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Mesoporous silica-immobilized aluminium chloride as a new catalyst system for the isopropylation of naphthalene

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Mesoporous MCM-41 silica immobilized aluminium chloride shows high catalytic activity and selectivity in the Friedel–Crafts alkylation of naphthalene with isopropanol.

Liquid phase Fridel–Crafts isopropylation of naphthalene over $AlCl_3$ catalysts is widely used in the chemical industry to manufacture 2,6-diisopropylnaphthalene (2,6-DIPN), an important chemical intermediate for making monomers of advanced polymers.[1] While $AlCl_3$ is catalytically efficient and readily available commercially, it has a number of drawbacks: (1) $AlCl_3$ catalyzes the formation of the desired 2,6-DIPN and the undesired 2,7-diisopropylnaphthalene (2,7-DIPN) in a thermodynamic ratio (2,6- : 2,7-DIPN = 1 : 1), requiring a costly separation step to isolate the 2,6 isomer; (2) significant quantities of other isopropylated derivatives such as 2-isopropylnaphthalene (2-IPN) are formed, which must also be separated and removed or recycled; (3) $AlCl_3$ is a stoichiometric reagent that cannot be regenerated and has to be hydrolyzed and disposed of, resulting in a large volume of solid waste. As a result, there has been an interest in finding environmentally friendly alternative catalyst systems.[1–3]

Immobilization of aluminium chloride onto inorganic support materials has been studied previously.[4–8] Of particular interest is the observation that aluminium chlorides immobilized on silica gel and on mesoporous HMS are highly active in the liquid-phase alkylation of aromatic molecules while the selectivity towards the formation of monoalkylates is considerably better than under homogeneous conditions, and the immobilized catalyst systems are recoverable and reusable.[7,8] Therefore, we initiated our investigation on the immobilization of aluminium chloride on mesoporous MCM-41[9] for the liquid-phase alkylation of naphthalene.

The pure-silica MCM-41 support was prepared using cetyltrimethylammonium bromide† as the template according to the method described by Beck *et al.*[9] Two immobilized catalysts designed as $AlCl_x$/MCM-41 and $AlCl_x$/MCM-41(ESM) (ESM refers for external surface modification) respectively were prepared. The preparation of $AlCl_x$/MCM-41 was similar to that reported by Clark *et al.*[8] The procedures of preparing catalyst $AlCl_x$/MCM-41(ESM) are described as follows. The external surface of the MCM-41 support was modified by silylation, using trimethylchlorosilane. It was achieved by modifying the as-synthesized MCM-41 sample before template removal (the template acts as protecting species equivalent to the protecting groups in the organic synthesis). The detailed modification procedures have been described previously.[10] After modification of the external surface, the surfactant template was removed by solvent extraction using 1 M HCl in ethanol at 50 °C under stirring (1 g of MCM-41 in 50 ml of solution), followed by calcination at 450 °C to achieve the maximum density of internal surface silanol groups[11] while maintaining the external surface-attached trimethylsilyl groups without burning off (according to thermogravimetric analysis, the thermal decomposition temperature of the trimethylsilyl species is about 650 °C). Aluminium chloride was grafted onto the internal surface of the MCM-41 support by refluxing benzene (99.99%) containing anhydrous $AlCl_3$ (BDH) and the support ($AlCl_3$: support : benzene = 2 g : 5 g : 100 ml) at room temperature for 4 h. No reaction occurred on the external surface because the silanol groups on the external surface had already been poisoned during the silylation step. The solid was filtered off, washed with benzene and dried at 110 °C. Other catalysts involved in this study included H/MCM-41 (Si : Al = 15 : 1) and H/Mordenite (Si : Al = 13 : 1).

The catalysts were characterized using the techniques of ICP-AES (Spectroflame Model P), XPS (PHI Model 560 XPS/SAM/SIMS I), XRD (PW 1050 diffractometer, Cu Kα radiation), Nitrogen adsorption (NOVA 1200, Quanta Chrome), and solid-state NMR (Bruker MSL 300 spectrometer). The properties of the catalysts are shown in Table 1.

