

CO₂-Free Ethylene Oxide Production via Liquid-Phase Epoxidation with Fe₂O₃/MSM Catalyst

Muhammad Maqbool,^[a] Nazia Parveen,^[a] Saima Jaffar,^[a] Sadaf Ul Hassan,^[b] Asif Mahmood,^[c] Waheed Al-Masry,^[c] Taewook Kim,^[d] Soo-Kyung Han,^[d] Chan Ho Park,^[d] Shumaila Razzaque,^{*,[e]} and Toheed Akhter^{*,[d]}

In this study, we present an approach for ethylene oxide (EO) production that addresses environmental concerns by eliminating greenhouse gas emissions. Our catalyst, Fe₂O₃/MSM, was synthesized using a hydrothermal method, incorporating Fe₂O₃ nanoparticles into a well-structured mesoporous silica matrix (MSM). We selected peracetic acid as the oxidant, enabling CO₂-free EO production while yielding valuable by-products such as acetic acid, monoethylene glycol, and diethylene glycol. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET) analyses confirmed the heteroatom structure of the catalysts and porosity, while Transmission

electron microscopy (TEM) analysis provided insights into its morphology. Then, the synthesized catalyst was used in the liquid-phase epoxidation of ethylene for EO production. Our systematic experiments involved varying critical parameters such as temperature, ethylene to oxidant ratio, catalyst dosage, and solvent to optimize EO selectivity and ethylene conversion. The results of this study demonstrated an 80.2% ethylene conversion to EO with an EO selectivity of 87.6%. The production process yielded valuable by-products without CO₂ emissions, highlighting its environmental friendliness.

1. Introduction

Ethylene oxide (EO) is a versatile compound widely utilized in industries such as plastics, solvents, detergents, and textiles.^[1] It is a colorless, flammable gas with a faintly sweet odor.^[2] EO is produced through the direct oxidation of ethylene, often catalyzed by silver or silver-based compounds.^[3] This reaction occurs under high temperatures and pressures and may involve various co-reactants and promoters.^[4] EO production demands meticulous optimization of reaction conditions and catalysts, along with rigorous attention to safety and environmental considerations.^[5] Despite these challenges, EO remains a critical component of many industrial processes, and demand for this compound continues to grow.^[6]

Studies in epoxidation have explored the effectiveness of different materials as catalysts for producing EO, polyethylene, and polyvinyl chloride.^[7] EO, in particular, is the third most significant ethylene derivative and is utilized as a raw material for the formation of various products.^[8] The most widely used approach for manufacturing EO involves employing oxygen (O₂) as the oxidizing agent, typically at elevated temperatures ranging from 200 to 240 °C, and pressures within the range of 10 to 30 bars. This process, known as gas-phase epoxidation (GPE) of ethylene, utilizes silver-based catalysts.^[9]

Despite its widespread use, the traditional method of EO production via silver-catalyzed epoxidation using oxygen as an oxidant has several drawbacks. One of the major concerns is the poor selectivity of the reaction, which results in the generation of a significant amount of CO₂ as a by-product. This by-product not only leads to environmental pollution but also poses a challenge in terms of sustainability.^[10] Indeed, this process is considered the second-highest CO₂-emitting chemical process, after ammonia synthesis.^[11] Scientists have attempted to replace the GPE process, which emits CO₂, with a liquid-phase epoxidation (LPE) that does not produce CO₂. The LPE method utilizes a homogeneous methyltrioxorhenium (MTO) catalyst and H₂O₂ as an oxidant and has demonstrated excellent catalytic activity with nearly 100% selectivity towards EO.^[9]

However, using MTO in this process has two drawbacks. Firstly, the catalyst becomes deactivated due to the accumulation of water, a by-product. Secondly, the high cost and limited availability of rhenium (Re) metal pose challenges for its use in this process. Therefore, replacing Re with readily available and less expensive catalytic materials that have high H₂O₂ utilization efficiency could improve process economics and practical feasibility.^[12] Hence, further research is required to develop alternative heterogeneous epoxidation catalysts.

[a] Mr. M. Maqbool, N. Parveen, S. Jaffar
Department of Chemistry
University of Management and Technology C-II, Johar Town, 54770, Lahore, Pakistan

[b] Prof. S. U. Hassan
Department of Chemistry
COMSATS University Islamabad, Lahore Campus, Lahore, Pakistan

[c] Prof. A. Mahmood, Prof. W. Al-Masry
Department of Chemical Engineering,
College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia

[d] Mr. T. Kim, S.-K. Han, Prof. C. H. Park, Prof. T. Akhter
Department of Chemical and Biological Engineering,
Gachon University, Seongnam 13120, Republic of Korea
E-mail: toheed.akhter@umt.edu.pk

[e] S. Razzaque
Institute of Physical Chemistry,
Polish Academy of Sciences,
Kasprzaka, 44/51, 01-224, Warszawa, Poland
E-mail: srazzaque@ichf.edu.pl

In the pursuit of efficient EO production catalysts, prior investigations have focused on transition metal-based catalysts with high oxidation states supported on mesoporous silica materials, such as MCM-41 and SBA-15.^[13] These studies have revealed the catalytic epoxidation mechanism, which involves redox reactions facilitating the transfer of oxygen from the oxidant to the alkene double bond.^[14] Notably, niobium (Nb)-based catalysts have been utilized for the epoxidation of cyclic alkenes, propene, and other chemical substrates, including carvone and limonene.^[15] These Nb-based catalysts demonstrate good thermal stability and resistance to metal leaching and hydrolysis, making them well-suited for LPE processes.^[16] The combination of Nb with MSM, known as Nb/MSM, has been extensively studied in previous research.^[16d,17] A notable study by Yan *et al.* investigated tungsten (W) and Nb-based MSM catalysts for ethylene epoxidation using H₂O₂ as the oxidant.^[12b] It was observed that both W-KIT-6 and Nb-KIT-6 catalysts demonstrated efficiency under normal conditions. Nonetheless, significant concerns were raised regarding metal leaching and H₂O₂ decomposition with W-KIT-6 and Nb-KIT-6-based catalysts.^[18] In alignment with prior research efforts, we have developed a highly efficient Nb/MSM catalyst for EO production in our previous research, where peracetic acid (PAA) was used as the oxidant instead of H₂O₂, resulting in both superior efficiency and the notable benefit of CO₂-free EO production.^[7a]

Similarly, the iron-based catalyst, [Fe(salophen)Cl].H₂O complex has been investigated for its potential in ethylene epoxidation using hydrogen peroxide as the oxidant.^[19] However, this approach has faced challenges related to catalyst stability and overall efficiency. In a separate research endeavor, Fe₂O₃ nanoparticles were incorporated into mesoporous silica materials and applied in the oxidation of alcohols and sulfides.^[20] Notably, the potential of employing Fe₂O₃ nanoparticles supported on mesoporous silica materials, along with PAA as the oxidant, for EO production remains unexplored.

In our current research endeavor, we have developed Fe₂O₃/MSM-based catalyst for EO production, demonstrating an approach that contributes to achieving zero greenhouse gas emissions during EO production. The catalyst was synthesized through a hydrothermal method, employing FeCl₃ to introduce Fe₂O₃ nanoparticle into a meticulously structured cubic large-pore mesoporous silicate (SiO₂) matrix, derived from tetraethyl orthosilicate (TEOS). The choice of PAA as the oxidant is a pivotal one, as it engages ethylene gas in a reaction that results in CO₂-free EO production, concurrently yielding valuable by-products such as acetic acid (AA), ethylene glycol (EG), and diethylene glycol (DEG). These by-products hold significant potential for diverse applications across various industrial sectors.^[21] We have thoroughly validated the heteroatom structure of the prepared Fe₂O₃/MSM catalyst, employing advanced techniques like XRD and XPS analysis. We employed BET analysis, a standard technique for surface area and pore volume characterization, to assess the material's porosity. For further morphological insights, we subsequently performed TEM analysis. Subsequently, we evaluated the potential of the Fe₂O₃/MSM catalyst in the LPE process for EO synthesis. In this process, ethylene gas compressed at 50 bars and then carefully

dissolved in a liquid reaction medium infused with PAA. Our efforts have been focused on achieving not just EO production but also the generation of valuable by-products, such as AA and ethylene glycols, all while adhering to a zero CO₂ emission strategy. Moreover, we conducted a series of experiments, systematically varying critical parameters such as temperature, ethylene to oxidant molar ratio, catalyst dosage, and solvent selection aiming for finding optimal reaction conditions than can yield the highest EO selectivity and ethylene conversion. Through gas chromatography (GC) analysis, we have substantiated 80.2% conversion of ethylene to EO, coupled with EO selectivity of 81.9%. Hence, throughout this process, we achieved the production of valuable EO, accompanied by useful by-products, all achieved with zero CO₂ emissions, exemplifying the environmentally friendly nature of this EO production method.

