Cation-exchanged Synthetic Saponite as a 'Heat-stable' Acidic Clay Catalyst

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A cation-exchanged synthetic saponite, $M^{n+}{}_y(Mg_3)^{oct.}(Si_{4-x}Al_x)^{tet.}O_{10}(OH)_2$ (interlayer cation; $M^{n+} = Al^{3+}$, Zr^{4+}, Ti^{4+}, *etc.*), has a large surface area at high temperatures and a high catalytic activity as a solid acid due to its 'card-house structure'.

Layered clay minerals, known to be solid acid catalysts, suffer from the disadvantage of interlayer collapse at temperatures >*ca.* 473 K with consequent loss of catalytic activity.[1] Pillaring the swellable clay with large inorganic hydroxy cations ('pillared clay')[2] has improved the situation. However, the variety of pillaring agents is restricted within narrow limits and pillaring causes the near total loss[3] of the original cation exchange capacity. Here we report a 'non-pillared but heat-stable' cation-exchanged synthetic saponite which gives a large surface area and a high activity comparable to pillared clay for some acid-catalysed reactions due to its 'card-house structure'.

The cation exchange clays were prepared by cation exchange of various cations from clay-dispersed aqueous nitrate or chloride solutions followed by calcination at 673—973 K for 4 h. The parent clays used here were a synthetic saponite $Na_x(Mg_3)^{oct.}(Si_{4-x}Al_x)^{tet.}O_{10}(OH)_2$ (Sumecton SA, Kunimine Ind.), a synthetic hectorite $Na_x(Mg_{3-x}Li_x)^{oct.}(Si_4)^{tet.}O_{10}(OH)_2$ (Laponite XLG, Laporte Ind.) and a natural montmorillonite $(Na,Ca)_y(Al_{2-x}Mg_x)^{oct.}(Si_4)^{tet.}O_{10}(OH)_2$ (Kunipia F, Kunimine Ind.). For comparison purposes, the pillared montmorillonite was prepared according to previously reported methods.[4] The catalytic reactions were carried out in a conventional continuous flow

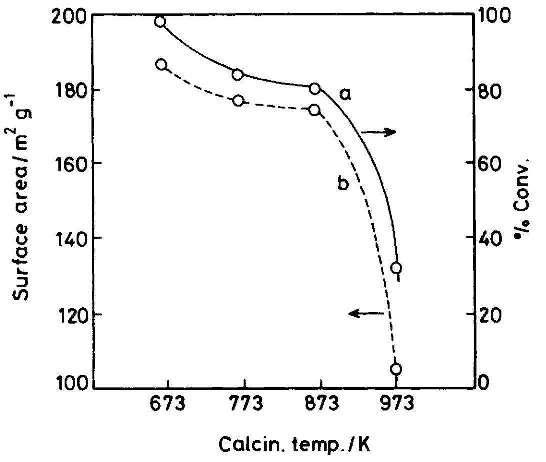

Figure 1. a = Dehydration activity of propan-2-ol (expressed in % conversion of propan-2-ol), b = B.E.T. surface area of Al^{3+}-S (units = m^2 g^{-1}) as a function of calcination temperature (reaction temp. = 523 K, W/F = 2.1 g cat. h mol^{-1}).

system with a fixed bed of catalyst, under atmospheric pressure. The reaction effluent was collected in an ice trap and analysed by g.l.c.

Table 1 shows the catalytic efficiencies of various catalysts for the cracking reaction of cumene. Al^{3+} exchanged saponite (Al^{3+}-S) calcined at 673 or 873 K has not only much greater activity than Al^{3+} exchanged montmorillonite (Al^{3+}-M) but also *ca.* double the activity of Al pillared montmorillonite (Al-PM). The catalytic efficiency of Al^{3+}-S for cracking cumene to benzene is nearly equal to that of H-ZSM-5 zeolite or SiO_2–Al_2O_3.

This high activity of Al^{3+}-S is characterized by its high surface area, the lack of long-range layer ordering, and its high acidity. Al^{3+}-M calcined at 673 K has a small B.E.T. (Brunauer–Emmett–Teller) surface area of 30 m^2 g^{-1} with basal spacing of 9.9 Å, indicating its face-to-face stacking of interlayer collapsed silicate sheets. However, *X*-ray diffraction spectra of Al^{3+}-S show a very weak and obscure (001) reflection compared with Al^{3+}-M, and Al^{3+}-S has a high surface area of 186 m^2 g^{-1}, as large as Al-PM (228 m^2 g^{-1}). In this connection, the N_2 adsorption isotherm at 78 K over Al-PM is Langmuir type, or microporous, whereas that over Al^{3+}-S is B.E.T. type, or non-microporous. Such behaviour[5] in saponite can be ascribed to its three-dimensional random 'card-house structure'[6] which is a common form of aggregate in fine clay particles. In fact, 60% of montmorillonite particles are >0.2 μm in diameter, whereas 90% of saponite are <0.2 μm. Although Al^{3+} exchanged laponite (Al^{3+}-L) also has such a 'card-house structure' with the largest surface area of 287 m^2 g^{-1}, it gives a lower activity than Al^{3+}-S due to its lower acidity. The solid acidity was estimated by means of temperature programmed desorption (TPD) of adsorbed NH_3. The acid amount calculated from the TPD peak area was 532 μmol g^{-1} for Al^{3+}-S and 216 μmol g^{-1} for Al^{3+}-L.

