



Faculty of Sciences

Department of Chemical and Forensic Sciences

**ALPHA MANGANESE OXIDE OCTAHEDRAL MOLECULAR SIEVES
(OMS-2) OXIDATION STATE TAILORING FOR SELECTIVE
COUPLING OF ANILINES TO AZOBENZENE.**

by

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ABSTRACT

Azobenzenes are a crucial class of molecules used as dyes, food additives, indicators, and therapeutic agents. Conventional methods used for preparation of azobenzene involve use of high stoichiometric/ toxic oxidant amounts which pose several drawbacks such as undesirable overoxidation products, harsh reaction conditions, limited functional group compatibility and environmentally unfriendliness. K-OMS-2 has superbly tailorable functionality which can be adjusted to favor formation of azobenzene. OMS-2 surface chemical property was successfully adjusted via etching with oxalic acid at room temperature and applied for oxidative coupling of anilines to azobenzene. Material characterization was carried out by XRD, SEM, TEM and BET to explore the relationship between material property and catalytic activity after acid treatment. The results show increase in surface area at lower acid concentration as regular K-OMS-2 has 72.6 m²/g, 0.025M OxH-OMS-2 has 81.9 m²/g and decrease to 53.6 m²/g as acid concentration was increased to 0.100M. The XRD shows retention of cryptomelane phase structure after etching and the nanorod morphology of the OMS-2 material is also maintained as is observed from SEM and TEM images. OMS-2 shows higher catalytic conversion of 72% compared to etched OMS-2 which shows 47% in 0.025M OxH-OMS-2, and 41% in 0.100M OxH-OMS-2 at 110° C which is attributed to less Mn⁴⁺ content on the catalytic surface due to reduction by oxalic acid from Mn⁴⁺ to Mn³⁺/Mn²⁺. Selectivity of azobenzene was observed to increase with the increase in concentration of the etchant in the following series, OMS-2 18%, 0.025M OxH-OMS-2 48% and 0.100M OxH-OMS-2 80% which can be ascribed to change on surface chemical state of the material. Calcined 0.100M OxH-OMS-2 shows higher performance of 57% than uncalcined catalyst which is 41%. Moreover, calcination decreased selectivity of azobenzene from 80 to 70% indicating oxidation of Mn²⁺/Mn³⁺ back to Mn⁴⁺ in air.

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DEDICATION

GOUTA BOTUMILE

I DEDICATE THIS TO MY MUM FOR NOT ONLY RAISING AND NURTURING ME BUT ALSO, SHE GAVE THE LITTLE SHE HAD TO SUPPORT MY EDUCATION AND INTELLECTUAL DEVELOPMENT. I HOPE THIS THESIS WILL SATISFY THE DREAM YOU HAD FOR ME IN ALL MY ACADEMIC CAREER.

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LIST OF ABBREVIATION

AMO- Amorphous Manganese Oxide

AOS- Average Oxidation State

BET- Brunnauer-Emmet-Teller

BJH- Barrett, Joyner, Halenda

GC-MS- Gas Chromatography Mass Spectrometer

HOMO- Highest Occupied Molecular Orbital

JCPDS- Joint Committee on Powder Diffraction Standards.

HTERM - High Resolution Transmission Electron Microscope

K-OMS-2- Cryptomelane manganese oxide Octahedral Molecular Sieves

LUMO- Lowest Unoccupied Molecular Orbital

NIST- National Institute of Standards and Technology

OMS- Octahedral Molecular Sieves

OxH-OMS-2- Oxalic acid etched cryptomelane manganese oxide Octahedral Molecular Sieves

SEM- Scanning Electron Microscope

SET- Single Electron Transfer

TBHP- Tert-Butyl Hydroperoxide

VOCs- Volatile Organic Compounds

Powder XRD- Powder X-ray Diffractometer.

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CHAPTER 1: INTRODUCTION

1.1 Manganese Oxide Octahedral Molecular Sieves (OMS-2)

Manganese Oxide Octahedral Molecular Sieves (OMS) are types of Manganese Oxides with tunnel structure constructed from edge and corner shared MnO_6 octahedra units forming a hollow tunnel structure. Most MnO_6 materials occur naturally in manganese nodules and the connectivity between these MnO_6 building blocks can be in form of the tunneled (e.g. cryptomelane, pyrolusite, ramsdellite), layered (e.g. buserite, birnessite) or three-dimensional networks (e.g. bixbyite, hausmannite)[1] (Figure 3). The composition of such manganese nodules is more varied and linked to watery habitats such as the middle Atlantic ridges and later exposure (after crystallization) to oceanic, lake, and river environments where cation exchange occurs. Hence much effort has been directed on preparation of these materials[2]. The methods of preparation of these materials have a direct influence on their ion sieves, electrochemical and catalytic properties though they exhibit similar structures[3]. Control of combination of MnO_6 is essential since it determines the size and the pore structure of these materials as it has been observed that 3x3 tunnel gives OMS-1, 2x2 OMS-2 tunnel, 2x4 tunnel OMS-5 and 1x1 tunnel OMS-7 etc. OMS-2 demonstrated remarkable performance among all OMS materials due to its catalytic activity, semiconductivity, myriad of synthetic routes, particle sizes and morphologies[2]. Tunnels usually contain water molecules, alkali metal or alkali earth counterions as a compensation for charge imbalance in a mixed valent system.

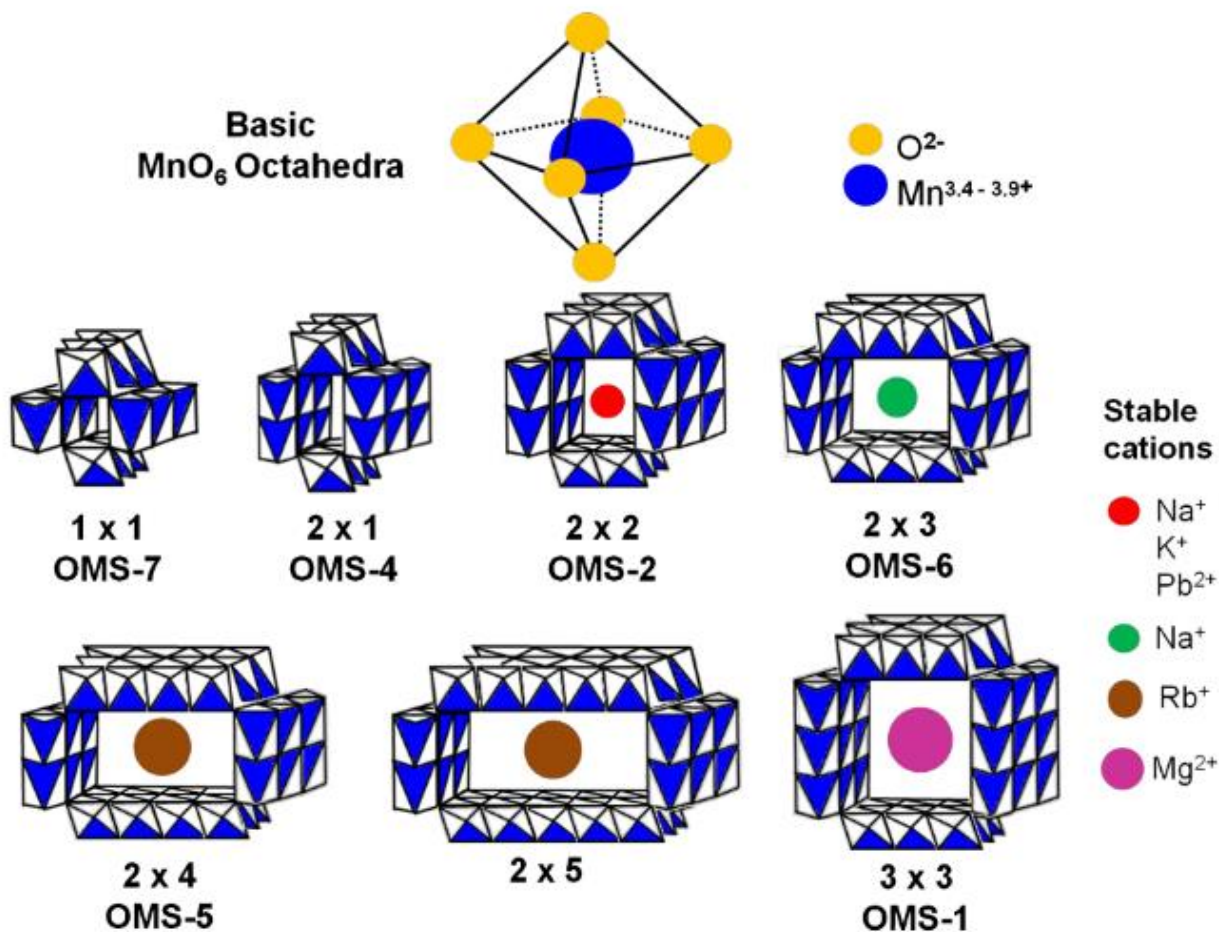


Figure 1: OMS materials with different tunnel structures and pore sizes[4].

Cryptomelane -type manganese oxide is an octahedral molecular sieve (K-OMS) which comprises of 2×2 edge-shared MnO₆ octahedra units, which are corner shared to form one-dimensional tunnels with K⁺ inside the tunnels (K-OMS)[5]. The square shaped tunnel has a size of 0.46 nm x 0.46 nm having diameter cross section in the range typical for that of zeolite pores. K-OMS-2 type material has myriad preparation method from Mn²⁺ precursors either in aqueous solution or in solid state using oxidants like KMnO₄, O₂, K₂Cr₂O₇, KClO₃, K₂S₂O₈ or maleic acid[6]. The chemical composition for K-OMS-2 (cryptomelane structure) is KMn₈O₁₆. This synthetic cryptomelane has been reported to invariably materialize into a tetragonal crystal structure. Manganese oxide octahedral molecular sieves (OMS) are a type of microporous transition metallic oxide with a variety of tunnel architectures that may be made by adjusting synthetic parameters including temperature, concentration, pH, and cations. Within the tunnels of

OMS materials, counterions such as K^+ , Na^+ , Ba^{2+} , other alkali, alkaline earth metal ions, and water play a role in charge balancing and material stability. The reduction of Mn^{4+} to Mn^{3+} , known as redox exchange, causes a charge imbalance on the octahedral framework of K-OMS-2 mixed valent α - MnO_2 , which is corrected by K^+ located in the tunnel site. This redox exchange's general formula is as follows:



Where K is a vacant site[7]. 16 oxygen sites, 8 six-coordinated Mn sites, and 2 eight-coordinated tunnel sites make up the unit cell (I4/ m). According to research, the synthesis of tunnel structure porous manganese oxides necessitates the use of hard cations as templates for adjusting tunnel size and concomitant pore structure also it has been discovered K^+ template 2x2 tunnel structures and Rb^+ ions were considered to specifically yield 2 x 4 structures[2]. Co-existence of mixed valence states of Mn^{4+} , Mn^{3+} and/or a small amount of Mn^{2+} sites in the K-OMS-2 framework with average oxidation state of ~ 3.8 is pivotal. The manganese oxides with multiple Mn oxidation states together with several features such as beneficial porous structure, hydrophobic nature, synergistic effect between K and Mn., the possibility to incorporate other transition metals as dopants, Lewis acidic sites and greater mobility of lattice oxygen at the catalytic surface have been reported as promising low cost- efficient, and environmentally benign catalysts for selective and complete oxidation reactions[8], [9] and also applied as molecular sieves. Typical example of these oxidations include oxidation of alkane or olefin epoxidations with tert-butyl hydroperoxide (TBHP) as oxidant, ethylbenzene oxidative dehydrogenation, side-chain oxidation of alkyl aromatics, alcohols oxidation and the total oxidation of VOC model compounds[6]. Mixed valency is seen in manganese redox enzymes in natural manganese oxide nodules, chemiluminescence systems, electrochromism, secondary non-aqueous rechargeable batteries, magnetics, electron transfer and electrocatalysis, ceramics, and biological systems.[10]. Microporous metal oxides have shown great deal of interest in heterogeneous catalysts due to their native distinctive attribute of high surface area and tunable pore sizes. High surface area provides a high active site which facilitates the binding of the substrate, whereas tunable pore size expedites adsorption and mass transfer[11].

1.2 AZOBENZENE

These are class organic compounds usually known as aromatic azo used as dyes, food additives, pigments, indicators, and therapeutic agents and as intermediates in the preparation of natural products[12]. Additionally azo compounds have shown great deal of interest in electronics and drug delivery where azobenzene due to their characteristics of being small in size, robust photo switching, synthetic accessibility, and low rate of photobleaching serves as excellent unit for the generation of elaborate optical devices applicable applications in variable sectors such as nonlinear optics, optical storage media, chemosensors, liquid crystals, photochemical molecular switches, molecular shuttles, nanotubes and in the manufacture of protective eye glasses and filters[13].

1.3 IMINES

Due to the unsaturated C=N double bonds, imines are highly reactive nitrogen-based chemicals. Imine derivatives are employed in the production of agricultural and pharmaceutical products as versatile intermediates.[11]. This class of compounds can be prepared from aldehydes, formamides, palladium catalyzed amination and by polymer supported[14]. Some imines, mostly N-salicylidene-anilines, have been found to have phototropic and thermotropic properties. The most common preparation of imines is through the reaction of aldehydes and ketones with amines[15] and their preparation is generally carried through refluxing with azeotroping agent when necessary and its usually acid catalyzed reaction.

1.4 PROBLEM STATEMENT

Azobenzene synthesis traditionally relied on azo coupling, Mills reactions and Wallach reactions[16]. Azo coupling reactions involves use of high stoichiometric amounts of nitrite salts (NaNO_2)/ toxic oxidants which will then require acid to liberate in situ nitrous acid from NaNO_2 in the formation of diazonium salt from primary amine[12]. The Mills reactions approach requires use of glacial acetic acid as a medium in coupling of nitroso derivatives with anilines. Oxidizing agents such as ferric chloride, Caro's acid (H_2SO_4) and chromates have been used in this reaction. Wallach reactions involve use of strong acid and Lewis acid, which are harmful to the environment[17]. This stoichiometric oxidant has various downsides, which are the

formation of unwanted hazardous waste, limited functional group compatibility, use of additives, harsh reaction conditions such as (high pressure, high temperatures) and complicated means of separation from the final product. Other azobenzene synthesis protocols which involve use of unfriendly oxidants such as mercury salts, lead salts and ferrates salts which are harmful to the environment have been recently reported[12]. Precious metals such as Au, Pt, or Pd nanoparticles have also been used as the catalyst for azobenzene where the reaction was carried under O₂ at high pressure which means the methods are industrially unfriendly and high cost-efficient. Chemists are focusing on greener synthesis techniques with high atom efficiency because of growing environmental concerns[18]. Homogeneous catalysts have several drawbacks hence replacing them with alternative solid (heterogeneous) catalysts such as non-precious metal oxides is a major goal in catalysis research and engineering. When compared to homogeneous catalysts, heterogeneous catalysts have the following advantages: low toxicity, increased environmental friendliness, elimination from the reaction mixture at a low cost via simple filtration or centrifugation, easy and safe disposal, safe storage, adaptability to a wide variety of pressures and temperatures, long lifetimes, regenerable and reusable[11]. The crystallinity, pore size, particle size distribution, oxidation state, morphology, thermal stability, and surface area of manganese oxide have all been methodically adjusted to achieve brilliantly tailorable functions[19]. This material can be adjusted to suit desired functions by simple treatment with low oxalic acid concentration as is being demonstrated in this research. Strong size/structure attribute functioning link has been recognized for this class of materials.