1.1. Experimental

1.1.1. Materials

Pluronic P123 (Mn = 8400, Sigma-Aldrich, Germany), Tetraethyl orthosilicate (TEOS) (98%, Sigma-Aldrich, Germany), Ferric (III) Chloride (99.99%, Sigma-Aldrich, Germany), Ethanol (99.8%, Sigma-Aldrich, Germany), *n*-Butanol (99.4%, Sigma-Aldrich, Germany), Peracetic acid (32%, Sigma-Aldrich, Germany), Acetonitrile (99.8%, Sigma-Aldrich, Germany), Chloroform (99.8%, Sigma-Aldrich, Germany), and Carbon tetrachloride (99.9%, Sigma-Aldrich, Germany) were used without further purification.

1.2. Synthesis of Fe₂O₃/MSM Catalyst

To synthesize the Fe₂O₃/MSM catalyst, Pluronic (6.0 g) was dissolved in a mixture of 216 mL of distilled water and 7.90 mL of 35% concentrated HCl at 35 °C with stirring. Subsequently, 7.42 mL of *n*-butanol was added dropwise to the solution, which was stirred for 1 hour at 35 °C. Following this, 1.539 g of FeCl₃ and 14.849 mL of TEOS were added to the mixture under the same conditions. The resulting mixture was stirred for 24 hours at 35 °C, followed by heating in a closed flask at 100 °C for an additional 24 hours. After allowing the reaction mixture to cool down to room temperature (approximately 30 °C), precipitates formed, which were then filtered off and dried overnight at 100 °C. The crude product was purified by washing with a mixture of ethanol and HCl (1:1). The purified product was then calcined at 550 °C for 5 hours. This synthesis procedure ensured the preparation of the Fe₂O₃/MSM catalyst for further investigation.^[22] To investigate the intrinsic properties of Fe₂O₃, bare nanoparticles were prepared through a modified Fe₂O₃/MSM catalyst synthesis process, excluding the surfactant and TEOS. To assess the properties, the support material for the catalyst, MSM, was prepared separately using the same process as for Fe₂O₃/MSM, except that FeCl₃ was omitted from the reaction mixture containing TEOS.

1.3. EO Production via LPE

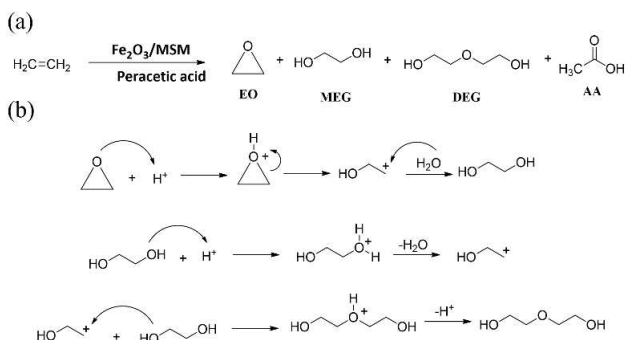
The synthesized $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst was used for ethylene EO production via LPE. The experimental setup involved adding PAA as the oxidant, acetonitrile as the solvent, and the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst to the reactor. Pure ethylene gas was introduced from a separate cylinder at a pressure of 50 bar. The consumption of ethylene gas was quantified using a precision weighing balance, while reactor pressure was controlled through a dedicated pressure controller located at the gas line outlet. A mass flow meter was connected with the reaction assembly to precisely control the flow rate and total volume of ethylene entering the reactor.

The experiments were conducted at various temperatures (40°C , 50°C , and 60°C) and reaction times ranging from 1 to 6 hours to determine the optimal reaction conditions, with a constant pressure of 50 bar maintained throughout. After each experiment, a specific volume of the sample was injected into the GC for analysis. As a reference, parallel experiments were conducted using MSM (catalyst support) to validate its inert nature. Additionally, a blank run was performed to experimentally confirm the inertness of acetonitrile. This blank run was conducted by carrying LPE experiment in the absence of ethylene gas, while all other reaction components remained unchanged. The simplified reactions for EO synthesis, as well as the production of its by-products, along with the reaction mechanism for MEG and DEG synthesis, are illustrated in Scheme 1 (a and b).^[11,23] Additionally, to identify the optimal reaction conditions, a series of experiments were conducted using $\text{Fe}_2\text{O}_3/\text{MSM}$ as the catalyst, investigating the influences of catalyst amount, temperature, ethylene to oxidant molar ratio, and solvent on the ethylene conversion and product selectivity.

The concentration of EO produced and the EO selectivity were determined using the following equations.

Conc. of EO

$$= \frac{\text{Conc. of std. sample}}{\text{Peak area of std. sample}} \times \text{peak area of EO produced} \quad (1)$$



Scheme 1. Production of EO and its derivatives from ethylene.

EO Selectivity

$$= \frac{\text{Moles of EO produced}}{\text{Total moles of all possible reaction products}} \times 100 \quad (2)$$

The utilization efficiency (U_{PAA}) and conversion efficiency (X_{PAA}) of peracetic acid (PAA) were determined using a previously established method.^[24]

$$U_{\text{PAA}} = \left(\frac{\eta_{\text{EO}} + \eta_{\text{MEG}} + \eta_{\text{DEG}}}{\eta_{\text{PAA}}^{\circ} - \eta_{\text{PAA}}} \right) \times 100 \% \quad (3)$$

$$X_{\text{PAA}} = \left(\frac{\eta_{\text{PAA}}^{\circ} - \eta_{\text{PAA}}}{\eta_{\text{PAA}}^{\circ}} \right) \times 100 \quad (4)$$

η_{EO} , η_{MEG} , and η_{DEG} = Moles of EO, MEG, and DEG, respectively. $\eta_{\text{PAA}}^{\circ}$ and η_{PAA} = Initial and final moles of PAA. Turn over frequency (TOF) is defined as moles of CH_3COOOH converted per atom of Fe per time.^[7a]

1.4. Characterization

The synthesis of the support (MSM) and the catalyst ($\text{Fe}_2\text{O}_3/\text{MSM}$) was examined using a Miniflex Benchtop powder X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ irradiation ($\lambda = 1.5418 \text{ \AA}$, 200 kV, 50 mA). The average crystallite size (with a size error of 0.5 nm) was estimated by the Scherrer equation.^[25] N_2 adsorption-desorption isotherms were obtained using Micro-metrics Gemini VII 2390 t at 77 K for specific surface area calculations. The Barret-Joyner-Halenda equation was used to determine pore size distributions and volumes.^[26] A TEM microscope (JEOL 2010F) was used to obtain high-resolution TEM images at a high voltage of 200 kV. The samples for the TEM analysis were prepared by diluting a suspension of samples with methanol and then drop-drying them on holey carbon-coated copper TEM grids. GC analysis was carried out using an Agilent GC-7890A equipped with a GC Column DB-WAX capillary column (30 m, 0.32 mm, 0.5 μm). The chemical composition of the sample was analyzed using XPS with an Al-K X-ray source operating at 1486.6 eV and a hemispherical energy analyzer (Specs EA 10 Plus) operating in vacuum better than 10^{-7} Pa. The core-level binding energies of photoelectrons emitted from the surface were determined and calibrated by fixing the C (1 s) core level at 284.5 eV. UV-Visible spectra were acquired employing a Rayleigh UV-1600 spectrophotometer. To obtain the UV-Vis absorption spectrum of a solid sample, a known quantity of the sample was introduced into spectral grade n-decane. A quartz window with a path length of 0.5 mm was employed for this purpose. It is worth noting that the solid sample exhibited minimal light scattering in the n-decane medium. This facilitated the acquisition of a high-quality spectrum, as the refractive index of n-decane closely matches with that of MSM support. The hydrodynamic size of the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst was characterized using dynamic light scattering (DLS). The measurements were conducted at 25°C with a

Zetasizer Nano-ZS instrument from Malvern Instruments (Malvern, UK).

2. Results and Discussion

2.1. XRD

The synthesis of the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst and MSM support was confirmed through XRD analysis, as displayed in Figure 1. The diffraction peaks of bare iron oxide (Figure 1a) can be attributed to the Fe_2O_3 phase, aligning with reported patterns in the literature and corresponding to JCPDS card no. 89–596. In the XRD pattern of MSM (Figure 1b), a single broad peak at $2\theta = 1.7^\circ$ indicated its complete amorphous nature resulting from calcination at 550°C for 5 hours. Whereas in the diffractograms of $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst (Figure 1c), a broad peak is observed at $2\theta = 23^\circ$. The addition of Fe_2O_3 to the silica framework may have hindered the material's transition to a crystalline phase. The dispersion and incorporation of Fe_2O_3 within the silica matrix might have prevented the formation of crystalline domains.^[22,27] This finding is significant because it indicates that the Fe_2O_3 nanoparticles are uniformly distributed on the MSM support, suggesting an even dispersion of Fe_2O_3 throughout the material without the formation of large clusters or aggregates. This uniform dispersion of iron Fe_2O_3 aligns with previous reports,^[28] confirming the successful achievement of a homogeneous Fe_2O_3 distribution in the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst using the employed preparation method.

