

Research Article

Synthesis of Propylene Carbonate from Epoxide and CO₂ Catalyzed by Carbon Nanotubes Supported Fe_{1.5}PMo₁₂O₄₀

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Carbon nanotubes (CNTs) were functionalized and were then used as supports of Fe_{1.5}PMo₁₂O₄₀ (FePMo) Keggin heteropolyanions catalysts. The characterization of the resulting catalysts was investigated by inductively coupled plasma spectrometry (ICP), Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) light spectroscopy, and transmission electron microscopy (TEM). FTIR and XRD results confirmed that FePMo was bounded on CNTs successfully and the Keggin structure was preserved. Characterization by TEM showed that solids with high FePMo content exhibited aggregation of FePMo in large particles. The as-prepared catalysts were tested in the synthesis of propylene carbonate (PC) from CO₂ and propylene oxide (PO) in a solvent-free reaction and under mild conditions. Effects of various parameters, such as reaction temperature, reaction time, FePMo content on the support, and catalyst loading on the reaction, were investigated. It has been found that CNTs supported FePMo achieved 57.7% PO conversion and 99.0% PC selectivity, whereas unsupported FePMo led only to 8.5% conversion and 48.6% selectivity. The remarkable enhancement of the catalytic activity over the supported catalyst can be attributed mainly to the better dispersion and reactivity of the FePMo catalyst in the supported material.

1. Introduction

The utilization of carbon dioxide as a raw material for the production of chemicals has attracted much attention [1]. Carbon dioxide has the advantages of being a cheap, nontoxic, and renewable C1 resource, and the development of methods for its activation at mild conditions is an attractive research axis [2, 3]. From the point of view of environment protection and resources availability, the transformation of CO₂ into valuable useful organic compounds represents an interesting alternative carbon feedstock. Unfortunately, carbon dioxide is thermodynamically stable and its activation requires high energy. Nevertheless, numerous reactions involving CO₂ are thermodynamically possible provided that an appropriate catalyst is used. Therefore, the design of a catalyst that can capture, activate, and convert CO₂ into useful chemicals is a key strategy. One of the most promising routes using CO₂ is its insertion into epoxides to form cyclic carbonates. Several homogeneous and heterogeneous catalysts have been explored for this reaction. Homogeneous catalysts include

polyoxometalates (POMs) [4], complexes of transition metals (Zn, Al, Cr, Co, Cu, Ni, and Sn) salen porphyrin and phthalocyanine [5–7], ionic liquids [8], and quaternary ammonium salts [9]. Although many homogeneous catalysts were found to be effective at low pressure and temperature [6, 7], the difficult and costly separation of the catalysts from the reaction products represents a serious drawback to their application. Consequently, various heterogeneous catalysts, such as metal oxides [10, 11], immobilized complexes or ionic liquids [12–14], titanosilicates [15], metal-organic frameworks [16–19], and zeolites [19], were tested. However, most of these heterogeneous systems require high pressures and high temperature. Taking into account the fact that several homogeneous based POMs catalysts have proven their performance in the cycloaddition of CO₂ [4, 20], their exploration as heterogeneous catalyst systems is a promising way. It is well known that redox and acid–base properties of POMs can be adjusted by varying the heteroatom, counter anion, and addenda atoms. Moreover, these kinds of materials do not undergo deactivation by water [21–23]. Since polyoxometalates are

known to be very active catalysts, it would be advantageous to load them on suitable supports, for example, on carbon nanotubes. Indeed, it has been mentioned in the literature that carbon nanotubes capture large quantities of carbon dioxide. It has been reported that CNTs modified with 3-aminopropyltriethoxysilane have a good potential for CO₂ capture [24, 25]. These features prompted us to investigate the catalytic potential of functionalized CNTs supported POMs for the synthesis of propylene carbonate from propylene oxide and CO₂. The synthesis of PC was achieved under mild conditions without using any solvent, which is attractive from both economic and environmental viewpoints.

2. Materials and Methods

2.1. Materials. Carbon nanotubes (CNTs) (>95%) were purchased from EMFUTUR Technologies. Molybdenum tungstate, Na₂MoO₄·2H₂O (98% purity), and propylene oxide were obtained from WINLAB Ltd., UK.

