Development and Mechanistic Investigation of Mixed Metal Oxides (MMOs) and Nanocomposites as Multi-Functional Catalysts

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Development and Mechanistic Investigation of Mixed Metal Oxides (MMOs) and Nanocomposites as Multi-Functional Catalysts

Laura Achieng Achola, PhD
University of Connecticut, 2020

Abstract
There are 4 chapters in this thesis. Chapter 1 presents photo-assisted PMS activation using cobalt doped mesoporous iron oxide with exceptional activity and stability up to 6 cycles and very low cobalt leaching. The effects of cobalt doping are shown using different characterization techniques. The high surface area and monomodal pore sizes are maintained with minimal cobalt incorporation. This study correlates the activity to increased labile oxygen induced by cobalt doping. Chapter 2 details the synthesis of mesoporous first-row transition metal ferrites. \(M^{2+}\) (Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\)) ferrite synthesis was systematically studied using a Biotage Initiator microwave apparatus and the effects of reaction time and initial \(M^{2+}\) concentration on the structure, morphology, composition, and catalytic activity were evaluated. These materials were then applied to electrochemical oxygen evolution reaction where NiFe\(_2\)O\(_4\) showed high activity vs. the other ferrites with a low overpotential of 278 mV at 10 mA/cm\(^2\). Chapter 3 presents a photo-assisted selective catalytic oxidation of acetonitrile to acetamide on octahedral molecular sieves.
(K-OMS-2) catalysts with oxygen as the sole oxidant. Under this protocol, the catalysts exhibit 100% selectivity towards the formation of acetamide and 15% conversion. The role of light and oxygen is discussed along with a kinetic study of the reaction. Kinetic isotope effect (KIE) studies were conducted in an effort to identify the rate-determining step (RDS) and an inverse KIE is observed. Chapter 4 is a review that surveys the chemistry of molecular oxygen, the generation mechanisms and detection methods of reactive oxygen species in heterogeneous selective catalytic oxidations.
Development and Mechanistic Investigation of Mixed Metal Oxides (MMOs) and Nanocomposites as Multi-Functional Catalysts

Laura Achieng Achola

B.Sc. Industrial Chemistry, University of Nairobi, 2014

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Development and Mechanistic Investigation of Mixed Metal Oxides (MMOs) and Nanocomposites as Multi-Functional Catalysts

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2020
DEDICATION

My Parents
Veronica Sabina Oriaro and Nicanor Achola Ogolla
&
My siblings
Maxwell, Dennis and Sharon
ACKNOWLEDGEMENTS

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## TABLE OF CONTENTS

APPROVAL PAGE .................................................................................................................. iii

DEDICATION ............................................................................................................................ iv

ACKNOWLEDGEMENTS ......................................................................................................... v

TABLE OF CONTENTS .......................................................................................................... vi

LIST OF FIGURES .................................................................................................................. x

LIST OF TABLES ..................................................................................................................... xv

Chapter 1  Enhanced Visible-Light-Assisted Peroxymonosulfate Activation on Cobalt-Doped Mesoporous Iron oxide for Orange II Degradation ................................................................. 1

1.1  Introduction ...................................................................................................................... 1

1.2  Experimental Section ....................................................................................................... 3

1.2.1  Materials ...................................................................................................................... 3

1.2.2  Synthesis of pristine and cobalt-doped iron oxide ......................................................... 3

1.2.3  Characterizations ......................................................................................................... 4

1.2.4  Orange II dye degradation by PMS activation ............................................................... 7

1.2.5  Reactive Oxygen Species study .................................................................................. 8

1.3  Results .............................................................................................................................. 9

1.3.1  Synthesis and characterization .................................................................................... 9

1.3.2  Photo-assisted peroxymonosulfate activation for Orange II dye degradation .......... 22

1.3.3  Reactive oxygen species ............................................................................................ 29
# Chapter 1

## 1.4 Discussion

- **1.4.1 Effect of cobalt doping on the structure of iron oxide.** ........................................... 33
- **1.4.2 Catalyst Performance** ................................................................................................. 36
- **1.4.3 Reactive Oxygen Species** ............................................................................................ 41
- **1.4.4 Mechanistic Ideas** ........................................................................................................ 42

## 1.5 Conclusions .......................................................................................................................... 43

## 1.6 Reference .............................................................................................................................. 44

# Chapter 2

## Chapter 2 Photo-assisted Selective Acetonitrile Catalytic Oxidation On Octahedral Molecular Sieve (K-OMS-2) ........................................................................................................... 53

- **2.1 Introduction** ...................................................................................................................... 53
- **2.2 Experimental Section** ....................................................................................................... 54
  - **2.2.1 Chemicals** .................................................................................................................... 54
  - **2.2.2 Catalyst Synthesis** ..................................................................................................... 55
  - **2.2.3 Catalyst Characterization** .......................................................................................... 56
  - **2.2.4 Catalytic Reaction Condition** .................................................................................... 57
- **2.3 Results** ............................................................................................................................. 57
  - **2.3.1 Catalytic Characterization** ........................................................................................ 57
  - **2.3.2 Catalytic Reaction Condition** .................................................................................... 60
- **2.4 Discussion** ....................................................................................................................... 67
- **2.5 Conclusions** .................................................................................................................... 70
Chapter 3  Microwave Hydrothermal Synthesis of Mesoporous First-row Transition-Metal Ferrites  77

3.1  Introduction ........................................................................................................... 77

3.2  Methods ............................................................................................................... 79

3.2.1  Materials .......................................................................................................... 79

3.2.2  Synthesis of M^{2+} ferrites ............................................................................. 79

3.2.3  Characterizations ............................................................................................ 80

3.2.4  Electrochemical Measurements ....................................................................... 81

3.3  Results .................................................................................................................. 81

3.3.1  XRD ................................................................................................................ 81

3.3.2  XRF ................................................................................................................ 85

3.3.3  Surface Area and Porosity .............................................................................. 86

3.3.4  Raman Analysis ............................................................................................... 91

3.3.5  SEM and TEM analyses .................................................................................. 92

3.3.6  Thermal Analysis ............................................................................................. 102

3.3.7  Magnetism studies .......................................................................................... 103

3.3.8  OER activity .................................................................................................... 106

3.4  Discussion .......................................................................................................... 107

3.5  Conclusion .......................................................................................................... 110
Chapter 4  Reactive Oxygen Species in Selective Heterogeneous Catalytic Oxidations: Generation, Detection, and Mechanistic Insights. ............................................................... 118

4.1  Introduction .................................................................................................................. 118
4.2  Electronic states and Redox properties ......................................................................... 120
4.3  Reactive Oxygen Species Generation ........................................................................... 125
  4.3.1  Singlet Oxygen ........................................................................................................ 126
  4.3.2  Superoxide Anion Radical ......................................................................................... 128
  4.3.3  Hydrogen Peroxide .................................................................................................. 134
  4.3.4  Hydroxyl radical ..................................................................................................... 135
4.4  Reactive Oxygen Species Detection .............................................................................. 137
  4.4.1  Singlet Oxygen ........................................................................................................ 139
  4.4.2  Superoxide anion radical ........................................................................................ 141
  4.4.3  Hydrogen Peroxide .................................................................................................. 142
  4.4.4  Hydroxyl Radical ..................................................................................................... 144
  4.4.5  In situ vs. Ex situ ..................................................................................................... 148
4.5  Conclusion .................................................................................................................... 154
4.6  References .................................................................................................................... 155
Appendix .............................................................................................................................. 172
LIST OF FIGURES

Figure 1-1. Characterization of the prepared materials: a) wide-angle XRD patterns, b) low
angle XRD patterns, c) Raman analysis, and d) FTIR analysis............................................. 11

Figure 1-2. SEM, TEM images of a), e) FeO$_x$; b), f)1%Co-FeO$_x$; c), g) 3%Co-FeO$_x$; d), h) 5%Co-FeO$_x$. Scale bar on the TEM images is 50 nm............................................................... 12

Figure 1-3. a,b) High-Resolution TEM image of 1%Co-FeO$_x$ with the SAED pattern (inset)
taken at the same location, c) HAADF-TEM-EDX, d,e) TEM-EDX mapping of Fe and Co, and f) overlaid Co and Fe maps................................................................. 13

Figure 1-4. TGA-DSC of prepared a) FeO$_x$; b) 1%Co-FeO$_x$; c) 3%Co-FeO$_x$; d) 5%Co-FeO$_x$
catalysts.................................................................................................................. 14

Figure 1-5. In situ XRD of a) FeO$_x$; b) 1%Co-FeO$_x$; c) 3%Co-FeO$_x$; d) 5%Co-FeO$_x$ catalysts
heated up in air from R.T to 800°C ........................................................................... 15

Figure 1-6. a) N$_2$ sorption isotherms, b) BJH desorption pore size distributions, c) TGA
analysis in air and argon, and d) H$_2$-TPR of pure and cobalt doped amorphous iron oxide....... 17

Figure 1-7. X-ray photoelectron spectroscopy (XPS) analysis: a) Fe 2p, b) Fe LMM, c) O 1s,
and Co 2p deconvoluted XPS spectra of FeO$_x$ and X%Co-FeO$_x$ x=1, 3, and 5). .................. 18

Figure 1-8. a) Magnetization vs. magnetic field (hysteresis loops) at 300 K, b) a) enlarged, c) Diffuse reflectance UV-Vis of the prepared samples, and d) Tauc plot from the DR-UV-Vis data.
........................................................................................................................................ 20

Figure 1-9. a) Adsorption capacity data, b) Dye degradation activity, c) Pseudo-first-order
kinetics plots of degradation of orange II, and d) Comparison of reaction rates after different quenching conditions. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3.................... 22

Figure 1-10. FTIR spectra of the 1% Co-FeO$_x$ before and after the reaction. ....................... 23

Figure 1-11. UV-Vis spectra of dye solution before and after 1 minute of degradation.
Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.
............................................................................................................................................. 24

Figure 1-12. 1% Co-FeO$_x$ catalyst performance under different a) calcination temperatures,
b) catalyst loading amounts, c) PMS loading amounts, and d) quenching agents. Reaction
condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K. ......... 25
Figure 1-13. Consecutive runs to probe the reusability of the 1% Co-FeOx catalyst. (The catalyst was recycled by filtration and washed thoroughly with DI water after each run and dried in a vacuum oven). Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K

Figure 1-14. ESI/MS plots of reaction solutions over 1%Co-FeOx. The intensity of each plot has been adjusted to the same scale to clearly show the observed m/z.

Figure 1-15. ESI/MS plots of reaction solutions over 1%Co-FeOx. The intensity of each plot has NOT been adjusted to the same scale to clearly show the observed m/z.

Figure 1-16. EPR spectra of a) \(^1\)O\(_2\) spin trapping using TMP under in situ conditions, b) ex situ conditions, and c) \(·\)OH spin trapping using BMPO under in situ and ex situ conditions. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.

Figure 1-17. UV-Vis spectra of Leuco crystal violet/HRP probe for the detection of H\(_2\)O\(_2\).

Figure 1-18. Fluorescence spectra of a) SOSG fluorescence probe for the detection of \(^1\)O\(_2\), and b) APF fluorescence probe for the detection of \(·\)OH radical. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.

Figure 1-19. (a) The transient photocurrent response of FeO\(_x\) and 1% Co-FeO\(_x\) catalyst electrodes with light on–off cycles under visible light irradiation [Na\(_2\)SO\(_4\)] = 0.1 M. (b) Photoluminescence spectra of FeO\(_x\) and 1% Co-FeO\(_x\).

Figure 1-20. Proposed mechanism of PMS activation for orange II dye degradation on cobalt doped mesoporous iron oxide.

Figure 2-1. Powder X-ray diffraction patterns of the synthesized catalysts.

Figure 2-2. a) Fourier-transform infrared spectroscopy (FTIR), b) Raman spectroscopy, c) BET isotherm, and d) NL-DFT pore size distribution of K-OMS-2\(_{\text{REF}}\) catalyst.

Figure 2-3. a) Transmission Electron Microscopy (TEM) micrographs, b) enlarged TEM image of the boxed area, c) Scanning Electron Microscopy (SEM) image, and d) SEM-EDX analysis of K-OMS-2\(_{\text{REF}}\) catalyst.

Figure 2-4. Kinetics of the photo-assisted acetonitrile and deuterated acetonitrile.

Figure 2-5. Mass-spectrometry fragmentation patterns of (from the top) CH\(_3\)CONH\(_2\) in CH\(_3\)CN, CD\(_3\)CONH\(_2\) in CD\(_3\)CN and (bottom) CH\(_3\)CONH\(_2\) and CD\(_3\)CONH\(_2\) in a mixture of CH\(_3\)CN and CD\(_3\)CN. Y-axis is relative abundance.
Figure 2-6. a) Effect of removal of catalyst on the reaction. Conditions: Acetonitrile (1 mL), RT, K-OMS-2REF- 25 mg, 2 hours, Visible light. b) Reusability test of the K-OMS-2REF catalyst.

Figure 2-7. a) FTIR and b) Thermogravimetric analysis (TGA) of the K-OMS-2REF catalyst before and after the reaction.

Figure 3-1. Wide-angle XRD patterns for synthesized a) manganese and b) nickel ferrite c) control experiments, and d) magnetite materials.

Figure 3-2. Wide-angle XRD patterns for synthesized cobalt iron mixed metal oxide system.

Figure 3-3. Wide-angle XRD patterns for synthesized copper iron mixed metal oxide system.

Figure 3-4. Wide-angle XRD patterns for synthesized zinc-iron mixed metal oxide system.

Figure 3-5. Summary of XRF and N₂ sorption data; a) trends in starting materials concentrations vs. final product metal concentrations, b) BET surface area, c) BJH pore size and, d) pore volume changes with changing starting material concentrations.

Figure 3-6. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized manganese iron mixed metal oxide system.

Figure 3-7. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized magnetite system.

Figure 3-8. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized cobalt iron mixed metal oxide system.

Figure 3-9. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized nickel-iron mixed metal oxide system.

Figure 3-10. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized copper iron mixed metal oxide system.

Figure 3-11. a) N₂ sorption isotherms, b) BJH desorption pore size distributions for synthesized zinc iron mixed metal oxide system.

Figure 3-12. Raman spectra for a) Manganese ferrite, b) magnetite, c) cobalt ferrite, d) nickel ferrite, e) copper ferrite and, f) zinc ferrite samples.
Figure 3-13. SEM images of a) MnFe-1 min, b) MnFe-20 mins, c) 0.5MnFe300, d) 0.25MnFe300, e) 0.125MnFe300 and, f) 0.0625MnFe300 (scale bar 1µm) ............................................................................ 93

Figure 3-14. SEM images of a) Fe304 -20 min, b) 0.5Fe300, c) 0.25Fe300, d) 0.125Fe300 and, e) 0.0625Fe300 ......................................................................................................................... 94

Figure 3-15. SEM images of a) CoFe-1 min, b) CoFe-20 mins, c) 0.5CoFe300, d) 0.25CoFe300, e) 0.125CoFe300 and, f) 0.0625CoFe300 ....................................................................................................... 95

Figure 3-16. SEM images of a) NiFe-1 min, b) NiFe-20 mins, c) 0.5NiFe300, d) 0.25NiFe300, e) 0.125NiFe300 and, f) 0.0625NiFe300 ....................................................................................................... 96

Figure 3-17. SEM images of a) CuFe-1 min, b) CuFe-20 mins, c) 0.5CuFe300, d) 0.25CuFe300, e) 0.125CuFe300 and, f) 0.0625CuFe300. Scale bar 1µm ........................................................................... 97

Figure 3-18. SEM images of a) ZnFe-1 min, b) ZnFe-20 mins, c) ZnFe-30 mins, d) ZnFe-40 mins, e) ZnFe-1hr f) 0.5ZnFe300, g) 0.25ZnFe300, h) 0.125ZnFe300 and, i) 0.0625ZnFe300 .. 97

Figure 3-19. Top row (from left to right) High-Resolution TEM image of MnFe-20 mins-300 with the lattice fringes, d (311) inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Mn, Fe, O, and an Mn-Fe overlaid map. .......................................................... 99

Figure 3-20. Top row (from left to right) High-Resolution TEM image of CoFe-20 mins-300 with the lattice fringes, d (311) inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Co, Fe, O, and a Co-Fe overlaid map. .......................................................... 99

Figure 3-21. Top row (from left to right) High-Resolution TEM image of NiFe-20 mins-300 with the lattice fringes, d (311) inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Ni, Fe, O, and a Ni-Fe overlaid map. .......................................................... 100

Figure 3-22 Top row (from left to right) High-Resolution TEM image of CuFe-40 mins-300 with the lattice fringes, d (311) inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Cu, Fe, O, and a Cu-Fe overlaid map. .......................................................... 101

Figure 3-23. Top row (from left to right) High-Resolution TEM image of CuFe-40 mins-300 with the lattice fringes, d (311) inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Cu, Fe, O, and a Cu-Fe overlaid map. .......................................................... 101

Figure 3-24. TGA-DSC in nitrogen plots for a) MnFe-20mins-AS, b) CoFe-20mins-AS, c) NiFe-20mins-AS, d) CuFe-20mins-AS, and e) ZnFe-20mins-AS. (AS means as-synthesized). 102

Figure 3-25. Thermogravimetric analyses of the a) Mn²⁺, b) Fe²⁺, c) Co²⁺, d) Ni²⁺, e) Cu²⁺, and f) Zn²⁺ synthesized samples in a nitrogen atmosphere. .......................................................... 103
Figure 3-26. Magnetization curves of the a) Mn$^{2+}$, b) Fe$^{2+}$, c) Co$^{2+}$, d) Ni$^{2+}$, e) Cu$^{2+}$, and f) Zn$^{2+}$ synthesized samples in nitrogen atmosphere. ................................................................. 104

Figure 3-27. Polarization curves of a) Mn$^{2+}$, b) Fe$^{2+}$, c) Co$^{2+}$, d) Ni$^{2+}$, e) Cu$^{2+}$, and f) Zn$^{2+}$ synthesized samples in nitrogen atmosphere. ] ................................................................. 105

Figure 3-28. Electrochemical characterization of OER in 0.1 M KOH. a) LSV of different catalysts at a scan rate of 5 mV s$^{-1}$, b) Tafel plots if the different catalysts, c) LSV of Nickel catalysts synthesized in this study, d) Overpotentials calculated at 10mAcm$^{-2}$ and 20mAcm$^{-1}$. 106

Figure 3-29. Representative profile of T, P, and p monitored when the reaction was performed at 160°C with a 20 min hold time. ................................................................................................... 107

Figure 4-1. Molecular orbital diagrams for ground-state molecular oxygen (O$_2$), dioxygenyl (O$_2^+)$, the two forms of singlet oxygen ($^1$O$_2$), superoxide radical anion (O$_2^-$) and peroxide ion O$_2^{2-}$. ................................................................. 121

Figure 4-2. Molecular O$_2$, $^1$O$_2$, O$_2^-$, and O$_2$ $^{2-}$, and the relationship between O$_2^-$ and H$_2$O$_2$. ................................................................................................... 122

Figure 4-3. Formation of radicals ........................................................................................................ 125

Figure 4-4. Workflow diagram for the analysis of reactive oxygen species. .............................. 137

Figure 4-5. UV-Vis spectra of aliquots of the reaction mixture that were added to a mixture of LCV and HRP to get the spectra of CV$^+$. Blank refers to the reaction mixture without the catalyst. Reaction conditions: phenylacetylene (0.5 mmol), catalyst (6 mol % of meso Cu/MnOx), toluene (5 mL), balloon of air, 105 °C........................................................................................................ 143

Figure 4-6. NBT evaluation as a good trapping agent under on/of switch configuration using curcumin. ........................................................................................................ 149

Figure 4-7. Quenching of the BMPO-OH adduct EPR signal by the addition of BHT under in situ conditions. ................................................................. 149
LIST OF TABLES

Table 1-1. Nitrogen Adsorption Analysis and Atomic ratio of cobalt doped iron oxide characterized by X-ray fluorescence (XRF). ...................................................................................................................... 16

Table 1-2. The summation of the surface elemental compositions obtained from the deconvoluted high-resolution Fe 2p, and O 1s XPS spectra of the cobalt doped iron oxide samples. .................................................................................................................. 19

Table 1-3. The summary of the magnetic and optical properties of the pure and cobalt doped iron oxide catalysts. ........................................................................................................................................... 21

Table 1-4. First-order kinetic parameters for degradation reactions by mesoporous iron oxides and turnover frequencies of catalysts. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K. ................................................................................................................................................. 28

Table 1-5. Catalytic performance comparison of recently reported Visible-light-assisted PMS activation ..................................................................................................................................................... 36

Table 1-6. Observed degradation products from ESI-MS fragmentation patterns. ........... 39

Table 2-1. Photo-assisted acetonitrile oxidation using different metal oxide catalysts and varied catalyst loading. ........................................................................................................................................... 61

Table 2-2. Photo-assisted acetonitrile oxidation using K-OMS-2REF catalyst under varied conditions. .................................................................................................................................................. 62

Table 2-3. Photo-assisted acetonitrile oxidation using K-OMS-2REF catalyst using different substrates and conditions. .................................................................................................................. 63

Table 3-1. Nitrogen Adsorption Analysis and mol. ratio of mixed metal oxides characterized by X-ray fluorescence (XRF).............................................................................................................................................. 90

Table 3-2. Summary of saturation magnetization M_s values and OER activity data........ 105

Table 4-1. Summary of standard one-electron reduction potentials that are of interest for predicting the course of a free radical relative to a standard hydrogen electrode (SHE). ........ 123

Table 4-3. Scavengers of Reactive Oxygen species.................................................................................. 138

Table 4-4. Summary Methods of detection of reactive oxygen species................................. 146
Chapter 1. Enhanced Visible-Light-Assisted Peroxymonosulfate Activation on Cobalt-Doped Mesoporous Iron oxide for Orange II Degradation

1.1 Introduction

Oxidation is one of the most important reactions in environmental remediation and chemical synthesis. Oxidation has been used for the destruction of pollutants, microbial and for chemical synthesis. Advanced oxidation processes (AOP) are typically characterized by the in situ generation of hydroxyl (•OH), and SO₄•⁻ radicals among other reactive oxygen species. These processes have been used for the non-selective oxidation of pollutant organics that are otherwise difficult to degrade using conventional methods. Hydroxyl radical generation has been extensively studied in the past decades with the most popular process being the Fenton reaction and several variations of this (e.g., Photo-Fenton, sono-Fenton, electro-Fenton, etc.). Recently, sulfate radical advanced oxidation processes have gained popularity for their considerable advantages over the hydroxyl radical. Other than its superior oxidation ability (oxidation potential of (2.5-3.1 vs. NHE)), wide range of pH applicability and its selective reactivity towards unsaturated and aromatic electrons, SO₄•⁻ has a longer half-life period (i.e., 30-40µs). The primary sources of the sulfate radical have been the activation of peroxymonosulfate (PMS, HSO₄⁻) and peroxydisulfate (PS, S₂O₈²⁻). Silver ion (Ag⁺) was found to perform the best for the homogeneous activation of PS while Cobalt ion (Co²⁺) performed the best for PMS. However, heterogeneous catalysts are preferred for their stability over a wide pH range, easier recovery, and lower metal loading for high concentrations of PMS. Given that cobalt is a rare, expensive, and
toxic pollutant even in very low concentrations, a lot of research has been dedicated to minimizing the amount of cobalt used as well as immobilizing the cobalt to avoid leaching.\textsuperscript{11–13}

Photo-assisted activation as an approach offers high efficiency in the generation of reactive oxygen species. Iron-based systems have been widely employed for catalysis because iron oxide (Fe\textsubscript{2}O\textsubscript{3}) is a benign, abundant, cost-effective, and efficient material.\textsuperscript{4,14} Iron oxide has been reported to be a good visible-light-driven photocatalyst for PMS activation.\textsuperscript{15} However, Fe\textsuperscript{3+}/Fe\textsuperscript{2+} systems are not as efficient for PMS activation as they tend to require higher PMS dosage.\textsuperscript{13} Co\textsuperscript{2+}-doped Fe\textsubscript{2}O\textsubscript{3} nanoparticles with enhanced photocatalytic activity have been reported for pararosaniline dye degradation. Suresh et al. proposed that Co\textsuperscript{2+} impurity energy levels where electrons are trapped are important.\textsuperscript{16} In the case of PMS activation, Co\textsuperscript{2+} would play several roles such as, i) increasing the kinetics of PMS activation, ii) introducing the impurity levels and, iii) increasing catalyst stability because of the strong Co\textsuperscript{2+}-Fe\textsuperscript{3+} interactions in the structure, which will suppress leaching. Thus, catalysts that are highly active with very low cobalt loading, chemically stable (little to no leaching), and magnetically recoverable are desired. Thus, mesoporous iron oxide with high surface area, narrow pore size distribution, prevalent multi-valency and tunable redox properties have great potential for this application.

