Styrene epoxidation in aqueous over triazine: Based microporous polymeric network as a metal-free catalyst

Anubhav Pradeep  
Research Scholar, Starex University, School of Physical Sciences, Department of Chemistry

Dr. Divya Tyagi  
Professor, Starex University, School of Physical Sciences, Department of Chemistry

Abstract---Epoxies are a popular kind of industrial chemical molecule used as an intermediate in agricultural and medicinal research. Metal-free catalyst for styrene epoxidation was found to be triazine-based microporous polymeric (TMP) network. H2O2 was used as a green oxidant in water as an ecologically friendly medium. The reactions were carried out at room temperature. In 6 hours, the process produced a greater yield of styrene oxide with a 90% conversion and 98% selectivity. Up to four times, the catalytic activity and selectivity of triazidine-based micro porous polymeric networks may be restored and reused.

Keywords---triazine micro, porouspolydendritic network, metal-free catalyst, aqueous medium, epoxidation, styrene.

Introduction

As a chemical intermediary in agricultural and pharmaceutical research, epoxides are a common kind of industrial chemical molecule. To manufacture epoxides, peracids are utilized in the direct epoxidation of alkenes to form the corresponding epoxides, although this process generates a lot of waste. Heterocyclic compound synthesis is of interest to chemists because of its potential use in the pharmaceutical and agricultural industries. Hydrogen peroxide is a good oxidant for styrene epoxidation because of both economic and environmental considerations. There are several benefits to using hydrogen peroxide as the primary oxidant, including its environmental friendliness, its harmless byproduct, and its cheap cost. [1]
Styrene-epoxide manufacturing is critical to both the environment and industrial processes, thus scientists have taken into account approaches that are both high-efficiency and short term effective. Contrary to this belief, transition metal oxides, which have advantages over homogeneous catalysts such as simple separation, biocompatibility selectivity, and recyclability over homogeneous catalysts, are commonly used in chemical processes as heterogeneous catalysts. Efforts should be made to minimize energy consumption in chemical processes since energy consumption has become one of the most pressing issues of our day. One of the catalyst's primary functions is to lower the amount of energy needed to initiate a reaction. [2]

The structure of crystals and their chemical and physical characteristics The oxidation of water and benzyl alcohol as well as the reduction of NOx and epoxidation of olefins, as well as the N-Alkylation of sulfonamides, as well as the decomposition of ozone, have all been reported to be possible with manganese oxide catalysts, which have been widely used in numerous chemical reactions. [3] Another important element in generating reusable catalyst is stabilising the catalyst. Traditional stabilising methods and procedures, such as coating catalyst, have been developed to create very stable and reusable catalysts. [4]. An aromatic and natural biomaterial, lignosulfonate, is a byproduct of the pulping and papermaking processes. It is now well accepted that lignosulfonate may be used as a prelude to more advanced uses. In their study, Modrzejewska and colleagues employed lignosulfonates as an affordable and environmentally friendly stabiliser. Catalytic epoxidation had previously been known to be expensive, but the nano MnO coated with calcium lignosulfonates as the long-term and reusable catalyst in the reduction of the chemical compound, Styrene, has not yet been reported. [5]

**Literature review**

**MANAL IBRAHIM (2022)**
Understanding how functional groups affect polymer materials' porosity structure and adsorption capacity is becoming more important. One-pot polycondensation of naphthalene and melamine (PAN-NA) building blocks yielded a new porous polyamine-linked polymer (PAN-NA) capable of adsorbing CO2 and heavy ions. The polymer was characterized using FTIR, NMR, powder X-ray diffraction, and mogravimetry, among other techniques. At 273 K and 1 pressure, the polymer absorbed 133 mg/g of CO2. Adsorbent dosage and contact time were also studied. Naphthalene has been shown to increase the polymer network's porosity, hence increasing CO2 adsorption and the adsorption of heavy metals. [6]