2.2. Preparation of the Catalysts

2.2.1. Heteropolyoxometalates Catalysts. The H₃PMo₁₂O₄₀ heteropolyacid was prepared according to Rocchiccioli-Deltcheff and Fournier method [26]. The heteropoly-molybdate salts, namely, Fe_{1.5}PMo₁₂O₄₀, Co_{1.5}PMo₁₂O₄₀, Cu_{1.5}PMo₁₂O₄₀, and Zn_{1.5}PMo₁₂O₄₀ (abbreviated as FePMo, CoPMo, CuPMo, and ZnPMo), were prepared as precipitates by slowly adding the required amount of Ba(OH)₂·8H₂O (to neutralize the 3 protons) to the aqueous solution of the H₃PMo₁₂O₄₀ heteropolyacid. Then, the required amount of MSO₄·xH₂O was added (M = Co, Cu, Fe, or Zn), leading to the formation of insoluble barium salt, which was removed by filtration. The resulting solutions were allowed to stand for a few days at 4°C to allow the precipitation of the salts which were then recovered from the solution by filtration.

2.2.2. Immobilization of FePMo on CNTs. To bind FePMo on carbon nanotubes (CNTs) support, oxygenated groups (functionalization) were created by using concentrated nitric acid according to the following steps: 0.1 g of sample of CNTs was suspended in 100 ml of nitric acid (65%) and heated for 5 hours at 80°C and then cooled at room temperature. The treated CNTs were then washed with deionized water at pH 7 and dried at 100°C overnight. The resulting functionalized CNTs were then added to the desired amount of FePMo already dissolved in acetone under stirring and heating at about 60°C until dryness evaporation. The prepared catalyst was dried overnight in an oven at 80°C. Various samples referred to as CNTs-FePMo-*x* (*x* is the weight in mg of FePMo per 100 mg of CNTs) were prepared.

2.3. Characterization of the Catalysts. Infrared spectra were recorded with an infrared spectrometer GENESIS II-FTIR (4000–400 cm⁻¹) using the KBr Pellet technique. X-ray diffraction (XRD) measurements were carried out employing an Ultima IV X-ray Rigaku diffractometer using Cu-K α radiation. Elemental analyses were carried out under inductively coupled plasma (ICP) spectrometry measurements

TABLE 1: Elemental analysis of the as-prepared unsupported heteropolyanions salt catalysts.

M _{1.5} PMo ₁₂ (theoretical formulas)	P	M Molar ratio	Mo
Fe _{1.5} PMo ₁₂	1	1,468	11,945
Co _{1.5} PMo ₁₂	1	1,515	11,810
Cu _{1.5} PMo ₁₂	1	1,589	12,567
Zn _{1.5} PMo ₁₂	1	1,496	12,259

using a PerkinElmer Nexion 300D Spectrometer. The UV-Vis spectra (in H₂O) were obtained with a double beam UV-Vis spectrophotometer (Philips 8800). Field emission transmission electron microscopy (TEM) experiments were performed on a JEOL JEM-2100F field emission electron microscope (JEOL, Japan) with an acceleration voltage of 110 kV.

2.4. General Procedure for Synthesis of PC. The reaction of propylene oxide and CO₂ was carried out in 80 mL stainless steel autoclave equipped with a magnetic stirrer. The temperature of the autoclave was adjusted by a heating jacket. In a typical experiment, catalyst, cocatalyst, and propylene oxide were charged into the reactor vessel without using any cosolvent. The reactor vessel was placed under a constant pressure of carbon dioxide and then heated to the required temperature and continuously stirred. When the desired reaction temperature was attained, the reaction mixture was pressurized with CO₂, while stirring, up to the desired level. When the desired time elapsed, the reactor was cooled by ice bath to room temperature and depressurized to atmospheric pressure. The products were analyzed with a gas phase chromatograph (PYE UNICAM) equipped with a flame ionization detector using a capillary column (HP-PLOT Q length 30 mID 0.53 mm). The identification of the products was achieved occasionally by gas chromatography-mass spectrometry (GC-MS) using a Thermo Trace GC Ultra gas chromatograph equipped with AI 3000. For the separation of target compounds, a TR-5 MS-SQC capillary column (30 m × 0.25 mm i.d., phase thickness 0.25 μ m) was used with helium as the carrier gas (at a flow rate of 1 mL/min).

3. Results and Discussion

3.1. Catalysts Characterization

3.1.1. Unsupported Heteropolyanions. Elemental analysis of the series of unsupported heteropolyanions salt catalysts was performed by ICP-MS and the results are reported in Table 1. The results were adjusted considering 1 atom of phosphorus per Keggin unit according to the nature of Keggin structure and were found to be in good agreement with the expected ones for molybdenum and counter ion.

