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Preparation and characterization of heteropolyacid/mesoporous carbon catalyst for the vapor-phase 2-propanol conversion reaction

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Abstract

$H_3PMo_{12}O_{40}$ catalyst was chemically immobilized on the surface modified CMK-3 (SM-CMK-3) support as a charge compensating component, by taking advantage of the overall negative charge of $[PMo_{12}O_{40}]^{3-}$. The supported $H_3PMo_{12}O_{40}$/SM-CMK-3 catalyst was characterized to have high surface area (≈1000 m^2/g) and relatively large pore volume (0.83 cm^3/g). The $H_3PMo_{12}O_{40}$/SM-CMK-3 catalyst was applied to the vapor-phase 2-propanol conversion reaction. The $H_3PMo_{12}O_{40}$/SM-CMK-3 catalyst exhibited higher 2-propanol conversion than the unsupported $H_3PMo_{12}O_{40}$ and the impregnated $H_3PMo_{12}O_{40}$ on CMK-3. Furthermore, the PMo_{12}/SM-CMK-3 catalyst showed the enhanced oxidation activity (acetone formation) and the suppressed acid catalytic activity (propylene formation) compared to the other two catalysts. It is believed that $[PMo_{12}O_{40}]^{3-}$ species were chemically and finely immobilized on the SM-CMK-3 support as charge matching species, and thus, the PMo_{12}/SM-CMK-3 catalyst showed an excellent oxidation activity.

Keywords: Heteropolyacid; CMK-3; Surface modified CMK-3; Immobilization; 2-Propanol

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1. Introduction

Heteropolyacids (HPAs) are early transition metal oxygen anion clusters that exhibit a wide range of molecular sizes, positions, and molecular architectures [1]. Among various HPA structural classes, the Keggin-type HPAs have been widely employed as homogeneous and heterogeneous catalysts for acid–base and oxidation reactions [2–4]. One of the disadvantages of HPA catalysts is that their surface area is very low. To overcome the low surface area, HPA catalysts have been supported on inorganic materials by conventional impregnation method. For example, a number of mesoporous materials have been extensively investigated for this purpose [5–8]. Another promising approach to enlarge the surface area of HPA catalysts is to take advantage of the overall negative charge of heteropolyanions. By this method, HPAs have been immobilized on ion-exchanged resins such as poly-4-vinylpyridine [9] or conjugated conducting polymers such as polyaniline [10] to obtain molecularly dispersed HPA catalysts. However, such an attempt utilizing inorganic supporting materials has been restricted due to the difficulty in forming positive charge on the inorganic materials. Among various supporting materials, porous carbon materials were found to have excellent thermal stability, high surface area, large pore volume, and uniform pore size distribution [11]. If porous carbon materials can be modified to have the positive charge, they can be utilized as excellent supporting materials for HPA catalysts. Porous carbon materials can serve as promising supports in catalysis because their pore structure and morphology can be easily controlled.

In this work, CMK-3 (mesoporous carbon having 2-dimensional pore structure) was synthesized using SBA-15 (mesoporous silica) as a template [12]. CMK-3 was chemically modified to have the positive charge, and thus, to provide the sites for HPA immobilization. $H_3PMo_{12}O_{40}$ (PMo_{12}) catalyst was then immobilized on the surface modified CMK-3 (SM-CMK-3). The supported PMo_{12}/SM-CMK-3 catalyst was applied to the

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model vapor-phase 2-propanol conversion reaction. For the comparison purpose, PMo_{12} catalyst impregnated on bare CMK-3 was also prepared (PMo_{12}/CMK-3).

2. Experimental

Mesoporous silica (SBA-15) was synthesized for use as a templating material for CMK-3 according to the method in a literature [13]. CMK-3 was synthesized as followings. The calcined mesoporous silica was impregnated with a solution of carbon precursor (sucrose) containing sulfuric acid. The resulting slurry was dried for 6 h at 373 K and further dried for 4 h at 433 K, followed by carbonization at 1073 K in a nitrogen stream. The silica template was finally removed using HF solution to yield the ordered mesoporous CMK-3 [12]. Surface modification of CMK-3 was done according to the reported method [14]. CMK-3 was activated with hydrogen stream at 373 K, and then it was successively treated with acetic anhydride, nitric acid, and sulfuric acid. The nitrated CMK-3 was washed with deionized water and dried overnight at 373 K. The nitrated CMK-3 was treated with sodium hydrosulfite (Aldrich) dissolved in an aqueous ammonia solution to yield the aminated CMK-3 (SM-CKM-3). In the preparation of PMo_{12}/SM-CMK-3, 1 g of SM-CMK-3 and 0.15 g of PMo_{12}were dissolved in 50 ml of acetonitrile (Aldrich). The slurry was washed several times with deionized water until the washing solvent became colorless. For the comparison purpose, PMo_{12} catalyst was also supported on bare CMK-3 by impregnation method (PMo_{12}/CMK-3).