1.5 AIM AND OBJECTIVES

1.5.1 Main Aim

- Prepare and characterize K-OMS-2 catalyst for catalytic synthesis of imines and azobenzene from aniline and benzyl alcohol

1.5.2 Specific Objectives

- To synthesize and characterize K-OMS-2 catalysts
- To conduct post etching on K-OMS-2 with oxalic acid at room temperature.

- To study the catalytic activity of OMS-2 towards benzyl alcohol and aniline oxidation to imines and azobenzene.

1.6 JUSTIFICATION AND SIGNIFICANCE

Recent concerns about the environment and energy are inspiring researchers to develop heterogeneous catalysts that can retain structure reactivity and selectivity and variable temperatures and pressures. Azobenzene has been previously prepared by techniques with several downsides such as use of strong acids, precious metals, harsh reaction conditions and non-precious metal oxides involving laborious techniques on their preparation hence there is need for alternative techniques with less drawbacks

After completion of this study, there will be inexpensive and environmentally benign technique suitable for azobenzene production which inspire green Chemistry and Sustainable development which is etching K-OMS-2 with low oxalic acid concentration to adjust its oxidation state to favor Azobenzene formation.

CHAPTER 2: LITERATURE REVIEW

2.1 CRYPTOMELANE OCTAHEDRAL MOLECULAR SIEVE (K-OMS-2)

These cryptomelane can be prepared via several methodologies such as hydrothermal treatment, reflux method, microwave heating, sol–gel and solvent- free method, having remarkable impact on the material's catalytic activity[6]. Solvent-free method cryptomelane-type manganese oxide presents several advantages when put next to standard preparation procedure (reflux method), such as shorter preparation time, absence of solvents which reflect green synthesis as there is no disposal of organic compounds leading to pollution and thermal treatment at lower temperature[20]. This solvent free method has also been found to yield material of higher surface area and higher catalytic activity more especially in volatile organic compounds (VOCs) oxidation as stated by[20]. On the other hand, reflux prepared OMS-2 materials by oxidation of Mn^{2+} by KMnO_4 in acidic media presents higher surface areas, smaller particle sizes, more acid sites, and more defects (primarily oxygen vacancies) as compared to other materials prepared by various methods [21]. Although the reflux approach has some advantages, it also has several disadvantages, including long reaction durations (24 h) and the use of highly concentrated HNO_3 , which is a strong oxidizing acid. As a result, reflux is unsuitable for large-scale production, which necessitates moderate conditions and a quick reaction time for high-volume production. The preparation route for K-OMS-2 material also affect its morphology as it was found that oxidation by $\text{K}_2\text{Cr}_2\text{O}_7$ produce crystallites in the form of needles grouped in dendritic patterns up to 4 mm diameter and reflux method in acidic medium yield fibrous agglomerates samples.

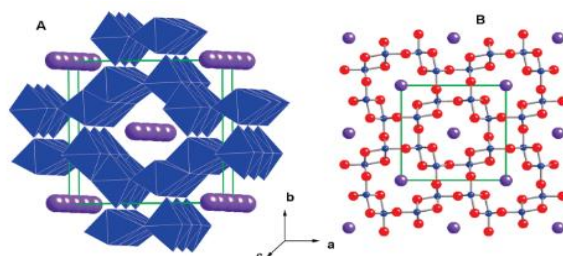


Figure 2. K-OMS-2 representation in polyhedral. (A and B) is a view from the c axis of a tetragonal unit-cell. The pink, blue, and red spheres represent K, Mn, and O, respectively[5].

Catalytic activity of the material can be enhanced by doping with transition metal or noble metals. Doping cryptomelane with various cations of different types has been observed to have an improved textural property, Mn average oxidation state (AOS) modification, thermal stability, increased structural defects, e.g., vacancies. It also enhances the catalytic oxidation of various organic pollutants [22]. These doped porous cryptomelane materials possess high surface areas (40-100 m²/g), more oxygen vacancies compared to undoped K-OMS-2, and there are more OH groups bonded to the surface[5]. The nature of doping metal and doping conditions of K-OMS-2 such as mode of incorporation and calcination temperature has an influence on physico-chemical properties. Doping K-OMS-2 can result in cations partially replacing K⁺ in the tunnel, Mn³⁺ or Mn⁴⁺ cations being substituted in MnO₆ octahedra, and/or distributed transition metal oxides supported on the cryptomelane phase. Metal dopants for K-OMS-2 are often chosen for their sizes, charges, and polarizabilities, which are like those of Mn²⁺, and are used to replace Mn²⁺ ions in the OMS-2 framework.[23]. The other means of modifying the surface/structure of material to enhance catalytic activity can be through etching where the materials are treated with acids[24]. Etching is carried on the K-OMS-2 material to enhance its catalytic activity as it creates newly formed point defects on the surface of the material. Defects play a crucial role in the application of OMS materials and the common type of defects in these materials is oxygen defects. Oxygen ion removal from OMS materials can markedly have an impact on the conductivity of the material[2]. Oxygen vacancies also have potential catalytic activity since those voids provide the area for substrates to dock in the material. Oxygen vacancies can also pave the way to doping of the materials since they can contribute to the charge balance of the material. Treatment of K-OMS-2 with acetic acid was investigated where the structure and phase purity monitored by XRD exhibited peaks corresponding to that of tetragonal cryptomelane structures of α -MnO₂ and it was concluded that etching has no effect on the phase structure of the material[24]. Further studies reveal that the effects of acetic acid on the surface morphology of K-OMS-2 using SEM were retained as nanorod morphology after acid treatment, also element mapping indicated continuous dispersion of the K, Mn and O elements. In the study of the K⁺ content a decrease in K⁺ from 5.5% (wt.) to 4.5% (wt.) from regular materials to the acid treated materials[24]. Characterization of the material was also carried using TEM on which lattice fringes of HRTEM images with d-spacing of 0.69 nm corresponding to 110 facet was found to be clearer in regular material than in acid treated materials which implies that the regular OMS-2

is more crystalline, and the acid treated materials has poor crystallinity with more defects. The average oxidation state (AOS) of Mn in the OMS-2 catalysts was deduced based on the Mn 3s spectra and the calculated AOS reduces from 3.75 to 3.62 after acid treatment further proving the more Mn^{3+} in the acid-treated OMS-2 than in the regular catalysts. Additionally, it was found that the surface adsorbed oxygen (O_{ads}) and lattice adsorbed oxygen has influence in catalytic activity of the catalyst[25]. The increasing of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio leads to increase in catalytic combustion of reactions. Time and temperature have influence on nucleation and growth of crystalline OMS-2 materials and the OMS-2 crystal growth is determined by the energy necessary for thermal transformation of amorphous manganese oxide (AMO) to OMS-2 which requires increase in temperature[19]. High crystal growth rate gives small particle size and the high thermal stability of the material which is associated with high crystallinity and vice versa. The post-thermal treatment of the materials also influences the phase and the crystallinity of the material[25]. The phase transformation was observed in the following pattern when the OMS-2 was calcined; MnO_2 , Mn_2O_3 , Mn_3O_4 and MnO which is in the phase of cryptomelane, bixbyite and hausmannite. This indicates that the calcination temperature increases with the reduction of manganese from Mn^{4+} to Mn^{3+} and eventually Mn^{2+} [25]. Calcination is pivotal in material physicochemical properties and its performance. The ideal aging temperature and time for the active K-OMS-2 sample shows high surface area and $\text{Mn}^{3+}/\text{Mn}^{4+}$ molar ratio hence high catalytic activity as a result. Uncalcined material required a high temperature of 250°C to complete benzene oxidation[25]. $\alpha\text{-Mn}_2\text{O}_3$ carries a complex orthorhombic crystal system having Mn^{3+} atoms octahedrally coordinated by oxygen, but with different distortion of MnO_6 octahedra sharing edges and corners. In case of Mn_3O_4 , Mn^{3+} ions are positioned in weakly distorted octahedral sites $[\text{MnO}_6]$ while Mn^{2+} ions are in tetrahedral sites $[\text{MnO}_4]$ with tetragonal symmetry and deformed spinel structure (space group, $I41/\text{amd}$)[26].

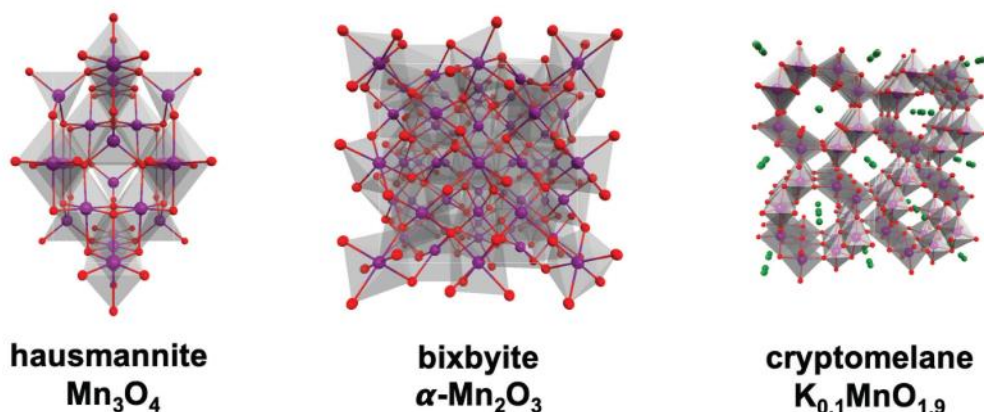
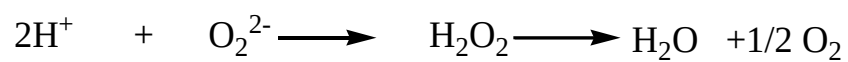
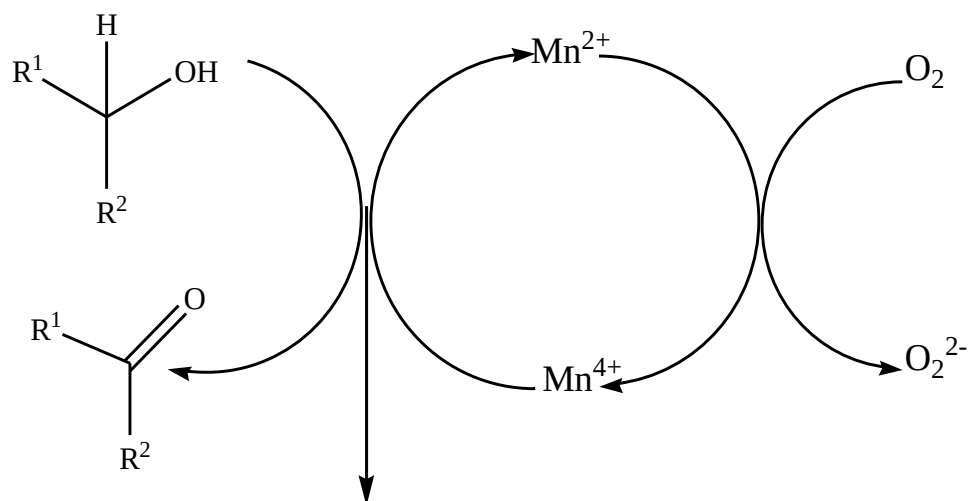


Figure 3; Structures of manganese oxides with different structural motifs having MnO₆ as building block[1].

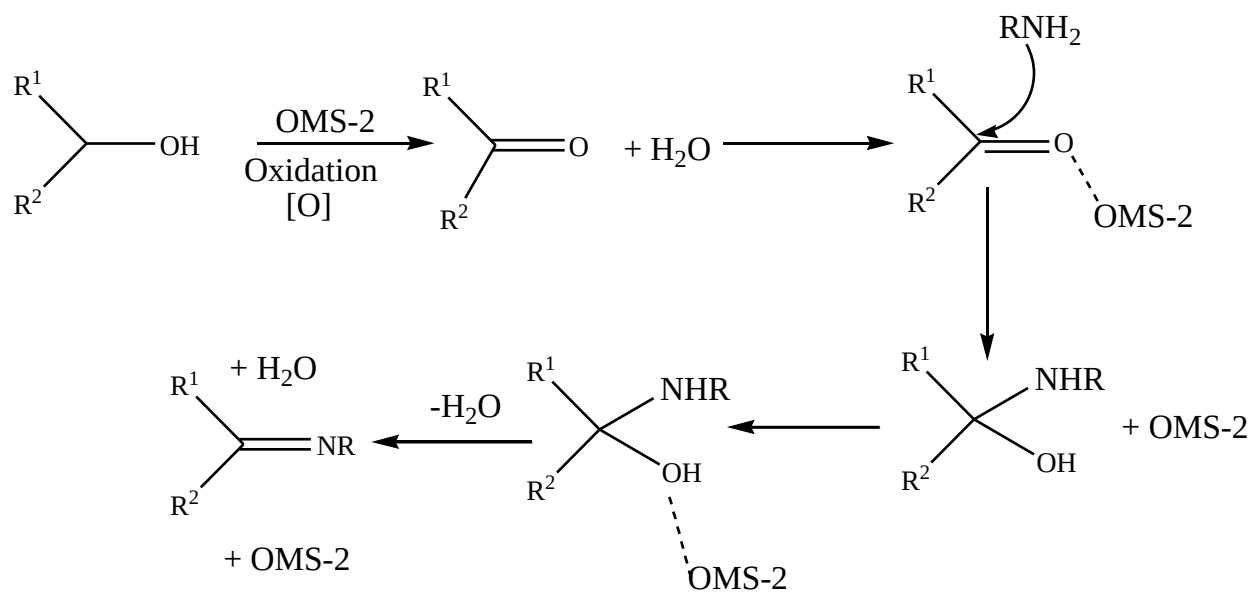
2.2 IMINES

This is a class of nitrogen containing organic compounds also known as Schiff bases which are useful in preparation of a variable of organic compounds such as pharmaceutical and fine chemicals. They are frequently utilized in a variety of biological activities, including lipoxygenase inhibition, anti-inflammatory, anti-cancer, antibacterial, and anti-fungal behavior[27]. This class of compounds was first discovered by Hugo Schiff in 1964 from condensation of carbonyl compounds with primary amines[27], hence they are often referred to as Schiff bases or azomethines. Many organic transformations, including cyclization, reduction, addition, condensation, aziridination, and others, have used this family of compounds as electrophiles. [28]. These classes of compounds are assigned structure of RR'C=NR'', where R groups represent alkyl or aryl substituents, or hydrogen connected to the imino (C=N) carbon or nitrogen. Imines containing the imino group as an integral element of a heterocyclic system, as well as compounds containing the imino group as an integral part of a heterocyclic system, have yet to be identified. However, a cyclic saturated system can be formed from R and R' [15]. This class of compounds has variable nomenclature depending on R and R' groups, compounds where R is alkyl or aryl and R' is a hydrogen are referred to as Aldimines, while those which both R and R' are alkyl or aryl are referred to as ketimines. Direct imine synthesis has been discussed which includes oxidation of secondary amines, dimerization of primary amines, and some other methods. However, these processes frequently necessitate extreme conditions, such as the use of alkaline or acidic chemicals, resulting in the generation of unwanted wastewater and harmful

byproducts. In the viewpoint of sustainable development aerobic oxidative coupling of an alcohol with amine has been proposed as a cost effective and environmentally benign approach for preparation of imines[29]. This is because coupling amine with alcohol produces water as only byproduct also alcohols are readily available which favors sustainable chemistry. One-pot catalytic processes for direct production of imines from alcohols and amines with manganese octahedral molecular sieves, ruthenium hydroxide supported on TiO_2 , and palladium nanoparticles supported on boehmite nanofibers was reported before. However, high reaction temperatures ($>363\text{ K}$) are required. Active manganese oxide has been found to undergo bifunctional tandem catalysis in imine formation from alcohol and amine. Tandem catalysis replaces multi-step synthetic routes with catalytic processes that are effective and can have substantial effect in the synthesis of fine chemicals and pharmaceutical intermediates. However, there are significant disadvantages to this approach, including the need for a large amount of active manganese oxide as the stoichiometric oxidant and dehydrating agents[14]. This tandem catalytic reaction was carried where benzyl alcohol diffuses and adsorb to the surface of K-OMS-2 and undergo oxidation to form benzaldehyde and subsequently the K-OMS-2 provide Lewis acid sites for oxygen in the carbonyl group to accelerate the amine's nucleophilic attack on the carbonyl group forming benzylideneaniline. This reaction was subjected to harsh conditions such as 110°C and 24 h. OMS-2 catalytic oxidation reactions proceed with Mars van Krevelen mechanism[30] in which, the substrate molecules adsorb to the surface and take advantage of the lattice oxygen from the OMS-2 structure and the gas phase oxygen from the atmosphere will then replenish the oxygen used in the material.



