Alkylation

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Sulfated Mesoporous Tantalum Oxides in the Shape Selective Synthesis of Linear Alkyl Benzene**

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Linear alkylbenzenes (LAB), the primary intermediates in detergent industry, are commercially manufactured by the alkylation of benzene with C_{10-14} *n*-alkenes.[1–3] Among LAB isomers, 2-phenyl isomers are the most favorable starting materials for the production of ecofriendly domestic and industrial detergents because of their high solubility and biodegradability.[4] The development of catalysts with a high selectivity to 2-phenyl isomers in benzene alkylations is an area of great interest. The alkylation of benzene with olefins proceeds through a carbonium ion mechanism.[5] The relative stabilities of the formed carbonium ions increase with the carbon number towards the center of olefin chains. When homogeneous catalysts such as HF or $AlCl_3$ are used, a thermodynamic mixture of LAB isomers is always obtained. In addition to their low selectivity to the desired 2-phenyl isomers, the use of highly corrosive and toxic HF or $AlCl_3$ poses disposal problems. Considerable efforts have been made to carry out alkylation reactions over environmentally friendly solid acid catalysts.[6–11] Strength, distribution and number of acid sites, surface area, pore size, geometry and pore size distribution, and hydrogenation/dehydrogenation ability of solid acid catalysts are the key factors that determine their activity and selectivity in alkylation reactions. Studies on the alkylation of benzene with 1-dodecene over FAU, BEA and EMT zeolites showed that the selectivity towards the least bulky 2-phenyldodecane increased with an increase of porous constraints, while activity decreased due to diffusion limitation in the channels.[12] The very low activity of H-ZSM5 indicated that its channels did not provide enough space for the formation of the potential bulky LAB isomers. The larger pore openings of H-USY improved the diffusion of reactants and products, leading to 100% conversion, but lower 2-phenyldodecane selectivity (25.5%).[13]

Mesoporous materials exhibiting surface areas from 300–2000 $m^2 g^{-1}$ and controlled pore sizes offer high reaction rates and overall efficiency because of a greater number of available surface sites per gram of catalyst and better diffusion rates. Furthermore, the selectivity to desired products can be tuned by optimizing the pore size of mesoporous catalysts. The monoalkylation selectivity for benzene alkylations was significantly enhanced to 89.9% when $AlCl_3$ was grafted onto mesoporous molecular sieves.[14] Shape selective synthesis of LAB has been carried out over AlMCM-41/Beta zeolite composites, which combined the advantages of both microporous and mesoporous materials.[15] Though a high 2-phenyldodecane selectivity (76%) was achieved, the upper conversion limit was only 48% even at 120°C after 2 h.

Nb and Ta oxides exhibit special properties such as high stability, variable oxidation states useful in tailoring catalytic properties, as well as variable acidic properties crucial to acid-catalyzed reactions. For example, niobic acid is an active catalyst for the alkylation of benzene with methanol and the catalytic activity is markedly enhanced when the catalyst was treated with a dilute phosphoric acid solution.[16,17] Because of their high surface area (400–900 $m^2 g^{-1}$) and controlled pore sizes (20–100 Å),[18–20] mesoporous Nb and Ta oxide could be potential catalysts for alkylation reactions and rival those of non-porous Nb and Ta oxides. In recent studies from our group, sulfated mesoporous Nb oxide showed extremely high catalytic activity, almost 200 times greater than sulfated bulk oxide in the benzylation of anisole with benzyl alcohol.[21] Mesoporous Ta oxide is more thermally stable[22] and thus shows even greater promise as a catalyst than its Nb counterpart. Herein, we report the catalytic properties of sulfated mesoporous Ta oxides for the alkylation of benzene with bulky olefins.

