

# Immobilization of aluminum chloride on MCM-41 as a new catalyst system for liquid-phase isopropylation of naphthalene

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## Abstract

A great deal of effort has been made at searching for alternative catalysts to replace conventional Lewis acid catalyst aluminum trichloride ( $\text{AlCl}_3$ ). In this paper, immobilization of  $\text{AlCl}_3$  on mesoporous MCM-41 silica with and without modification was carried out. The catalytic properties of the immobilized catalyst systems for liquid-phase isopropylation of naphthalene were studied and compared with those of H/MCM-41 and H/mordenite. The structures of the surface-immobilized aluminum chloride catalysts were studied and identified by using solid-state magic angle spinning nuclear magnetic resonance (MAS NMR), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), nitrogen adsorption, and X-ray diffraction (XRD) techniques. The catalytic activity of the immobilized catalysts was found to be similar to that of acidic mordenite zeolite. A significant enhancement in the selectivity of 2,6-diisopropylnaphthalene (2,6-DIPN) was observed over the immobilized aluminum chloride catalysts. Immobilization of aluminum chloride on mesoporous silica coupled with surface silylation is a promising way of developing alternative catalyst system for liquid-phase Friedel–Crafts alkylation reactions. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Aluminum chloride; MCM-41; Isopropylation of naphthalene; Silylation

## 1. Introduction

Liquid-phase Friedel–Crafts isopropylation of naphthalene is a process currently used in the chemical industry to produce 2,6-diisopropylnaphthalene (2,6-DIPN), an important chemical intermediate for manufacturing advanced polymers and polyesters [1]. The catalyst used in this process is Lewis acid  $\text{AlCl}_3$  [2]. While  $\text{AlCl}_3$  is catalytically efficient and readily available commercially, the use of it as a

catalyst is environmentally problematic [1]: (i) the  $\text{AlCl}_3$  catalyst produces the thermodynamic ratio of the desired linear 2,6-DIPN and the undesired nonlinear 2,7-diisopropylnaphthalene (2,7-DIPN) and other DIPN isomers, requiring a costly separation step to isolate the 2,6 isomer; (ii) significant quantities of other naphthalene derivatives such as 2-isopropylnaphthalene (2-IPN) are formed, which must also be separated and removed or recycled; (iii) the  $\text{AlCl}_3$  catalyst cannot be regenerated and must be hydrolyzed and disposed of, resulting in a large volume of solid waste. Consequently, much research effort has been directed towards zeolite alternatives

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[1,3–10]. Despite the improved selectivity towards 2,6-DIPN, coking and pore blocking have been found to be unavoidable for zeolite catalysts, resulting in rapid catalyst deactivation.

Immobilization of aluminum chloride on inorganic supports (mainly porous materials such as silica and alumina) was achieved and the immobilized materials were used as catalysts in previous studies [11–17]. It has been demonstrated that immobilized aluminum chloride catalysts display high activity for gas-phase isomerization and cracking reactions [11]. For liquid-phase Friedel–Crafts alkylations, a much lower activity than that of aluminum chloride itself has been observed [13]. Recently, Clark et al. reported that immobilized aluminum chloride on porous supports possesses a high activity in the liquid-phase alkylation of aromatics [16,17]. Of particular interest is the observation that substantial increases in selectivity towards monoalkylation of benzene can be achieved through the use of hexagonal mesoporous silica (HMS) [18] as a support [17].

As part of our effort to develop environmentally friendly alternative catalysts for replacing the currently used environmentally unfriendly ones in naphthalene alkylation, this study aims to immobilize aluminum chloride on ordered mesoporous molecular sieves. A preliminary study showed that immobilized aluminum chloride on mesoporous MCM-41 silica is a promising alternative catalyst system for liquid-phase isopropylation of naphthalene [19]. The appropriate acidic properties and the mesoporous structure coupled with controllable surface properties afford high catalytic activity, easy diffusion and transport of isopropylated products, and high selectivity of 2,6-DIPN. In this paper, we report a more detailed study on the catalytic performance of the various catalysts, the catalytic species, the catalyst structures and the observed high selectivity of 2,6-DIPN in the reaction of isopropylation of naphthalene in a liquid-phase.

