



Reliable Method for the Synthesis of Mixed Metal Oxides (Zr-Mo-Si)

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ABSTRACT

The increasing demand for eco-friendly and sustainable chemical processes has led to the exploration of green synthesis methods in the preparation of mixed oxides. Mixed oxides are vital in a variety of catalytic applications, and traditional synthesis methods often involve energy-intensive processes with the use of toxic chemicals. This paper explores green and sustainable methods for synthesizing mixed oxides, focusing on innovative approaches such as sol-gel, hydrothermal, and bio-template methods. The study aims to reduce the environmental impact while maintaining high catalytic performance. The research presents a comprehensive analysis of synthesis routes, optimization of process parameters, and the structural characterization of the oxides.

3.3.1 Synthesis of ZrO₂/ MoO₃/SiO₂ catalysts:

Zirconyl Nitrate Hydrate in distilled water was gently added to the aforementioned solution, resulting in the formation of a greenish gel, which was dried and calcined at 500°C, 600°C, and 700°C for 7 hours. Similarly, catalysts containing 5%, 10%, 15%, and 20% ZMS were produced using varying amounts of zirconyl nitrate hydrate.

INTRODUCTION

Mixed oxides have gained significant attention due to their wide application in catalysis, environmental remediation, and energy storage. Traditional synthesis methods of mixed oxides, such as co-precipitation and solid-state reactions, often require high temperatures, use hazardous chemicals, and generate considerable waste [1]. With the growing need for sustainable processes, green chemistry offers a promising alternative to the traditional synthesis routes, aiming to minimize energy consumption, reduce waste, and employ renewable or less hazardous resources. This paper investigates green methods for the synthesis of mixed oxides and explores their effectiveness in achieving high-performance catalysts in an environmentally friendly manner.

Green synthesis of mixed oxides has emerged as a critical focus of research in recent years, driven by the growing need for environmentally sustainable chemical processes. Mixed oxides play a significant role in various catalytic applications, including energy conversion, environmental remediation, and chemical production [2-4]. However, traditional methods of synthesizing mixed oxides often involve energy-intensive procedures, the use of toxic solvents, and non-sustainable raw materials, which pose significant environmental challenges.

The structural characterization of mixed oxides synthesized through green methods is a critical component of the research, as it allows for the evaluation of the material's properties and performance in catalytic applications. Several advanced techniques are used for this purpose, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) [5]. XRD provides information about the crystallographic structure of the mixed oxides, allowing researchers to determine the phase purity and crystallite size of the materials. SEM and TEM are used to investigate the morphology and surface structure of the mixed oxides, revealing important details about particle size, porosity, and the distribution of the metal components within the oxide matrix. These structural characteristics are closely linked to the catalytic performance of the materials, as factors such as surface area, pore size, and metal dispersion directly influence the reactivity and stability of the catalysts [6].

One of the key findings of the research is that the green synthesis methods not only reduce the environmental impact but also enhance the catalytic performance of the mixed oxides in many cases. For instance, mixed oxides synthesized using the bio-template method often exhibit higher surface areas and improved porosity compared to those produced by conventional methods, leading to better catalytic activity in reactions such as oxidation, hydrogenation, and pollutant degradation. Similarly, materials prepared via the sol-gel and

hydrothermal methods tend to have smaller particle sizes and higher degrees of crystallinity, which contribute to increased reactivity and durability under harsh reaction conditions [7-10].

The research also highlights the potential for further development and optimization of green synthesis methods for mixed oxides. One promising area of future research is the exploration of alternative bio-templates that can offer even greater control over the morphology and structure of the mixed oxides. Additionally, the development of scalable green synthesis processes is crucial for the industrial application of these methods. While many green synthesis techniques have been demonstrated on a laboratory scale, translating these processes to larger-scale production remains a challenge. Overcoming this hurdle will be essential for realizing the full potential of green synthesis in the production of mixed oxides for catalytic applications.

Moreover, the integration of renewable energy sources into the green synthesis of mixed oxides presents another avenue for reducing the environmental impact of these processes. For example, the use of solar energy to drive hydrothermal reactions or the application of microwave-assisted sol-gel methods can significantly lower the energy requirements of the synthesis process. These approaches not only contribute to the sustainability of the process but also offer potential cost savings, making green synthesis more attractive for industrial applications.