Mesoporous C_{12}-Ta oxide was prepared using the ligand-assisted templating approach with 1-dodecylamine surfactant. The sulfated samples were produced by treating the template-free Ta oxides with sulfuric acid. The (100) reflection in the XRD pattern of sulfated mesoporous C_{12}-Ta oxide demonstrates the retention of the mesoporous structure after sulfuric acid treatment. The type IV N_2 adsorption/desorption isotherms further confirmed the confined mesoporous structure in the sulfated sample. The BET surface area was found to be reduced from 582.7 $m^2 g^{-1}$ to 292.2 $m^2 g^{-1}$ by sulfuric acid treatment.

The Hammett acidity and acid amounts of Ta catalysts are summarized in Table 1. Sulfuric acid treatment leads to the increase in both acid strength and acid amount of mesoporous C_{12}-Ta oxide, which are essential to alkylation reactions. The FT-IR spectrum in Figure 1 shows that the sulfated mesoporous C_{12}-Ta oxide possesses mainly Brønsted-acid sites (1538 cm^{-1}) with a smaller number of Lewis-acid sites (1448 cm^{-1}), while Lewis-acid sites are dominant on H-Y and H-ZSM5 zeolites.

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Table 1: Hammett acidity and acid amount of solid acid catalysts.

Catalyst	H_0	Acid amount [mmol g^{-1}]
Meso C_{12}-Ta	−6.6	0.40
Meso SO_4^{2-}/C_{12}-Ta	−8.2	19.8
Meso C_{12}-Nb	−6.6	2.48
Meso SO_4^{2-}/C_{12}-Nb	−8.2	31.78
H-Y zeolite	−6.6	1.55
H-ZSM5	−4.4	16.1

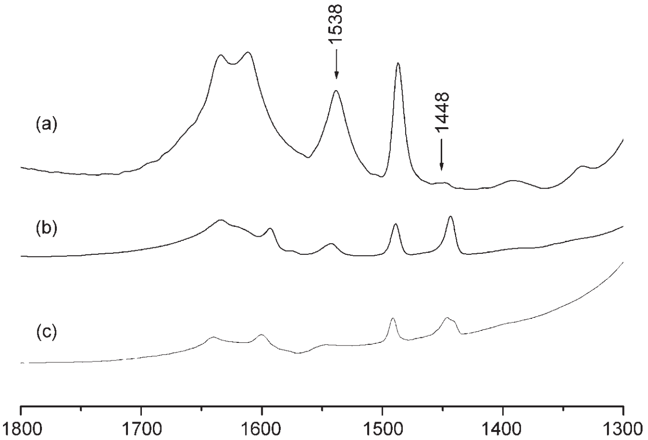

Figure 1. FT-IR spectra of pyridine adsorbed on a) sulfated mesoporous C_{12}-Ta oxide, b) H-Y and c) H-ZSM5 zeolites.

The catalytic properties of sulfated mesoporous C_{12}-Ta oxide were evaluated in terms of olefin conversion and the selectivity towards 2-phenyl isomers. At 80 °C and a benzene/olefin molar ratio of 10:1, no oligomerization of 1-dodecene was observed and only monoalkylated phenyldodecanes were detected. As shown in Figure 2, 100 % 1-dodecene conversion was achieved within 0.5 h. However, the conversion was only 1.2 % over sulfated mesoporous C_{12}-Nb at 0.5 h, despite of larger number of relatively strong acid sites. The reason for this is not understood, and cannot be rationalized by the acid strength data in Table 1. Recent work in our group on the ^{17}O NMR of mesoporous Nb oxide showed a much more highly ordered crystal structure in the walls of this material than its Ta counterpart, which may account for the observed difference in catalytic behavior.[23] The alkylation reaction is dependent on the chemisorption of reactants, surface reaction and desorption of products on the internal pore surface of solid acid catalysts, which are determined by their pore structures and sizes. GC results showed that all possible phenyldodecane isomers were formed. In contrast to homogeneous catalysts, the non-attainment of thermodynamic equilibrium over solid acid catalysts leads to a more favorable isomer distribution. As shown in Figure 3, the selectivity towards phenyldodecane isomers remains unchanged even after 6.0 h when sulfated mesoporous Ta oxide was employed as catalyst. This suggests that it is difficult for the reaction system to reach thermodynamic equilibrium due to the limited diffusion of bulky phenyldodecane isomers in the mesoporous channels.

