Synthesis and characterization of Al-HMS catalysts and their application for t-butylation of toluene

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Al-HMS (hexagonal mesoporous silica) with Al content in the range 2 - 10 mol% has been synthesized using dodecylamine surfactant as template and aluminum s-butoxide as the aluminum source. The mesoporous structure has been confirmed by XRD and the surface area and pore size calculated by BET equation and BJH method using nitrogen adsorption-desorption technique. The aluminum atom coordination has been determined by 27Al MAS NMR. The total acidity and the type of acid sites have been studied using TPD of chemisorbed 2,6-di-tert-butylpyridine and IR spectra of pyridine adsorption, respectively. The Al-HMS materials possess abundant tetrahedral aluminum in the HMS framework and also Brönsted and Lewis acid sites. The catalytic activities of the materials have been tested in 4-t-butylation reaction of toluene in liquid phase. Maximum conversion (85.1%) of toluene has been achieved with 10%Al-HMS catalyst, and high selectivity (> 80%) for 4-t-butyltoluene is observed over 2 - 4.8% Al-HMS catalysts. The conversion of toluene increases with increase of Al content, and the selectivity of 4-t-butyltoluene decreases to 70% when Al content is increased up to 10% in HMS materials.

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The alkylation of aromatic hydrocarbons is an important process in chemical production processes. Industrial alkylation processes are usually catalyzed by strong mineral acids (HCl, H2SO4, H3PO4), or Lewis acids such as AlCl3, BF3. These traditional catalysts have disadvantages such as environmental pollution hazard, reactor corrosion and difficulty in handling. Therefore, considerable research effort has been directed towards the development of solid acid catalysts to overcome these drawbacks. In many cases, solid acid heterogeneous catalysts show better selectivity than mineral acids towards a specific isomer in a mixture of reaction products. Also, they are safer and more environmentally friendly.

4-t-Butyltoluene is an intermediate in the production of 4-t-butylbenzaldehyde, used in perfumery in large quantities and of 4-t-butylbenzoic acid, used in plastics and resins. The alkylation of toluene with t-butylation alcohol, isobutylene, disobutylene, etc. has been carried out with solid acid catalysts to produce 4-t-butylation toluene. Selvaraj and co-workers have reported the use of mesoporous Al-MCM-41 materials as solid acid catalysts in t-butylation reaction of toluene to 4-t-butylation toluene with t-butylation alcohol in the liquid phase, and a maximum conversion of 86.3% of 4-t-butylation toluene and a selectivity to 4-t-butylation toluene of 92.3% were achieved over Al-MCM-41 (Si/Al=21). A conversion of 59.2% of toluene and a selectivity of 87.2% of 4-t-butylation toluene were observed in liquid phase t-butylation of toluene by t-butanol over large pore zeolite catalysts (Si/Al=17.5). Sebastian and co-workers have studied vapour phase butylation of toluene with t-butylation alcohol over mordenite based catalysts. The mordenite catalyst (Si/Al=180) offered 17.6% conversion of toluene and 67.4% selectivity of 4-t-butylation toluene. To our knowledge, Al-HMS used as catalyst in t-butylation of toluene has not been reported so far.

Al-MCM-41 used as solid acid catalysts has been largely studied, whereas Al-HMS has received comparatively less attention. MCM-41 has uni-directional mesoporous structure. A similar material, HMS, has three-directional wormhole hexagonal framework structure. Both exhibit very high surface area of about 1000 m²/g and uniform framework mesopores. HMS materials contain significant volumes of irregular mesovoids distributed within the primary particles, which facilitates organic molecule transport to the framework reaction centers.
Besides, HMS synthesis condition is mild, and the template can be extracted without pollution. These advantages of HMS motivated us to study Al-HMS molecular sieves and their applications.

In the present work, we have synthesized and characterized Al-HMS molecular sieves with different Al contents, and evaluated their catalytic activities by t-butylation of toluene by t-butanol in the liquid phase as a test reaction.

**Materials and Methods**

**Synthesis and characterisation**

Al-HMS with various Al content (2, 2.5, 3.6, 4.8 and 10 mol%) was synthesized using Al(OBu')₃ as the source for aluminum. Tetraethylorthosilicate (TEOS) was added to a mixture of dodecylamine (DDA), water and ethanol (EtOH) at room temperature. The mixture was stirred for 1 h and then Al(OBu')₃ in s-butanol was added with vigorous stirring. After a reaction time of 20 h at 45°C, the solid was filtered, washed, dried at room temperature, and calcined in air at 550°C for 4 h. The molar composition of the final gel was 1.00SiO₂: (0.02-0.01)Al : 0.25DDA : 15.0EtOH : 48.6H₂O. These calcined samples are labeled mol% Al-HMS.