The observed frequencies and assignments of the IR bands are given in Table 2. The four bands observed and assigned to the asymmetric stretching vibrations

TABLE 2: Infrared absorption bands and symbol frequencies for the Keggin-type heteropolyanions catalysts (M = W or Mo).

Catalyst	Wavenumbers (cm^{-1})			
	$\nu_{\text{as}}(\text{P-Oa})$	$\nu_{\text{as}}(\text{Mo-Od})$	$\nu_{\text{as}}(\text{Mo-Oc-Mo})$	$\nu_{\text{as}}(\text{Mo-Oc-Mo})$
CuPMo	1064.74	964.66	872.43	782.61
ZnPMo	1065.59	963.72	873.63	779.10
FePMo	1065.42	963.22	869.94	781.21
CoPMo	1062.04	962.61	883.43	796.87

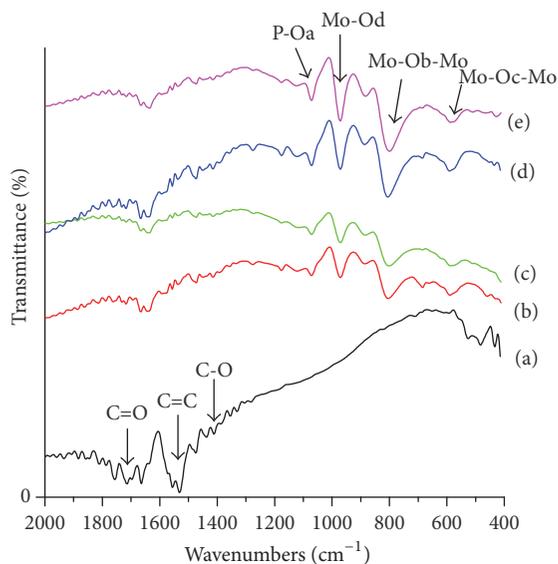


FIGURE 1: FTIR spectra of the functionalized CNTs and CNTs-PMo- x series of catalysts. (a) Functionalized CNTs; (b) CNTs-FePMo-150; (c) CNTs-FePMo-200; (d) CNTs-FePMo-250; (e) CNTs-FePMo-300; (f) CNTs-FePMo-350.

of the $\nu_{\text{as}}(\text{P-Oa})$, $\nu_{\text{as}}(\text{Mo-Od})$, $\nu_{\text{as}}(\text{Mo-Oc-Mo})$, and $\nu_{\text{as}}(\text{Mo-Oc-Mo})$ bonds are the main characteristic bands of the Keggin structure [26, 27]. In Keggin structure, Oa is the oxygen atom common to PO_4 tetrahedron and one trimetallic group Mo_3O_{13} , Ob is the oxygen shared by two trimetallic groups, Oc binds two octahedral trimetallic groups MoO_6 , and Od refers to the terminal oxygen atom.

3.1.2. CNTs Supported Heteropolyanions. Figure 1 shows the IR spectra of the CNTs support and the CNTs-FePMo- x catalysts. As already reported in a previous paper [28], oxidized CNTs exhibit, in the $1300\text{--}1900\text{ cm}^{-1}$ range, three main bands at 1386 , 1720 , and 1585 cm^{-1} assigned to C-O, C=O, and C=C groups, respectively. In the $3000\text{--}4000\text{ cm}^{-1}$ range, two bands, one at 3448 cm^{-1} and the other at 3720 cm^{-1} , are assigned to O-H and -COOH groups, respectively. As for the IR spectra of the CNTs supported catalysts, it can be seen that, for all the catalysts, the main characteristic bands of the Keggin structure were observed in the fingerprint region ($700\text{--}1100\text{ cm}^{-1}$), indicating that the Keggin structure was maintained. The characteristic bands of FePMo, observed at 1065.42 cm^{-1} , 963.22 cm^{-1} , 869.94 cm^{-1} , and 781.21 cm^{-1} ,

