

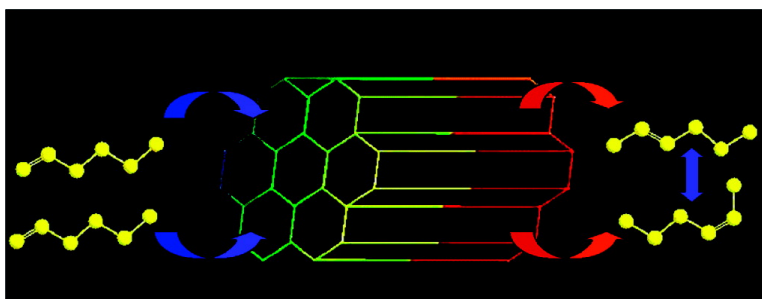
Communication

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# 1-Hexene Isomerization over Sulfated Mesoporous Ta Oxide: The Effects of Active Site and Confinement

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Template-synthesized meso- and microporous materials composed of transition metal oxides are attractive solid catalysts.<sup>1,2</sup> Since the first synthesis of group V mesoporous metal oxides (Nb, Ta-TMS1) were described in 1996,<sup>3</sup> only a few papers have been reported on their catalytic properties.<sup>4–6</sup> These materials have potential applications in petrochemical processes because of facile tuning of pore size, moderate thermal stability, high surface area, and high surface acidity, all of which are crucial properties in industrial catalysis. The relatively large pores (12–30 Å) overcome the size constraint of most zeolites, allowing more facile diffusion of bulky substrates, while the very high surface areas (200–1200 m<sup>2</sup>/g) create a high concentration of active sites per mass of material. The transition metal centers in the inorganic framework of the mesoporous structure also possess variable oxidation states and empty d-orbitals, properties which allow electron transfer to occur between the reactants and active site during any catalytic process.<sup>4a</sup> Recent work in our group showed that sulfated mesoporous Nb and Ta oxides were effective catalysts for benzylolation reaction<sup>5a</sup> due to their combination of strong acidity and large pore size. In this report, we investigate the catalytic properties of mesoporous Ta oxide in the isomerization of 1-hexene and compare the catalytic activities and selectivity with commercially available zeolites<sup>7,8</sup> (HY-zeolite and H-ZSM5) and the ion exchange resin<sup>9</sup> Amberlyst 15. The former are currently the most effective catalysts in catalytic reforming, a process which is important because branched-chain hydrocarbons are better automotive fuels than their straight-chain isomers. This reaction is also widely used by many researchers in both homogeneous<sup>10</sup> and heterogeneous<sup>11</sup> processes as a test of a material's effectiveness as an acid catalyst.

The synthesis of a tantalum oxide molecular sieve (Ta-TSM1) was successfully achieved by using the ligand-assisted templating approach<sup>3</sup> with different chain-length amine surfactants (C<sub>6</sub>–C<sub>18</sub>). The as-synthesized samples were further treated with 1 M sulfuric acid in methanol solution to obtain sulfated mesoporous Ta oxides. The BJH pore sizes slightly decreased after acid treatment, possibly due to the deposit of SO<sub>4</sub><sup>2-</sup> ions inside their wormhole channels (Table S1). The strong reflections (100) at low angle in the XRD pattern showed the retention of the mesoporous structure after acid treatment (Figure S1). This was further confirmed by the type IV isotherm obtained in the nitrogen adsorption/desorption measurements (Figure S2), although materials synthesized with the smaller hexylamine displayed a type I isotherm. The pore size of the C<sub>6</sub> material was estimated as 12 Å on the basis of previous work on microporous Nb oxide<sup>5b</sup> and Ti oxide.<sup>5c</sup> These studies used TEM and XRD as a gauge of the pore size, which falls below that of the BJH method using N<sub>2</sub> as an adsorbent.

