

Talc-derived Pillared Clay as an Acidity-tunable Catalyst

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A novel pillared clay can be prepared from talc $[(\text{Mg}_3)^{\text{oct}}(\text{Si}_4)^{\text{tet}}\text{O}_{10}(\text{OH})_2]$ via a swellable mica, and its catalytic activity for cumene cracking is not only greatly enhanced by La^{3+} cation modification but also tunable by choosing the type of cation.

Over the past ten years, a new family of microporous crystals referred to as 'pillared clays' have attracted considerable interest owing to their wide range of applications from catalysts to molecular devices.¹ The number of materials has increased further with the use of specific clays, such as rectorite² and synthetic fluor-mica.^{3,4} However, pillaring has hitherto been restricted to swellable clays as starting materials. Here we report the synthesis and catalytic properties of a novel pillared clay derived from talc which neither swells, nor has cation-exchange capacity.

The formation of a pillared derivative can be judged by a distinct expansion of the interlayer spacing. Fig. 1 shows X-ray diffraction patterns of various clay samples. For the original talc, collected from Kanshi deposits in China, the basal spacing, d_{001} , of 9.3 Å is not expanded after attempts to cause

pillaring using an aluminium hydroxy polycation³ because of its non-swellable, or water-repellent nature. The swellable nature was conferred on the talc by reaction with Na_2SiF_6 at 1123 K for 2 h.⁵ In the reaction product, or fluor-mica (FM),⁵ a double-layer hydrated basal spacing is evident at 15.4 Å. This material gives a strong (001) reflection with a d_{001} value of 18.7 Å after pillaring. The value of the interlayer spacing, 9.1 Å, calculated from d_{001} and the silicate layer thickness of 9.6 Å, is the same as those of typical Al-pillared clays³ and is retained even after calcination at 573 K. In addition, the pillaring brings about a marked increase in surface area from 20 m² g⁻¹ for FM to 320 m² g⁻¹. The isotherm for nitrogen adsorption over this pillared fluor-mica (PFM) fits a Langmuir-type well, indicating its microporous nature.

An increase in swellable nature should be accompanied by

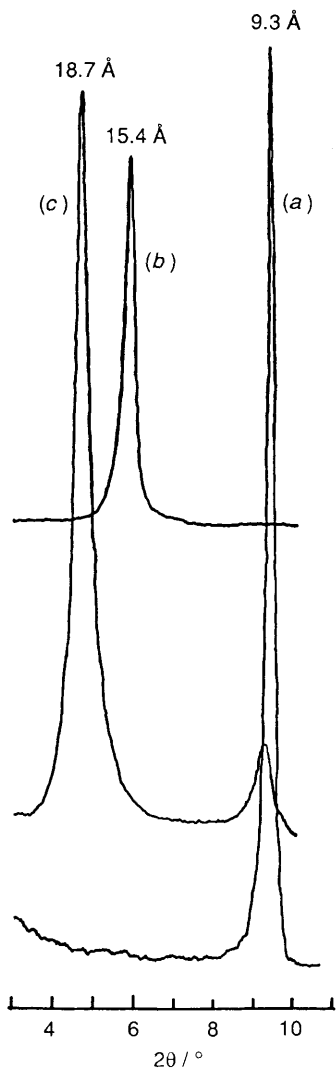


Fig. 1 X-Ray diffraction patterns of various clay samples: (a) original talc (sens., 800 counts s^{-1}); (b) fluor-mica (20 000 counts s^{-1}); (c) pillared fluor-mica (2000 counts s^{-1})

an increase in negative charge in the silicate layer, or cation exchange capacity (CEC). The CEC value of fluor-mica was 80 mequiv. per 100 g according to the Methylene Blue adsorption method. The amount of exchanged interlayer Na^+ by pillaring was determined analytically to be 84.5 mequiv. per 100 g, in agreement with the above CEC value. A negative charge in the silicate layer may also be characterized by the chemical shift of the MAS ^{29}Si NMR signal.⁶ Fig. 2 shows the MAS ^{29}Si NMR spectra of various clay samples. The original talc with a neutral silicate layer shows an intense ^{29}Si signal at δ -97.6 ppm assigned to $Q^3(0Al)$. This chemical shift is in fair agreement with the reported value (-98.0 ppm).⁷ The swellable fluor-mica and its pillared variant have $Q^3(0Al)$ signals at δ -94.4 and -94.6 ppm, respectively, shifted to lower magnetic field compared with talc. These values are close to the reported chemical shifts⁷ for fluorophlogopite mica (δ -92.9) or hectorite (δ -95.3 ppm). More interestingly, they coincide with the chemical shift of δ -93.8 ppm shown by the tetrasilicic mica³ [TSM; $Na(Mg_{2.5})_{oct} \cdot (Si_4)_{tet} \cdot O_{10}F_2$] synthesized by the melting method. The above NMR data are easy to understand on the basis of the gain of negative charge in the silicate layer causing deshielding at the Si nucleus,⁶ leading to a low-field shift of the ^{29}Si signal.