In this study, we utilize visible-light-assisted peroxymonosulfate activation on cobalt-doped mesoporous iron oxide for orange II degradation. Sol-gel based inverse micelle methods were used to synthesize cobalt doped amorphous iron oxide.\textsuperscript{5} This is the first report of this kind of cobalt-doped amorphous iron oxide applied to visible-light-assisted PMS activation. The materials were thoroughly characterized and the structural and electronic effects of the cobalt doping on the amorphous iron oxide were studied. These materials were then applied to the visible-light-assisted peroxymonosulfate activation of orange II dye degradation. Two distinct techniques (electron
paramagnetic resonance (EPR) and fluorescence trapping) were utilized to evaluate the ROS present in the reaction system. ROS scavenging techniques were conducted to reveal the dominant pathway. This study attempts to tie the structural and electronic changes induced by cobalt doping to the enhanced performance.

1.2 Experimental Section

1.2.1 Materials

Iron nitrate nonahydrate (≥98%), poly (ethylene glycol)-block-pol (propylene glycol)-block-pol-(ethylene glycol), Pluronic P123, PEO$_{20}$PPO$_{70}$PEO$_{20}$, molar mass 5750 g/mol, nitric acid (≥70%), 1-butanol (≥99.4%), iron(III) oxide (99.98%, metal basis) and Oxone (KHSO$_5$·0.5KHSO$_4$·0.5K$_2$SO$_4$, PMS) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

1.2.2 Synthesis of pristine and cobalt-doped iron oxide

Pure iron oxide was synthesized following the procedure described in the literature. $^{17}$ Co-doped iron oxides were synthesized similar to the procedure of pristine iron oxide except for the introduction of the Co salt. In a typical synthesis 0.01 mol of iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) (depending upon the dopant percentage) and 0.134 mol of 1-butanol were added into a 120 mL beaker. To this solution, 0.0034 mol of Pluronic P123 and 0.032 mol of concentrated nitric acid (HNO$_3$) were added and stirred at room temperature until the solution became clear (light orange). The resulting clear solution was then kept in an oven at 95°C for 2 h. The product was collected and washed with excess ethanol,
centrifuged, and dried in a vacuum oven overnight. Afterward, the dried powders were subjected to a heating cycle. First, they were heated to 250°C at a heating rate of 2°C and kept at this temperature for 4 h. The powder was then cooled down to room temperature under ambient conditions. The material was then subjected to the following heating cycle to obtain differently calcined materials: 350°C for 3 h, 450°C for 2 h and 550°C for 1 h respectively.

1.2.3 Characterizations

Powder XRD data were collected on a Rigaku UltimaIV instrument using Cu Kα (1.54 Å) radiation at a beam voltage of 40 kV and a 45 mA beam current. High- and low-angle patterns were obtained by continuous scans in a 2θ range of 5−75° and 0.5−5° with a scan rate of 2°/ min and 0.5°/min, respectively. In situ XRD was performed in air atmosphere while heating up 100 mg of the sample from room temperature to 700°C and the diffraction patterns were collected every 100 °C. The surface area, pore size distribution, and pore volume of iron oxides were determined in a Quantachrome Autosorb-I-1C automated adsorption system. The samples were treated at 150°C for 6 h under helium prior to measurement. The isotherms of N₂ at 77 K were obtained from physisorption. The pore size distributions of the iron oxides were determined from the N₂ desorption isotherms at 77 K, using the Barrett–Joyner–Halenda (BJH) method. Raman spectra were obtained using a Renishaw 2000 Raman scope which has an optical microscope (0.024 in. focus length), grating (1800 mm⁻¹), and CCD detector. A laser excitation source with 514 nm wavelength was used. Fourier-transform infrared spectroscopy (FT-IR) was performed on a NICOLET MAGNA 560 FT-IR spectrometer in transmission mode (32 scans, 4 cm⁻¹ resolution). The laser focus was set to 40% to prevent local damage. For each sample, three different locations were analyzed to verify the spectra. Field-Emission Scanning Electron
Microscope (FE-SEM) and Elemental Dispersive X-Ray Spectroscopy (EDS) were taken on an FEI Nova NanoSEM 450 and an Oxford 553 EDS. High-Resolution Transmission Electron Microscopy (HR-TEM) was conducted on an FEI, Talos F200X microscope with an operating voltage of 200 kV and the ability to conduct Energy Dispersive X-Ray Spectroscopy (EDS). The quantitative elemental compositions of samples were determined by X-ray fluorescence (XRF) with a Rigaku ZSX Primus IV sequential wavelength-dispersive XRF spectrometer (4 kW Rh anode).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are employed to study the thermal stability of the samples. The experiments were performed on a TA instruments SDT Q-600. The temperature was ramped from RT to 1400°C at 10°C/min in an argon environment. TG-MS analyses were performed with a TG 209 F1 Libra thermogravimetric analyzer coupled to a QMS 403C quadrupole mass spectrometer. The samples (20 mg) are heated to 800 °C with a 10°C/min heating rate under 50 mL/min argon and air atmosphere. A scanned bar graph mode was used for MS measurements. The UV–vis diffuse reflectance spectra (DRS) were obtained at room temperature using a GBC Cintra apparatus equipped with an integrated sphere attachment with BaSO₄ as background. The optical band gap of it could be calculated from the Tauc plot. This curve of converted \((\alpha hν)^r\) versus \(hν\) was obtained from the UV–vis spectrum, in which \(\alpha\), \(h\), and \(ν\) were the absorption coefficient, Planck’s constant, and light frequency, respectively. When \(r = 2\), a direct band gap could be determined.

X-ray photoelectron spectroscopy (XPS) analysis of the synthesized materials was conducted on a PHI model Quantum 2000 spectrometer with a scanning ESCA multiprobe (Φ Physical Electronics Industries Inc.) using Al Kα radiation (\(λ = 1486.6\) eV) as the radiation source. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 187.85 eV.
and 29.35 eV for recording survey and high-resolution spectra, respectively. The powder samples were pressed on a double-sided carbon tape mounted on an Al coupon pinned to the sample stage with a washer and screw then placed in the analysis chamber. Binding energies (BE) were measured for Co 2p, Fe 2p, and O 1s regions. The XPS spectra were analyzed and fitted using CasaXPS software (version 2.3.16). Sample charging effects were eliminated by correcting the observed spectra with the C 1s BE value of 284.8 eV. XPS spectra were also collected using monochromatic Mg Kα X-ray source on PHI VersaProbe II X-ray Photoelectron Spectrometer with a 0.47 eV system resolution. The energy scale has been calibrated using Cu 2p3/2 (932.67 eV) and Au 4f7/2 (84.00 eV) peaks on a clean copper plate and a clean gold foil. Temperature programmed mass spectrometry analyses were conducted in a programmable tube furnace equipped with a gas analyzer MKS coupled with a quadrupole mass selective detector. About 100 mg of materials were packed in a quartz tube reactor mounted into the tube furnace. The loaded samples were pretreated in an inert gas flow (Ar) at 200 °C for 1 h to clean the catalyst surface before each test. Temperature programmed measurements were performed from room temperature to 800 °C with a heating ramp rate of 10 °C/min. In H2-TPR measurements, 10% H2/Ar flow was passed through the catalyst bed at a flow rate of 50 sccm, while the temperature was ramped from room temperature (RT) to 800 °C. DC magnetization versus magnetic field was evaluated using a vibrating sample magnetometer system attached to an Evercool Physical Property Management System from Quantum Design Inc. The samples were scanned at a rate of 20 Oe/s when the field strength is smaller than 2000 Oe and a rate of 150 Oe/s when the field is larger than 2000 Oe.
1.2.4 Orange II dye degradation by PMS activation

A 1000 W Xenon lamp was used as a light source with wavelength \( \lambda > 400 \) nm. In a typical degradation experiment, 5 mg of catalyst was dispersed in 100 mL Orange II aqueous solution (0.1 mM). Before visible light irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium among the catalyst, Orange II dye, and water. Then, 30 mg of Oxone was added to the solution. About 3 mL of analytical sample was drawn from the reaction suspension every 1 min, and the catalyst was removed by centrifugation. The reaction progress was monitored by measuring the absorbance (A) of the clarified solution at 485 nm for Orange II using a UV−vis spectrophotometer (Shimadzu Scientific Instruments, Tokyo, Japan). Atomic absorption spectroscopy was used to study cobalt leaching in the solution. The substrate concentration \( (C_e) \) remaining in the supernatant was analyzed. The decreased concentration \( (C_0 - C_e) \) was then used to calculate the amount of adsorption in units of milligrams per gram of catalyst. The degradation (%) was calculated from the formula: degradation (%) = \((C_e - C)/C_e \times 100\%\), where \( C_0 \) was the initial dye concentration, \( C_e \) was the concentration after equilibration and \( C \) was the concentration at homologous times. A series of external standard dye solutions were used for calibration. An API 2000 mass spectrometer (Applied Biosystem/MDS SCIEX, CA) using electrospray ionization (ESI) source in the negative mode was used to analyze the dye degradation products under different conditions. A 1:1 ratio of HPLC-grade acetonitrile to dye sample solution was used. The solvent flow rate was set at 10 \( \mu L \) min−1 while the injection volume was 50 \( \mu L \). The needle voltage was −4500 V. The desolation temperature was 250 \( ^\circ C \). Quenching experiments were conducted under identical conditions with the addition of quenching agents such as methanol, tert-butyl alcohol (TBA), and furfuryl alcohol (FFA). For the recycle tests, the catalyst was filtered, washed with deionized water dried at 90 °C.
for 12 h, and used for a recycle test in the next round under identical conditions. Most of the experiments were carried out in triplicate.

1.2.5 Reactive Oxygen Species study

The production of \(^{\cdot}\)OH radicals by the 1\%Co-FeO\(_x\) catalyst was measured by using aminophenyl fluorescein (APF). APF selectively reacts with \(^{\cdot}\)OH radical to form a strongly emissive fluorescein molecule (\(\lambda_{\text{em}} = 515\) nm) but does not react with the other ROS, such as O\(_2^{\cdot-}\), \(^{1}\)O\(_2\), and H\(_2\)O\(_2\). The catalyst (5 mg) was dispersed in 100 mL of water or dye solution. Three milliliters of this dispersion was mixed with 6 \(\mu\)L of APF and irradiated with a 1000 W Xenon lamp. The photoluminescence spectra were recorded in order to estimate the evolution of \(^{\cdot}\)OH (\(\lambda_{\text{ex}} = 490\) nm). The production of H\(_2\)O\(_2\) by was measured by using leuco crystal violet (LCV), which forms a violet cation (LCV\(^+\)) absorbing at 596 nm in the presence of horseradish peroxidase (HRP) and H\(_2\)O\(_2\). For the preparation of the HRP solution, 10 mg of HRP was dissolved in 10 mL of water. For the LCV solution, 5 mg of LCV was dissolved in 10 mL of 0.5\% HCl solution. The acetate buffer was prepared by mixing equal volumes of sodium acetate (2 M) and acetic acid followed by pH adjustment at 4.5 using glacial acetic acid. A dispersion of photocatalyst (5 mg) in 100 mL of water was irradiated for 10 min. 200 \(\mu\)L of the irradiated solution was collected every minute and added to 9.8 mL of distilled water. Next, 1 mL of the LCV solution and 0.5 mL of the HRP solution and 5 mL of acetate buffer were added. The mixture was stirred in the dark at room temperature for 60 min.

The production of \(^{1}\)O\(_2\) was measured by using the Singlet Oxygen Sensor Green (SOSG) probe. About 100 \(\mu\)g of SOSG were dispersed in 6.6 mL of methanol in order to prepare a stock solution of SOSG (25 \(\mu\)M). The 1\% Co-FeO\(_x\) catalyst (5 mg) was dispersed in 100 mL of water or dye
solution, 2.5 ml of the dispersion, and 100 µL of SOSG solution was irradiation for a minute. The production of $^1$O$_2$ was evaluated by measuring the photoluminescence of SOSG–endoperoxide (SOSG-EP) ($\lambda_{\text{ex}} = 480$ nm and $\lambda_{\text{em}} = 525$ nm).$^{18}$ The production of superoxide $\text{O}_2^{-}$ radicals was measured using the nitroblue tetrazolium (NBT). The reduction of the yellowish NBT into purple formazan derivatives results in an increase of the absorbance between 450 and 700 nm. The 1% Co-FeO$_x$ catalyst (5 mg) was dispersed in 100 mL of water. NBT (8 mg) was added to the photocatalyst dispersion under light protection. Then the solution was irradiated with a 1000 W Xe lamp for various durations (0, 1, 15 and 30 minutes).

For EPR analysis, 5-tert-Butyloxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO)$^{19}$ was used as a spin trapping agent for $\text{SO}_4$•− and ‘OH radicals. The compound 2,2,6,6-tetramethyl-4-piperidinol (TMP)$^{20}$ was used as a $^1$O$_2$ spin trap. EPR spectra of the aqueous 1% Co-FeO$_x$/PMS suspensions were recorded at 298 K with an X-Band (9 GHz) Bruker EMX spectrometer.

1.3 Results

1.3.1 Synthesis and characterization

The powder X-ray Diffraction (PXRD) pattern of amorphous iron oxide is characterized by 2 broad low-intensity peaks centered at d-spacings of 2.53 Å (35.4°) and 1.47 Å (63.0°), which are assigned to the (110) and (115) planes of 2-line ferrihydrite (JCPDS card number 29-0712) (Figure 1-1a).$^{21}$ No impurity peaks were observed in the pure and cobalt doped iron oxide samples. A single low-angle PXRD is expected for UCT materials as the materials are formed by the packing of monodispersed nanoparticles in a random manner. Since the mesopores in the typical UCT material are a network of intraparticle voids, the observed low angle peaks are an indication of
small building blocks (nanoparticles). Following the synthesis of the Co-doped catalysts, all the catalysts show a peak in the low-angle PXRD patterns. This indicates that the materials preserved their mesostructure with cobalt doping. The $d$-spacings of FeO$_x$, 1%Co-FeO$_x$, 3%Co-FeO$_x$ and 5%Co-FeO$_x$ are 38Å (2.30°), 54Å (1.65°), and 41 Å (2.14°), respectively.

Figure I-1c shows the Raman spectra of the synthesized materials. The FeO$_x$ material shows strong Raman bands at 219 cm$^{-1}$, 284 cm$^{-1}$, 396 cm$^{-1}$ and weaker bands at 500 cm$^{-1}$, 600 cm$^{-1}$, and 1300 cm$^{-1}$. The 1%Co-FeO$_x$ and 3%Co-FeO$_x$ samples show a peak shift (219 cm$^{-1}$ to 222 cm$^{-1}$) from the FeO$_x$ sample. This can be attributed to compressive strain as cobalt is incorporated into the iron oxide structure. This shift is not observed in the 5%Co-FeO$_x$ sample. The infrared spectrum in the range 400-4000 cm$^{-1}$ (Figure I-1d) is consistent with previous reports for the UCT iron material. In general, the absorption band at 3379 cm$^{-1}$ is attributed to the hydroxyl stretching modes of physically adsorbed H$_2$O molecules or to hydrogen-bonded surface OH groups while the bands at 1358 cm$^{-1}$, 1500 cm$^{-1}$, and 1628 cm$^{-1}$ are assigned to hydroxyl bending vibrations. Additionally, the bands at 450 cm$^{-1}$ and 575 cm$^{-1}$ are attributed to Fe-O-Fe stretching vibrations.
Figure 1-1. Characterization of the prepared materials: a) wide-angle XRD patterns, b) low angle XRD patterns, c) Raman analysis, and d) FTIR analysis.

SEM analysis shows a pin-cushion morphology for all the materials (Figure 1-2a-d). These materials have spherical, hedgehog-like, or pin-cushion aggregates that consist of radially oriented nanoparticles. The FeO\textsubscript{x} sample shows the smallest particle size with near-spherical particles in the agglomerates. The largest particle size is observed for the 1%Co-FeO\textsubscript{x} sample. The 5% Co-FeO\textsubscript{x} sample showed a needle-like morphology. As more cobalt ions are incorporated into the iron oxide structure, the particle size increases up to the 3% doping level. The 5% Co-FeO\textsubscript{x} were smaller and needle-like.
Figure 1-2. SEM, TEM images of a), e) FeO_; b), f)1%Co-FeO_; c), g) 3%Co-FeO_; d), h) 5%Co-FeO_. Scale bar on the TEM images is 50 nm.

The spikes observed in the transmission electron microscopy (TEM) images (Figure 1-2e-h) are formed by small crystalline nanosized particles and pores are formed among these nanosized particles. All the TEM images are collected at the same magnification, therefore, the effects of cobalt doping on pore sizes and aggregation of nanoparticles can be observed. The TEM images clearly show changes in the morphology of the samples with Co doping. Generally, the cobalt doping leads to more elongated spikes. The selected area electron diffraction (SAED) (Figure 1-3a) of the 1%Co-FeO_x shows two rings that correspond to the two broad peaks that were observed in XRD analysis. High-Resolution TEM (Figure 1-3b) shows the individual needles and further confirms the amorphous nature of the nanoparticles. The presence of cobalt is confirmed using TEM-EDX (Figure 1-3c-f), further indicating a uniform distribution of Co and Fe.
Figure 1-3. a,b) High-Resolution TEM image of 1%Co-FeO$_x$ with the SAED pattern (inset) taken at the same location, c) HAADF-TEM-EDX, d,e) TEM-EDX mapping of Fe and Co, and f) overlaid Co and Fe maps.

*In situ* XRD patterns (*Figure 1-5*) show the α-Fe$_2$O$_3$ phase emerges at 500 °C in the FeO$_x$ and 1%Co-FeO$_x$ samples but at higher temperature (600 °C) for the 3%Co-FeO$_x$ and 5%Co-FeO$_x$ samples. As the temperature was increased, the peaks for the Fe$_2$O$_3$ phase became sharper and
more intense; an indication of increasing crystallinity. No impurity peaks were observed in any of the samples.

**Figure 1-4.** TGA-DSC of prepared a) FeOx; b) 1%Co-FeOx; c) 3%Co-FeOx; d) 5%Co-FeOx catalysts.

The Thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) (**Figure 1-4**) data show two exothermic peaks at \(\sim 300^\circ\text{C}\) and a second one at \(\sim 490^\circ\text{C}\). The first peak corresponds to weight loss due to the decomposition of the P\(_{123}\) surfactant since these samples were the as-synthesized materials, while the second peak corresponds to crystallization, specifically hematite.
phase formation. At this temperature, no further weight loss is observed. There is a peak shift from 479°C to 504°C as the dopant amount was increased.

Nitrogen sorption experiments were conducted to confirm a regular mesoporous structure as is typical of UCT materials. All the samples showed a type IV adsorption isotherm with an H1 hysteresis loop (Figure 1-6a) suggesting that the mesoporous structure is maintained with increasing cobalt ion doping. All the materials showed monomodal pore size distributions with average pore sizes lower than 4 nm (Figure 1-6b). Doping cobalt has significantly reduced the surface area (Table 1) from 386 m2/g in the FeOx sample to 269 m2/g in the 3%Co-FeOx sample. The lowest pore size was observed for the 1%Co-FeOx catalyst and the highest being the 3%Co-
FeOx. The 5%Co-FeOx sample showed a similar pore size as the FeOx material. In general, the pore volume was lower in the doped sample. Notably, the 1%Co-FeOx samples showed the highest BET surface area, lowest pore size, and a low pore volume among the doped catalysts.

Table 1-1. Nitrogen Adsorption Analysis and Atomic ratio of cobalt doped iron oxide characterized by X-ray fluorescence (XRF).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area</th>
<th>BJH des. Pore size (nm)</th>
<th>Pore volume (cc/g)</th>
<th>Feeding molar ratio of Fe: Co</th>
<th>Co/Fe, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOx</td>
<td>368</td>
<td>2.3</td>
<td>0.27</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1%Co-FeOx</td>
<td>319</td>
<td>1.8</td>
<td>0.20</td>
<td>1:0.01</td>
<td>0.42</td>
</tr>
<tr>
<td>3%Co-FeOx</td>
<td>269</td>
<td>3.2</td>
<td>0.23</td>
<td>1:0.03</td>
<td>1.48</td>
</tr>
<tr>
<td>5%Co-FeOx</td>
<td>274</td>
<td>2.3</td>
<td>0.29</td>
<td>1:0.05</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis (TGA) experiments carried out in argon and air atmospheres are compiled in Figure 1-6c. In an argon atmosphere, the TGA curves have similar features with a low-temperature weight loss between RT to 175 ºC followed by a slower weight loss between 175 ºC-400 ºC but the degree of weight loss increases with increasing Co²⁺ content. In air, the opposite effect is observed, where the thermal stability increases with increasing dopant amount. The FeOx has three weight loss regions as compared with the rest of the samples with a second, fast weight loss at around 300 ºC. This could be an indication of air atmosphere encouraging the loss of the strongly bound water (O_mw). The cobalt doped materials show a clear reverse behavior from the undoped material, where they are more stable in air atmosphere than in argon and this can be an indication of oxygen evolution.²⁴
H$_2$-TPR measurements were performed to investigate the effect of cobalt doping on the reducibility of FeO$_x$ (Figure 1-6d). The FeO$_x$ sample shows 2 major hydrogen consumption peaks. The first broad peak starts at $\sim$300 °C and is centered at $\sim$350 while the second broader peak starts at $\sim$450°C and is centered at $\sim$670°C. The first peak is related to the reduction of readily reducible surface oxygen while the second peak corresponds to bulk oxygen. In the H$_2$-TPR profile of the doped samples, both reduction peaks shifted to lower temperatures, indicating the higher reducibility of the doped materials.

Figure 1-6. a) N$_2$ sorption isotherms, b) BJH desorption pore size distributions, c) TGA analysis in air and argon, and d) H$_2$ -TPR of pure and cobalt doped amorphous iron oxide.
For Fe 2p (Figure 1-7a) FeO$_x$ has signals at 709.8 and 722.6 eV with a separation of 12.8 eV and a small satellite structure at ~734 eV that have all been reported for Fe$^{3+}$. We also observe a peak at ~708 eV that indicates Fe$^{2+}$. However, the Fe$^{2+}$ and Fe$^{3+}$ satellites overlap and, therefore, the satellite structure is completely obscured. When cobalt is doped the Fe$^{2+}$ shoulder at ~708 eV disappears and the Fe$^{3+}$ satellite at 720 eV becomes more prominent. On the other hand, deconvolution of O 1s spectra (Figure 1-7b) showed the existence of three different binding oxygen species, namely, structural or lattice oxygen (O$_s$), surface adsorbed oxygen (O$_{ads}$), and adsorbed water or hydroxyl groups (O$_{mw}$).

Figure 1-7. X-ray photoelectron spectroscopy (XPS) analysis: a) Fe 2p, b) Fe LMM, c) O 1s, and Co 2p deconvoluted XPS spectra of FeO$_x$ and X%Co-FeO$_x$ x=1, 3, and 5).
In comparison to the reference catalyst (FeO$_x$), the doped samples do not show a peak at ~533 eV. Table 1-2 shows the relative amounts of oxygen species with increasing cobalt content. All the cobalt doped samples show higher O$_s$ than O$_{ads}$ whereas the reference material shows the reverse (higher O$_{ads}$ than O$_s$). The deconvoluted O 1s spectra also suggest a predominance of lattice oxygen (O$_2$) near the surface of cobalt doped catalysts. The Co 2p transition could not be observed in XPS since the Fe LLM peak overlaps with the Co 2p region while using an Al anode. A Mg anode was utilized to shift the Fe LMM region so the Co 2p region could be observed even considering the low cobalt doping amounts in this study. The presence of cobalt was confirmed by the broadening of the Co LMM peak when cobalt is doped (Figure 1-7c) and XRF analysis (Table 1-1).

Table 1-2. The summation of the surface elemental compositions obtained from the deconvoluted high-resolution Fe 2p, and O 1s XPS spectra of the cobalt doped iron oxide samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe 2p3/2 peak position (eV)</th>
<th>ΔE Fe 2p (eV)</th>
<th>O$_{lattice}$ (530.1 eV) %Area</th>
<th>O$_{hydroxyl}$ (531.8 eV) %Area</th>
<th>O$_{mw}$ (533.6 eV) %Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO$_x$</td>
<td>709.8</td>
<td>12.8</td>
<td>38.1</td>
<td>54.2</td>
<td>4.97</td>
</tr>
<tr>
<td>1%Co-FeO$_x$</td>
<td>710.8</td>
<td>13.6</td>
<td>64.7</td>
<td>35.3</td>
<td>N/A</td>
</tr>
<tr>
<td>3%Co-FeO$_x$</td>
<td>710.9</td>
<td>13.5</td>
<td>80.4</td>
<td>19.6</td>
<td>N/A</td>
</tr>
<tr>
<td>5%Co-FeO$_x$</td>
<td>710.9</td>
<td>13.7</td>
<td>43.6</td>
<td>56.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 1-8. a) Magnetization vs. magnetic field (hysteresis loops) at 300 K, b) a) enlarged, c) Diffuse reflectance UV-Vis of the prepared samples, and d) Tauc plot from the DR-UV-Vis data.