2.2. BET

The surface properties of the bare Fe_2O_3 nanoparticles, $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst and its corresponding support were examined via BET analysis at 77 K. According to the IUPAC nomenclature, both $\text{Fe}_2\text{O}_3/\text{MSM}$ and MSM exhibited type IV isotherms characterized by a distinctive hysteresis loop, signifying the presence of cage-like pore structures, as depicted in Figure 2 (a,b). Interestingly, following the incorporation of Fe_2O_3 into the MSM support, the isotherms of the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst retained their cage-like structural integrity. This observation suggests that the process of incorporating Fe_2O_3 into the MSM support does not modify the well-ordered mesoporous architecture of the material. It is noteworthy that there was a notable decrease in pore volume, reducing from $0.701\text{ cm}^3/\text{g}$ for MSM to $0.623\text{ cm}^3/\text{g}$ for $\text{Fe}_2\text{O}_3/\text{MSM}$. Simultaneously, a significant reduction in surface area was observed, diminishing from $796\text{ m}^2/\text{g}$ for MSM to $250\text{ m}^2/\text{g}$ for $\text{Fe}_2\text{O}_3/\text{MSM}$. To assess the pore size distribution of both $\text{Fe}_2\text{O}_3/\text{MSM}$ and MSM, the Barrett-Joyner-Halenda (BJH) method was employed.^[29] The uniformity of pore sizes was evaluated through capillary condensation analyses performed on both the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst and its corresponding support, utilizing the adsorption-desorption curve. The sharp inflection observed in the adsorption isotherm, occurring at a relative pressure (p/p°) between 0.5 and 0.7, is indicative of capillary condensation of nitrogen within the pores, as

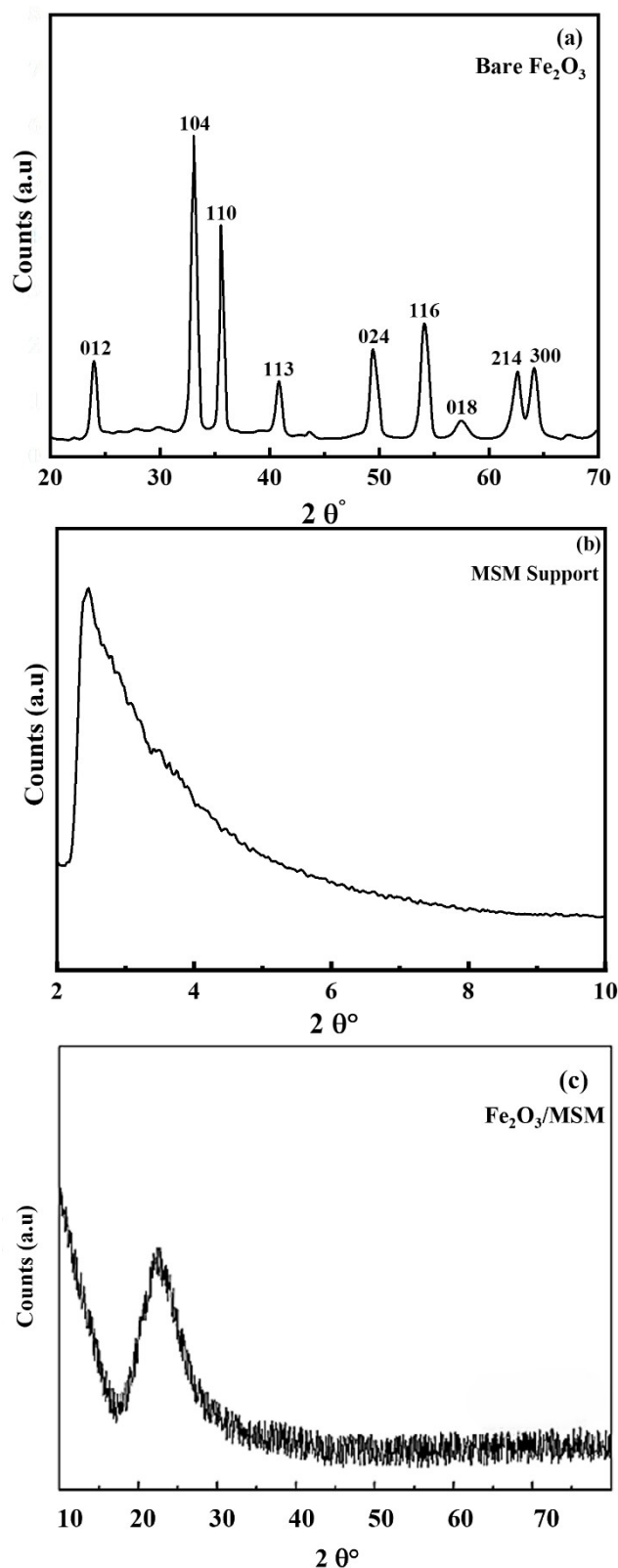


Figure 1. XRD pattern of (a) bare Fe_2O_3 , (b) MSM and $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst.

illustrated in Figure 2(b). The extent of pore size uniformity is assessed by examining the height and sharpness of this inflection. The measurements revealed an average pore diame-

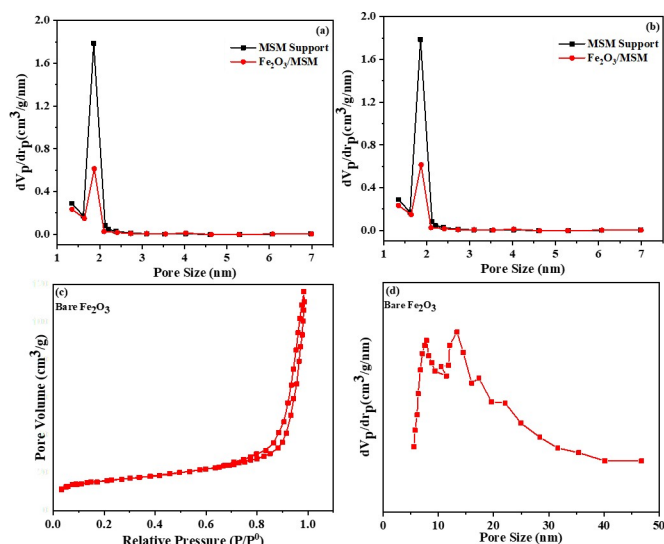


Figure 2. N₂ adsorption-desorption isotherm of (a,b) bare Fe₂O₃, (c,d) MSM support and Fe₂O₃/MSM catalyst.

ter of 3.5 nm for Fe₂O₃/MSM and 3.8 nm for the support. This decrease can be attributed to the presence of Fe₂O₃ within the pores of Fe₂O₃/MSM, which occupies pore space, consequently reducing both the overall pore volume and surface area.^[30] It is significant to observe that the structural parameters also underwent changes in comparison to the values associated with the bare Fe₂O₃ (Figure 2c,d), indicating a high level of interaction between them. Table 1 provides an overview of various textural parameters obtained from the BET analysis, including surface area (S_{BET}), cumulative pore volume (V_{BJH}), and mesoporous diameter (D_{BJH}).

2.3. TEM

The structural properties and porous nature of Fe₂O₃/MSM catalyst were examined utilizing TEM images at resolutions of 50 nm and 200 nm, as presented in Figure 3. These TEM micrographs not only affirm the mesoporous nature of the calcined Fe₂O₃/MSM catalyst but also provide invaluable insights into its morphology. The images clearly depict the distribution of Fe₂O₃ nanoparticles within the MSM support, showing particle sizes within the range of 20 to 30 nm. This observation demonstrate that the overall morphology of the silica material remains unaltered subsequent to the introduction

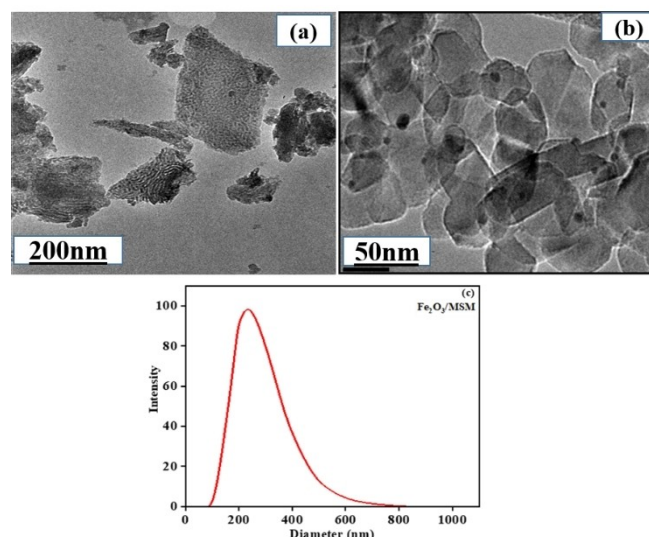


Figure 3. TEM images of Fe₂O₃/MSM catalyst at (a) 200 nm, (b) 50 nm, and (c) DLS data of Fe₂O₃/MSM.

of Fe₂O₃ nanoparticles into the MSM support.^[31] Moreover, these findings are corroborated by both XRD and BET analyses, which consistently validate the preservation of structural integrity and porous characteristics throughout the catalyst.^[31] The incorporation of Fe₂O₃ nanoparticles into the mesoporous silica matrix resulted in a gradual increase in particle size, as shown in Figure 3c. Upon encapsulation within the MSM support, Fe₂O₃/MSM catalyst exhibited a significantly larger average hydrodynamic diameter of 240 nm. The average hydrodynamic diameter of the Fe₂O₃/MSM nanoparticles was 32.48 nm, as depicted in Figure 3d.