Powder XRD patterns were obtained on a Rigaku Rotaflex diffractometer using Cu Kα radiation (\(\lambda = 1.542 \ \text{Å}\)). The diffraction data were collected every 0.02°(2θ) at a scan speed of 1°(2θ)/min from 1° to 10°.

N₂ adsorption-desorption isotherms were recorded at -196°C on a Micromeritics ASAP 2010 sorptometer. Prior to adsorption, the samples were outgassed at 150°C and 10⁻⁶ torr for a minimum of 12 h. BET surface areas were calculated from the linear part of the BET plot. The pore size distributions were calculated using the adsorption branches of the N₂ adsorption isotherms and the Barret-Joyner-Halenda (BJH) formula.

\(^{27}\)Al MAS NMR spectra were recorded on a Varian VXR 400 MHz spectrometer at 104.26 MHz under single pulse mode with a 7 mm zirconia rotor and a sample spinning frequency of 4 kHz. A pulse duration of 9 μs and a pulse delay of 1 s allowed for a full relaxation of the Al nucleus. The external Al(H₂O)₆³⁺ was used as a standard reference to determine the chemical shift values.

**Acidity analysis**

The acidities of Al-HMS were obtained by the temperature-programmed desorption (TPD) of chemisorbed 2,6-di-tert-butyl pyridine according to earlier method\(^ {11} \). IR spectra of Bronsted and Lewis acid-site chemisorbed pyridine on the samples were obtained with a Galaxy series FT-IR 3000 instrument using self-supported wafers of 10 mg/cm² prepared from the sample powders. The wafers were calcined under vacuo (1 mtorr) at 450°C for 2 h before addition of pyridine. The sample wafers adsorbed pyridine for 30 min at room temperature, were then degassed at 200°C for 30 min and cooled to room temperature. The infrared spectra of all the samples were recorded at room temperature. Bronsted to Lewis pyridine ratio (B/L) was obtained by measuring the integrated absorbance of bands for Bronsted and Lewis acid-site chemisorbed pyridine and by using the correlation developed by Emeis\(^ {12} \) for porous aluminosilicates.

**Catalytic activity**

The alkylation reaction tests were carried out in a stirred batch autoclave reactor at the reaction temperature of 175°C and autogeneous pressure. In a typical run, the catalyst (300 mg) was added to a mixture of s-butanol (10 mmol) and toluene (20 mmol) with n-decane (80 ml) as solvent. The finally reaction mixture was filtered, and the filtrate was analysed by mass spectrometry (MS) and gas chromatography (GC) instrument equipped with a flame ionization detector (FID).

**Results and Discussion**

**X-ray diffraction**

Figure 1 illustrates the powder XRD patterns of calcined Al-HMS. Clearly, the patterns for the Al-HMS materials exhibit intense [100] reflections at low angles, which is typical of HMS wormhole structures with lack of long-range symmetry assembled from long alkyl chain neutral amines as surfactants\(^ {13} \). The regularity of the mesoporous structure still remained intact when incorporation of aluminum was high up to 10 mol%. Physico-chemical properties of HMS materials are summarized in Table 1. It is evident that the Al-HMS materials have considerably high pore volumes and surface areas. Increase in Al incorporation into the HMS framework leads to slight decrease in the unit cells and BET surface areas, as well as increase in the pore volumes.

**Nitrogen adsorption-desorption isotherms**

The nitrogen adsorption-desorption isotherms and the corresponding pore size distributions of Al-HMS
TABLE 1 — Physico-chemical properties of Al-HMS calcined at 550°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al molar ratio</th>
<th>Unit cell (nm)</th>
<th>(S_{\text{BET}}) (m²/g)</th>
<th>Pore vol. (cm³/g)</th>
<th>BJH pore size (nm)</th>
<th>Acidity (mmol/g)</th>
<th>(B/L) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Al-HMS</td>
<td>49</td>
<td>4.33</td>
<td>1179.6</td>
<td>0.80</td>
<td>2.0</td>
<td>0.071</td>
<td>2.22</td>
</tr>
<tr>
<td>2.5%Al-HMS</td>
<td>39</td>
<td>4.29</td>
<td>1165.9</td>
<td>0.83</td>
<td>2.0</td>
<td>0.078</td>
<td>2.18</td>
</tr>
<tr>
<td>3.6%Al-HMS</td>
<td>27</td>
<td>4.25</td>
<td>1127.7</td>
<td>0.87</td>
<td>2.0</td>
<td>0.086</td>
<td>2.03</td>
</tr>
<tr>
<td>4.8%Al-HMS</td>
<td>20</td>
<td>4.18</td>
<td>1124.5</td>
<td>0.92</td>
<td>2.0</td>
<td>0.102</td>
<td>1.94</td>
</tr>
<tr>
<td>10%Al-HMS</td>
<td>9</td>
<td>4.12</td>
<td>992.5</td>
<td>0.99</td>
<td>2.0</td>
<td>0.135</td>
<td>1.17</td>
</tr>
</tbody>
</table>

*Brønsted : Lewis pyridine ratio*
aluminum up to 10% resulted in a disruptive effect on the mesopores. Differences can be appreciated in the pore size distributions shown in Fig. 2B. The 10% Al-HMS sample presented a wider pore size distribution.