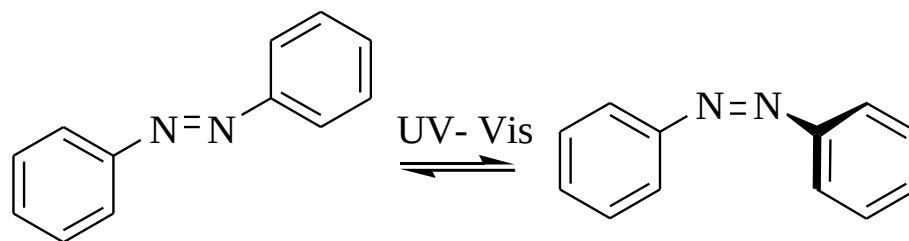
Scheme 1: Mechanism for oxidation of alcohol by K-OMS-2[14]



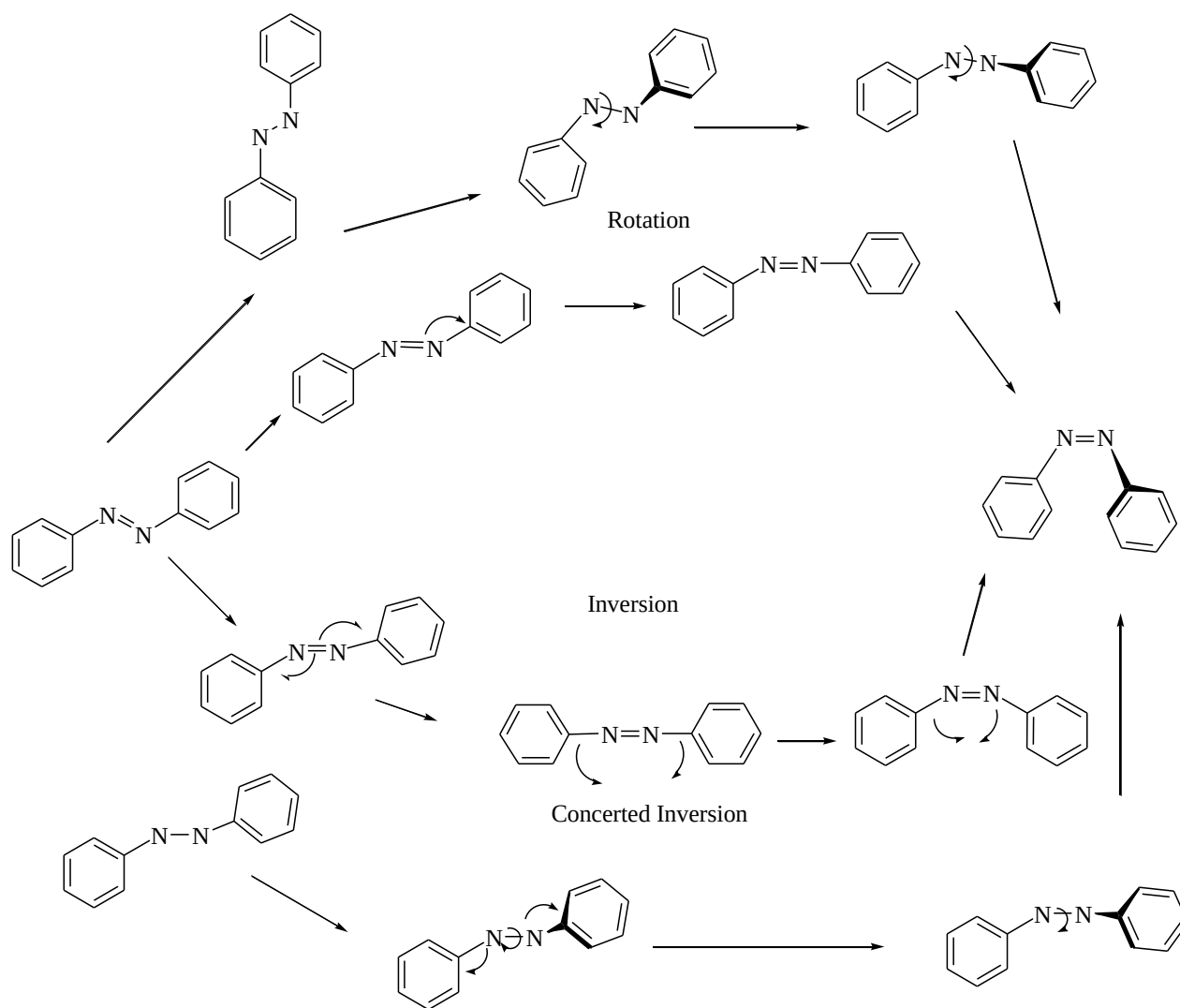
Scheme 2: Mechanism for formation of Imine[14]

2.3 AZOBENZENES

Azobenzenes are class organic compounds usually known as aromatic azo used as dyes, food additives, pigments, indicators, and therapeutic agents and as intermediates in the preparation of natural products[12]. Additionally azo compounds have shown great deal of interest in electronics and drug delivery. Their properties of being small, robust photo switching, synthetic accessibility, and low rate of photobleaching serves as excellent units for the generation of elaborate optical devices. These devices are applicable in variable sectors such as nanotubes, chemosensors, liquid crystals, photochemical molecular switches, molecular shuttles, nonlinear optics, optical storage media, chemosensors, molecular shuttles, and filters for safety glasses. Azobenzene can be used as a stabilizer by incorporating it into polymer matrices and due to its rigid rod-like form, it can behave as liquid-crystal mesogens in a variety of materials[31]. Activity of enzymes and polypeptides in biological systems can be modified by photo-response of azo compounds. Azo compounds also have promising ability in giving accurate results during diagnosis of Alzheimer's disease. They can also be applied as probes for diagnosis in amyloid plaques visualization in mentally deteriorating patient's brain due to their physiological activity. Azobenzene exists as two isomers which are E/trans and Z/cis. The E isomer is more thermodynamically stable than the Z isomer with 50 kJ/mol consequently this different spatial arrangement has different chemical and physical properties[32]. E- azobenzene is planar with dihedral angle around N, N, C, C being $\sim 17.5^\circ$ whereas for Z- azobenzene one of benzene ring occupies a plane tilted by 56° from the plane of the other ring. Two mechanisms for isomerization of azobenzene have been suggested which involves the N–N double bond rotation and includes complete rupture of π -bond giving a highly dipolar activated complex leading to rotamers and the other proceed with one (or both) azo-nitrogen atom inversion with simultaneous $sp^2 \rightarrow sp$ rehybridization during the activation process leading to invertomers[33]. The E to Z isomerization pathway can be through rotational and/or inversion due to photoirradiation whereas for thermal there is only inversion from Z to E isomerization. Photo-isomerization of azobenzene between E and Z isomers and their recovery to the starting E isomer is one of fascinating features about these compounds. The dipole moment is induced during the E to Z-photoisomerization of azobenzene (μ - E-azobenzene= 0.5 D vs μ - Z-azobenzene= 3.1 D), which simultaneously determines the hydrophobicity and hydrophilicity for both isomers.



Scheme 3: E and Z isomers of azobenzene due to photoisomerization upon UV-Vis irradiation[32].

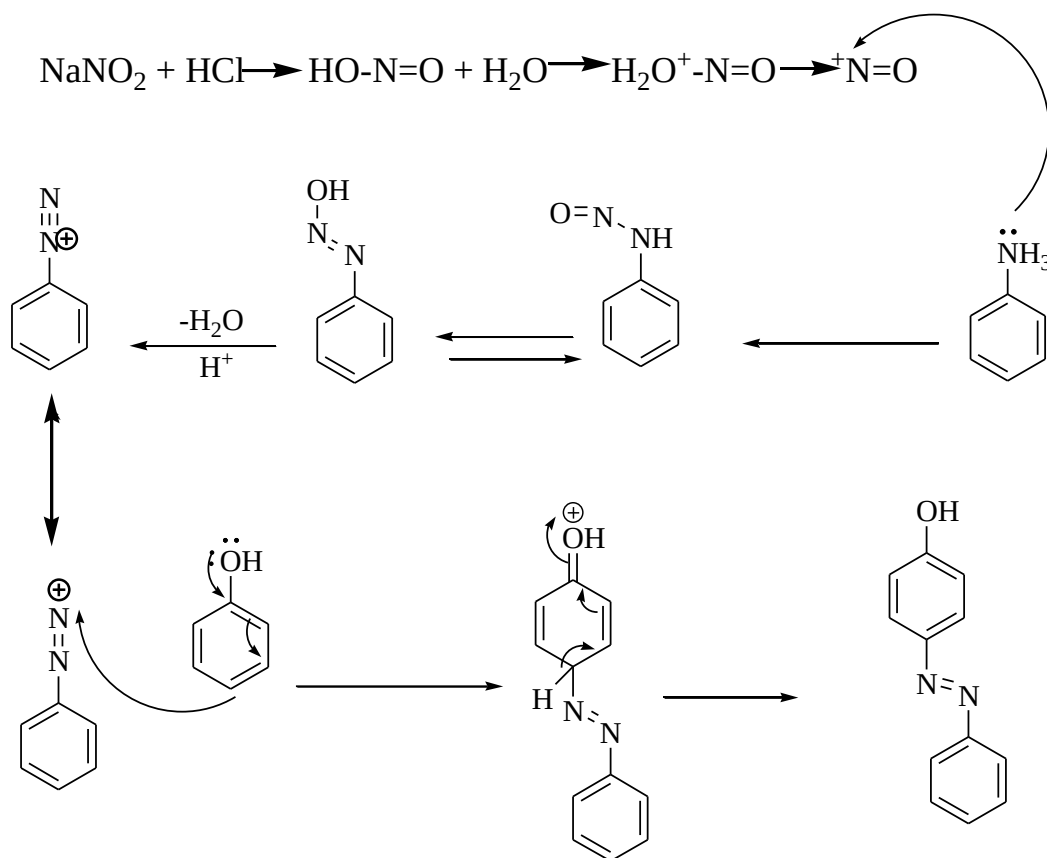


Scheme 4: Proposed mechanism for trans-cis isomerization of azobenzene[34].

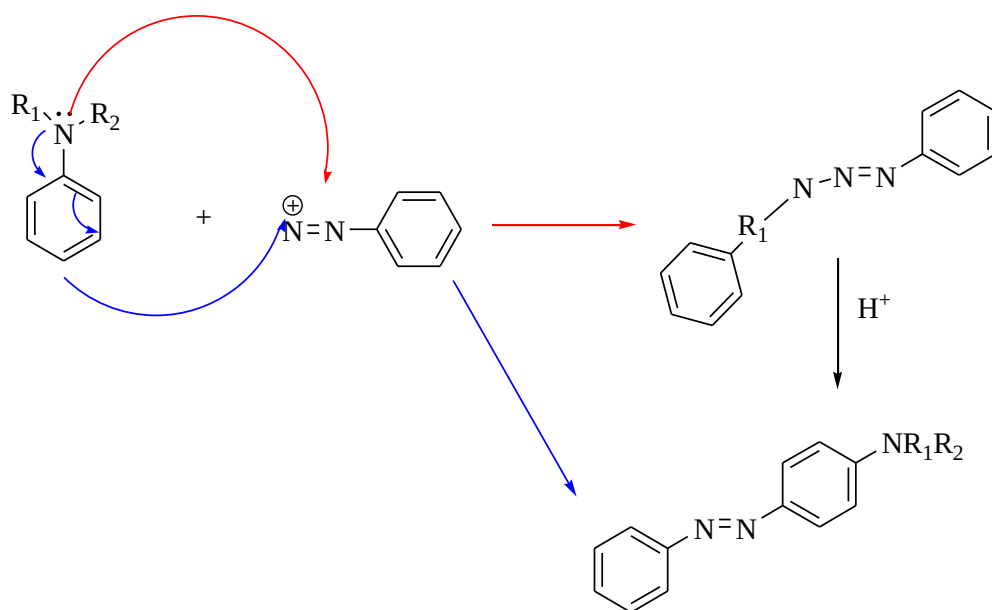
The classical methods for azobenzene synthesis are azo coupling reaction, the Mills, and the Wallach reactions, although there are other methods that have been discovered for azobenzene preparation such as reduction of nitro compounds, the dehydrogenation of arylhydrazines, and the rearrangement of aryl triazenes[35].

2.3.1 Azo Coupling Reactions

Azo coupling involves initial diazotation of aromatic primary amine at low temperature which will then react with an aromatic nucleophile in an acidic or basic medium. This method requires short reaction times and high yield is recorded[13]. This method involves use of high stoichiometric amounts of nitrite salts (NaNO_2). Acid is required in the formation of diazonium salt from primary amine to liberate in situ nitrous acid from NaNO_2 . Protonation and elimination of H_2O gives the nitrosating agent ($^+\text{N}=\text{O}$), which reacts with the amine to give N-nitroso derivative which will tautomerize to diazohydroxide[17]. Further protonation and elimination of H_2O lead to diazonium salt which is resonance stabilized. Phenol in ionized form must couple with diazonium salt since it will be sufficiently nucleophilic. Slightly alkaline solutions are crucial since diazonium salt develops into diazohydroxide in the basic condition which then will inhibit coupling. Therefore, the coupling of phenols must be carried in a mild basic condition with pH controlled whereas for aromatic amines weak acidic medium is required to avoid N-coupling without lowering the nucleophilicity of nitrogen that must be protonated in strongly acidic medium. Maximum rate for phenol coupling is observed at $\text{pH} \approx 10$. There are two possible pathways when aromatic amine is used as a nucleophilic reagent which involves N-N bond formation resulting in amino diazo compound which undergoes further rearrangement to azo compound[17]. The other pathway takes place when the reactivity of aryl ring is enhanced by electron donating group as a substituent or fused rings in which it will lead to direct formation of C-N bond between aryl ring and diazonium salt yielding azo compound.



Scheme 5: Mechanism of formation of diazonium from primary amine to couple with phenol[17].

