Pillared Synthetic Saponite as an Efficient Alkylation Catalyst

Kazuo Urabe,* Hiroaki Sakurai, and Yusuke Izumi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

A novel pillared synthetic saponite, prepared by exchanging Na^+ in the interlayer of saponite [idealized formula; $Na^+_x(Mg_3)^{oct.}(Si_{4-x}Al_x)^{tet.}O_{10}(OH)_2$] with an Al hydroxy cluster cation followed by calcination, gives a high catalytic activity and a high yield of *p*-xylene isomer for toluene alkylation by methanol.

The advent of 'pillared clay,' or a porous material holding inorganic pillars between silicate layers of clay, in the field of zeolite chemistry during the last decade has attracted considerable interest due to its large surface area and thermal stability,[1] molecular sieving ability,[2] and applicability to potential shape-selective catalysis.[3] Nevertheless, the pillared clays have been restricted exclusively to montmorillonite-based sheet silicates because it occurs abundantly in nature. In this communication we present a novel pillared synthetic saponite catalyst which is very efficient for toluene alkylation by methanol, as well as our findings on other pillared clays.

The pillared clays were prepared by the cation exchange of the Al hydroxy cluster cation,[2] $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, in a clay-dispersed aqueous solution (OH/Al = 2) followed by calcination according to the known method[1] except that $Al(NO_3)_3$ was used instead of $AlCl_3$ as an Al source. The swellable clays used here, except montmorillonite (Kunipia F, Kunimine Ind.), were all synthetic ones; saponite (Kunimine Ind., see ref. 4 for its synthesis and full characterization), fluor-hectorite, fluor-tetrasilicic mica (TSM),[5] and taeniolite.[6] The latter 3 samples were supplied by Topy Ind. The alkylation of toluene to xylene by methanol was carried out in

Table 1. Physical properties of various clays before and after pillaring manipulation.

	Basal spacing: $d(001)$ (Å)			Surface area[b] ($m^2\,g^{-1}$)	
Clay[a]	Before[c]	After (dry)	After (calcin.)[d]	Before[c]	After (calcin.)[d]
Montmorillonite	12.4	19.0	17.3	8.4	228
Saponite	12.4	18.0	17.3[e]	168[f]	191[f]
Hectorite	12.3	18.0	18.0	4.2	73
Tetrasilicic mica	12.4	19.2	18.0	0.5	238
Taeniolite	12.2	15.4	12.4	4.5	5.0

[a] The first 3 clays belong to the smectite mineral group and the last 2 are micas. The structural formulae of these clays are as follows; montmorillonite: $(Na,Ca)_y(Al_{2-x}Mg_x)^{oct}\cdot(Si_4)^{tet}\cdot O_{10}(OH)_2$, saponite: $Na_x(Mg_3)^{oct}\cdot(Si_{4-x}Al_x)^{tet}\cdot O_{10}(OH)_2$, fluor-hectorite: $Li_{1/3}(Mg_{8/3}Li_{1/3})^{oct}\cdot(Si_4)^{tet}\cdot O_{10}F_2$, fluor-tetrasilicic mica: $Na(Mg_{5/2})^{oct}\cdot(Si_4)^{tet}\cdot O_{10}F_2$, taeniolite: $Li(Mg_2Li)^{oct}\cdot(Si_4)^{tet}.O_{10}F_2$. [b] Measured after evacuation at 573 K for 1 h unless otherwise stated. [c] Before pillaring. [d] After pillaring followed by calcination at 673 K. [e] Broad peak. [f] Measured after evacuation at 573 K for 30 min.

Table 2. Catalytic efficiencies[a] of various pillared clays and zeolites for toluene alkylation by methanol.

Original clay or zeolite	Abbreviation of pillared clay	Toluene conv. (%)	Xylene selec. (%)	*p*-Xylene fraction (%)
Montmorillonite	PM[b]	11.6	73.6	43.2
Saponite	PS[b]	10.8	72.9	37.6
Hectorite	PH[c]	0.6	93.1	32.1
Tetrasilicic mica	PTSM[c]	0.5	100	26.4
Taeniolite	PT[c]	0.2	100	31.1
HZSM-5[b]		23.9	66.5	25.5
HY[b]		31.2	68.8	33.2

[a] 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 and xylene selectivity obtained 1 h after feeding of reactants. [b] Reaction temp. 623 K. [c] Reaction temp. 673 K.

a conventional continuous flow system with a fixed bed of catalyst (0.4 g) under atmospheric pressure. The reaction effluent was collected in an ice trap and analysed by g.l.c. using a Bentone 34 + DNP column (4 m).

