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Preparation of $H_5PMo_{10}V_2O_{40}$ catalyst immobilized on nitrogen-containing mesostructured cellular foam carbon (N-MCF-C) and its application to the vapor-phase oxidation of benzyl alcohol

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Abstract

Nitrogen-containing mesostructured cellular foam carbon (N-MCF-C) was synthesized by a templating method using mesostructured cellular foam silica (MCF-S) and polypyrrole as a templating agent and a carbon precursor, respectively. The N-MCF-C was then modified to have a positive charge, and thus, to provide a site for the immobilization of $[PMo_{10}V_2O_{40}]^{5-}$. By taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$, $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) catalyst was chemically immobilized on the N-MCF-C support as a charge-matching component. Characterization results showed that the $PMo_{10}V_2$ catalyst was finely dispersed on the N-MCF-C support via strong chemical interaction, and that the pore structure of N-MCF-C was still maintained even after the immobilization of $PMo_{10}V_2$. In the vapor-phase oxidation of benzyl alcohol, the $PMo_{10}V_2$/N-MCF-C catalyst showed a higher conversion and a higher oxidation activity (formation of benzaldehyde) than the unsupported $PMo_{10}V_2$ and $PMo_{10}V_2$/MCF-S catalysts.

Keywords: Heteropolyacid; Nitrogen-containing mesostructured cellular foam carbon; Chemical immobilization; Benzyl alcohol oxidation

1. Introduction

Heteropolyacids (HPAs) are early transition-metal oxygen anion clusters that have found successful applications in homogeneous and heterogeneous catalysis [1–3]. Among various HPA structural classes, the Keggin [4] HPAs have been used as commercial catalysts [1–3]. The Keggin HPA has a soccer ball shape with a molecular size of ca. 1 nm [5]. One of the great advantages of HPA catalysts is that their acid–base and redox properties can be tuned in a systematic way by changing the identity of counter-cation, central heteroatom, and framework polyatom [1–3].

A disadvantage of HPA catalysts, however, is that their surface area is very low (<10 m^2/g). To overcome the low surface area, HPA catalysts have been supported on various inorganic materials by a conventional impregnation method [6]. 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, HPAs have been immobilized on polymer materials such as poly-4-vinylpyridine [7], polyaniline [8], and polystyrene [9]. Although such an attempt utilizing inorganic supporting materials has been restricted due to the difficulty in forming a positive charge on the inorganic supporting materials, HPAs have also been

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successfully immobilized on inorganic mesoporous materials such as HMS [10], MCM-41 [11], SBA-15 [12], CMK-3 [13], and mesostructured cellular foam silica [14] through a surface modification process.

Mesoporous carbon materials have high surface area, large pore volume, and uniform pore size distribution [15]. In spite of the difficulty in forming a positive charge on the mesoporous carbon materials, mesoporous carbon materials still have merit as catalyst supports due to their excellent thermal stability and controllable textural properties. If mesoporous carbon materials are modified to have a positive charge by an easy method, they can serve as efficient supports for HPA catalyst.

In this work, nitrogen-containing mesostructured cellular foam carbon (N-MCF-C) was synthesized by a templating method using mesostructured cellular foam silica (MCF-S) and polypyrrole as a templating agent and a carbon precursor, respectively. The N-MCF-C was then modified to have a positive charge for the immobilization of $[PMo_{10}V_2O_{40}]^{5-}$. By taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$, $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) catalyst was chemically immobilized on the N-MCF-C support as a charge-matching component. The $PMo_{10}V_2$/N-MCF-C catalyst was characterized and applied to the vapor-phase oxidation of benzyl alcohol.

2. Experimental

MCF-S was synthesized for use as a templating material for N-MCF-C according to the method in the literature [16]. N-MCF-C was synthesized as follows. $FeCl_3$ (1.0 g) dissolved in an aqueous HCl solution (1.5 ml, 1.0 M) was impregnated on the MCF-S (1.0 g) by an incipient wetness method. The yellow-colored slurry was dried at 100 °C in a convection oven. The resulting solid was reacted with pyrrole monomer (0.5 g) at room temperature under vacuum for the polymerization of pyrrole. The composite of MCF-S and polypyrrole was dried at 80 °C, 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 the treatment with HF and HNO_3. After washing the solid with de-ionized water several times, the resulting solid was finally dried at 100 °C in a convection oven to yield the N-MCF-C [17].