Figure 1-8a presents the magnetization loop of pure and cobalt doped iron oxide at 300K. The magnetization values of the nano-magnetic materials are in general very sensitive to the particle size. The low value of magnetization in the present samples could be attributed to the small size of the iron oxide particles due to spin disorders. The total magnetization decreases with decreasing particle size, due to increasing dispersion on the exchange integral. This shows superparamagnetic properties, where each particle acts as a “spin” with suppressed exchange interaction between the particles.\textsuperscript{27,28} The coercivity field (H_c) and the magnetization (M) values of the present FeO_x are
89 G (1T = 10000 G) and 1.2 emu/g, respectively at an applied external magnetic field of 2 T. The $H_c$ and M values for the 3%Co-FeO$_x$ sample were 11 G and 2.4 emu/g, respectively under the same conditions and the M values were found to increase with increasing dopant loading up to the 3% loading amount (*Table 1-3*). The hysteresis for the 1%Co-FeO$_x$ and 5%Co-FeO$_x$ samples are very close to zero (*Figure 1-8b*) indicating the superparamagnetic behavior of these samples at room temperature. For these reasons, the present nanoparticles are small enough to exhibit superparamagnetic behavior. Diffuse reflectance UV-Vis spectra are shown in *Figure 1-8c*, and the Tauc plots are in *Figure 1-8d*. The samples show slight changes in the band gap with the 5%Co-FeO$_x$ sample showing the smallest band gap.

*Table 1-3.* The summary of the magnetic and optical properties of the pure and cobalt doped iron oxide catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic coercivity ($H_c$) Oe</th>
<th>Magnetization (Ms) (emu g$^{-1}$)</th>
<th>Anisotropy at 20000 Oe</th>
<th>Band gap from Tauc plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO$_x$</td>
<td>89</td>
<td>1.2</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>1%Co-FeO$_x$</td>
<td>N/A</td>
<td>2.1</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>3%Co-FeO$_x$</td>
<td>11</td>
<td>2.4</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td>5%Co-FeO$_x$</td>
<td>N/A</td>
<td>2.2</td>
<td>1.75</td>
<td></td>
</tr>
</tbody>
</table>
1.3.2 Photo-assisted peroxymonosulfate activation for Orange II dye degradation.

Figure 1-9. a) Adsorption capacity data, b) Dye degradation activity, c) Pseudo-first-order kinetics plots of degradation of orange II, and d) Comparison of reaction rates after different quenching conditions. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3

Figure 1-9a shows the adsorption capacities of the pure and Co-doped iron oxide. The adsorption capacity follows the same trend as the BET surface area where the high surface area material (FeOₓ) has a high capacity of 43 mg/g and the lower capacity was recorded for the lower surface area material (3%Co-FeOₓ) with 12 mg/g capacity. Figure 1-9b shows the dye degradation efficiency of the synthesized materials. Without PMS, the dye was not degraded instead being
adsorbed. When PMS was added and the reaction mixture kept in the dark, 20% of the dye was degraded within 15 minutes. When PMS was added and the reaction mixture placed in front of the xenon lamp, the cobalt doped catalysts showed exceptional activity for PMS activation. The FeO\textsubscript{x} only degraded about 40% of the dye after 20 minutes whereas the 1%Co-FeO\textsubscript{x} sample was the most efficient with 100% of the dye degraded within 1 minute.

![FTIR spectra of the 1% Co-FeO\textsubscript{x} before and after the reaction.](image)

**Figure 1-10.** FTIR spectra of the 1% Co-FeO\textsubscript{x} before and after the reaction.

**Figure 1-9c** shows the pseudo-first-order kinetic plot of dye degradation reactions by the pure and doped iron oxide. The corresponding rate constants are listed in **Table 1-4** with the apparent rate constant of 1%Co-FeO\textsubscript{x} being about 12 times that of the FeO\textsubscript{x}. Chen et al. utilized a 1000W Xenon
lamp for their system and achieved 100% degradation efficiency within 80 mins.\textsuperscript{29} Compared with other catalyst systems, the lamp power utilized in our system is slightly high and not monochromatic. \textsuperscript{3031}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{UV-Vis spectra of dye solution before and after 1 minute of degradation. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.}
\end{figure}

The degradation efficiency is influenced by the amount of catalyst loading. \textbf{Figure 1-12a} shows the degradation with varied catalyst loadings. At 0.025 g/L catalyst loading, 40% of the dye was degraded within a minute and as the loading was increased to 0.05 g/L 40% of the dye was degraded within a minute. Further increase in the catalyst loading showed fast kinetics for the degradation. The amount of PMS added was also optimized for the lowest loading with the highest
rate as shown in Figure 1-12b. The effect of calcination temperature was evaluated, and the degradation degree reduced with increasing calcination temperature (Figure 1-12c).

![Figure 1-12](image.png)

**Figure 1-12.** 1% Co-FeOx catalyst performance under different a) calcination temperatures, b) catalyst loading amounts, c) PMS loading amounts, and d) quenching agents. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.

In order to study the stability of the catalyst, seven cycle experiments were carried out under optimized conditions (Figure 1-13). The regenerated catalyst shows good performance and stability. Leaching is typically a major issue with the cobalt-mediated SR-AOP, hence the need for strategies to reduce leaching in heterogeneous catalysts applied in this process. Therefore, the
concentration of leached Co was as low as 0.12 -0.50 ppm (Table 1-4), which is well below the permissible level (1 ppm).\textsuperscript{33} Notably, the activity of the catalyst drops slightly after 3 cycles which is probably due to the loss of active sites through cobalt leaching.\textsuperscript{34} However, the removal efficiency of orange II is still high at 90%.

**Figure 1-13.** Consecutive runs to probe the reusability of the 1\% Co-FeOx catalyst. (The catalyst was recycled by filtration and washed thoroughly with DI water after each run and dried in a vacuum oven). Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.

ESI/MS data provide great insight into the degradation of Orange II dye. From **Figure 1-14**, the intensity of the PMS peak at 327 m/z drops drastically under the reaction conditions. With further
evaluation of the peaks as shown in Figure 1-15, there is an appearance of some new peaks over time.

Figure 1-14. ESI/MS plots of reaction solutions over 1%Co-FeO$_x$. The intensity of each plot has been adjusted to the same scale to clearly show the observed m/z.
Figure 1-15. ESI/MS plots of reaction solutions over 1%Co-FeOx. The intensity of each plot has NOT been adjusted to the same scale to clearly show the observed m/z.

Table 1-4. First-order kinetic parameters for degradation reactions by mesoporous iron oxides and turnover frequencies of catalysts. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and T = 298 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K \text{ min}^{-1}$</th>
<th>$R^2$</th>
<th>Co$^{2+}$ leaching amount</th>
</tr>
</thead>
</table>

28
<table>
<thead>
<tr>
<th>FeOx</th>
<th>0.030</th>
<th>0.945</th>
<th>n/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Co-FeOx</td>
<td>2.72</td>
<td>0.881</td>
<td>0.12</td>
</tr>
<tr>
<td>3%Co-FeOx</td>
<td>0.46</td>
<td>0.993</td>
<td>0.21</td>
</tr>
<tr>
<td>5%Co-FeOx</td>
<td>0.38</td>
<td>0.988</td>
<td>0.50</td>
</tr>
</tbody>
</table>

1.3.3 Reactive oxygen species

Radical trapping experiments were carried out to identify the reactive oxygen species present in the reaction system. The study focused on detecting $^1\text{O}_2$, $\text{O}_2^-$, $\cdot\text{OH}$, $\text{H}_2\text{O}_2$, and $\text{SO}_4^{\cdot-}$. Radical quenching experiments were conducted to identify the active radical species generated during PMS activation. As shown in (Figure 1-9d), if tert-butanol (TBA) or methanol (radical scavenger for $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$, respectively) were added into the reaction mixture,\textsuperscript{29} the orange II degradation efficiency decreased slightly, which indicates that they are not the only active species responsible for the observed degradation. However, when FFA, a unique scavenger for $^1\text{O}_2$,\textsuperscript{30} was added into the reaction system, the efficiency of orange II degradation was significantly reduced, suggesting the crucial role of singlet oxygen.
**Figure 1-16.** EPR spectra of a) $^1$O$_2$ spin trapping using TMP under in situ conditions, b) ex situ conditions, and c) ·OH spin trapping using BMPO under in situ and ex situ conditions. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and $T = 298$ K.

*Ex situ* studies were conducted and these involved analyses of the reaction mixture in the absence of the dye while *in situ* studies involved the dye solution. This presents an opportunity to evaluate the catalyst’s performance on its own and its performance with respect to dye molecules. Spin trapping experiments were conducted to trap the $^1$O$_2$ using TMP as spin traps and ·OH and SO$_4$$^-$$^-$ using BMPO. The TMP- $^1$O$_2$ adduct is observed in both *ex situ* (Figure 1-16a) and *in situ* (Figure 1-16b) conditions. *In situ* studies reveal a significant drop in the TMP- $^1$O$_2$ adduct signal when PMS was added to the reaction mixture followed afterwards by a typical signal. BMPO-OH and
BMPO-SO₄ adducts are not observed for *ex situ* and *in situ* conditions (Figure 1-16c). Following the above observations, a second detection method was used to observe the ROS.

¹O₂ was trapped using the fluorescent dye SOSG that provides a positive indication of the presence of singlet oxygen due to its very selective reactivity towards singlet oxygen.¹⁸ This study confirms that the catalyst can generate ¹O₂ in *ex situ* and *in situ* conditions (Figure 1-18a). The catalyst on its own in the presence of light generates singlet oxygen and in the presence of the dye (*in situ*) a lower intensity peak is observed. But when PMS is added into the reaction mixture, no singlet oxygen was trapped. This is consistent with the observation made when the spin trapping agent (TMP) was used. The presence of ·OH is confirmed by trapping with a fluorescent probe (APF).³⁵ The catalyst can generate a detectable level of ·OH when exposed to light and the amount of ·OH radical detected increases when PMS was added (Figure 1-18b). When the same test was conducted *in-situ* with the dye solution, no detectable amount of ·OH is observed. No ·OH radical is detected under dark conditions.
Leuco Crystal violet (CV)/horse radish peroxidase (HRP) was used to detect the generation of H$_2$O$_2$ in the absence of the dye (Figure 1-17). The test was not done in the presence of the dye since there is significant peak overlap between orange II dye and the crystal violet peak. The production of superoxide O$_2^-$ was measured using nitroblue tetrazolium (NBT). The reduction of the yellowish NBT into purple formazan derivatives results in an increase of the absorbance between 450 and 700 nm. A faint purple color was observed when the reaction mixture was irradiated for
a minute. But the concentration was too low to observe using the UV/Vis spectrometer. Even after longer exposure periods (30 minutes) the intensity was significantly higher.

![Fluorescence spectra](image)

**Figure 1-18.** Fluorescence spectra of a) SOSG fluorescence probe for the detection of $^{1}$O$_{2}$, and b) APF fluorescence probe for the detection of ·OH radical. Reaction condition: [Orange II] = 0.1 mM, [PMS] = 0.3 g/L, catalyst = 0.05 g/L, and $T = 298$ K.

### 1.4 Discussion

#### 1.4.1 Effect of cobalt doping on the structure of iron oxide.

In this study, cobalt doped mesoporous iron oxide was prepared based on a sol-gel method developed by our group.$^{17}$ The PXRD results suggest that the material’s amorphous structure and mesostructure are maintained after cobalt doping. No cobalt oxide related diffraction lines were observed during PXRD analysis, suggesting that either doping of cobalt into the iron oxide lattice or well-dispersed nano-oxide (polymeric form) clusters were produced on the surface of iron oxide. No cobalt oxide clusters can be detected in Raman spectroscopy analysis, which further supports that cobalt may enter the iron oxide lattice and substitute for part of the Fe$^{3+}$. The relatively similar ionic radius of cobalt (Co$^{2+} = 0.61$ Å) compared to iron (Fe$^{3+} = 0.64$ Å) makes
this substitution possible.\textsuperscript{16} The N\textsubscript{2} sorption results suggest the preservation of mesoporosity and high surface area with cobalt doping.

The morphology of the iron oxide nanoparticles changed with cobalt incorporation. TEM images of the doped samples reveal significant changes in the morphology and assembly of the nanoparticles as the amount of dopant increases from 1 to 5 mol %. Erwin et al.\textsuperscript{36} mention that adsorption of impurities is a key factor in the doping mechanism and is governed by three factors: morphology, nanocrystal shape, and surfactants in the growth solution. The adsorption energies will govern through which facet the doping will preferentially occur and the doping efficiency. Consequently, the energies of the facets along with their reactivities will be changed by either cobalt incorporation of cobalt species adsorbed on the surface. A possible side effect of the changes in reactivities would be anisotropic growth of nanoparticles. In the case of cobalt doped ZnO, the nanoparticle shape changed from spherical to triangular.\textsuperscript{37} This explains the morphology changes observed with increased cobalt doping amounts. These morphology changes could be responsible for the slight drop in surface area that is reported. The doping efficiency (confirmed by XRF data) is also low as would be expected due to a ‘self-cleaning mechanism’ that has been reported in the literature.\textsuperscript{36,38,39}

The transition to hematite has been reported to occur between 300 and 600 °C and the factors that determine the rate and the extent of ferrihydrite phase transition have been extensively studied. They involve pH, reaction temperature, inorganic and organic impurities, and temperature.\textsuperscript{40} In the TG-DSC curves, the exothermic peak appears due to excess energy release from the system which takes place during the phase transition from ferrihydrite to the \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} phase and the amount of energy released or absorbed during phase transition is represented by \(\Delta H\) which is the change in enthalpy. This indicates the possibility of a transition taking place in the system. In the present
case, the peak transition temperatures increasing with increasing dopant level can be explained by the fact that increasing cobalt content resulted in the system becoming more stable, thus requiring higher temperatures to drive a phase transformation. The changes in phase transformation temperature are consistent with the in situ XRD studies. In comparison, the FeO\textsubscript{x} and 1\%Co-FeO\textsubscript{x} samples required lower transformation temperatures (∼480 °C), whereas 3\%Co-FeO\textsubscript{x} and 5\%Co-FeO\textsubscript{x} require a higher transformation temperature (∼504°C).

The thermal stability of the materials increased with cobalt incorporation when heated in air atmosphere and the contrary is observed in an argon atmosphere. This suggests that the cobalt doped materials have labile oxygen that is not replenished; instead oxygen species are desorbed when the materials are heated in argon.\textsuperscript{24} High-resolution XPS O 1s spectra further confirm that FeO\textsubscript{x} has adsorbed water on the surface, unlike the doped samples which could be responsible for its lower stability in air atmosphere due to the desorption of water. Additionally, the undoped material undergoes a different mechanism of thermal decomposition since this material shows the best thermal stability under an argon atmosphere, a lower phase transformation temperature and a different surface oxygen composition.

The oxidation states of cobalt in the lattice could not be determined from XPS due to the low concentration of dopant however the increase in Fe\textsuperscript{3+} present from the 1\% to 5\% dopant is typically indicative of cobalt incorporation. The Fe 2p\textsubscript{3/2} primary photoelectron peaks of binding energies 709.8 eV and 710.8 eV are indicative of Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, respectively\textsuperscript{42}. The electronic configuration of Fe\textsuperscript{2+} is 3d\textsuperscript{6} whereas Fe\textsuperscript{3+} is 3d\textsuperscript{5}. This means that Fe\textsuperscript{3+} may have a shorter lifetime compared to Fe\textsuperscript{2+}; therefore, the FWHM of Fe\textsuperscript{3+} are expected to be slightly larger than the Fe\textsuperscript{2+} peaks. The satellite peak indicative of the presence of Fe\textsuperscript{3+} is 8 eV higher than the primary Fe\textsuperscript{3+} peak. The doped materials show the characteristic Fe\textsuperscript{3+} satellite peak while the undoped sample has a
broadened Fe 2p3/2 peak and the satellite peak is completely absent. This behavior was observed for a commercial Fe3O4 sample and was ascribed to the overlap of Fe2+ and Fe3+ satellite peaks.\textsuperscript{43} Since O2- is a weak-field ligand, this allows octahedrally oriented Fe2+ to have an overall high spin, resulting in a wider Fe 2p3/2 spectrum.\textsuperscript{44} For this reason, coupled with the increased doublet separation with cobalt doping, cobalt increases the Fe3+ character of the amorphous material. A look at the O 1s spectra further confirms that lattice oxygen amounts are increased with cobalt doping. These results suggest that the 1- 5% cobalt doped into the material had an effect on the surface redox properties of the material. The materials were therefore evaluated for SR-AOP.

### 1.4.2 Catalyst Performance

Visible-light-assisted PMS activation for orange II dye degradation was chosen as a model system to verify surface modification by cobalt doping. The adsorption capacity (mg dye/g catalyst) of mesoporous amorphous iron oxide in this study is 43 mg/g which is close to the previously reported value and this has been attributed to the large surface area of this material. As the surface area is decreased with the increasing cobalt doping levels, the adsorption capacity also decreases.\textsuperscript{5} A continuous increase in reaction kinetics with increased catalyst loading was observed and indicates the absence of mass transfer limitations or adsorption.

**Table 1-5.** Catalytic performance comparison of recently reported Visible-light-assisted PMS activation.

<table>
<thead>
<tr>
<th>Catalyst (loading, g L\textsuperscript{-1})</th>
<th>PMS (mM)</th>
<th>Pollutant (mM/ mg/L\textsuperscript{a})</th>
<th>Removal Efficiency</th>
<th>Rate constant (min\textsuperscript{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon [0.75]</td>
<td>8</td>
<td>2,4,6-trichlorophenol (5)\textsuperscript{a}</td>
<td>&gt;65</td>
<td>0.0521</td>
<td>57</td>
</tr>
<tr>
<td>Co/Al2O3 [0.25]</td>
<td>1</td>
<td>2,4,6-trichlorophenol (0.1)\textsuperscript{a}</td>
<td>100</td>
<td>n.d</td>
<td>58</td>
</tr>
</tbody>
</table>
The cobalt doped amorphous iron oxide catalyst exhibited higher reactivity, as high as 100% degradation in 1 min, than the FeO\textsubscript{x}. To verify the role of Co, samples with various amounts of cobalt were synthesized. Reactivity did not increase with increasing cobalt loading, instead, the reactivity decreased with decreasing surface area (a measure of active site density). This suggests that the adsorption of orange II on the surface of the material is a key component of the reaction kinetics as observed in many prior dye abatement studies. But the surface area isn’t the only...
determining factor since the FeOₓ material having the highest surface area still had a lower performance in this reaction.

Lattice oxygen content and lack of adsorbed H₂O may also be important. Adsorbed water can have negative effects on the reactivity of catalysts since there is active site competition between the water molecules and the substrate. This was not the case for the adsorption of the orange II molecule but could be the case for the PMS ions. In this case, two major components for the reactivity are important; the orange II adsorption and PMS adsorption. The impact of lattice oxygen was further studied by utilizing 1%Co-FeOₓ catalyst calcined at higher calcination temperatures. An increase in calcination temperature increases lattice oxygen content but lowers the surface area of mesoporous materials synthesized using this method.¹⁷ The performance was enhanced when compared with the FeOₓ material and the higher dopant level samples. These higher lattice oxygen content samples also required higher PMS loading amounts judging by the fast kinetics at the beginning followed by an equilibration which is characteristic of lower PMS or the lower catalyst loadings studied during the optimization reaction conditions.

To examine the charge separation and electron hole pair recombination rate of the catalysts, PL and photocurrent were measured (Figure 1-19). Transient photocurrent response was investigated under visible light irradiation at 0.6 V (Ag/AgCl). The photocurrent value was higher for 1%Co-FeOₓ than FeOₓ, implying that the doped sample has a higher electron-hole separation efficiency and a lower recombination rate. FeOₓ and 1%Co-FeOₓ have similar PL spectra while the FeOₓ peak is of a higher intensity. This suggests that the introduction of Co into the iron oxide structure has enhanced the electron-hole pair separation capacity, therefore offering an advantage in the migration and separation of photogenerated charge.
Figure 1-19. (a) The transient photocurrent response of FeOₓ and 1% Co-FeOₓ catalyst electrodes with light on–off cycles under visible light irradiation [Na₂SO₄] = 0.1 M. (b) Photoluminescence spectra of FeOₓ and 1% Co-FeOₓ.

The balance between Co²⁺/Co³⁺, O²⁻/O₂, PMS, and Orange II is crucial for the activity enhancement between the undoped vs the doped samples. The increased reducibility and increased labile lattice oxygen suggest a replenishment cycle for the Co²⁺/Co³⁺ redox cycle since the reduction of Co³⁺ by Fe²⁺ is thermodynamically feasible. Other studies show that the introduction of dopants introduces defect sites, inhibiting the recombination of photoinduced holes and electrons. Oₐ and O_ads are important for the generation of reactive oxygen species. The labile lattice oxygen will be utilized to regenerate oxygen vacancies generated during the reaction and are replenished. Reactive oxygen species were studied to give an insight into the surface redox chemistry as well as the mechanism of the reaction.

Table 1-6. Observed degradation products from ESI-MS fragmentation patterns.

<table>
<thead>
<tr>
<th>Entry</th>
<th>m/z</th>
<th>Proposed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>327</td>
<td><img src="image" alt="Proposed structure" /></td>
</tr>
</tbody>
</table>
1.4.3 Reactive Oxygen Species

Comparing the redox potentials puts into perspective which redox cycles are feasible. Co$^{2+}$/Co$^{3+}$ redox pair (1.80 V) and PMS has a redox potential of HSO$_5^-$/SO$_4^{2-}$ (1.82 V) and HSO$_5^-$/SO$_5^{2-}$ (1.1 V) which are slightly higher with respect to SO$_4^{2-}$ and would require a low overpotential to drive the reaction. However, the Fe$^{2+}$/Fe$^{3+}$ redox pair (0.8 V), shows a negative redox potential of -0.3 V vs HSO$_5^-$/SO$_5^{2-}$ which results in a thermodynamically unfavorable redox cycle. This one electron donating potential can initiate the one-electron reduction of PMS leading to the generation of ROS.

Radical quenching experiments were used to identify the active radical species generated during the process. When methanol (•OH and SO$_4^{2-}$ scavengers) and TBA (•OH scavenger) are added to the reaction, there was no effect on the kinetics of the reaction. While when FFA (1O$_2$ scavenger) was added, orange II degradation efficiency was significantly reduced, suggesting a crucial role played by singlet oxygen. Singlet oxygen was detected using two distinct methods. Ex situ EPR spin trapping confirmed that the 1%Co-FeO$_x$ material generates singlet oxygen in the dark both in the absence and presence of PMS with a higher signal for the latter. Typically, this signal is taken as a good indication for the presence of singlet oxygen. Considering the fast rate of reaction and disregarding the role of the orange II dye, in situ studies would be more informative. In situ studies further indicate that when the dye and PMS are present in the dark, 1O$_2$ is generated and the peaks being broader indicate a higher amount of singlet oxygen as well as a broad distribution. Immediately after the mixture is exposed to light, the signal drops drastically, which is an indication of 1O$_2$ consumption. After the first minute, most of the dye has been degraded and the signals resemble those of the ex situ study. •OH, and SO$_4^{2-}$ were not detected using BMPO. APF
has been shown to be a very good indicator for the presence of *OH and is more sensitive.\textsuperscript{51} This method confirmed that the catalyst can generate *OH in the presence and absence of PMS. In situ studies suggest that the *OH radical isn’t generated. \textsuperscript{1}\textsubscript{O}_2 is also confirmed by the SOSG probe but the singlet oxygen signal is highest in the absence of the dye. From EPR and fluorescence trapping methods the same behavior is observed with ROS being absent when light is introduced. Two things may be occurring at that moment, i) the ROS are consumed at a rate higher than their reactions with the trapping agents and, ii) there is a change in the dominant mechanism and ROS are not generated at that moment. Yun et al.\textsuperscript{52} recently suggested that singlet oxygen generated during PMS activation is a minor route for the activation.

### 1.4.4 Mechanistic Ideas

The above-mentioned experimental data led to the proposal of a mechanism to explain the present catalytic protocol. Visible light introduces a level of complexity to the mechanism of degradation. First, the catalyst will absorb visible light and electrons will be excited from the valence band to the conduction band of the material. Notably, iron oxide suffers increased recombination of the photogenerated holes, and that recombination occurs predominantly via surface states associated with other sites on the surface that are effectively ‘passivated’ by the adsorption of cobalt.\textsuperscript{53,54} Therefore, cobalt improves electron transfer in the material. Second, visible light cannot activate PMS but orange II dye can be excited and undergo intersystem crossing (ISC) to the corresponding triplet state with transition energy (\textit{\Delta E}) of 0.29 eV. The photosensitization of orange II can accelerate the Co\textsuperscript{3+/2+} catalytic cycle as well as the reactions with the ROS, specifically singlet oxygen.\textsuperscript{55}

Recently, reports have suggested a nonradical mechanism as the major pathway of PMS activation. Three dominant pathways such as electron transfer between surface activated complex (or surface-
bound radicals), electron transfer (between the adsorbed pollutant and the adsorbed oxidant), and the involvement of singlet oxygen exist. All three of the pathways are likely in the current system and most likely a combined mechanism occurs. The quenching studies suggest that singlet oxygen plays a dominant role in this system. This activity enhancement is achieved by a simple doping strategy that balances maintaining structural integrity while altering electronic and catalytic properties. Figure 1-20 summarizes this proposed mechanism.