Table 1 shows the physical properties of these five kinds of pillared clays as well as those before pillaring. In each case, except taeniolite, the basal spacing, $d(001)$, increases to 18—19 Å from an original value of about 12 Å by Al hydroxy cluster cation pillaring manipulation. The values of interlayer spacing, 8.4—9.4 Å, calculated from the $d(001)$ value and the silicate layer thickness of 9.6 Å suggest that the interlayer pillar is an Al hydroxy cluster cation itself since this cation has a diameter of about 9 Å.[2] Furthermore these pillared clays with orderly layer structure are thermally stable enough to retain their basal spacings even with calcination at 673 K. In addition, the pillaring brings about a marked increase in surface area for each case except taeniolite which seems to fail in holding pillars. In this connection, Langmuir-type isotherms for nitrogen adsorption at 78 K are observed for all pillared clays except taeniolite in accord with the previous information on Al[7] and Zr hydroxy cluster cation[8] pillared montmorillonite.

Table 2 shows the catalytic efficiencies† of these pillared clays for toluene alkylation by methanol, compared with two types of proton-exchanged zeolite catalysts. None of the original Na^+ or Li^+ type clays without pillaring exhibit alkylation activities. In contrast, all the pillared clays reveal substantial activities which depend on the kind of clay. Pillared saponite (PS) and montmorillonite (PM) have greater activities (toluene conv.; 11—12% at 623 K) compared with the other pillared clays (0.2—0.6% even at 673 K). Although the activities of PS and PM are one third or half compared with HY or HZSM-5 zeolite, the fraction (about 40%) of *p*-xylene among the produced xylenes over PS and PM is significantly larger than those over zeolites (the thermodynamic equilibrium fraction of the *p*-form is 23.7% at 623 K). This high *p*-xylene fraction is very attractive, suggesting a shape-selectivity due to the unique pore structure of PM[2,7] or PS. These different characteristics among pillared clays may be understood with regard to the different cation exchange capacity (C.E.C.) as well as the different extent or position of isomorphous substitution in each original clay.

Subsequently, focusing on the effect of C.E.C. of the original clay on the catalytic efficiency of the corresponding pillared clay, it is noticeable that PS and PM exhibit comparable activities in spite of the smaller C.E.C. (72.4 m equiv./100 g) of unpillared saponite than the C.E.C. (115) of unpillared montmorillonite used as starting sheet silicates. Montmorillonite samples with extensively different C.E.C. are not available in nature. However, in the synthetic saponite the preparation of samples with various C.E.C.s (63—101) is possible. The PS prepared from the saponite with C.E.C. of 101, despite this value still being smaller than that of natural montmorillonite, displays much higher activity (toluene

---

† Since the toluene conversion decreases with the time on stream owing to possible coke formation, the averaged toluene conversion and xylene selectivity obtained 1 h after the reactant feed are taken as the standard catalytic efficiency data. The activity decay is quite reproducible in all cases.

conv.; 15.5%, *p*-xylene fraction; 37% at 623 K) than PM. More interestingly, the activity (toluene conv.; 6.8 to 15.5% at 623 K) of the corresponding PS tends to increase with increased C.E.C. (63 to 101 m equiv./100 g) of unpillared saponite. This finding is in agreement with the observation that the enlargement ratio (12 to 82%) of surface area due to pillaring increases with increased C.E.C. of unpillared saponite, suggesting an obvious gain in the number of active sites.

We thank Mr. Makoto Koga (Research Laboratories, Kunimine Ind.) for supplying the synthetic saponite samples and Dr. Seitaro Namba (Tokyo Institute of Technology) for HZSM-5.

Received, 14th March 1986; Com. 334

References

1 G. W. Brindley and R. E. Sempels, *Clay Miner.*, 1977, **12**, 229; N. Lahav, U. Shani, and J. Shabtai, *Clays. Clay Miner.*, 1978, **26**, 107.
2 D. E. W. Vaughan and R. J. Lussier, Proceedings 5th International Conference on Zeolites, Naples, 1980, p. 94.
3 J. Shabtai, R. Lazar, and A. G. Oblad, Proceedings 7th International Congress on Catalysis, Tokyo, 1980, p. 828.
4 M. Kondo and M. Koga, Abstracts 20th Meeting on Powder, Japan, 1982, p. 41.
5 K. Kitajima and N. Daimon, *Nippon Kagaku Kaishi*, 1975, 991.
6 K. Kitajima and N. Daimon, *Chem. Lett.*, 1973, 241; *Nippon Kagaku Kaishi*, 1975, 44.
7 M. Matsumoto, M. Suzuki, H. Takahashi, and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1.
8 S. Yamanaka and G. W. Brindley, *Clays. Clay Miner.*, 1979, **27**, 119.