

Immobilization of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst on the nitrogen-containing mesoporous carbon and its application to the vapor-phase 2-propanol conversion reaction

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Abstract—Nitrogen-containing mesoporous carbon (N-MC) with high surface area ($=1,115 \text{ m}^2/\text{g}$) and large pore volume ($=1.18 \text{ cm}^3/\text{g}$) was synthesized by a templating method. The surface of N-MC was then modified to form a positive charge, and thus, to provide sites for the immobilization of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. By taking advantage of the overall negative charge of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}) was chemically immobilized on the N-MC support as a charge matching component. It was found that the $\text{PMo}_{12}/\text{N-MC}$ still retained relatively high surface area ($=687 \text{ m}^2/\text{g}$) and large pore volume ($=0.67 \text{ cm}^3/\text{g}$) even after the immobilization of PMo_{12} . It was also revealed that PMo_{12} species were finely and molecularly dispersed on the N-MC support via chemical immobilization. In the vapor-phase 2-propanol conversion reaction, the $\text{PMo}_{12}/\text{N-MC}$ showed a higher conversion than the unsupported PMo_{12} . Furthermore, the $\text{PMo}_{12}/\text{N-MC}$ showed an enhanced oxidation catalytic activity and a suppressed acid catalytic activity compared to the unsupported PMo_{12} . This catalytic behavior of $\text{PMo}_{12}/\text{N-MC}$ was due to the molecular dispersion of PMo_{12} on the N-MC support formed via chemical immobilization by sacrificing the proton.

Key words: Heteropolyacid Catalyst, Immobilization, Nitrogen-containing Mesoporous Carbon, 2-Propanol Conversion Reaction, Oxidation Catalysis

INTRODUCTION

Heteropolyacids (HPAs) are early transition-metal oxygen anion clusters that have been widely investigated as homogeneous and heterogeneous catalysts for acid-base and oxidation reactions [1-10]. One of the great advantages of HPA catalysts is that their catalytic properties can be controlled in a systematic way by replacing protons or by substituting framework transition-metal atoms with different metals [11-22]. Their excellent thermal stability also makes HPAs good candidates for application in catalysis that may require extreme environments [23].

A disadvantage of HPA catalysts, however, is that their surface area is very low ($<10 \text{ m}^2/\text{g}$). To overcome the low surface area, HPAs have been supported on inorganic materials by a conventional impregnation method [24-26]. Another promising approach for increasing the surface area of HPA catalysts is to take advantage of the overall negative charge of heteropolyanions. By this method, HPA catalysts have been immobilized on polymer materials such as poly-4-vinylpyridine [27], polyaniline [28], and polystyrene [29] to obtain molecularly dispersed HPA catalysts. Although such an attempt utilizing inorganic supporting materials has been restricted due to the difficulty in forming a positive charge on the inorganic supports, a few successful examples for the chemical immobilization of HPA catalysts on the inorganic supporting materials have been reported recently by forming a positive charge on the inorganic supports through a surface modification process [30-33]. Some of these examples include HPA catalysts immobilized on mesoporous carbon [30],

mesostructured cellular foam silica [31], MCM-41 [32], and SBA-15 [33].

Mesoporous carbons with high surface area and uniform pore size have attracted considerable attention in many fields of science and engineering, such as adsorption and catalysis [34-38]. However, it is difficult to introduce a functional group onto the carbon material due to its hydrophobic nature and chemical inertness. If mesoporous carbon materials have a nature that can be easily modified to form a positive charge, and consequently, to provide anchoring sites for heteropolyanions, they can serve as an excellent support for the preparation of molecularly dispersed HPA catalyst.

In this work, nitrogen-containing mesoporous carbon (N-MC) was synthesized by a templating method using SBA-15 and polypyrrole as a silica template and a carbon precursor, respectively. The N-MC was then modified to have a positive charge for the immobilization of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. By taking advantage of the overall negative charge of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}) catalyst was immobilized on the N-MC support as a charge matching component. The $\text{PMo}_{12}/\text{N-MC}$ catalyst was applied to the vapor-phase 2-propanol conversion reaction, with the aim of utilizing $\text{PMo}_{12}/\text{N-MC}$ as an oxidation catalyst.