2.4. XPS

The XPS was used to determine the chemical composition and valence states of Fe species in bare iron oxide nanoparticles and the catalyst. The XPS survey spectrum of Fe₂O₃/MSM (Figure 4a) shows sharp peaks for Si (103.6 eV), O (533 eV), C (284.5 eV), and a weak Fe (711 eV) peak. The carbon peak is ascribed to environmental contamination originating from the XPS instrument itself. In Figure 4b, the Fe 2p region of the XPS spectrum exhibits two distinct peaks at 711.1 eV (Fe 2p_{3/2}) and 723.5 eV (Fe 2p_{1/2}), accompanied by a shake-up satellite at 718.9 eV. These findings are consistent with the presence of Fe³⁺ in Fe₂O₃, aligning well with prior literature.^[32] As shown in Figure 1c, the XPS survey spectrum confirmed the presence of Fe and O, the key elements constituting Fe₂O₃. Collectively, XRD patterns, N₂ adsorption-desorption isotherms, and TEM images validate the structural integrity of the synthesized catalyst, affirming its stability throughout the preparation process.

Table 1. Textural parameters of support Bare Fe₂O₃ nanoparticles, Fe₂O₃/MSM and MSM.

Entry	Material	(S_{BET}) (m ² /g)	(V_{BJH}) (cm ³ /g)	Average pore diameter (nm)
1	MSM support	796	0.701	3.8
2	Fe ₂ O ₃ /MSM	250	0.623	3.5
3	Bare Fe ₂ O ₃	53.9	0.102	1.3

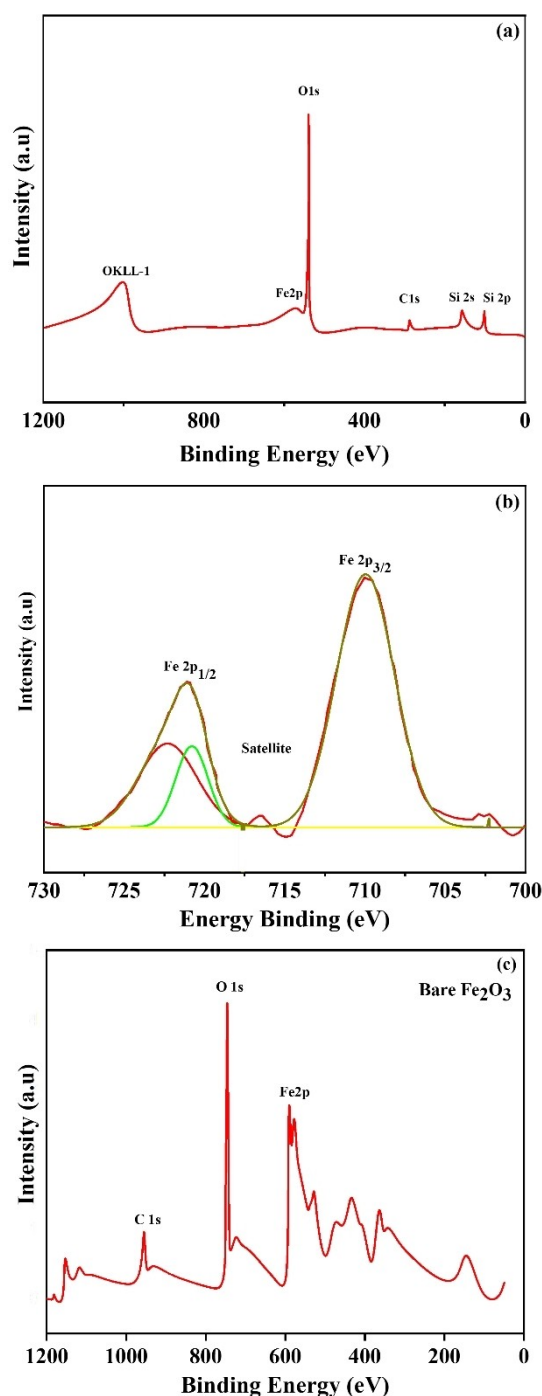


Figure 4. (a) XPS graph of bare Fe_2O_3 nanoparticles (b) XPS survey scan of $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst, (b) Fe 2p XPS spectra of $\text{Fe}_2\text{O}_3/\text{MSM}$ (10 wt %).

2.5. UV-Visible Spectroscopy

The co-ordination geometry of metal oxides is significantly influenced by various factors, including the type and composition of the support, the amount of metal loaded, the heat treatment, and the surface chemistry of the support.^[33] In our study, we investigated the co-ordination of bare Fe_2O_3 nanoparticles, iron species on MSM support using UV-Visible

spectroscopy. UV-Visible spectra of MSM, $\text{Fe}_2\text{O}_3/\text{MSM}$, and bare Fe_2O_3 are shown in Figure 5a, b, and c, respectively.

Figure 5a shows the two absorption peaks at 270 nm and 320 nm, which is possibly due to spherical and mesoporous morphologies of the silica nanoparticles.^[34] In Figure 5c, the

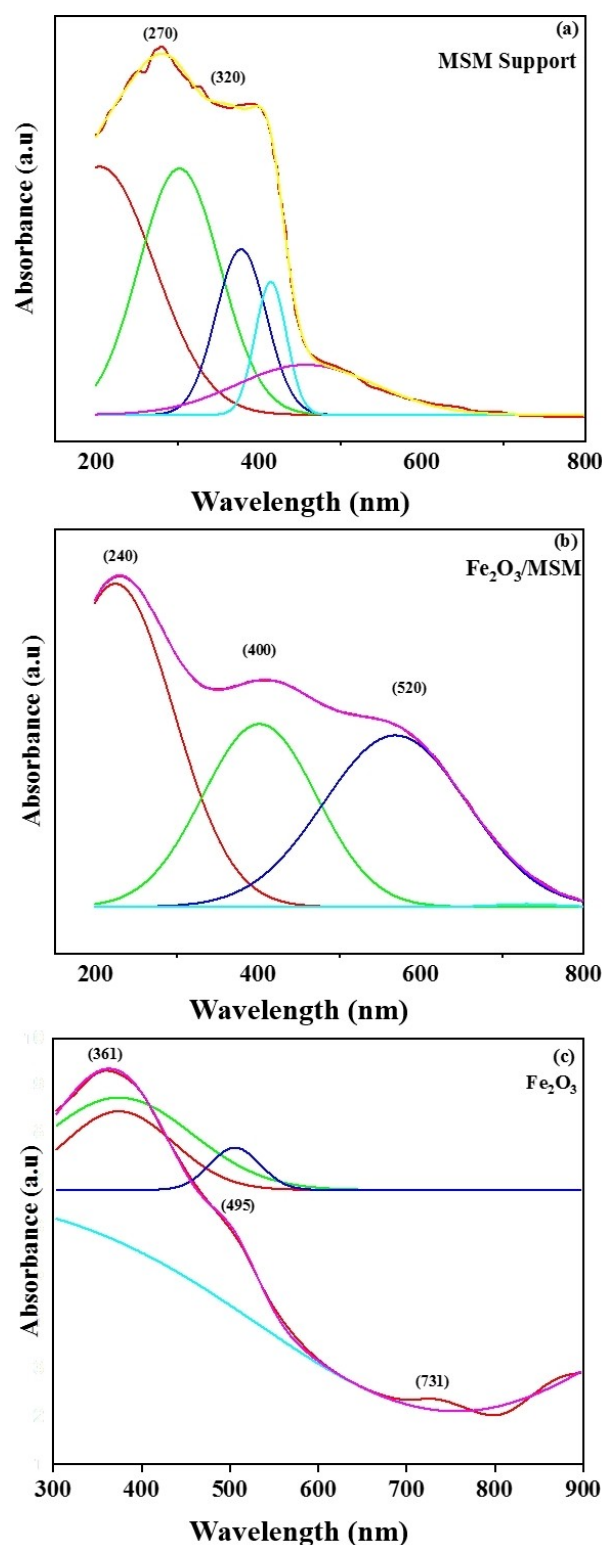


Figure 5. (a) UV-Visible spectra of MSM support, (b) UV-Visible spectra of $\text{Fe}_2\text{O}_3/\text{MSM}$, and (c) UV-Visible spectra of Fe_2O_3 .

absorption band observed at 240 nm can be ascribed to ligand-to-metal charge transfer (LMCT) arising from isolated Fe^{3+} species on the MSM support. These Fe^{3+} species adopt a tetrahedral geometry. Indeed, a single Fe^{3+} ion at the center can engage in a reaction with two silanol groups situated on the surface of the support. Within our findings, we can attribute the absorption band at 400 nm to oligomerized iron species, while a shoulder band at 520 nm corresponds to aggregated iron species.^[24,28, 35] Both UV-Visible and XPS analyses demonstrate that Fe (III) is the predominant oxidation state of iron in the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst.