N_2 adsorption–desorption isotherms of supports and supported catalysts were obtained with an ASAP-2010 instrument (Micromeritics). Small angle X-ray scattering (SAXS) patterns were recorded on a GADDS apparatus (Bruker) using Cu Kα radiation. Supports and supported catalysts were further characterized by TEM (Jeol, JEM-200CX) and XRD (Mac Science, M18XHF) measurements. Infrared spectra of supports and supported catalysts were obtained with a FT-IR spectrometer (Nicholet, Impact 410).

Vapor-phase 2-propanol conversion reaction was carried out in a continuous flow fixed-bed reactor at an atmospheric pressure. Known amounts of each catalyst were charged into a tubular quartz reactor, and pretreated at 523 K with an air stream (20 ml/min) for 1 h. The catalytic reaction was carried out at 493 K. 2-Propanol (6.55×10^{-3} mol/h) was sufficiently vaporized and fed into the reactor continuously together with air carrier (20 ml/min). In each run, contact time was maintained at 4.6 g-PMo_{12}-h/2-propanol-mole. The product stream was periodically sampled and analyzed with an on-line GC (HP 5890II).

3. Results and discussion

Physical properties of supports and supported catalysts are listed in Table 1. CMK-3 support showed high surface area (≈1400 m^2/g) and large pore volume (1.45 cm^3/g). PMo_{12}/CMK-3 catalyst exhibited slightly lower surface area and pore volume than CMK-3. Surface area and pore volume of SM-CMK-3 and PMo_{12}/SM-CMK-3 were slightly decreased compared to those of unmodified samples. However, SM-CMK-3 support and PMo_{12}/SM-CMK-3 catalyst still retained relatively large surface area and pore volume. The changes in surface area and pore volume of each support after supporting of PMo_{12} imply that PMo_{12} catalyst was successfully supported on each support. PMo_{12} loadings in two supported catalysts were almost the same. Fig. 1 shows the nitrogen adsorption–desorption isotherms of supports and supported catalysts. CMK-3 and PMo_{12}/CMK-3 showed IV type isotherm and H2 type hysteresis loop. On the other hand, however, isotherms patterns of SM-CMK-3 and PMo_{12}/SM-CMK-3 were somewhat different from those of CMK-3 and PMo_{12}/CMK-3. This may be due to partial deformation of SM-CMK-3 caused by the treatment with a strong acidic solution during the modification step.

Table 1
Physical properties of supports and supported catalysts

BET surface area (m^2/g)	Pore	Volume (cm^3/g)	PMo_{12} content (wt.%)
CMK-3	1418	1.45	–
PMo_{12}/CMK-3	1306	1.32	2.1
SM-CMK-3	1116	0.90	–
PMo_{12}/SM-CMK-3	1011	0.83	2.3
Unsupport PMo_{12}	11	–	–

Fig. 2 shows the SAXS patterns of CMK-3 and supported catalysts. Scattering peaks of (1 0 0), (1 1 0), and (2 0 0) appeared in all samples and the ratio of peak positions