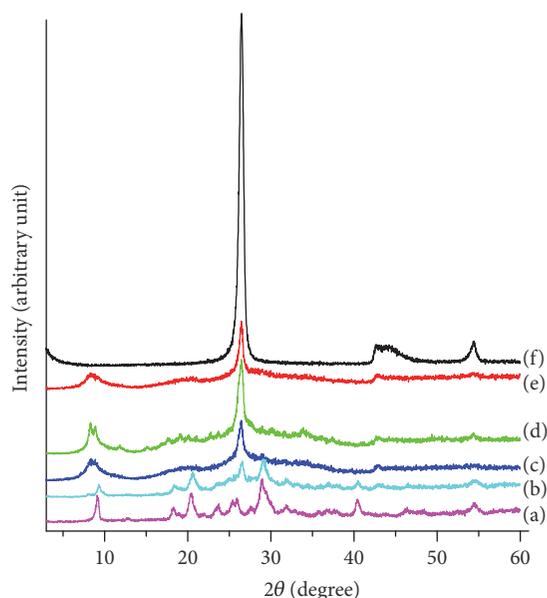


FIGURE 2: XRD spectra of the functionalized CNTs and CNTs-PMo- x series of catalysts. (a) CNTs-FePMo-350; (b) CNTs-FePMo-300; (c) CNTs-FePMo-250; (d) CNTs-FePMo-200; (e) CNTs-FePMo-150; (f) functionalized CNTs.

indicated that the Keggin structure was preserved on the support [26, 27].

3.1.3. X-Ray Diffraction. The XRD patterns of the CNTs, FePMo, and CNTs-FePMo- x are illustrated in Figure 2. The three peaks at 26.1° , 43.1° , and 53.5° observed in the XRD pattern of the oxidized CNTs which were indexed to the (002), (100), and (004) diffractions of hexagonal graphite [29, 30], respectively, indicated that the graphitic structure of the CNTs was not destroyed after oxidation treatment. The reflections at 7.2° , 20.5° , and 27.2° , observed in the pattern of FePMo, are the characteristic peaks of the Keggin structure of the phosphomolybdate phase [31]. These diffraction peaks could be readily indexed to cubic structure (JCPDS 09-0412). In the case of CNTs-FePMo- x catalysts, the characteristic lines of the Keggin structure at 25.6° and 29.7° can be observed easily for the samples with high FePMo content, showing that the Keggin structure was preserved on the support. It is worth noting that the intensity of the hexagonal graphite structure on CNTs was stronger than that of CNTs-FePMo- x samples. A similar finding was observed by Li et al. [32]. In fact, when comparing the XRD patterns of pure CNTs and Fe_3O_4 -CNTs nanocomposite, they found that the

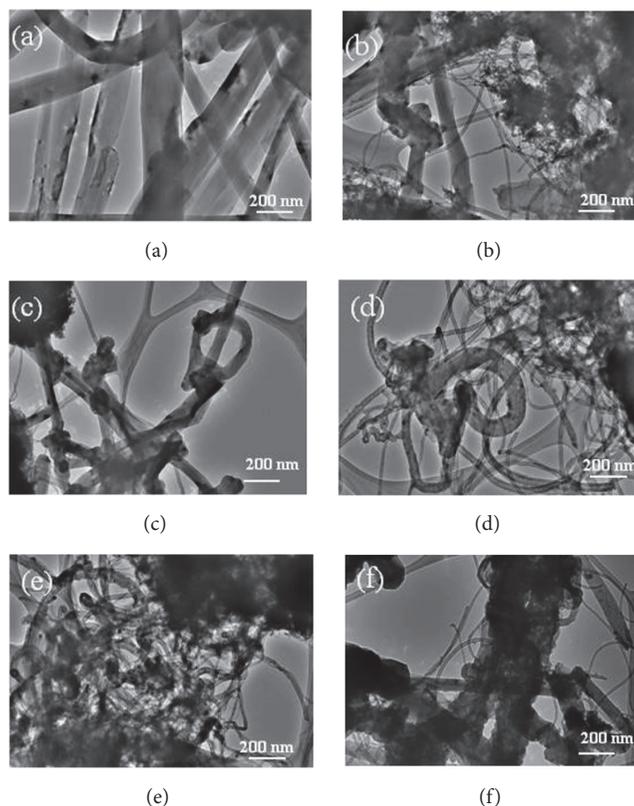


FIGURE 3: TEM images of the functionalized CNTs and CNTs-PMo- x series of catalysts. (a) Functionalized CNTs; (b) CNTs-FePMo-150; (c) CNTs-FePMo-200; (d) CNTs-FePMo-250; (e) CNTs-FePMo-300; (f) CNTs-FePMo-350.

intensity of the pure CNTs was stronger than that of Fe_3O_4 -CNTs nanocomposite. In the opinion of the authors, this might be due to the fact that grafted Fe_3O_4 on the CNTs surface weakened the diffraction peak at 26.1° . Thus, the XRD patterns combined with FTIR spectra indicated that the active phase FePMo on CNT conserved the Keggin-type structure and the as-prepared CNTs-FePMo- x catalysts were successfully synthesized.