The absorption peak depicted in Figure 5c corresponds to Fe_2O_3 nanoparticles, exhibiting significant absorption at a wavelength of approximately 400 nm, indicating the successful incorporation of Fe_2O_3 into the MSM support.

2.6. Catalytic Activity

2.6.1. LPE of Ethylene Using $\text{Fe}_2\text{O}_3/\text{MSM}$ Catalyst

For the synthesis of EO, a well-established procedure was followed.^[36] A reaction mixture comprising 3.29 mmol of ethylene, 5.5 mmol of PAA, 0.3 g of $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst, and 20 mL of acetonitrile was subjected to a controlled heating process at 40 °C for a duration of 6 hours. The successful formation of EO was confirmed through GC analysis, with the corresponding chromatograms presented in Figure 6. In Figure 6(a), the GC chromatogram exhibits a distinct peak at a retention time of 9.01 minutes, attributable to EO, confirming successful production of EO. Furthermore, this LPE method yielded valuable by-products, including AA, MEG, and DEG, as evidenced by peaks observed at retention times of 23.6, 27.2, and 31.2 minutes, respectively. This GC analysis also highlights the environmentally friendliness of our EO production process. Notably, no discernible peak corresponding to CO_2 production is detected at a retention time of 3.5 minutes, as illustrated in Figure 6(a).

To facilitate a comprehensive comparison, a control experiment was rigorously conducted, employing only PAA and MSM support, excluding the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst from the reaction system. The results of this control experiment, illustrated in Figure 6b, demonstrate the absence of EO production or any by-products.

The conversion of ethylene and selectivity towards EO exhibited notable differences between the bare Fe_2O_3 nanoparticles and the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst based on support. Specifically, the bare Fe_2O_3 nanoparticles displayed a conversion of 46.2% for ethylene, with a selectivity towards EO of 67.5%, whereas the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst demonstrated improved ethylene conversion at 61.4% and significantly enhanced selectivity towards ethylene oxide at 92.7% as shown in Figure 6c. Complementary data, including conversion efficiency (11.2%) and PAA utilization efficiency (14.7%), are documented in Table 2 for ethylene epoxidation employing the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst. As obvious from the Table 2, when MSM was employed in place of $\text{Fe}_2\text{O}_3/\text{MSM}$, no PAA decomposition or EO production

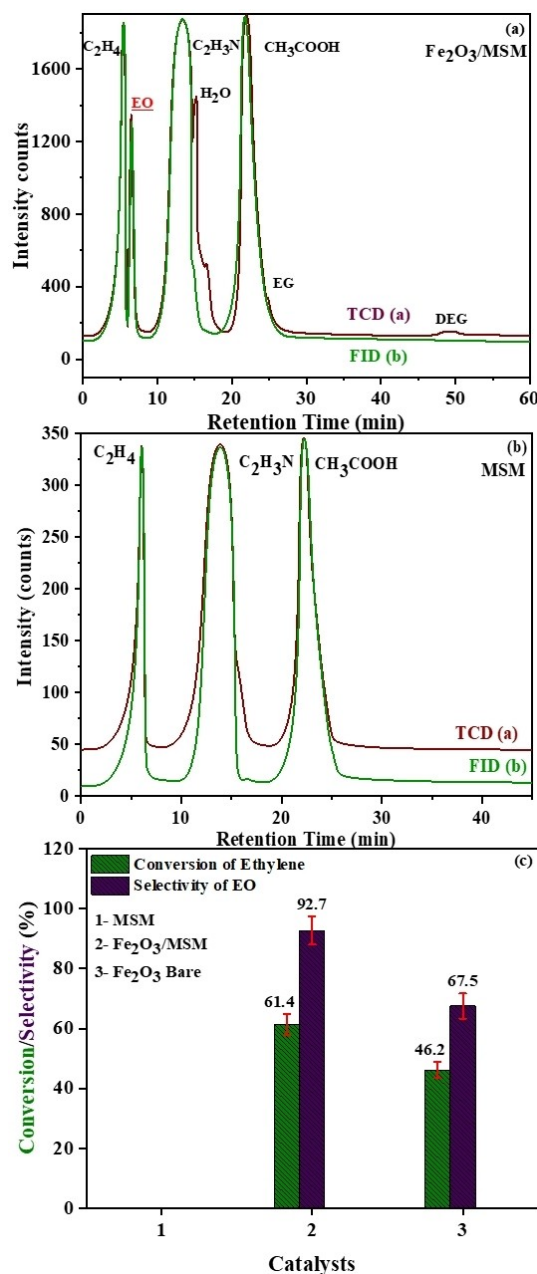


Figure 6. GC chromatogram of (a) $\text{Fe}_2\text{O}_3/\text{MSM}$ (b) MSM support and (c) Ethylene conversion and selectivity of bare Fe_2O_3 , MSM, and $\text{Fe}_2\text{O}_3/\text{MSM}$ towards EO production. [Reaction condition: Ethylene = 3.29 mmol, PAA = 5.6 mmol, Temperature = (50 °C), Amount of catalyst (10 wt%) = 0.3 g, Solvent = Acetonitrile (20 mL), Time = 6 h].

was observed. However, in the blank run, a notable PAA conversion efficiency of 8.4% was evident. This PAA decomposition in the blank run may be ascribed to the inherent acidity of the catalyst stemming from the incorporation of iron oxide into the MSM support, a phenomenon well-documented in the existing literature.^[12b] To provide deeper insights into catalytic efficiency, the TOF of $\text{Fe}_2\text{O}_3/\text{MSM}$ was determined through the methodology reported in reference.^[37] In our experimental setup, employing PAA as the oxidant and $\text{Fe}_2\text{O}_3/\text{MSM}$ as the catalyst, we calculated the TOF to be 178. In striking

Entry	Catalyst	TOF (mol ⁻¹ Fe ⁻¹ s ⁻¹)	X _{PAA} (%) (±3)	U _{PAA} (%) (±3)
1	Fe ₂ O ₃ /MSM	178	11.2	14.7
2	MSM	0	0	0
3	Fe ₂ O ₃ /MSM1	0	8.4	0
4	Bare Fe ₂ O ₃	98	9.6	10.3

¹Blank run was conducted under identical conditions to the original experiment, except that ethylene was not added, all other components like catalyst, ethylene, and PAA, were present. TOF is the no. moles of CH₃COOOH converted per Fe atom per unit of time.^[12b]

contrast, Wu *et al.* previously reported a TOF of 89 when employing H₂O₂ as the oxidant and Nb/MSM catalyst.^[37] These results collectively underscore that, for EO production, the utilization of Fe₂O₃/MSM in combination with PAA is substantially more efficient than the deployment of Nb/MSM or any other metal oxide catalyst/MSM system in conjunction with H₂O₂ as the oxidant.

For optimizing the selectivity catalyst for EO production and enhancing the conversion of ethylene to EO, we conducted a series LPE experiments. These experiments were designed to systematically vary critical reaction parameters, including temperature, catalyst dosage, ethylene to PAA molar ratio, and the utilization of various solvents. Our aim was to comprehensively explore the factors influencing the catalytic process and to identify the most favorable conditions for achieving optimal EO yields with superior selectivity.

2.6.1.1. Effect of Temperature

We examined how the temperature affects the ethylene conversion and catalyst selectivity for EO production at different temperatures (50 °C, 60 °C, and 70 °C). The remaining reaction parameters, such as the ethylene to PAA molar ratio (1:2) and catalyst amount (0.3 g), were kept constant. The reaction time was set at 6 hours, and acetonitrile served as the solvent. The results of this investigation are presented in Figure 7. According to the results, when the temperature was 50 °C, the ethylene conversion was 61.4%, and the catalyst showed a selectivity of 92.7%. However, when the temperature was raised to 60 °C, the ethylene conversion increased from 61.4% to 77.6%, but the selectivity decreased from 92.7% to 88.1%. Furthermore, at 70 °C, the ethylene conversion decreased from 77.6% to 75.3%, and the selectivity of the catalyst also declined further 88.1% to 83.2%. The observed decrease in catalyst selectivity towards EO production at elevated temperatures can be ascribed to the formation of AA and glycol derivatives as by-products. This phenomenon is well-established and attributed to the reaction pathway proceeding through the formation of EO intermediates. At higher temperatures, the stability of carbon-carbon (C–C) bonds becomes more favorable when compared to carbon-oxygen (C–O) bonds.^[38] Furthermore, the accelerated

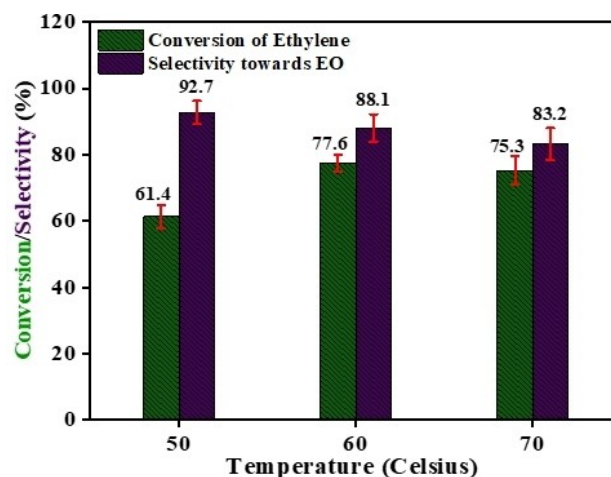


Figure 7. Effect of temperature [Reaction Conditions: Ethylene = 3.29 mmol, (32%) PAA = 5.6 mmol, Time = 6 h, Catalyst dose = 0.3 g, Solvent (Acetonitrile) = (20 mL)].

decomposition of PAA at elevated temperatures leads to enhanced ethylene conversion and a consequent reduction in catalyst selectivity towards EO production.^[39] Therefore, it can be inferred that 60 °C represents the optimal temperature at which the highest ethylene conversion and catalyst selectivity for EO production can be achieved when utilizing Fe₂O₃/MSM as the catalyst.