Solid-state $^{27}$Al MAS NMR spectroscopy
$^{27}$Al MAS NMR spectroscopy can provide information on the environment of the incorporated aluminum atom in the Al-HMS framework. Figure 3 shows $^{27}$Al MAS NMR spectra of Al-HMS. Two clear chemical shift peaks centred at 50 and 0 ppm are observed in the samples. The signal at around 50 ppm may be assigned to tetrahedrally coordinated framework aluminum (potential Brönsted acidity). The signal at around 0 ppm may be ascribed to octahedrally coordinated nonframework aluminum (potential Lewis acidity)\cite{16}. The resonances from the intra-framework Al at about $\delta$=50 ppm are stronger than those from the additional Al framework at about $\delta$=0 ppm regardless of the Al content in the samples. This suggests that significantly higher amounts of tetrahedral framework Al have been incorporated into the framework of the HMS sample.

Acidity analysis
The acidities (mmol/g) of the samples are presented in Table 1. As the aluminum content increases, the total acidity increases in the samples in the order of the Si/Al ratio 9>20>27>39>49. The infrared spectra of the pyridine-adsorbed Al-HMS are shown in Fig. 4. Peaks are observed at ca. 1454 and 1545 cm$^{-1}$ due to pyridine adsorbed on Lewis and Brönsted acid sites, respectively. The peaks near 1490 cm$^{-1}$ correspond to Lewis and Brönsted (L+B) sites. The intensities of bands for adsorbed pyridine on Bronsted and Lewis acid sites increase with increasing Al content, indicating that the numbers of Bronsted and Lewis acid sites in Al-HMS catalysts increase with increase in Al content. As seen from Table 1, the number of Bronsted acid sites is higher than that of the Lewis acid sites, although the B/L acid site ratio decreases with increasing Al content.

Catalytic activity of Al-HMS
Table 2 provides data on toluene conversion and selectivity of $t$-butyltoluene for Al-HMS catalysts. To avoid the formation of coking, the $t$-butylation reaction was carried out under reflux conditions with
reaction time of 4 h and at a temperature of 175 °C (i.e., at the boiling point of decane). The activity of Al-HMS catalysts decreases according to the conversion of toluene in the order: 10% Al-HMS > 4.8% Al-HMS > 3.6% Al-HMS > 2.5% Al-HMS > 2% Al-HMS. The catalytic activity depends strongly on Al content due to different acidity behavior of the Al-HMS catalysts. In all the cases, the main reaction product was identified as 4-t-butyltoluene. 3-t-Butyltoluene and 2-t-butyltoluene were present in the reaction products only in small amounts. The main product is 4-t-butyltoluene because the para-position is favored due to the steric hindrance of the methyl group on one side and voluminous t-Bu group. The 10% Al-HMS sample showed maximum conversion (85.1%) of toluene due to the high Al content and the higher number of Bronsted acid sites. This sample also showed a low selectivity (70.0%) of 4-t-butyltoluene due to the higher number of Lewis acid sites and the mesoporous property of 10% Al-HMS catalyst. Considering activity and valuable product selectivity for 4-t-butyltoluene, the best catalytic performance was obtained over 4.8% Al-HMS with an intermediate Al content (Si/Al molar ratio of 20). The 4.8%Al-HMS offered a maximum yield of 65.4% of 4-t-butyltoluene.

Conclusions
The above study shows that 2~10 mol %Al-HMS materials may be synthesized by neutral templating pathway and successfully used as catalysts for the 4-t-butylation of toluene. The Al-HMS materials possess well-ordered mesoporous, high BET surface areas, Lewis and Bronsted acid sites. The numbers of Lewis and Bronsted acid sites increase with increasing Al content in the mesoporous structure. Incorporation of excess Al (10 mol%) results in a wide pore size distribution and a disruptive effect on the mesopores and high numbers of Lewis acid sites. The aluminium content of Al-HMS materials significantly influences the conversion of toluene and the selectivity of 4-t-butyltoluene. The 4.8% Al-HMS sample shows a high yield of 65.4% of 4-t-butyltoluene. The study indicates that Al-HMS is a potent solid acid catalyst for alkylation of aromatic hydrocarbons.

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References