Figure 1-20. Proposed mechanism of PMS activation for orange II dye degradation on cobalt doped mesoporous iron oxide.

1.5 Conclusions

In summary, we demonstrate efficient visible-light assisted PMS activation for orange II degradation on cobalt doped mesoporous iron oxide. The effects of cobalt doping on the structure are confirmed by SEM, TEM, UV-Vis, Raman, XPS and magnetism studies. The high surface area maintained during this study led to high adsorption capacities observed for the doped materials (27.4 mg orange II/g cat for 1%Co-FeO₃), which is more than half the undoped material (42.9 mg orange II/g cat). The best catalyst is 91 times more active than the undoped material, suggesting
that cobalt had more than just a structural effect on the material. The combined effect of multivalent metal species and lattice oxygen were critical for the enhanced activity. ROS studies were conducted using two distinct methods and helped to support a plausible mechanism while radical scavenging studies elucidated the dominant mechanism. Singlet oxygen is the active species. Our study details the first heterogeneous visible -light-assisted PMS activation on iron oxide with low cobalt loading. The results indicate that the combination of cobalt doping and visible light assistance is a viable approach towards water remediation with high activity. We anticipate that our ROS studies will shed light on the development of other activated PMS systems.

1.6 References


(28) Montha, W.; Maneepakorn, W.; Buatong, N.; Tang, I. M.; Pon-On, W. Synthesis of Doxorubicin-PLGA Loaded Chitosan Stabilized (Mn, Zn)Fe₂O₄ Nanoparticles: Biological Activity and PH-


Chapter 2. Photo-assisted Selective Acetonitrile Catalytic Oxidation On Octahedral Molecular Sieve (K-OMS-2)

2.1 Introduction

Based on worldwide production of 8 billion pounds per year of acrylonitrile, about 3 to 4% acetonitrile is generated. Acetonitrile is generated as a by-product of the catalytic ammoxidation of propylene and ammonia to acrylonitrile. Because of its relatively high chemical stability, acetonitrile has found limited application as a chemical intermediate, in turn, they are safe organic solvents. Only in the presence of powerful catalysts and rigorous conditions do they undergo chemical reactions under solvent conditions. Recently, the hydrolysis of nitriles has become of interest because the amide bond is present in proteins and is essential for the sustenance of life. Nitriles are a synthetically versatile synthons distributed in several biologically active molecules. The nitrile group is mechanistically interesting kinetically inert, and thermodynamically unstable. The complete hydrolysis to acetic acid and ammonia is typical and follows a two-step pathway where acetonitrile is first hydrolyzed to acetamide then further hydrolyzed to acetic acid. The rate of amide hydrolysis is faster than nitrile hydrolysis in hydrating environments.

Conversion of acetonitrile into acetamide has been studied for many transition metal catalysts such as ruthenium, gold, copper, as well as alloys. Transition metal-catalyzed systems have shown high selectivity for the amide formation with manganese oxide showing excellent selectivity. Battilocchio et al. demonstrated a mild and selective approach utilizing manganese dioxide in a flow system. Whereas, Mehta et al. demonstrated a photocatalytic approach in both neutral and basic media. Although ammonia generated during the over hydrolysis to acetic acid can poison the catalyst’s acid sites, acetamide, on the other hand isn’t innocent either. Acetamide
bound to the surface will require higher desorption energy than acetonitrile. Barbosa et al. demonstrated that the type of medium could lower the acetamide desorption energy. More specifically, a water medium works to lower desorption energy.\textsuperscript{17,18}

Herein, we report photo-assisted selective acetonitrile oxidation under conditions utilizing oxygen as the oxygen source. The catalyst shows 100\% selectivity towards acetamide with a 15\% conversion. The mechanism was studied using KIE studies and isotope scrambling. The material synthesis method played a key role in the activity of the best material. This study evaluates the kinetics of the reaction and an inverse secondary kinetic isotope effect was observed. The roles of lattice oxygen, dissolved oxygen, and light have been discussed. On top of this, the adsorption of the reactant and desorption of the product are discussed and are also key to driving the reaction.

The best catalyst (K-OMS-2\textsubscript{REF}) is stable and reusable up to 6 cycles.

2.2 Experimental Section

2.2.1 Chemicals

All chemicals were used as received without further purification. All chemicals used were reagent-grade. Potassium permanganate (KMnO\textsubscript{4}), manganese sulfate (MnSO\textsubscript{4}), cobalt(II) nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, \geq98.0\%), 1-butanol (anhydrous, 99.8\%), and poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) PEO\textsubscript{20}−PPO\textsubscript{70}−PEO\textsubscript{20} (Pluronic P\textsubscript{123}) were purchased from Sigma-Aldrich. Concentrated nitric acid (68\%−70\% HNO\textsubscript{3}) and concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) were purchased from J. T. Baker.
2.2.2 Catalyst Synthesis

Preparation of meso-\(\text{MnO}_x\). Amorphous mesoporous manganese oxide was synthesized using the procedure of Poyraz et al.\(^1\) In a typical synthesis, 5.0 g (0.02 mol) of \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) was dissolved in a solution containing 14 g (0.188 mol) of 1-butanol, 2 g (0.032 mol) of \(\text{HNO}_3\) and 2 g (3.44x10\(^{-4}\) mol) of P\(_{123}\) surfactant in a 150 ml beaker at room temperature (RT) and under magnetic stirring. The obtained clear gel is placed in an oven at 120 °C for 4 h. The obtained powder was washed several times with ethanol and then the powder is centrifuged. Finally, the powder is dried in a vacuum oven overnight. The dried powder was heated to 150 °C for 12 h followed by 250 °C for 3 h under air atmosphere.

Preparation of meso-\(\text{Co}_3\text{O}_4\). Briefly, 5 g (0.017 mol) of \(\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) was dissolved in a solution containing 17 g (0.33 mol) of 1-butanol, 2.4 g (0.038 mol) of \(\text{HNO}_3\), and 2.5 g (4.31 \times 10^{-4} \text{ mol}) of P\(_{123}\) in a 400 mL beaker. After magnetic stirring at room temperature, a clear gel was formed. The clear gel was then placed in an oven at 120 °C for 3.5 h. The obtained powder was washed with ethanol several times, centrifuged, and dried in a vacuum oven. The powders were calcined at 150 °C for 12 h and further heated to 250 °C for 1 h with a heating rate of 1 °C/ min under air.\(^2\)

Preparation of \(\text{KOMS-2SF}\). In general, 9.48 g (0.06 mol) of \(\text{KMnO}_4\) and 22.05 g (0.09 mol) of \(\text{Mn(Ac)}_2\cdot4\text{H}_2\text{O}\) powders were mixed and ground homogeneously in a mortar. The mixed powders were then placed in a capped glass bottle and maintained at 80 °C for 4 h. The resulting black product was thoroughly washed with deionized water several times to remove any ions which may remain in the product and finally dried at 80 °C in a vacuum oven overnight.\(^3\)

Preparation of \(\text{KOMS-2HT}\). A typical synthesis was as follows: 5.89 g of \(\text{KMnO}_4\) in 100 mL of water was added to a solution of 8.8 g of \(\text{MnSO}_4\cdot\text{H}_2\text{O}\) in 30 mL of water and 3 mL concentrated
HNO₃. The solution was refluxed at 100 °C for 24 h, and the product was filtered, washed, and dried at 120 °C.

*Preparation of AMO.* Eighty ml of a KMnO₄ solution (0.01 M) was added to 100 ml of a 0.25 M oxalic acid solution which led to an exothermic reaction. A dark brown precipitate is formed in a period of 30 min. The precipitate is washed with distilled deionized water, and dried in a vacuum oven overnight.²²

*Preparation of K-OMS-2REF.*

Briefly, a 0.4 M solution of KMnO₄ (13.3 g in 225 mL of distilled, deionized water) was added to a mixture of a 1.75 M solution of MnSO₄·H₂O (19.8 g in 67.5 mL of DDW) and 6.8 mL of concentrated H₂SO₄. The resulting black precipitate was stirred vigorously and refluxed at 373 K for 24 h. The precipitate was filtered and washed with DDW until neutral pH and dried overnight at 393 K. This gave the K⁺ form of OMS-2.²³ The main difference in the synthesis is the use of sulfuric acid instead of Nitric acid.

### 2.2.3 Catalyst Characterization

Powder XRD data were collected on a Rigaku UltimaIV instrument using Cu Kα (1.54 Å) radiation at a beam voltage of 40 kV and a 45 mA beam current. Wide-angle patterns were obtained by continuous scans in a 2θ range of 5–75° with a scan rate of 2°/ min. The surface areas, pore size distributions, and pore volumes of manganese oxide catalysts were determined in a Quantachrome Autosorb-1-1C automated adsorption system. The samples were treated at 150°C for 6 h under helium prior to measurement. The isotherms of N₂ at 77 K were obtained from physisorption. The pore size distributions were determined from the N₂ desorption isotherms at 77 K, using the NL-DFT method. Field-Emission Scanning Electron Microscope (FE-SEM) and Elemental Dispersive X-Ray Spectroscopy (EDS) were taken on an FEI Nova NanoSEM 450 and Oxford 553 EDS.
Raman spectra were obtained using a Renishaw 2000 Ramascope which has an optical microscope (0.024 in. focus length), graphic grating (1800 mm−1), and CCD detector. A laser excitation source with 514 nm wavelength was used. For each sample, three different locations were analyzed to verify the spectra.

2.2.4 Catalytic Reaction Condition

One mL of acetonitrile was put in a small vial with 25 mg of catalyst being added and this mixture was covered with a lid with a septum. A balloon was filled with pure oxygen and bubbled into the liquid for 5 minutes. The reaction mixture was irradiated by a 1000 W Xenon lamp was used as a light source with wavelength \( \lambda > 400 \) nm.

2.3 Results

2.3.1 Catalytic Characterization

Wide-angle Powder X-Ray Diffraction (WA-PXRD) patterns of the synthesized materials are displayed in Figure 2-1. Meso-MnO\(_x\) showed the typical UCT manganese oxide amorphous pattern\(^{19}\) while meso-Co\(_3\)O\(_4\) had a typical spinel Co\(_3\)O\(_4\) crystalline pattern (JCPDS 09-0418). The PXRD pattern of the K-OMS-2\(_{SF}\), K-OMS-2\(_{HT}\), and K-OMS-2\(_{REF}\) materials was indexed to a tetragonal cryptomelane phase characteristic of the octahedral molecular sieve material K-OMS-2 (JCPDS 29-1020).\(^{24,25}\) No impurity peaks were observed.
Figure 2-1. Powder X-ray diffraction patterns of the synthesized catalysts.

FTIR spectra match those reported in the literature\textsuperscript{26-29} as shown in Figure 2-2. The sample exhibits the vibrational modes characteristic of K-OMS-2 between the range of 400 to 800 cm\textsuperscript{-1}. The Raman spectrum (Figure 2-2b) features three characteristic peaks at around 635 cm\textsuperscript{-1}, 325 cm\textsuperscript{-1}, 170 cm\textsuperscript{-1}, and a shoulder at 580 cm\textsuperscript{-1}.\textsuperscript{28} The weak shoulder band around 580 cm\textsuperscript{-1} and strong band at approximately 635 cm\textsuperscript{-1} correspond to the stretching modes of Mn-O while the first two (325 and 170 cm\textsuperscript{-1}) to the deformation mode of the Mn-O-Mn chain.\textsuperscript{30}
Nitrogen sorption experiments show that K-OMS-2\textsubscript{REF} catalyst has a surface area of 76 m\textsuperscript{2}/g, a high pore volume of 0.56 cm\textsuperscript{3}/g, and 25 nm pore size. Figure 2-2c shows the N\textsubscript{2} adsorption-desorption isotherm of the as-synthesized K-OMS-2. The material exhibits a type II adsorption isotherm according to the IUPAC classification with micropore filling at low P/P\textsubscript{0} while at higher P/P\textsubscript{0} a multilayer of adsorption occurs. The isotherm hysteresis loop can be classified as H3 since the adsorption branch resembles a type II isotherm and the lower limit of the desorption branch is located at the cavitation-induced P/P\textsubscript{0}.\textsuperscript{31} The pore size distribution (Figure 2-2d) shows that the pore diameter of the as-synthesized K-OMS-2 is 25 nm with a broad distribution.
Morphology studies K-OMS-2REF were conducted using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As shown in Figure 2-3, the material exhibited a fine and uniform nanorod shape. The nanorods exhibit well-defined lattice fringes as shown in Figure 2-3b. The spacing of the lattice fringes is 0.48 nm, corresponding to the (200) plane of the cryptomelane structure. The EDX analysis confirms the presence and uniform distribution of Mn, K, and O throughout the material.

![Figure 2-3](image)

**Figure 2-3.** a) Transmission Electron Microscopy (TEM) micrographs, b) enlarged TEM image of the boxed area, c) Scanning Electron Microscopy (SEM) image, and d) SEM-EDX analysis of K-OMS-2REF catalyst.

### 2.3.2 Catalytic Reaction Condition

Different metal oxide catalysts were evaluated for the selective photo-assisted oxidation of acetonitrile. *Table 2-1* shows the conversions and selectivity of the different catalysts. Among the
manganese oxide materials evaluated, K-OMS-2 type materials performed better than the meso-
MnO\textsubscript{x} and Amorphous Manganese Oxide (AMO). Cobalt oxide showed lower catalytic activity as
compared to the K-OMS-2 type material. The highest conversion was observed for the K-OMS-2
synthesized by the above-mentioned method with a conversion of 15%. All the materials tested
showed a high selectivity of $>$99\% for acetamide. When the catalyst loading was changed from 25
mg to 100 mg (Table 2-1, Entries 6-8), no increase in conversion is observed and the selectivity
still remains at 100%.

**Table 2-1.** Photo-assisted acetonitrile oxidation using different metal oxide catalysts and varied catalyst
loading.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Catalyst (25mg)</th>
<th>Conversion (%)\textsuperscript{b}</th>
<th>Selectivity I (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Meso-MnO\textsubscript{x}</td>
<td>0.1</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>2.</td>
<td>Meso-CoO\textsubscript{x}</td>
<td>1.5</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>3.</td>
<td>K-OMS-2\textsubscript{SF}</td>
<td>5</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>4.</td>
<td>K-OMS-2\textsubscript{HT}</td>
<td>3</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>5.</td>
<td>AMO</td>
<td>0</td>
<td>n.d</td>
</tr>
<tr>
<td>6.</td>
<td>K-OMS-2\textsubscript{Reflux}</td>
<td>15</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>7.</td>
<td>K-OMS-2\textsubscript{Reflux}\textsuperscript{d}</td>
<td>15</td>
<td>$&gt;$ 99</td>
</tr>
<tr>
<td>8.</td>
<td>K-OMS-2\textsubscript{Reflux}\textsuperscript{e}</td>
<td>15</td>
<td>$&gt;$ 99</td>
</tr>
</tbody>
</table>
Conversions and selectivity were determined by GC-MS. Different catalyst loadings where \(^{c}\) 25 mg catalyst, \(^{d}\) 50 mg and \(^{e}\) 100 mg of the catalyst were used. Acetamide was not formed in the absence of light and while under wavelengths higher than 500 nm (Table 2-2, Entries 1,2). Notably, the conversion is significantly lower when the light is restricted to the visible region (>400 nm). No product was observed in an argon atmosphere (Table 2-2, Entry 5). The highest activity was observed under an oxygen environment.

**Table 2-2.** Photo-assisted acetonitrile oxidation using K-OMS-2\(_{\text{REF}}\) catalyst under varied conditions.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Conditions</th>
<th>Conversion (%)(^{b})</th>
<th>Selectivity I (%)(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No Light</td>
<td>0</td>
<td>n.d</td>
</tr>
<tr>
<td>2</td>
<td>&gt;500 nm</td>
<td>0</td>
<td>n.d</td>
</tr>
<tr>
<td>3</td>
<td>&gt;400 nm</td>
<td>5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>No cut-off filter</td>
<td>15</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>Argon</td>
<td>0</td>
<td>n.d</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction condition: Acetonitrile (1 mL), RT, Catalyst- 25 mg, 2 hours, Visible light, ice bath. \(^{b}\) 500nm cut off filter, \(^{c}\) 400 nm cut-off filter. \(^{d}\) Conversions and selectivities were determined by GC-MS.

Subsequently, the reaction conditions were applied to different substrates to assess the scope and limitations of the protocol. Acrylonitrile was oxidized to acrylamide under the same conditions while trichloroacetonitrile was over-oxidized to trichloroacetic acid. Malonitrile was not
hydrolyzed under similar conditions. The conversion was slightly lower in the presence of CD$_3$CN and in a 1:1 mixture of CD$_3$CN: CH$_3$CN (Table 2-3, entries 4,5). When water was added to the reaction, the conversion was similar to the reaction in the absence of water (Table 2-3, entry 6). The conversion is still maintained at 15% in the absence of N$_2$ (Table 2-3, entry 7).

Table 2-3. Photo-assisted acetonitrile oxidation using K-OMS-2REF catalyst using different substrates and conditions.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Substrate</th>
<th>Conversion (%)$^b$</th>
<th>Selectivity I (%)$^b$</th>
<th>Selectivity II (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acrylonitrile</td>
<td>5</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Trichloroacetonitrile</td>
<td>10</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3.</td>
<td>Malonitrile</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>CD$_3$CN</td>
<td>15</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>CD$_3$CN/CH$_3$CN$^c$</td>
<td>15</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Acetonitrile/H$_2$O$^d$</td>
<td>15</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>Acetonitrile/H$_2$O/N$_2$</td>
<td>15</td>
<td>&gt;99</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Reaction condition: Acetonitrile (1 mL), RT, K-OMS-2REF- 25 mg, 2 hours, Visible light.  $^b$ Conversions and selectivity were determined by GC-MS.  $^c$ 1:1 mixture of acetonitrile to deuterated acetonitrile.  $^d$ 4:1 mixture of acetonitrile to H$_2$O.

Reaction kinetics under reaction conditions were investigated and were fitted to first-order kinetics with a rate constant of 0.0023 min$^{-1}$. The rate of the reaction was also evaluated using deuterated acetonitrile (CD$_3$CN) and a rate constant of 0.00188 min$^{-1}$ was calculated. An evaluation of the
rate of the kinetics of the reaction reveals the rate of the reaction (Figure 4). An inverse secondary kinetic isotope effect is calculated, $K_{H}/K_{D}=0.814$.

Figure 2-4. Kinetics of the photo-assisted acetonitrile and deuterated acetonitrile

Figure 2-5 shows mass spectrometry data for the acetamide peak when the reaction was run using CH$_3$CN, CD$_3$CN and a 1:1 mixture of CH$_3$CN and CD$_3$CN. Oxidation of deuterated acetonitrile (CD$_3$CN) gave a deuterated acetamide (CD$_3$CONHD and CD$_3$COCD$_2$) with a mass to charge ratio (m/z) of 63 amu and 64 amu respectively. In the 1:1 mixture of acetonitrile to deuterated acetonitrile, two main products are observed, CH$_3$CONH$_2$ (m/z =59 amu) and CD$_3$CONH$_2$ (m/z = 62 amu). There is a peak at 60 amu, suggesting the presence of acetamide with one of the hydrogens substituted by a deuterium atom. Another peak was observed at 63 amu.
Figure 2-5. Mass-spectrometry fragmentation patterns of (from the top) CH$_3$CONH$_2$ in CH$_3$CN, CD$_3$CONH$_2$ in CD$_3$CN and (bottom) CH$_3$CONH$_2$ and CD$_3$CONH$_2$ in a mixture of CH$_3$CN and CD$_3$CN. Y-axis is relative abundance.

Hot filtration after 20 minutes of the reaction (about 7% conversion) was conducted. The resulting filtrate was then subjected to reaction conditions for an additional 90 min. Aliquots were collected successively after each hour and were analyzed with GC-MS to track the progress of the reaction. No further improvement in conversion was observed, indicating the reaction is completely heterogeneous. In the event that manganese ions leach from the catalyst, they are not responsible for the activity observed. To verify reusability, the retrieved catalyst was washed with ethanol and dried in a vacuum oven overnight. The catalyst was reactivated after this cleaning and drying procedure. As evidenced from Figure 2-6, there was no significant drop in the catalytic activity. Therefore, the catalyst can be considered heterogeneous, stable, and reusable.
Figure 2-6. a) Effect of removal of catalyst on the reaction. Conditions: Acetonitrile (1 mL), RT, K-OMS-2REF-25 mg, 2 hours, Visible light. b) Reusability test of the K-OMS-2REF catalyst.

Figure 2-7. a) FTIR and b) Thermogravimetric analysis (TGA) of the K-OMS-2REF catalyst before and after the reaction.

FTIR analysis of the fresh K-OMS-2REF catalyst as compared to the used catalyst (Figure 2-7a) shows the existence of adsorbed acetamide, which has absorptions at 1651, 1594, 1531, 1406, and 1330 cm⁻¹, and OH and NH groups around 3100-3600 cm⁻¹.²²,²³ Additionally, the catalyst has a
lower thermal stability after the reaction and this is an indication of the loss of adsorbed species on the surface of the catalyst being desorbed during heat treatment.

### 2.4 Discussion

Octahedral molecular sieve materials have been utilized for selective catalytic organic transformations. Such transformation can be achieved through different stimuli such as heating (thermal), ultrasound, microwave, and light. K-OMS-2 has been used for oxidation of ethanol and acetaldehyde\(^\text{34}\), benzyl alcohol oxidation\(^\text{23}\), primary amines to primary amides\(^\text{35}\), thermal and photo-assisted isopropanol oxidation to acetone\(^\text{36,37}\), and photochemical water oxidation\(^\text{38}\). Additionally, K-OMS-2 type materials have been synthesized using different methods to date, such as sol-gel, high-temperature, hydrothermal, microwave, phase-transfer, solvent-free, reflux, among others\(^\text{39}\).

As illustrated in **Table 2-1**, this system exhibits high selectivity (100%) for the photo-assisted oxidation of acetonitrile. Manganese oxide has been reported to have higher activity towards this reaction. However, the results seem to indicate that crystalline manganese oxide materials are better than amorphous materials (i.e. AMO and Meso-MnOx) and even if the materials are crystalline, the synthesis method is also key. The findings of this study clearly show that acetonitrile was selectively oxidized to acetamide by the K-OMS-2 catalyst synthesized by the reflux method. Other catalysts applied to the same reaction did not convert acetonitrile to the same magnitude as K-OMS-2\textsubscript{REF}. The K-OMS-2\textsubscript{REF} material properties matched the ones reported in the literature\(^\text{23}\), but its catalytic activity towards acetonitrile oxidation stood out. Catalytic studies suggest that each of these different chemical preparation methods can lead to materials that are not exactly the same\(^\text{40}\). The average oxidation number that represents the ratio of Mn\(^{2+}\), Mn\(^{3+}\), and
Mn$^{4+}$ influences the strength of Lewis acidity of the catalysts and may play a role in the activity observed. However, a detailed investigation to relate the catalytic activity to their properties is still in progress. Furthermore, increasing the catalyst amount did not lead to a proportional increase in product yield, presumably due to the reaction approaching equilibrium.

Previous studies have reported that higher manganese valence could lead to higher CO oxidation rates over Cu(Co, Ag)-OMS-2 catalysts, in nitrous oxide abatement, and producing high yields in the synthesis of quinoxalines. The reaction reported here does not proceed in the absence of oxygen. However, added H$_2$O can also act as a source of oxygen. When H$_2$O was added and oxygen removed by bubbling nitrogen, the reaction proceeded in a similar manner as with oxygen. The catalyst shows no activity in the absence of oxygen. This suggests that oxygen plays an important role in this reaction. Previous mechanisms suggest that the lattice oxygen or surface hydroxyl groups form excited oxygen species in the presence of irradiation due to oxygen mobility from the manganese oxide structure. These species bring about the oxidation reaction of the acetonitrile. The replenishment of these species seems important to driving the reaction forward, therefore, another source of oxygen is required (H$_2$O and molecular oxygen). Three key steps hypothesized to be involved are electron transfer due to light adsorption by K-OMS-2$_{REF}$, reduction of the manganese species, and the consumption of lattice oxygen that is then replenished by dissolved oxygen. This is similar to the Mars–van Krevelen mechanism of selective oxidation over transition metal oxides.

Along with the above-mentioned steps, the adsorption of the reactant molecule and its subsequent desorption are very important for driving the reaction forward. This behavior indicates that acetamide-like species are less sensitive to photo-oxidation than acetonitrile adsorbed in molecular
form. These species can exhibit a poisoning effect towards part of the photocatalytic surface sites.\textsuperscript{44} The adsorbed trichloroacetamide was further oxidized to trichloroacetic acid. This is because the acyl carbon is more susceptible to nucleophilic substitution. When the catalyst was washed with ethanol and reused, the activity was fully restored up to 6 times (Figure 7b). This indicates that the poisoning species can be removed easily and the catalyst reused. The hot filtration analysis suggests that the catalyst is stable during the reaction and no leaching occurs during the reaction. TGA analysis before and after the reaction shows a greater weight loss due to the desorption of the adsorbed species.

