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SHORT COMMUNICATION

Preparation of $H_5PMo_{10}V_2O_{40}$ catalyst immobilized on spherical carbon and its application to the vapor-phase 2-propanol conversion reaction

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Abstract−Spherical carbon (SC) with a diameter of ca. 9 μm was synthesized by a hydrothermal method using sucrose as a carbon precursor. The spherical carbon was then modified to have a positive charge, and thus, to provide a site for the immobilization of $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) catalyst. The $PMo_{10}V_2$ catalyst was immobilized on the surface-modified spherical carbon by taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$. The $PMo_{10}V_2$ catalyst immobilized on the spherical carbon ($PMo_{10}V_2$/SC) was applied to the vapor-phase 2-propanol conversion reaction. In the catalytic reaction, the $PMo_{10}V_2$/SC catalyst showed a higher 2-propanol conversion than the unsupported $PMo_{10}V_2$ catalyst. Furthermore, the $PMo_{10}V_2$/SC catalyst showed enhanced oxidation catalytic activity (formation of acetone) and the suppressed acid catalytic activity (formation of propylene and isopropyl ether) compared to the unsupported $PMo_{10}V_2$ catalyst. The enhanced oxidation activity of $PMo_{10}V_2$/SC catalyst was due to the fine dispersion of $[PMo_{10}V_2O_{40}]^{5-}$ on the spherical carbon formed via chemical immobilization.

Key words: Heteropolyacid Catalyst, Spherical Carbon, Chemical Immobilization, 2-Propanol Conversion

INTRODUCTION

Heteropolyacids (HPAs) have been widely employed as homogeneous and heterogeneous catalysts for acid-base and oxidation reactions [1-8]. A great advantage of HPA catalysts is that their oxidation catalytic properties can be controlled in a systematic way by changing the identity of counter-cation, central heteroatom, and framework polyatom [9-14]. However, a disadvantage of HPA catalysts is that their surface area is very low (<10 m^2/g) [3]. To overcome the low surface area, HPAs have been supported on various inorganic materials by a conventional impregnation method [15-17]. Another promising approach for enlarging the surface area of HPA catalysts is to take advantage of the overall negative charge of heteropolyanion [18-25]. By this method, HPA catalysts have been immobilized on the positively charged supporting materials.

Carbon materials have found successful applications as supporting materials due to their excellent thermal and mechanical stability [26-28]. Among various carbon materials, spherical carbon can be potentially available as a supporting material due to its spherical morphology, non-toxicity, and availability [29]. If spherical carbon is modified to have a positive charge for the immobilization of heteropolyanion, it can serve as an efficient support for HPA catalyst.

In this work, spherical carbon (SC) was synthesized by a hydrothermal method using sucrose as a carbon precursor. The surface of spherical carbon (SC) was then modified to have a positive charge. $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) catalyst was chemically immobilized on the surface-modified spherical carbon (SC) as a charge-matching component, by taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$. The prepared $PMo_{10}V_2$/SC catalyst was characterized and applied to the vapor-phase 2-propanol conversion reaction.

EXPERIMENTAL

Spherical carbon (SC) was prepared by a hydrothermal method using sucrose as a carbon precursor. 61.6 g of sucrose (Sigma-Aldrich) was dissolved in 120 ml of de-ionized water. The solution was then charged into a stainless steel autoclave. The mixture was hydrothermally treated without stirring at 190 °C for 7 h. After the autoclave was cooled to room temperature, the precipitate was filtered and washed with de-ionized water. The solid product was dried in an air stream at 80 °C for 24 h. The resulting solid was finally pyrolyzed in a nitrogen stream at 900 °C for 4 h to yield the spherical carbon (SC).

The schematic in Fig. 1 shows the procedures for the surface modification of spherical carbon (SC) and the subsequent immobilization of $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) on the surface-modified spherical carbon (SC). SC was activated by flowing hydrogen at 200 °C, and then it was successively treated with acetic anhydride (Samchun), nitric acid (Samchun), and sulfuric acid (Samchun). The resulting nitrated SC was washed with de-ionized water and dried at 80 °C for 24 h. It was then treated with sodium hydrosulfite (Samchun) dissolved in an ammonium hydroxide solution (29 wt% NH_3) to form an amine group on the surface. The solid product was washed with de-ionized water and dried at 80 °C for 24 h to yield the surface-modified SC. The surface-modified SC (0.5 g) was reacted with $PMo_{10}V_2$ (0.5 g, Sigma-Aldrich) dissolved in acetonitrile (50 ml, Sigma-Aldrich) for the immobilization of $PMo_{10}V_2$ on the surface-modified SC. The resulting solid product was washed with de-ionized water several times, until the washing solvent became colorless. It was finally dried at 80 °C for 24 h to yield the $PMo_{10}V_2$/SC.