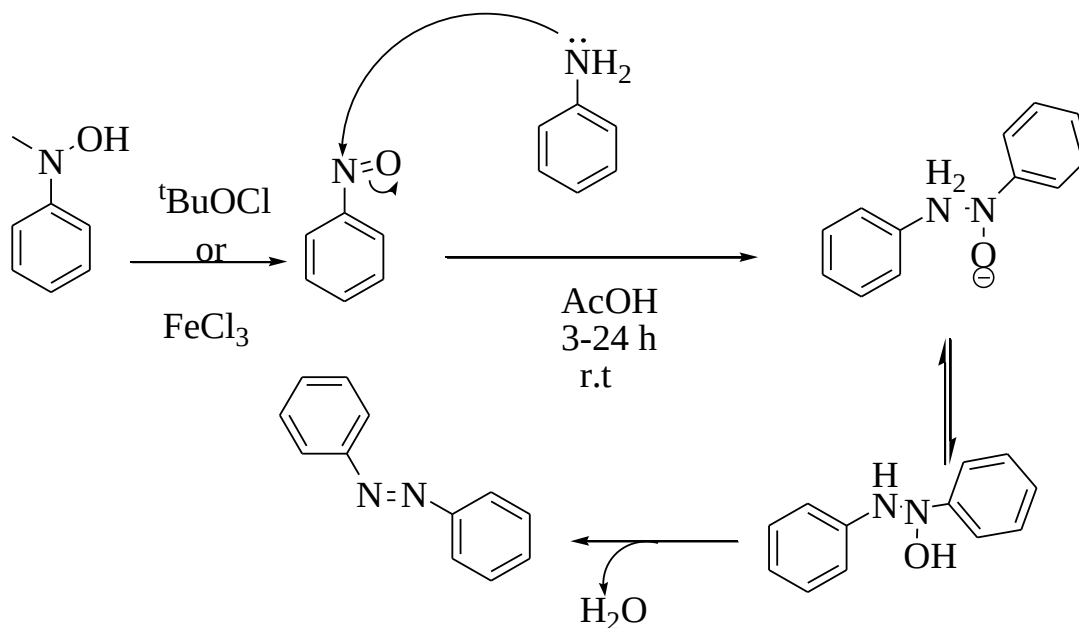


Scheme 6: Diazonium salt from primary amine coupling with an amine to form azobenzene[13].

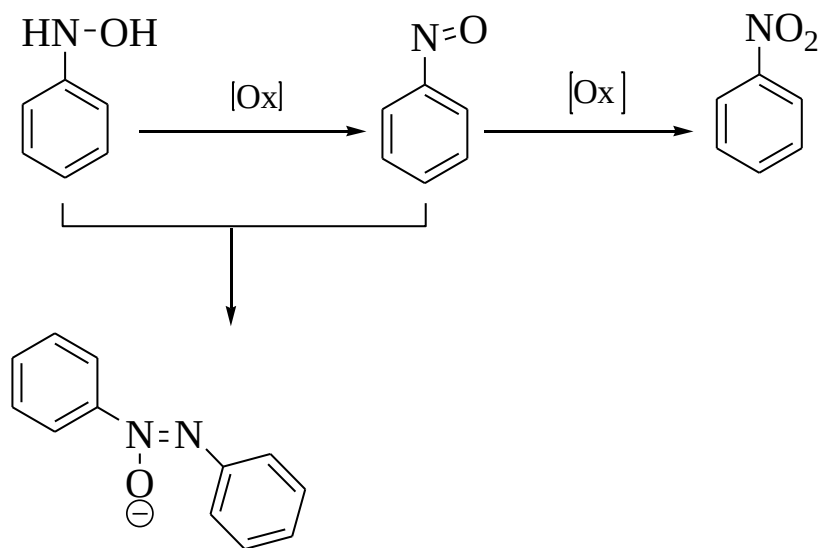
2.3.2 Mills Reaction

This involves coupling of primary arylamines with nitroso compounds to produce dissymmetrical azobenzene. Anilines and nitroso compound's reactions give a good yield of corresponding azobenzene when coupling in presence of glacial acetic acid. The most conventional method for nitroso compound preparation involves oxidation of the analogous hydroxylamine, using iron (III) chloride[16] in the heterogeneous system. This heterogeneous oxidation is usually slow and several hours are required for completion and this can lead to production of corresponding azoxy compounds due to coupling of unconverted hydroxyl amine with nitroso compound. These heterogeneous oxidation reactions are frequently sluggish and provide low yields in cases where either the starting hydroxyl- amine or the nitrous product has limited stability and decomposes during the reaction progress. There can be side reaction taking place during the oxidation of hydroxylamine which involves formation of nitro derivatives because of further oxidation of nitroso compound, also condensation reaction that produces azoxybenzenes from N- aryl hydroxylamine and nitroso compound[17]. These side products are predominantly observed when anilines are less activated due to attachment of electron withdrawing substituents in either ortho, meta and para position which renders its poor reactivity and the prolonged reaction times. Nitroso compounds can also be prepared by oxidation of methyl hydroxyl amine with tert-butyl hypochlorite, this reaction occurs rapidly and occurs at - 78 °C with high dilution to impede over oxidation[17]. High yield is recorded for this reaction. In this type of reaction there could be different substituent in either aryl amine or nitroso compound in ortho, meta or para position whether electron donating group or electron withdrawing group[32]. Oxone which is a two-phase heterogeneous system consisting of (2KHSO₅.KHSO₄. K₂SO₄) in H₂O/CH₂Cl₂ is efficient in preparation of nitrosoarenes which then undergo a condensation reaction with anilines to form azobenzene. Slightly water-soluble nitroso compounds from N-arylhydroxylamine intermediates are separated by this biphasic system to avoid unwanted condensation reactions[17]. There are heterogeneous procedures that have been also employed for preparation of nitroso compound which involves use of several oxidant such as Caro's acid (H₂SO₅), sodium or potassium dichromate and sulfuric acid, acetic acid/H₂O₂, m-chloroperbenzoic acid, potassium permanganate, ferric chloride, diethyl azodicarboxylate, iodine/NaI/NaOAc, silver carbonate (diacetoxyiodo)benzene, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and peroxyformic acid. [17] also highlighted that nitroarenes can

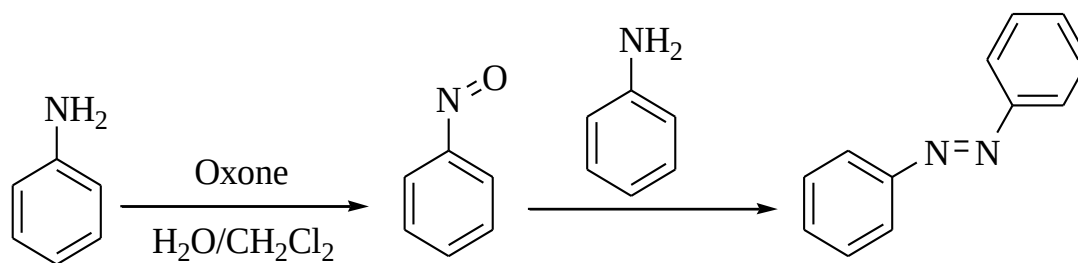
be prepared from hydrogen peroxide using rhenium, tungsten or molybdenum giving high yield.



Scheme 7: Mechanism for formation of Azobenzene by Mills reaction from nitroso compound coupling with aniline[17].



Scheme 8; Mechanism leading to overoxidation of Nitroso compound leading to low yield[17].



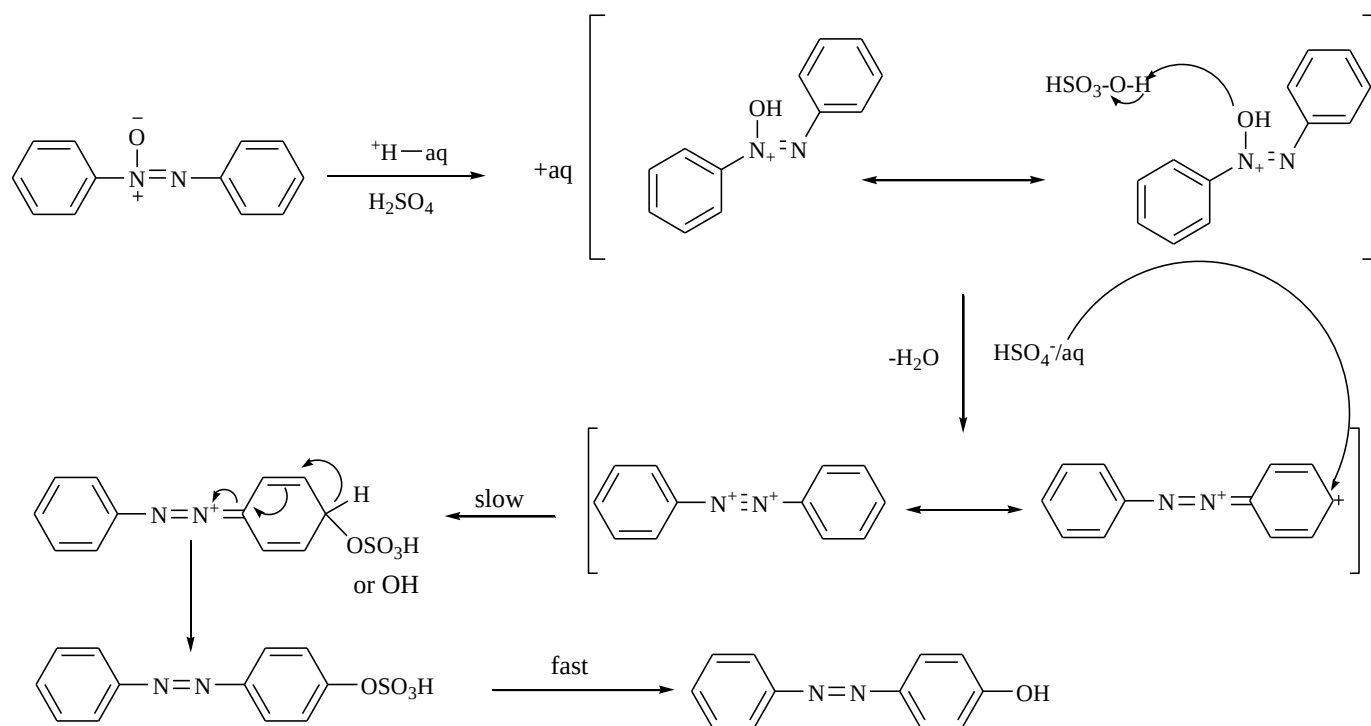
Scheme 9: Preparation of nitroarenes condensing with anilines from Oxone[13].

2.3.3 Wallach Reactions

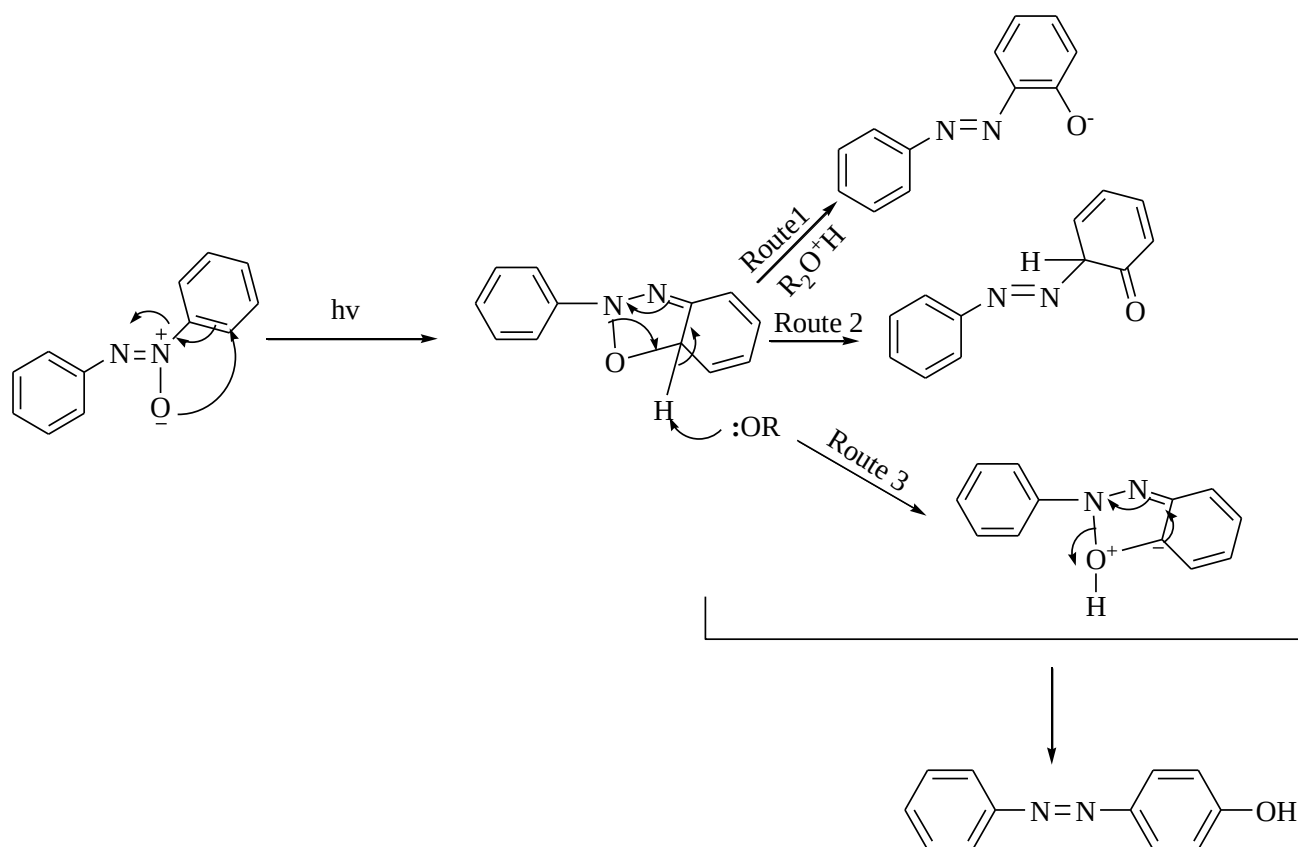
This type of reaction was first reported in 1880 by Wallach and Belli[36]. This process was found to take place in a harsh acid condition (also Lewis acids) but sulfuric acid is the most effective acid for this reaction [37]. The rate of rearrangement relies much on the acidity of the reaction medium, raising acid concentration from 75 to 100% will have a five-order magnitude increase[38]. Acidic zeolites can also promote transformation of azoxy compounds to mainly para-hydroxy azobenzene and ortho-hydroxy azobenzene is expected in small quantities or sometimes can be preferred in case para has been occupied, on the other hand deoxygenation of azoxybenzene in the presence of benzophenone and nitrogen yields azobenzene without hydroxyl substituent[37]. The migration of oxygen atom from one of the nitrogen mechanisms was studied using sulphuric acid with labeled ^{18}O isotope and it proved that the Wallach reaction proceeds with an intermolecular pathway[39]. In this study it was found that dicationic, delocalized intermediate was formed due to dehydration and deprotonation, followed by attachment of HSO_4^- to the aromatic ring at a para position by nucleophilic substitution mechanism and finally hydrolysis take place to yield the final product[40][41].

Photo-Wallach rearrangement is the transformation of azobenzene from azoxybenzene in the singlet state when there is light irradiation which will lead to oxygen atom migration from nitrogen to more distant aromatic ring bonded to other nitrogen atom[39]. The photo driven process yields to ortho-hydroxy azobenzene because of the closer distance between the plane of the $\text{N}=\text{N}$ bond and the ortho position of the benzene ring, which supports the second nitrogen atom. The mechanism of photochemical Wallach rearrangement transposition has been identified to be an intramolecular pathway[13]. Azobenzene can be achieved from azoxybenzene by

thermal and photochemical Wallach rearrangement [36]. Though the transformation mechanism for photochemical Wallach rearrangement has not been yet known, there are some propositions which have been made as possible routes[13]. Ring opening and concomitant deprotonation by basic solvents is one of the possible mechanisms proposed (Route 1). Photo irradiation of azoxybenzene leading to formation of diazonium ions taking place in benzene solution has been discussed. In this case the product is obtained by intramolecular 1,2- hydrogen atom shift accompanied by scission giving diazonium ion or prototropy (Route 2). Then lastly intramolecular H-migration which gives the final product and diazonium ion by the [1,5]-sigmatropic rearrangement of H through the face of heterocyclic ring. The H atom can be brought to the O atom by solvent reliant migration of the H atom's LUMO over the excited eight-electron ring system's HOMO through prototropy (Route 3).