## 2. Experimental

### 2.1. Synthesis and modification of MCM-41 silica

The synthesis of pure-silica MCM-41 support followed the procedures of Beck et al. [20], where cetyltrimethylammonium bromide surfactant was used

as the template. The details were reported previously [21]. Selective modification of the external-surface of MCM-41 was achieved by silylation of the as-synthesized sample using trimethylchlorosilane [22,23]. In brief, 2 g of as-synthesized MCM-41 powder was extensively washed using a mixture of ethanol and water (1:1 v/v) to clean up the external-surfaces, followed by filtration and drying at 110 °C. The sample was soaked in a trimethylchlorosilane solution in toluene with a concentration of 5 wt.% (solid:liquid = 1 g:50 ml) at room temperature under stirring. The solid was then filtered off, washed with toluene and acetone to rinse away any residual trimethylchlorosilane, and dried again at 110 °C. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements confirmed the presence of trimethylsilyl species because of the appearance of a resonance peak at 14 ppm [23]. By modifying the as-synthesized MCM-41, only the external-surface of the sample was silylated while the interior surface remained unaffected due to the existence of the surfactant template.

### 2.2. Template removal

Template removal was carried out using solvent extraction method as briefed later. One gram solid was combined with 100 ml 1 M HCl solution in dimethyl ether under stirring at 50 °C overnight. In order to achieve complete removal of the template, the experiment was repeated until no further mass loss was observed at the temperature range of 200–450 °C using the technique of thermogravimetric analysis (TGA).

### 2.3. Immobilization of aluminum chloride

Two types of immobilized catalysts were prepared. One was prepared by immobilization of aluminum chloride on MCM-41 silica without modification, designed as  $\text{AlCl}_x\text{-MCM-41}$  ( $x = 1$  or  $2$ ). The other one was prepared by immobilization of aluminum chloride on the external-surface-silylated MCM-41 support, denoted  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  (ESM: external-surface modification). The preparation of both catalysts was essentially similar to that reported by Clark et al. [16,17]. In brief, template-free MCM-41 support was heated at 400 °C for 2 h prior to being introduced into a flask containing benzene

(99.99%) and anhydrous  $\text{AlCl}_3$  (BDH) ( $\text{AlCl}_3$ : support:solvent = 2 g:5 g:100 ml). The flask was stirred at room temperature for 4 h. The solid was filtered off, washed with benzene, and dried at  $110^\circ\text{C}$ . The only difference between the two catalysts is MCM-41 silica without surface modification was used for preparing catalyst  $\text{AlCl}_x$ -MCM-41 while external-surface-modified MCM-41 was used for preparing catalyst  $\text{AlCl}_x$ -MCM-41 (ESM).

Other catalysts involved in this study were H/MCM-41 (Si/Al = 15) and H/mordenite (Si/Al = 13). The H/MCM-41 catalyst was prepared by ion-exchange of the calcined MCM-41 using 1 M  $\text{NH}_4\text{NO}_3$  solution at  $80^\circ\text{C}$  followed by washing, drying, and calcination. The preparation of the H/mordenite catalyst has been described previously [3].

#### 2.4. Catalyst characterization

The chemical compositions of samples were determined by using ICP–AES (Spectroflame Model P) and XPS. XPS data were collected on a PHI Model 560 XPS/SAM/SIMS I multi-technique surface analysis system. Atomic concentrations were calculated from peak areas by using linear baselines and “in-house” experimentally determined sensitivity factors as described by Ward and Wood [24]. XRD spectra were recorded on a PW 1050 diffractometer (Philips) using  $\text{Cu K}\alpha$  radiation. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature on a NOVA 1200 microanalyzer (Quanta Chrome). Before analysis, samples were degassed at  $200^\circ\text{C}$  for 4 h under vacuum ( $10^{-3}$  Torr). Total surface area was calculated by using the multi-point BET method in the relative pressure range of 0.05–0.2 while total pore volume was derived from the nitrogen adsorption amount at the relative pressure of 0.95. Pore diameter was estimated from the peak position of a BJH pore size distribution curve. Nuclear magnetic resonance (NMR) measurements were conducted on a Bruker MSL 300 spectrometer using a 7 mm Bruker magic angle spinning (MAS) probe.  $^1\text{H}$ - $^{29}\text{Si}$  CP/MAS NMR spectra were collected at a frequency of 59.63 MHz using the standard cross polarization (CP) pulse sequence, with a spinning rate of 2.9 kHz, reported relatively to TMS.  $^{27}\text{Al}$  MAS NMR spectra were recorded at a frequency of 78.21 MHz and a spinning rate of 8 kHz, reported

relatively to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . FTIR spectra of chemically adsorbed pyridine were collected on a Perkin-Elmer 2000 FTIR spectrometer. Catalyst was activated in an IR cell at  $250^\circ\text{C}$  under vacuum for 4 h, cooled down to  $120^\circ\text{C}$ , followed by exposure to pyridine at this temperature for 30 min. The sample was then evacuated at this temperature under vacuum ( $10^{-5}$  Torr) for 1 h to remove physically adsorbed pyridine. Finally, the spectrum was recorded at room temperature.