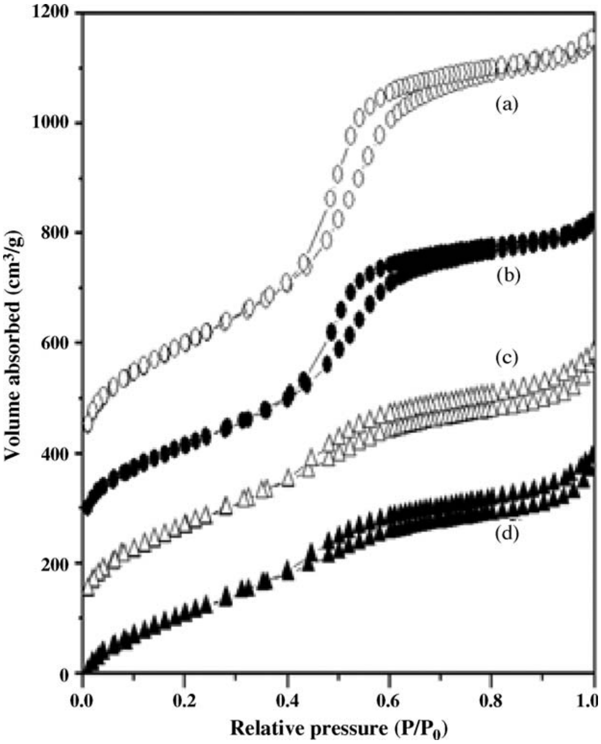

Fig. 1. N_2 adsorption–desorption isotherms of (a) CMK-3, (b) PMo_{12}/CMK-3, (c) SM-CMK-3, and (d) PMo_{12}/SM-CMK-3. The adsorption data for (a), (b), (c), and (d) were offset vertically by 450, 300, 150, and 0 cm^3 (STP)/g, respectively.

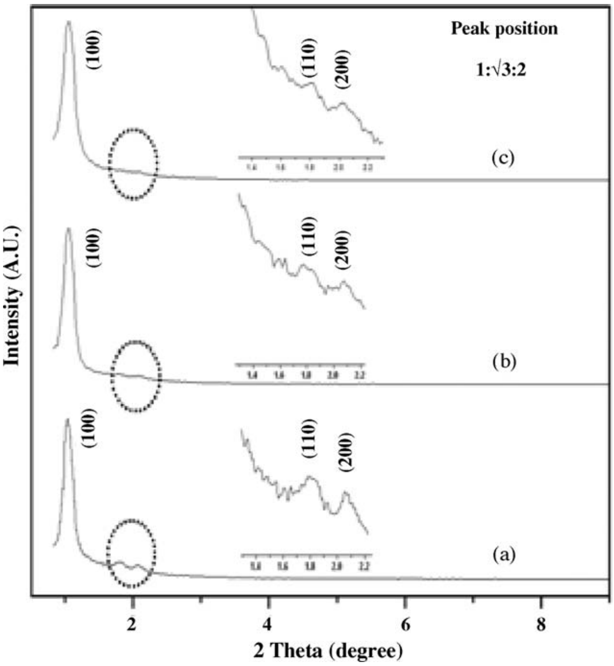

Fig. 2. SAXS patterns of (a) CMK-3, (b) PMo$_{12}$/CMK-3, and(c) PMo$_{12}$/SM-CMK-3.

corresponded to $1{:}\sqrt{3}:2$, indicating a highly ordered 2-dimensional hexagonal type arrangement (*P6mm*). Although PMo$_{12}$/CMK-3 and PMo$_{12}$/SM-CMK-3 showed slightly weak SAXS patterns compared to bare CMK-3, the above result indicates that hexagonal structural orderness of CMK-3 was maintained even after the supporting of PMo$_{12}$ catalyst.

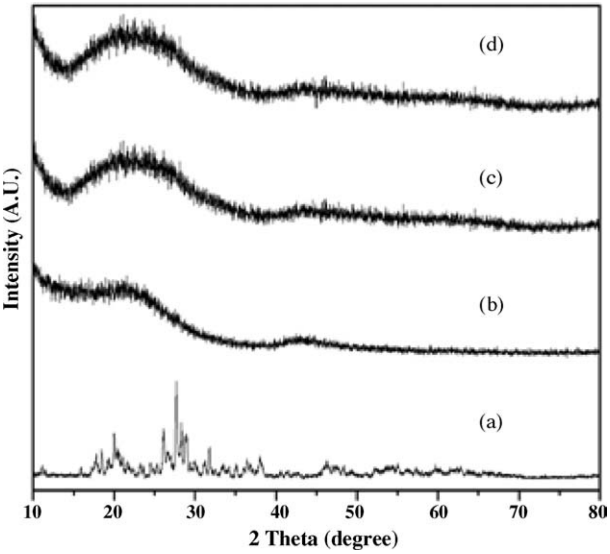

Fig. 4. XRD patterns of (a) unsupported PMo$_{12}$, (b) CMK-3, (c) PMo$_{12}$/CMK-3, and (d) PMo$_{12}$/SM-CMK-3.