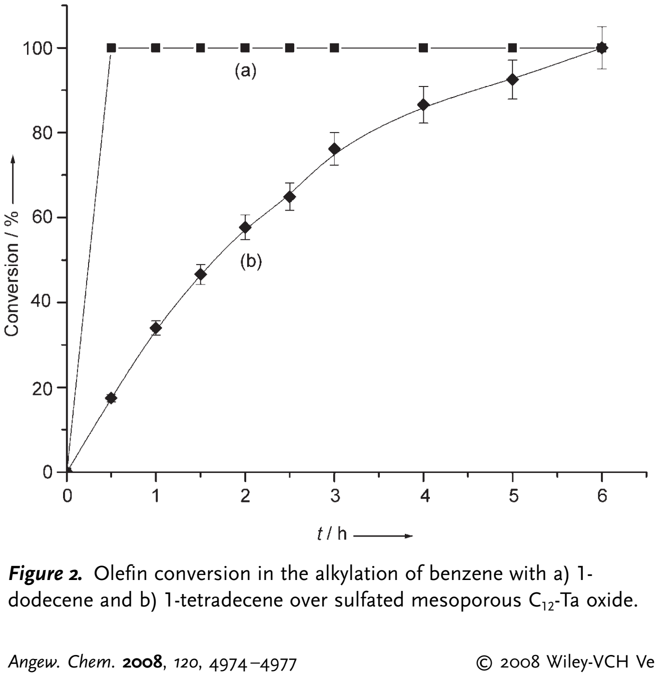

Figure 2. Olefin conversion in the alkylation of benzene with a) 1-dodecene and b) 1-tetradecene over sulfated mesoporous C_{12}-Ta oxide.

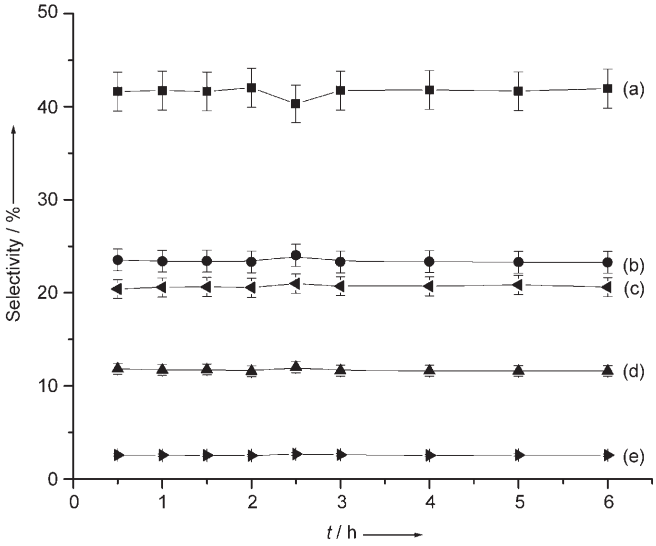

Figure 3. Distribution of phenyldodecane isomers over sulfated mesoporous C_{12}-Ta oxide as a function of reaction time. a) 2-phenyldodecane, b) 3-phenyldodecane, c) 5-phenyldodecane, d) 4-phenyldodecane, and e) 6-phenyldodecane. Reaction conditions: 80 °C, catalyst loading = 4.0 wt. %.