A study of the kinetic isotope effect revealed an inverse secondary kinetic isotope effect with $K_{H}/K_{D}=0.814$. Typically, there are three reasons associated with a KIE that are <1. The first effect is associated with surface crowding. Since the C-D bond is shorter than the C-H bond. This could lead to a less crowded active site, resulting in a less hindered pathway for reactants to diffuse to the metal oxide surface. As a result, the less bulky CD$_3$CN allows for more adsorption of the reactants as compared to CH$_3$CN. The second reason is the change in hybridization during the rate-determining step. The $\alpha$-carbon and nitrogen are both sp hybridized in acetonitrile and are either sp$^2$ or sp$^3$ hybridized depending on the resonance state of acetamide.\textsuperscript{45} The typical KIE observed for the change in hybridization is ~0.9 as observed in the solvolysis of methyl esters containing iodide and their deuterated derivatives. A change in the hybridization state is accompanied by a change in the $\Delta$ZPE (zero-point energy) of the transition state than in the $\Delta$ZPE in the ground state.

The adsorption of acetonitrile on the metal center could lead to the change in the hybridization of the metal center, leading to an inverse KIE. Thus, the $\Delta$ZPE when CD$_3$CN is the incoming species will be larger than that of the CH$_3$CN case.\textsuperscript{46} Third, the argument involves an electronic effect. Inductive KIE typically has a magnitude of ~0.95, a less significant effect than the aforementioned
cases. Since D is more electropositive than H, D is more electron releasing. Due to the difference in the electron-donating ability, C-D is more polar than C-H, therefore a higher flux occurs towards the positively charged metal center.\(^{47}\)

Isotope scrambling suggests that the hydrogen source is possibly a second acetonitrile molecule. CH\(_3\)CONH\(_2\) (m/z 59), CH\(_3\)CONHD or CH\(_2\)DCONH\(_2\) (m/z 60), CD\(_3\)COCNH\(_2\) or CD\(_2\)HCONDH or (m/z 62) and CD\(_3\)CONHD (m/z 63) are possible products after isotope scrambling. While CH\(_3\)COCND\(_2\) or CD\(_2\)HCONH\(_2\) or CH\(_2\)DCONHD (m/z 61), and CD\(_3\)COCND\(_2\) are conspicuously missing from the isotopic mixture. Ma et al. observed that the addition of acetaldoxime helped increase the yield in their copper (II) catalyzed system.\(^{11}\) Thus it is hypothesized that the second reactive species is possibly an oxime and this reacts with acetonitrile adsorbed at a different but nearby site to drive this reaction forward.

### 2.5 Conclusions

In conclusion, we report an efficient method for the photo-assisted selective hydration of nitrile to amide using the K-OMS-2\(_{\text{REF}}\) catalyst with 100% selectivity and 15% conversion. Under this protocol, the role of lattice oxygen, dissolved oxygen, and light are addressed. O\(_2\) was utilized as an oxygen source instead of water although water can still be utilized. The kinetics of the reaction are evaluated and the KIE study suggests an inverse secondary kinetic isotope effect. The present study allows a deep understanding of the mechanism of acetonitrile oxidation on the surface of a metal oxide catalyst. This catalyst is stable and reusable up to 6 times with the activity fully maintained. However, systematic studies and general structure-reactivity relationships still have to be established within this highly promising field of research with a possible commercial significance. This work brings us a step closer to understanding the mechanism of photo-assisted acetonitrile oxidation on the surface of metal oxide catalysts.
2.6 References


https://doi.org/10.1002/chem.201503076.


Chapter 3. Microwave Hydrothermal Synthesis of Mesoporous First-row Transition-Metal Ferrites

3.1 Introduction

Earth-abundant iron oxide is well known as a promising material for both fundamental scientific interests and technological applications of industrial and environmental significance in the last few decades.\(^1\)–\(^5\) Iron oxide has a series of attractive properties, including its abundance and nontoxic nature, remarkable stability in an aqueous environment.\(^6\) Iron oxides also have unique biochemical, magnetic, catalytic, and other properties that provide suitability for specific technical and biomedical applications.\(^7,8\) Ferrites are of particular interest due to their demonstrated role in biomedical, magnetic devices, rechargeable batteries, sensors, catalysis, and water treatment.\(^9,10\) The structure of ferrites is a cubic spinel structure.\(^11\) Typically, three types of spinel, namely normal spinel A\([\text{B}_2\text{O}_4]\), where A\(^{2+}\) ions occupy the tetrahedral sites only and B\(^{3+}\) are in the octahedral sites, e.g., ZnFe\(_2\)O\(_4\). Inverse spinel B\([\text{ABO}_4]\) where A\(^{2+}\) occupying the octahedral sites and B\(^{3+}\) in both tetrahedral and octahedral sites, e.g., NiFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\), CuFe\(_2\)O\(_4\), Fe\(_3\)O\(_4\). Mixed Spinel where A\(^{2+}\) and B\(^{3+}\) distributed over both tetrahedral and octahedral sites, e.g., MnFe\(_2\)O\(_4\).\(^12\) The synthesis of ferrite materials can be grouped into four main groups; one, physical methods that include gas-phase deposition, electron beam lithography, and ball milling. Second, chemical methods, including co-precipitation, micro-emulsion, hydrothermal processes, solvothermal, electrochemical methods and, continuous flow techniques. Third, biological methods that involve the use of micro-organisms and forth, green methods that utilize plants and plant extracts.\(^13\) Microwave hydrothermal has attracted a lot of attention in the last two decades due to its simplicity and ease of operation. Microwave heating provides rapid volumetric heating, short reaction period,
and increased yield. However, control of size and shape can be challenging, and microwave systems can be costly.\textsuperscript{14} Nanocrystalline and monomodal pore size multivalent mesoporous transition metal oxides have attracted much attention in the past two decades and have been the subject of thousands of research studies. The interest in multivalent mesoporous transition metal oxides originates from their catalytic, electronic, sorption, and magnetic properties which are superior to those of nonporous materials.\textsuperscript{15,16} Mesoporous structures possess interconnected networks and high surface areas and have shown advantages when used for different catalytic applications, with improved characteristics such as electron transport, dye loading, electrolyte permeation, and oxidative capabilities when compared to those of typical nanostructured catalysts.\textsuperscript{17} Our lab has done a lot of work with the synthesis of mesoporous metal oxides in the past few years.\textsuperscript{18–22} Expanding these studies to mixed metal oxides has been of interest in the hope that combining the unique advantages of mesoporous materials with those of mixed metal oxide systems could yield better catalysts. Mesoporous ferrites have been utilized for pollutant degradation have shown exceptional activity.\textsuperscript{13,23} Moreover, catalyst regeneration is made easy with the use of a magnet for successive uses.

Herein, we report the synthesis of mesoporous first-row transition metal ferrites and apply them to the electrochemical oxygen evolution reaction. $\text{M}^{2+}$ (Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$) ferrite synthesis was systematically studied using a Biotage Initiator microwave apparatus. The effects of reaction time and initial $\text{M}^{2+}$ concentration on the structure, morphology, composition, and catalytic activity were evaluated. The synthesis involves using the high surface area, small crystallite size, and mesoporous UCT-5 (UCT-Fe)$^{24}$ as the precursor that is further reacted in the presence of $\text{M}^{2+}$ ions under microwave irradiation. The ferrite phase formation is confirmed using
XRD and Raman analysis with the ferrite phase forming after 20-40 min of the reaction. The morphology changes suggest that longer reaction times lead to larger particle sizes, and different conditions produce unusual morphologies such as hollow microspheres. The NiFe$_2$O$_4$ catalyst shows exceptional OER activity with an overpotential of 273 mV at 10 mA/cm$^2$.

3.2 Methods

3.2.1 Materials

Iron nitrate nonahydrate (≥98%), poly (ethylene glycol)-block-pol (propylene glycol)-block-poly-(ethylene glycol), Pluronic P$_{123}$, PEO$_{20}$PPO$_{70}$PEO$_{20}$, molar mass 5750 g/mol, nitric acid (≥70%), 1- butanol (≥99.4%), manganese (II) nitrate tetrahydrate (Mn(NO$_3$)$_2$·4H$_2$O, ≥97.0), cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, ≥98.0), nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, ≥98.5), Ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O, 99.5%) Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 98%) reagent grade, 98% were all purchased from Sigma-Aldrich. Concentrated nitric acid (HNO$_3$, 68–70%) was purchased from J.T. Baker. were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

3.2.2 Synthesis of M$^{2+}$ ferrites

Pure iron oxide was synthesized following the procedure described in the literature. The M$^{2+}$ source (0.02-0.33 M$^{2+}$ to Fe mole ratio) was dissolved in a suspension of 0.003 mol UCT-Fe (approximately 0.479) and stirred magnetically for 15 minutes. 0.003 mol NaOH is then added, and the solution is placed in the Biotage Initiator microwave apparatus, where the mixture is pre-stirred for 2 minutes before starting the magnetron. After the reaction, the reaction mixture is washed with water, centrifuged, and placed in a vacuum oven to dry overnight. The dried powders were subjected to a heating cycle where they were heated to 300°C at a heating rate of 2°C and kept at this temperature for 3 h. The powder was then cooled down to room temperature under ambient conditions.
### 3.2.3 Characterizations

Powder XRD data were collected on a Rigaku UltimaIV instrument using Cu Kα (1.54 Å) radiation at a beam voltage of 40 kV and a 45 mA beam current. High- and low-angle patterns were obtained by continuous scans in a 2θ range of 5–75° and 0.5–5° with a scan rate of 2°/min and 0.5°/min, respectively. The surface area, pore size distribution, and pore volume of iron oxides were determined in a Quantachrome Autosorb-1-1C automated adsorption system. The samples were treated at 150°C for 6 h under helium before measurement. The isotherms of N₂ at 77 K were obtained from physisorption. The pore size distributions of the iron oxides were determined from the N₂ desorption isotherms at 77 K, using the Barrett–Joyner–Halenda (BJH) method. Raman spectra were obtained using a Renishaw 2000 Raman scope, which has an optical microscope (0.024 in. focus length), graphic grating (1800 mm⁻¹), and CCD detector. A laser excitation source with 514 nm wavelength was used. For each sample, three different locations were analyzed to verify the spectra. Field-Emission Scanning Electron Microscopy (FE-SEM) and Elemental Dispersive X-Ray Spectroscopy (EDS) data were taken on an FEI Nova NanoSEM 450 and an Oxford 553 EDS. High-Resolution Transmission Electron Microscopy (HR-TEM) was conducted on an FEI, Talos F200X microscope with an operating voltage of 200 kV and the ability to perform Energy Dispersive X-Ray Spectroscopy (EDS). The quantitative elemental compositions of samples were determined by X-ray fluorescence (XRF) with a Rigaku ZSX Primus IV sequential wavelength-dispersive XRF spectrometer (4 kW Rh anode).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) is employed to study the thermal stability of the samples. The experiments were performed on a TA instruments SDT Q-600. The temperature was ramped from RT to 1400°C at 10°C/min in an argon environment. TG-MS analyses were performed with a TG 209 F1 Libra thermogravimetric analyzer coupled to a QMS 403C quadrupole mass spectrometer. The samples (20 mg) are heated to 800 °C with a 10°C/min heating rate under 50 mL/min argon atmosphere.
DC magnetization versus magnetic field was evaluated using a vibrating sample magnetometer system attached to an Evercool Physical Property Management System from Quantum Design Inc. The samples were scanned at a rate of 20 Oe/s when the field strength is smaller than 2000 Oe and a rate of 150 Oe/s when the field is larger than 60000 Oe.

### 3.2.4 Electrochemical Measurements

The electrochemical measurements were performed using a CHI 760E electrochemical workstation using a three-electrode cell. Coated carbon cloth worked as the working electrode and a Hg/HgO reference electrode for measurements in 1.0 M KOH. IrO$_2$ ink was typically made by dispersing 5 mg of the catalyst into 0.96 mL of water/ethanol (v/v = 1:1) solvent. After adding 40 μL of 5 wt % of the Nafion solution and sonicated for at least 30 minutes, 300 μL of this ink was loaded onto a carbon cloth to achieve the sample loading of 1.6 mg cm$^{-2}$. The OER activity of the catalysts was evaluated using linear sweep voltammetry (LSV) at the scan rate of 5 mV s$^{-1}$ after 20 cycles of cyclic voltammetry (CV). The overpotential required to deliver a current density of 20 mA cm$^{-2}$ (η$^{20}$) is chosen as the primary parameter for OER comparison.

### 3.3 Results

#### 3.3.1 XRD

The wide-angle X-ray diffraction patterns for the synthesis of cobalt ferrite are shown in Error! Reference source not found.a after 1 minute of microwave exposure in the presence of Co$^{2+}$ ions; the material is still amorphous with a cobalt oxalate peak (JCPDS 25-0250) showing up at $\sim$20 °. When time is increased to 10 minutes, more cobalt oxalate is observed with the appearance of higher intensity peaks that are sharper. After 20 minutes, the cobalt ferrite phase is observed (JCPDS 22-1086). At even longer times (30 mins), more cobalt oxalate is found. The effect the cobalt to iron precursor ratio was evaluated by varying the starting cobalt ion amount (Error! Reference source not found.b). Lower cobalt amounts lead to broader cobalt ferrite peaks up to the 0.125 ratios. Here we observe a mixture of cobalt ferrite and hematite (JCPDS 86-0550) with hematite being the dominant phase. When these materials were calcined to 300°C, there were
no observable crystal structure changes. When Mn$^{2+}$ ions are added, the material stays amorphous in the first minute, and the MnFe$_2$O$_4$ phase (JCPDS 10-0913) is observed after 20 minutes (Figure 3-1). At lower Mn$^{2+}$ loadings, there is a mixture of MnFe$_2$O$_4$ and hematite with hematite being the dominant phase. The materials stayed the same after calcination at 300°C.

In the presence of Ni$^{2+}$ ions, the materials stay amorphous after 1 minute of exposure to microwaves, but a nickel oxalate peak is observed at ~20° after 20 minutes of the reaction (JCPDS 44-1485). At lower Ni$^{2+}$ loadings, a mixture of nickel oxalate and hematite is observed. The 0.125 Ni-Fe-AS sample showed a higher intensity peaks for nickel oxalate as compared to the other low nickel loading (0.0625-0.5) samples. After calcination at 300°C, there were no observable crystal phase changes (Figure 3-1b). In the presence of Cu$^{2+}$ ions, the hematite phase is observed within 1 minute of the reaction. When the reaction was run for longer (20 mins), the material became amorphous, and after 40 minutes, a mixture of copper ferrite (JCPDS 34-0425) is observed with CuFe$_2$O$_4$ being the dominant phase. At lower Cu$^{2+}$ loading amounts, hematite is the dominant phase. There were no significant changes observed after calcination to 300°C (Error! Reference source not found.). The iron oxide precursor maintained its amorphous structure in the presence of Zn$^{2+}$ ions when the reaction was run for 20 minutes (Error! Reference source not found.). After 30 minutes, the zinc ferrite phase (JCPDS 22-1012) is observed, after which a mixture of hematite and zinc ferrite is observed. After calcination, there were no observable changes in the XRD patterns. The 0.5Zn-Fe sample, both calcined and uncalcined, showed the ferrite phase as the most dominant.
Figure 3-1. Wide-angle XRD patterns for synthesized a) manganese and b) nickel ferrite c) control experiments, and d) magnetite materials.

To synthesize Fe$_3$O$_4$, the calcination step was employed before the microwave treatment step to prevent Fe$^{2+}$ in Fe$_3$O$_4$ from being oxidized to Fe$^{3+}$. Magnetite phase of iron oxide was observed after 20 minutes at 160°C in the microwave reactor (JCPDS 19-0629). When the ratio of Fe$^{2+}$ to Fe$^{3+}$ was decreased, a mixture of the hematite and magnetite phase was observed. Additionally, the peaks appeared broader as the amount of Fe$^{2+}$ was reduced. (Figure 3-1c,d) shows XRD patterns of the UCT-Fe material before the microwave treatment, after microwave treatment in water, and after microwave treatment with the addition of NaOH.
Microwave treatment leads to the evolution of the hematite phase, while in the presence of NaOH, the material was amorphous.

**Figure 3-2.** Wide-angle XRD patterns for synthesized cobalt-iron mixed metal oxide system.

**Figure 3-3.** Wide-angle XRD patterns for synthesized copper-iron mixed metal oxide system.
3.3.2 XRF

The XRF data show the effect of metal ion concentration in the starting solution on the $M^{2+}$: Fe ratio of the final product. (Figure 3-5) indicates that a large portion of the ratios reported here was above the starting ratios; therefore, there is iron dissolution occurring during the synthesis. The $M^{2+}$ decreased with decreasing starting mole ratios.
Figure 3-5. Summary of XRF and N₂ sorption data; a) trends in starting materials concentrations vs. final product metal concentrations, b) BET surface area, c) BJH pore size and, d) pore volume changes with changing starting material concentrations.

### 3.3.3 Surface Area and Porosity

The synthesized materials show Type IV and H1 hysteresis, as shown in other UCT type materials. Most samples show the characteristic type IV adsorption isotherm, indicating the existence of a mesopore structure. The pore size distributions, as shown in Figure 3-6 to Figure 3-11b, are all monomodal within the 2-15 nm range, except for the Fe₃O₄ sample synthesized under microwave radiation for 20 minutes. A summary of the nitrogen sorption data is shown in Table 3-1. The BET surface areas were in the range of 221 m²/g to 44 m²/g. Considering that the typical UCT iron oxide calcined to 300°C has been reported to have a surface area of 223 m²/g, the MnFe₂O₄ and ZnFe₂O₄ materials maintained the high surface area while the others showed a significant drop. The general observable trend is that the surface area drops as...
the $M^{2+}:Fe^{3+}$ ratio decreases except for the $Fe_3O_4$ sample where the surface area is increasing with increasing $M^{2+}:Fe^{3+}$ ratio. The pore sizes were within the mesoporous range (2-50 nm) with an apparent pore size of 25 nm observed for the $Fe_3O_4$ sample. In general, the pore sizes observed for the synthesized materials are slightly larger than the pure starting material which is reported to be 3.4 nm.\textsuperscript{25} The pore volume was between 0.4 and 0.14 cc/g with slight fluctuations within sample sets.

**Figure 3-6.** a) N\textsubscript{2} sorption isotherms, b) BJH desorption pore size distributions for synthesized manganese iron mixed metal oxide system.

**Figure 3-7.** a) N\textsubscript{2} sorption isotherms, b) BJH desorption pore size distributions for synthesized magnetite system.
Figure 3-8. a) N\textsubscript{2} sorption isotherms, b) BJH desorption pore size distributions for synthesized cobalt iron mixed metal oxide system.

Figure 3-9. a) N\textsubscript{2} sorption isotherms, b) BJH desorption pore size distributions for synthesized nickel-iron mixed metal oxide system.
Figure 3-10. a) N$_2$ sorption isotherms, b) BJH desorption pore size distributions for synthesized copper iron mixed metal oxide system.

Figure 3-11. a) N$_2$ sorption isotherms, b) BJH desorption pore size distributions for synthesized zinc iron mixed metal oxide system.
Table 3-1. Nitrogen Adsorption Analysis and mol. ratio of mixed metal oxides characterized by X-ray fluorescence (XRF).

<table>
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<tr>
<th>Sample</th>
<th>Mol % (starting)</th>
<th>Mol % (XRF)</th>
<th>Surface area $S_{BET}$(m$^2$/g)</th>
<th>BJH Pore size (nm)</th>
<th>Pore Volume (cc/g)</th>
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### 3.3.4 Raman Analysis

Raman analysis was conducted to study the structure of the materials. Figure 3-12 shows the room temperature Raman spectra of the presented materials indicating changes in structure with changing precursor ratios. The spinel structure is known to have 39 vibrational modes with five Raman active modes, namely $A_{1g}$, $E_g$, and $3T_{2g}$.

The modes below 600 cm$^{-1}$ correspond to metal-oxygen bending (symmetrical, anti-symmetrical bending) in octahedral sites, while the modes above 600 cm$^{-1}$ are due to metal-oxygen symmetric stretching at tetrahedral sites. The materials synthesized with a 1:2 $M^{2+}$ to Fe$^{3+}$ ratio show three broad predominant peaks at ~700 cm$^{-1}$, 500 cm$^{-1}$, and 350 cm$^{-1}$, which correspond to the $A_{1g}$, $T_{2g}$ (1) and $T_{2g}$ (2). The other modes, $E_g$ and $T_{2g}$ (3), were buried in the broad peaks that were observed.

The hematite phase of iron oxide (observed in the XRD data) has seven signature peaks, namely $2A_{1g}$ and $5E_g$. Hematite is also known to exhibit a Raman forbidden, IR active longitudinal optical (LO) $E_u$ band that occurs at 660 cm$^{-1}$. This mode is activated by disorder within the hematite crystal. The Raman shifts and assignments are as follows: 229 ($A_{1g}$), 249 ($E_g$), 295 ($E_g$), 302 ($E_g$), 414 ($E_g$), 500 ($A_{1g}$), 615 ($E_g$), 660 (LO $E_u$). The peak at ~ 660 cm$^{-1}$ could arguably be due to the ferrite $A_{1g}$ peak, although Bersani et al. showed that only by making a 1:1 mixture of hematite to magnetite were they able to observe such high relative intensities as observed in the synthesized materials. Therefore, the peak at ~ 660 will be attributed to the ferrite phase. The Raman analysis confirms the synthesis of the ferrite materials and the dominance of the hematite phase with decreasing $M^{2+}$ amounts. Notably, as when non-stoichiometric amounts are utilized, mixed-phase materials are formed with the ferrite phase coexisting with the hematite phase. These results are consistent with the phase assignments made for the XRD data.
Figure 3-12. Raman spectra for a) Manganese ferrite, b) magnetite, c) cobalt ferrite, d) nickel ferrite, e) copper ferrite and, f) zinc ferrite samples.

3.3.5 SEM and TEM analyses

Figure 3-13 shows the SEM images of the Mn$^{2+}$ ion introduced samples. The particle size increased with longer reaction times while also increasing when the Mn: Fe ratio was decreased. Similar behavior is observed in the case of Co$^{2+}$ (Figure 3-15) and Ni$^{2+}$ (Figure 3-16). When the Ni: Fe was at its lowest, two different morphologies are observed. There are both nanosheets and nanoparticles. In the case of Cu$^{2+}$ ions (Figure 3-17), the particle size increases with longer reaction times. The lower Cu: Fe ratios showed similar morphology with two apparent particle sizes. There are large agglomerates made up of smaller nanoflakes with larger nanoparticles around the agglomerates. The Zn$^{2+}$ system showed different morphologies (Figure 3-18). As the reaction time is increased from 1 minute to 20 minutes to 30 minutes to 40 minutes, the morphology changes from nanospheres to nanoflakes back to nanospheres and, finally, nanorods. When
the time was increased further, nanospheres are observed. Decreasing the Zn: Fe ratio led to the particle size increase with decreasing Zn: Fe ratio. **Figure 3-18h** shows hollow microsphere formation when the Zn$^{2+}$ concentration is 0.04 mol%.

High-Resolution TEM images of the First-row transition metal ferrite materials prepared at a 0.33 M$^{2+}$: Fe$^{3+}$ ratio for 20 minutes in the case of Co$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, 30 minutes for Zn$^{2+}$ and 40 minutes for Cu$^{2+}$. The TEM images of CoFe-20 mins-300 (**Figure S16**) clearly shows spherical nanoparticles with a diameter of approximately 10 nm with pores formed between the particles. The selected area electron diffraction (SAED) pattern from the sample shows a distinct ring pattern that can be indexed to CoFe$_2$O$_4$. The lattice fringes can be observed clearly from the HRTEM image with the distance between neighboring fringes being around 0.25 nm, which is indexed to the (311) planes. The Energy Dispersive X-ray analysis (EDX) maps show a uniform distribution of Co and Fe, therefore, showing an orange color, but excess Co flakes are also observed at the surface, suggesting that a thin cobalt oxide layer exists.

**Figure 3-13.** SEM images of a) MnFe-1 min, b) MnFe-20 mins, c) 0.5MnFe300, d) 0.25MnFe300, e) 0.125MnFe300 and, f) 0.0625MnFe300 (scale bar 1µm).
Figure 3-14. SEM images of a) Fe304 -20 min, b) 0.5FeFe300, c) 0.25FeFe300, d) 0.125FeFe300 and, e) 0.0625FeFe300.
Figure 3-15. SEM images of a) CoFe-1 min, b) CoFe-20 mins, c) 0.5CoFe300, d) 0.25CoFe300, e) 0.125CoFe300 and, f) 0.0625CoFe300.
Figure 3-16. SEM images of a) NiFe-1 min, b) NiFe-20 mins, c) 0.5NiFe300, d) 0.25NiFe300, e) 0.125NiFe300 and, f) 0.0625NiFe300.
Figure 3-17. SEM images of a) CuFe-1 min, b) CuFe-20 mins, c) 0.5CuFe300, d) 0.25CuFe300, e) 0.125CuFe300 and, f) 0.0625CuFe300. Scale bar 1µm.