Scheme 10: Mechanism for Wallach rearrangement in Sulfuric acid[41].

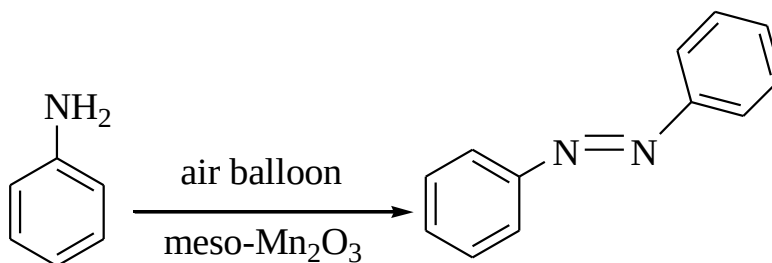


Scheme 11: Photo Chemical Wallach rearrangement proposed mechanisms[13]

Azobenzene preparation was previously achieved through inverse-micelle-templated mesoporous manganese oxide materials [12]. Nonionic surfactant micelles are used as a soft template in the preparation method of amorphous manganese oxide (Meso-Mn). Meso-Mn was then heated to transform it to amorphous mesoporous manganese oxide (Meso-Mn-A). Meso-Mn-A intermediate was further heated at higher temperatures for transformation into crystalline manganese oxide of Meso-Mn₂O₃ phase which is rich in Mn³⁺[42]. Meso-MnO_x under aerobic oxidation led to coupling of anilines. This coupling is initiated when radical intermediates are formed through single electron transfer (SET) from aniline to metal center. Azobenzene is formed because of the sequential loss of protons and electrons from matching intermediates. The meso-MnO_x reported in this was in a crystalline Mn₂O₃ phase structure with a mesoporous size distribution, the surface area calculated for this material was 100 m²g⁻¹ with pore size of 5.3 nm. The optimal conditions for catalytic oxidation of aniline using meso-Mn₂O₃ were found to be 50

mg of meso-Mn₂O₃, 0.5 mL of toluene and 110 °C with an air balloon. This reaction gave conversion of aniline as >99% and selectivity of aniline as >99% in h. Introduction of tert-butyl hydroperoxide (TBHP) led to low conversion of 58% and increased selectivity of imine to 79% when 10 mL of toluene solvent was used.[12]. Increase in selectivity of imine was also observed when the toluene was increased in the presence of TBHP of which was then ascribed to condensation of toluene to form benzaldehyde. The following results were obtained from the previous work[12].

Amount of solvent(mL)	Aniline conversion	Azobenzene selectivity	Imine selectivity
1.0	97	>99	<1
5.0	75	>98	<2
10	71	70	30
25	39	62	38

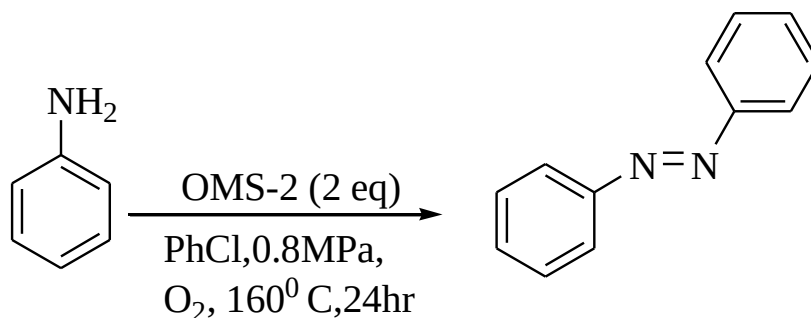


Scheme 12: Catalytic route for oxidation of aniline to azobenzene using meso-Mn₂O₃[12].

This method presents multi-step preparation since the catalyst used requires laborious techniques as surfactants are involved to prepare meso-Mn as the starting material and further subject it to higher temperatures to form meso-Mn-A as an intermediate. Amorphous mesoporous manganese oxide is also heated at high temperatures to yield meso-Mn₂O₃. Furthermore, the catalytic method is more suitable with a small quantity of solvent, as the amount of solvent increases the reaction favors the formation of side product which impedes large scale production.

Another previous work was reported using regular K-OMS-2 prepared from reflux method, the

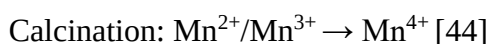
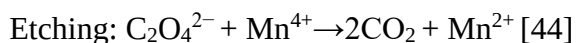
azobenzene was prepared from chlorobenzene as solvent, under O₂ at higher temperature and prolonged reaction time[43]. Conversion and selectivity observed through use of this catalyst was 95% and >99%, respectively. Increasing temperature leads to an increase in conversion. Although the catalyst is prepared through low energy cost techniques and without additives, the catalytic process was carried out at high temperatures as compared to the previous method where meso-Mn₂O₃ and toluene was used. This method also requires prolonged reaction times since 24 h gives the highest conversion as compared to previous method where higher selectivity has been obtained at a period of 8 h.

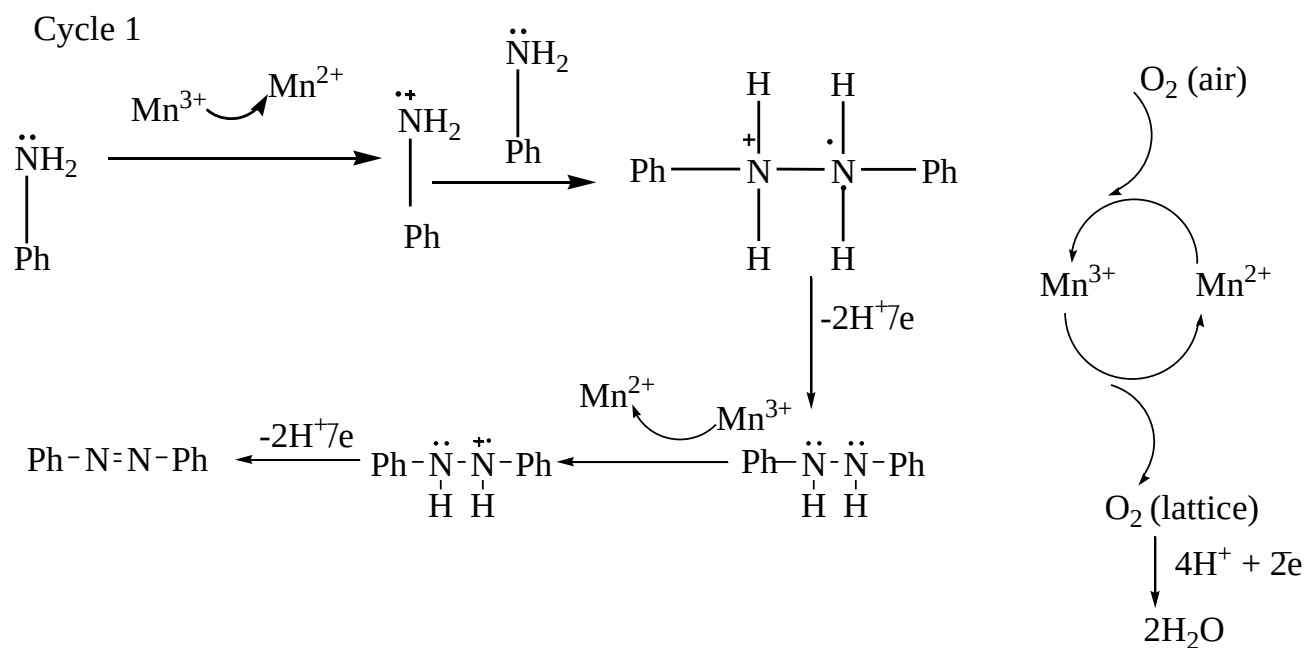


Scheme 13: Azobenzene preparation using OMS-2[43]

The focus of this work is to tailor oxidation state of K-OMS-2 material by etching with Oxalic acid to suite formation of azobenzene as it is a cheap and environmentally benign approach when compared to previous studies, where they used Mn₂O₃ which involves introduction and removal of surfactants using complicated techniques. Etching OMS-2 with low concentrated oxalic acid to adjust oxidation state of K-OMS-2 was employed in this work. Lower oxidation state occurs due to redox reactions between oxalic acid and Mn⁴⁺ which produce Mn at lower oxidation state (Mn²⁺) in solution or on the surface [44].

Proposed mechanism for post etching and calcination





Scheme 14: Proposed mechanism for coupling of anilines under aerobic oxidation using manganese oxides[43][12]

CHAPTER 3: METHODOLOGY

3.1 CHEMICALS

Chemical Name and Purity	Supplier
Tertbutyl Hydroperoxide	Sigma Aldrich
Manganese Sulphate Monohydrate 98%	Alpha Chemika
Potassium Permanganate 99.5%	Associated Chemical Enterprises (ACE)
Oxalic Acid 99%	Alpha Chemika
Nitric Acid 56%	Alpha Chemika
Aniline 99%	Sigma Aldrich
Benzyl Alcohol > 99%	Honeywell
Toluene	Sigma Aldrich

3.2 INSTRUMENTS

3.2.1 X-ray Diffractometer (XRD)

X-ray diffraction data from a Bruker D8 Advance powder diffractometer, a Cu tube X-ray source, and a LynxEye XE energy-dispersive strip detector were used to investigate the phase purity and crystalline phases of the materials prepared. The radiation utilized was a Cu-K with a wavelength of 1.54056 Å in stages of 0.02 degrees with a duration of 0.500 seconds each step between 0 and 80 degrees. The instrument operated at a current of 40 mA and a voltage of 40 kV.

3.2.2 Scanning Electron Microscope (SEM)

Morphological studies were carried out by Jeol JSM-7100F, Tokyo, Japan source Scanning Electron Microscope coupled with Elemental Dispersion X-ray (SEM-EDX). This technique involves scanning samples with a focused beam of electrons to capture images. The electron-atom interaction gives various signals which can provide data about the surface topography and composition.

3.2.3 Transmission Electron Microscope (TEM)

High resolution transmission electron microscope (HRTEM) (JEOL JEM-2100) was conducted at 300 kV, which was used to assess the microstructure and morphology of the prepared materials from HRTEM micrographs.

3.2.4 Brannuer-Emmet-Teller (BET)

N₂ adsorption-desorption isotherms were carried out by Micrometrics 3flex 3500 Chem-TCD Loop accelerated surface area system at 77K. The specific surface area was determined based on the BET methodology. Barrett-Joyner-Halenda (BJH) techniques were used to compute the micropore and mesopore respectively.

3.2.5 Gas Chromatography-mass spectroscopy (GC-MS)

The product mixtures were analyzed qualitatively and quantitatively using the Agilent 7890A, Santa Clara, United States of America source gas chromatography-mass spectroscopy (GC-MS) method. The MS employed NIST (National Institute of Standards and Technology) software for identification of peaks in the spectra.

3.3 PREPARATION OF THE MATERIALS

3.3.1 Synthesis of K-OMS-2

The K-OMS-2 was prepared by conventional reflux method[24], the KMnO₄ (0.042 mol, 6.65 g) was dissolved in 112 mL deionized and MnSO₄·H₂O (9.90g, 0.066 mol) was dissolved in 34 mL of deionized water both at room temperature. MnSO₄·H₂O solution was acidified with 3 mL concentrated HNO₃ (65%). KMnO₄ (0.042 mol, 6.65 g) solution was added dropwise to MnSO₄·H₂O (9.90g, 0.066 mol) under constant agitation to achieve a MnO₄⁻/Mn²⁺ molar ratio of 0.76. The resultant mixture was refluxed at 110 °C for 24 h. The reaction product was washed with deionized water and dried in the oven overnight[45].

3.3.2 Acid treatment of OMS-2

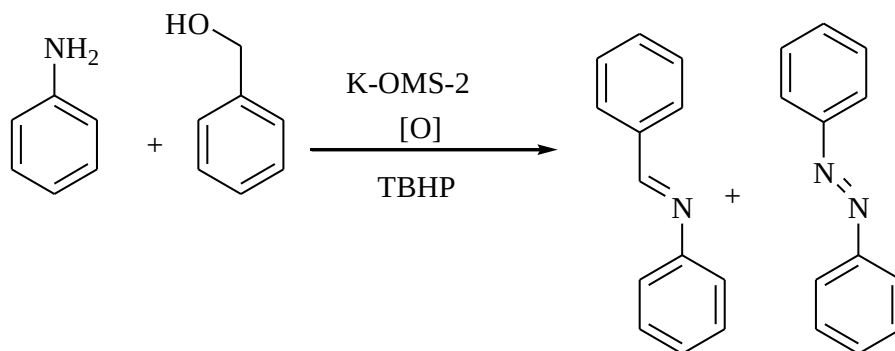
Aqueous solution of oxalic acid was prepared by dissolving 3.1518 g (0.250 mol) in minimum amount of deionized water and made up to 250 mL of solution. Series of 0.10, 0.05 and 0.025 M were prepared from the stock solution. 0.5 g of OMS-2 was stirred in 10 mL of standard solutions for each concentration of oxalic acid for 5 min. After the time for etching was reached, distilled water was quickly added to the reaction mixture and immediately transferred to the Buchner funnel for suction filtration. The product was then rinsed multiple times with distilled water, and it was oven dried overnight.

0.10 M etched OMS-2 was calcined at 350 °C for 1h to burn insoluble impurities which might have formed during the process of etching and as such might interfere with collision between material and the substrate thus reducing conversion.

3.4 REACTION PROCEDURE FOR CATALYTIC SYNTHESIS.

3.4.1 General Reaction Procedure for Catalytic Synthesis.

The reaction was carried with benzyl alcohol (1 mmol), toluene (10 mL), tert-butyl hydroperoxide (1 mmol), aniline (1 mmol), and K-OMS-2 (50 mg) were added to a 50 mL round- bottomed flask[14]. The mixture was stirred under reflux for 4 h at 110 C with continuous supply of atmospheric gas phase through the condenser. After the end of reaction, reaction mixture was allowed to cool at room temperature and the material was filtered from reaction mixture by gravity filtration. Finally, the mixture was analyzed by GC-MS.



Scheme 15: Synthesis of Benzylideneaniline and Azobenzene using OMS-2 material.

3.5 PARAMETER OPTIMIZATION

Temperature, time, oxidant amount and sample loading were studied to determine their effect on the catalytic activity.

3.5.1 Time

A general procedure for catalytic synthesis was followed and time for reaction was varied as it was performed at 3, 4 and 7 h, respectively. All other parameters were kept constant.

3.5.2 Temperature

Reaction temperatures varied at 100, 110 and 120 °C whilst all other factors were kept constant.

3.5.3 Sample (K-OMS-2) Amount

K-OMS-2 sample loading was varied at 50 and 100 mg whereas keeping all other parameters in general procedure constant.