#### 2.5. Catalytic tests

The isopropylation of naphthalene was carried out in a Parr batch reactor equipped with a temperature controller. Naphthalene (0.02 mol), isopropyl alcohol (0.04 mol) and freshly calcined catalyst (1.5 g) were loaded in the reactor containing 200 ml (some 1.8 mol) of cyclohexane (solvent). The reactor was flushed with nitrogen before temperature was increased to remove the air in the reactor. Temperature was then raised to  $200^\circ\text{C}$ . After 4 h, the reactor was cooled to room temperature. The contents of the reactor were washed with acetone. The solid catalyst was filtered off, washed with hot benzene and stored for further characterization and reuse. The liquid products were analyzed by using a GC–FID with a DB-17 column (30 m  $\times$  0.25 mm). Products were identified with a GC–MS system using the same column. The detailed qualitative and quantitative analyses are similar to those reported previously [25].

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

A comprehensive characterization of the catalysts was performed by using XRD, TEM, nitrogen adsorption and XPS. The textural and compositional properties of the catalysts involved in this study along with the parent MCM-41 are presented in Table 1. XRD and TEM characterization data confirmed that the MCM-41 support is a high-quality mesoporous material. The XRD and TEM data also demonstrated that the structure of the mesoporous supporting material remained intact through the silylation and template removal processes. The observed features in terms of structural property after immobilizing

Table 1  
Physicochemical properties of catalysts and catalyst supports

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume (ml/g)	Pore diameter (nm)	Atomic ratio <sup>a</sup>		
				Al:Si <sub>Bulk</sub>	Al:Si <sub>XPS</sub>	Cl:Al <sub>XPS</sub>
AlCl <sub>x</sub> -MCM-41	723	0.67	2.3	0.019	0.023	1.56
AlCl <sub>x</sub> -MCM-41 (ESM)	778	0.70	2.0	0.020	0.021	2.08
Parent MCM-41	1230	1.2	3.0	Nil	Nil	N/A <sup>b</sup>
H/MCM-41	1040	1.1	3.0	0.058	0.064	0
H/Mordenite	444	0.32	0.65 × 0.70	0.076	0.075	0

<sup>a</sup> The atomic ratio of Al:Si was measured using both ICP–AES (denoted Al:Si<sub>Bulk</sub>) and XPS (denoted Al:Si<sub>XPS</sub>) while the atomic ratio of Cl:Al was measured using only XPS.

<sup>b</sup> Not measured.

aluminum chloride were the decreases in surface area, pore volume, and diameter (see Table 1). These changes are due to the surface attachment of AlCl<sub>x</sub> species, which resulted in the decreased surface area, pore volume and diameter. The data in Table 1 also show that both Cl and Al atoms are present in catalysts AlCl<sub>x</sub>-MCM-41 (ESM) and AlCl<sub>x</sub>-MCM-41, whereas neither Cl nor Al was detected on the parent MCM-41 silica, further demonstrating the success in the immobilization of aluminum chloride. For catalyst AlCl<sub>x</sub>-MCM-41 (ESM), the value of atomic ratio of Cl:Al measured by XPS is 2.08, very close to 2, indicating that the most possible Al species is –AlCl<sub>2</sub>. For catalyst AlCl<sub>x</sub>-MCM-41, the atomic ratio of Cl:Al measured by XPS is 1.56, smaller than that of catalyst AlCl<sub>x</sub>-MCM-41 (ESM), indicating the presence of not only –AlCl<sub>2</sub> but also –AlCl species. In addition, the value of Al:Si ratio measured by XPS is larger than that measured by ICP–AES for both AlCl<sub>x</sub>-MCM-41 (ESM) and AlCl<sub>x</sub>-MCM-41 catalysts, indicating surface enrichment of Al. These

quantitative-analysis results suggest that aluminum chloride was essentially grafted on the surface rather than inserted into the framework of the MCM-41 support. For catalysts H/MCM-41 and H/mordenite, the surface area and Al:Si ratio indicate that the chemical compositions and the framework structures were hardly affected during the NH<sub>4</sub><sup>+</sup>-exchange and subsequent calcination steps.