Figure 3-18. SEM images of a) ZnFe-1 min, b) ZnFe-20 mins, c) ZnFe-30 mins, d) ZnFe-40 mins, e) ZnFe-1hr f) 0.5ZnFe300, g) 0.25ZnFe300, h) 0.125ZnFe300 and, i) 0.0625ZnFe300.

MnFe-20mins-300 TEM images (Figure 3-19) show irregularly shaped nanoparticles of different sizes. The lattice fringes are shown inset with the distance between neighboring fringes being 0.25 nm, which is
indexed to the (311) planes. The SAED show perfect concentric circles confirming the formation of 
MnFe$_2$O$_4$ crystals of spinel cubic structure. The EDS elemental maps show a uniform distribution of Mn, 
Fe, and O. The overlaid Mn and Fe maps show that these elements are homogeneously distributed and 
therefore give an orange color. NiFe-20 mins-300 TEM image (Figure 3-20) shows nanoparticles with a 
diameter of approximately 5 nm that are organized to reveal pores. The lattice fringes were observed under 
HRTEM and the (311) planes of NiFe$_2$O$_4$. The SAED pattern shows two distinct rings that can be indexed 
to Nickel ferrite. The EDX elemental maps reveal a core-shell structure with nickel oxide coating the iron 
oxide particles. Oxygen was homogeneously distributed throughout the sample. The CuFe-40mins-300 
TEM image (Figure 3-21) shows nanoflakes as observed by SEM The lattice fringes are observed using 
HRTEM, and the distance between neighboring fringes was measured to be 0.25 nm. This distance is 
indexed to the (311) planes of copper ferrite, while the SAED pattern shows distinct rings that can be 
indexed to the copper ferrite phase. The TEM-EDS elemental maps show that Cu is mostly homogeneously 
distributed in the sample, except for certain spots that show higher Cu concentration.

The ZnFe-30 mins-300 sample TEM images (Figure 3-22) show nanoflakes morphology, as observed in 
the SEM images. The lattice fringes were observed using HRTEM and show a 0.25 nm distance between 
neighboring lattices. The EDS elemental maps show that the Zn and Fe are not homogeneously distributed. 
Instead, there are distinct regions of zinc oxide and iron oxide. The SAED pattern indicates a set of rings 
instead of spots due to the random orientation of the crystallites, corresponding to reflection from six crystal 
planes, indicating (220), (311), (400), (422), (511) and (440). The SAED data also support the formation 
of the spinel cubic phase of the magnetic nanoparticles.33
Figure 3-19. Top row (from left to right) High-Resolution TEM image of MnFe-20 mins-300 with the lattice fringes, $d_{(311)}$ inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Mn, Fe, O, and an Mn-Fe overlaid map.

Figure 3-20. Top row (from left to right) High-Resolution TEM image of CoFe-20 mins-300 with the lattice fringes, $d_{(311)}$ inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Co, Fe, O, and a Co-Fe overlaid map.
Figure 3-21. Top row (from left to right) High-Resolution TEM image of NiFe-20 mins-300 with the lattice fringes, $d_{(311)}$ inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Ni, Fe, O, and a Ni-Fe overlaid map.
Figure 3-22 Top row (from left to right) High-Resolution TEM image of CuFe-40 mins-300 with the lattice fringes, d_{(311)} inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Cu, Fe, O, and a Cu-Fe overlaid map.

Figure 3-23. Top row (from left to right) High-Resolution TEM image of CuFe-40 mins-300 with the lattice fringes, d_{(311)} inset, SAED pattern taken at the same location, TEM-EDX elemental mapping of Cu, Fe, O, and a Cu-Fe overlaid map.
3.3.6 Thermal Analysis

Figure 3.24. TGA-DSC in nitrogen plots for a) MnFe-20mins-AS, b) CoFe-20mins-AS, c) NiFe-20mins-AS, d) CuFe-20mins-AS, and e) ZnFe-20mins-AS. (AS means as-synthesized).

Figure 3.24 shows the TGA-DSC curves of the ferrite materials before they were calcined. This analysis was done first to determine the calcination temperatures for the samples and to check for any unexpected crystal phase changes that could be occurring at temperatures higher than the calcination temperature. All the samples go through a majority of the weight loss at temperatures below 300°C; therefore, they were calcined at this temperature. One can also observe apparent differences between the different ferrites prepared. In the case of MnFe₂O₄ four exothermic events are accompanied by mass loss. Notably, the CuFe₂O₄ curve shows an endotherm at approximately 220°C and an exothermic event at around 600°C that doesn’t have a corresponding weight loss.
The TGA data (Figure 3-25) of the final materials calcined at 300°C were used to study the effect of varying the M^{2+}: Fe^{3+} ratio. For the Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} systems, the thermal stability generally decreases with this increasing ratio. The Fe^{2+} system is entirely different since the thermal stability increases with decreasing precursor ratio. Additionally, the Fe_{3}O_{4} material shows two distinct weight gain regions, which is an indication of oxidation events.

Figure 3-25. Thermogravimetric analyses of the a) Mn^{2+}, b) Fe^{2+}, c) Co^{2+}, d) Ni^{2+}, e) Cu^{2+}, and f) Zn^{2+} synthesized samples in a nitrogen atmosphere.

3.3.7 Magnetism studies

Figure 3-26 shows the magnetic hysteresis loops of the M^{2+}Fe_{2}O_{4} samples, and Table 3-2 summarizes the values of saturation magnetization \( M_{s} \). Based on the \( M_{s} \) values, the order was Fe_{3}O_{4} > ZnFe_{2}O_{4} > NiFe_{2}O_{4} > CoFe_{2}O_{4} > MnFe_{2}O_{4} > CuFe_{2}O_{4}. Judging by the shape and the value of the mass magnetization, Fe_{3}O_{4} and ZnFe_{2}O_{4} are classified as ferromagnetic due to the high \( M_{s} \) observed. The NiFe_{2}O_{4}, CoFe_{2}O_{4}, MnFe_{2}O_{4},
and CuFe$_2$O$_4$ samples tested exhibit superparamagnetism, and the remnant magnetism fades to zero when the intensity of the applied magnetic field decreases to zero.

**Figure 3-26.** Magnetization curves of the a) Mn$^{2+}$, b) Fe$^{2+}$, c) Co$^{2+}$, d) Ni$^{2+}$, e) Cu$^{2+}$, and f) Zn$^{2+}$ synthesized samples in nitrogen atmosphere.
**Figure 3-27.** Polarization curves of a) Mn$^{2+}$, b) Fe$^{2+}$, c) Co$^{2+}$, d) Ni$^{2+}$, e) Cu$^{2+}$, and f) Zn$^{2+}$ synthesized samples in nitrogen atmosphere.

**Table 3-2.** Summary of saturation magnetization $M_s$ values and OER activity data.

<table>
<thead>
<tr>
<th>$M^2$Fe$_2$O$_4$ sample</th>
<th>$M_s$ (emu/g)</th>
<th>Overpotential @10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>3.9</td>
<td>450</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>73.5</td>
<td>482</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>6.7</td>
<td>330</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>8.9</td>
<td>278</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>2.2</td>
<td>396</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>25.9</td>
<td>n/a</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>n/a</td>
<td>285</td>
</tr>
</tbody>
</table>
3.3.8 OER activity

The OER activity in 1.0 M KOH was studied for the synthesized transition metal ferrites (Figure 3-26), and the activity followed the order NiFe$_2$O$_4$ > CoFe$_2$O$_4$ > CuFe$_2$O$_4$ > MnFe$_2$O$_4$ > Fe$_3$O$_4$. The best material requires 278 mV overpotential to drive 10 mA/cm$^2$, which is lower than the overpotential for IrO$_2$ (320 mV). Upon decreasing the amount of Ni$^{2+}$, the OER activity dropped drastically, indicating the superiority of the nickel ferrite material over the other mixed-phase materials.

**Figure 3-28.** Electrochemical characterization of OER in 0.1 M KOH. a) LSV of different catalysts at a scan rate of 5 mV s$^{-1}$, b) Tafel plots if the different catalysts, c) LSV of Nickel catalysts synthesized in this study, d) Overpotentials calculated at 10mAcm$^{-2}$ and 20mAcm$^{-1}$. 
3.4 Discussion

In this work, $M^{2+}$ ferrites were prepared using a microwave-assisted synthetic route in aqueous media under hydrothermal conditions. The precursor was synthesized utilizing the unique inverse micelle sol-gel method for the synthesis of UCT materials (University of Connecticut mesoporous materials). These materials show exceptional catalytic activity in many applications.\textsuperscript{18,19,21,22,34} The surface area, pore sizes, and nanocrystallinity of these materials are tunable.\textsuperscript{25} Based on the synthesis procedure, 2-line ferrihydrite (UCT-5), which is an amorphous mesoporous iron oxide, was synthesized.\textsuperscript{24} The as-synthesized material was then placed in a microwave vial with water, sodium hydroxide, and varying amounts of $M^{2+}$ salts. This mixture was then heated using microwave radiation. Figure 3-29 shows the temperature (T), pressure (P), and power (p) profiles where the reaction was conducted at 160°C for 20 minutes. The temperature was maintained at 160°C for 20 minutes, the pressure was maintained at 7 bar, and the power was initially high at 400 W then lowered and maintained at 50 W for the rest of the experiment. This indicates overall low energy consumption throughout the process.

![Figure 3-29](image_url)

**Figure 3-29.** Representative profile of T, P, and p monitored when the reaction was performed at 160°C with a 20 min hold time.
The PXRD data suggest that reaction time is a major factor in synthesis. Longer reaction times lead to desired ferrite phase formation. The hydrothermal synthesis of ferrites mainly consists of dispersion, dissolution, precipitation, growth of the precipitates, and structure ordering. Each of these processes will be affected by many factors, and time is one of them.\textsuperscript{35} With the appropriate extension of time, the corresponding process will be carried out more thoroughly, which can explain the presence of ferrite after more extended reaction periods. For larger ions such as Zn\textsuperscript{2+}, longer reaction times were utilized. To eliminate the possibility of ferrite forming in the absence of the respective M\textsuperscript{2+} ions, control experiments were conducted where the UCT-Fe in water turns into hematite under microwave irradiation, while when NaOH is added the 2-line ferrihydrite phase is maintained. When the M\textsuperscript{2+} concentration was decreased, mixed-phase materials were formed. Ahn et al. proposed a dissolution-precipitation mechanism for the hydrothermal synthesis of barium titanate.\textsuperscript{36} This mechanism suggests that the metal oxide first gets dissolved, and the amount of dissolved metal is governed by the precursor (UCT-Fe) particle size. This is followed by a nucleation and crystal growth step. This explains the higher M\textsuperscript{2+}: Fe\textsuperscript{3+} ratios observed using XRF. Dissolution under hydrothermal conditions differs depending on the matrix compositions. In the Cu\textsuperscript{2+} system, the ratio of Cu\textsuperscript{2+}: Fe\textsuperscript{3+} in the starting mixture was significantly lower than that found in the final CuFe\textsubscript{2}O\textsubscript{4} material (0.33 vs. 1.08), therefore suggesting significant dissolution and loss of Fe\textsuperscript{3+} ions during the synthesis.

Ostwald ripening has been documented as the process responsible for the crystal growth in hydrothermal systems.\textsuperscript{37,38} The SEM images show that the particle sizes increase with longer reaction times, which is typical of Ostwald ripening.\textsuperscript{39} The particle sizes are also different between different M\textsuperscript{2+} systems, although the starting precursor is the same. Tjisse et al. suggest that the rate of crystal growth is limited by the diffusion of ions between the free solution and particle surface.\textsuperscript{39} The different M\textsuperscript{2+} ions have different diffusion rates in the free solution and particle surface as well as through the particle; therefore, different particle sizes are observed. The morphology of the materials varied with changing growth solution composition. The adsorption of the M\textsuperscript{2+} ion especially governs the crystal growth step and the key factors
involve adsorption depending on initial morphology, nanocrystal shape, and surfactants in solution. For most of the catalysts, the morphology didn’t show significant changes other than increased particle size. The Zn$^{2+}$ showed several changes and indicates that this system is most affected by changes in reaction mixture composition. Cho et al. observed several morphologies for ZnO under microwave irradiation in their study which explains the different morphologies observed.$^{40}$

The thermal stability of the synthesized catalysts increases with increasing M$^{2+}$ concentration. This is seen in the case of Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ systems. Small size nanoparticles have lower thermal stability, while larger nanoparticles have higher thermal stability. This behavior is similar to TiO$_2$ nanoparticles. The decreased thermal stability in smaller nanoparticles was primarily due to the reduced activation energy as the size-related surface enthalpy and stress energy increase.$^{41}$

The magnetization data presented show the variation of magnetization with the applied field. Fe$_3$O$_4$ has a large hysteresis loop, which is characteristic of ferromagnetism. The composition and the average size of the nanoparticles affect the saturation magnetization values.$^{42}$ The magnetization increases with increasing particle size,$^{43}$ and this statement coincides with the particle sizes observed in SEM. The ferrite structure is described as a closely packed face-centered cubic arrangement of oxygen ions, with metal cations and Fe$^{3+}$ at two different crystal sites.$^{44}$ They are defined to have a collinear ferrimagnetic structure where the magnetization at the A (tetrahedral) site is antiparallel to that of the B (octahedral) site and the magnetic moments are mutually compensated.$^{45}$ The magnetic moments of these divalent cations follow the following order: Fe$^{2+}$ > Co$^{2+}$ > Ni$^{2+}$ > Cu$^{2+}$. The reported data follow this order, except the NiFe$_2$O$_4$ sample had a higher M$_s$ value. Mn$^{2+}$ preferentially occupies A sites while taking a mixed spinel structure; therefore, this material cannot be compared to the other samples.

Nickel/iron-based compounds have been known as active OER catalysts since the last century.$^7$ It is therefore not surprising that NiFe$_2$O$_4$ showed such high activity as compared to the other synthesized materials. Additionally, previous studies indicate that NiFe mixed compound (spinel NiFe$_2$O$_4$) outperforms Fe alone (spinel Fe$_3$O$_4$) and Ni alone (cubic NiO) in OER electrocatalytic activity.$^{7,46}$ Smith et al. compared
various oxide films synthesized using the same method, and found that NiFe oxide and a mixed oxide containing Ni and Fe outperformed other catalysts with low overpotential and low Tafel slope.\textsuperscript{47} To probe further the importance of merely having Ni in the structure, the lower Ni loading samples were evaluated for electrochemical OER activity. The activity drops significantly when the amount of Ni is reduced. From the Raman analysis and XRD patterns, the lower Ni loading samples are mixed-phase materials with hematite and nickel ferrite. Hematite has demonstrated inferior OER activity under multiple experimental conditions, significantly worse than that of Co or Ni-based oxides.\textsuperscript{48} This explains the low activity observed when hematite is the dominant phase.

### 3.5 Conclusion

In summary, we demonstrate microwave hydrothermal synthesis of first-row transition metal ferrite catalysts. The synthesis approach involves utilizing high surface area, small particle size, mesoporous UCT-Fe as the precursor. The ferrite phase formation is confirmed using XRD and Raman analysis, while the textural properties were studied using N\textsubscript{2} sorption studies. The materials were further evaluated using SEM, TEM, BET, XRF, and TGA analysis. The synthesis was studied against changing M\textsuperscript{2+} concentration and effects on the morphology, crystal structure, thermal stability, and textural properties have been detailed. The synthesized ferrites were then evaluated for electrochemical oxygen evolution reaction where NiFe\textsubscript{2}O\textsubscript{4} showed exceptional activity vs. the other ferrites with a low overpotential of 278 mV at 10 mA/cm\textsuperscript{2}. The results of this study capture the synthesis mechanism and demonstrate the potential of ferrites as OER catalysts. Ferrites have several applications, and we anticipate this study is simply the start of a world of possible ferrites that exist, along with their attractive potential applications.

### 3.6 References


(10) Du, Y.; Ma, W.; Liu, P.; Zou, B.; Ma, J. Magnetic CoFe2O4 Nanoparticles Supported on Titanate


(36) Song, W.; Poyraz, A. S.; Meng, Y.; Ren, Z.; Chen, S.-Y.; Suib, S. L. Mesoporous Co3O4 with Controlled Porosity: Inverse Micelle Synthesis and High-Performance Catalytic CO Oxidation at −60 °C. https://doi.org/10.1021/cm502106v.


4.1 Introduction

Heterogeneous catalysis is a type of catalysis where the catalyst and the reactant(s) are in different physical states (solid, liquid, or gas). This makes it easier to separate and recycle the catalysts at the end of the reaction as compared to the corresponding homogeneous systems. Additionally, the difference between the phases of reactants and catalysts leads to the reaction pathways differing from those of homogeneous systems. Heterogeneous catalysts are widely exploited in many industries, particularly the chemical, petrochemical, agrochemical, and pharmaceutical sectors. Since the presentation of the first mesoporous material (MCM-41) by Mobil Company, the field of mesoporous materials has expanded enormously. A lot of effort has gone into the development of novel synthetic approaches as well as the application of mesoporous materials in unique applications. Our group has been successful in both the development of novel synthetic approaches2–5, and the use of these materials to various applications such as cathode material in zinc ion batteries,5 adsorptions,6–8 catalysis,9–11 and magnetic materials.12 In the area of selective oxidations, we have studied the mechanisms of redox catalytic cycles in the oxidation of alcohols,13 CO,14 toluene,15 phenol,16 olefins,17 dyes,18 and oxidative coupling reactions such as amine coupling19, and alkyne coupling reactions.20

Factors such as catalyst morphology, particle size, mixed valency, surface area, thermal and chemical stability, electronic effects, active sites, among others, are critical to the design of
selective oxidation catalysts. Robert Grasselli mapped out the seven pillars of selective heterogeneous oxidation catalysis, and they include lattice oxygen, metal-oxygen bond, host structure, redox, multifunctionality of active sites, site isolation, and cooperation of phases.\textsuperscript{21} Mesoporous transition metal oxides have been characterized by various characterization methods and their structure, electronic effects, and chemical properties are often well studied.\textsuperscript{22} When these materials are used as catalysts in selective heterogeneous catalytic oxidations, the typical practice is to draw a structure-activity relationship to explain the observed selectivity and high conversions.\textsuperscript{23} One key factor that needs further work is the detection and potential correlation of reactive oxygen species (ROS) in these selective oxidations. Generally, any research program aiming at a description of the elementary steps of a catalytic process should include the study of the kinetics and equilibria of chemisorption, identification of the real adsorbed species present at the catalyst surface, and the behavior of these species in the course of the catalytic reaction.\textsuperscript{24} In the case of reactions of catalytic oxidation, the role of oxygen, the most commonly used oxidizing agent, is of particular interest. No one method can reliably monitor the multitude of reactive oxygen species that could be generated.\textsuperscript{25} Therefore, a combination of material characterization, reactant and intermediates, and reactive oxygen species analysis is key to a better understanding of these selective heterogeneous catalytic oxidations.

Reactive Oxygen Species (ROS) define highly reactive oxygen-bearing molecules typically formed upon the incomplete reduction of molecular oxygen.\textsuperscript{26} Four major ROS are recognized, comprising superoxide radical anion (O\textsubscript{2}\textsuperscript{−}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), (singlet oxygen (\textsuperscript{1}O\textsubscript{2})), and hydroxyl radical (\textsuperscript{·}OH). Other ROS include ozone (O\textsubscript{3}), ozonide (O\textsubscript{3}−), and oxide (O\textsubscript{2}−), although they do not often appear in common selective catalytic oxidation reactions. The different ROS are
typically difficult to track, especially under heterogeneous systems, and the methods used to study them are generally complicated, expensive and time consuming.\textsuperscript{27}

Over the years, several review articles and books have been published related to reactive oxygen species. Most of these have been focused on biological systems,\textsuperscript{28} medicine,\textsuperscript{29} and most recently photocatalysis.\textsuperscript{30,31} In this review, we have surveyed the chemistry of molecular oxygen, the generation mechanisms and detection methods proposed for the individual ROS in heterogeneous selective catalytic oxidations which have appeared in the literature published in these five decades, and pointed out the specific challenges on researching these heterogeneous systems.

4.2 Electronic states and Redox properties

Ground state triplet oxygen is a paramagnetic biradical with two electrons occupying separate $\pi^*$ orbitals with parallel spins. Most nonradical organic molecules are diamagnetic, with pairs of electrons with opposite spins. A spin restriction applies to molecular oxygen to undergo redox reactions with other atoms or molecules due to accepting a pair of nondiamagnetic electrons from the reductant to fit them into the vacant spaces in the $\pi^*$ orbitals of oxygen.\textsuperscript{28,29} This spin restriction has led to oxygen undergoing one-electron reductions during redox reactions, and therefore O$_2$ can react with other radicals by single-electron transfer. Additionally, O$_2$ may react with other species bearing unpaired electrons such as transition metals. In 1928, Mulliken predicted that the electronic configuration of oxygen should give rise to three energetically closely lying electronic states of O$_2$, the $\Sigma$ triplet ground state, and the excited $\Sigma$ and $\Delta$ singlet states.\textsuperscript{30} Therefore, ground-state oxygen could lead to the formation of singlet oxygen (more reactive) through energy transfer.\textsuperscript{31} Dioxygenyl ion is an oxycation formed from the removal of one electron (oxidation) of oxygen. The ionization energy related to this process is very high (1175 kJ/mol); as a result, the scope of
the chemistry of $O_2^+$ is limited. Dioxygenyl cation containing dioxygenyl hexafluoroplatinate ($O_2^{+}\text{PtF}_6$) can be prepared at room temperature by direct reaction of oxygen gas ($O_2$) with platinum hexafluoride ($\text{PtF}_6$).\(^{32}\) $O_2^+$ can also be generated by the oxidation oxygen by fluoride ions to form oxygen fluorides.\(^{33}\) The oxygenyl ion is rarely encountered in heterogeneous selective catalytic oxidations and will not be discussed in further in this review.

\[ \text{Figure 4-1.} \text{ Molecular orbital diagrams for ground-state molecular oxygen (O}_2\text{), dioxygenyl (O}_2^+\text{), the two forms of singlet oxygen (O}_2^1\text{), superoxide radical anion (O}_2^-\text{) and peroxide ion O}_2^{2-}\text{.}^{34} \]

Since both reduction and oxidation take place concurrently, ROS may be produced sequentially both from $O_2$ and $\text{H}_2\text{O}$. Namely, ROS of `$\text{OH}$, $\text{H}_2\text{O}_2$, $O_2^-$, and $^1\text{O}_2$' would be generated in this order by the stepwise oxidation of $\text{H}_2\text{O}$. On the other hand, the stepwise reduction of $O_2$ generates $O_2^-$, $\text{H}_2\text{O}_2$ and `$\text{OH}$, as shown in Figure 4-2.
Figure 4-2. Molecular O$_2$, $^1$O$_2$, O$_2^-$, and O$_2^{2-}$, and the relationship between O$_2^-$ and H$_2$O$_2$.

The knowledge of the thermodynamics of reactive oxygen species is necessary in order to understand the direction of electron flow. Table 4-1 shows a summary of standard one-electron reduction potentials that are of interest for predicting the course of a free radical compiled from McCoy-Messer et al.\textsuperscript{35} The redox potential of O$_2$ (−0.33 V) is for the standard gas state of 1 atm. The reduction potentials are organized in order of decreasing reduction potential; therefore, OH is the most potent oxidant with a one-electron reduction potential of 2.31V vs. SHE reacting at diffusion control rates with organic molecules.

When protonated of O$_2^{•-}$, the peroxyl radical (·OOH) is obtained (pK$_a$=4.8).\textsuperscript{36} The peroxyl radical has an increased reduction potential and is a better oxidant.
**Table 4-1.** Summary of standard one-electron reduction potentials that are of interest for predicting the course of a free radical relative to a standard hydrogen electrode (SHE).