Figure 4 shows the effect of catalyst loading on 1-dodecene conversion and 2-phenyldodecane selectivity over sulfated mesoporous C_{12}-Ta oxide. When catalyst loading was increased from 0.5 to 4.0 wt. %, 1-dodecene conversion increased from 28.8 % to 100 %, whereas the selectivity to 2-phenyldodecane decreased from 52.9 to 41.6 % at the reaction time of 0.5 h. With increased catalyst loading, the greater number of acid sites leads to higher activity, while the kinetic availability of external surface acid sites is increased relative to internal sites resulting in a decrease in the 2-phenyldodecane selectivity. Further increase in catalyst load-

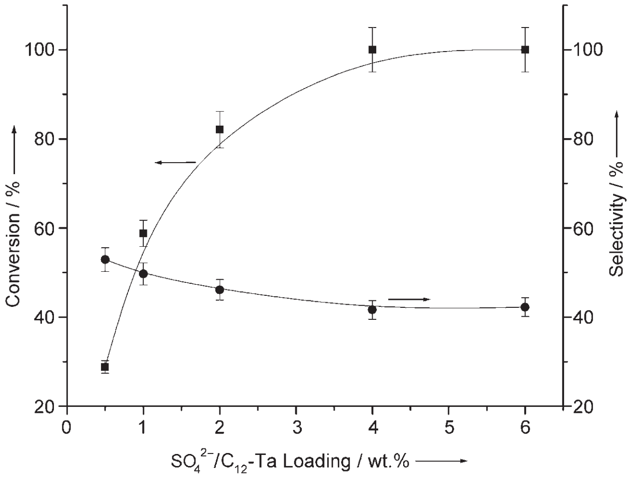

Figure 4. 1-Dodecene conversion and 2-phenyldodecane selectivity as a function of catalyst loading. Reaction conditions: 80 °C, 0.5 h.

ing to 6.0 wt.% had no obvious effect on 2-phenyldodecane selectivity.

The effect of the bulkiness of the olefin on the conversion over mesoporous C_{12}-Ta oxide was studied (Figure 2). When bulkier 1-tetradecene was used, olefin conversions at 0.5 h decreased greatly to 17.5%. The longer the olefin chain, the more difficult for the olefin molecules to access to the active sites in mesopores. Therefore, activity decreased with an increase in olefin chain length. In order to further clarify the effect of pore structure on activity, the alkylation reaction was carried out over sulfated mesoporous C_6-Ta and C_{18}-Ta oxide prepared by using 1-hexylamine and 1-octadecylamine as templates. The catalytic activity data is given in Table 2. The lower activity of C_6-Ta oxide is attributed to the strong diffusion resistance offered by the pore blocking in smaller pores.[24] Despite its larger pore size, sulfated C_{18}-Ta oxide showed very low activity. The low 1-dodecene conversion offered by sulfated C_{18}-Ta oxide may be caused by its relatively low surface area and extremely low pore volume, but may also be related to relative optimization of the reaction transition state by the two pore sizes. The large C_{18} pores are less effective at bringing the benzene and alkyl cation together than the intermediate C_{12} pores, while the small C_6 pores cause diffusion hindrances. Although more study may be necessary to fully elucidate this effect, a similar trend in pore size versus activity was observed in the isomerization of 1-hexene over sulfated mesoporous Ta oxide.[25]

Table 2: Catalytic properties of solid acid catalysts in alkylation reactions.

Catalyst	Olefin	Conversion [%][a]
SO_4^{2-}/C_6-Ta	1-dodecene	46.9
SO_4^{2-}/C_{12}-Ta	1-dodecene	100
SO_4^{2-}/C_{18}-Ta	1-dodecene	2.3
SO_4^{2-}/C_{12}-Nb	1-dodecene	1.2
H-Y zeolite	1-dodecene	100
H-ZSM5	1-dodecene	0
Amberlyst	1-dodecene	13.5

[a] 0.5 h at 80 °C, catalyst loading = 4.0 wt.%.

As one of the best solid acid catalysts for benzene alkylations,[5] H-Y zeolite (Zeolyst, Si/Al = 80) was tested for comparison. This material gave 100% 1-dodecene conversion at 80 °C within 0.5 h. Though the acid amount on H-ZSM5 zeolite is comparable to that on sulfated mesoporous C_{12}-Ta oxide, no alkylation reaction was detected over H-ZSM5 at 80 °C. This can be rationalized by the diffusion limitation in the channels with smaller openings.[12] An alkylation reaction was conducted over Amberlyst 15 ion exchange resin (Aldrich). Despite the presence of strong acid sites, Amberlyst resin showed lower catalytic activity for the alkylation reaction, due to its lower surface area ($55.1\ m^2 g^{-1}$) and thus smaller amount of active sites on the internal surface of pores.