### 3.2. Catalytic properties

The catalytic properties of the various catalysts were evaluated in terms of the conversion of naphthalene (activity) and the yields of products and are shown in Table 2. Theoretically, there are more than 12 products in naphthalene isopropylation: two monoisopropyl naphthalene (MIPN) including 1- and 2-IPN, 10 DIPN isomers including 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- and 2,7-DIPN, and polyalkylated naphthalenes such as triisopropyl naphthalene, etc. It can be seen from Table 2 that both AlCl<sub>x</sub>-MCM-41

Table 2  
Comparison of catalyst performance in the isopropylation of naphthalene

Catalyst	Conversion (mol%) <sup>a</sup>	Product distribution (mol%)			Selectivity of DIPNs (mol%)						
		DIPNs	MIPNs <sup>b</sup>	Others <sup>c</sup>	2,6	2,7	1,3	1,4	1,5	1,6	1,7
AlCl <sub>x</sub> -MCM-41	88.5	65.5	25.5	4.50	41.0	18.6	14.0	8.60	6.08	4.90	6.82
AlCl <sub>x</sub> -MCM-41 (ESM)	85.2	72.3	25.4	2.30	60.9	21.6	7.50	2.00	2.00	2.15	3.85
AlCl <sub>3</sub>	96.4	56.3	33.1	10.6	36.7	37.2	5.90	5.32	5.05	5.44	4.40
H/MCM-41	60.4	38.4	51.8	9.80	38.6	23.5	18.0	0.00	6.80	4.55	8.55
H/Mordenite	84.8	44.5	55.5	0.00	44.3	22.2	13.7	2.20	1.88	10.5	5.32

<sup>a</sup> Conversion of naphthalene.

<sup>b</sup> MIPNs including 1- and 2-IPN.

<sup>c</sup> Others including tri- and tetra-IPNs, etc.

and  $\text{AlCl}_x\text{-MCM-41}$  (ESM) exhibited good catalytic activity, similar to that of H/mordenite. Despite a slightly lower activity, catalysts  $\text{AlCl}_x\text{-MCM-41}$  and  $\text{AlCl}_x\text{-MCM-41}$  (ESM) produced much more DIPNs with a higher selectivity of 2,6-DIPN than that of  $\text{AlCl}_3$ . The Lewis  $\text{AlCl}_3$  catalyzed the formation of 56.3% of DIPNs and the selectivity of 2,6-DIPN was 36.7% with 2,6-/2,7-DIPN = 0.987. For catalyst  $\text{AlCl}_x\text{-MCM-41}$ , the yield of DIPNs was 65.5% and the selectivity of 2,6-DIPN was 41.0% with 2,6-/2,7-DIPN = 2.20. Most significantly, catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM) produced 76.3% DIPNs with a 2,6-DIPN selectivity of 69.9% and 2,6-/2,7-DIPN = 2.82. The earlier results indicate that 2,6-DIPN can be selectively produced over the two immobilized catalyst systems, in particular over catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM), whose external-surface has been selectively modified by silylation. The significant enhancement of selectivity of 2,6-DIPN was not expected and cannot be explained from the shape selectivity point of view because the pore diameter of catalysts  $\text{AlCl}_x\text{-MCM-41}$  and  $\text{AlCl}_x\text{-MCM-41}$  (ESM) is between 2 and 2.3 nm, whereas, the kinetic diameter of 2,6-DIPN is about 0.72 nm. The most probable reasons could be the difference in electronic properties between 2,6- and 2,7-DIPN isomers [26]. At present, we are carrying out fundamental study in combination with computational analysis in order to elucidate the observed enhancement in selectivity. However, the further improvement on both catalytic activity and selectivity of 2,6-DIPN after selective silylation of the external-surface of the MCM-41 silica support can be explained in terms of (1) the poisoning of the external active sites by silylation and (2) the enhancement of surface hydrophobicity so that isopropyl alcohol-adsorption-induced catalyst deactivation was largely avoided.

For the acidic mordenite catalyst, the yield of 2,6-DIPN was about 44% with a 2:1 ratio of 2,6-DIPN:2,7-DIPN, which is in good agreement with the previously reported data [3]. The H/MCM-41 catalyst gave rise to the formation of the lowest amount of DIPNs and the highest amount of by-products.