EXPERIMENTAL

1. Preparation of Nitrogen-containing Mesoporous Carbon (N-MC)

Highly ordered mesoporous silica (SBA-15) was synthesized for use as a templating material for nitrogen-containing mesoporous carbon (N-MC), according to the method in the literature [39]. As-synthesized SBA-15 was calcined at 550°C for 5 h in a stream of

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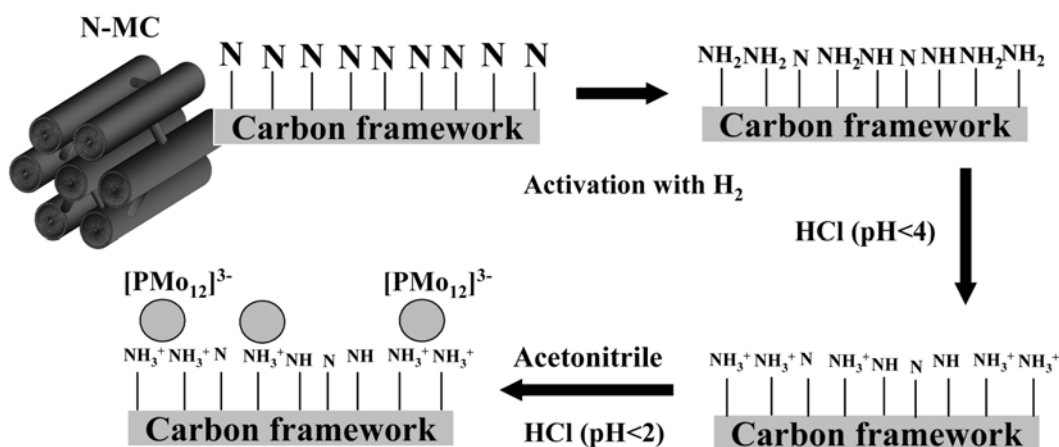


Fig. 1. Schematic procedure for the surface modification of N-MC and the subsequent immobilization of H₃PMo₁₂O₄₀ (PMo₁₂) on the N-MC support.

air. The typical procedure for the preparation of N-MC support was followed. 2.0 g of FeCl₃ dissolved in an HCl solution (3.0 ml, 1.0 M) was impregnated onto SBA-15 (2.0 g) by an incipient wetness method. The yellow-colored slurry was dried in an oven at 100 °C for 6 h. The resulting solid was reacted with 1.0 g of pyrrole monomer at room temperature under vacuum for the polymerization of pyrrole. The SBA-15/polypyrrole composite was dried at 80 °C for 4 h, and it was then carbonized at 900 °C for 5 h in a stream of nitrogen (40 ml/min). The silica template was removed by using HF and HNO₃. After the resulting solid was washed with deionized water several times, it was finally dried at 100 °C in a convection oven to yield the N-MC [40,41].

2. Immobilization of H₃PMo₁₂O₄₀ (PMo₁₂) on N-MC

Fig. 1 shows the schematic procedure for the surface modification of N-MC and the subsequent immobilization of H₃PMo₁₂O₄₀ (PMo₁₂) on the N-MC support. In order to create amine groups on the surface of N-MC, the N-MC was activated by flowing hydrogen (10 ml/min) at 150 °C for 2 h. The activated N-MC was then treated with an aqueous HCl solution (pH<4.0) for 12 h to form a positive charge. After the resulting N-MC support was washed with deionized water several times until the pH of the washing solvent became 5.0-6.0, it was dried overnight at 100 °C to yield the surface-modified N-MC support. For the preparation of PMo₁₂/N-MC, PMo₁₂ (1.0 g) and surface-modified N-MC (1.0 g) were dissolved in acetonitrile (100 ml). The pH of the mixed slurry was maintained below 2.0 by using an aqueous HCl solution. The slurry was stirred for 24 h at room temperature for the immobilization of PMo₁₂ species on the surface-modified N-MC support. After the solid product was recovered by filtration, it was washed several times with deionized water until the washing solvent became colorless. The solid product was dried at 100 °C overnight and calcined at 200 °C for 3 h to yield the PMo₁₂/N-MC.

