

ALUMINIUM CHLORIDE GRAFTED ON SILICA MESOPOROUS MOLECULAR SIEVES AS ALKYLATION CATALYSTS

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Introduction For decades sulfonated linear alkylbenzenes (LABs) have been among the most important detergents. The LABs synthesis is carried out by Friedel Craft alkylation of benzene by linear olefins using hydrogen fluoride or aluminium chloride as catalyst. The use of these catalysts presents severe problems. For example, aluminium chloride is difficult to separate after reaction and produces a large amount of waste effluent. To solve these problems, attempts have been made to chemically support aluminium chloride on the surface of silica mesoporous molecular sieves (MMSs) [1]. Products can be easily separated and the catalyst can be recycled. This study deals with the characterisation of the $\text{AlCl}_{(x)}$ supported on different surfaces of MMSs and their catalytic activity in alkylation of benzene with 1-dodecene. Compared to homogeneous AlCl_3 , $\text{AlCl}_{(x)}$ MMSs increase selectivity to monoalkylation.

Experimental Four samples of Aluminium chloride supported on four mesostructured silicates (2 hexagonal and 2 wormhole like with different pore diameters) were prepared by post synthesis reaction in dry conditions (Schlenk technique). The physico-chemical properties were monitored by N_2 adsorption, XRD, atomic absorption, ^{29}Si and ^{27}Al MAS NMR and surface OH density measurements. The acidity data were obtained by TPD NH_3 , and FTIR of adsorbed pyridine. The alkylation of benzene by 1-dodecene was conducted in a Schlenk tube under dry conditions: catalyst weight 0,5g, 5mL benzene, 5mL 1-dodecene (molar ratio 2,5:1), at 80°C. Products were analysed by GC-MS.

Results and discussion As shown in Table 1, specific surface area of each catalyst decreases with aluminium loading. The analysis of acidity by TPD NH_3 shows an intense signal at 190°C and a smaller one at 250°C in Fig.1. This indicates the presence of two types of Lewis acid sites. At 190°C, the aluminium chloride is grafted at two Si-OH groups and the second peak at 250°C corresponds to aluminium chloride grafted at one Si-OH on the MMS walls. A small signal around 400°C indicates the presence of a low amount of Brönsted acid sites. In dry conditions, the amount of NH_3 desorbed is high. Thus the density and strength of surface Lewis acid sites are very high. In the presence of moisture the amount of NH_3 desorbed decreases dramatically. The moisture neutralizes the aluminium chloride to form an aluminium oxide with very low content of Lewis acid sites. These results are also confirmed by ^{27}Al MAS NMR, in Fig 2, that shows two types of Lewis acid sites at 85 and 70 ppm. This Lewis acidity is further confirmed by catalytic tests in the alkylation reaction of benzene by 1-dodecene (1-Dd). As shown in Table 1, a better selectivity to monoalkylate products is obtained over $\text{AlCl}_{(x)}$ grafted on MMSs compared to AlCl_3 in homogeneous solution. This behaviour is believed to be associated

to the highly polar MMS support, which allows a fast out ward diffusion of the monoalkyl product, thus limiting the secondary alkylation.

Table 1. Physico-chemical properties and catalytic activity for the benzene alkylation reaction of AlCl_x grafted on hexagonal and wormhole like MMS.

Catalyst	Loading	S_{BET}	P. Size	OH density	Ratio	%Mono	%Di
	(mmolAl/g)						
D ₁₋₀	-----	1018	33	2,33	-----	-----	-----
D ₂₋₀	-----	874	26	2,15	-----	-----	-----
D ₁₋₁	2,00	654	30	0,62	2,5 : 1	81,5	18,5
D ₂₋₁	2,30	675	23	0,25	2,5 : 1	69,6	30,4
AlCl_3	-----	-----	-----	-----	2,5 : 1	52,8	47,2

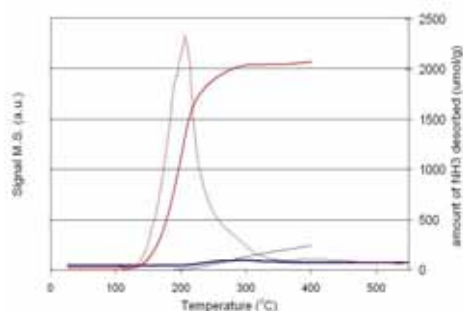


Fig. 1. TPD- NH_3 on D₁₋₁ – Ramp = 10K/min in 20mL/min He.

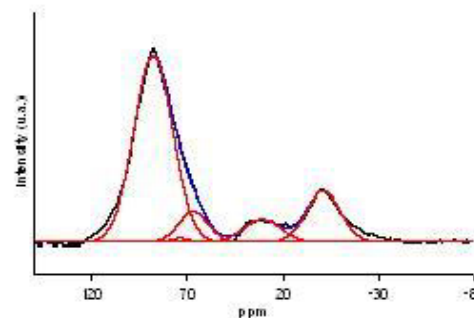


Fig. 2. ^{27}Al MAS NMR. spectra on D₁₋₁.

References

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