2

Functional Mesoporous Alumina Materials
Sheela Chandren, Zainab Ramli and Hadi Nur

2.1 INTRODUCTION

Catalytic technologies play a key role in the economic development and growth of the chemicals industries and contribute to around 20% of the world Gross National Product. A major emerging and challenging area of heterogeneous catalysis is that of environmental pollution control, with tightening legislation on the release of waste and toxic emissions having serious implications for the chemical industry. While heterogeneous catalyzed processes are widely used within petrochemical industry, many fine and specialty chemicals manufacturers rely on homogeneously catalyzed liquid-phased reactions. Many of these processes were developed at the turn of the century, and focused on product yield, disregarding the environmental impact of inorganic wastes and toxic by-products formed during the reaction.

In recent years, environmental and economic considerations have raised strong interest to redesign commercially important processes so that the use of harmful substances and the generation of toxic waste could be avoided. In this respect, there is no doubt that heterogeneous catalysis play a key role in the development of environmentally benign processes in petroleum chemistry and in the production of fine chemicals, for instance by substitution of liquid acid catalysts with solid materials.

Zeolites have attracted strong attention as solid acid catalysts and also as base and redox catalysts. However, zeolites present severe limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the
case in the synthesis of fine chemicals, due to the fact that mass transfer limitations are very severe for microporous solids.

The discovery of ordered mesoporous solids of the MCM-41 type and related materials in the early 1990s has been a breakthrough in materials engineering. This discovery revealed exciting possibilities for new types of molecular sieves with significantly larger pores than zeolites and narrow pore size distribution, with applications not only in catalysis but also in other areas of chemistry. The invention of mesoporous molecular sieves by the researchers at the Mobil Research and Development Corporation, enabled escape from the “1 nm prison” imposed by zeolite-based microporous molecular sieves. Since then there has been impressive progress in the development of many new mesoporous solids.

Mesoporous alumina has been widely used as catalyst supports and absorbents, and its physical properties such as surface area, pore distribution and volume have significant effect on its performance in application. Modified mesoporous alumina has been widely employed in several catalytic processes. Mesoporous alumina modified with copper was tested as a catalyst for selective hydrogenation of cinnamaldehyde (Valange et al., 2005). The remarkable selectivity of this catalyst towards the formation of unsaturated alcohol was observed compared to conventional alumina. Rhenium oxide finely dispersed on mesoporous alumina is significantly more active and selective in metathesis of terminal and inner olefins compared to γ-alumina (Oikawa et al., 2004).

### 2.2 RELATED WORKS

Friedel-Crafts reactions are of considerable importance in the productions of fine chemicals (DeCastro et al., 2000). Many industrial processes for the production of pharmaceutical products, fragrances, antioxidants, paint additives, cosmetics and others involve an intermediate step that is the Friedel-Crafts reaction. This type of reaction requires the present of acidic catalyst in order to allow the reaction to proceed at a convenient rate.
Unfortunately, the use of homogenous conventional Lewis and Brönsted acid catalysts such as AlCl₃, BF₃, FeCl₃, ZnCl₂, H₂SO₄, HCl and HF lead to several problems such as they need more than stoichiometric amount because of complexation of reactant or product, disposal of potentially highly polluting and toxic wastes and corrosiveness (Smith et al., 1998). Homogeneous catalysts also give rise to problems in products separation as the catalyst is in the same phase with the products.

Present day heterogeneous catalysts are used in the processing of high-molecular–weight hydrocarbons. Because of this reason, the demand for mesoporous materials (pore diameter higher than 1.0 nm and lower than 25 nm) has triggered major synthetic efforts in academic and industrial laboratories (Hou et al., 1994). As these materials have very-well scattered Brönsted acid sites and large-pore diameters with less diffusional constraints, they are expected to discourage consecutive alkylations and deactivation of the catalyst by coke deposition (Umamaheswari et al., 2002). In addition, unlike microporous zeolites, where simultaneous diffusion of many molecules is prevented, these materials, in contrast, allow simultaneous entry of many reactant molecules into their pores, thereby permitting high conversion.

Aluminas are important industrial chemicals that have found wide application in adsorbents, ceramics, abrasives, catalysts and catalyst supports (Bai et al., 2005). Alumina, mainly in its γ form, is widely used in catalysis as inert carrier of metal catalysts and as part of bifunctional catalysts, largely because it is inexpensive and reasonably stable, and can provide high surface area for many catalytic applications. As a general rule, the alumina used in catalytic reactions always requires a controlled pore size distribution (Yao et al., 2001).