Crystalline phases of unsupported $PMo_{10}V_2$, SC, and $PMo_{10}V_2$/SC samples were examined by XRD measurements (Mac Science, M18XHF-SRA). Surface morphologies of SC and $PMo_{10}V_2$/SC were examined by FE-SEM analyses (Jeol, JSM-6700F). Nitrogen

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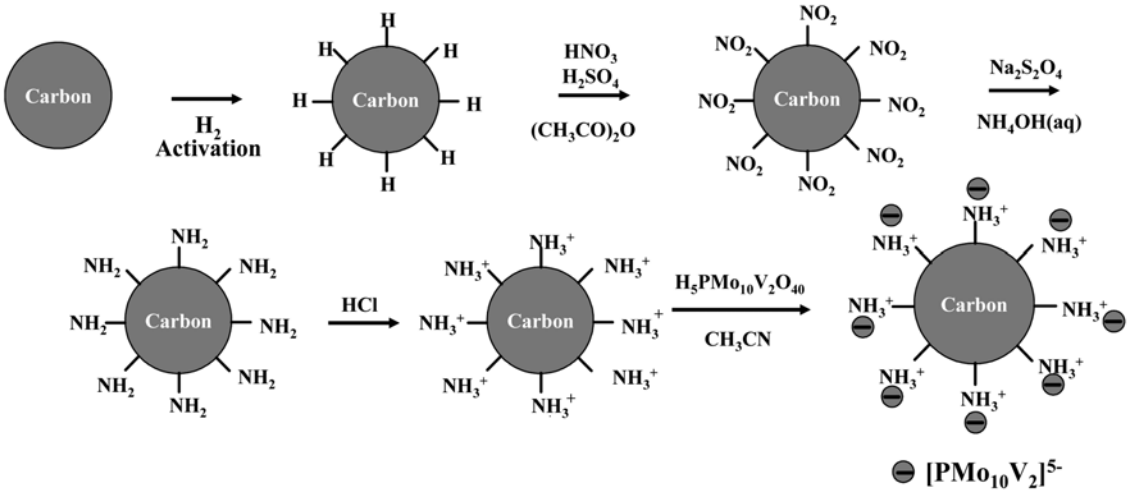

Fig. 1. Schematic procedures for the surface modification of spherical carbon (SC) and the subsequent immobilization of $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) on the surface-modified spherical carbon (SC).

content of surface-modified SC was measured by CHN elemental analysis (EC Instrument, EA 1110). $PMo_{10}V_2$ content of $PMo_{10}V_2$/SC was measured by ICP-AES analyses (Shimadzu, ICP-1000IV). Thermal analyses of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2$/SC were conducted in an air stream by using a TGA-50 instrument (Shimadzu) at a heating rate of 5 °C/min. Chemical states of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2$/SC were examined by ^{31}P CP-MAS NMR (Bruker, AVANCE 400WB, DSX-400) analyses.

Vapor-phase 2-propanol conversion reaction was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. Unsupported $PMo_{10}V_2$ (30 mg on $PMo_{10}V_2$ basis) or $PMo_{10}V_2$/SC (30 mg on $PMo_{10}V_2$ basis) was charged into a tubular quartz reactor, and then it was pretreated with a mixed stream of nitrogen (10 ml/min) and oxygen (10 ml/min) at 240 °C for 1 h. The reaction temperature was maintained at 220 °C. 2-Propanol (1.05×10^{-2} mol/h) was sufficiently vaporized by passing a pre-heating zone and was continuously fed into the reactor together with a mixed stream of nitrogen (10 ml/min) and oxygen (10 ml/min). The contact time was maintained at 2.86 g-$PMo_{10}V_2$-h/2-propanol-mole. The catalytic reaction was carried out for 5 h. The reaction products were periodically sampled and analyzed with a gas chromatograph (HP 5890 II).

RESULTS AND DISCUSSION

The nitrogen content of surface-modified SC was measured by CHN elemental analysis. As expected, no nitrogen was detected in the bare SC sample. The nitrogen content of surface-modified SC was 1.7 wt%, indicating that amine functional groups were successfully formed on the SC via surface modification step. The amine functional group on the surface-modified SC played an important role for the immobilization of $PMo_{10}V_2$. The amount of $PMo_{10}V_2$ catalyst immobilized on the SC was measured to be 2.0 wt%. Thermal analyses conducted in an air stream revealed that the $PMo_{10}V_2$ catalyst was decomposed at around 420 °C. The decomposition temperature of $PMo_{10}V_2$/SC was almost identical to that of unsupported $PMo_{10}V_2$, indicating that the decomposition of $PMo_{10}V_2$/SC was attributed to the thermal decomposition of $PMo_{10}V_2$ component. This result implies that $PMo_{10}V_2$/SC can be utilized as a thermally stable catalyst in the oxygen-involved oxidation reaction which will be performed below 420 °C.

