

Synthesis, characterization, and catalytic activities of tungstophosphoric acid supported on metal oxide modified SBA-15

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Introduction

Heteropoly acids (HPA) are receiving considerable attention due to their interesting catalytic properties for commercial acid catalyzed reactions and because they provide well defined structures for fundamental studies.

However, one of the limitations for HPA's applications in gas phase reactions is its low surface area, which can be overcome by two different approaches. One is to exchange protons with larger sized cations such as Cs, K etc to create micro- and mesoporous structures. This approach may affect the number of available acid sites, and the acid properties of residual protons. A second approach is to support the HPA on high surface area catalyst supports such as silica, alumina etc.

In this presentation, we report catalytic activities of HPA supported on various metal oxide modified SBA-15 supports synthesized using a novel atomic layer deposition method. Specifically, the morphological variance of the supports was minimized so that the effects of support identify on the catalytic activity of supported HPA could be systematically studied. The physical and chemical properties of HPA were studied by high resolution TEM, solid state ³¹P-NMR, and FTIR. The catalytic properties were evaluated using gas phase 2-butanol dehydration as a probe reaction.

Experimentals

The SBA-15 used for this work was synthesized using a previously reported protocol, and has a surface area of ~860m²/g and an average pore size of 7 nm after calcining at 500°C for 4 hours. Metal oxide modified SBA-15 samples were prepared using a solution based atomic layer deposition method described in our previous papers [1,2]. We prepared SBA-15 samples with their surfaces modified by aluminum, titanium and zirconium oxides. H₃PW₁₂O₄₀ (HPA Fluka, 99.9%) was dissolved in methanol and impregnated on both the metal oxide modified- and parent-SBA-15 samples using an incipient wetness method. The amount of HPA in the methanol solution was chosen to provide 30wt% HPA on the supports. 2-butanol dehydration on these catalysts was studied at 70°C in a quartz flow reactor.

Results and Discussion

High resolution TEM images of HPA directly supported on SBA-15 shows agglomeration of HPA inside the mesopore channels. On the other hand, HPA supported on Al₂O₃ modified SBA-15 exhibits bimodal distributions of HPA, with a small fraction of the HPA forming large agglomerants, similar to that of HPA/SBA-15, with the rest being highly dispersed clusters. Solid state ³¹P-NMR spectra of HPA/SBA-15 and HPA/MOx/SBA-15 (M

= Al, Ti, Zr) are quite different. HPA/SBA-15 shows only a single peak at ~ -15ppm which was assigned to the intact Keggin structure of HPA due to a lack of significant interaction with the SiO₂ surface. However, HPA/MOx/SBA-15 samples exhibit a main peak at ~ 13 ppm which is due to the interaction of the Keggin-structured HPA with the metal oxide modified surface, and a relatively small peak at ~-15ppm. *In-situ* pyridine titration experiments suggest that the peak at ~13 ppm is *not* due to partial decomposition of the HPA Keggin structure, a process that typically leads to formation of the lacunary structure, H₇PW₁₁O₃₉.

Figure 1 shows catalytic activity and selectivity of the 2-butanol dehydration reaction for HPA catalysts supported on oxide modified SBA-15. The TOF of HPA/SBA-15 is very high over the entire conversion range and actually increases with conversion. However, HPA supported on oxide modified SBA-15 show a decrease in TOF with increasing conversion and lower activity than HPA/SBA-15. The trans- and cis-2-butene ratio are also different between the HPA/SBA-15 and HPA/MOx/SBA-15 catalysts. These selectivity changes with oxide modification of the surface of mesoporous silica suggest that the mechanisms of 2-butanol dehydration over these two catalysts may be different. These activity and selectivity changes may be attributable to acidity changes of supported HPA due to the surface modification of mesoporous silica by metal oxides.

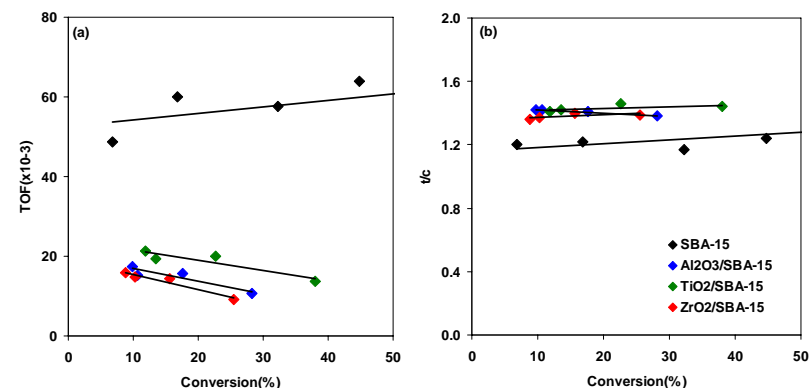


Figure 1. Changes in the TOF (a) and trans/cis 2-butene ratio (b) with 2-butanol conversion on HPA supported on (♦) SBA-15, (♦) TiO₂/SBA-15, (♦) Al₂O₃/SBA-15 and (♦) ZrO₂/SBA-15.

Significance

The results clearly indicate how the catalytic activity and selectivity of HPA can be tailored by modifying the anchoring phase of the mesoporous support.

References

1. Ja Hun Kwak, Jose E. Herrera, Jian Zhi Hu, Yong Wang and Charles H.F. Peden, *Appl. Catal. A* **300** 109 (2006).
2. Jose E. Herrera, Ja Hun Kwak, Jian Zhi Hu, Yong Wang, Charles H.F. Peden, Josef Macht, and Enrique Iglesia, *J. Catal.* **239** 200 (2006).