One of the most promising green methods for synthesizing mixed oxides is the sol-gel process. This method allows for the preparation of mixed oxide materials at relatively low temperatures, using non-toxic solvents and reducing agents. The sol-gel process involves the transition of a system from a colloidal solution (sol) into a solid phase (gel), enabling the formation of highly homogenous mixed oxides. The key advantage of this method is its ability to control the morphology and structure of the final material by fine-tuning the processing parameters, such as pH, temperature, and concentration of precursors. This level of control is vital for optimizing the catalytic properties of the resulting mixed oxides. Moreover, the sol-gel method can be performed in aqueous media, which aligns with the goals of green chemistry by minimizing the use of harmful organic solvents.

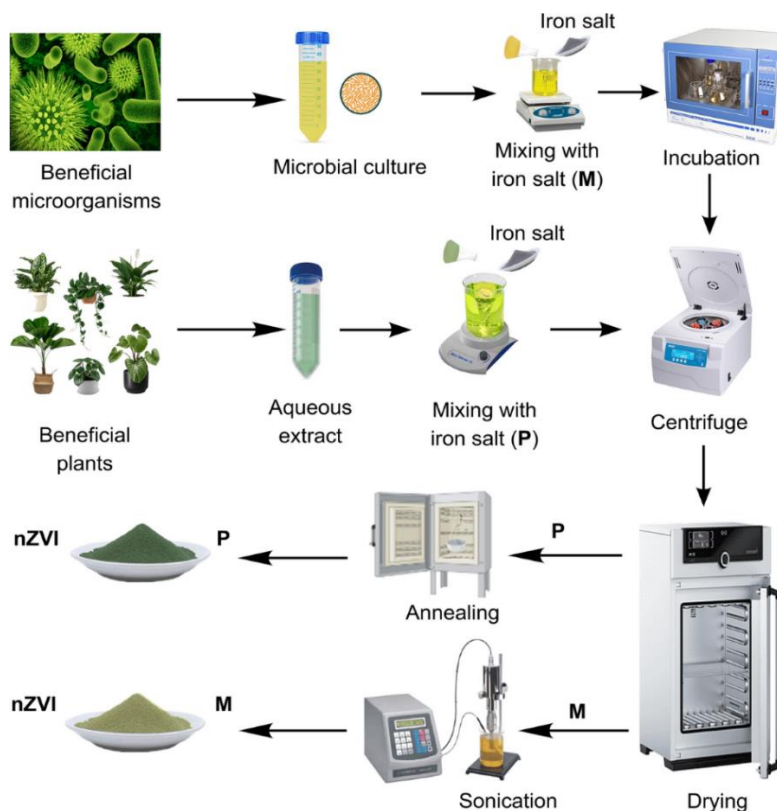


Figure 1: Representation of synthesis of mixed oxides.

Another innovative green synthesis approach is the bio-template method. This technique involves using natural, renewable materials such as plant extracts, microorganisms, or biomolecules as templates for the formation of mixed oxides. The bio-template method offers several advantages, including the ability to create highly porous structures and the use of mild reaction conditions. Biomolecules such as proteins, polysaccharides, and even plant leaves have been successfully employed as templates for synthesizing mixed oxides with unique morphologies. After the oxide is formed, the organic template is usually removed through calcination, leaving behind a highly porous and well-defined oxide structure. This method not only reduces the environmental impact by using renewable resources but also enhances the catalytic properties of the resulting materials, as the porosity and high surface area contribute to increased catalytic activity.

MATERIALS AND METHODS

Materials

Hydrated salts of all the metals (Zirconyl Nitrate Hydrate, Tetraethyl Ortho Silicate, Ammonium heptamolybdate tetrahydrate) were purchased from Sigma-Aldrich. Other chemicals (Iso-propyl alcohol etc.) obtained from SD Fine Chemicals of Analytical Grade and were used without further purification.