The isopropylation of naphthalene was carried out in a Parr batch reactor equipped with a temperature controller. Naphthalene (0.02 mol), isopropanol (0.04 mol) and fresh catalyst (1.5 g) were loaded in an autoclave containing 200 ml of cyclohexane (solvent). The reaction temperature was 200 °C and the pressure was autogenous. After 4 h, the reactor was cooled to room temperature, and the liquid products were analyzed using a GC-FID with a DB-17 column (30 m × 0.25

Table 1 Physical and chemical properties of catalysts

				Atomic ratio[a]		
Sample	Surface area/$m^2\,g^{-1}$	Pore volume/$ml\,g^{-1}$	Pore diameter/nm	$Al:Si_{Bulk}$	$Al:Si_{XPS}$	$Cl:Al_{XPS}$
$AlCl_x$/MCM-41	723	0.67	2.3	0.019	0.023	1.56
$AlCl_x$/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
H/MCM-41	1040	1.1	3.0	0.058	0.064	0
H/Mordenite	444	0.32	0.65 × 0.70[12]	0.076	0.075	0

[a] The atomic ratio of Al : Si was measured using both ICP-AES (denoted $Al:Si_{Bulk}$) and XPS (denoted $Al:Si_{XPS}$) while the atomic ratio of Cl : Al was measured using XPS only.

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Table 2 Catalytic properties of catalysts

Catalyst	Conv.[a] (mol%)	DIPN yield (mol%)	DIPN selectivity (mol%)			Other products[c] (mol%)
			2,6	2,6:2,7	Other[b]	
$AlCl_x$/MCM-41	88.5	65.5	41.0	2.20	40.4	34.3
$AlCl_x$/MCM-41(ESM)	85.2	72.3	60.9	2.82	17.5	27.7
$AlCl_3$	96.4	56.3	36.7	0.986	26.1	43.7
H/MCM-41	60.4	38.4	38.6	1.64	37.9	61.6
H/Mordenite	84.8	44.5	44.3	2.00	33.6	55.4

[a] Conversion of naphthalene. [b] Other DIPN isomers. [c] Other products except DIPNs including MIPN, tri-, and tetra-IPNs, *etc*.

mm). Product identification was carried out using a GC/MS system. Comparisons of the catalytic performance of the catalysts are summarized in Table 2.

Table 1 shows that both the pure-silica and the aluminosilicate MCM-41 materials are of high quality with a pore diameter of 3.0 nm. As expected, immobilization of aluminium chloride on MCM-41 silica resulted in a reduction of surface area, pore volume, and pore diameter. The chemical analysis data further prove the attachment of aluminium chloride on the surface of the MCM-41 silica. The Al contents analyzed using ICP-AES are consistent with that analyzed using XPS.

It can be seen from Table 2 that the highest activity was observed on $AlCl_3$ while the lowest activity was observed on H/MCM-41. The two immobilized catalysts exhibit a reasonable catalytic activity, similar to that of H/Mordenite. Despite a slightly lower activity for catalysts $AlCl_x$/MCM-41 and $AlCl_x$/MCM-41(ESM) compared to $AlCl_3$, there are significant differences in the yield and selectivity of products. With $AlCl_x$/MCM-41 and $AlCl_x$/MCM-41(ESM) as the catalysts, DIPNs were the major products, whereas the other catalysts produced a large amount of other products. Very remarkably, $AlCl_x$/MCM-41(ESM) catalyzed the formation of 72.3% DIPNs with a selectivity of 2,6-DIPN of 60.9% while $AlCl_x$/MCM-41 produced 65.5% DIPNs with a selectivity of 2,6-DIPN of 41.0%. The significant enhancement of selectivity towards 2,6-DIPN after modification of the external surface of the MCM-41 support is explicable only in terms of the differences in the pore-opening size and the nature of the external surfaces of the two catalysts. The selective modification of the external surface of the MCM-41 support resulted in a reduction of the pore-opening size (see Table 1) and the poisoning of the external catalytically active sites. The former probably enabled shape-selectivity while the latter led to the avoidance of the catalytic reaction taking place on the external surface of the $AlCl_x$/MCM-41(ESM) catalyst.

After the 4 h reaction, catalyst $AlCl_x$/MCM-41(ESM)† was filtered off, washed with hot benzene and calcined at 450 °C for 2 h. Subsequent characterization using ^{27}Al NMR and catalytic tests were carried out. The chemical shifts of ^{27}Al before and after the 4 h reaction were found to be about 53.0 and 52.2 ppm, respectively, indicating that the immobilized aluminium chloride species had hardly changed. It was also observed that both the activity and selectivity towards 2,6-DIPN remained unchanged.

Overall, the results discussed above demonstrate that immobilization of aluminium chloride on mesoporous MCM-41 silica can create substantial density of acidic sites, which are catalytically responsible for the liquid-phase isopropylation of naphthalene. Most remarkably, a significant increase in selectivity towards 2,6-DIPN can be achieved through the use of external surface-silylated MCM-41 support. The immobilized catalyst system is recyclable and reusable without observable loss in activity and selectivity, demonstrating its promise as an environmentally friendly alternative catalyst for the isopropylation of naphthalene.

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Notes and references

† The IUPAC name for cetyl is hexadecyl.

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