The performance of alumina, however, is limited due to uncontrolled porosity, deactivation by coke formation and plugging of the micropores which hinders the diffusion of reactants and products (Kim et al., 2005). In order to overcome the weakness of conventional alumina, efforts to develop alumina that
has uniform mesoporous distribution were made. Mesoporous alumina is a very interesting material with broad applicability as a support for various catalytically-active phases, which are employed in industry in a high number of large-scale technological processes (Čejka, 2003). Although several papers were reported on the synthesis of mesoporous alumina by utilizing cationic, anionic and non-ionic templates as the structural directing agents since the first in 1996 (Shan et al., 2003; Hicks et al., 2003; Deng et al., 2002), these methods usually use the expensive and toxic aluminum alkoxides as precursors, and/or strictly control the synthetic conditions, which make them inconvenient for the industrial scaling-up.

The sol gel process has been used for the last 20 years to prepare different alumina with uniform particles size and high surface area (Kaneko et al., 2002). In contrast, common method of preparation involves the precipitation of salts such as, nitrates or chlorides with bases. The removal of water from the precipitate results in pore collapse and shrinkage. Hence, these xerogels have a low surface area. The sol-gel-derived mesoporous alumina materials, besides exhibiting a large surface area and the presence of mesopores, are characterized by very good mechanical properties (Kirszensztejn et al., 2005). Preparation of good quality alumina especially in the form of granules by the sol-gel method from a cheaper precursor is critical to lowering the costs of the sol-gel derived sorbents or catalysts for many industries.

Mixed-metal oxide systems produced via the sol-gel method are of particular interest for generating materials intermixed almost at the atomic level. Such systems have the potential of exhibiting chemical properties that differs notably from those of the corresponding single component oxide. The mixed oxide systems, whose initial components differ considerably in their acid-base properties, are especially interesting. Characterization of some mixed-metal oxides with unique properties has been reported in the literature, some devoted to the modification of its acid-base characteristics in the presence of other species (Díaz et al., 1999; Sheng et al., 1994; Kirszensztejn
Due to the importance of alumina as catalysts, several attempts have been made to synthesize alumina having uniform mesopore size distribution, which can be applied in the catalytic processing of large molecules (Vaudry et al., 1996). Previous works done by other researchers using the existing sol gel method to synthesize mesoporous alumina (Bai et al., 2005; Yao et al., 2001; Kim et al., 2005; Čejka, 2003; Shan et al., 2003), has managed to synthesize alumina with uniform pore size distribution. However, mesoporous alumina with narrow pore size distribution was not obtained each and every time. So far, it has proven to be very difficult to obtain mesoporous alumina with narrow pore size distribution. Meanwhile works done by Yusoff (2006) in the preparation of zeolitic mesoporous ITQ6 by using ultrasonic treatment has proven to be successful in obtaining a very uniform pore size distribution in the mesopore range material. The same method could be applied with some modifications in the synthesis of mesoporous alumina nanoparticles. The new concept involves firstly the preparation of nanosize particles and then the incorporation of templates to create the mesoporosity.

Alumina is known to possess Lewis acidity and basicity. However, it lacks Brønsted acidity. In order to introduce acidity, Brønsted acid precursors have been loaded on the surface of catalyst. One method to enhance the amount and acid strength of mesoporous alumina is by modifying it with sulfuric acid. The use of sulfate as acidity promoting additives for catalytic aluminas have been reported by Ertel et al. (1997) and Mekhemer et al. (2005) and this effect has been suggested to increase the changes of its acidity by twofold. Sulfates play an important role as support stabilizer; the stabilizing effect seems to delay the most undesired phase transition of \( \gamma-\text{Al}_2\text{O}_3 \) (Mekhemer et al., 2005). The introduction of sulfur compounds onto metal oxides enhanced remarkably the acidic properties of the oxides, regardless of the types of the introduced sulfur compounds.