3. Characterization

Nitrogen adsorption-desorption isotherms of N-MC and PMo₁₂/N-MC were obtained with an ASAP-2010 instrument (Micromeritics). Pore structures of N-MC and PMo₁₂/N-MC were examined by TEM (Jeol, JEM-2000EXII). Chemical immobilization of PMo₁₂ on the N-MC support was confirmed by ³¹P CP-MAS NMR analyses (Bruker, AVANCE 400 WB, DSX-400). N-MC and PMo₁₂/

N-MC were further characterized by XRD (Mac Science, M18XHF) and ICP-AES (Shimadzu, ICPS-1000IV) measurements.

4. Catalytic Reaction

Vapor-phase 2-propanol conversion reaction was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. PMo₁₂/N-MC or unsupported PMo₁₂ (35 mg on PMo₁₂ basis) was charged into a tubular quartz reactor, and pretreated at 260 °C for 1 h with a mixed stream of oxygen (10 ml/min) and nitrogen (10 ml/min). 2-Propanol (1.3×10⁻² mol/h) was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with oxygen (10 ml/min) and nitrogen (10 ml/min). The

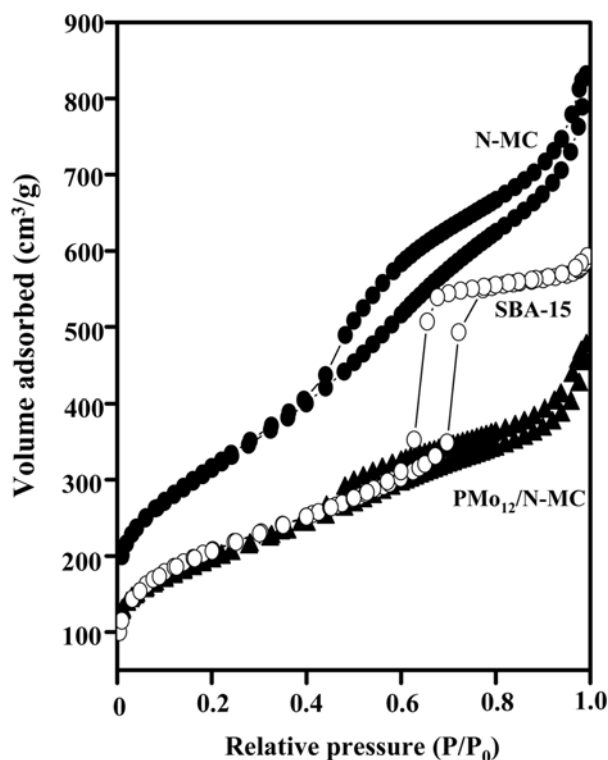


Fig. 2. Nitrogen adsorption-desorption isotherms of SBA-15, N-MC, and PMo₁₂/N-MC.

catalytic reaction was carried out at 200 °C, and the contact time was maintained at 2.2 g- PMo_{12} -h/2-propanol-mol. Reaction products were periodically sampled and analyzed with a gas chromatograph (HP 5890 II).

RESULTS AND DISCUSSION

1. Physical and Chemical Properties of N-MC and PMo_{12} /N-MC

Fig. 2 shows the nitrogen adsorption-desorption isotherms of SBA-15, N-MC, and PMo_{12} /N-MC. SBA-15 retained high surface area ($\approx 760 \text{ m}^2/\text{g}$) and large pore volume ($\approx 0.90 \text{ cm}^3/\text{g}$), and exhibited type IV isotherm and type H1 hysteresis loop [39]. On the other hand, both N-MC and PMo_{12} /N-MC showed type IV isotherm and type H2 hysteresis loop. This indicates that the pore structure of N-MC was still maintained even after the immobilization of PMo_{12} . Surface area and pore volume of N-MC were $1,115 \text{ m}^2/\text{g}$ and $1.18 \text{ cm}^3/\text{g}$, respectively. PMo_{12} /N-MC still retained relatively high surface area ($\approx 687 \text{ m}^2/\text{g}$) and large pore volume ($\approx 0.67 \text{ cm}^3/\text{g}$) even after the immobilization of PMo_{12} . Nitrogen content of N-MC determined by CHN elemental analysis was 3.6 wt%. ICP-AES analysis revealed that the loading of PMo_{12} in the PMo_{12} /N-MC was 14.0 wt%. We attempted to immobilize PMo_{12} on the nitrogen-free mesoporous carbon such as CMK-3. In this case, however, PMo_{12} species were totally dissolved out during the washing step due to the absence of anchoring sites for PMo_{12} on the nitrogen-free mesoporous carbon. This result indicates that nitrogen in the N-MC played an important role in forming a nitrogen-derived functional group (amine group) for the immobilization of PMo_{12} catalyst. It also implies that PMo_{12} species were chemically immobilized on the N-MC support by the aid of amine functional group.