Methods: Synthesis of Zr-Mo-Si mixed oxides (ZMS) and Characterization

The sol-gel method is one of the most widely used green synthesis techniques for preparing mixed oxides. It involves the transition of a sol, which is a colloidal solution of nanoparticles, into a gel-like network through hydrolysis and condensation reactions. This technique is particularly advantageous due to its ability to utilize environmentally benign solvents, such as water or alcohols, and to operate at relatively low temperatures, which minimizes energy consumption. The sol-gel process allows for precise control over the composition and morphology of the mixed oxides by adjusting various parameters such as pH, precursor concentration, and reaction time. For instance, by modifying the pH, researchers can influence the particle size and surface area of the final product. Additionally, the sol-gel method can produce highly homogeneous materials with uniform distribution of metal components, which is crucial for achieving optimal catalytic performance.

Hydrated salts of all the metal oxides were taken for the synthesis of Zr-Mo-Si mixed oxides (ZMS). The Hydrated salts were mixed with distilled water with continuous stirring in an Erlenmeyer Flask (Capacity 250 mL) with a bed, resulting in the formation of a greenish gel, which was dried and calcined at 500°C, 600°C, and 700°C for 7 hours. Similarly, catalysts containing 5%, 10%, 15%, and 20% ZMS were produced using varying amounts of zirconyl nitrate hydrate.

Instrumental analytical techniques were used to examine the structural, morphological, textural, and chemical properties of ZMS materials discussed herein:

X-Ray Diffraction (XRD)

To identify crystalline phases, degree of crystallinity, and estimate crystallite size (using Scherrer's equation) XRD patterns were analysed.

Fourier Transform Infrared Spectroscopy (FTIR)

In order to assess the functional groups and the presence of M–O (M = Zr, Mo, Si) bonds and network formation FTIR was used for the synthesized material.

Energy Dispersive X-ray Spectroscopy (EDX)

To analyze the elemental analysis and verification of Zr, Mo, and Si incorporation EDX technique was employed.

SEM and TEM Analysis

To study the morphological features of the synthesized Zr-Mo-Si (ZMS) mixed oxides, SEM and TEM analyses were conducted. SEM images revealed agglomerated, irregularly shaped particles with a rough, porous surface texture, indicating mesoporosity and particle sintering during calcination. The average particle sizes were in the submicron to nanometer range, and the images showed interconnected grains, suggesting good textural development. TEM analysis further confirmed the formation of quasi-spherical nanoparticles in the 10–50 nm size range.

RESULTS AND DISCUSSION

The synthesized mixed oxides exhibited various crystal structures depending on the synthesis route. Sol-gel and hydrothermal methods produced oxides with high surface areas, essential for catalytic performance. Bio-template methods using plant extracts resulted in well-dispersed oxide particles with reduced aggregation.

Characterization

XRD and FTIR Analysis

X-ray Diffraction (XRD) analysis was carried out to investigate the crystalline structure and phase composition of the synthesized Zr-Mo-Si (ZMS) mixed oxides. The XRD patterns showed broad and low-intensity diffraction peaks, indicating that the material is predominantly amorphous or poorly crystalline in nature, which is typical for sol-gel-derived oxides calcined at moderate temperatures. In some cases, weak diffraction peaks corresponding to tetragonal ZrO_2 or MoO_3 phases were observed, suggesting partial crystallization depending on the calcination conditions. The absence of sharp peaks associated with crystalline silicon dioxide indicates that Si was incorporated into the amorphous matrix. These results confirm the formation of a homogeneously mixed oxide system with a predominantly amorphous structure, which is advantageous for catalytic and surface-related applications due to enhanced dispersion of active sites (Fig. 2).

The FT-IR spectra of 10ZM samples were shown. The results showed only one peak for Zr-O at 545 cm^{-1} in the sample calcined at 500°C , which is diminished at high temperature. Peaks for $\alpha\text{-MoO}_3$ may be found at 870 cm^{-1} and 1000 cm^{-1} , which decrease in intensity at 700°C . The following observations were found- $1000\text{--}1100\text{ cm}^{-1}$ due to Si-O-Si asymmetric stretching, $800\text{--}950\text{ cm}^{-1}$ due to Zr-O-Si and Mo-O-Si linkages and $500\text{--}700\text{ cm}^{-1}$ on account of Mo-O and Zr-O vibrations (Fig. 3).