Overall, the earlier catalytic data demonstrate that substantial increases in DIPN yield and 2,6-DIPN selectivity have been achieved through the use of mesoporous silica-immobilized aluminum chloride catalysts. The increases are remarkable particularly

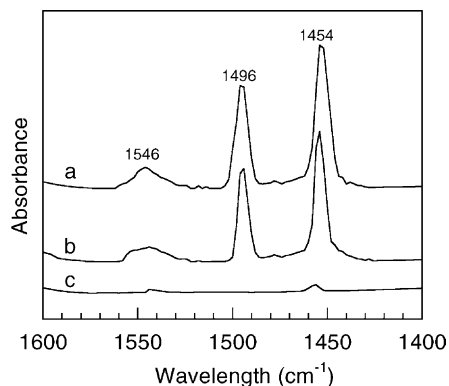


Fig. 1. Pyridine-FTIR spectra of (a)  $\text{AlCl}_x\text{-MCM-41}$  (ESM), (b)  $\text{AlCl}_x\text{-MCM-41}$ , and (c) siliceous MCM-41.

when the external-surface of the silica support was poisoned by silylation to remove the hydroxyl groups and to enhance the surface hydrophobicity of the support. These observations indicate the potential application of immobilized aluminum chloride as an alternative catalyst system for the liquid-phase isopropylation of naphthalene.

### 3.3. Catalyst characterization

The catalysts were characterized by using a number of techniques. Fig. 1 shows the pyridine-FTIR spectra of (a)  $\text{AlCl}_x\text{-MCM-41}$  (ESM), (b)  $\text{AlCl}_x\text{-MCM-41}$  and (c) the parent MCM-41 silica. It can be seen that both  $\text{AlCl}_x\text{-MCM-41}$  and  $\text{AlCl}_x\text{-MCM-41}$  (ESM) exhibit bands at 1546, 1496 and 1454  $\text{cm}^{-1}$ . According to a recent study [27], the band at 1546  $\text{cm}^{-1}$  is attributed to Brönsted acid sites, the band at 1454  $\text{cm}^{-1}$  is assigned to Lewis acid sites and the band at 1496  $\text{cm}^{-1}$  is assigned to a combination signal associated with both Brönsted and Lewis acid sites. For the parent MCM-41 silica, no significant signal was observed in the wavelength region between 1400 and 1600  $\text{cm}^{-1}$  upon pyridine adsorption except for a very weak peak at 1458  $\text{cm}^{-1}$ , indicating that the siliceous MCM-41 possesses little acidity. From Fig. 1 it can also be seen that Lewis acid sites are the predominant acid species on the two immobilized aluminum chloride catalysts.

Fig. 2 compares the  $^1\text{H}\text{-}^{29}\text{Si}$  CP/MAS NMR spectrum of the parent MCM-41 with that of

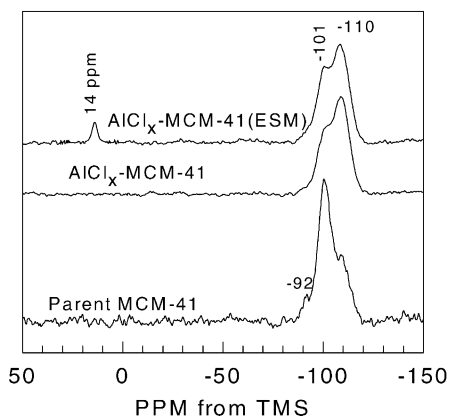


Fig. 2.  $^1\text{H}$ - $^{29}\text{Si}$  CP/MAS NMR spectra of MCM-41 silica support before and after immobilization of aluminum chloride.