2.6.1.2. Effect of Catalyst Dose

The amount of catalyst used in the epoxidation process of ethylene plays a significant role in determining the selectivity towards EO production and the catalyst's stability. To evaluate this effect, we conducted the reaction at a temperature of 60 °C and an ethylene-to-oxidant molar ratio of 1:2 in an acetonitrile for 6 hours while varying the catalyst amount from 0.1 g to 0.5 g (Figure 8). It was noticed that when catalyst amount was increased, there was a significant improvement in the conversion of ethylene and a small increase in the selectivity toward producing EO. These results can be explained by the fact that increasing the amount of catalyst leads to a higher concentration of active metal oxide species, resulting in a faster reaction rate. Based on the data in Figure 6, increasing the amount of catalyst used from 0.1 g to 0.3 g resulted in a significant improvement in ethylene conversion, with values increasing from 56.2% to 77.6%. However, further increasing the amount of catalyst beyond 0.3 g only showed a minor enhancement in ethylene conversion. Furthermore, the selectivity towards EO production was marginally increased from 82.4% to 88.9% by increasing the catalyst amount from 0.1 g to 0.5 g. After analyzing the results, it was determined that the optimal catalyst amount under the given reaction conditions is 0.3 g.

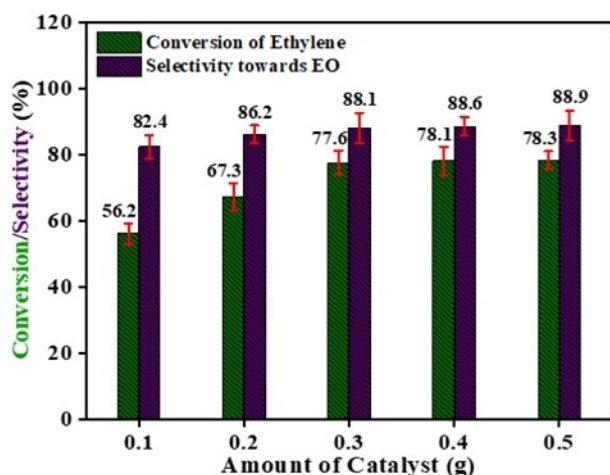


Figure 8. Effect of catalyst dosage; [Reaction Conditions: Ethylene = 3.29 mmol, (32 %) PAA = 5.6 mmol, Time = 6 h, Solvent (Acetonitrile) = (20 mL), Temperature = 60 °C.

2.6.1.3. Effect of Ethylene to Oxidant Molar Ratio

To determine how the ratio of ethylene to PAA affects the conversion of ethylene and the selectivity of EO, we conducted LPE of ethylene under optimal conditions of temperature (60 °C) and catalyst amount (0.3 g) while using acetonitrile as a solvent. In these experiments, we systematically examined different molar ratios of ethylene to PAA, including 1:1, 1:2, 1:3, and 1:6 (ethylene: PAA), as presented in Figure 9. Our findings reveal that an ethylene conversion of 69.4% was attained at the 1:1 ratio. With the incremental addition of PAA, the conversion exhibited a consistent rise, culminating at a maximum of 81.3% at the 1:6 ratio. On the other hand, it was observed that increasing amounts of PAA led to a decrease in EO selectivity. This was due to the decomposition of PAA at higher concentrations, rather than its attachment to the active catalyst sites. From these findings, it can be concluded that an excess of

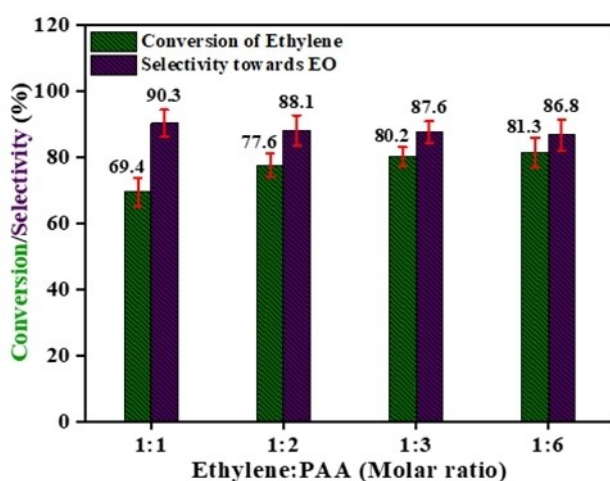


Figure 9. Effect of ethylene to oxidant molar ratio; [Reaction Conditions: Ethylene = 3.29 mmol, catalyst dose = 0.3 g, Time = 6 h, Solvent (Acetonitrile) = (20 mL), Temperature = 60 °C.

oxidant does not improve the activity of the catalyst. An optimal molar ratio of ethylene to PAA is considered to be 1:3, as it strikes a balance between ethylene conversion and selectivity towards EO production.

2.6.1.4. Solvent Effect

The selection of solvents in ethylene epoxidation reactions plays a pivotal role in determining the performance and efficiency of the catalyst employed. In our investigation, the ability of Fe₂O₃/MSM catalyst to catalyze the conversion of ethylene into EO was rigorously assessed using various solvents, including ethyl acetate, acetonitrile, chloroform, and acetone, all within the framework of optimized reaction conditions: temperature (60 °C), ethylene-to-oxidant molar ratio (1:3), and catalyst amount (0.3 g). The results of this study are given in Figure 10. Notably, utilizing acetonitrile as the solvent for EO production resulted in an impressive ethylene conversion rate of 80.2%. In contrast, decreasing solvent polarity exerted a detrimental effect on ethylene conversion. Specifically, ethylene conversions in acetone, ethyl acetate, and carbon tetrachloride were recorded at 40.5%, 22.8%, and 17.2%, respectively.

The observed enhancement in ethylene conversion in a more polar solvent can be attributed to enhanced mass transfer and a greater degree of uniformity across the various phases involved.^[38a] In the present study, the EO selectivity exhibited a random pattern, indicating that it is not significantly influenced by the alteration in solvent.

Based on the findings from these studies, we have ascertained that the optimal conditions for maximizing both EO selectivity and ethylene conversion entail a temperature of 60 °C, a catalyst amount of 0.3 g, and an ethylene-to-PAA molar ratio of 1:3. The use of acetonitrile as a solvent, in conjunction with the Fe₂O₃/MSM catalyst and PAA oxidant, has emerged as the most effective approach for EO production in LPE.

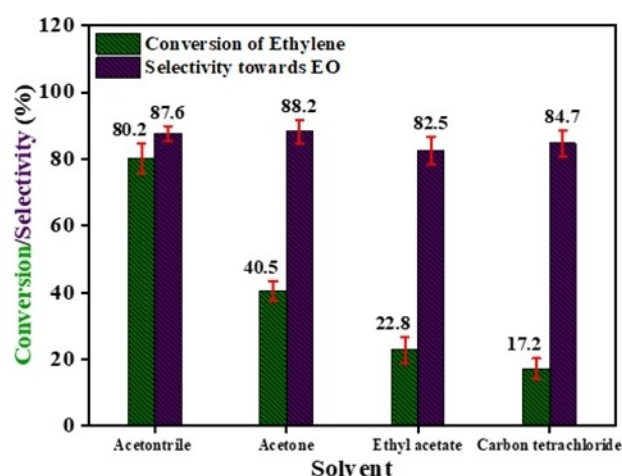


Figure 10. Effect of different solvents; [Reaction Conditions: Ethylene = 3.29 mmol, (32 %) PAA = 5.6 mmol, Temperature = 60 °C, Time = 6 h, Catalyst = 0.3 g, Solvent (ACN) = (20 mL)].

