High Conversion and Selectivity for Cracking of n-Heptane on Cerium–Aluminium Montmorillonite Catalysts

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The synthesis and catalytic properties of an aluminium pillared clay modified by inclusion of cerium are described; very high catalytic activity and selectivity for the cracking of n-heptane are observed.

Recently pillars of various metal–polyoxy cationic species have been intercalated between the layers of clays. Polymeric compounds of Al, and Zr and Fe[1–4] are among the principal species quoted in the literature; compounds of Cr, Ti, Sn and Si[5–8] have also been utilized but to a lesser extent. These pillared smectites have acidic properties which make them suitable for use in petrochemical cracking where they can successfully replace zeolites. An advantage that pillared clays (PILC) have with respect to zeolites is that the diameter of their micropores is greater, which allows larger molecules, and therefore heavier oil fractions, to be cracked. Pillaring with mixed cations has been investigated[9–12] in order to increase

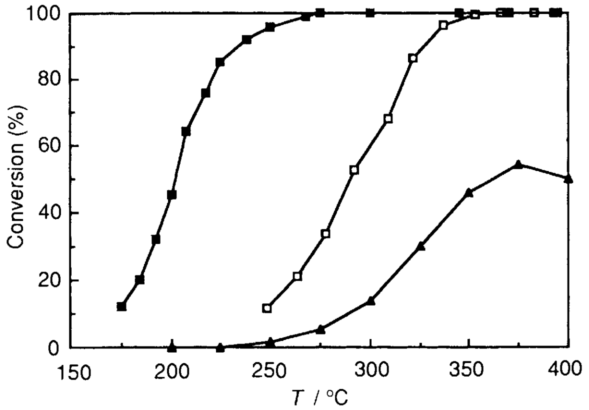

Fig. 1 Conversion of n-heptane *vs.* reaction temperature over □, Ce–Al-PILC and reference samples ■, HY-zeolite; ▲, Al-PILC

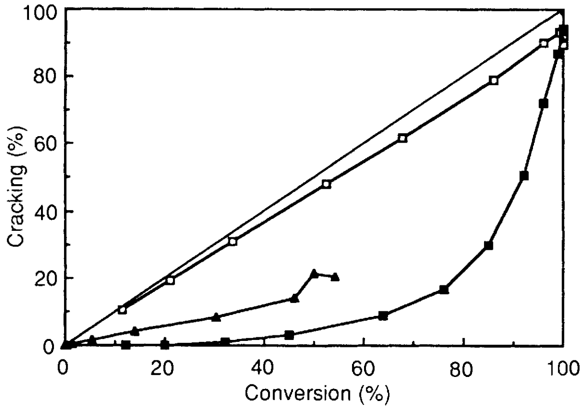

Fig. 3 Yield of cracking product *vs.* conversion of n-heptane; symbols as in Fig. 1

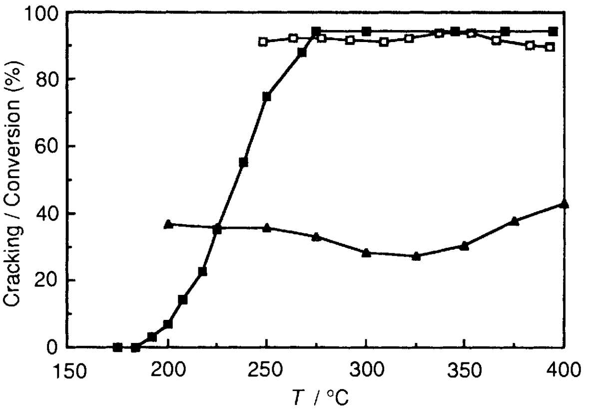

Fig. 2 Yield of cracking products of n-heptane *vs.* reaction temperature; symbols as in Fig. 1

the stability of the pillars and to improve the catalytic properties of the products.

H-Zeolites impregnated with Pt have been used extensively for hydroisomerization–hydrocracking of n-alkanes. Indeed, this process gives a good evaluation of the strength of the acid sites. Moreover, the chain length of the alkanes obtained by cracking, *i.e.* the distribution and nature of the isomer, can yield information on the pore size and shape of a catalyst. Three types of products can be obtained: products of isomerization, cyclization and cracking. In these bifunctional catalysts, the main role of the metal is to dehydrogenate the alkane, which is then isomerized or cracked on the acid sites.

This work describes the preparation of a catalyst of montmorillonite pillared with mixed Al and Ce cations, impregnated with Pt. The activity and selectivity of this catalyst are studied in comparison with Al-PILC catalysts, obtained from homoionic Na-montmorillonite (Na-mont) and Ce-montmorillonite (Ce-mont), and with a commercial zeolite, by means of the hydroisomerization–hydrocracking reaction of n-heptane.