The high catalytic efficiency of saponite can be observed with different cations. Table 2 shows the catalytic activities of various cation exchanged saponites for toluene alkylation by methanol. Alkylation activity depends entirely on the kind of exchanged cation. In particular, the saponite exchanged with Zr^{4+}, Al^{3+}, or Ti^{4+}, which has a large hydration energy, exhibits high activity (toluene conv. >10%), comparable to Al-PM.

The high thermal stability of Al^{3+}-S can be seen in Figure 1, where the dehydration activity of propan-2-ol and the B.E.T. surface area of Al^{3+}-S are plotted as a function of calcination temperature. The activity and surface area both have high values up to 873 K, indicating the 'card-house structure' of saponite to be stable even at the high temperature of 873 K.

Table 1. Catalytic efficiencies^{a} of various catalysts for cumene cracking.

Catalyst^{b}	Calcination temp./K	% Cumene conv.	% Benzene selec.
Al^{3+}-M	673	34.1	91.2
Al^{3+}-S	673	84.2	92.5
Al^{3+}-M	873	9.5	85.1
Al^{3+}-S	873	66.7	95.0
Al-PM	873	34.9	90.8
Al^{3+}-L	873	14.9	87.8
H-ZSM-5^{c}	873	99.0	68.8
SiO_2–Al_2O_3^{d}	673	87.2	96.8

^{a} Reaction temp. = 673 K, W/F = 139 g cat. h mol^{-1} (W = weight of catalyst, F = feed rate of reactant), flow rate of N_2 carrier gas = 200 ml h^{-1}, averaged cumene conversion and benzene selectivity obtained 1 h after feeding of reactant. ^{b} Calcined in air at each temperature for 4 h. ^{c} Reference catalyst of Catalysis Society of Japan; JRC-Z5-70H. ^{d} Reference catalyst; JRC-SAL-2.

Table 2. Catalytic activities^{a} of various cation exchanged saponites and other catalysts for toluene alkylation by methanol.

Catalyst^{b}	% Toluene conv.	Catalyst^{b}	% Toluene conv.
Zr^{4+}-S	14.2	Fe^{3+}-S	4.6
Al^{3+}-S	12.2	Ca^{2+}-S	0.3
Ti^{4+}-S	10.2	Na^{+}-S	0
Ga^{3+}-S	8.4	Al^{3+}-L	3.8
Mg^{2+}-S	7.9	Al^{3+}-M	1.6
La^{3+}-S	7.5	Al-PM	11.6

^{a} Reaction temp. = 623 K, W/F = 60 g cat. h mol^{-1} (W = weight of catalyst, F = feed rate of reactants), toluene : methanol = 2 : 1 (mol ratio), averaged toluene conversion obtained 1 h after feeding of reactants. ^{b} Calcined in air at 673 K for 4 h.

In conclusion, the synthetic saponite consisting of fine particles gives a high external surface area even at 873 K due to its 'card-house' arrangements of layers, and works as cation-support to make an efficient solid acid catalyst.

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References

1 R. Gregory, D. J. H. Smith, and D. J. Westlake, *Clay Miner.*, 1983, **18**, 431.

2 For recent reviews see: *Catalysis Today*, ed. R. Burch, 1988, **2**, nos. 2—3, and references cited therein.

3 G. Poncelet and A. Schutz, in 'Chemical Reactions in Organic and Inorganic Constrained Systems,' ed. R. Setton, Reidel, Dordrecht, 1986, p. 165; D. T. B. Tennakoon, W. Jones, and J. M. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 3081.

4 K. Urabe, H. Sakurai, and Y. Izumi, *J. Chem. Soc., Chem. Commun.*, 1986, 1074.

5 Similar phenomena were reported on laponite pillared with Al_{13} hydroxy polycations and described as 'delamination' by Prof. Pinnavaia; T. J. Pinnavaia, M.-S. Tzou, S. D. Landau, and R. H. Raythatha, *J. Mol. Catal.*, 1984, **27**, 195.

6 H. van Olphen, 'An Introduction to Clay Colloid Chemistry,' 2nd edn., John Wiley & Sons, New York, 1977, p. 95.