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>( E^0/V ) vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>'OH, H⁺/H₂O</td>
<td>2.31</td>
</tr>
<tr>
<td>O₃⁻, 2H⁺/H₂O + O₂</td>
<td>1.80</td>
</tr>
<tr>
<td>RO⁻, H⁺/ROH (aliphatic alkoxy radical)</td>
<td>1.60</td>
</tr>
<tr>
<td>'CH₂OH, H⁺/CH₃OH</td>
<td>1.20</td>
</tr>
<tr>
<td>'OOH, H⁺/H₂O₂</td>
<td>1.06</td>
</tr>
<tr>
<td>ROO⁻, H⁺/ROOH (alkylperoxyl radical)</td>
<td>1.00ᵇ</td>
</tr>
<tr>
<td>Allyl⁻, H⁺/allyl-H (propene)</td>
<td>0.96</td>
</tr>
<tr>
<td>O₂⁻⁻, 2H⁺/H₂O₂</td>
<td>0.94</td>
</tr>
<tr>
<td>C₆H₅O⁻, H⁺/C₆H₅OH</td>
<td>0.90</td>
</tr>
<tr>
<td>O₃/ O₃⁻⁻</td>
<td>0.89</td>
</tr>
<tr>
<td>(^1)O₂/O₂⁻⁻</td>
<td>0.65</td>
</tr>
<tr>
<td>H₂O₂, H⁺/H₂O, 'OH</td>
<td>0.32</td>
</tr>
<tr>
<td>TEMPO (R₂NO⁻, H⁺/R₂NOH)</td>
<td>0.08</td>
</tr>
<tr>
<td>O₂/ O₂⁻⁻</td>
<td>-0.33</td>
</tr>
<tr>
<td>O₂, H⁺/HO₂⁻</td>
<td>-0.46</td>
</tr>
<tr>
<td>CO₂/ CO₂⁻⁻</td>
<td>-1.80</td>
</tr>
<tr>
<td>( \text{H}<em>2\text{O} / \text{e}^{−}</em>{\text{aq}} )</td>
<td>-2.87</td>
</tr>
</tbody>
</table>

Although these reduction potentials are very informative, we have to keep in mind that the calculated values are those that are in aqueous solutions.\textsuperscript{37} Similar data in aprotic solvents is not available. It is a commonly held view that apparent concerted multi-electron transfer reactions actually represent atom-transfer processes.\textsuperscript{38,39} Therefore, their kinetics and mechanisms are strongly dependent on the substrate and the catalysts. Typically, selective catalytic oxidations involve the reduction of \( \text{O}_2 \) to a more reactive species/ radicals as well as the incorporation into the oxidized products. Beyond the reversible one-electron process, the effective energetics for oxidations by \( \text{O}_2 \) is dependent on substrate and catalyst and typically limited to one- or two-electron rate controlled step. Although the overall thermodynamics due to the reduction of oxygen is determined by its final state, the reduction potentials can be set as an upper limit that is rarely realized.\textsuperscript{40}
4.3 Reactive Oxygen Species Generation

In nature, several triggers lead to the generation of reactive oxygen species that can lead to oxidative stress in plants and animals. These triggers include air pollution, heavy metals, soil salinity, drought, high light intensity, and high temperatures, and biotic stress.\textsuperscript{41} In catalysis, ROS can be generated through two main ways: radiation and redox reactions (\textbf{Figure 4-3}). Under radiation, ionization, ultra-violet light, visible light (typically through photosensitization), and thermal radiation are responsible for the generation of ROS. Redox reactions that are catalyzed by transition metals play an integral part in the production of ROS on the surface of transition metal oxide catalysts. Enzyme catalyzed redox reactions have also been studied in biological systems with examples such as superoxide dismutase (SOD) playing critical roles in ROS generation.\textsuperscript{42}
4.3.1 Singlet Oxygen

There are three main ways to generate singlet oxygen in solution phase heterogeneous catalysis. One is the direct optical excitation of ground-state oxygen to form excited state singlet oxygen. Second, energy transfer from the excited state of an organic molecule (photosensitization). Last, chemical formation through reactions that do not involve light.\textsuperscript{43,44} Considering that the three electronic transitions are forbidden as electric dipole transitions, due to the quantum mechanical selection rules regarding spin, parity, symmetry, and angular momentum, generating singlet oxygen by this method is very inefficient and requires high power input over long periods of time.\textsuperscript{31,45} The most common singlet oxygen generation pathway is through photosensitization. A typical photosensitization process only requires oxygen, the light of an appropriate wavelength, and a photosensitizer capable of absorbing ultraviolet, visible, or near-infrared radiation in a one- or two-photon transition, thereby forming an excited singlet state ($^1\text{Sen}_n$). Relaxation of the excited singlet state of the photosensitizer yields the lowest excited singlet state of the sensitizer ($^1\text{Sen}_1$). This can either undergo phosphorescence or internal conversion back to the ground state ($^1\text{Sen}_0$). Alternatively, $^1\text{Sen}_1$ can undergo intersystem crossing to the triplet state $^3\text{Sen}_1$. This can be followed by phosphorescence to the triplet ground state ($^3\text{Sen}_0$) or intersystem convert to the singlet ground state ($^1\text{Sen}_0$). Under specific conditions, the quenching of excited state singlet and triplet states can lead to the generation of singlet oxygen through an energy transfer process when the excited state sensitizier collides with triplet oxygen.\textsuperscript{28,46} An alternative process that leads to the generation of free radicals is the chemical quenching of the excited state photosensitizer. In this case, hydrogen-atom abstraction or electron-transfer between the excited sensitizer and a substrate leads to the generation of yielding free radicals. These radicals can react with oxygen to form other active oxygen species such as the superoxide anion radical.\textsuperscript{47,48} Derosa et al. has compiled a
comprehensive review of the types of photosensitizers. In summary, there are five major groups; organic dyes and aromatic hydrocarbons, porphyrins, phthalocyanines, and related tetrapyrroles, transition metal complexes, semiconductors, and immobilized photosensitizers.

Singlet oxygen is also generated through reactions that do not involve light. Singlet oxygen can be generated by the oxidation of hydrogen peroxide using hypochlorite. This oxidation reaction is allowed on both thermodynamic and spin-conservation grounds, but the reaction is kinetically restricted; the rate is extremely low at low temperatures. Bahme et al. have reported the generation of singlet oxygen from the disproportionation of hydrogen peroxide into $\text{H}_2\text{O}$ and $^1\text{O}_2$ catalyzed by molybdate ions.

$$2\text{H}_2\text{O}_{aq} \rightarrow 2\text{H}_2\text{O} + O_2^1$$

Equation 1

With respect to heterogeneous catalysis, several mineral compounds were studied with respect to singlet oxygen generation in basic aqueous hydrogen peroxide. The results of this screening study are clearly represented in regards to the periodic table. This study shows that four families of mineral compounds lead to the generation of $^1\text{O}_2$: the oxides of the alkaline earth Ca, Sr, and Ba; the derivatives of elements of groups 3A, 4A, 5A, and 6A in d⁰ configuration (except niobium); the oxides of actinides and lanthanides; and finally the oxidizers $\text{ClO}^-$, $\text{BrO}^-$, $\text{Au}^{3+}$, $\text{IO}_3^-$, and $\text{IO}_4^-$. Molybdate- and tungstate- exchange LDHs were later studied for this reaction and LDH-$\text{MoO}_4^{2-}$ generated more $^1\text{O}_2$ than the LDH-$\text{WO}_4^{2-}$.

Singlet oxygen can also be generated for the decomposition of ozonides and endoperoxides. When superoxide anion radical undergoes oxidation, there are three ways for the electrons to be removed therefore generating three different electronic states of molecular oxygen. One of the five
states among them three triplet states and two singlet states will be selected with the same probability. Since the $^1\Sigma_g$ state with the highest energy immediately transfers to the $^1\Delta_g$ state, the distribution to the singlet state, $^1\text{O}_2(1\Delta_g)$, is two against three for that in the triplet state. Thus, it is statistically probable that $^3\text{O}_2$ will be generated while $^1\text{O}_2$ could still be generated.\textsuperscript{55} Alternatively, singlet oxygen can be generated through the Haber-Weiss reaction.\textsuperscript{56–58} This involves the reaction of hydrogen peroxide with superoxide anion radical to produce molecular oxygen, hydroxide anion, and hydroxide radical. There are two main steps reported for this reaction. One, the reduction of a Fe$^{3+}$ to Fe$^{2+}$ by O$_2$ $^\cdot$ producing singlet oxygen. Second, the hydrogen peroxide Fenton reaction leading to the generation of $^\cdot$OH.\textsuperscript{55} Notably, these two steps can be driven by other transition metal systems considering their redox potentials with respect to the superoxide radical anion oxidation and the Fenton reaction. Recently, unprecedented singlet oxygen mediated Fenton's reaction occurred inside carbon nanotube with an inner diameter of $\sim$7 nm (under nanoconfinement) was reported. This shows exotic catalytic activities, unforeseen adsorption-dependent selectivity, and pH stability for the oxidation of organic compounds.\textsuperscript{59} The nonradical peroxymonosulfate activation pathway is another recent process that leads to the generation of singlet oxygen although the exact mechanism is yet to be studied.\textsuperscript{60,61}

### 4.3.2 Superoxide Anion Radical

Superoxide anion radicals can be generated from the reduction of molecular oxygen (Error! Reference source not found.). This reduction can be achieved using chemical, electrochemical, photochemical, photocatalytic methods. Chemically, O$_2^-$ can be generated from the synthesis of superoxide salts followed by the dissolution of the salts in appropriate solvents to release the O$_2^-$. 

128
Alkali and alkali earth metals such as potassium, rubidium, cesium, barium, and strontium can react at atmospheric pressure with $O_2$ to produce thermodynamically stable superoxide compounds.$^{36,62,63}$ The solubility of these compounds is very low in aprotic solvents such as DMSO, making it challenging to access the superoxide species. One tested approach to curb this is the introduction of quaternary ammonium salts to increase the nucleophilicity of $O_2\cdot$-$\cdot$. Some studies have used crown ethers for the $O_2\cdot$-$\cdot$ reaction with organic molecules, but highly soluble salts such as tetramethylammonium superoxide have been used.$^{64,65}$

The first step of the Haber-Weiss reaction involves the reduction of $O_2$ by $Fe^{2+}$ to generate singlet oxygen.$^{66}$ The electrochemical reduction of oxygen offers a convenient method with no byproduct formation. Studies have shown that ORR (Oxygen Reduction Reaction) is significantly improved when an electrolyte with low viscosity, high $O_2$ solubility and weak adsorption species.$^{67}$ $O_2\cdot$-$\cdot$ also has a longer lifetime in aprotic solvents but is very reactive and spontaneously disproportionates in protic solvents forming $O_2$ and hydroperoxide anion ($HO_2\cdot$) (Error! Reference source not found.).$^{68}$ Sawyer et al. were able to show that the electrochemical reduction of $O_2$ in dimethyl sulfoxide (DMSO) yields $O_2\cdot$-$\cdot$ in a stable state.$^{69}$ The electrochemical reduction of $O_2$ in aprotic solvents occurs at $E=\mp(-1.0)$ V Vs. The standard calomel electrode (SCE).

$$O_2(g) + e^- \leftrightarrow O_2^\cdot(g)$$

Equation 2

$$2O_2^\cdot(g) + H_2O(l) \rightarrow O_2(g) + OH^-(aq) + O\cdotH(aq)$$

Equation 3
Photochemically, sunlit surface waters typically contain $O_2^-$ due to the reaction of molecular oxygen with excited state substrate molecule through an electron transfer mechanism. Notably, the $O_2^-$ yields reduce over prolonged photolysis since superoxide anion radical inevitably reacts with the substrate molecules in oxygen-depleted solutions. Bielski et al. were able to prepare and stabilize alkaline aqueous and/or ethanolic superoxide solutions utilizing high energy ionizing radiation or vacuum-UV photolysis. Overall the mechanism of $O_2^-$ generation can be summarized below;

$$H_2O(\text{l}) \xrightarrow{\text{Ionizing radiation or vacuum-UV photolysis}} O_2^- \xrightarrow{\text{Oxygen, KOH, HCOONa or ethanol}} O_2(\text{g})$$

Equation 4

The CH$_3$CH$_2$O$^-$ radicals formed in this system were rapidly converted to the CH$_3$CCHOH radicals by rearrangement or reaction with the excess alcohol.

$$\text{CH}_3\text{CHOH} + O_2(g) \xrightarrow{} \text{CH}_3\text{CCHOH}$$

Equation 5

$$\text{CH}_3\text{CCHOH} + \cdot \text{OH}(\text{aq}) \xrightarrow{} \text{CH}_3\text{CHO} + \text{H}_2\text{O}(\text{l}) + \cdot O_2(g)$$

Equation 6

Adsorbed superoxide anion can be used as a probe of the surface crystal field of a metal oxide catalyst. Since the unpaired electron of the superoxide ions is confined in a $\pi$ orbital, it’s EPR
spectrum is intrinsically orthorhombic because three axes of the molecule are magnetically inequivalent. Anpo et al. explained that the $g_{zz}$ is the $g$-tensor element that is most sensitive to the cationic field felt by the adsorbed anion and therefore is suitable for measuring the extent of the surface electrostatic interaction and the value of $g_{zz}$ depends on the ionic charge of the metal to which $O_2^-$ is adsorbed (more precisely, its charge to radius ratio). On metal oxide surfaces, adsorbed $O_2^-$ species can be generated through photoinduced electron transfer, the reaction with $H_2O_2$, surface intermolecular electron transfer, and the direct oxide-oxygen electron transfer. In principle, when the oxygen is adsorbed in the surface of a metal oxide, the $O_2^-$ formation will only occur if the energy of the adsorbed negative moiety lies below the Fermi level of the solid oxide.

The direct oxide-oxygen electron transfer on the surface of oxide catalysts occurs in three significant ways. First, electron transfer from isolated transition metal ions embedded in an insulating matrix is possible. Insulators such as MgO are not capable of direct electron transfer since all the valence band electrons lie at lower energy than that of a hypothetical adsorbed superoxide ion. However, when transition metals such as $Co^{2+}$ are introduced into the framework of the oxide, the band structure is modified due to the formation of new localized states which typically lie within the bandgap of the insulator. This phenomenon was demonstrated by Giamello et al. and they were able to spectroscopically (EPR) study the formation of superoxide species adsorbed onto a MgO-CoO solid solution. Cobalt-oxygen superoxide adducts were characterized by EPR and IR and the structures of the surface species proposed. The study also reveals that the adsorption of oxygen is reversible, and therefore the oxide material can be used as an oxygen carrier. Considering that a lot of studies on heterogeneous selective catalytic oxidations involve metal or non-metal doping to increase catalyst activity, the introduction of defect states in the band structure has been argued for by several studies as a reason for the enhanced catalytic activity. But
these defect states play an important role in the generation of ROS, which translates to increased catalyst activity.

Second, electron transfer from reducible oxides can occur. The reduction of molecular oxygen at the surface of slightly reduced transition metal oxides is an essential step in the redox cycle taking place at the surface of mixed or supported oxide systems with at least one reducible oxide phase. The Mars Van Krevelen mechanism was first proposed for the selective oxidation of aromatic hydrocarbons where the reaction is split into two significant steps, namely, the reaction between the aromatic and the oxygen on the surface, and the re-oxidation of the partly reduced surface by means of oxygen. A good candidate for a catalyst for the selective oxidation reaction is described to have a certain tendency to lose oxygen and good electronic conductivity to ensure a highly efficient redox process.\textsuperscript{45,72,73} The reduction of the adsorbed O\textsubscript{2} isn’t the only factor as to how it is bound on the surface has been called into question as well. Recently, the mono- and diatomic ROS generated upon O\textsubscript{2} interaction with the (111) facets of spinel cobalt oxide at different conditions were studied. This study was conducted using molecular DFT and atomistic thermodynamic investigations, and a reaction pathway is proposed involving mono- and bidentate oxygen-binding modes. The first principle thermodynamic modeling predicted that under typical catalytic pressures ($p_0/p^\circ\sim$0.01 to 0.1 atm), the bridging Co-O\textsubscript{2}-Co species is stable below 375°C while above this temperature the surface is covered by monoatomic species.\textsuperscript{74} This study is of particular interest since some reactions have very different product distributions as a factor of temperature, suggesting a temperature-dependent selectivity.

Third, the electron transfer from localized electron defect centers has been observed in the case of zeolite systems. Tuel et al. found that superoxide radical ions adsorbed on Ti\textsuperscript{4+} ions incorporated into a silicate framework in the case of TS-1 catalyst (titanium silicate) exhibit different $g_{zz}$ features
from superoxide adsorbed on titanium ions introduced in the zeolite channels by ion exchange.\textsuperscript{75} This is valuable information when trying to distinguish between two TS-1 samples with isomorphous substitution. On the other hand, these isomorphous catalysts will show very different reactivity towards the same substrate and, in some cases, different product distributions. This further confirms the critical role played by superoxide species adsorbed on the surface of oxide catalysts.

Other than direct oxide-oxygen electron transfer, surface intermolecular electron transfer also leads to the generation of superoxide anion radical. Here low coordinate surface oxygen $\text{O}^{2-}$ ions are able to split the hydrocarbon molecule heterolytically, forming a proton stabilized $\cdot\text{OH}$ and a carbanion.

$$\text{R-H} + \text{O}^{2-}_{\text{surf}} \rightarrow \text{R}^-_{(l)} + \cdot\text{OH}_{(aq)}$$

Equation 7

$$\text{R}^-_{(aq)} + \cdot\text{OH}_{(aq)} + \text{O}_2(g) \rightarrow \text{O}_2(g) + \text{R}^- + \cdot\text{OH}_{(aq)}$$

Equation 8

The carbanion is unstable towards molecular oxygen and readily transfers an electron to $\text{O}_2$. The remaining species probably in the protonated form ($\text{HO}_2$) will react with the $\text{R}^-$ radical, leading to the cleavage $\text{HO}_2$ and the formation of an oxidized product. In this case the basic strength of the surface oxide ions is significant.\textsuperscript{76}

Lastly, superoxide radical anion can be generated from the interaction at the surface of the metal oxide with hydrogen peroxide. The distinguishing factor from all the on the superoxide anion radical generation is the lack of electron transfer step on the surface of the oxide; instead, the
radical anion is formed from the disproportionation of HO₂⁻, which is formed in the liquid phase. The oxide's only role is to stabilize the resulting proton and radical anion.⁷⁵

\[
\begin{align*}
H_2O_2\text{ (aq)} & \rightarrow 2\cdotOH \\
\cdotOH + H_2O_2\text{ (aq)} & \rightarrow H_2O\text{ (l)} + H\dot{O}_2 \\
H\dot{O}_2 & \rightarrow H^+\text{ (aq)} + \cdotO_2\text{ (aq)}
\end{align*}
\]

Equation 9

Equation 10

Equation 11

4.3.3 Hydrogen Peroxide

Hydrogen peroxide presents an interesting middle ground, with one side being a two-electron reduction of molecular oxygen and the other side being the two-hole oxidation of water. Industrially H₂O₂ generation is achieved through the electrochemical generation for pulp bleaching, and Fe²⁺ is generated at the cathode to minimize sludge formation.⁷⁷ There are a lot of publications on the electrochemical oxygen reduction reaction (ORR) as well as the water oxidation reaction to generate hydrogen peroxide. This has been the most efficient and controllable hydrogen peroxide generation process. Currently, the anthraquinone oxidation process is the most widely used method, generating H₂O₂ with concentrations as high as 70 wt% through several distillation steps.⁷⁸ Several metal oxide catalysts have been evaluated to this cause, with supported catalysts being more prevalent. The effects of factors such as the choice of metal, choice of support,
effect of acidity, synthetic method, the use of metal promoters, and nonmetal promoters have been heavily discussed.\textsuperscript{79,80} But how all these factors come together and are affected by the ROS generated and stabilized at the surface is yet to be studied. From our studies, hydrogen peroxide was generated at the surface of most of the catalytic systems we evaluated, although it wasn't the ROS responsible for the overall catalyst performance.\textsuperscript{81–83} Notably, hydrogen peroxide can be generated from the oxidation and reduction of other ROS, such as the coupling of two hydroxyl radicals, the HO\textsubscript{2} protonation, and the superoxide reduction.

### 4.3.4 Hydroxyl radical

Hydroxyl radicals can be generated through several photolytic processes that involve different combinations of UV exposure coupled with other stimuli such as plasma, microwave, heterogeneous catalysts, among others.\textsuperscript{58,79,84} Fenton reaction is one of the most commonly used reactions for the generation of hydroxyl radicals. This reaction involves the reduction of hydrogen peroxide in the presence of Fe\textsuperscript{2+} to generate hydroxyl radical, hydroxyl ion, and Fe\textsuperscript{3+}.

$$\text{Fe}^{2+}_{(aq)} + \text{H}_2\text{O}_2_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{HO}_2^-_{(aq)} + \cdot\text{OH}$$

Equation 12

Several heterogeneous Fenton-type systems have emerged since its discovery, and examples include Photo-Fenton, sono-Fenton, and electro-Fenton.\textsuperscript{85,86} Also sulfate radically advanced oxidation processes have seen the use of other oxidants such as peroxymonosulfate as sources of the hydroxyl radical as well as the sulfate radical to achieve faster and more efficient pollutant degradation.\textsuperscript{87–89 90}

Additionally, when considering the surface O species as terminal OH and bridged OH groups, potential hydroxyl radical generation sites are introduced.\textsuperscript{90} Basic metal oxides such as MgO, CaO,
BaO, and SrO have proven to be suitable catalysts for the rapid generation of OH. The concentration of OH radicals generated from the reaction with water or oxygen changed with changes in temperature or pressure over the Al$_2$O$_3$ catalyst. Noda et al. attributed this to the possible consumption of the generated hydroxyl radical.$^{90}$ Hydroxyl radical can also be electrochemically or photo electrochemically generated from the one-electron oxidation of water. Siahrostami et al. recently studied the water oxidation reaction incorporating the formation of the hydroxyl radical.$^{91}$ Their study shows several catalysts such as manganese oxide, bismuth vanadate, titanium oxide, iridium oxide, and platinum oxide. The authors were able to generate a selectivity plot with the major oxygen species product being predicted. The study reiterated that titanium oxide was a great candidate for hydroxyl radical generation, while PtO$_2$ was best for the four-electron O$_2$ evolution reaction. Manganese oxide was right at the cusp of the two-electron H$_2$O$_2$ production and oxygen evolution. So far, no metal oxide catalysts were shown to be great hydroxyl radical generation catalysts. Keeping in mind that the calculations were in terms of purely thermodynamic constraints.
4.4 Reactive Oxygen Species Detection

The first step in conducting a ROS study for any heterogeneous catalytic system is to determine whether or not ROS plays any role in the reaction. Therefore, selective scavenging is the easiest way to determine this. A reactive oxygen species scavenger is a substance that can react with the ROS to effectively prevent participation in the reaction it normally facilitated. If the ROS is highly reactive (e.g., \(^{1}\text{OH}\) radical), then the scavenger must be able to penetrate to the ROS generation site since the diffusion of said ROS is restricted. Subsequently, the ROS have short lifetimes; consequently, the scavenger has to be present at the right time to compete with the substrate molecules. Additionally, the scavenger will require an unfair advantage in this competition so that
the major reaction occurs with the scavenger and not the substrate. Hence, the scavenger concentration should be locally higher than that of the substrate.

**Table 4-2. Scavengers of Reactive Oxygen species**

<table>
<thead>
<tr>
<th>ROS</th>
<th>Selective scavenger</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2^{\cdot-}$ (Superoxide anion radical)</td>
<td>Curcumin$^{94-96}$</td>
</tr>
<tr>
<td></td>
<td>p-Benzoylquinone$^{97}$</td>
</tr>
<tr>
<td>$^1\text{O}_2$ (singlet oxygen)</td>
<td>Sodium azide$^{98}$</td>
</tr>
<tr>
<td></td>
<td>Furfuryl alcohol$^{99,100}$</td>
</tr>
<tr>
<td></td>
<td>1,4-diazabicyclo[2.2.2]octane (DABCO)$^{67}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ (hydrogen peroxide)</td>
<td>Sodium pyruvate$^{101,102}$</td>
</tr>
<tr>
<td>$\cdot\text{OH}$ (hydroxyl radical)</td>
<td>Tert-butylalcohol$^{103,104}$</td>
</tr>
<tr>
<td></td>
<td>Isopropanol$^{105,106}$</td>
</tr>
<tr>
<td></td>
<td>Mannitol$^{107-109}$</td>
</tr>
</tbody>
</table>

**Table 4-2** summarizes the most commonly used selective scavengers with respect to the ROS that are scavenged. The addition of quenchers can potentially disrupt the nature of the system, and their suitability must be based on the system's needs. Factors such as the solubility, the working pH and concentration range, potential interactions with other molecules in the system, and potential photo-oxidation of the scavenging agent should always be considered before selecting a suitable scavenger.

Once the involvement of reactive oxygen is suspected, direct and indirect observation techniques should be utilized to confirm the presence of said ROS. Since these species interconvert with each
other and also may possibly play more roles than one in the reaction system, merely identifying one ROS without checking for the others is not enough. The main questions to ask are ‘which ROS are present?’ and ‘which one(s) most important to the observed conversion and selectivity?’