Fig. 3 shows the TEM images of PMo$_{12}$/CMK-3 and PMo$_{12}$/SM-CMK-3 catalysts. Regular cylindrical pore structure of CMK-3 was clearly observed even after the supporting of PMo$_{12}$ in both catalysts. Although PMo$_{12}$ species could not be resolved by TEM images, fine dispersion of PMo$_{12}$ catalyst was confirmed by XRD measurements as shown in Fig. 4. Unsupported PMo$_{12}$ catalyst exhibited characteristic XRD patterns, while pure CMK-3 showed no characteristic XRD patterns due to its amorphous nature. It is noticeable that both PMo$_{12}$/CMK-3 and PMo$_{12}$/SM-CMK-3 catalysts showed no characteristic XRD patterns. This demonstrates that PMo$_{12}$ catalyst was not in a crystal state but in an amorphous-like state, indicating fine dispersion PMo$_{12}$ catalyst on CMK-3 and SM-CMK-3 supports.

Immobilization states of PMo$_{12}$ on CMK-3 and SM-CMK-3 were confirmed by FT-IR analyses, as shown in Fig. 5. The primary structure of PMo$_{12}$ could be identified by four characteristic IR bands appearing within the range 700–1200 cm^{-1}. Characteristic IR bands of the unsupported PMo$_{12}$ catalyst appeared at 1064(P–O band), 964(Mo=O band), 868, and 789 cm^{-1} (Mo–O–Mo bands). The CMK-3 support showed no characteristic IR bands within the range 700–1200 cm^{-1}. It is noticeable that the characteristic IR bands of PMo$_{12}$/CMK-3

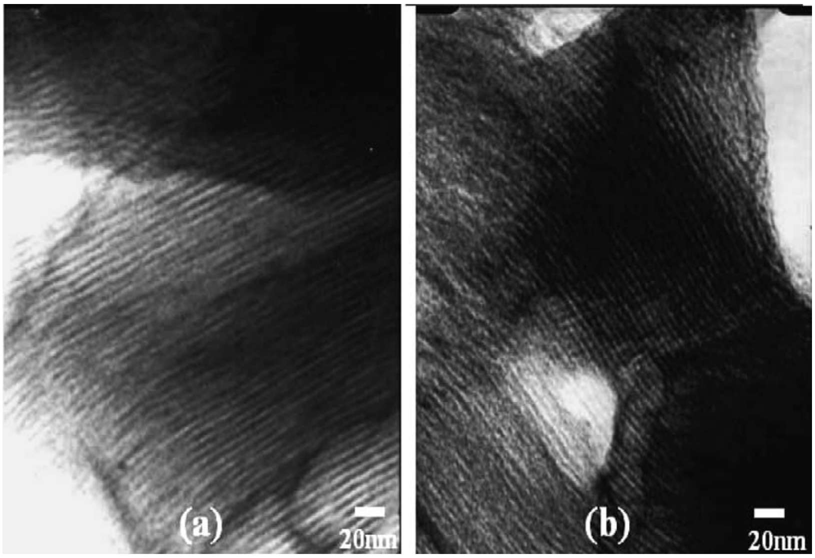

Fig. 3. TEM images of (a) PMo$_{12}$/CMK-3 and (b) PMo$_{12}$/SM-CMK-3.