The selectivities towards the 2-phenyldodecane isomer were compared at the same conversion and summarized in Table 3. The selectivity over sulfated mesoporous C_{12}-Ta oxide, H-Y zeolite, and Amberlyst resin at 1-dodecene conversion of ca. 60% were 49.19%, 25.31%, and 38.31%, respectively. The high selectivity of sulfated mesoporous C_{12}-Ta oxide can be attributed to “confinement effects”, which indicates that selectivity as well as conversion rate are pore size dependent.[26] Jaenicke et al. reported the shape-selective catalysts prepared by immobilizing $AlCl_3$ onto a series of MCM-41 mesoporous silica with different pore sizes.[27] They found that the selectivity towards monoalkylation product in the synthesis of linear alkyl benzenes can be controlled by changing the pore size of the MCM-41 supports. The mesoporous structure in our sulfated Ta oxide may offer a similar confined space for the establishment of shape selective reactions.

Table 3: 2-Phenyldodecane selectivity over solid acid catalysts.

Catalyst	Conversion [%]	Selectivity [%]
SO_4^{2-}/C_{12}-Ta	60.0	49.19
H-Y zeolite	61.1	25.31
Amberlyst	60.4	38.31

In order to examine the reusability of sulfated mesoporous C_{12}-Ta oxide, the catalyst was separated by filtration after the first run and then dried at 120 °C for 12 h. The reaction was repeated under the same conditions using the recovered catalyst. The XRD pattern and N_2 adsorption/desorption isotherm after the first run confirmed the retention of mesoporous structure. However, the catalyst lost 17.4% of its initial surface area after the first run. The catalyst used in the second run gave a 1-dodecene conversion of 26.8% at 0.5 h. The deactivation of the catalyst could be due to the blockage of the mesoporous pore by the accumulation of bulky phenyldodecane isomers during previous runs, or a small loss of sulfate by leaching as observed for the sulfated mesoporous Nb oxide in the benzylation of anisole and toluene.[21] Elemental analysis showed that the sulfur content in the sulfated mesoporous C_{12}-Ta oxide was 4.18%, while the sulfur content was slightly decreased to 4.06% after alkylation reaction. Therefore, the deactivation is not related to sulfate loss. The deactivated catalyst could not be regenerated by the treatment with sulfuric acid.

In summary, mesoporous Ta oxides were prepared and employed as solid acid catalysts in the alkylation of benzene with bulky olefins. The catalysts with optimal pore size displayed comparable activity to H-Y zeolite, but much higher selectivity towards the desired isomer. Because of this ideal balance between high activity and selectivity, it is anticipated that this catalyst may see applications in industrial acid catalyzed reactions.

Experimental Section

Mesoporous Ta and Nb oxides were prepared as described previously.[18] The sulfated oxides were produced by stirring the template-free oxides with 1.0 M sulfuric acid for 12 h.

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5000-2 diffractometer using $Cu_{K\alpha}$ radiation. Nitrogen adsorption/desorption data were collected on Micromeritics ASAP 2010. FT-IR experiments were performed on Bruker Vector 22 FT-IR spectrometer. The Hammett acidity and acid amounts were measured according to literatures.[28,29] Elemental analysis was conducted in Galbraith Laboratories, Inc.

Before reaction, H-Y and H-ZSM5 zeolites were activated at 500°C for 3 h in air, whereas sulfated mesoporous Ta and Nb oxides were dried at 120°C for 12 h. The liquid-phase alkylation reactions were carried out in a 100 mL 3-neck round-bottom flask with a reflux condenser, a nitrogen inlet and a septum. The reactant mixture was refluxed at atmospheric pressure in an oil bath. Samples were periodically withdrawn and analyzed using a Varian CP-3800 gas chromatograph.

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