The starting material was a bentonite from La Serrata de Nijar, Almeria, in SE Spain. Its mineralogical composition is: 97% montmorillonite, 3% feldspar and traces of calcite. The bentonite was purified by means of conventional sedimentation, with the <2 μm fraction being collected. Its structural formula, obtained by chemical analysis is: $(\mathrm{Ca^{2+}}_{0.13}\mathrm{Mg^{2+}}_{0.26}\mathrm{Na^{+}}_{0.23}\mathrm{K^{+}}_{0.02})(\mathrm{Si}_{8.00})_{\mathrm{T}}(\mathrm{Al}_{2.69}\mathrm{Fe}_{0.32}\mathrm{Mg}_{0.97})_{\mathrm{O}}\mathrm{O}_{20}(\mathrm{OH})_4$. The homoionic Na-mont was obtained by washing a sample with 1 mol dm^{-3} NaCl solution at 25 °C. Its specific surface area was 87 m^2 g^{-1} and it had a cation exchange capacity of 59 mequiv. (100 g clay)$^{-1}$.[13] Its basal spacing of 15.4 Å decreased to 9.9 Å when the sample was heated at 500 °C. The homoionic Ce-mont was obtained in the same way, with $\mathrm{CeCl_3}$ solution; its original basal spacing of 15.8 Å was reduced to 9.9 Å by heating at 500 °C.

The Ce-Al-PILC sample was synthesized by adding a solution of the pillaring agent to a specific volume of clay slurry so as to adjust the (aluminium + cerium) content to the desired value. The system used in the experiment was 10 mequiv. Al and 10 mequiv. Ce per g clay. The method of preparation of the pillaring agent was the same as that described by Shabati *et al.*[14] A suitable volume of 0.5 mol dm^{-3} NaOH was gradually added to a stirred solution of 0.2 mol dm^{-3} $\mathrm{AlCl_3\cdot 6H_2O}$ + $\mathrm{CeCl_3\cdot H_2O}$, in order to obtain an OH/(Al + Ce) ratio of 2.0. The resulting solution was then aged at 60 °C for 2 h before being used in the pillaring process. The solution of the pillaring agent obtained in this way was added to the clay slurry (2.5 g of clay per 100 ml of solution) and the resulting mixture was left for 24 h with constant stirring at room temperature. The suspension was then dialysed until chloride free. Finally, the sample was freeze-dried.

The Ce/Al ratio intercalated in the resulting product was found to be 0.44 by chemical analysis of the Ce and Al remaining in the liquid after centrifuging the reaction mixture. In corroboration of this value, the solid sample was analysed by EDXRA (energy-dispersive X-ray analysis); 6.5 g of Ce were incorporated per 100 g of original clay.

Expansion of the basal spacing of montmorillonite by exchange of oligomeric species was followed by X-ray diffraction performed on thin layers of the clay on glass slides. The basal spacing was found to be 17.5 Å with a shoulder at higher values. After heating at 500 °C it decreased to 13.2 Å, and the shoulder appeared as a low-intensity peak at 25.9 Å. These results seem to indicate the existence of oligomers of different composition between the sheets of montmorillonite. Sterte[15] and McCauley[16] obtained Al/La-mont and Al/Ce-mont, respectively, with a basal spacing of 25–28 Å, and very little evidence for residual unpillared material.

The specific surface area (S_{BET}) of the material that we obtained was 165 m^2 g^{-1}; its micropore volume obtained by the *t*-plot method[17] was 0.048 cm^3 g^{-1}.

IR studies were carried out after degassing the samples for 2 h at 200 °C *in vacuo* followed by pyridine adsorption–desorption. The ratio of Brønsted to Lewis acidity in the Ce–Al-PILC sample was higher than that in the Al–PILC sample.

An Al-PILC sample synthesized by us,[18] whose specific surface area is 350 m^2 g^{-1}, and a commercial HY zeolite were included in the evaluation as references. The samples were impregnated with an ammoniacal complex of Pt to 1% (w/w). The WHSV (weight hour space velocity) was 0.9 g n-heptane (g cat. h)$^{-1}$. Fig. 1 shows how the conversion changes with reaction temperature. The HY zeolite used as reference is the most active, with a conversion of 100% from 275 °C upward. The Ce–Al-PILC shows complete conversion at 350 °C. By contrast, the two Al-PILC-samples obtained from Na-mont and Ce-mont show the same catalytic behaviour, reaching a maximum conversion of 53% at 375 °C. The Ce–Al-PILC sample is more active than Al-PILC throughout the entire temperature range. The homoinic samples, Na-mont and Ce-mont, do not show catalytic activity for the conversion of n-heptane.

Fig. 2 shows the selectivity in cracking products *vs.* temperature. The yields of cracking products *vs.* conversion of n-heptane over Ce–Al-PILC and reference catalysts are shown in Fig. 3. The straight line in Fig. 3 corresponds to the situation where all the products obtained are cracking products (100% selectivity). The selectivity is 93% over Ce–Al-PILC, while over Al-PILC it is only 30–40% in all the ranges of temperature tested. In comparison, the HY zeolite only shows high cracking selectivity above 275 °C (high conversions); between 175 and 275 °C the selectivity increases with the conversion.

The results clearly show that the presence of Ce in the pillars has a marked influence on the activity of the PILC products. The incorporation of Ce increases the total conversion and yields high selectivity for cracking in the entire temperature range tested, approaching results obtained for the reference zeolite. At lower temperatures the selectivity of the Ce-PILC is higher than that of the zeolite.

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