3.5.4 Amount of Oxidant (TBHP)

The oxidant amount varied at 0.5, 1.0 and 2.0 mmol and all other factors were not altered from general procedure.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 OMS-2 CHARACTERIZATION

4.1.1 Structure and Phase Purity

The OMS-2 materials were prepared by conventional reflux method from Mn^{2+} and Mn^{7+} precursors by synproportionation in acidic aqueous suspension. The structure and phase purity were studied by XRD, the material presented an XRD pattern with no discernible shifts on the peaks when indexed to standard tetragonal cryptomelane mineral compound using ($\text{KMn}_8\text{O}_{16}$, JCPDS 42-1348). XRD pattern for etched OMS-2 material was found to be consistent when indexed to a regular form of the tetragonal $\alpha\text{-MnO}_2$ (Figure 4) indicating that 0.025, 0.050 and 0.100 M acid treatment has no impact on the phase structure of the material [24].

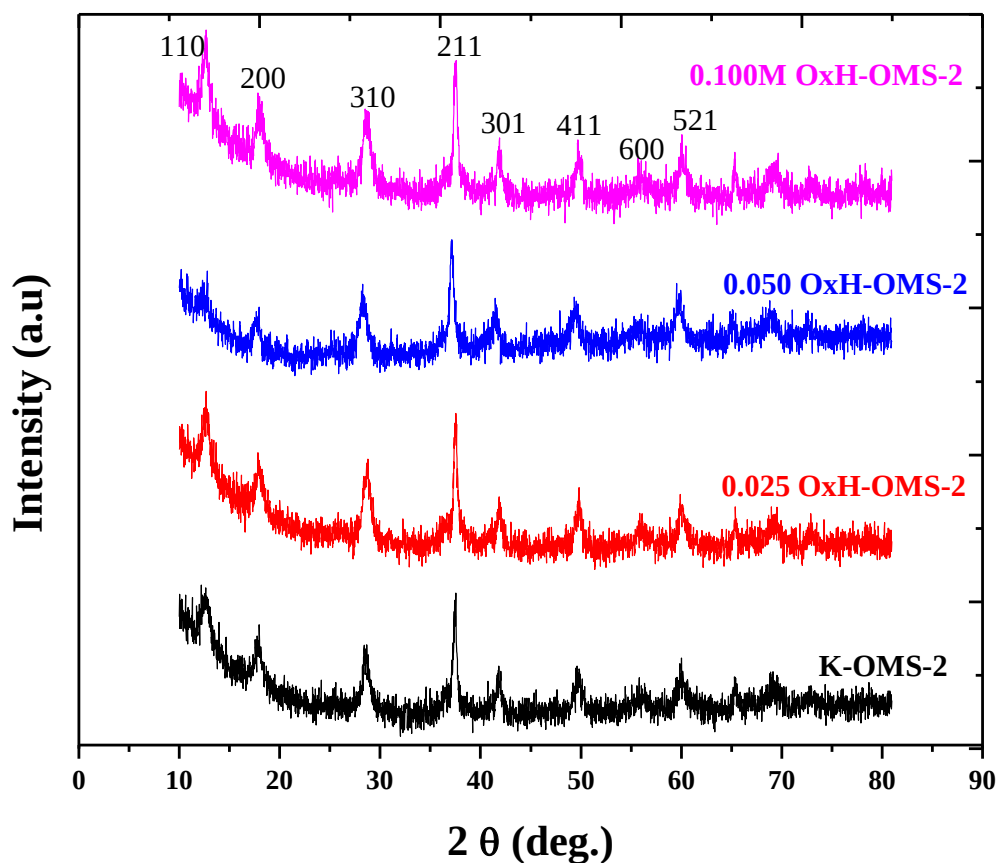


Figure 4: XRD patterns for OMS-2 Materials.

0.100M-OxH-OMS-2 sample was calcined at 350 °C for 1 h and the XRD pattern for calcined 0.100M-OxH-OMS-2 presented similar pattern to that of uncalcined 0.100M-OxH-OMS-2 without noticeable shift in peaks and their intensities. This implies that the calcination did not have the impact on the crystallographic phase structure of the OMS-2 material.

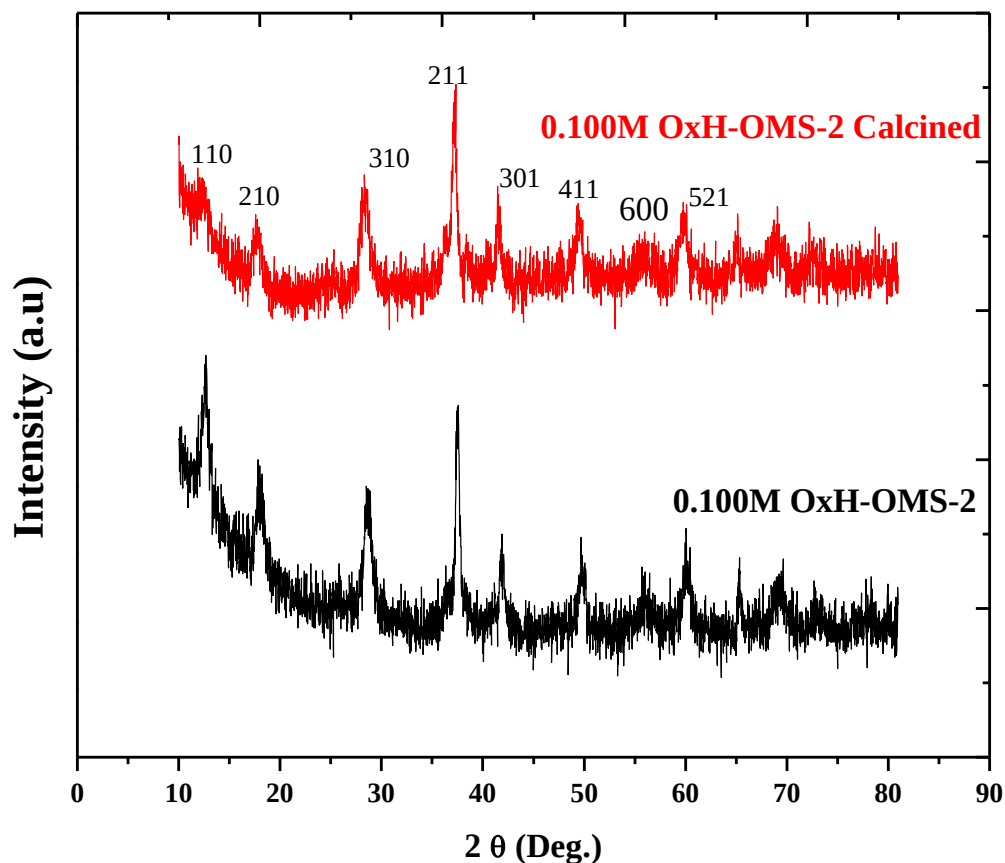


Figure 5: XRD patterns for calcined 0.10 M OMS-2 Materials.

4.1.2 Morphological Characterization (SEM and TEM)

The morphology of the OMS-2 materials was studied by SEM. The K-OMS-2 depicted nanorods shapes typical to that of K-OMS-2 prepared by reflux method (Figure 6a) [6]. After treating K-OMS-2 material with the acid, there was no change observed on the nanorods shapes (Figure 6b, 6c and 6d). The morphology of the OMS-2 material was retained regardless of acetic acid and oxalic acid etching[24]. The acid treated materials presented some newly developed pits on the nanorod which implies that the acid has formed new voids on the surface of the nanorod. The

pits are attributed to the leaching of some Mn into the solution. There was also a decrease in the length of nanorods in etched materials as compared to material indicating that the acid has deleterious effects on the nanorods[44]. The agglomeration of nanorods is observed when the material is treated with an acid as the nanorods are now bonded together.

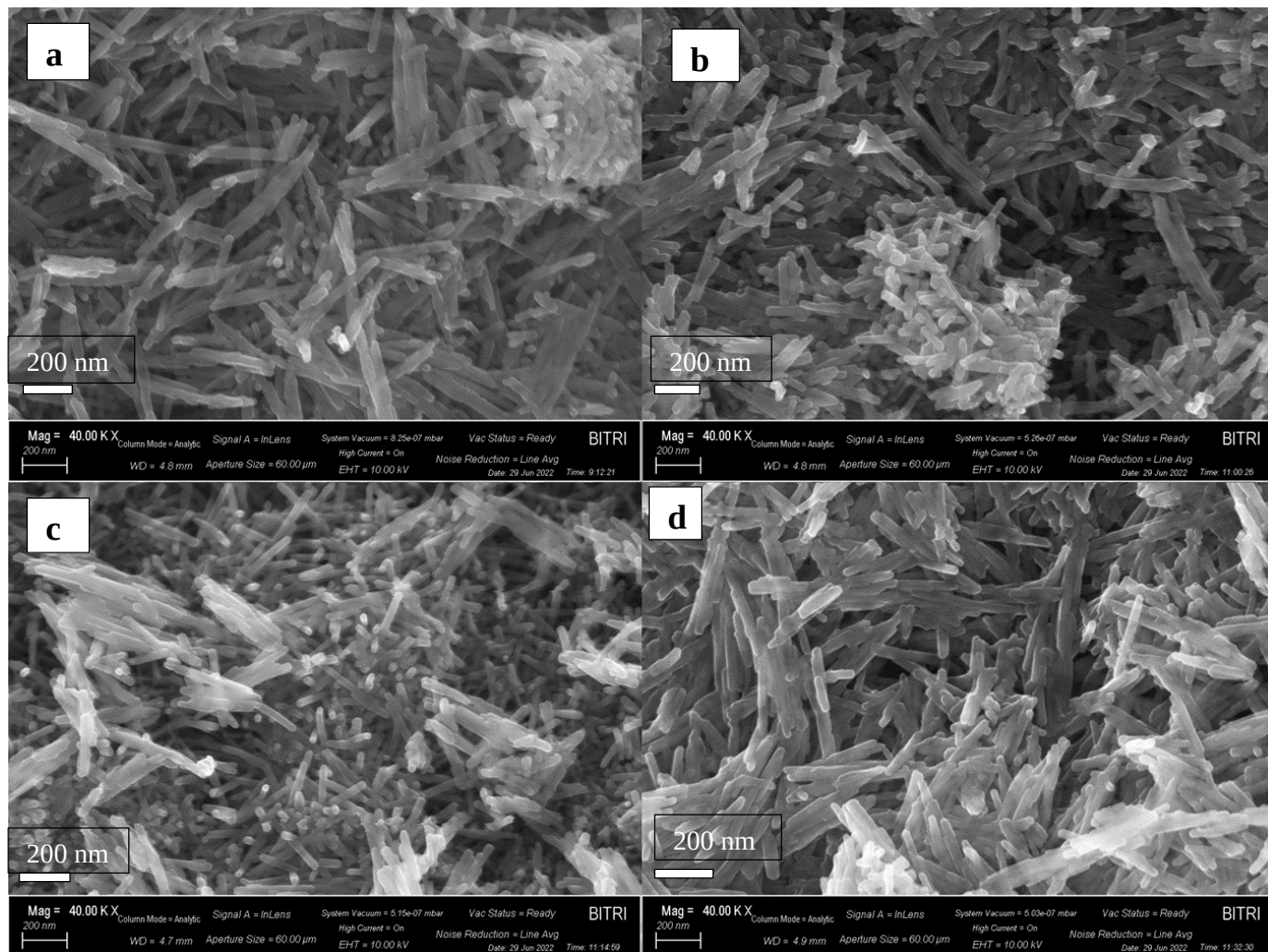


Figure 6: SEM image for (a) K-OMS-2, (b) 0.025 M OxH-OMS-2, (c) 0.05 M OxH-OMS-2 and (d) 0.10 M OxH-OMS-2.

The calcination has no impact on the morphology of the material since the nanorods were still maintained after the calcination of 0.10 M sample at 150 °C for 1 h.

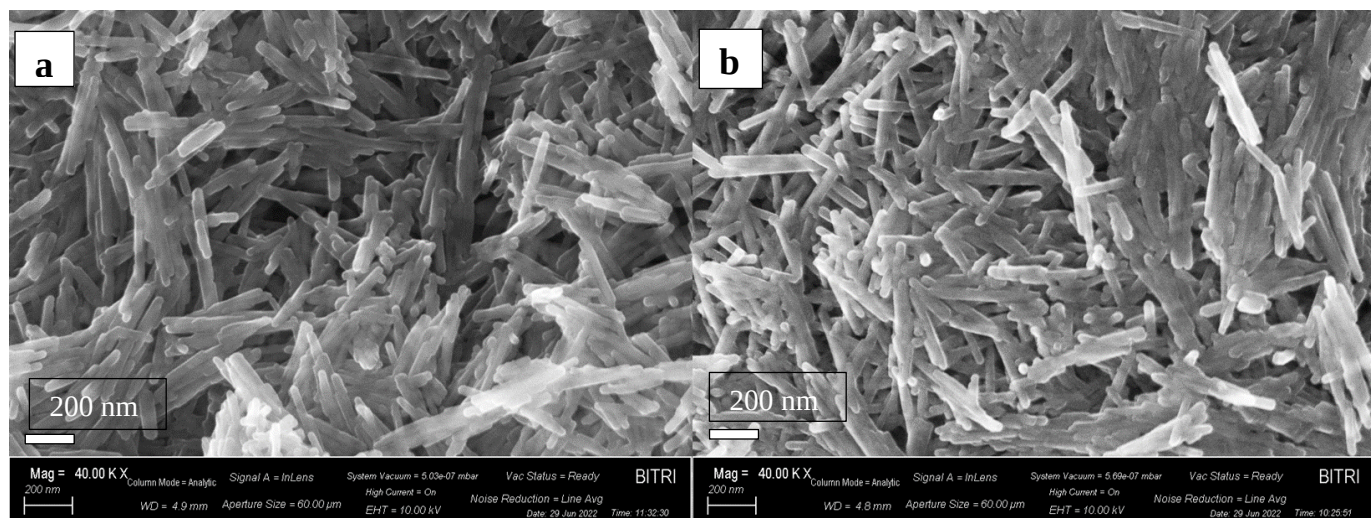


Figure 7: SEM image for (a) 0.10 M OxH-OMS-2 and (b) 0.10 M OxH-OMS-2 calcined.

TEM and HRTEM images display nanorod morphology (Figure 8) which is consistent with SEM images for all samples. The lattice fringes from HRTEM micrographs of regular OMS-2, 0.025 M OxH-OMS-2, 0.05 M OxH-OMS-2 and 0.10 M OxH-OMS-2 displays interplanar spacing of 0.51, 0.32, 0.19 and 0.50 nm corresponding to (200), (310), (211) and (200) facets of K-OMS-2. The lattice spacing from HRTEM images is accordant with the XRD results. The clear lattice fringes indicate that the OMS-2 (Figure 9 a) tetragonal prisms exist as single crystalline. By careful inspection, it is important to note that the lattice fringes of etched materials (Figure 8 b, c, d) are not clear when put next to regular material (Figure 8 a). This indicates that the acid has an impact on the surface microstructure of the OMS-2 material due to alteration of the strains causing disorientation of the atoms on the lattice surface. This is attributed to leaching of some Mn^{4+} atoms on the surface of the material during etching which led to more defects on the material hence poor crystal structure. The leaching of Mn^{4+} can be confirmed by an increase of surface micropore area from 2.2 to 8.2 m^2/g as presented by BET results. It can be concluded that the decrease in the crystallinity as observed from HRTEM because of loss of some more active Mn^{4+} ions on the surface, has led to decrease of catalytic activity as the conversion has decreased after etching.