**GUIPENGJIAYANFEIZHAO (2022)**
Recent years have seen a lot of interest in the conversion of carbon dioxide (CO2) into fuels and chemicals. Research on materials with certain functions has shown that CO2 collection and conversion need these types of materials. Due to its unique features like as tailorable functionalization, vast surface areas and changeable porosity, as well as diverse polymerizations, porous organic polymers (POPs) have gained a lot of attention in the scientific community as a developing material platform. The polymer architectures of this research group’s POPs comprise functional groups such as azo, Tröger’s base, fluorine, and polyphenolic–OH, which are subsequently
immobilised with metal-activated species for CO2 transformation. An overview of POP-based catalysts for CO2 transformation is presented in this review article, including those that use cycloaddition reactions of epoxides and propargylic alcohols with CO2, H2 reduction, and photo catalytic/electro catalytic reduction as starting points. POP-based catalysts for CO2 transformation are also discussed in this study. [7]

JING DU (2021) In order to combat climate change and environmental deterioration, we must lower the amount of carbon dioxide (CO2) in the atmosphere. To reduce carbon dioxide concentrations in the atmosphere, it may be conceivable to create ecologically acceptable techniques of absorbing carbon dioxide and translating it into value-added products. As a result of their large surface area and chemical stability, as well as their nanoscale porosity and wide structural range, porous organic polymers (POPs) have showed tremendous promise as CO2 selective adsorbents and as heterogeneous catalysts based on POPs for CO2 conversion. Photo catalytic CO2 reduction, electro catalytic POPs in various processes, as well as the challenges and present development trends they face, are explored in this paper. [8]

NEHA SHARMA (2021) In order to combat global warming and energy crises, the collection and intriguing and sustainable possibility is the conversion of CO2 into high-value compounds. Porous organic polymers rich in nitrogen are excellent materials for CO2 collection and separation. Heptazine microporous polymer, which is nitrogen-rich, may be used to synthesize carbon dioxide-based cycloaddition reactions in the absence of metals and solvents, as shown in this study when it came to CO2 uptake, HMP-TAPA performed well due to its high nitrogen content, registering A selectivity of 30.79 for CO2 over N2HMP-TAPA also exhibited excellent chemical and water stability with no loss in structural integrity throughout testing. The cycloaddition of CO2 and terminal epoxides were assessed after the HMP-catalytic TAPA activity had been sorbed with CO2, leading to the formation of carbonate with a highly converted rate of CO2 (98 percent). They were able to be recycled up to five times without losing any of their functionality. Overall, this research shows that POPs (HMP-TAPA) may be rationally designed for diverse applications for the first time. [9]. MOHD BISMILLAH ANSARI (2012) Metal-free catalyst for the epoxidation of styrene was reported to be trazine-based micro porous polymeric (TMP) network. At room temperature, the reactions were carried out using H2O2 as a green oxidant and water as an ecologically friendly medium. For the first six hours, the process produced 90% conversion of styrene and 100% selectivity for styrene oxide. Up to four cycles of reuse of the triazine-based micro porous polymeric network are possible, with no noticeable reduction in catalytic activity or selectivity. [10]

**Research Methodology**

**Experimental Chemicals**

There was no need to purify any of the compounds before usage since they were all analytical-grade materials. Sigma Aldrich supplied the styrene. Duksan chemicals in South Korea supplied NaHCO3 and 28 percent H2O2. Young Lin,
Korea’s Aqua MaxTM basic water purification technology was utilised to remove ions from the water.

**Catalyst Preparation**

As previously described, a slightly modified technique was used to produce the 1,3,5-triazine micro porous network. There was a condenser and a magnetic stirring bar attached to a two-necked round bottom flask that contained a terephtalaldehyde solution dissolved in dimethyl sulfoxide. It was held at 100°C until a yellow solution developed in the flask. Solution of terephtalaldehyde was heated and combined with melamine solution under nitrogen. For three hours, a hot solution is sonicated at 100°C to keep the temperature constant. It took up to 48 hours for the combination to reach a temperature of 180°C when cooked in an inert atmosphere. The precipitated TMP network was separated using a Buchner funnel and rinsed with excess acetone, tetrahydrofuran, and dichloromethane after cooling to room temperature. At 60 °C overnight, a vacuum-dried TMP network separated from the rest of the network yielded 75%.

