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COMMUNICATIONS

Published on Web 10/11/2006

Sulfated and Phosphated Mesoporous Nb Oxide in the Benzylation of Anisole and Toluene by Benzyl Alcohol

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Acid catalyzed conversions of hydrocarbons have been studied for several decades. Because of the environmental hazards associated with the use of liquid acids, much effort has been put into developing more environmentally friendly solid acids to perform the same function. Solid acids are mineral oxides such as sulfated zirconia that contain both Lewis and Brønsted acid sites. These materials are used in the isomerization of alkanes and other petrochemical processes such as alkylation of aromatics and hydrocarbon cracking. Isomerization of linear hydrocarbons is performed commercially using solid Pt/chlorided Al_2O_3 catalysts in the case of *n*-butane (UOP Butamer process or BP process), and Pt/mordenite zeolite (Shell Hysomer) in the case of C5/C6 alkanes.[1] Trace amounts of transition metals such as Fe, Mn, or Pt[2] can promote isomerization by sulfated zirconia to the extent that the catalyst performs at room temperature or lower, rivaling the performance of liquid acid agents[2]. Despite this high activity, sulfated zirconia has two major problems. These are (a) the low surface area and porosity of the material and (b) rapid deactivation owing to build up of carbonaceous deposits on the oxide surface. Thus, a higher surface area transition metal oxide catalyst with larger pores, resistant to blockage by carbonaceous deposits, is required. While the tailoring of superacidity into mesoporous silica has been thwarted by deactivation and instability to acids, MCM-41 has been used as a support for sulfated zirconia,[3] although extension to more active Fe/Mn doped systems has not yet been reported. Al-Daous et al.[4] described the synthesis 3-d ordered macroporous sulfated zirconia with ~120 m^2/g surface area that shows catalytic activity for *n*-butane isomerization. Mesoporous phosphated zirconias with high surface acidity have also been studied by Wong and Ying, although competing layered phases were observed under the conditions of study.[5] Because of the ease of preparation, enormous surface areas (400−900 m^2/g), controlled pore sizes, and accessible variable oxidation states, amine-templated mesoporous Nb (Nb-TMS1) and Ta oxides (Ta-TMS1)[6] are ideal catalyst materials.[6] Nb and Ta oxides exhibit special properties such as high stability, strong metal support interaction (SMSI), and potential for the formation of unique mixed metal oxides, as well as variable acidic properties, crucial to alkane isomerization and alkylation reactions.[7] Hydrated Nb and Ta oxides are highly acidic in the amorphous form,[8] while partially hydrated Nb oxide, calcined at moderate temperatures, is an effective solid acid catalyst. These properties can be maintained even in the presence of water.[9] Nb oxides pretreated with phosphoric or sulfuric acid are solid acid catalysts with a high ratio of Lewis acidity to Brønsted acidity.[10,11] Generally, Lewis acidity is found in all of the supported Nb oxide systems, while Brønsted acid sites are only detected in niobia supported on alumina and silica.[12] Precious metal dopants improve the activity of Nb and Ta oxides in many hydrocarbon reactions while maintaining their high selectivity.[13] Herein we provide a report of the synthesis, characterization, and catalytic properties of mesoporous sulfated and phosphated Nb oxides. The catalytic activity in the benzylation of anisole is studied and compared to standard Nb phosphate and sulfate acid catalysts.

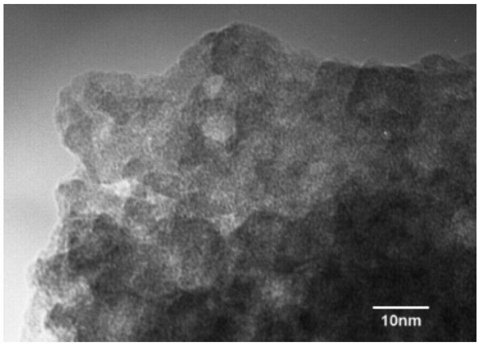

Figure 1. TEM image of sulfated mesoporous Nb oxide synthesized with a dodecylamine template.

The synthesis of niobium oxide molecular sieve (Nb-TMS1) was successfully achieved by using the ligand-assisted liquid crystal templating approach; the optimized ratio of dodecylamine-to-Nb-$(OEt)_5$ used was 0.3:1.[6] The as-synthesized samples were further treated with 1 M sulfuric acid or phosphoric acid (in methanol solution) separately to obtain mesoporous sulfated and phosphated Nb oxides. Elemental analyses showed that the samples were 1.15 wt % P and 2.03 wt % S for the phosphated and sulfated samples, respectively.

Figure S1 shows the XRD patterns of pure Nb oxide and sulphated and phosphated Nb oxides. The strong reflection at $d = 32$ Å in all samples demonstrates the retention of the mesoporous structures after acid treatment. Nitrogen adsorption/desorption measurements (Figure S2) show a typical type IV isotherm for the sulfated and phosphated materials, further confirming that the mesoporous structure was retained. This stability to acid is surprising considering that mesoporous silica and alumina lose their pore structure under these conditions. Figure 1 shows a transmission electron micrograph (TEM) of mesoporous Nb oxide treated with sulfuric acid, clearly illustrating the wormhole pore structure of this material. It can be estimated from the image that the average pore size of H_2SO_4/Meso Nb is around 20 Å.