### 4.4.1 Singlet Oxygen

Owing to the fact that singlet oxygen is an excited state of molecular oxygen, this species can be quenched to the ground state without chemical reactions. Two emission lines can be observed for singlet oxygen, namely, phosphorescence ($^1\Delta g \rightarrow ^3\Sigma_g^-$) at 1270 nm in the near-IR region and the dimol emission ($2^1\Delta_g \rightarrow 2^3\Sigma_g^-$) occurring at 634 nm.\(^{34,44,110,111}\) The phosphorescence at 1270 nm is deemed the most reliable for direct detection. However, the intensity of this emission is too weak to be useful at low $^1\text{O}_2$ concentrations. Consequently, the use of this technique has been restricted to transient luminescence studies initiated by laser irradiation.\(^{67,112}\) $^1\text{O}_2$ possesses no electron spin, but exhibits paramagnetic properties caused by the orbital angular momentum. An Electron paramagnetic resonance (EPR) spectrometer with a microwave frequency of about 9 GHz (X-band) could be used to observe the quartet signal of $^1\text{O}_2$ in the gas phase at 950 mT.\(^{113}\)

Due to the challenges of direct observation methods, singlet oxygen trapping methods have emerged. A good trapping agent should be highly reactive towards singlet oxygen and compatible with the reaction system being studied. Additionally, trapping agents should not be active in the spectral range of the incident light to avoid photosensitization by the trap.

There are three groups of spin traps; compounds with nitrone, nitroso, and piperidine/pyrrolidine groups. Piperidine-type spin traps are the most commonly used with examples such as 2,2,6,6-tetramethylpiperidine (TEMP), 4-oxo-TEMP, 4-hydroxy-2,2,6,6-tetramethylpiperidine (HTMP) among others.\(^{26,114,115}\) In the case of 4-oxo-TEMP, as stable nitrooxide radical (4-oxo-TEMPO), is formed as shown in Error! Reference source not found.. The observation of the signal is typically
not enough for complex systems such as heterogeneous catalytic systems. Control experiments should be conducted to ensure the integrity of the chosen probe. Checking the EPR signal of the probe molecule in the solvent alone, in the solvent and substrate mixture, and finally, the complete reaction mixture can help ensure the integrity of the data collected.

![Chemical structure of 4-oxo-TEMP and 4-oxo-TEMPO](image)

Equation 13

Suitable fluorescence probes are also utilized to trap singlet oxygen. Majima et al. selectively detected airborne $^1$O$_2$ molecule that diffused from the surface of the TiO$_2$ nanoparticles at the single-molecule level using total internal reflection fluorescence microscopy. Here terylenediimide (TDI) molecule reacted with singlet oxygen to form a less fluorescent endoperoxide that subsequently undergoes rearrangement when heated or exposed to light forms a strongly fluorescent diepoxide. The diepoxide is easily detected upon 532 nm laser excitation.\cite{116,117} In the past, MCLA (2-methyl-6-(p-methoxyphenyl)-3,7-dihydropyrindazo[1,2-a]pyrazin-3-one) was commonly used for singlet oxygen detection.\cite{28,32,34,55} But since MCLA also reacts with O$_2^-$, other fluorescent probes are utilized instead.\cite{67} Singlet oxygen sensor green (SOSG) is commonly used for trapping singlet oxygen. Upon reacting with $^1$O$_2$, an endoperoxide is formed that fluoresces at 528 nm by excitation at 488 nm (Equation 14).\cite{118,119} Caution should be used when working under light illumination since photosensitization and/or photodecomposition may occur.\cite{120}
4.4.2 Superoxide anion radical

In aqueous media, UV-Vis spectrophotometry can be used to detect $\text{O}_2\cdot^{-}$ because it has an absorption at 245 nm. The optical absorption at 245 nm has a low absorption coefficient that reduces from 2350 M$^{-1}$cm$^{-1}$ to 1400 M$^{-1}$cm$^{-1}$ when $\text{O}_2\cdot^{-}$ protonated to $\text{HO}_2\cdot$.\textsuperscript{121} In aprotic media, the absorbance is at 255 nm, which in turn overlaps with the cutoff wavelengths of such solvents.\textsuperscript{122} In the gas phase, the absorption of $\text{HO}_2\cdot$ in the near-IR region for the vibrational transition (2$\nu_1$ band at 6638.2 cm$^{-1}$) could be measured by continuous-wave CRDS (cavity ring down spectroscopy).\textsuperscript{123}

The presence of three electrons in the 2$\pi^*$ antibonding orbitals for the superoxide anion radical renders a paramagnetic species. However, the EPR spectrum is only observed when the degeneration of the two orbitals is removed by an external perturbation. This can occur when the superoxide anion radical is trapped in the bulk of an ionic solid or when this radical is adsorbed at the surface of an oxide.\textsuperscript{70} This characteristic of $\text{O}_2\cdot^{-}$ has been used to study the surface of metal
oxides. Attempts have been made to trap O\textsubscript{2} \textsuperscript{−} using spin traps, but the superoxide anion adduct is typically very unstable and subsequently decomposes spontaneously to the hydroxyl adduct.\textsuperscript{124} Furthermore, fluorescence probes such as Luminol and 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroirnidazo[1,2-a]pyrazin-3-one (MCLA) have been used for the detection of O\textsubscript{2} \textsuperscript{−}. The challenge with these probes is their lack of selectivity. Luminol can be oxidized by all four of the ROS while MCLA also reacts with singlet oxygen.\textsuperscript{67}

Nitro blue tetrazolium chloride (NBT) is a classical reagent used for O\textsubscript{2} \textsuperscript{−} detection.\textsuperscript{67,83,121,124–127} NBT is reduced by O\textsubscript{2} \textsuperscript{−} and its color changes from yellow to purple (Error! Reference source not found.). The visual results obtained using this method are qualitative or semiquantitative and do not reflect quantitative O\textsubscript{2} \textsuperscript{−} accurately. But, diformazan is insoluble in water, and its precipitation leads to an inconsistency in absorbance readings. Therefore, modified NBT derivatives that have water-soluble end products have been used 3′-{1-[(phenylamino)-carbonyl]-3,4-tetrazolium} -bis(4-methoxy-6-nitro)benzenesulfonic acid hydrate (XTT)\textsuperscript{124,126,128}

\[ \text{Nitrotetrazolium blue chloride (yellow)} \quad \text{Nitrotetrazolium blue-formazan (purple)} \]

\[ \text{Equation 15} \]

### 4.4.3 Hydrogen Peroxide

The molar absorption coefficient of 0.01 M\textsuperscript{−1} cm\textsuperscript{−1} at 360 nm is too low for detection. Therefore, trapping methods are employed. Since hydrogen peroxide is fairly stable at room temperature,
activation is required for some of its selective probe reactions. For instance, the reaction of H$_2$O$_2$ with Leuco crystal violet (LCV) catalyzed by horseradish peroxidase is exploited for its detection. LCV is oxidized by hydrogen peroxide, forming a purple-colored crystal violet ion (CV$^+$), which is stable for days.$^{127,129,130}$ Other probes that work in a similar way include DPD (N, N-dimethyl-p-phenylenediamine) and Leuco malachite green (LMG). Other metals utilize the transition metal ions to catalyze the reaction with the probe molecule such as 2-((5-Bromopyridyl)azo)-5-(N-propyl- N-sulfopropylamino)phenol + Ti$^{4+}$ (Ti-PAPS).$^{67}$ This technique cannot be coupled with heterogeneous catalytic reaction systems since they may cause interference with the system. 

**Figure 4-5** shows the UV-Vis spectra of aliquots of the reaction mixture that were added to a mixture of LCV and HRP to get the spectra of CV$^+$. Blank refers to the reaction mixture without the catalyst. The reaction conditions are from the optimized for the oxidative coupling of phenylacetylene.$^{131}$

![UV-Vis spectra](image)

**Figure 4-5.** UV-Vis spectra of aliquots of the reaction mixture that were added to a mixture of LCV and HRP to get the spectra of CV$^+$. Blank refers to the reaction mixture without the catalyst. Reaction conditions: phenylacetylene (0.5 mmol), catalyst (6 mol % of meso Cu/MnOx), toluene (5 mL), balloon of air, 105 °C.
Correspondingly, fluorescence probe molecules have been utilized to detect H$\text{}_2$O$\text{}_2$. Lucegenin is one such molecule. Lucigenin’s optimal pH is under basic conditions, but, lucigenin sensitizes superoxide production, is quenched by Cl$^-$, and reacts with hydroperoxides.\textsuperscript{132} Other fluorescence probes that involve selective catalysis using horseradish peroxidase (HRP) or other transition metals were chosen to focus on those of HRP. For instance, Luminol (phthalic cyclic hydrazide), Amplex Red (also known as APOXA; N-acetyl-3,7-dihydroxyphenoxyanine), p-Hydroxyphenylacetic acid (POHPAA), Redox sensor red CC-1, and dihydrorhodamin 123 were studied.\textsuperscript{55,67} Raza et al. analyzed the benzylamine coupling reaction mixture during the middle of the reaction by $^1$H NMR to confirm the production of H$\text{}_2$O$\text{}_2$; in the NMR spectrum, the peak for H$\text{}_2$O$\text{}_2$ clearly appeared at 10.95 ppm in NMR experiments.\textsuperscript{131}

\textbf{4.4.4 Hydroxyl Radical}

The hydroxyl radical is a non-selective oxidant that reacts at near-diffusion-controlled rates with many substrates, resulting in low steady-state concentrations of $\cdot$OH. The corresponding low concentrations and short lifetimes pose significant challenges in quantifying this ROS. Although $\cdot$OH absorbs light in the UV region, direct observation is not typically possible because of its limited lifetime and the presence of other chromophores absorbing in a similar wavelength region. Therefore, $\cdot$OH is quantified either through the loss of a reagent or accumulation of a product. The key challenge is obtaining a compound that will react selectively and unambiguously with $\cdot$OH, which does not interfere with the other aspects of the chemistry of the system under study. The time-resolved evolution of the $\cdot$OH at low concentration has been observed at pressures between 4 and 600 Torr and at varying distances between the photocatalytic surface and the
detection volume using laser-induced fluorescence (LIF). The fluorescence emitted from \( ^{\cdot} \text{OH} \) appearing at 310 nm was measured as a function of the excitation wavelength by using a dye laser. The presence of \( ^{\cdot} \text{OH} \) radicals was confirmed from the obtained LIF spectrum with the characteristic rotational structure of the transition energies.\(^{133}\) Though the LIF method is one of a few methods with which \( ^{\cdot} \text{OH} \) can be directly detected; its application is limited to the gas phase.\(^{134}\) EPR spin traps have also been utilized for the detection of \( ^{\cdot} \text{OH} \). Several spin traps have been studied for instance, DMPO (5,5-Dimethyl-1-pyrroline N-oxide)\(^{135}\), POBN (\( \alpha \)-4-pyridyl-1-oxide)-N-tert-butyl nitroside), and BMPO (5-diethoxyphosphoryl-5-methyl-1-pyrroline N-oxide).\(^{124}\) DMPO is one of the most commonly used spin trapping agents, but this material is not reliable in distinguishing superoxide anion radical form hydroxyl radical since the superoxide anion radical adduct spontaneously decomposes to the hydroxyl adduct. Therefore extra care should be taken when using this reagent. Actively scavenging the superoxide radical anion when analyzing for \( ^{\cdot} \text{OH} \) can help clarify the source of the adduct under observation. Conversely, the \( ^{\cdot} \text{OH} \) may also be quenched, and the superoxide radical anion adduct confirmed.\(^{115}\) Recently, BMPO has gained popularity due to the adduct lifetime of 20 minutes. This gives ample time for analysis.\(^{60,136}\) The \( ^{\cdot} \text{OH} \) radicals produced during the reaction reacts with BMPO to convert to stable BMPO-OH adducts, which are detected by ESR spectroscopy (Error! Reference source not found.).

\[
\begin{align*}
\text{BMPO} + ^{\cdot} \text{OH} & \rightarrow \text{BMPO-OH} \\
\text{Equation 16}
\end{align*}
\]

Fluorescence probes such as DST (Disodium Terephthalate),\(^{127}\) APF (3\(^{\prime}\)-(p-aminophenyl) fluorescein), CCA (coumarin-3-carboxylic acid) have also been used for \( ^{\cdot} \text{OH} \) detection. The
solubility of terephthalic acid (TA) is low in aqueous but markedly higher in common organic solvents such as toluene and 1,4 dioxane. While DST is typically utilized for its increased solubility in water, TA can be used in organic solvent systems. APF (3′-(p-aminophenyl) fluorescein) and HPF (2-[6-(4′-hydroxy)phenoxy-3H-xanthen-3-on-9-yl]benzoic acid) have been proven to be powerful fluorescence probes for the detection of hydroxyl radical (Equation 17).

![Equation 17](image)

Table 4-3 is a summary of various detection methods that are available for the detection of reactive oxygen species. These detection methods are not a plug and chug process; they should be carefully selected and modified based on the reaction conditions. Factors such as light, pH, temperature, and in some cases, the catalyst will affect the decision to use a specific method.

Table 4-3. Summary Methods of detection of reactive oxygen species.

<table>
<thead>
<tr>
<th>ROS</th>
<th>Detection method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)O(_2) (singlet oxygen)</td>
<td>Direct light emission</td>
<td>Phosphorescence ((^1\Delta_g \rightarrow \Sigma_g)) at 1270 nm in the near-IR region and the dimol emission ((2\Delta_g \rightarrow 2\Sigma_g^-)) occurring at 634 nm.</td>
</tr>
<tr>
<td><strong>O₂</strong> •⁻ (Superoxide anion radical)</td>
<td><strong>H₂O₂</strong> (hydrogen peroxide)</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>Direct EPR</td>
<td>Molar absorption coefficient of 0.01 M⁻¹ cm⁻¹ at 360 nm. Too low for detection.</td>
<td></td>
</tr>
<tr>
<td>ESR</td>
<td>Spin trapping agents such as HTMP (4-hydroxy-2,2,6,6-tetramethylpiperidine),</td>
<td></td>
</tr>
<tr>
<td>Fluorescence probes</td>
<td>SOSG (singlet oxygen sensor green), is sensitive to photodecomposition. TDI (terrylenediimide) 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazin-3-one (MCLA)</td>
<td></td>
</tr>
<tr>
<td>Optical absorption</td>
<td>Optical absorption at 245 nm with a low absorption coefficient that reduces to 1400 M⁻¹ cm⁻¹ when protonated to HO₂⁺.¹²¹</td>
<td></td>
</tr>
<tr>
<td>CRDS</td>
<td>Cavity Ring Down Spectroscopy.¹²³ Great for gas-phase superoxide.</td>
<td></td>
</tr>
<tr>
<td>ESR</td>
<td>DMPO, BMPO adducts decompose to ·OH adducts.</td>
<td></td>
</tr>
<tr>
<td>UV-Vis</td>
<td>NBT (Nitrotetrazolium Blue), XTT (2,3-bis(2- methoxy-4-nitro-5-sulfopheny), has a higher solubility in water and form an XTT-formazan with an absorption peak at 470 nm.</td>
<td></td>
</tr>
<tr>
<td>Fluorescence probes</td>
<td>Luminol, MCLA (6-(4-methoxyphenyl)-2-methyl-3,7-dihydroimidazo- [1,2-a]pyrazin-3-one hydrochloride) reacts with (^1)O₂.</td>
<td></td>
</tr>
<tr>
<td><strong>LIF</strong></td>
<td>Laser-Induced-Fluorescence Method</td>
<td></td>
</tr>
<tr>
<td>OH (hydroxyl radical)</td>
<td>ESR</td>
<td>DMPO, CPYMPO, BMPO, POBN spin trapping agents</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Fluorescence probes</td>
<td>DST (Disodium Terephthalate), APF (3′-(p-aminophenyl) fluorescein)(^{139}), CCA (coumarin-3-carboxylic acid)</td>
</tr>
</tbody>
</table>

### 4.4.5 In situ vs. Ex situ

Reactive oxygen species generation and reactivity different under *ex-situ* vs. *in situ*. Studying the ROS on the surface of the catalyst under ex situ conditions can not tell much about the overall reaction, but when compared to the in situ studies, a lot more information can be gathered. For instance, Achola et al. found that when conducting the detection of singlet oxygen ex situ, the amount of singlet oxygen was increasing over time, but under in situ conditions, the singlet oxygen is almost immediately consumed under visible light irradiation. This helped narrow down the moment the reaction was taking place and also confirmed the integral role played by singlet oxygen.\(^{60}\)

In some cases combining the trapping methods with scavenging can help validate the integrity of the ROS probe in an on/of switch type of way. In this case the in the absence of the scavenger, the trapping agent is switched on, and it is switched off when the scavenger is added. One such example was utilized to study the phenylacetylene homocoupling reaction.\(^{20}\)
Figure 4-6. NBT evaluation as a good trapping agent under on/of switch configuration using curcumin.

Additionally, when BHT (butylated hydroxytoluene) was used to quench the \(^\cdot\)OH adduct signal under EPR detection,\textsuperscript{25,83} the BMPO-OH adduct signal was markedly diminished for the amine to imine transformation using a CuO/Al\(_2\)O\(_3\) mixed oxide catalyst.\textsuperscript{142}

Figure 4-7. Quenching of the BMPO-OH adduct EPR signal by the addition of BHT under \textit{in situ} conditions.
4.5 Our Contributions

These methods were used to study the heterogeneous aerobic oxidative coupling of amines to imines where reactive oxygen species play an integral role in the mechanism. Three different catalysts were studied; cobalt doped mesoporous manganese oxide, mesoporous copper aluminum mixed metal oxide, and mesoporous copper sulfide material. The first catalyst (Cu_methAlbutox) was used for the heterogeneous aerobic oxidative coupling of amines to imines. Here, the generation of *OH, H_2O_2, O_2*, and ^1^O_2 was confirmed by the above mentioned methods. These observations led to Dissanayake et al. proposing a mechanism that included all four of the observed ROS. Interestingly, a radical cation was also trapped using BHT and the adduct presence confirmed using GC-MS.¹⁴⁴

Figure 4-8. Proposed mechanism containing all for ROS observed.¹⁴⁴
The second catalyst (1%Co-MnO₃) was used for the thermal heterogeneous selective catalytic protocol for amine-alcohol cross-coupling to produce symmetric or asymmetric imines. In this system, a detailed investigation was carried out to identify the reactive oxygen species (ROS) formed during the reaction. The superoxide anion radical (O₂⁻) was detected by the characteristic UV-Vis peak in between 450-700 nm in the presence of nitro tetrazolium blue chloride (NBT) probe molecule. An increase in intensity of the characteristic UV-Vis peak (at 596 nm, in the presence of leuco crystal violet) confirmed the presence of hydrogen peroxide (H₂O₂) during the reaction. The hydroxyl radical (·OH) was detected by the characteristic fluorescent peak at 430 nm in the presence of disodium terephthalate (DST). The fluorescence peak intensity observed when SOSG was added was low and therefore isn’t indicative of the presence of singlet oxygen ¹O₂.
Figure 4-9. Hydroxyl radical test, Peroxide test, Singlet oxygen, and super oxide anion test for the 1%Co-MnOx catalyst system.\textsuperscript{85}

The detection of the three ROS, led the authors to probe further to find out the terminal ROS. Therefore, ROS quenchers curcumin and butylated hydroxytoluene (BHT) were introduced to scavenge the superoxide anion radical and hydroxyl radical, respectively. The quenching of hydroxyl radicals inhibited the formation of imines. Whereas, a considerable amount (~15 %) of imine was obtained, despite quenching superoxide anions. This confirmed the hydroxyl radical to be the terminal ROS.\textsuperscript{85}

The third catalyst was a hydrothermally synthesized mesoporous copper sulfide. This catalyst was used for the visible-light-driven catalytic process for amine to imine transformations. In this system, the presence of superoxide radical anion ($\text{O}_2^-$), hydrogen peroxide ($\text{H}_2\text{O}_2$), singlet oxygen
(1O2) and hydroxyl radical (·OH)) were detected and therefore reactive oxygen species were investigated using different detection methods.

Multiple reactive oxygen species were detected in the reaction mixture using UV-vis and fluorescence spectroscopy in the presence of different indicators. Among these, superoxide radical anions and singlet oxygen (produced by the reaction between superoxide anion (O2·−) electron hole (h+) on the surface) are prone to abstract electrons, which is required to drive the reaction forward. Hence, to identify the ROS responsible for this process, specific quenchers were used. In the presence of p-benzoquinone (pBQ), the superoxide radical anion quencher, no significant drop in conversion (93%) was observed as compared to the unquenched system (97%). However, the conversion decreased significantly to 37% in the presence of sodium azide (NaN3), a singlet oxygen quencher. This indicated the major role played by singlet oxygen in catalyzing the meso-CuS driven photocatalytic transformation of amines to imines. This led us to propose a reaction mechanism using singlet oxygen, which initiated the reaction by abstracting electrons from the substrate and produced superoxide radical anions.83

Additionally, copper oxide supported on mesoporous manganese oxide (meso Cu/MnOx) was synthesized by an inverse micelle templated evaporation induced self-assembly procedure. The catalyst had exceptional catalytic activity in the aerobic oxidative coupling of terminal alkynes with a conversion and selectivity of >99% in both homocoupling and cross-coupling of alkynes using the optimized reaction conditions. The labile lattice oxygen of the meso Cu/MnOx was implicated in the deprotonation of the alkyne proton, as supported by TPD and TGA studies. Therefore, further studies were conducted to investigate the reactive oxygen species in this system.145 The aforementioned methods were used to detect ·OH, H2O2, O2·− and 1O2. The ·OH and H2O2 species were found to be present in this system.
Figure 4-10. Hydroxyl radical test, Peroxide test, Singlet oxygen, and super oxide anion test for the 1%Cu-MnO₃ catalyst system.

4.6 Conclusion

These studies reviewed above hypothesize that identifying the ROS and understanding their generation may enable us to further control reaction products. Reactive oxygen species control through catalyst design to achieve specific activity is a subject of great interest. We have outlined above many of the methods that can be used to study ROS. Some important points are that such species are transient, *in situ* methods must be used to observe and follow these ROS. Nonetheless, *ex situ* studies should not be completely disregarded since they also generate a great deal of valuable data. Albeit, said methods reveal the presence of ROS, their contributions could be either
in parallel or in series. A combination of previous knowledge deduced from different indirect methods such as catalyst characterization, substrate scope analysis, and computational predictions; and the existing knowledge of reactive oxygen species properties, generation mechanisms, and detection methods is a valuable tool for the understanding of heterogeneous selective catalytic oxidations. There needs to be considerable more work done on the heterogeneous selective catalytic oxidations before the design of ROS specific catalysts to achieve select reactions and selectivities.

### 4.7 References


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APPENDIX I: FUTURE WORK

The third chapter of this thesis describes a novel synthetic technique for the synthesis of first-row transition metal ferrites using microwave assisted hydrothermal methods. Mesoporous mixed metal oxides have high surface area, ultrafine particle size, and monomodal pore size distribution make them unique and interesting for different applications. The multivalency of transition metal ferrite nanoparticles provides a potential for oxidative reactions. These materials have been shown to be reactive towards the Suzuki-Miyaura cross-coupling reaction, the selective dehydrogenation of butene. Of particular interest is the catalyst recoverability, recyclability and leaching circumvention. Along with selective catalytic oxidations, their applications as electrode materials for lithium-ion batteries and electrochemical capacitors, and efficient electrocatalysts for the oxygen reduction reaction in metal–air batteries and fuel cells are of particular interest too. They also perform exceptionally as catalysts for the photoelectrocatalytic and photochemical water oxidation.

The fourth chapter reviews reactive oxygen species in heterogeneous catalytic selective oxidation research. The research described here may lead to new catalysts that can be used for water splitting, clean hydrogen generation, activation of other hydrocarbons like methane, and use of selectively oxidized products in chemical and pharmaceutical applications. Pre-existing catalysts that have proven exceptional activity should be studied as well to elucidate the root of their exceptional activity. We hypothesize that some of these systems are reliant on ROS stabilization and control. Some of the best catalysts in the world are found in our bodies and they have efficiently driven numerous processes to keep homeostasis. Studies in biological systems have shown that some of these catalysts are able to stabilize and control ROS to achieve exceptional selectivity. Therefore,
studying the ROS is selective catalytic oxidations is a step in the right directions towards catalyst design. Pre-existing catalysts that have proven exceptional activity should be studied as well to further probe the mechanisms.
APPENDIX II: LIST OF PUBLICATIONS


17. Liu, P; Dang, Y; He, J; Shirazi Amin, A; Achola, L; Dissanayake, S; Liang, X; Suib, S. Effects of Zr substitution on soot combustion over cubic fluorite-structured ceria: Soot-ceria contact and interfacial oxygen evolution. Under review- Langmuir.

18. Kankanamage, R; Ghosh, A; Jiang, D; Gkika, K; Keyes, T; Achola, L; Suib, S; Rusling, J Metabolites of Tobacco- and E-Cigarette-related Nitrosamines Can Drive Cu²⁺-mediated DNA Oxidation. Under review- Chemical Research in Toxicology.

**To be submitted**


APPENDIX III: CONFERENCES AND TALKS


4. (Oral) Laura A. Achola “X-rays for Structural and Elemental Analysis.” Western Connecticut State University, Danbury, Connecticut, February 08, 2019

5. (Poster) Laura A. Achola, Aaron Ghebrehiwet, Steven L. Suib "Water oxidation catalysis by manganese oxide/cobalt oxide@ iron oxide core-shell nanocomposites." American Chemical Society (ACS) Conference, Boston, Massachusetts, August 19-23, 2018