**Characterization**

To further understand the catalyst’s chemical structure, FT-IR and Raman spectroscopy were used. Varian UnityNOVA NMR spectrometers were utilised to collect the data. Five hours of degassing samples at 160°C prior to measurement SEM pictures were captured using a JEOL 630-F microscope. GC and GC-MS were utilised to analyse an aliquot of the reaction mixture.

**Catalytic Activity**

Styrene To retain the catalyst, H2O, and one millimole, a vial with a magnetic bar was utilised. In one millilitre of water, dissolve 0.5 - 2.0 mol of NaHCO3 and add it to the liquid under reaction. After 30 minutes of stirring at room temperature, the reaction mixture received a dropwise addition of H2O2. After the reaction was completed, the reaction mixture was separated using a separating funnel and diethyl ether. Filtered and concentrated by rotation-evaporation before being submitted to GC examination of the dried ether layer collected over anhydrous sodium sulphate. GC-MS was used to identify the products. The mole percent of styrene was used to compute the conversions, and to get the response factor, the beginning mole percent of styrene was multiplied by the starting area percent. This was estimated by multiplying response factor by the area percentage obtained for CYA from a GC peak using styrene moles still present in the reaction mixture. Styrene was used as the basis for the conversion. To calculate selectivity, multiply the GC peak area of styrene oxide by 100.

**Data Analysis**

**Catalyst Preparation and Characterization**

An improved method of synthesising terephtalaldehyde-melamine condensation-catalyzed free polymerization yielded the TMP network (Scheme 1). In addition to reducing the reaction time from 72 to 48 hours, the redesigned technique resulted
in a 75% increase in yield. The absence of a band at 1690 cm\(^{-1}\) that corresponded to the carbonyl function of aldehydes confirmed their carbonyl function. At and show well-defined quadrant vibrations and semicircle stretching vibrations in FTIR spectra of heteroaromatic ring systems. Imine connections are not represented in any of the bands.

![FTIR spectra](image1)

**Figure 1. Melamine and TMP network FTIR spectra**

Stretching vibrations of C=N are found at a wavelength of 1600 cm\(^{-1}\). Figure 2 shows the UV spectrum, which shows the K and B bands that emerge from the to * transitions when an aromatic ring is connected to a group with numerous bonds. A shift of between 220 and 250 nm has been found for bath chromic shifts in the K band and between 300 and 350 nm in the B band after introduction of the melamine. NMR spectra of 13C cross-polarization magic angle spinning (CPMAS) exhibit resonances at 167, 114, and 54 parts per million (ppm). The melamine triazine ring’s carbon atoms are responsible for the peak at 167 ppm, while the benzene’s C-H aromatic carbons are responsible for the signal at 114 ppm and the melamine’s tertiary carbon atoms are responsible for the resonance at 54 ppm. 215 ppm and 287 ppm were found in the 15N spectrum by 15N CPMAS on the TMP network (Figure 4). It is possible that the secondary amine in the aminal motif, which contains nitrogen, is responsible for the –287 ppm peak. All of the characterization findings were consistent with those previously published.

![UV spectrum](image2)

