

Synthesis and Catalytic Properties of Pillared Nickel Substituted Mica Montmorillonite Clays

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Nickel substituted mica montmorillonite (Ni-SMM) clay can be intercalated successfully with aluminium and silica-alumina oligomers leading to pillared clays; transmission electron microscopy has revealed agglomeration of the particles, which leads to suppression of hydroisomerization catalysis.

It is known¹⁻⁵ that swelling clays can be crosslinked with inorganic metal hydroxide oligomers to yield thermally stable pillared clays with properties reminiscent of zeolites.

We report here the application of this technique to the pillaring of nickel substituted montmorillonite (Ni-SMM) clay. This may be of interest because Ni-SMM impregnated with a noble metal salt is an active hydroisomerization catalyst.^{6,7} Ni-SMM clay is hydrothermally prepared from a solution of silicate, nickel salt, aluminium alcoholate, ammonia, and ammonium fluoride and by heating the gel in an autoclave for several hours at 200–350 °C. The optimum catalytic activity is found for Ni:Al ratios of the order of 5:6. The material prepared according to the method of Swift and Black⁶ is not water-swellable. We prepared a water-swellable material by choosing the Si:Al:Ni ratios in the synthesis mixture so that enough, but not too much Al is in a tetrahedral co-ordination. Good results are found for Al^{IV}:Si^{IV} (ratios of tetrahedral atoms) of 0.15–0.3:1 and the material shows after metal exchange and reduction at 300 °C a good catalytic activity for the hydroisomerization of n-pentane (Table 1).

Crosslinking of such a Ni-SMM clay with a solution of a hydroxy-alumina oligomer in H₂O leads to considerable

Table 1. Hydroisomerization of n-pentane at 250 °C, using samples reduced at 343 °C.^a

Pd-Ni-SSM sample ^b	X.R.D. ^c	<i>k</i> (g g ⁻¹ h ⁻¹)
Before cross-linking	1.26	2.5
(1) ^d	1.73	3.6
(2) ^e	1.26 1.96	0.3

^a Weighted hourly space velocity = 2 g g⁻¹ h⁻¹; H₂/feed = 1.25 mol/mol; *p*(H₂) = 30 bar; *k* = first-order rate constant.^b Stoichiometry of Pd-Ni-SSM: tetrahedral, Si_{6.72}Al_{1.28}; octahedral, Al_{1.62}Ni_{0.57}.^c 001 reflection, nm, after drying at 110 °C. ^d Cross-linked with Al oligomer. ^e Cross-linked with Si-Al oligomer.

catalytic enhancement (sample 1, Table 1). Table 1 shows the first-order rate constant, *k* for catalysis, before and after crosslinking. For sample 1 we used as crosslinking agent a hydroxy-aluminium oligomeric solution, made by refluxing metallic aluminium in 1 M HCl for 8 h and ageing this solution for at least 10 days. Crosslinking took place by stirring a slurry of the clay with this solution at 70 °C for 20 h. We used a ratio of 6 mmol Al/g clay in the mixture. The Brunauer-

Emmett-Teller surface area of the clay after calcination at 350 °C had increased from 170 to 230 m²/g.

The X-ray diffraction (X.R.D.) peak corresponding to a repeat distance of 1.26 nm for the non-crosslinked sample had been completely replaced by the peak corresponding to the expanded lattice with a repeat distance of 1.73 nm.

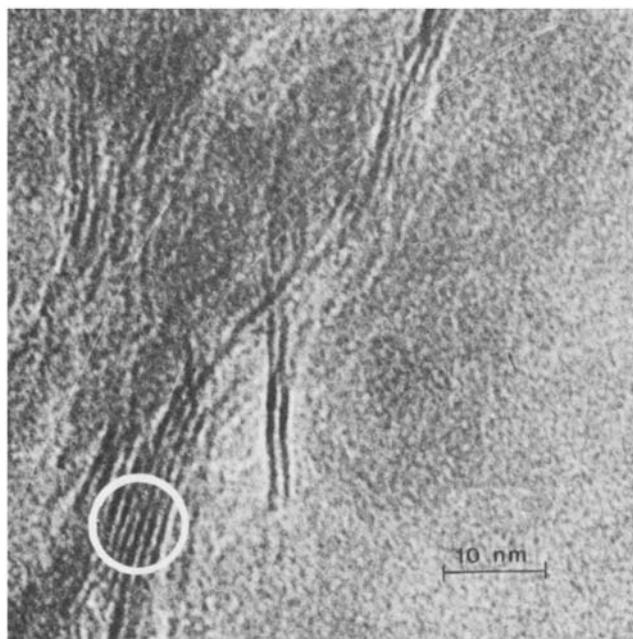


Figure 1. Transmission electron micrograph of Ni-SMM.

Completely different results were obtained with a Ni-SMM sample treated with a solution containing a silica-alumina oligomer. Crosslinking was carried out at a pH of 4.8, using a solution prepared by refluxing a mixture of chlorhydrol and a sodium silicate solution for 24 h.

With X.R.D, only a weak signal of the basal spacing of the expanded structure was detected, whereas the original 001 reflection at 1.26 nm was still present. The surface area of the sample treated as such had now decreased to 125 m²/g.

Figures 1 and 2 show transmission electron micrographs of sample 2 before and after crosslinking. Figure 1 clearly reveals the stacking of layers (each dark line corresponds to one triple layer). The distance between the basal planes agrees, within experimental accuracy, with the values obtained by X.R.D. In the product crosslinked with the silica-alumina oligomer solution (Figure 2), two features are interesting: two different stacking distances can be observed (see circles), and an enormous degree of agglomeration in the basal direction has taken place. The observation of two different stacking distances agrees with the observation of a weak X.R.D. signal of the expanded structure. We ascribe this larger stacking distance to crosslinking with the oligomer.

The strong growth of the Ni-SMM particles in the basal direction is probably the cause for the decrease in total surface area observed after treatment with the silica-alumina oligomer solution. The large decrease in catalytic activity (sample 2, Table 1) indicates that the major part of the catalytically active sites is located in the basal layers. The cause of agglomeration is basically the same as that which induces pillaring of the clays. The positively charged oligomers exchange with the surface cations. In this particular case the charge of the oligomers is such that it is not only compensated



Figure 2. Transmission electron micrograph of Ni-SMM cross-linked with Si-Al oligomer.

by the negative charge in the surface layer of one crystallite, but can also exchange with charge of another surface.

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