2. Fine Dispersion of PMo_{12} on N-MC

Fig. 3 shows the XRD patterns of unsupported PMo_{12} , N-MC, and PMo_{12} /N-MC. Unsupported PMo_{12} showed the characteristic XRD peaks of the HPA. On the other hand, N-MC showed the characteristic diffraction peaks for (002) and (101) planes at around $2\theta =$

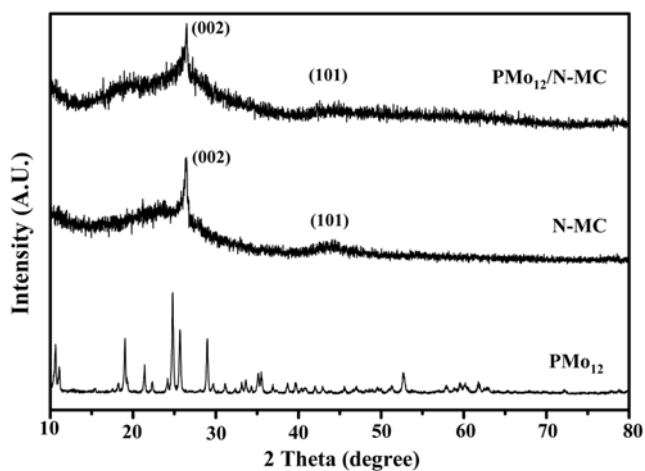


Fig. 3. XRD patterns of unsupported PMo_{12} , N-MC, and PMo_{12} /N-MC.

26.3° and 43°, respectively, indicating that the N-MC retained a graphitic structure. However, PMo_{12} /N-MC exhibited no characteristic XRD peaks of PMo_{12} but showed the same XRD patterns as N-MC, even though 14.0 wt% of PMo_{12} was loaded in the PMo_{12} /N-MC. This result indicates that PMo_{12} species were not in a crystal state but in an amorphous-like state, demonstrating that PMo_{12} species were molecularly dispersed on the N-MC via chemical immobilization.

Fig. 4 shows the TEM images of N-MC and PMo_{12} /N-MC. Two-dimensionally interconnected pore arrays can clearly be observed in both N-MC and PMo_{12} /N-MC. This result supports the conclusion that the pore structure of N-MC was still maintained in the PMo_{12} /N-MC even after the immobilization of PMo_{12} , as evidenced by nitrogen adsorption-desorption isotherm measurements (Fig. 2). Furthermore, no visible evidence representing PMo_{12} species was found in the PMo_{12} /N-MC, indicating that PMo_{12} species were finely dispersed on the N-MC support.

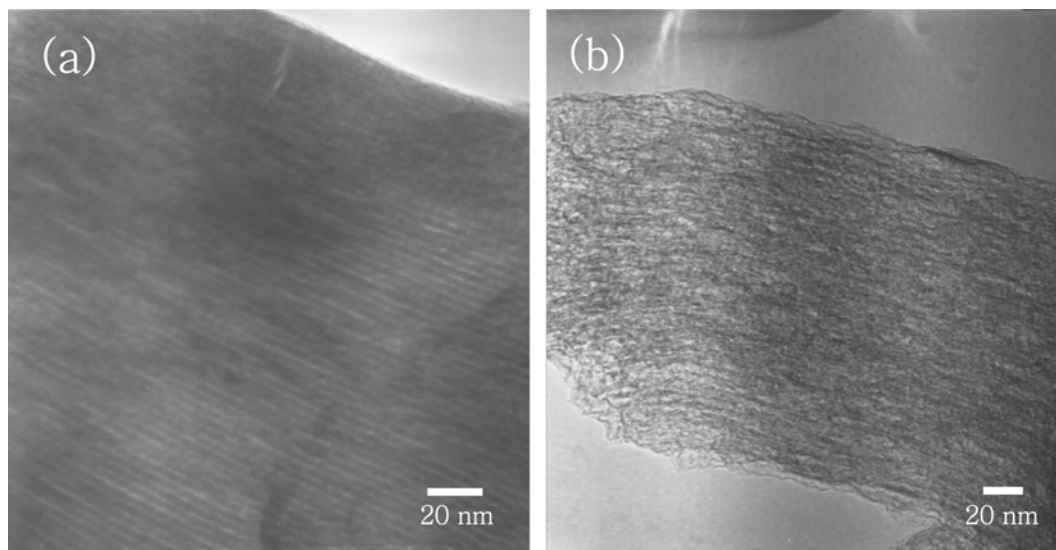


Fig. 4. TEM images of (a) N-MC and (b) PMo_{12} /N-MC.