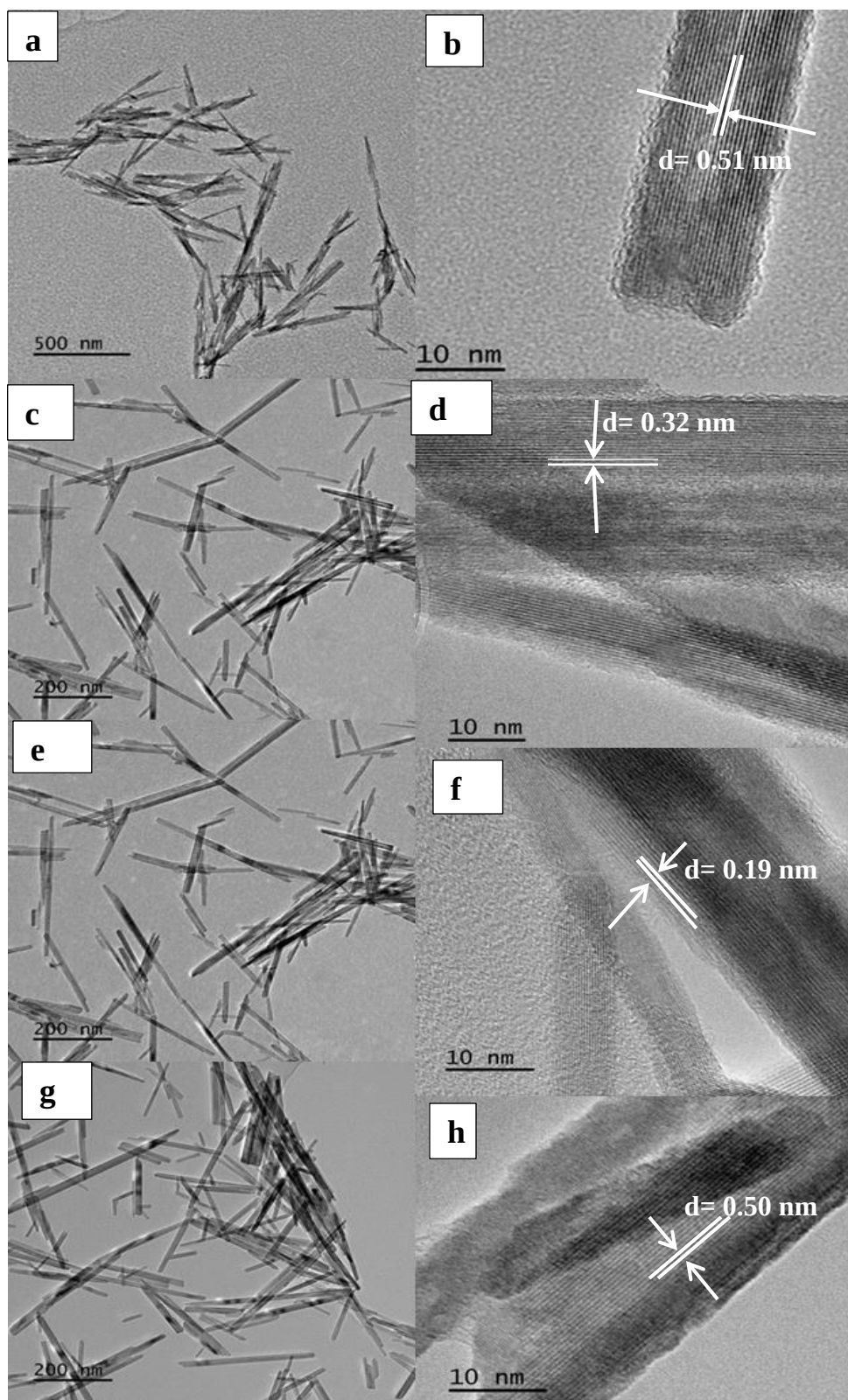


Figure 8: TEM and HRTEM images of (a, b) K-OMS-2, (c, d) 0.025 M OxH-OMS-2, (e, f) 0.05 M OxH-OMS-2 and (g, h) 0.10 M OxH-OMS-2.

Nanorod morphology is still maintained after the calcination of 0.10 M OxH-OMS-2 which agrees with SEM results. There is no evident impact on the microstructure of the material after the calcination as the lattice spacing was found to be 0.50 nm which correspond to (200) crystal planes from the XRD in both calcined and uncalcined 0.10 M OxH-OMS-2. This implies that the calcination has no impact on the microstructure of the 0.10 M OxH-OMS-2 material since the calcination affects the oxidation state not the stress of the material which is consistent with XRD results as there are no noticeable peak shifts observed.

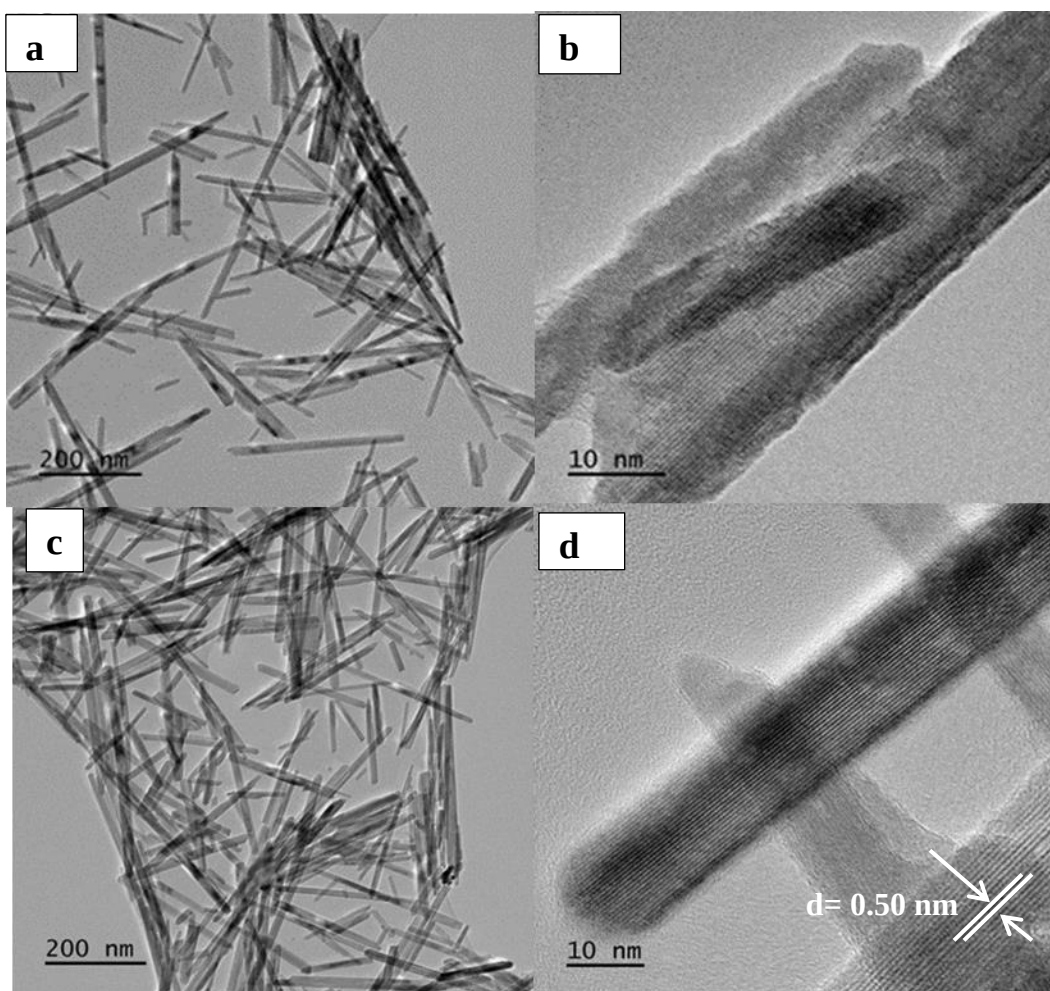
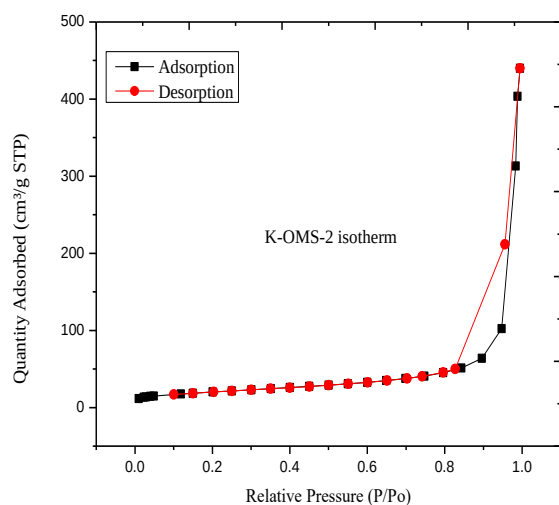


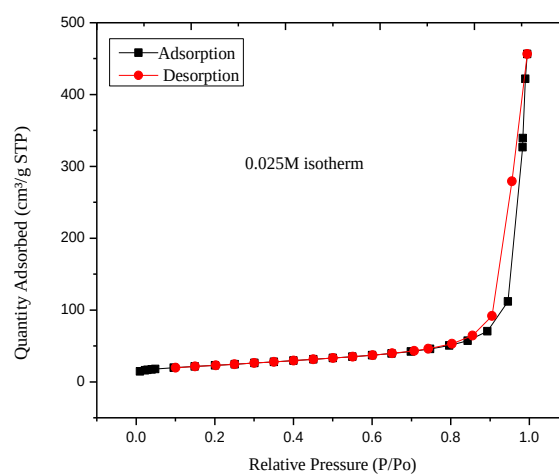
Figure 9: TEM and HRTEM image for (a, b) 0.10 M OxH-OMS-2 and (c, d) 0.10 M OxH-OMS-2 calcined.

4.1.3 Surface Area and Porosity

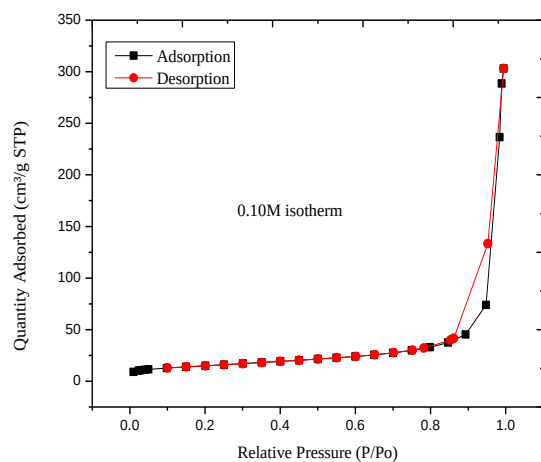
The N₂ adsorption/desorption of regular K-OMS-2 and acid treated materials were obtained and all the materials displayed type IV isotherm as classified by IUPAC. These isotherms confirm the existence of micropores and mesopores of the material. All samples revealed formation of monolayer at low relative pressure (P/P_0) and as relative pressure increases the multilayer adsorption prevailed. K-OMS-2 surface area obtained by the Brunauer-Emmett-Teller (S_{BET}) was found to be 72.7 m²/g, upon treating the material with 0.025M acid the surface area increased to 81.9 m²/g. K-OMS-2 material had a micropore surface area of 2.3 m²/g and external surface area of 70.4 m²/g. After treating the K-OMS-2 with 0.025M of oxalic acid the micropore surface area increased to 8.2 m²/g and external surface area increased to 73.7 m²/g. This implies that the acid opened micropores on the surface of the material since the micropores contributed the most in the increase in the S_{BET} . The results agree with SEM results as it revealed more incisions in acid treated materials than in regular material. Increase in the acid concentration from 0.025 to 0.10M led to decrease in the S_{BET} to 53.6 m²/g with micropore surface area being 4.0 m²/g and external surface area of 49.6 m²/g. This is attributed to more agglomeration leading to reduced inter-particle spaces hence reducing external surface area inhibiting N₂ adsorption. Barrett, Joyner and Halenda (BJH) average pore diameter of sample was found to range from 23-40 nm, 0.025 M sample as 31-38 nm and 0.10M material was 29-39 nm which confirms the mesoporous nature. From the pore size distribution, it can be concluded that treating OMS-2 with an acid increases the pore sizes as observed from the range of pore diameter. This indicates that some Mn go into solution during acid treatment leaving bigger pores on the surface of the material. Table 1 shows contribution of micropore surface area and external surface area to BET surface area.



(a)



(b)



(c)

Figure 10: N₂ adsorption/desorption isotherm for (a) K-OMS-2, (b) 0.025 M OxH-OMS-2, (c) 0.100 M OxH-OMS-2.

Table 1: Showing micropore surface area and external surface area in contribution to BET surface area.

Catalyst	S _{micropore} (m ² /g)	S _{external} (m ² /g)	S _{BET} (m ² /g)
K-OMS-2	2.2	70.4	72.6
Ox-H 0.025-OMS-2	8.2	73.7	81.9
Ox-H 0.100-OMS-2	4.0	49.6	53.6

4.2 CATALYTIC STUDIES OF OMS-2

The catalytic reactions of regular and etched materials were carried out, and analysis of the analyte was carried out using the GC-MS instrument. Conversion and selectivity were calculated from peak areas of aniline, azobenzene and benzylideneaniline using the following formulas.

$$\% \text{ Conversion} = \frac{\text{Peak Area of all products}}{\text{Peak Area of aniline} + \text{Peak Area of all products}} \times 100$$

$$\% \text{ Selectivity} = \frac{\text{Peak area of Product A}}{\text{Peak Area of all Products}} \times 100$$

Where products are azobenzene and benzylideneaniline and product A can be either azobenzene or benzylideneaniline. The selectivity is denoted by **S** and the peak area is **A** as presented on the tables.

4.2.1 Study of effect of oxalic acid concentration on the catalytic activity

The reactions were carried out at the temperature of 110 °C, with 50 mg sample, 1 µL TBHP with continuous supply of atmospheric air. The etchant concentration was the only parameter which varied as the investigation was on the effect of etchant concentration on the catalytic activity of the material. From the results obtained in general reaction conditions, it was observed that regular K-OMS-2 has the highest rate of aniline conversion being 72%, highest selectivity of imine as 82% and lowest azobenzene selectivity as 18%. Upon etching with 0.025 M oxalic acid conversion dropped drastically from 72 to 47%, selectivity of imine reduced from 82 to 52% whilst for azobenzene increased from 18 to 48% indicating the acid affects catalytic activity as it reduces the conversion rate of the material. Etching material with oxalic acid was found to reduce Mn^{4+} to $\text{Mn}^{2+}/\text{Mn}^{3+}$ into solution or the surface[44], decrease in the conversion rate can be attributed to this decrease in the oxidation state of Mn^{4+} leading to less Mn^{4+} content responsible for tandem catalysis in condensation of alcohols with amines as the Lewis acidity has been reduced. The acid also has been shown to have an impact on the selectivity of products formed during the catalytic process as it favors the selectivity of azobenzene. Increasing acid concentration on the material to 0.050 and 0.10M led to decrease of conversion from 47 to 34%

and increase to 41% which shows no relationship between conversion and acid concentration. Selectivity of azobenzene increased to 70% and 80% as acid concentration was increased to 0.050M and 0.10M which concludes that acid concentration has a significant effect on the selectivity of azobenzene. 0.10M was observed to give the highest selectivity of azobenzene. Increase in the selectivity of azobenzene can be due to less amount of Mn^{4+} is reduced to lower oxidation states (Mn^{2+}/Mn^{3+}) by oxalic acid which leaches into solution and some on the catalytic surface hence forming mesoporous site which facilitate coupling of aniline with Mn^{3+} metal center to form azobenzene in toluene at 110 °C[12].

