Study of acidic properties of heteropolyacid catalysts supported on various substrates

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Abstract: $H_4SiW_{12}O_{40}$ (HSiW), one of the heteropolyacids with Keggin units structure, was supported on SBA-15, [Al]-SBA-15 and γ-Al_2O_3. The prepared catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption methods and infrared (IR) observation of pyridine adsorption. XRD and N_2 adsorption-desorption results indicated that HSiW supported on SBA-15 and [Al]-SBA-15 maintained the ordered two dimensional hexagonal mesoporous structures. The presence of Brønsted and Lewis acid sites on HSiW-supported samples was confirmed by IR observation of pyridine adsorption. In addition, the dispersion of HSiW on [Al]-SBA-15 was found to be higher than that of non-porous γ-Al_2O_3.

Keywords: Heteropolyacid, Mesoporous silica, Pyridine adsorption.

1. Introduction

Heteropolyacids (HPAs) are molecular metal oxide clusters, and they have been widely used as acid and oxidation catalysts for several reactions[1]. Especially, HPAs with Keggin units represented by $H_4SiW_{12}O_{40}$ (HSiW) and $H_3PW_{12}O_{40}$ (HPW) have strong Brønsted acidity, and show high catalytic activity for a variety of acid-catalyzed reactions in homogeneous and heterogeneous systems[2]. However, the surface area of HPAs is as small as about 5 m^2 g^{-1}. Therefore, any improvement of surface area is necessary to utilize them as solid catalysts. In this study, highly dispersed HPAs on various materials were prepared for overcoming of their small surface area. Moreover, we characterized the effect of the type of supports on their acidic properties.

2. Experimental

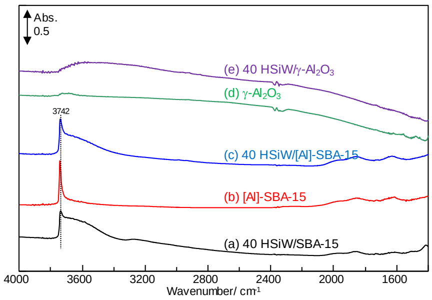
SBA-15 was synthesized by referring to the previous report[3]. [Al]-SBA-15 was prepared as follows[4]. SBA-15 was stirred in sodium aluminate aqueous solution (Si/Al=20) at room temperature for 20 h. The mixture was filtered, washed and dried at 373 K overnight, followed by calcination at 823 K for 5 h. HSiW was supported on SBA-15, [Al]-SBA-15 and γ-Al_2O_3 (JRC-ALO-9) by impregnation methods, and they were calcined at 423 K for 4 h. The prepared catalysts were characterized by XRD, N_2 adsorption-desorption method and IR observation of pyridine adsorption. IR measurement was carried out using an FT/IR-6300 spectrometer (JASCO). Before the IR measurement, about 20 mg of samples pressed into a self-supported disk (20 mm in diameter) was placed in a quartz cell connected to a conventional closed gas circulation system. SBA-15, [Al]-SBA-15 and γ-Al_2O_3 were pretreated at 773 K for 1 h under vacuum conditions and HSiW-supported samples were pretreated at 523 K for 2 h under vacuum conditions before pyridine adsorption. The pretreated samples were exposed to sufficient amount of pyridine at 423 K, and heated at 523 K in vacuum conditions to remove hydrogen-bonded pyridine species. The measurement temperature of IR spectra was 423 K.

3. Results and discussion

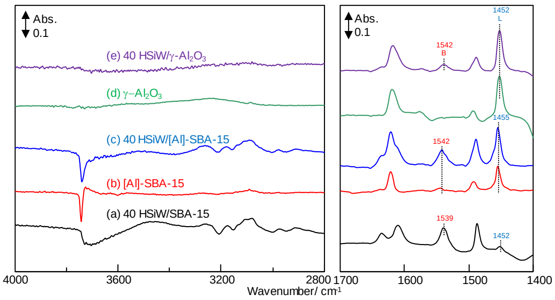
SBA-15 and [Al]-SBA-15 with ordered two dimensional hexagonal mesoporous structures were confirmed by XRD patterns, and HSiW-supported samples maintained the original structures. From results of N_2 adsorption-desorption, BET surface areas of SBA-15 and [Al]-SBA-15 were estimated as 1000 and 818 m^2 g^{-1}, respectively. In addition, the pore diameter and the pore volume did not change before and after supporting HSiW on SBA-15 and [Al]-SBA-15. These results indicate that pore blocking of the samples did not occur.