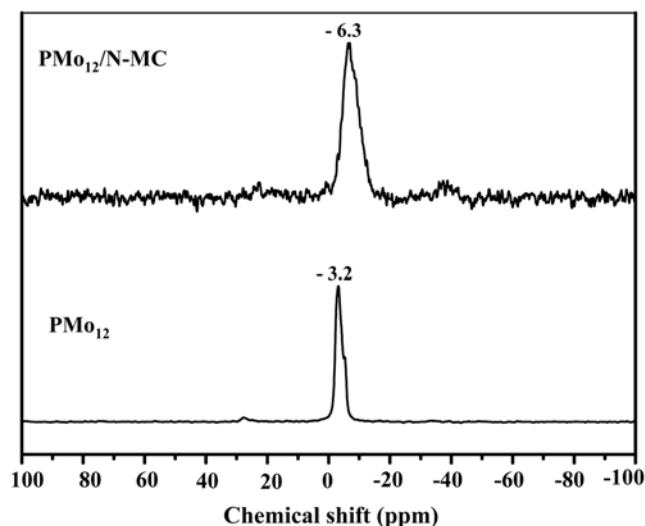


Fig. 5. ^{31}P CP-MAS NMR spectra of unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$.

3. Chemical Immobilization PMo_{12} on N-MC

Chemical immobilization of PMo_{12} on the M-MC support was confirmed by ^{31}P CP-MAS NMR analyses. Fig. 5 shows the solid-state ^{31}P CP-MAS NMR spectra of unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$. Unsupported PMo_{12} showed a chemical shift at $\delta = -3.2$ ppm. This resonance peak corresponds to the structural phosphorus in the PMo_{12} , in good agreement with the previous report [6]. On the other hand, the chemical shift of $\text{PMo}_{12}/\text{N-MC}$ appeared at $\delta = -6.3$ ppm. This result indicates that the surroundings of phosphorous atom were remarkably changed, suggesting that PMo_{12} species were successfully immobilized on the N-MC support via chemical interaction. The chemical immobilization of PMo_{12} on the N-MC support was further confirmed by the shifts of characteristic IR bands of

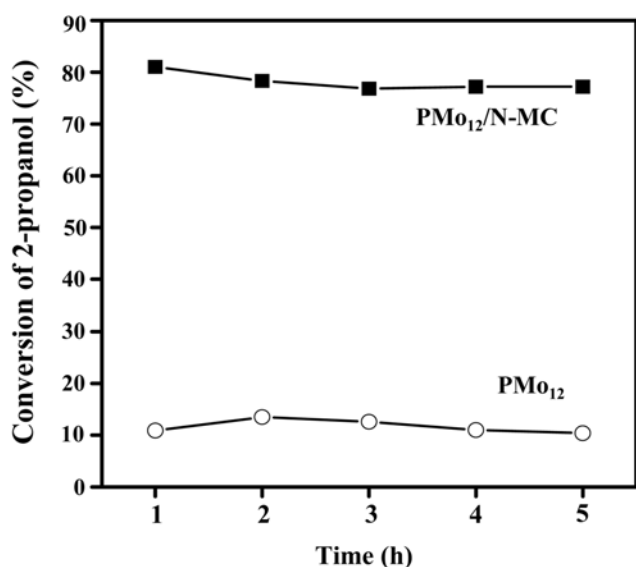


Fig. 6. Conversions of 2-propanol over unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$ catalysts in the vapor-phase 2-propanol conversion reaction at $200\text{ }^{\circ}\text{C}$.