3.1.4. UV-Visible Spectroscopy. The amount of FeMo_{12} loaded on CNTs support was determined by using the UV-visible technique. The UV-visible spectrum of the Keggin FePMo sample shows a large band with multiplicity in the domain of wavelengths 250–500 nm. According to the literature, this band constituted several components, due to the changes from the double-occupied oxo orbital to the unoccupied Mo d orbitals ($\text{O}^{2-} \rightarrow \text{Mo}^{6+}$) in the Keggin anion [33, 34]. It constituted several components (200–250, 270–350, and 400–450 nm ranges) having different energies associated with ligand–metal charge transfers from oxygen to $\text{Mo}^{(\text{VI})}$. The results of FeMo_{12} loaded on CNTs support in aqueous solution, reported in Table 3, showed that the nominal concentrations were slightly different from the experimental ones.

3.1.5. Transmission Electronic Microscopy. The results of TEM analysis of the functionalized CNTs support and the

TABLE 3: Determination of the amount of $\text{Fe}_{1.5}\text{PMo}_{12}$ loaded on the CNTs support by UV-visible spectroscopy.

Catalyst	Nominal mass (mg)	Experimental mass (mg)
CNTs- FePMo-150	150	124
CNTs- FePMo-200	200	180
CNTs- FePMo-250	250	224
CNTs- FePMo-300	300	310
CNTs- FePMo-350	350	345

CNTs-FePMo- x supported catalysts are shown in Figure 3. It can be seen that at lower contents FePMo clusters are well dispersed ((b), (c), and (d)) while at higher contents ((e) and (f)) agglomeration into larger crystallites is formed. The aggregation of FePMo clusters into large particles at high contents might be due to the insufficient number of binding sites (functional groups) to anchor all the FePMo particles.

3.2. Catalytic Activity

3.2.1. Effect of Counter Ion. The experiments were carried out at 65°C during a period of 7 h under 5-bar CO_2 pressure using 0.150 g of the catalyst and 0.050 g of tetraethyl ammonium bromide (TEABr) as a cocatalyst. The results are shown in Table 4. It can be seen that ZnPMo led to the highest

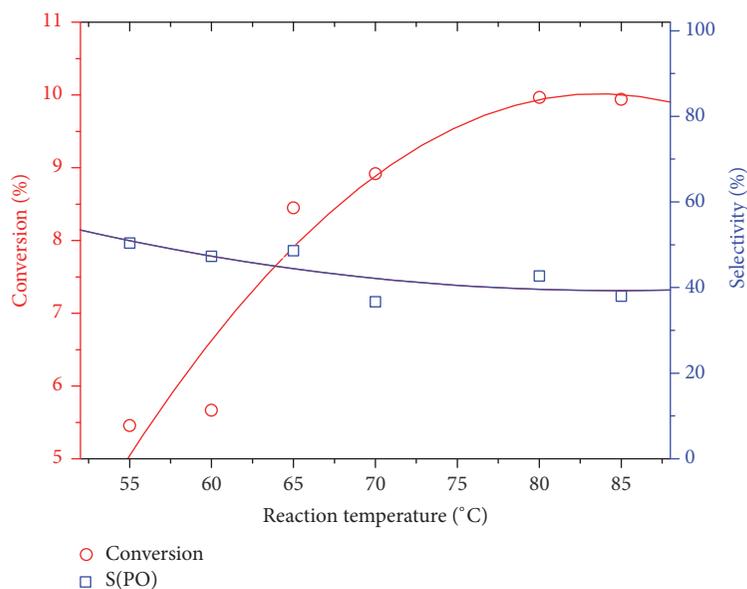


FIGURE 4: Effect of reaction temperature on the conversion and selectivity of PC over FePMo. Reactions carried out under 5-bar CO_2 pressure during a period of 7 h by using 0.150 g of catalyst and 0.050 g of TEABr (cocatalyst).

TABLE 4: Effect of counter ion on the PO conversion and PC selectivity. Reaction conditions: $P_{(\text{CO}_2)} = 5$ bar; reaction temperature 65°C ; reaction time = 7 h; m (catalyst) 0.150 g; m (TEABr: cocatalyst) 0.050 g.