EDX analysis

To confirm the elemental composition and uniform distribution of components in the synthesized Zr-Mo-Si (ZMS) mixed oxides, Energy Dispersive X-ray Spectroscopy (EDX) analysis was performed. The EDX spectra revealed the presence of zirconium (Zr), molybdenum (Mo), silicon (Si), and oxygen (O), verifying the successful incorporation of all intended elements into the oxide matrix. No significant peaks corresponding to impurities were detected, indicating the high purity of the synthesized material. Elemental mapping further demonstrated a homogeneous spatial distribution of Zr, Mo, and Si across the sample, suggesting effective mixing at the nanoscale during the sol-gel synthesis. These results confirm the compositional integrity and uniformity of the ZMS mixed oxides.

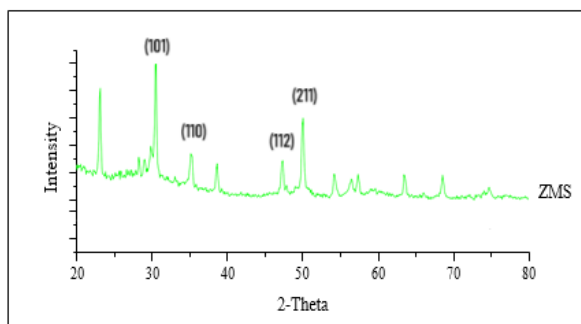


Figure 2: XRD Spectra of ZMS material.

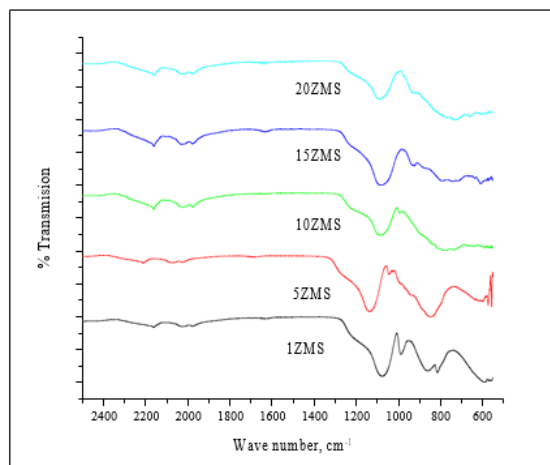


Figure 3: FT-IR Spectra of ZMS material.

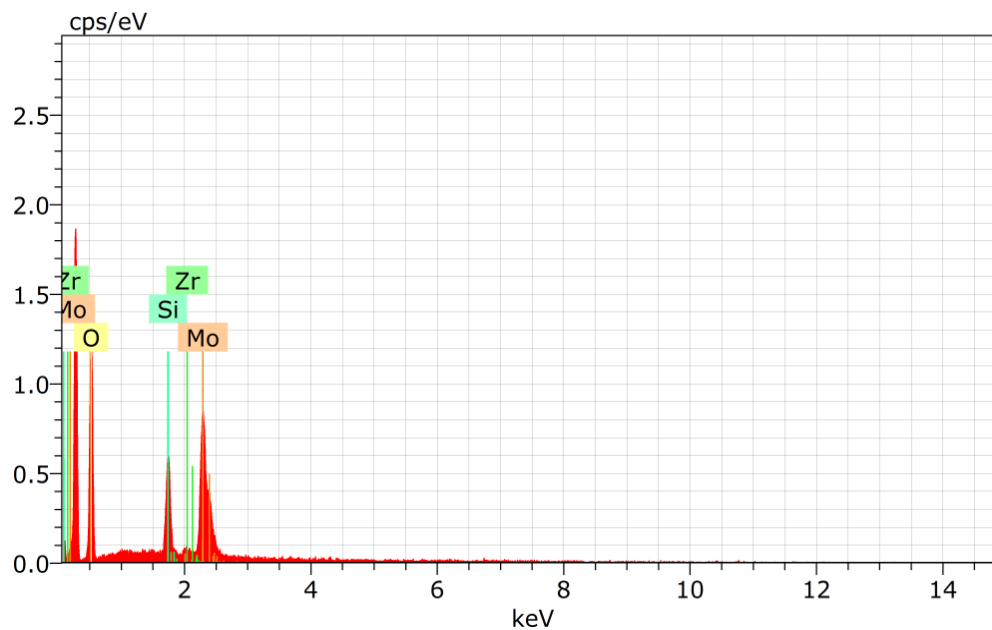


Figure 4: EDX analysis of ZMS material.