**Figure 2. TMP network spectra in the ultraviolet**
Catalytic Results

TMP networks were employed as catalysts for styrene epoxidation with different oxidants in the presence and absence of a promoter in the TMP network. Initial studies focused on optimising the oxidant-to-substrate molar ratio using acetonitrile as the solvent solution and NaHCO₃ as a promoter. Styrene-to-styrene oxide conversion was minimal due to the lack of oxidant in the reaction, while increasing the molar ratio was extremely successful in increasing conversion of styrene (Table 1, Entries 2-4). One:5 molar ratio was found to have the maximum conversion rate (50 percent) and selectivity (90%), however when the quantity of oxidant is increased, conversion rises but selectivity decreases. (Table 1, Entry 6). Aqueous and organic (DMF, acetonitrile) solvent system reactions were carried out after the oxidant to substrate molar ratio was optimised. The conversion of styrene-to-styrene oxide (98 percent selectivity) in aqueous conditions was found to be 60% intriguing. DMF and DMSO, the other two non-aqueous solvents, exhibited lower conversion and selectivity than acetonitrile, which had the greatest conversion and the highest selectivity. For this reason, subsequent investigations were conducted in aqueous media employing other oxidants such as H₂O₂, tert-Butyl hydroperoxide, and iodosylbenzene, which had a greater selectivity and conversion rate. However, compared to H₂O₂, TBHP and iodosylbenzene had worse conversion and selectivity than H₂O₂, which may be explained by a lower degree of oxidant solvation in the reaction media. NaHCO₃ concentrations ranging from 0.0 - 2.0 mole percent were employed to further enhance promoter variation. When NaHCO₃ was not present, the conversion rate was poor (5 percent). At a concentration of 1 mole percent NaHCO₃ (Table 3, Entry 3), the maximum conversion was 90.8 percent and the maximum selectivity was 97.2 percent (Table 3, Entry 3).
Table 1  
Optimization substrate to H2O2 molar ratio

| Entry | Styrene:H2O2 | Conversion of Styrene % | Selectivity for Styrene Oxide % |
|-------|--------------|-------------------------|---------------------------------|
| 1     | 1:1          | 10                      | 96                              |
| 2     | 1:2          | 22                      | 96                              |
| 3     | 1:3          | 30                      | 94                              |
| 4     | 1:4          | 36                      | 93                              |
| 5     | 1:5          | 50                      | 90                              |
| 6     | 1:6          | 54                      | 85                              |

Table 2  
Influence of solvent and oxidant on conversion

| Entry | Solvent | Oxidant | Conversion of Styrene % | Selectivity for Styrene Oxide % |
|-------|---------|---------|--------------------------|--------------------------------|
| 1     | ACN     | H2O2    | 50.0                     | 90.0                            |
| 2     | DMF     | H2O2    | 45.5                     | 75.0                            |
| 3     | DMSO    | H2O2    | 38.9                     | 65.0                            |
| 4     | H2O     | H2O2    | 60.3                     | 98.7                            |

Table 3  
Effect of base and temperature on conversion

| Entry | NaHCO3 (mmol) | Time | Conversion of Styrene % | Selectivity for Styrene Oxide % |
|-------|---------------|------|-------------------------|--------------------------------|
| 1     | 0             | 12   | 5.0                     | ND                             |
| 2     | 0.5           | 6    | 60.3                    | 98.7                           |
| 3     | 1             | 6    | 90.0                    | 97.8                           |
| 4⁹    | 1             | 6    | 30.3                    | 99.0                           |
| 5⁹    | 1             | 6    | >99                     | 59.2                           |
| 6     | 1.5           | 6    | 92.2                    | 70.2                           |
| 7     | 2             | 6    | 97.1                    | 65.2                           |
| 8⁹    | 1             | 12   | 10.0                    | ND                             |

However, the selectivity for ep-oxide was lost due to the addition of NaHCO3 (Table 3, Entries 6 and 7). One mole percent of NaHCO3 was discovered to be the optimal quantity of base. Styrene to styreneoxide conversion was tested at various temperatures in order to determine the influence of temperature on the process (Table 3, Entries 3-5). The selectivity (98%) was greater at a lower temperature (15 C), but the conversion (30.3 percent) was lower. Styrene oxide was converted to diol at a temperature of 40 degrees Celsius, but the ring opening lowered the selectivity of styrene oxide to 59.2 percent, resulting in the formation of diol. (Table
Higher temperatures reduce selectivity. The optimal temperature was discovered to be 25°C, and this yielded great conversion (90.8 percent) and high levels of selectivity (97.8 percent) (Table 3, Entry 5).

**Conclusion**

The styrene epoxidation process may be efficiently catalysed in aqueous medium using the TMP-network. Dual route and the "Breslow effect" are cited for the improved water performance. An eco-friendly method of epoxidation utilising hydrogen peroxide at ambient temperature resulted in a 90.9 percent conversion of styrene to styrene oxide with 97.8 percent selectivity. Without a substantial loss in conversion or selectivity, the catalyst may be reused several times.

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