Catalyst	Conversion (%)	S (PC)
CuPMo	7.94	16.6
ZnPMo	2.86	56.2
CoPMo	6.42	31.0
FePMo	8.45	48.6

selectivity in PC (56.2%) but to the lowest conversion (2.86%), whereas FePMo catalyst led to the highest conversion (8.45%) and to a relatively higher selectivity in PC (48.6%). These results indicated that FePMo was the suitable catalyst for the conversion of PO into PC. Therefore, it was selected for further investigations such as the effect of reaction temperature, content on CNTs support, and reaction time.

3.2.2. Effect of Temperature. The selected FePMo catalyst was tested for the reaction of PO with CO_2 at different reaction temperatures. The experiments were carried out under a pressure of CO_2 equal to 5 bar for 7 hours. The results depicted in Figure 4 showed that the temperature has a strong effect on the conversion. With the increase of temperature from 55 to 65°C , PO conversion increased sharply from 5.46 to 8.92%. Further rise of temperature to 85°C resulted in only a slight increase of PO conversion (9.94%) due to the decrease of CO_2 solubility in the reaction mixture. In fact, an increase in the reaction temperature increased the conversion but at the same time decreased the solubility of carbon dioxide in the reaction system. A similar finding was reported in the literature [35, 36]. Contrary to PO conversion, PC selectivity decreased slightly and can be considered as

remaining unchanged as the temperature increased. This very slight decrease in the selectivity of PC might be caused by the increase of secondary reactions such as isomerization to acetone, as well as the hydrolysis to diol, favored at high temperatures [37, 38]. Based on the above results, it can be concluded that 65°C was the optimum reaction temperature and all the subsequent experiments for PC synthesis were performed at this temperature.

3.2.3. Effect of CNTs Support. It is well known that both the conversion and the selectivity depend on the size and dispersion of the catalyst particles on the support. A strong interaction between the particles and the support leads to high dispersion of the particles on the support which in turn leads to high conversion and selectivity. Functionalized CNTs are among the supports that possess these properties. Moreover, they have high specific surface areas, good thermal properties, and excellent adsorption properties [39]. That is why we have selected CNTs as a catalyst support to investigate the influence of FePMo content on PO conversion. The experiments were carried out at 65°C under 5-bar CO_2 pressure during a period of 7 hours and the results are shown in Figure 5. As expected, PO conversion increased with increasing FePMo content, whereas PC selectivity decreased slightly. This result can be explained by the fact that, at high loading, the amount of FePMo loaded on the CNTs was larger than the available functional groups created on the support, which influenced the dispersion of FePMo on the support. When the concentration of the functional groups is less than that of the FePMo particles on the support, there will be poor dispersion (aggregation) of FePMo particles (as evidenced by TEM) and consequently the selectivity decreases. Similar findings were observed by the authors of [40] in their study of the hydrogenation of phenylacetylene over CNTs supported Pt catalyst. The authors mentioned that the high conversion

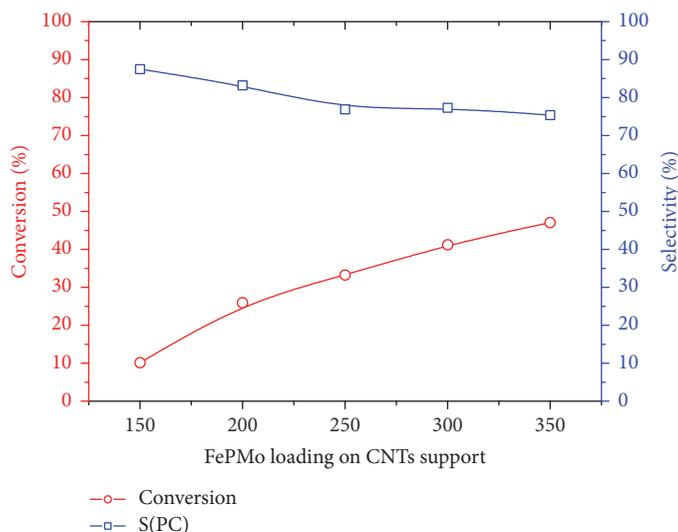


FIGURE 5: Effect of FePMo contents on the conversion and PC selectivity. Reactions carried out under 5-bar CO_2 pressure during a period of 7 h by using 0.150 g of catalyst and 0.050 g of TEABr (cocatalyst).

and selectivity to styrene obtained might be due to the higher dispersion (i.e., smaller particle size) of the Pt particles size.