Nonetheless, it is important to consider that PAA might potentially induce the hydrolysis of EO, leading to diminished EO selectivity. To mitigate the risk of epoxide ring opening, it is advisable to employ a lower catalyst loading on the support during the epoxidation process. This strategic choice is guided by the understanding that elevated catalyst acidity can trigger heightened oxidant decomposition and subsequent hydrolysis of the EO ring.^[24] Additionally, it is well-established that water, which is produced during the process, can block Lewis's acid sites and enhance Bronsted acid sites. It has been also observed that the presence of extra Bronsted acid sites can result in higher levels of hydrolysis of the epoxide ring.^[12b]

2.7. Leaching Property of Fe₂O₃/MSM

To investigate the leaching behavior of the metal, a leaching test was conducted utilizing a Fe₂O₃/MSM catalyst. This involved the separation of the catalyst from the heated reaction mixture after 6 hours, followed by the continuation of the supernatant reaction solution for an additional 6 hours, resulting in a total reaction time of 12 hours.^[40] Ethylene conversion at both 6 hours and 12 hours was analyzed using gas chromatography. As depicted in Figure 11, the study demonstrates that there was no further ethylene conversion. This observation provides compelling evidence that the Fe₂O₃/MSM catalyst, particularly when used in conjunction with PAA, effectively mitigates the issue of leaching that commonly afflicts primitive metal-based

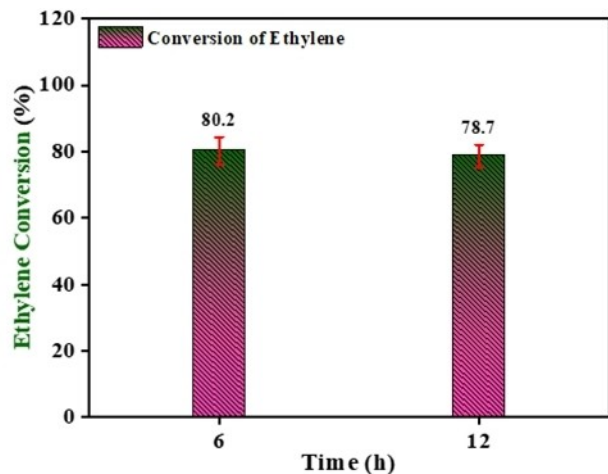


Figure 11. Leaching of Fe₂O₃/MSM catalyst.

catalysts employed in EO production. As outlined in the published literature,^[41] the observed leaching resistance and absence of further epoxidation can likely be attributed to the presence of specific leached species. During the epoxidation reaction, it is known that certain oligomerized metal oxide particles form on the catalyst surface in the presence of an oxidant. Importantly, these oligomerized metal oxide particles have been reported to exhibit limited catalytic activity for the epoxidation reaction, as documented by Das *et al.*^[41]

While the precise characteristics of these metal species, should they exist within the acetonitrile solvent, remain beyond the scope of this study, they are presently the subject of ongoing investigation by our research group.

Furthermore, Table 3 compares the catalytic performance of the catalyst prepared in this study with that reported in the literature.

Our Fe₂O₃/MSM catalyst demonstrates competitive performance for EO production compared to other reported catalysts. With an ethylene conversion of 80.2% and EO selectivity of 87.6%, it surpasses catalysts like Nb/KIT (50.1% conversion, 58.1% selectivity) and W/SBA-16 (68.2% conversion, 80.1% selectivity) while achieving comparable values to Nb/MSM (79.5% conversion, 84.3%) and Ag/MCM (79.3% conversion, 82.5%). Notably, our catalyst utilizes the environmentally friendly PAA as the oxidant, offering an advantage over H₂O₂-based systems in terms of sustainability. Furthermore, Fe₂O₃/MSM catalyst exhibits an upright TOF of 178, demonstrating its catalytic efficiency. This comparative analysis highlights the promising potential of our Fe₂O₃/MSM catalyst for sustainable EO production in the current landscape. This work holds potential for industrial EO production with enhanced selectivity, reusability, and cost efficiency.

2.8. Reusability of the Catalyst

An investigation into the potential for reusing the Fe₂O₃/MSM catalyst was carried out, as exhibited in Figure 12. This entailed removing the catalyst from the reaction mixture via filtration, conducting a thorough solvent wash, and subsequently drying it at 100 °C for 6 hours. It was noted that, even under the optimized reaction conditions, there was a slight decrease in both the conversion of ethylene and EO selectivity, which remained consistent through the fifth cycle of catalyst use. These findings validate the ability to reuse the Fe₂O₃/MSM catalyst.

Table 3. A comparative analysis of our catalyst for EO production in relation to previously reported catalysts.

	Catalysts	Ethylene Conversion	EO Selectivity	Oxidant	TOF (mol ⁻¹ Fe ⁻¹ s ⁻¹)	Reference
1	Nb/MSM	79.5%	84.3 %	PAA	163	7a
2	Nb/KIT	50.1%	58.1 %	H2O2	284	12b
3	Ag/MCM	79.3%	82.5 %	O2	159	42
4	W/SBA-16	68.2%	80.1 %	H2O2	153	43
5	Fe2O3/MSMM	80.2%	87.6 %	PAA	178	This work

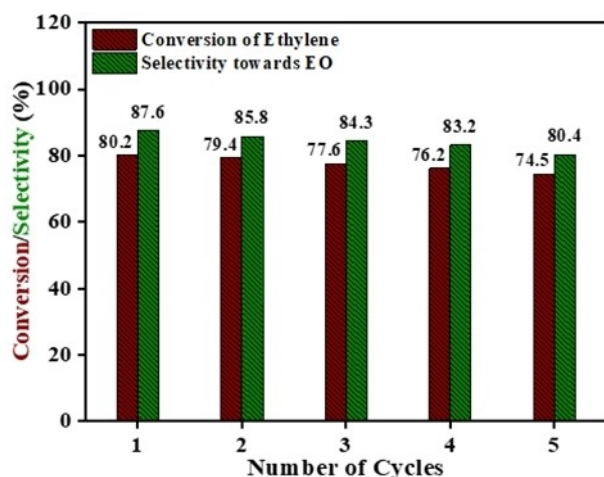


Figure 12. Reusability of the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst under optimized reaction conditions.

3. Conclusions

In conclusion, our research has successfully developed a $\text{Fe}_2\text{O}_3/\text{MSM}$ -based catalyst for EO production, presenting an approach that significantly reduces greenhouse gas emissions during the EO manufacturing process. This catalyst was synthesized through a hydrothermal method, incorporating Fe_2O_3 nanoparticles into a well-structured cubic large-pore SiO_2 matrix derived from TEOS. The selection of peracetic acid as an oxidant played a crucial role in enabling the eco-friendly production of EO without CO_2 emissions. Additionally, it yielded valuable by-products, including AA, MEG, and DEG, which have wide-ranging industrial applications. Our research validated the heteroatom structure of the $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst through advanced techniques such as XRD and XPS analysis. Furthermore, BET analysis confirmed its porosity, while TEM provided insights into its morphology. The $\text{Fe}_2\text{O}_3/\text{MSM}$ catalyst's potential in the LPE process for EO synthesis was thoroughly assessed. We conducted a series of experiments systematically varying critical parameters, including temperature, ethylene to oxidant molar ratio, catalyst dosage, and solvent selection. The GC analysis confirmed 80.2% conversion of ethylene to EO, coupled with EO selectivity of 87.6%. In conclusion, our research has successfully demonstrated an environmentally friendly approach to EO production, emphasizing not only the efficient generation of EO but also the valuable by-products, all achieved with zero CO_2 emissions. This represents a significant step forward in sustainable EO manufacturing, with the potential for broad industrial applications and a substantial reduction in environmental impact.

4. List of Abbreviations

(EO) Ethylene Oxide
(MSM) Mesoporous silica material
(AA) Acetic acid

(MEG) Mono ethylene glycol
(DEG) Diethylene glycol
(LPE) Liquid phase epoxidation
(GPE) Gas phase epoxidation
(GC) Gas chromatography
(XRD) X-ray diffraction
(XPS) X-ray photoelectron spectrometer
(BET) Brunauer-Emmett-Teller
(TEM) Transmission electron microscopy
(MTO) Homogeneous Methyltrioxorhenium
(PAA) Per acetic acid
(CO_2) Carbon dioxide

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Catalyst on support • CO_2 free production • mesoporous silica material • ethylene oxide • liquid phase epoxidation

- [1] S. Han, C. Cheng, M. He, R. Li, Y. Gao, Y. Yu, B. Zhang, C. Liu, *Angew. Chem.* **2023**, *135*, e202216581.
- [2] a) M. Ghanta, B. Subramaniam, H. J. Lee, D. H. Busch, *AIChE J.* **2013**, *59*, 180–187; b) J. Schalck, J. Hereijgers, W. Guffens, T. Breugelmans, *Chem. Eng. J.* **2023**, *472*, 144741.
- [3] C. He, X. Lu, Y. Liu, Z. Yan, R. Zhang, X. Liu, *Catal. Commun.* **2023**, *178*, 106669.
- [4] T. E. Jones, R. Wyrwich, S. Böcklein, E. A. Carbonio, M. T. Greiner, A. Y. Klyushin, W. Moritz, A. Locatelli, T. O. Mentş, M. A. Niño, *ACS Catal.* **2018**, *8*, 3844–3852.
- [5] C.-C. Tsai, Z. Y. Kong, A. Yang, V. S. K. Adi, J. Sunarso, *Chem. Eng. J.* **2023**, *475*, 146331.
- [6] T. E. Jones, T. C. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl, S. Piccinin, *ACS Catal.* **2015**, *5*, 5846–5850.
- [7] a) M. Maqbool, T. Akhter, M. Faheem, S. Nadeem, C. H. Park, A. Mahmood, *RSC Adv.* **2023**, *13*, 1779–1786; b) M. Kurańska, H. Beneš, A. Prociak, O. Trhliková, Z. Walterová, W. Stochlińska, *J. Cleaner Prod.* **2019**, *236*, 117615; c) M. S. Shaw, M. R. Bates, M. D. Jones, B. D. Ward, *Polym. Chem.* **2022**, *13*, 3315–3324.