2.3 EXPERIMENTAL

2.3.1 Preparation of Mesoporous Alumina

The mesoporous alumina nanoparticles were prepared from gels with the following molar composition:

\[ 1 \text{Al}(\text{C}_3\text{H}_7\text{O})_3 : 0.3 \text{CTABr} : 1.8 \text{HCl} : 17 \text{C}_3\text{H}_7\text{OH} : 22 \text{H}_2\text{O} \]

The procedure comprises of three steps. Firstly, the hydrolysis of aluminum iso-propoxide (\(\text{Al}(\text{C}_3\text{H}_7\text{O})_3\), Merck, 98%) by hydrochloric acid (HCl, Merck, 37%) at room temperature was carried out for 4 h in the presence of the surfactant cetyltrimethylammonium bromide (CTABr; 99% Fluka) and iso-propanol (\(\text{C}_3\text{H}_7\text{OH}\), Fluka, 99%). The second step was the condensation of aluminum hydrolyzed species by heating the reacting mixture at 80 °C. Then the sol gel obtained underwent ultrasonic treatment for 30 minutes in order to disperse the particles. Drying was then carried out at 100 °C. Finally, the resulting material is calcined at 600 °C for 4 h. Sulfated mesoporous alumina samples were prepared according to the literature (Ng et al., 2006). Four samples with different loading percentage of sulfate were prepared using sulfuric acid as the precursor. The desired amount of sulfuric acid was then added to toluene before adding the pre-dried MA (200°C for 24h). The mixture was stirred at 50°C for 1 h and dried at 130°C for 12 h. The samples were designated as YS/MAN, with Y as the percentage of sulfate (\(\text{SO}_4^{2-}\)) in wt%. Sample niobic acid on mesoporous alumina (NbA/MAN) with four different loadings of niobium were prepared by impregnation technique using niobium(V) ethoxide as the precursor as described in literature (Prasetyoko et al., 2005). The needed amount of niobium(V) ethoxide was dissolved in iso-propanol to obtain the desired metal loading. Then, the required quantity of pre-dried MA (200 °C for 24h) was immediately added to the clear solution with stirring. The mixture was stirred at room temperature for 3 hours before recovering the solid by evaporating the iso-propanol at 80°C. The hydrolysis was then performed by adding 20 mL 0.5 M HNO\(_3\) in distilled water and aged overnight, followed by drying at 120 °C.
The solid was washed with distilled water for three times and finally dried at 200 °C for 24 h. Sample denoted as XNbA/MAN, in which X is the percentage of the niobium in wt%.

2.3.2 Acidity Study and Morphology Study

About 20 mg of sample was ground and pressed under 5 tons of pressure for 1 second in order to obtain 13 mm diameter of self-supporting wafer. The wafer was placed in the sample holder then put inside a homebuilt IR cell that consists of Pyrex glass and fitted with CaF2 window. Prior to the adsorption, samples were dehydrated under vacuum (<103 mbar) at 400 °C (MAN) and 200 °C (S/MAN and NbA/MAN) for 16 hours. Acidity of the sample was determined by adsorption of pyridine (as probe molecule) on the evacuated sample at room temperature for a minute at 10 torr, followed by desorption of pyridine at 150 °C under vacuum for one hour. Infrared spectra of the pyridine vibration region were monitored in the range of 1700–1400 cm\(^{-1}\) in adsorbance mode, using Perkin Elmer Spectrum One FTIR Spectrometer.

Field Emission Scanning Electron Microscope (FESEM), Zeiss Supra Series model was used to determine the morphology of the samples.

2.3.3 Catalytic Testing

The catalysts performances were tested in the Friedel-Crafts alkylation reaction of resorcinol (SigmaAldrich, 99%) with tert-butyl methyl ether (MTBE, Fischer, 99.8%). Nitrobenzene (J.T. Baker, 99%) was used as the internal standard. The reaction mixture containing resorcinol, MTBE and internal standard was placed in a round-bottom flask equipped with a condenser. About 0.2 g of the samples were activated for 4 hours and then added at once to the reaction mixture. Sample MAN was activated at 400 °C, while samples S/MAN and NbA/MAN were activated at 200 °C. The reaction was done under reflux in an oil bath with stirring using magnetic bar at 80 °C for 8 hours. The ratio of the resorcinol,
MTBE and internal standard is 2:3:1. For reusability test, the reaction condition for the first cycle is the same as described previously. However, for the subsequent runs the amount of substrates and solvent were scaled down according to the available amount of catalyst. The catalysts were filtered, washed with ethanol and reactivated before being used again. Products of reactions were separated and analysed using gas chromatography with FID detector using Ultra-1 column (length: 25 metres; internal diameter I.D: 0.2 mm; film: 0.11 µm).