Table 2: Effect of OMS-2 at different concentration of oxalic acid on the catalysis of azobenzene

Sample	Aaniline	Aazobenzene	Abenzylideneaniline	%Conversion	Sazobenzene	Sbenzylideneaniline
OMS-2	2079003.81	973560.39	4324191.48	72	18	82
0.025 M OxH-OMS-2	3147939.95	1358167.96	1450179.22	47	52	48
0.050 M OxH-OMS-2	26505079.46	9677022.66	4181145.69	34	70	30
0.100 M OxH-OMS-2	7774258.16	4264982.41	1053339.04	41	80	20

4.2.2 Study of effect of temperature on the catalytic activity

The reactions were conducted at temperatures of 100, 110 and 120 °C, time was kept constant at 4 h, with 50 mg sample and 1 µL TBHP for 0.050 M oxalic acid. The supply of atmospheric air was also continuously supplied then GC-MS analysis was carried out to determine conversion and selectivity. Conversion was found to be 42, 34 and 41% which shows no significant change since the difference is less than 10% and no relationship observed between acid concentration and conversion. Selectivity of azobenzene increased as the temperature increased by 10 °C where values of 63, 70 and 81% were recorded. Temperature is observed to have a significant impact on the selectivity of azobenzene since the difference between 110 and 120 °C was 11% which exceeds 10% and 120 °C was observed to give highest azobenzene selectivity. Some changes

observed in the conversion can be attributed to activity of the oxidant under different reaction temperatures as the oxidant is active.

Table 3; Effect of OMS-2 treated with 0.050 M of oxalic acid on the catalysis of azobenzene at different reaction temperatures.

Temperature	A _{aniline}	A _{azobenzene}	A _{benzylideneaniline}	%Conversion	S _{azobenzene}	S _{benzylideneaniline}
100	7266082.64	3331981.4	1945519.39	42	63	37
110	26505079.46	9677022.66	4181145.69	34	70	30
120	7201687.75	4101384.52	935983.07	41	81	19

The reactions were conducted at temperatures of 100, 110 and 120 °C, time was kept constant at 4 h, with 50 mg sample and 1 µL TBHP for 0.10 M oxalic acid sample. The supply of atmospheric air was constantly supplied. Conversion was found to be 38, 41 and 48% which was concluded that there isn't significant increase in the conversion of substrate as the temperature was increased by 10 °C. Selectivity of azobenzene was found to be 62, 80 and 62% indicating drastic increase of 18% in the selectivity when temperature was raised by 10 from 100 to 110 °C, when temperature increased by 10 °C from 110 selectivity dropped by 18% giving 62%. This now concludes that 110 °C is the optimum temperature for selectivity of azobenzene. 0.050 and 0.10M presented average conversion of 39 and 42% which has insignificant difference. The irregularities observed in the selectivity might arise from the activity of the oxidant as the temperature increases since the organic peroxides are mostly affected by changes in the temperature.

Table 4; Effect of OMS-2 treated with 0.100 M of oxalic acid on the catalysis of azobenzene at different reaction temperatures.

Temperature	A _{aniline}	A _{azobenzene}	A _{benzylideneaniline}	%Conversion	S _{azobenzene}	S _{benzylideneaniline}
100	12305762.13	4652770.51	2803402.61	38	62	38
110	7774258.16	4264982.41	1053339.04	41	80	20
120	11892672.29	6779345.89	4095308.21	48	62	38

4.2.3 Study of the effect of time on the catalytic activity of the material.

In this study time was varied, 3, 4 and 7 h were investigated on the catalytic activity of the material while keeping temperature constant at 110 °C, with 50 mg sample and 1 µL TBHP for 0.050 M oxalic acid sample. Constant supply of atmospheric air was also carried. Conversion values obtained for 0.050 M were 31, 30 and 33% which shows no significant change as reaction time was varied. Selectivity obtained for this material were 66, 70 and 79% which indicate no significant increase between 3 and 4 but as for 4 and 7 h there is significant increase as the difference is close to 9%.

Table 5; Effect of OMS-2 treated with 0.050 M of oxalic acid on the catalysis of azobenzene at different reaction times.

Time	A _{aniline}	A _{azobenzene}	A _{benzylideneaniline}	%Conversion	S _{azobenzene}	S _{benzylideneaniline}
3	9890402.74	2926970.9	1488589.81	31	66	34
4	26505079.46	9677022.66	4181145.69	34	70	30
7	10638439.09	4199683.99	1135940.65	33	79	21

Time was varied as seen in (table 6) 3,4 and 7 h was investigated on the catalytic activity of the material while keeping temperature constant at 110 °C, 50 mg sample and 1 µL TBHP for 0.10 M oxalic acid sample. 0.100 M gave conversions of 46, 41 and 47%, which shows no significant change as the time is varied also for azobenzene selectivity values obtained were 84, 80 and 82% having no significant change. It is observed that 7 h gives the highest selectivity for both 0.050 and 0.100 M gives high selectivity for all times selected. The average conversion of 0.050 and 0.100 M are 33 and 45% which has a significant change of 12%.

Table 6; Effect of OMS-2 treated with 0.100 M of oxalic acid on the catalysis of azobenzene at different reaction times.

Time(hrs.)	Aaniline	Aazobenzene	Abenzylideneaniline	%Conversion	Sazobenzene	Sbenzylideneaniline
3	9233162.04	6585888.29	1238209.74	46	84	16
4	7774258.16	4264982.41	1053339.04	41	80	20
7	15098457.13	10945577.46	2371115,07	47	82	18

4.2.4 Study of oxidant amount on the catalytic activity of the material.

The following study was carried out to investigate the effect of the TBHP amount on the catalytic activity of the material where the amount was varied from 0.5, 1.0 and 2.0 μL . Temperature was kept constant at 110 $^{\circ}\text{C}$, with 50 mg sample and time at 4 h for OMS-2 sample. Conversion rate obtained for regular OMS-2 were 28, 72 and 37%, increasing oxidant amount by 0.5 M increased catalytic activity by 44% which is a drastic increase moreover further increase by 1.0 μL led to significant decline by 19% which implies that there is no uniform relationship between oxidant amount and rate of conversion. Selectivity of azobenzene obtained were 28, 18 and 37%, the results show increase in oxidant amount by 0.5 μL leads to 10% decrease in the selectivity and further increase by 1.0 μL lead to increase by 19%. The optimum oxidant amount for substrate conversion was found to be 1.0 μL since it gives 72% conversion whilst for selectivity was 2.0 μL with 37%. In general, it is observed that there are more irregularities in conversion and selectivity values of both regular and etched materials. This can be ascribed to variation of active oxidant amount due to its ability to form free radicals which can attack some compounds in reaction hence affecting the results.

Table 7; Effect of OMS-2 on the catalysis of azobenzene at variable oxidant amount.

Oxidant amount(μL)	A_{aniline}	A_{azobenzene}	A_{benzylideneaniline}	%Conversion	S_{azobenzene}	S_{benzylideneaniline}
0.5	8805542.45	1227500.9	3117636.8	33	28	72
1.0	2079003.81	973560.39	4324191.48	72	18	82
2.0	797421.02	302730	598847.68	53	37	66

The following study was carried out to investigate the effect of the TBHP amount on the catalytic activity of the material where the amount was varied from 0.5, 1.0 and 2.0 μ L. Temperature was kept constant at 110 $^{\circ}$ C, with 50 mg sample, time at 4 h for 0.0250 M oxalic acid sample. Conversion values were 34, 47 and 52% which implies that an increase of oxidant amount by 0.5 μ L influences the conversion rate since the difference is 13% which is noticeable, increasing the oxidant amount by 1.0 μ L didn't produce any significant difference since its less than 10%. In the case of selectivity of azobenzene, values obtained were 74, 52 and 68% indicating a decline in the selectivity by 22% when oxidant is increased by half and further doubling the oxidant amount reduced selectivity by 16%. These results conclude that there is no proportional relationship between oxidant amount and selectivity.

Table 8; Effect of OMS-2 treated with 0.0250 M of oxalic acid on the catalysis of azobenzene at variable oxidant amount.

Oxidant amount(μL)	A_{aniline}	A_{azobenzene}	A_{benzylideneaniline}	%Conversion	S_{azobenzene}	S_{benzylideneaniline}
0.5	4911216.17	1824286.86	650268.78	34	74	26
0.1	3147939.95	1358167.96	1450179.22	47	52	48
2.0	9423569.45	3324602.42	6952656.28	52	68	32

The following study was carried out to investigate the effect of the TBHP amount on the catalytic activity of the material where the amount was varied from 0.5, 1.0 and 2.0 μL . Temperature was kept constant at 110 $^{\circ}\text{C}$, 50 mg sample, and time at 4 h for 0.050 M oxalic acid sample. Conversion rate of 38, 34 and 50% in which a significant increase of 16% was only observed when 1.0 μL was doubled. As for selectivity, obtained values were 65, 70 and 55% where there was 15% decline as 1.0 μL was doubled.

Table 9; Showing results of the effect of OMS-2 treated with 0.050 M of oxalic acid on the catalysis of azobenzene at variable oxidant amount.

Oxidant amount(μL)	A_{aniline}	A_{azobenzene}	A_{benzylideneaniline}	%Conversion	S_{azobenzene}	S_{benzylideneaniline}
0.5	25418444.9	10063368.25	5326871.92	38	65	35
0.1	26505079.46	9677022.66	4181145.69	34	70	30
2.0	5497251.95	2960899.17	2437429.3	50	55	45

The following study was carried out to investigate the effect of the TBHP amount on the catalytic activity of the material where the amount was varied from 0.5, 1.0 and 2.0 μL . Temperature was kept constant at 110 $^{\circ}\text{C}$, 50 mg sample, time at 4 h for 0.10 M sample. Conversions were found to be 67, 41 and 47%, conversion dropped immediately, oxidant amount was increased and further increase did not have any noticeable change. The drastic increase in the selectivity when 0.5 μL was doubled was noted to have magnitude of 38 which is almost double up. Further doubling the oxidant amount reduced selectivity by 24%. From these results it was concluded that 1.0 μL presented highest conversion with regular OMS-2 which is 72% and highest selectivity with 0.100M which is 80%, hence it is a suitable oxidant amount for the reaction.

Table 10; Effect of OMS-2 treated with 0.10 M of oxalic acid on the catalysis of azobenzene at variable oxidant amount.

Oxidant amount(μL)	A_{aniline}	A_{azobenzene}	A_{benzylideneaniline}	%Conversion	S_{azobenzene}	S_{benzylideneaniline}
0.5	18302745.87	15824984.28	21736795.25	67	42	58
0.1	7774258.16	4264982.41	1053339.04	41	80	20
2.0	21729817.84	10890774.57	8435322.51	47	56	44

4.2.5 Study of effect of sample loading on catalytic activity of the material.

The effect of amount of the catalyst was studied by varying the mass between 50 and 100 mg as to investigate qualitative effect when doubling sample amount. This was achieved by keeping the temperature constant at 110 °C, time at 4 h and 1.0 μ L TBHP for 0.05 M oxalic acid sample. Conversions obtained for 0.050M were 47 and 53% which indicate there is no significant influence of the sample amount since doubling the sample amount increased conversion by 6% which is less than 10%. There was a dramatic increase in the selectivity when the sample amount was doubled where it increased from 52 to 80%.

Table 11; Showing results of the effect of OMS-2 treated with 0.05 M of oxalic acid on the catalysis of azobenzene at variable sample amount.

Sample amount (mg)	A_{aniline}	A_{azobenzene}	A_{benzylideneaniline}	%Conversion	S_{azobenzen}-e	S_{benzylideneaniline}
50	3147939.95	1358167.96	1450179.22	47	52	48
100	4970004.61	4414475.59	1119658.03	53	80	20

Qualitative study on the amount of the catalyst was studied by varying the mass between 50 and 100 mg, this was achieved by keeping the temperature constant at 110 °C, time at 4 h and 1.0 μ L

TBHP for 0.10 M oxalic acid sample. Conversions were 41 and 52% which shows a significant increase on the conversion since doubling up sample amount led to 11% increase. There was an insignificant increase in the selectivity when sample amount was double as the values obtained were 80 and 76% respectively. 100mg was concluded to be a suitable amount for both materials and both 50mg and 100 mg were optimal amounts for a 0.100M sample.

Table 12; Effect of OMS-2 treated with 0.10 M of oxalic acid on the catalysis of azobenzene at variable sample amount.

Sample amount(mg)	Aaniline	Aazobenzene	Abenzylideneaniline	%Conversion	Sazobenzene	Sbenzylideneaniline
50	7774258.16	4264982.41	1053339.04	41	80	20
100	13956616.24	11622493.32	3608943.78	52	76	24

4.2.6 Study of effect of calcination on the catalytic activity of the material.

Post- thermal treatment was studied to investigate its effect on the catalytic activity on 0.10 M sample. The material was calcined at 350 °C for 1h and the reaction was carried using the conditions from general procedure. Uncalcined material was found to have 41% conversion whereas calcined one had 57% conversion. These results indicate that there is a noticeable effect of post-thermal treatment since there was a 16% increase after calcination was performed. Selectivity for both uncalcined and calcined was 80 and 71% which implies that there is a slight significance of post-thermal treatment on selectivity of azobenzene since it declined by 9%. The increase in the conversion can be ascribed to an increase in the Mn^{4+} which was reduced by oxalic acid on the catalytic surface as the Mn^{2+}/Mn^{3+} burns in air.

Table 13; Effect of calcination on 0.10 OxH-OMS-2 sample on the catalysis of azobenzene.

Sample	Aaniline	Aazobenzene	Abenzylideneaniline	%Conversion	Sazobenzene	Sbenzylideneaniline
0.10	7774258.16	4264982.41	1053339.04	41	80	20
0.10 Calcined	971120.79	898651.5	370000.56	57	71	29

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1: CONCLUSION

K-OMS-2 was successfully prepared through reflux method at a temperature of 110 °C and the resultant product was etched by oxalic acid. Different techniques such as Powder X-Ray diffraction (XRD), scanning electron microscope coupled with an elemental dispersive X-ray (SEM-EDX), high resolution transmission electron microscope (HRTEM) and Brannuer Emmet Teller were employed. XRD confirmed retention of the crystallographic phase structure and SEM, TEM confirmed the retention of nanorod morphology of the OMS-2 after acid treatment. BET showed an increase in the surface area at lower concentration of an acid and a decrease as the concentration of an acid increased.

The catalyst was used in one pot synthesis of imine and azobenzene through reflux in toluene for reaction period of 4 h at 110 °C, the conversion of aniline was dropped as the etching process was introduced hence selectivity of azobenzene increased indicating that the functionality of catalyst was tailored to favor the formation of azobenzene. The optimal conditions for selectivity of azobenzene were found to be 0.100 M oxalic acid etchant, reaction period of 4 h, 1.0 μ L TBHP at 110 °C. Calcination of 0.100M OxH-OMS-2 catalyst increased conversion of aniline from 41 to 57% and decreased selectivity of azobenzene from 80 to 71% indicating re-oxidation of $\text{Mn}^{2+}/\text{Mn}^{3+}$ back to Mn^{4+} on the catalytic surface as it increases high catalytic activity and selectivity of imine.

5.2: RECOMMENDATIONS

Further characterization such as X-ray Photoelectron Spectroscopy (XPS) and Thermogravimetric Analysis will be performed to get more information on the changes on surface chemical composition and state and thermal stability of the materials as etching is carried on it. Studies of different solvents will be performed to investigate the optimum solvent for synthesis of azobenzene. More structural modification including doping will be carried out prior to etching process to enhance catalytic performance of the materials. Optimistically etching K-OMS-2 with oxalic acid will be adopted in the manufacture of azobenzene on the large scale since its cheap hence promoting sustainable development and it is an environmentally benign approach.

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