$\text{AlCl}_x\text{-MCM-41}$  and  $\text{AlCl}_x\text{-MCM-41 (ESM)}$ . Three peaks centered at  $-92$ ,  $-101$ , and  $-110$  ppm, assigned to  $\text{Q}^2$  (geminal silanol groups),  $\text{Q}^3$  (single silanol groups), and  $\text{Q}^4$  [23], respectively, can be seen on the parent MCM-41 surface. After immobilization of aluminum chloride,  $\text{Q}^2$  sites disappeared while the intensity of the  $\text{Q}^3$  sites decreased. There was a substantial increase in intensity of the  $\text{Q}^4$  sites, indicating that reaction between  $\text{AlCl}_3$  and geminal and single silanol groups occurred, resulting in the transformations of  $\text{Q}^3$  sites to  $\text{Q}^4$  sites, as well as  $\text{Q}^2$  sites to  $\text{Q}^3$  and/or  $\text{Q}^4$  sites. The reaction between  $\text{AlCl}_3$  and the single silanol groups (associated with  $\text{Q}^3$  sites) was not complete because of the observation of the  $\text{Q}^3$  sites. This is in agreement with our previous studies [22,23], which found the maximum degree of surface coverage of trimethylsilyl groups to be about 80%. The peak at about 14 ppm on  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  is due to the presence of the Si sites of trimethylsilyl groups because of the silylation prior to grafting of aluminum chloride.

$^{27}\text{Al}$  NMR technique is among the most powerful methods for obtaining structural information on aluminosilicates. It has been demonstrated that  $^{27}\text{Al}$  chemical shifts vary with not only the coordination number of the aluminum species but also the types of ligands [14,28–30]. Shown in Fig. 3 are the  $^{27}\text{Al}$  MAS NMR spectra of (a)  $\text{AlCl}_3$ , (b)  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  and (c)  $\text{AlCl}_x\text{-MCM-41}$ . Only one resonance peak at about 8.1 ppm is seen on  $\text{AlCl}_3$ . This peak is readily assigned to six-coordinate Al species. Catalyst

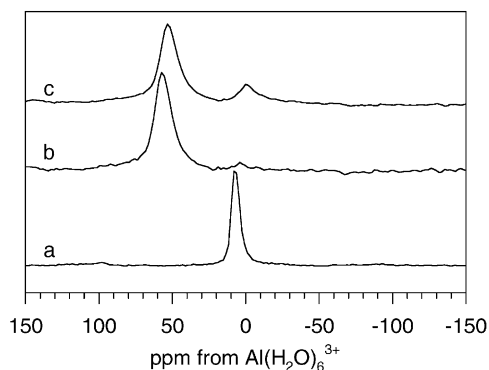


Fig. 3.  $^{27}\text{Al}$  MAS NMR spectra of catalysts (a)  $\text{AlCl}_3$ , (b)  $\text{AlCl}_x\text{-MCM-41}$ , and (c)  $\text{AlCl}_x\text{-MCM-41 (ESM)}$ .

$\text{AlCl}_x\text{-MCM-41 (ESM)}$  has a very strong peak at 57.3 ppm with a very small shoulder peak at 4.2 ppm, assigned to four- and six-coordinate Al atoms, respectively. Catalyst  $\text{AlCl}_x\text{-MCM-41}$  exhibits a main peak at 53.3 ppm and a shoulder peak at 0 ppm, attributed to four- and six-coordinate Al species, respectively. The observed differences in chemical shifts of both four- and six-coordinate Al atoms between  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  and  $\text{AlCl}_x\text{-MCM-41}$  are probably due to the difference in coordinate ligands. It can therefore be concluded that there are two types of Al species on both catalysts  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  and  $\text{AlCl}_x\text{-MCM-41}$ , namely six- and four-coordinate Al.

### 3.4. Proposed catalyst structures

Based on the earlier NMR results and the XPS data (see Table 1) and previous studies [11–15,22,23], four possible types of catalyst structures are proposed as shown in Fig. 4. Structure (a) with a  $^{27}\text{Al}$  chemical shift of 51–57 ppm, derived from the reaction of  $\text{AlCl}_3$  with two adjacent isolated silanol groups, constitutes the major Al species, accounting for the catalytic activity. Structure (b) with a  $^{27}\text{Al}$  chemical shift of 51–57 ppm, derived from the reaction of  $\text{AlCl}_3$  with geminal silanol groups, constitutes a very small part of the catalyst species because of the very low density of geminal silanol groups on MCM-41 silica [23]. Catalyst  $\text{AlCl}_x\text{-MCM-41 (ESM)}$  contains only species (a) and (b). Apart from these two structures, other two catalytic species can be found on catalyst  $\text{AlCl}_x\text{-MCM-41}$ , namely, (c) and (d). Structure (c) is believed to be derived from structure (a) because of the

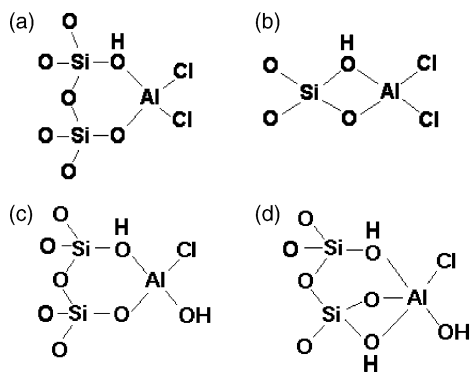


Fig. 4. Proposed catalyst structures.

hydrolysis of Al–Cl while structure (d) can be formed the further reaction of species (b) with a closest free silanol group under the induction of moisture.