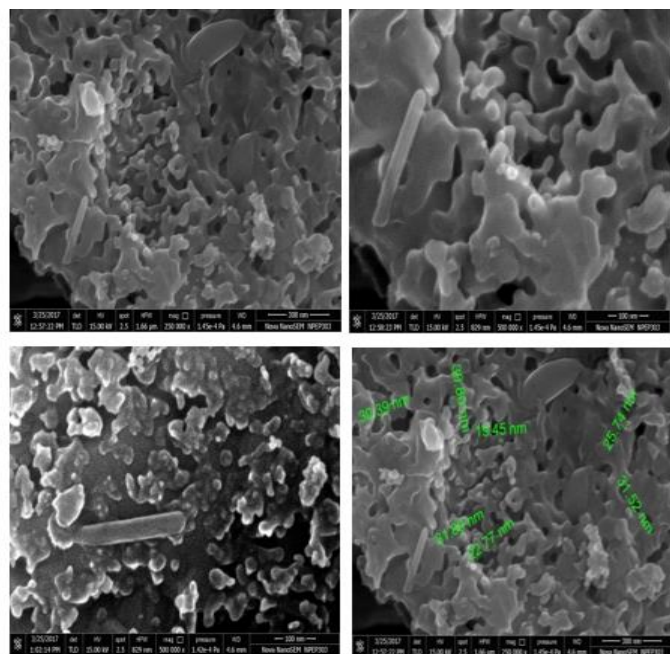


Figure 5: FESEM images of ZMS material calcined at 500°C.

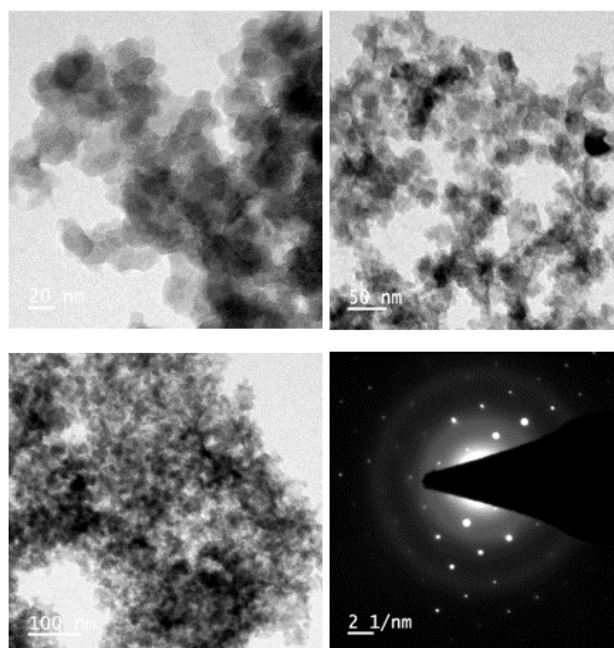


Figure 6: TEM micrograph of ZMS material.

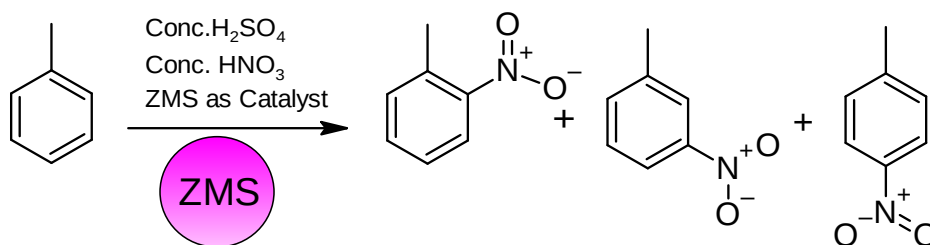
Figure 5 showed FESEM micrographs of the ZMS material. The images show that the size and shape have altered to an agglomerated form with a mixture of spherical and cylindrical nanoparticles. This could be attributed to the increased amount of zirconia on $\text{MoO}_3/\text{SiO}_2$ support. The average particle size was between 14 and 36 nm. In another set of ZMS catalysts, the 1ZMS is shown in fig. 5 (d), demonstrating that the particle size remains spherical after ZrO_2 is added to $\text{MoO}_3/\text{SiO}_2$.