Acid properties of each catalyst were clarified by IR observation of pyridine adsorption. It is known that the pyridine is adsorbed on acid sites in two ways; receiving proton from Brønsted acid sites to form pyridinium ion and coordination to Lewis acid sites donating electron lone pair on nitrogen. Pyridinium species and the coordinated species are observed at around 1545 and 1450 cm^{-1}, respectively.

IR spectra of (a) 40 HSiW/SBA-15, (b) [Al]-SBA-15, (c) 40 HSiW/[Al]-SBA-15, (d) γ-Al_2O_3 and (e) 40 HSiW/γ-Al_2O_3 are compared in Figure 1. The band at 3742 cm^{-1} was observed on SBA-15, [Al]-SBA-15 and 40 HSiW/[Al]-SBA-15 (spectra (a), (b) and (c)), which are attributed to silanol groups. On the other hand, a broad band at 3700-3200 cm^{-1} was observed only for HSiW-supported samples (spectra (a), (c) and (e)), which are due to $H_5O_2^+$ in HSiW. Figure 2 shows IR spectra of pyridine adsorption on each catalyst. IR observation of pyridine adsorption on 40 HSiW/SBA-15 (Figure 2 (a)) clarified acidic properties of HSiW alone, because acid sites do not exist on SBA-15. Consequently, the band of silanol groups did not change, while that of $H_5O_2^+$ of HSiW decreased producing pyridinium ion species (1539 cm^{-1}). In addition to Brønsted acid sites, a small amount of Lewis acid sites (1452 cm^{-1}) was observed. Brønsted and Lewis acid sites are attributed to $H_5O_2^+$ of HSiW and WO_3 species, respectively. The formation of WO_3 species is considered to be due to the decomposition of a part of HSiW during impregnation. In case of [Al]-SBA-15 (Figure 2 (b)), the presence of both Brønsted and Lewis acid sites was confirmed. Brønsted acid sites are considered to be amorphous silica-alumina like acid sites and bringing hydroxyl group between partially incorporated Al atoms and Si atoms. Lewis acid sites are attributed to Al species outside of amorphous siloxane networks. In case of 40 HSiW/[Al]-SBA-15 (Figure 2 (c)), the amount of Brønsted acid sites increased from those of [Al]-SBA-15, and the bands of $H_5O_2^+$ of HSiW were consumed. We carried out IR observation of pyridine adsorption on γ-Al_2O_3 and 40 HSiW/γ-Al_2O_3 (Figure 2 (d) and (e)) to discuss the effect on type of supports to acidic properties. The presence of only Lewis acid sites on γ-Al_2O_3 were confirmed. In the case of 40 HSiW/γ-Al_2O_3, Brønsted acid sites appeared in addition to Lewis acid sites of γ-Al_2O_3. However, the bands of $H_5O_2^+$ of HSiW did not decrease. It is considered that HSiW supported on γ-Al_2O_3 was condensed because of small surface area about 270 m^2 g^{-1} and pyridine could not be efficiently adsorbed on each Brønsted acid site. On the other hand, the bands of $H_5O_2^+$ of HSiW on 40 HSiW/[Al]-SBA-15 decreased, indicating that HSiW supported on [Al]-SBA-15 is highly dispersed.



Figuer 1. IR spectra of (a) 40 HSiW/SBA-15, (b) [Al]-SBA-15, (c) 40 HSiW/[Al]-SBA-15, (d) γ-Al_2O_3 and (e) 40 HSiW/γ-Al_2O_3.



Figuer 2. IR spectra of pyridine adsorption on (a) 40 HSiW/SBA-15, (b) [Al]-SBA-15, (c) 40 HSiW/[Al]-SBA-15, (d) γ-Al_2O_3 and (e) 40 HSiW/γ-Al_2O_3.

4. Conclusions

HSiW supported on γ-Al_2O_3 was condensed comparing with HSiW supported on [Al]-SBA-15. Thus, the dispersion of HSiW was different depending on the surface area and acidic properties of substrates.

References

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