- [8] W. H. Faveere, S. Van Praet, B. Vermeeren, K. N. Dumoleijn, K. Moonen, E. Taarning, B. F. Sels, *Angew. Chem.* **2021**, *60*, 12204–12223.
- [9] W. Diao, C. D. DiGiulio, M. T. Schaal, S. Ma, J. R. Monnier, *J. Catal.* **2015**, *322*, 14–23.
- [10] C. Backx, J. Moolhuysen, P. Geenen, R. Van Santen, *J. Catal.* **1981**, *72*, 364–368.
- [11] L. Pinaeva, A. Noskov, *Pet. Chem.* **2020**, *60*, 1191–1206.
- [12] a) D. M. Minahan, G. B. Hoflund, *J. Catal.* **1996**, *158*, 109–115; b) W. Yan, A. Ramanathan, M. Ghanta, B. Subramaniam, *Catal. Sci. Technol.* **2014**, *4*, 4433–4439.
- [13] a) M. Selvaraj, D.-W. Park, I. Kim, S. Kawi, C. Ha, *Dalton Trans.* **2012**, *41*, 9633–9638; b) M. Selvaraj, M. Kandaswamy, D. Park, C. Ha, *Catal. Today* **2010**, *158*, 377–384; c) M. Selvaraj, P. Sinha, *New J. Chem.* **2010**, *34*, 1921–1929.
- [14] a) R. A. Sheldon, M. Wallau, I. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485–493; b) C. Copéret, M. Chabanas, R. P. Saint-Arroman, J. Basset, *Angew. Chem.* **2003**, *42*, 156–181; c) V. Dal Santo, M. Guidotti, R. Psaro, L. Marchese, F. Carniato, C. Bisio, *Proc. Roy. Soc. A* **2012**, *468*, 1904–1926.
- [15] G. Hayes, M. Laurel, D. MacKinnon, T. Zhao, H. A. Houck, C. R. Becer, *Chem. Rev.* **2022**, *123*, 2609–2734.
- [16] a) A. Feliczak-Guzik, A. Wawrzyńczak, I. Nowak, *Microporous Mesoporous Mater.* **2015**, *202*, 80–89; b) J. V. Coelho, L. C. Oliveira, F. C. Moura, P. P. de Souza, C. A. Silva, K. B. Batista, M. J. da Silva, *Appl. Catal. A* **2012**, *419*, 215–220; c) P. Chagas, H. S. Oliveira, R. Mambri, M. Le Hyaric, M. V. de Almeida, L. C. Oliveira, *Appl. Catal. A* **2013**, *454*, 88–92; d) Y. Liu, K. Murata, M. Inaba, *Chem. Lett.* **2003**, *32*, 992–993.
- [17] a) I. Nowak, A. Feliczak, I. Nekoksová, J. Čejka, *Appl. Catal. A* **2007**, *321*, 40–48; b) F. Quignard, A. Choplin, R. Teissier, *J. Mol. Catal. A* **1997**, *120*, L27–L31; c) E. Gianotti, M. E. Raimondi, L. Marchese, G. Martra, T. Maschmeyer, J. M. Seddon, S. Coluccia, *Catal. Lett.* **2001**, *76*, 21–26; d) K. Kang, W. Ahn, *J. Mol. Catal. A* **2000**, *159*, 403–410; e) W. Adam, W. Malisch, K. J. Roschmann, C. R. Saha-Möller, W. A. Schenk, *J. Organomet. Chem.* **2002**, *661*, 3–16; f) A. Held, P. Florczak, *Catal. Today* **2009**, *142*, 329–334.
- [18] J. Zhang, Z. Xin, X. Meng, Y. Lv, M. Tao, *Fuel* **2014**, *116*, 25–33.
- [19] M. Ghazizadeh, A. Badiei, I. Sheikhshoae, *Arab. J. Chem.* **2017**, *10*, S2491–S2498.
- [20] H. Atashin, R. Malakooti, *J. Saudi Chem. Soc.* **2017**, *21*, S17–S24.
- [21] N. A. Halim, N. A. Rahman, J. M. Ali, *J. Kajian Kejuruteraan* **2023**, *35*, 937–943.
- [22] P. M. Machado, L. M. Lube, M. D. Tiradentes, C. Fernandes, C. A. Gomes, A. M. Stumbo, R. A. San Gil, L. C. Visentin, D. R. Sanchez, V. L. Frescura, *Appl. Catal. A* **2015**, *507*, 119–129.
- [23] a) V. Berg, M. Geske, O. Korup, M. Schmidt, F. Rosowski, A. Karpov, M. Kraemer, R. Horn, *Ind. Eng. Chem. Res.* **2024**; b) J. R. Lockemeyer, T. L. Lohr, *ChemCatChem* **2023**, *15*, e202201511; c) A. Fazeli, A. Naseri, F. Eslamjamal, *Kinet. Catal.* **2020**, *61*, 603–612; d) T. Salmi, M. Roche, J. H. Carucci, K. Eränen, D. Murzin, *Curr. Opin. Chem. Eng.* **2012**, *1*, 321–327.
- [24] W. Yan, A. Ramanathan, P. D. Patel, S. K. Maiti, B. B. Laird, W. H. Thompson, B. Subramaniam, *J. Catal.* **2016**, *336*, 75–84.
- [25] a) S. Linic, M. A. Barteau, *J. Am. Chem. Soc.* **2003**, *125*, 4034–4035; b) S. Linic, P. Christopher, *ChemCatChem* **2010**, *2*, 1061–1063.
- [26] X. Zhao, S. Veintemillas-Verdaguer, O. Bomati-Miguel, M. Morales, H. Xu, *Phys. Rev. B* **2005**, *71*, 024106.
- [27] M. Davidson, C. Ngo, S. H. Gage, S. Pylypenko, B. G. Trewyn, *Microporous Mesoporous Mater.* **2019**, *276*, 270–279.
- [28] Y. Li, Y. Chen, L. Li, J. Gu, W. Zhao, L. Li, J. Shi, *Appl. Catal. A* **2009**, *366*, 57–64.
- [29] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.
- [30] G. Somorjai, R. Rioux, *Catal. Today* **2005**, *100*, 201–215.
- [31] M. R. Sazegar, A. Davdand, A. Mahmoudi, *RSC Adv.* **2017**, *7*, 27506–27514.
- [32] N. Rizkalla, Google Patents, **1994**.
- [33] a) A. L. Linsebigler, G. Lu, J. T. Yates Jr, *Chem. Rev.* **1995**, *95*, 735–758; b) V. I. Bukhtiyarov, A. I. Nizovskii, H. Bluhm, M. Hävecker, E. Kleimenov, A. Knop-Gericke, R. Schlögl, *J. Catal.* **2006**, *238*, 260–269.
- [34] J. Berty, *Appl. Ind. Catal.* **1983**, *1*, 207.
- [35] R. Huang, B. Lan, Z. Chen, H. Yan, Q. Zhang, L. Li, *Chem. Eng. J.* **2012**, *180*, 19–24.
- [36] B. Kalita, P. Phukan, A. K. Talukdar, *Catal. Sci. Technol.* **2012**, *2*, 2341–2350.
- [37] X. Lu, W.-J. Zhou, Y. Guan, A. Liebens, P. Wu, *Catal. Sci. Technol.* **2017**, *7*, 2624–2631.
- [38] a) S. Narayanan, J. J. Vijaya, S. Sivasanker, C. Ragupathi, T. Sankaranarayanan, L. J. Kennedy, *J. Porous Mater.* **2016**, *23*, 741–752; b) J. Liu, Z. Wang, P. Jian, R. Jian, *J. Colloid Interface Sci.* **2018**, *517*, 144–154.
- [39] W. Zhan, Y. Guo, Y. Wang, X. Liu, Y. Guo, Y. Wang, Z. Zhang, G. Lu, *J. Phys. Chem. B* **2007**, *111*, 12103–12110.
- [40] A. Boro, A. K. Talukdar, *J. Porous Mater.* **2019**, *26*, 1185–1196.
- [41] D. R. Das, P. Kalita, A. K. Talukdar, *J. Porous Mater.* **2020**, *27*, 893–903.
- [42] J. Van Den Reijen, W. Versluis, S. Kanungo, M. d'Angelo, K. de Jong, P. de Jongh, *Catal. Today* **2019**, *338*, 31–39.
- [43] D. Ren, G. Cheng, J. Li, J. Li, W. Dai, X. Sun, D. Cheng, *Catal. Lett.* **2017**, *147*, 2920–2928.

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