Catalytic activity

The synthesized catalysts were employed for a variety of processes, including toluene nitration. Different parameters were tested to optimize the reaction conditions.

The nitration process of aromatic substrates produces substantial commercial products such as intermediates, explosives, dyes, and polymers. The classic process for synthesizing nitro-aromatic molecules using H_2SO_4 as a catalyst is not environmentally friendly because it produces a large amount of dilute H_2SO_4 as a by-product due to the formation of H_2O during the reaction. This acid must be separated and concentrated from the reaction mixture, which is very energy intensive and causes environmental problems. For these reasons, nitration reactions using solid acid instead of liquid acid, i.e. H_2SO_4 , are gaining popularity. Numerous sulphated solid acid catalysts for nitration reactions have been identified, including sulphated titania, zirconia-ceria, and sulphated carbon.

Simple nitration reactions were carried out using the developed catalysts ZMS. In a typical run, a 1:4 combination of toluene and 50% nitric acid with 0.3g of catalyst was heated to 100°C with magnetic stirring and monitored by GC. When the reaction was finished, the liquid was filtered to remove the catalyst, which was then utilized for recycling studies with a new reaction mixture.



Scheme 1: Scheme of nitration of toluene to nitrotoluenes (*o*, *m* and *p* forms).

Nitration of toluene was performed with 50% nitric acid in the presence of the catalyst ZMS. Several parameters, including the effect of temperature, catalyst quantity, catalyst concentration, molar ratio, and reaction time, are used to optimize the reaction conditions. Temperature affects the conversion of toluene. Increasing the temperature resulted in a 99% conversion of toluene at 100°C, indicating that raising the reaction temperature is helpful for accelerating the process. However, at 120°C, no increase in conversion was found, possibly due to faster decomposition of HNO₃, resulting in loss of mass. The optimal temperature for nitration of toluene was 100°C. All reactions resulted in nitro toluene with ortho, Meta, and para isomers, with no synthesis of dinitro.

Table 1 shows the results of testing different concentrations of ZrO₂ on the MoO₃/SiO₂ catalyst during toluene nitration. In the first run, we carried out the reaction without a catalyst, and conversion reached 30%. It suggested that the reaction was somewhat self-catalysing due to the use of dilute HNO₃ as a reagent; however, using a number of ZMS catalysts, high catalytic activity of up to 99% was observed, and all catalysts demonstrated excellent toluene conversion. TPD data from 10ZMS showed only strong acid sites in the high temperature zone. These acid sites were responsible for the production of nitronium ions.

Table 1: Effect of different concentration on nitration of Toluene.

ZMS Catalyst	Conversion (%)	Selectivity (%)		
		ONT	MNT	PNT
Blank	30	52.1	9.9	38.5
1% ZMS	75	58.1	8.9	34.5
5% ZMS	78	54.7	10.0	35.5
10% ZMS	99	53.3	7.5	39.0
15% ZMS	90.9	56.1	8.0	35.2
20% ZMS	90.0	56.0	7.9	35.1

Note: Toluene: HNO₃-1:4, conc. of HNO₃ -50%, temp. 100°C, 0.3 g of catalyst, 5h.

Different catalyst amounts were utilized to investigate their effect on the nitration reaction; the results are shown in Table 2. The table shows that increasing the amount of catalyst (0.1 g - 0.3 g) boosted toluene conversion by

up to 99%. The optimal acid sites required for toluene nitration, which could be achieved with 0.3g of catalyst. Further increasing the catalyst amount resulted in no increase in conversion.