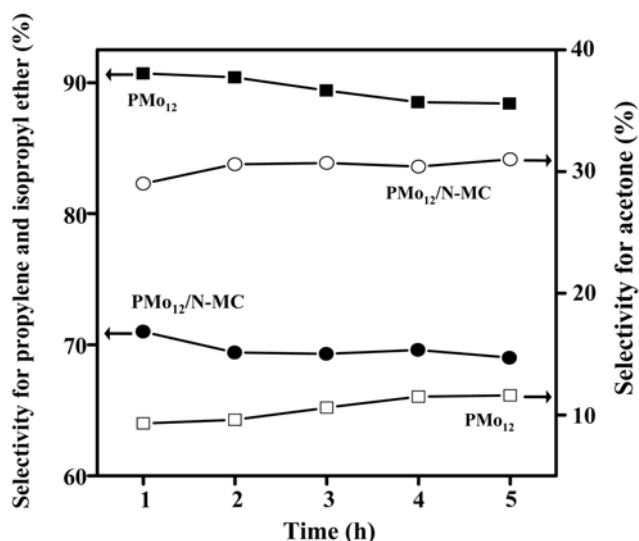


Fig. 7. Selectivities for products over unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$ catalysts in the vapor-phase 2-propanol conversion reaction at $200\text{ }^{\circ}\text{C}$.

$[\text{PMo}_{12}\text{O}_{40}]^{3-}$ in the $\text{PMo}_{12}/\text{N-MC}$, although these are not shown here.

4. Catalytic Activity of $\text{PMo}_{12}/\text{N-MC}$

Fig. 6 shows the conversions of 2-propanol over unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$ catalysts in the vapor-phase 2-propanol conversion reaction. The $\text{PMo}_{12}/\text{N-MC}$ catalyst showed a higher conversion than the unsupported PMo_{12} catalyst. The enhanced catalytic performance of $\text{PMo}_{12}/\text{N-MC}$ was due to the fine dispersion of PMo_{12} species on the surface of N-MC formed via chemical immobilization. Fig. 7 shows the selectivities of products over unsupported PMo_{12} and $\text{PMo}_{12}/\text{N-MC}$ catalysts in the vapor-phase 2-propanol conversion reaction. It is known that propylene (a product of dehydration reaction) and isopropyl ether (a product of dehydration and coupling reactions) are formed by the acid function of HPA catalyst, while acetone (a product of dehydrogenation reaction) is formed by the oxidation catalysis of HPA. As shown in Fig. 7, the $\text{PMo}_{12}/\text{N-MC}$ catalyst exhibited a better oxidation catalytic activity (formation of acetone) and a lower acid catalytic activity (formation of propylene and isopropyl ether) than the unsupported PMo_{12} catalyst. Unsupported PMo_{12} catalyst retains its own acid and oxidation catalytic function. However, PMo_{12} catalyst in the $\text{PMo}_{12}/\text{N-MC}$ was chemically immobilized on the positive site of N-MC by losing the proton. As attempted in this work, it is believed that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ was molecularly and chemically immobilized on the N-MC support as a charge matching component by sacrificing its proton (Brönsted acid site). Therefore, the $\text{PMo}_{12}/\text{N-MC}$ catalyst showed an enhanced oxidation catalytic activity and a suppressed acid catalytic activity compared to the unsupported PMo_{12} catalyst. This implies that the $\text{PMo}_{12}/\text{N-MC}$ served as an efficient oxidation catalyst in this model reaction.

CONCLUSIONS

Nitrogen-containing mesoporous carbon (N-MC) was prepared by a templating method. The surface of N-MC was then modified to have a positive charge, and thus, to provide sites for the immobi-

lization of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. By taking advantage of the overall negative charge of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, PMo_{12} catalyst was chemically immobilized on the N-MC support as a charge compensating component. It was revealed that PMo_{12} species were finely and molecularly dispersed on the N-MC support via chemical immobilization. In the vapor-phase 2-propanol conversion reaction, the PMo_{12} /N-MC showed a higher conversion than the unsupported PMo_{12} . Furthermore, the PMo_{12} /N-MC showed an enhanced oxidation catalytic activity and a suppressed acid catalytic activity compared to the unsupported PMo_{12} . This catalytic behavior of PMo_{12} /N-MC was attributed to the molecularly dispersed PMo_{12} , which was chemically immobilized on the positive site of N-MC by sacrificing the proton. Thus, the PMo_{12} /N-MC served as an efficient oxidation catalyst in the 2-propanol conversion reaction.

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