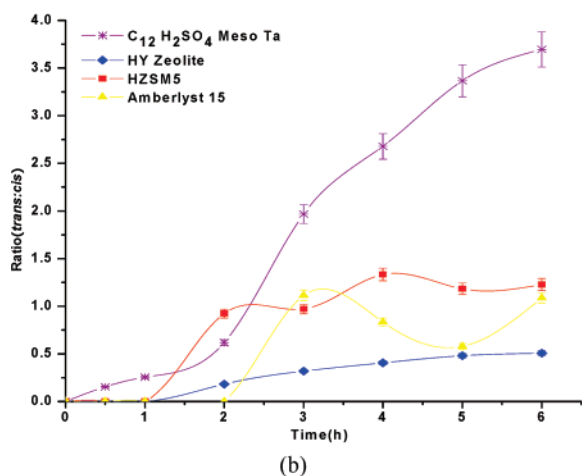
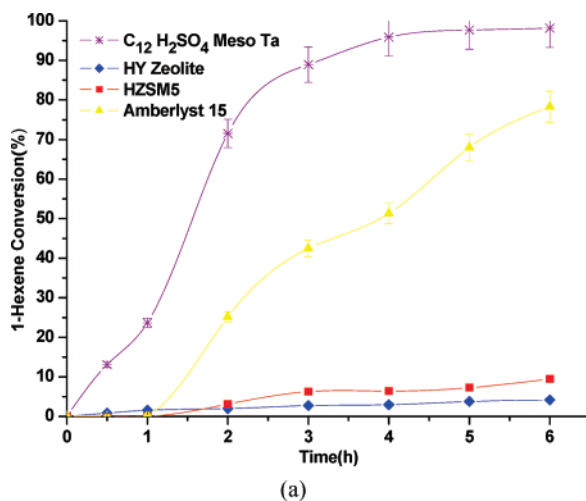
The FTIR spectrum for C<sub>12</sub> mesoporous Ta oxide (Figure S3) showed a strong peak corresponding to Brønsted acid sites (~1538 cm<sup>-1</sup>) which was enhanced after acid treatment. In contrast, HY-zeolite and H-ZSM5 possess mainly Lewis acid sites (~1448 cm<sup>-1</sup>) with only a weak absorbance observed for Brønsted acid sites. The majority of research indicates that Brønsted acid sites are chiefly

involved in isomerization reactions.<sup>12</sup> The Hammett acidity and *n*-butylamine titration methods were employed to measure acid strength and acid amount of all the samples. The results are summarized in Table 1. As is seen from this table, both acid strength and acid amount of the C<sub>12</sub> mesoporous Ta oxide increased after acid treatment, consistent with previous work on mesoporous Nb oxide.<sup>5a</sup>

C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxide was evaluated in 1-hexene isomerization at reflux temperature (343 K) and compared to Amberlyst 15, HY-zeolite, and H-ZSM5 (Figure 1a). This new material showed much higher activity than HY-zeolite and H-ZSM5 (roughly 10 times greater) and ca. 50% higher activity than Amberlyst 15. In order to investigate the effect of pore size on this reaction, C<sub>6</sub> and C<sub>18</sub> mesoporous Ta oxides were also synthesized and tested. The results are shown in Figure S4. Among these three samples, C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta showed the highest activity (~95% in 4 h), which can be attributed to a combination of pore size and its higher BET surface area (292.19 m<sup>2</sup>/g, Table S1). The C<sub>6</sub> sample has the second highest surface area (206.40 m<sup>2</sup>/g), but its smaller pore size leads to the lowest observed activity. The C<sub>18</sub> sample has the largest pore size (22.5 Å) but the lowest surface area (188.79 m<sup>2</sup>/g) and thus displays an activity that falls between that of its two congeners. GC analysis confirmed that *trans*- and *cis*-2-hexene isomers were formed as the only two principal products. Skeletal isomerization, which requires more energy and can only be performed at elevated temperature (>523 K),<sup>13</sup> was not observed at 343 K. C<sub>6</sub> and C<sub>18</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxides showed very similar selectivity, the ratio of *trans*/*cis*-2-hexene is less than 1, which is close to the ratios observed from HY-zeolite, H-ZSM5, and Amberlyst 15. However, for the C<sub>12</sub> sample, the ratio of *trans*:*cis* isomers can reach up to 3.7 after 6 h, which is very close to thermodynamic equilibrium (3.37).<sup>14</sup> Tanchoux et al.<sup>15</sup> studied the impact of confinement and nesting effects in the isomerization of 1-hexene by MCM-41, demonstrating that selectivity as well as conversion rate were pore size dependent. This is consistent with the results observed in the present study. The pore size of the C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxide is 18.2 Å (Table S1), which allows linear *trans*-2-hexene to pass more easily through its channels than nonlinear *cis*-2-hexene. Because of the large pore size (22.5 Å) of C<sub>18</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxide, both products can be formed inside its channel structure and diffuse out freely, leading to poor selectivity. As for C<sub>6</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxide, the limitation of its small pore size (12 Å) blocks the penetration of the reactant, allowing most of the reaction to occur on the exterior of the wall, not inside the pores. This leads to low selectivity. The increase of selectivity over time to the thermodynamic mixture in the case of the C<sub>12</sub> catalyst can be attributed to the more efficient conversion of *cis*-2-hexene to *trans*-2-hexene by this material relative to the other catalysts in this study. This faster rate of conversion is consistent with Tanchoux's observations on the higher activity of moderate pore size MCM-41 materials in this reaction. The isomerization of 1-hexene to 2-hexene is a proton