3.2.4. Effect of Reaction Time. The influence of reaction time on PO conversion and PC selectivity was investigated in the time interval 3–7 h. The experiments were performed using CNT-FePMo-350 catalyst at 65°C under CO_2 pressure of 5 bar and the results are depicted in Figure 6. It is observed that the conversion of PO increases progressively, reaching PO conversion of 47.1% at 7 hours, whereas the selectivity of the PC increases within the first 5 hours only. Beyond 5 hours, it remains approximatively at 75% throughout.

3.2.5. Effect of Catalyst Amount. The effect of the amount of CNTs-FePMo-350 on the conversion and selectivity was investigated in the range of 0.15–0.3 g at 65°C for 7 h under a 5-bar CO_2 pressure. The results depicted in Figure 7 showed that when the catalyst amount was increased from 0.15 g to 3 g, the conversion increased from 26.6% to 57.7%, whereas no significant change in the selectivity was observed. Compared to the unsupported FePMo catalyst, CNTs supported FePMo enhanced the conversion of epoxide remarkably. Conversion of 57.7% and selectivity of 99% were achieved, whereas unsupported FePMo led only to 8.5% conversion and 48.6% selectivity. The enhancement in activity of CNT-FePMo catalyst can be attributed to the capture of CO_2 by the highest porous CNTs combined with the highest activity of FePMo and also by the high dispersion of FePMo clusters owing to the oxygenated groups created on the CNTs [41, 42]. Thus, CNTs play a role not only in increasing the dispersion of FePMo clusters, but also in lowering the high pressure required to dissolve CO_2 gas in the reactant mixture. It is worth noting that most of the reactions of cyclic carbonate involving CO_2 gas, reported in the literature, were carried out under very high pressure of CO_2 [36, 37, 43, 44]. In

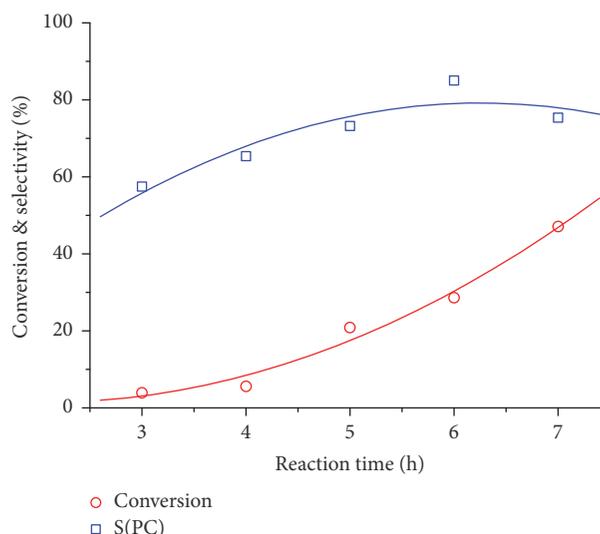


FIGURE 6: Effect of reaction time on the conversion and PC selectivity. Reactions carried out under 5-bar CO_2 pressure at 65°C by using 0.150 g of catalyst and 0.050 g of TEABr (cocatalyst).

our research work, experiments were carried out under mild conditions, that is, 65°C and 5 bar.

3.2.6. Effect of CO_2 Pressure. Figure 8 depicts the effect of CO_2 pressure on the conversion and selectivity of PC. It can be seen that the conversion depends strongly on the CO_2 pressure. Indeed, when CO_2 pressure was increased from 5 to 8 bar, the conversion increased from 47.1% to 64.6%, which represents an increase of 27%. Further increase in CO_2 pressure led to a slight decrease in the conversion. This can be explained by the pressure effect on the concentrations of CO_2 and epoxide in the two phases of reaction medium [45]. The top phase is the CO_2 -rich phase, and the bottom phase