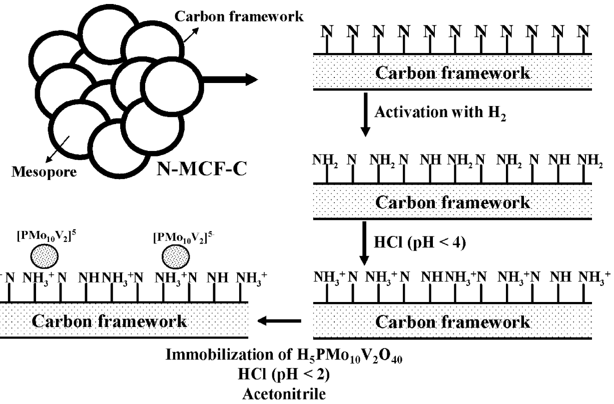

Fig. 1. Schematic procedures for the surface modification of N-MCF-C and the subsequent immobilization of $PMo_{10}V_2$ on the N-MCF-C.

Fig. 1 shows the schematic procedures for the surface modification of N-MCF-C and the subsequent immobilization of $PMo_{10}V_2$ on the N-MCF-C. N-MCF-C (1.0 g) was activated by flowing hydrogen (10 ml/min) at 150 °C for 2 h to create amine groups on the surface of the N-MCF-C. The activated N-MCF-C was then treated with an aqueous HCl solution (pH < 4) for 12 h to form a positive charge. The resulting N-MCF-C was washed with de-ionized water several times, and subsequently, dried overnight at 100 °C to yield the surface-modified N-MCF-C. For the preparation of $PMo_{10}V_2$/N-MCF-C, $PMo_{10}V_2$ (1.0 g) and surface-modified N-MCF-C (1.0 g) were dissolved in acetonitrile (100 ml). The pH of the mixed slurry was maintained below 2.0 using an aqueous HCl solution. The slurry was stirred for 24 h at room temperature for the immobilization of $PMo_{10}V_2$ on the surface-modified N-MCF-C. After the solid product was recovered by filtration, it was washed with de-ionized water several times 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 $PMo_{10}V_2$/N-MCF-C. For comparison, $PMo_{10}V_2$ supported on MCF-S was also prepared by an impregnation method ($PMo_{10}V_2$/MCF-S).

N_2 adsorption–desorption isotherms of support and supported catalyst were obtained with an ASAP-2010 instrument (Micromeritics). Surface areas and pore volumes of the prepared samples were calculated using the BET equation and the BJH model, respectively. Nitrogen contents were determined by CHN elemental analyses (EC Instrument, EA1110). $PMo_{10}V_2$ content in the $PMo_{10}V_2$/N-MCF-C was measured by ICP-AES analyses (Shimadz, ICP-1000IV). Support and supported catalyst were further characterized by TEM (Jeol, JEM-200CX), XRD (Rigaku, D-MAX2500-PC), FT-IR (Nicolet, Impact 410), and ^{31}P CP-MAS NMR (Brunker, AVANCE 400 WB, DSX-400) analyses.

The vapor-phase oxidation of benzyl alcohol was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. Unsupported $PMo_{10}V_2$, $PMo_{10}V_2$/MCF-S or $PMo_{10}V_2$/N-MCF-C (40 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 280 °C for 1 h. Benzyl alcohol (2.90×10^{-3} 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 carrier (10 ml/min). The contact time was maintained at 13.8 g $PMo_{10}V_2$-h/benzyl alcohol-mol. The catalytic reaction was carried out at 260 °C for 5 h. The reaction products were periodically sampled and analyzed with an on-line gas chromatograph (HP 5890 II).

3. Results and discussion

Physical properties and chemical compositions of support and supported catalyst are listed in Table 1. The nitrogen content of N-MCF-C was 3.75 wt%, while that of $PMo_{10}V_2$/N-MCF-C was measured to be 2.86 wt%. The decreased nitrogen content of the $PMo_{10}V_2$/N-MCF-C was due to the loading of