**Table 1.** Acid Strength and Acid Amount of Solid Acid Catalysts (measured by Hammett Indicators and *n*-Butylamine Titration)

sample	<i>H</i> <sub>0</sub>	acid amount (mmol/g)
C <sub>12</sub> meso Ta	−6.6	0.40
C <sub>12</sub> H <sub>2</sub> SO <sub>4</sub> meso Ta	−8.2	19.8
HY-zeolite	−6.6	1.55
H-ZSM5	−4.4	16.1
Amberlyst 15	N/A	N/A

**Figure 1.** 1-Hexene isomerization on different catalysts: (a) 1-hexene conversion rate with time; (b) ratio of *trans*/*cis*-2-hexene with time.

transfer process.<sup>16</sup> The initial proton is transferred from the acid sites on the surface of the catalyst to the double bond of 1-hexene, and then the hydride shift along the linear chain produces *cis*-2-hexene and *trans*-2-hexene. To eliminate the potential effect of free H<sub>2</sub>SO<sub>4</sub> on selectivity, a separate experiment was performed using a drop of pure sulfuric acid as catalyst (Figure S5), the conversion of 1-hexene reached 31.18% after 6 h, and an only slightly higher ratio (1.5) was obtained as compared to the C<sub>6</sub> and C<sub>18</sub> samples. Nevertheless, this value is still far behind the selectivity of C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta oxide, which establishes that pore size is crucial to the selectivity in this system.

The reusability of C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta was tested by conducting three continuous runs using the same catalyst. The results showed that its catalytic activity declined linearly, the conversion of 1-hexene decreased from almost 100% conversion for the first run to 76% for the second run, and then to 40% for the third run. This can be attributed to partial pore blockage caused by isomerization products deposited inside the channel, which occupy

some of the active sites on the surface and cause the BET surface area to decrease from 292 to 133.25 m<sup>2</sup>/g (Figure S6). The loss of catalytic activity can also be ascribed to sulfate leaching during each catalytic run. This is demonstrated by the fact that the used catalyst can be partially regenerated to 60% its original activity by treatment with new sulfuric acid. Elemental analysis shows no increase in %C, demonstrating that loss of surface area is not due to build up of polymers.

In summary, this study provides a straightforward demonstration of the influence of acid sites and confinement effect in 1-hexene isomerization catalyzed over sulfated mesoporous Ta oxides. These catalysts showed higher activities than Amberlyst 15, HY-zeolite, and H-ZSM5. Among the three different pore sizes of sulfated mesoporous Ta oxides studied, C<sub>12</sub> H<sub>2</sub>SO<sub>4</sub> mesoporous Ta showed both the highest activity and selectivity, which can be attributed to its high BET surface area, increased concentration of Brønsted sites on the surface of the mesoporous channels, and optimal pore size for this particular reaction.

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**Supporting Information Available:** Detailed experimental procedure, powder X-ray diffraction patterns, N<sub>2</sub> 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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