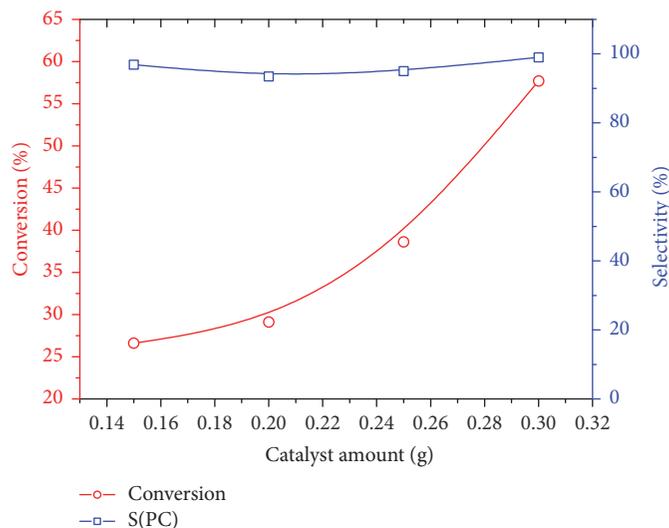


FIGURE 7: Effect of catalyst amount on the conversion and PC selectivity. Reactions carried out under 5-bar CO_2 pressure at 65°C during a period of 7 h. $m(\text{catalyst})/m(\text{cocatalyst}) = 3$.

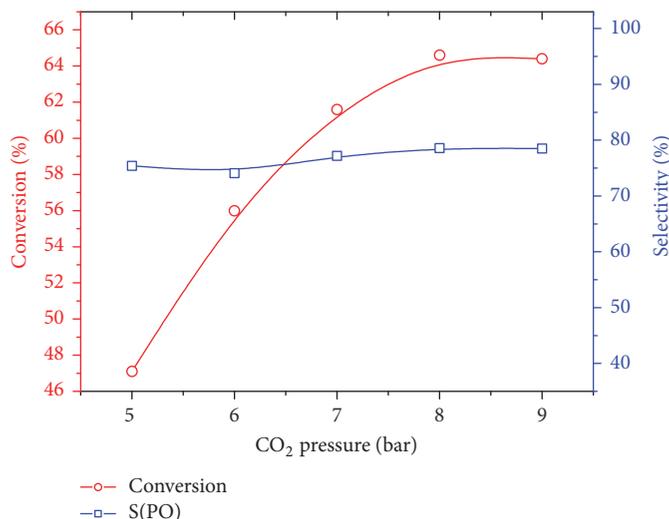


FIGURE 8: Effect of CO_2 pressure on conversion and PO selectivity. Reactions catalyzed by 0.150 g of catalyst and 0.050 g of TEABr (cocatalyst) at 65°C during a period of 7 hours.

is the epoxide-rich phase. The reactions occur in the liquid phase because of the presence of the catalyst in this phase. The conversion increased when the concentration of CO_2 increased in the bottom phase at low pressure, and decreased when the concentration of PO decreased in the bottom phase at high pressure (>9 bar). As for PC selectivity, it can be seen that CO_2 pressure has no significant influence. It can be concluded from this result that 8-bar CO_2 pressure is the optimized condition for the synthesis of PC from PO and CO_2 for the reaction conducted at 65°C over CNTs-FePMo catalyst system.

4. Conclusions

A series of unsupported Keggin-type heteropolyanions ($\text{M}_{1.5}\text{PMo}_{40}$, $\text{M} = \text{Zn}, \text{Cu}, \text{Co}, \text{and Fe}$) and a series of

CNTs supported FePMo heteropolyanions were prepared and characterized by means of ICP, FTIR, XRD, UV, and TEM. It has been found that the Keggin structure of FePMo heteropolyanions was preserved on the CNTs support.

The as-prepared catalysts were tested for the reaction of carbon dioxide with propylene oxide. It has been found that the heteropolyanions having Fe as counter anion (FePMo) were the most active of the series of unsupported catalysts. When supported on CNTs, FePMo exhibited high catalytic performance compared to the unsupported FePMo.

The enhanced activity can be attributed mainly to the better dispersion and reactivity of the FePMo catalyst in the supported material.

The CNTs play a role not only as a solid support to heterogenize the catalyst for easy separation, but also in

lowering the high pressure required to dissolve CO₂ gas in the reactant mixture.

The reaction of propylene oxide with CO₂ leading to propylene carbonate can be catalyzed by CNT-FePMo, with high conversion and selectivity without using a solvent and under mild reaction conditions (temperature of 65°C and CO₂ pressure of 5 bar).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

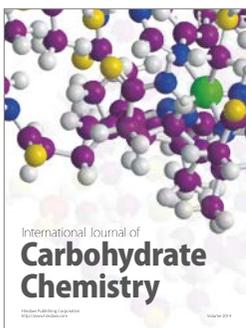
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