2.4 RESULTS AND DISCUSSION

In the Friedel-Crafts alkylation of resorcinol with tert-butyl methyl ether, 4-tert-butylresorcinol and 4,6-di-tert-butylresorcinol were obtained as the major and minor products respectively. The results displayed in Table 2.1 shows that the alkylation of resorcinol with MTBE required the presence of a catalyst. This proved that without the presence of catalyst, the reaction did not produce any product because MTBE was not converted into the reactive species (electrophile). No product was obtained too when mesoporous alumina alone was used as the catalyst in the reaction. This indicates that the reaction needs the presence of Brønsted acid sites is necessary to initiate the reaction, as mesoporous alumina only possesses Lewis acidity as shown in the IR spectra in pyridine vibration region in Figure 2.1.

MAN with a loading as low as 2% of sulfuric acid, produced both monobutylated and dibutylated. This is in agreement with report by Khalaf et al. (2005) which reported that the introduction of a small amount of sulfur compounds onto metal oxides enhanced remarkably the acidic properties of the oxides, regardless of the types of the introduced sulfur compounds. So even though only 2% of sulfuric acid was loaded to the mesoporous alumina, the increase in the acidity was obvious and significant. The trend of the yield of both the dibutylated and mono butylated products corresponding to the niobic acid loading percent showed no significant differences in the yields produced by each of the
samples. Theoretically, the activity of the catalyst should increase with increasing niobium loading on the alumina. However, the results of the catalytic activity contradict with the theory. The results could be caused by the agglomeration among the Nb₂O₅ particles, thus lowering the amount of active sites on the surface of the catalyst. In order to confirm this finding, the morphology of sample 15NbA/MAN was investigated using FESEM.

Table 2.1 Product yield obtained using mesoporous alumina nanoparticles modified with different Brønsted acid precursors

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>4-tert butylresorcinol Yield (mmole)</th>
<th>Selectivity (%)</th>
<th>4,6-diterbutylresorcinol Yield (mmole)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MAN</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2S/MAN</td>
<td>3.52</td>
<td>80.4</td>
<td>0.86</td>
<td>19.6</td>
</tr>
<tr>
<td>5S/MAN</td>
<td>3.18</td>
<td>81.1</td>
<td>0.74</td>
<td>18.9</td>
</tr>
<tr>
<td>10S/MAN</td>
<td>2.85</td>
<td>83.6</td>
<td>0.56</td>
<td>16.4</td>
</tr>
<tr>
<td>15S/MAN</td>
<td>6.08</td>
<td>59.3</td>
<td>4.17</td>
<td>40.7</td>
</tr>
<tr>
<td>2NbA/MAN</td>
<td>3.39</td>
<td>84.3</td>
<td>0.63</td>
<td>15.7</td>
</tr>
<tr>
<td>5NbA/MAN</td>
<td>3.49</td>
<td>82.9</td>
<td>0.72</td>
<td>17.1</td>
</tr>
<tr>
<td>10NbA/MAN</td>
<td>1.83</td>
<td>91.0</td>
<td>0.18</td>
<td>9.0</td>
</tr>
<tr>
<td>15NbA/MAN</td>
<td>3.73</td>
<td>81.3</td>
<td>0.86</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Figure 2.2 shows the FESEM images for samples MAN and 15NbA/MAN magnified by 100,000 times. For sample MAN, a uniform distribution of particles can be seen. Sample 15NbA/MAN on the other hand, showed that aggregation among the particles occurred. EDX analysis was also carried out for sample 15NbA/MAN. EDX results (Table 2.2) show that the amount of niobium species in the sample was higher than aluminium, despite the fact that the amount of aluminium should be higher than niobium. This proved that high loading of niobic acid on mesoporous alumina will leads to agglomeration of the particles, which explains the catalytic testing results.
Figure 2.1 The FTIR spectra of samples MAN, 15S/MAN and 15NbA/MAN after desorption for 1h at 150 °C.

Figure 2.2 FESEM images of samples (a) MAN and (b) 15NbA/MAN magnified by 100,000 times.