Fig. 2 shows the SEM images of SC and $PMo_{10}V_2$/SC. The images clearly showed that SC with a diameter of ca. 9 μm was successfully prepared by a hydrothermal method. It is interesting to

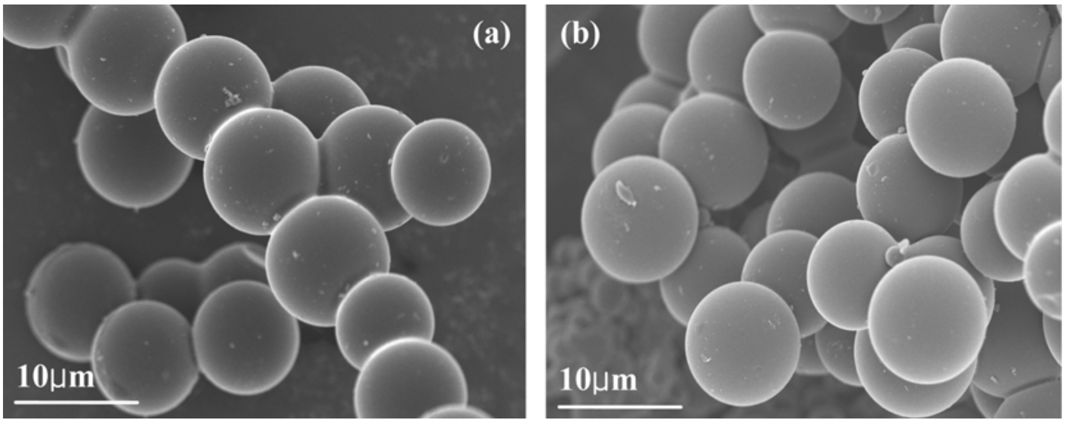

Fig. 2. SEM images of (a) SC and (b) $PMo_{10}V_2$/SC.

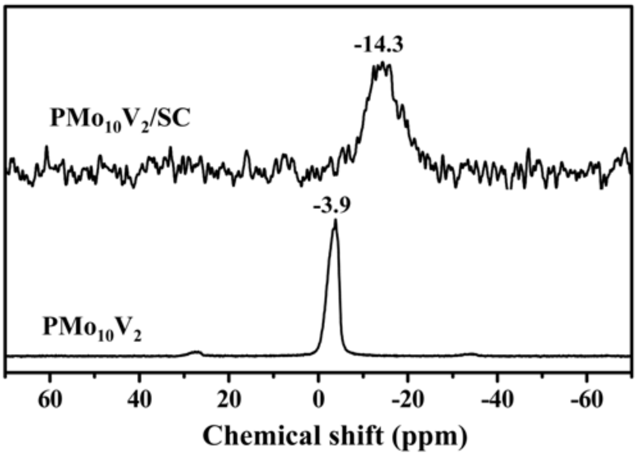

Fig. 3. **^{31}P CP-MAS NMR spectra of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2/SC$.**

note that there was no significant difference in surface morphology between SC and $PMo_{10}V_2/SC$. This indicates that SC was morphologically stable even after the surface modification step and the subsequent immobilization step of $PMo_{10}V_2$. Furthermore, no visible evidence representing $PMo_{10}V_2$ agglomerates was found in the SEM image of $PMo_{10}V_2/SC$, indicating that $PMo_{10}V_2$ catalyst was finely dispersed on the surface of SC.

Fig. 3 shows the ^{31}P CP-MAS NMR spectra of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2/SC$. The unsupported $PMo_{10}V_2$ catalyst showed a chemical shift at $\delta=-3.9$ ppm, in good agreement with a previous report [30]. However, the $PMo_{10}V_2/SC$ catalyst showed a chemical shift at $\delta=-14.3$ ppm. It is believed that the great difference in chemical shift of structural phosphorous between $PMo_{10}V_2$ and $PMo_{10}V_2/SC$ was attributed to the strong chemical immobilization of $PMo_{10}V_2$ on the SC support [31].

Fig. 4 shows the XRD patterns of unsupported $PMo_{10}V_2$, SC, and $PMo_{10}V_2/SC$. The unsupported $PMo_{10}V_2$ catalyst showed the characteristic XRD pattern of the HPA catalyst. On the other hand, the SC exhibited a typical amorphous XRD pattern of carbon materials prepared using sucrose [32,33]. It is noticeable that the $PMo_{10}V_2/SC$ catalyst also showed an amorphous XRD pattern. This result indicates that $PMo_{10}V_2$ species were finely and molecularly dispersed on the SC support, as attempted in this work. It should be noted that the amine functional group on the surface-modified SC efficiently served as an anchoring site for the chemical immobilization of $[PMo_{10}V_2O_{40}]^{5-}$.