Because of the presence of Al species of (c) and (d) in catalyst  $\text{AlCl}_x\text{-MCM-41}$ , this catalyst showed a lower catalytic activity than catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM). Because of the partial hydrolysis of Al–Cl bonds in catalyst  $\text{AlCl}_x\text{-MCM-41}$ , the Cl:Al atomic ratio of this catalyst is lower than that of catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM).

### 3.5. Stability of catalysts

After 4 h reaction,  $\text{AlCl}_x\text{-MCM-41}$  and  $\text{AlCl}_x\text{-MCM-41}$  (ESM) were recovered and washed with hot benzene followed by calcination at  $400^\circ\text{C}$ . The catalytic properties were examined using the same conditions as the fresh catalyst. Catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM) exhibited 85.2% conversion of naphthalene and a 2.64:1 ratio of 2,6-DIPN:2,7-DIPN, similar to that of the fresh catalyst. However, catalyst  $\text{AlCl}_x\text{-MCM-41}$  showed a much lower catalytic activity with 33.5% conversion of naphthalene than the fresh catalyst, which was 88.5% (see Table 1). Fig. 5 compares the  $^{27}\text{Al}$  MAS NMR spectra of the catalysts before and after 4 h reaction. It can be seen that the  $^{27}\text{Al}$  MAS NMR spectrum of catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM) after 4 h reaction is essentially identical to that of the fresh catalyst, showing that this catalyst is stable under the reaction conditions. However, the  $^{27}\text{Al}$  MAS NMR spectrum of catalyst  $\text{AlCl}_x\text{-MCM-41}$  after 4 h reaction became less resolved with a strong background of noise, indicating that Al leaching may

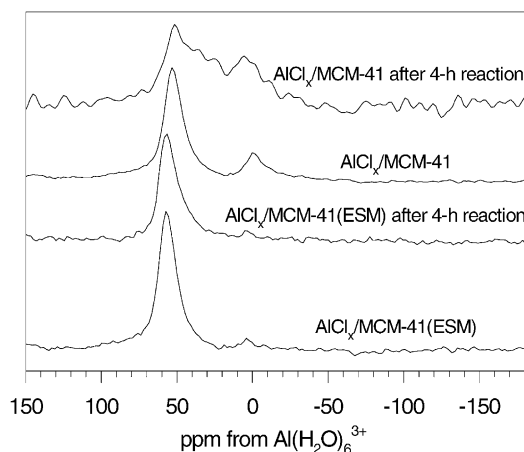


Fig. 5.  $^{27}\text{Al}$  MAS NMR spectra of catalysts  $\text{AlCl}_x\text{-MCM-41}$  (ESM) and  $\text{AlCl}_x\text{-MCM-41}$  before and after 4 h catalytic reaction.

have occurred during the 4 h reaction. It can be concluded that that catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM) is stable under the reaction conditions and is reusable while catalyst  $\text{AlCl}_x\text{-MCM-41}$  has a poor stability. The enhanced surface hydrophobicity due to surface silylation accounts for the significant improvement of the stability of catalyst  $\text{AlCl}_x\text{-MCM-41}$  (ESM).

## 4. Conclusions

Immobilization of  $\text{AlCl}_3$  on MCM-41 silica surface results in the formation of both Brönsted and Lewis acidic sites, which are the active sites for liquid-phase isopropylation of naphthalene. Selective silylation of the external-surface of MCM-41 silica support can significantly improve catalyst performance owing to the removal of external-surface silanol groups as well as enhanced surface hydrophobicity. Immobilization of  $\text{AlCl}_3$  on surface-modified MCM-41 silica is a promising method for developing environmentally friendly alternative catalyst for the isopropylation of naphthalene in liquid-phase. Such a catalyst system may find applications in other Friedel–Crafts reactions.

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