The FTIR (Fourier transform infrared, Figure S3) analysis of the spectra of pyridine adsorption show that Brønsted (1540 cm^{-1}) and Lewis (1450 cm^{-1}) acid sites coexist in a roughly 50:50 mixture on the surfaces of the parent material and that the sulfated and phosphated materials exhibit a strong dominance of Brønsted sites. This distribution of acid sites is unusual from the standpoint of bulk niobia (see above),[12] and demonstrates the unique nature of

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10.1021/ja0647147 CCC: $33.50

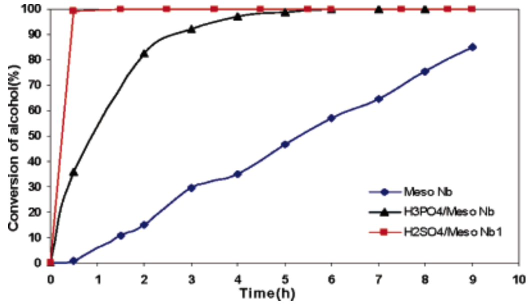

Figure 2. Percent conversion of benzyl alcohol in benzylation of anisole catalyzed by different mesoporous Nb oxides.

the inner surface of the Nb oxide mesostructure. To further probe the surface acidity of these mesoporous Nb oxides, the Hammett acidity and *n*-butylamine titration methods[14] were employed.

Commercially available bulk niobium pentoxides were used here as standards to gauge the effect of the mesoporous structure on acidity (Table S1, S2). From these data it is clear that bulk niobia possesses only very weak acidic sites on the surface ($pK_a = +3.3$), even for the sulfated and phosphated samples ($pK_a = -3.0$).

In contrast, pure mesoporous Nb oxide has a surprising $H_o < -6.6$, and after being treated with 1 M sulfuric or phosphoric acid, its H_o value can reach as low as −8.2, equal to 90% sulfuric acid.[14] Table S2 shows the *n*-butylamine titration data for these materials. The sulfated mesoporous material possesses 10 times more total Lewis and Brønsted acid sites (31.78 mmol/g) than the parent (2.478 mmol/g) or phosphated (3.086 mmol/g) oxides, and almost 100 times more acid sites than the bulk samples (0.024−0.338 mmol/g). The higher BET surface areas (Table S3) of the mesoporous materials can account for some of this difference, although it is also clear that sulfate is more effective than phosphate in generating surface acid sites.

The catalytic activities of these mesoporous Nb oxide materials and bulk Nb oxides were evaluated in the benzylation of anisole with benzyl alcohol in liquid phase at reflux temperature of the mixture[10a] (Figure 2). These relatively bulky substrates were used to illustrate the diffusion advantages of the mesoporous system. Bulk Nb_2O_5 show moderate catalytic activities similar to those reported by Morais et al.[10a] (Figure S4). The untreated mesoporous Nb oxide has an activity of ca. 8 times (80% in 9 h) that of the sulfated bulk material (10% in 9 h), while the phosphated mesoporous sample possesses an activity almost 20 times higher than this value. The best results were achieved with the sulfated mesoporous oxide, which showed 100% conversion in only 30 min. This activity is ca. 200 times greater than that of the sulfated bulk oxide, and can be attributed to the higher acid strengths, greater number of acid sites, and more ideal diffusion properties in the mesoporous sample. Since the phosphated and sulfated materials possess a similar strength and distribution of acid sites, the greater activity of the latter over the former is likely due to the greater number of acid sites in the sulfated material. This material also showed >50 times greater activity than the phosphated or parent mesoporous sample in the benzylation of toluene (Figure S5). A mixture of products was obtained in all cases, and surface areas of catalyst ca. 10 m^2/g after reactions and >12 wt % C indicated that rapid polymerization of the neat reactants may have occurred over the course of the reaction, resulting in pore blockage. This excess C could not be washed out. The S content droped in the used catalyst to ca. 0.5%, and the catalyst could not be reused. To offset the effects of sulfate leaching and formation of polymers, further optimization of reaction conditions is obviously necessary.

Amberlyst 15 and MCM-41 were chosen as standards to compare the catalytic activities in this study. The results showed that Amberlyst 15 possesses roughly 1.5 times higher activity than sulfated mesoporous Nb oxide, while MCM-41 has no activity at all. Our catalyst is also three times more active in this reaction than $SiO_2{-}Si{-}SCF_3$.[16] Since our material has tunable pores in the 15−30 Å range, it is anticipated that it may find applications in size and shape selective acid-catalyzed reactions for molecules too large to fit in zeolite pores, yet small enough that the macroporous (200−300 Å) structure of Amberlyst 15 would have no effect on the steric profile of the reaction.

In summary, a series of high surface area mesoporous niobium oxide materials with a range of acidity of H_o value from −6.6 to −8.2 were prepared and screened for activity in the acid-catalyzed benzylation of anisole. The sulfated material showed the highest activity, almost 200 times greater than bulk sulfated standard. The high activities were attributed to the mesoporosity and increased concentration of Brønsted sites on the surface of the mesoporous channels.

Acknowledgment. The authors wish to acknowledge NSERC for the financial support of this research. We are also grateful to Haining Liu for the artwork of reaction and Ahmad Hamaed for the MCM-41 sample.

Supporting Information Available: Detailed experimental procedure, power X-ray diffraction patterns, N_2 adsorption/desorption isotherm and FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0647147