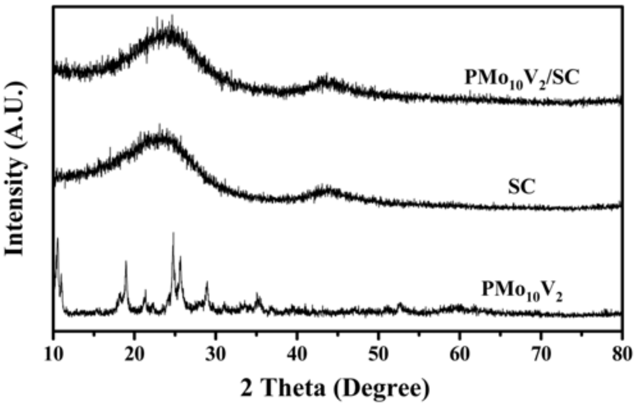

Fig. 4. XRD patterns of unsupported $PMo_{10}V_2$, SC, and $PMo_{10}V_2/SC$.

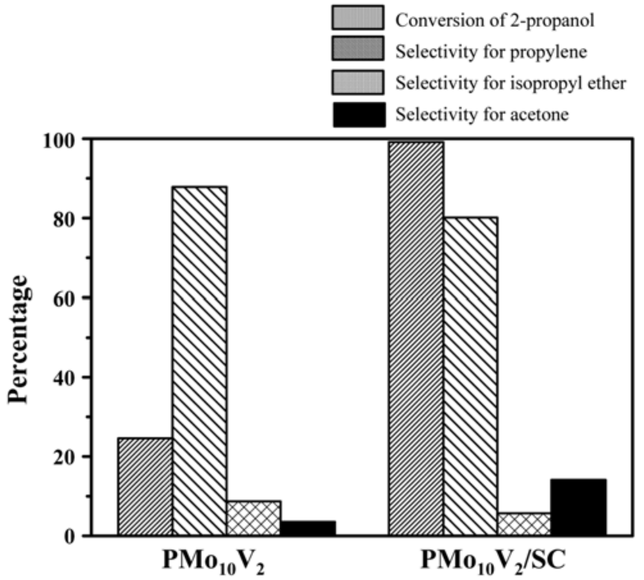

Fig. 5. Catalytic performance of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2/SC$ catalysts in the vapor-phase 2-propanol conversion reaction at 220 °C after 5 h-reaction.

Fig. 5 shows the catalytic performance of unsupported $PMo_{10}V_2$ and $PMo_{10}V_2/SC$ catalysts in the vapor-phase 2-propanol conversion reaction at 220 °C after 5 h-reaction. The $PMo_{10}V_2/SC$ catalyst showed a higher 2-propanol conversion than the unsupported $PMo_{10}V_2$ catalyst. The enhanced catalytic performance of $PMo_{10}V_2/SC$ was attributed to the fine dispersion of $PMo_{10}V_2$ species on the SC support formed via chemical immobilization. It is known that propylene and isopropyl ether are formed by the acid catalysis of HPA catalyst, while acetone is produced by the oxidation catalysis of HPA catalyst [34]. Experimental results revealed that the $PMo_{10}V_2/SC$ catalyst showed the enhanced oxidation catalytic activity (formation of acetone) and the suppressed acid catalytic activity (formation of propylene and isopropyl ether) compared to the unsupported $PMo_{10}V_2$ catalyst. The enhanced oxidation activity of $PMo_{10}V_2/SC$ catalyst was due to the fine dispersion of $[PMo_{10}V_2O_{40}]^{5-}$ on the SC. Thus, the $PMo_{10}V_2/SC$ catalyst served as a selective oxidation catalyst in the 2-propanol conversion reaction.

CONCLUSIONS

Spherical carbon (SC) with a diameter of ca. 9 μm was prepared by a hydrothermal method using sucrose as a carbon precursor. The $PMo_{10}V_2$ catalyst was successfully immobilized on the SC support, by taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$. The amine functional group formed on the surface-modified SC played an important role for the immobilization of $PMo_{10}V_2$. It was found that $PMo_{10}V_2$ was finely dispersed on the SC via chemical interaction. In the vapor-phase 2-propanol conversion reaction, the $PMo_{10}V_2/SC$ catalyst showed a higher 2-propanol conversion than the unsupported $PMo_{10}V_2$ catalyst. Moreover, the $PMo_{10}V_2/SC$ catalyst showed enhanced oxidation catalytic activity and suppressed acid catalytic activity compared to the unsupported $PMo_{10}V_2$ catalyst.

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