Table 2: Effect of catalyst amount on nitration.

Amount of Catalyst, gm	% Conversion	Selectivity %		
		ONT	MNT	PNT
0.1	85	53.5	-	46.9
0.3	99	53.3	7.5	39
0.7	97.8	59.55	5.9	35.6
1	97.8	56.85	6.7	33

Note: toluene: HNO_3 -1:4, conc. of HNO_3 -50%, temp. 100°C , 5h, 10 ZMS catalyst

In Fig. 7, a combination of toluene and 50% HNO_3 at various molar ratios was tested; the results showed that increasing HNO_3 level resulted in a significant rise in toluene conversion up to 1:4 molar ratio, which was due to the creation of additional NO^{2+} ions from nitric acid. As a result, the optimal volume ratio of 1:4 was chosen, and no dinitro-toluene was generated at varied nitric acid concentrations.

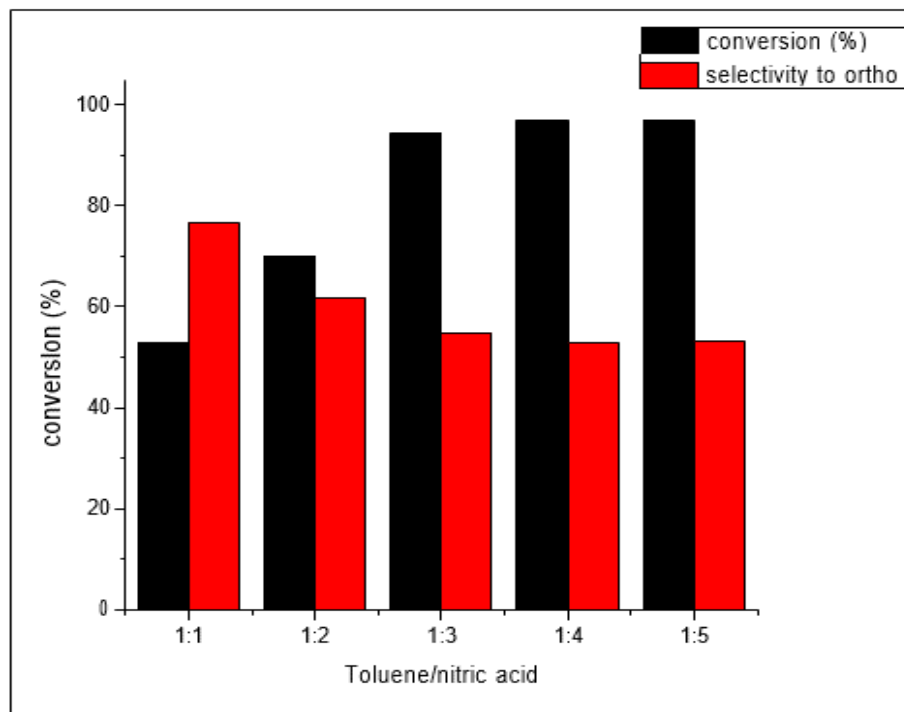


Figure 7: Effect of molar ratio on nitration (Reaction condition: (0.3g) of 10 ZMS, conc. of HNO_3 -50%, temp. 100°C , 5h)

CONCLUSION

In conclusion, the green synthesis of mixed oxides represents a significant advancement in the field of sustainable chemistry. By utilizing environmentally friendly methods such as sol-gel, hydrothermal, and bio-template synthesis, researchers can produce mixed oxides with high catalytic performance while minimizing the environmental impact. These methods offer several advantages over traditional synthesis techniques, including lower energy consumption, the use of non-toxic solvents and precursors, and the ability to fine-tune the material properties. The optimization of process parameters and the use of advanced characterization techniques have further enhanced the understanding of how green synthesis can improve the performance of mixed oxides in catalytic applications. As the demand for eco-friendly chemical processes continues to grow, the development and implementation of green synthesis methods for mixed oxides will play a crucial role in achieving sustainability goals in various industries, particularly in the fields of energy, environmental protection, and chemical production. The ongoing research in this area promises to yield even more innovative and efficient methods for producing mixed oxides, contributing to a greener and more sustainable future.

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