Table 2.2 EDX results for sample 15NbA/MAN

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>6.62</td>
</tr>
<tr>
<td>Niobium</td>
<td>11.88</td>
</tr>
<tr>
<td>Oxygen</td>
<td>52.06</td>
</tr>
<tr>
<td>Carbon</td>
<td>29.44</td>
</tr>
</tbody>
</table>
The yield of both of the monobutylated and dibutylated products was higher when mesoporous alumina incorporated with sulfuric acid was used as the catalyst. The same pattern was observed when the reusability tests of the catalysts were carried out. Table 2.3 shows the percent of the yield of the reused catalysts relative to the yield obtained from first time utilization. At 2% loading both 2S/MAN and 2NbA/MAN did not manage to produce any dibutylated product. However, monobutylated resorcinol can still be obtained using 2S/MAN, even though at a reduced amount. None of the catalysts impregnated with niobic acid were active in the production of dibutylated resorcinol in the reusability test. This could be caused by the change of active sites in the Nb species. According to Braga et al. (2005) acidity of the catalyst depends strongly on the Nb species present. When changes in the Nb species occur, the Nb species that present may not be active anymore. Although the amount of yield was decreased, all three 5S/MAN, 10S/MAN and 15S/MAN remained active in the production of both dibutylated and monobutylated resorcinol. By comparison with S/MAN and NbA/MAN, the alumina incorporated with sulfuric acid was more active in the alkylation of resorcinol with tert-butyl methyl ether. This is further supported by the results from pyridine-FTIR (Figure 2.1). Results obtained by pyridine adsorption on pure mesoporous alumina show only the presence of Lewis type acidity. As expected, the FTIR results given in Figure 2.1 confirmed the absence of Brönsted type acidity with the absence of adsorption band near 1540 cm$^{-1}$, characteristics of Brönsted acid sites, whereas the characteristics band at 1451 cm$^{-1}$ that correspond to the vibration of pyridine in sites Lewis type are present. As for sample 15S/MAN and 15NbA/MAN, it is clearly shown that the peak corresponding to Brönsted acid sites at 1540 cm$^{-1}$ is larger for sample 15S/MAN as compared to that of sample 15NbA/MAN. This confirms that even though the loading percents were the same, sulfuric acid is the better source for creating Brönsted acidity on mesoporous alumina. The incorporation of both sulfuric acid and niobic acid also increased the amount of Lewis acid sites on mesoporous alumina.
Table 2.3 Reuse of the catalysts for alkylation of resorcinol with MTBE

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>4-tertbutylresorcinol</th>
<th>4,6-diterbutylresorcinol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S/MAN</td>
<td>12.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5S/MAN</td>
<td>80.5</td>
<td>58.1</td>
<td></td>
</tr>
<tr>
<td>10S/MAN</td>
<td>145.6</td>
<td>196.4</td>
<td></td>
</tr>
<tr>
<td>15S/MAN</td>
<td>70.9</td>
<td>35.7</td>
<td></td>
</tr>
<tr>
<td>2NbA/MAN</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5NbA/MAN</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10NbA/MAN</td>
<td>23.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15NbA/MAN</td>
<td>14.2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

2.5 CONCLUSION

This study was aimed at understanding the reactivity of incorporated niobic acid and sulfuric acid on mesoporous alumina nanoparticles in the alkylation of resorcinol with tert-butyl methyl ether. The amount of products obtained was higher when sulfated mesoporous alumina nanoparticles were used as the catalyst as compared to mesoporous alumina nanoparticles incorporated with niobic acid. The reusability test also showed that the acid sites created by sulfuric acid were more stable and S/MAN remains active in the alkylation of resorcinol. It indicates that sulfuric acid has created a more stable and higher strength of Brönsted acidity in alumina as compared to niobic acid.

In this research, Brönsted acid precursors were incorporated on mesoporous alumina nanoparticles by post synthesis modifications. Some of the Brönsted acid precursors were easily leached out, therefore unable to enhance the acidity of mesoporous alumina. Therefore Brönsted acid precursors should be incorporated on mesoporous alumina via direct synthesis method in order to promote greater interaction between alumina and the Brönsted acid precursors. The porosity of the catalysts could also be tested by carrying out alkylation reactions using
bulkier reactants such as napthol.

REFERENCES


Chemistry and Physics. 93: 443 – 449.