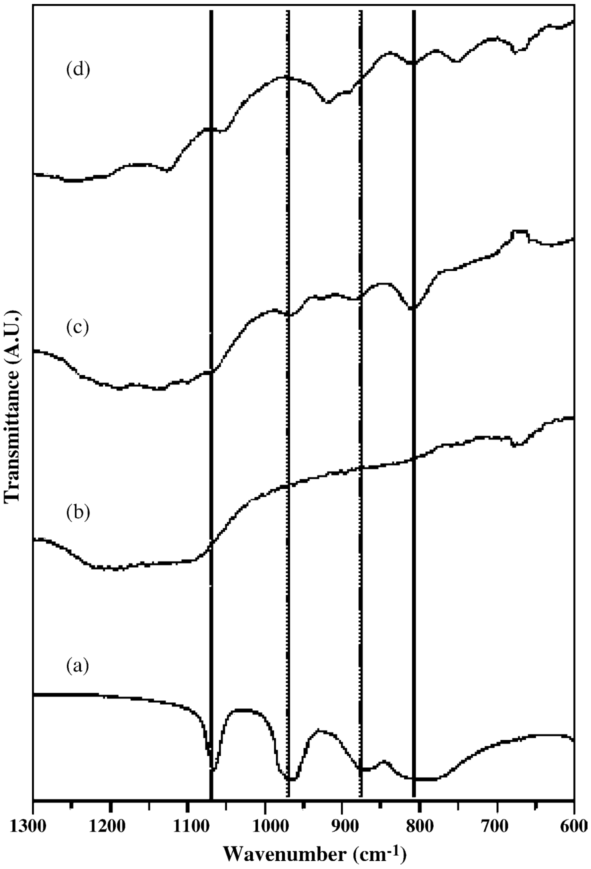

Fig. 5. FT-IR spectra of (a) unsupported PMo_{12}, (b) CMK-3, (c) PMo_{12}/CMK-3, and (d) PMo_{12}/SM-CMK-3.

catalyst appeared at almost the same positions without significant band shifts compared to those of mother catalyst, indicating that PMo_{12} species were physically supported on CMK-3 in the PMo_{12}/CMK-3 catalyst. On the other hand, however, the characteristic IR bands observed in the PMo_{12}/SM-CMK-3 catalyst were not identical to those of unsupported PMo_{12} or PMo_{12}/CMK-3 catalysts. This demonstrates that PMo_{12} species in the PMo_{12}/SM-CMK-3 catalyst were immobilized on the surface of SM-CMK-3 via strong chemical interaction.

Fig. 6 shows the typical catalytic performance of bulk and supported catalysts in the vapor phase 2-propanol conversion reaction. The supported catalysts exhibited excellent catalytic performance than the unsupported PMo_{12}. 2-Propanol conversions were increased in the following order; unsupported PMo_{12} < PMo_{12}/CMK-3 < PMo_{12}/SM-CMK-3. The enhanced catalytic performance of the supported catalysts was due to the fine dispersion of PMo_{12} species on the supports. The difference in catalytic performance between PMo_{12}/CMK-3 and PMo_{12}/SM-CMK-3 catalysts may be due to different level of PMo_{12} dispersion. It is believed that PMo_{12} species were more finely dispersed on the SM-CMK-3 via chemical immobilization than on the CMK-3. Fig. 7 shows the propylene and acetone selectivities over the bulk and supported PMo_{12} catalysts. It is known that propylene is formed by the acid function of HPA catalyst, while acetone is formed by the redox function of HPA [15]. Propylene selectivity increased in the order of PMo_{12}/SM-CMK-3 < unsupported PMo_{12} < PMo_{12}/CMK-3, while acetone selectivity increased in the order of PMo_{12}/CMK-3 < unsupported PMo_{12} < PMo_{12}/SM-CMK-3. The PMo_{12}/CMK-3 catalyst showed the enhanced acid catalytic activity and the suppressed oxidation catalytic activity than the unsupported PMo_{12} catalyst. On the other hand, the PMo_{12}/SM-CMK-3 catalyst showed the enhanced oxidation catalytic activity and the suppressed acid catalytic activity than the unsupported PMo_{12} catalyst. PMo_{12}/CMK-3 is an impregnated catalyst, therefore, it retains both acid and redox function of

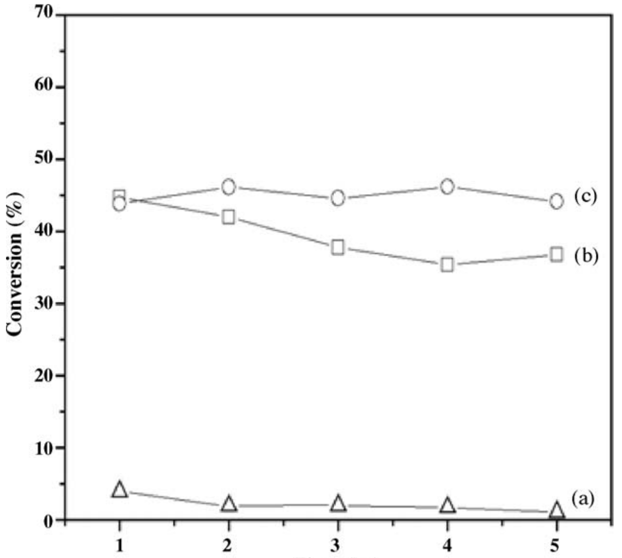

Fig. 6. 2-Propanol conversions over (a) unsupported PMo_{12}, (b) PMo_{12}/CMK-3, and (c) PMo_{12}/SM-CMK-3.

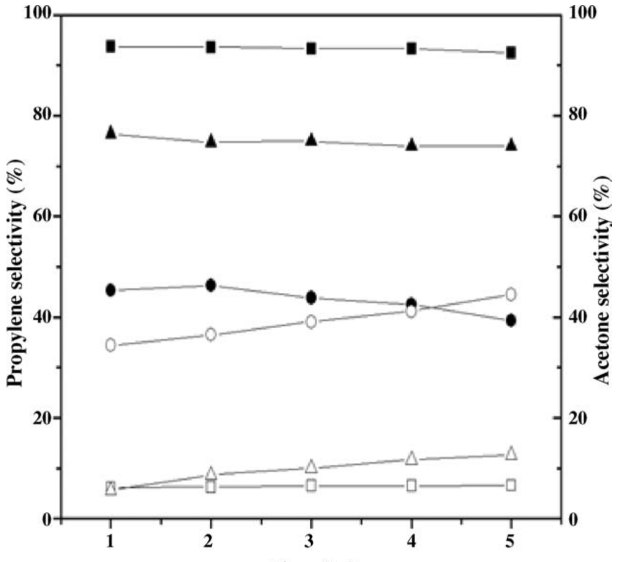

Fig. 7. Propylene and acetone selectivities over unsupported PMo_{12}, PMo_{12}/CMK-3, and PMo_{12}/SM-CMK-3: closed symbol = propylene selectivity, open symbol = acetone selectivity: (△, ▲) = unsupported PMo_{12}, (□, ■) = PMo_{12}/CMK-3, (○, ●) = PMo_{12}/SM-CMK-3.

PMo_{12} catalyst. It is believed that fine dispersion of PMo_{12} in the PMo_{12}/CMK-3 catalyst favorably served to enhance the acid catalytic activity. Unlike the PMo_{12}/CMK-3, the PMo_{12}/SM-CMK-3 is a chemically immobilized catalyst. This implies that the supporting states of PMo_{12} on CMK-3 and SM-CMK-3 were different. As attempted in this work, it is believed that $[PMo_{12}O_{40}]^{3-}$ species were chemically and strongly immobilized on the SM-CMK-3 support as charge matching components by losing protons (acid sties). Therefore, the PMo_{12}/SM-CMK-3 catalyst showed the enhanced oxidation catalytic activity and the suppressed acid catalytic activity compared to the other two catalysts. This implies that PMo_{12}/SM-CMK-3 catalyst may serve as an efficient catalyst for a certain oxidation reaction.

4. Conclusions

By taking advantage of the overall negative charge of $[PMo_{12}O_{40}]^{3-}$, PMo_{12} catalyst was chemically immobilized on the surface modified CMK-3 (SM-CMK-3) as a charge compensating component. The supported PMo_{12}/SM-CMK-3 catalyst was applied to the vapor-phase 2-propanol conversion reaction. For the comparison purpose, PMo_{12}/CMK-3 was also prepared by impregnation method. It was revealed that PMo_{12} was finely dispersed in both PMo_{12}/CMK-3 and PMo_{12}/SM-CMK-3 catalysts. In the 2-propanol conversion reaction, the PMo_{12}/SM-CMK-3 catalyst exhibited higher conversion than the unsupported PMo_{12} and the PMo_{12}/CMK-3 catalysts. Furthermore, the PMo_{12}/SM-CMK-3 catalyst showed the enhanced oxidation activity for acetone formation and the suppressed acid catalytic activity for propylene formation. It is concluded that $[PMo_{12}O_{40}]^{3-}$ species were chemically and strongly immobilized on the SM-CMK-3 support as charge matching species, and thus, the PMo_{12}/SM-CMK-3 catalyst served as an excellent oxidation catalyst (KOSEF R01-2004-000-10502-0).

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