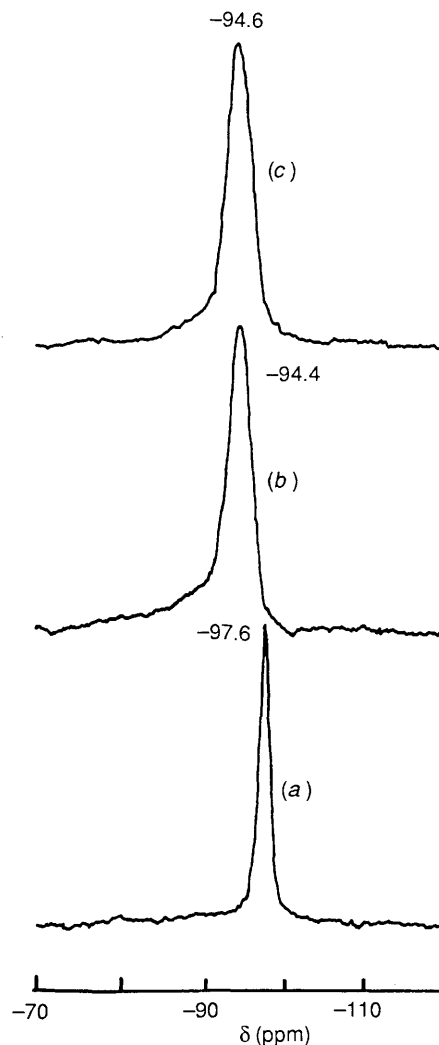


Fig. 2 Magic angle spinning (MAS) ^{29}Si NMR spectra of various clay samples: (a) original talc; (b) fluor-mica; (c) pillared fluor-mica

Table 1 Catalytic activities^a for cumene cracking and physical properties of various cation-modified catalysts (M^{n+} -PFM)

Catalyst ^b	Hydration energy of cation /kJ (g ion) ⁻¹	Basal spacing $d_{001}/\text{\AA}$	Surface area ^c /m ² g ⁻¹	Cumene conv. (%)
PFM	—	18.3	320	0.2
Ba ²⁺ -PFM	1376	18.7	343	1.8
Sr ²⁺ -PFM	1519	18.4	360	5.2
Ca ²⁺ -PFM	1666	19.2	364	5.6
Be ²⁺ -PFM	2550	17.0	268	11.0
La ³⁺ -PFM	3390	18.8	215	13.9
PM	—	17.3	228	15.4

^a Reaction temp. = 573 K, W/F = 33 g cat. h mol⁻¹, flow rate of N_2 carrier gas = 600 ml h⁻¹, averaged cumene conversion obtained 1 h after feeding of reactant. ^b Calcined in air at 573 K for 3 h. ^c Measured after evacuation at 573 K for 1 h. All samples show Langmuir-type N_2 adsorption isotherms.

The talc-derived pillared clay, or pillared fluor-mica (PFM), is unusually inert as a solid acid catalyst despite its microporous structure and high surface area. In the cracking of cumene, it manages only a 0.2% conversion of cumene at 573 K and W/F = 33 g cat. h mol⁻¹ (W = weight of catalyst,

F = feed rate of reactant). In catalytic efficiency, PFM strongly resembles the pillared tetrasilicic mica (PTSM) which gives the same low conversion, but contrasts with the conventional pillared montmorillonite (PM) which exhibits a high conversion of 15.4%.

We found previously that the catalytic activity of PTSM is greatly enhanced through the modification of cation exchange sites by lanthanum ions.⁸ Following the same modification⁸ for PFM, the La^{3+} modified catalyst (La^{3+} -PFM) displays a high activity, with a cumene conversion of 13.9%, twice as much as La^{3+} -PTSM⁸ and comparable to that of an active PM. IR studies of adsorbed pyridine as an example of a basic molecule confirmed the genesis of strong acidic sites by the fixation of La^{3+} . Table 1 shows the catalytic activities of various cation-modified catalysts (M^{n+} -PFM) along with the basal spacings and surface areas. Each catalyst has a similar and distinct pillared structure but a different activity depending on the type of cation, the sequence of which relates with the hydration energy of the cation, or the acidity of the aquocation, as shown in the first column of Table 1. This means that M^{n+} -PFM catalysts may have a tunable activity for various acid-catalysed reactions by the choice of cation (M^{n+}).

We thank Dr Hiroshi Tateyama (Government Industrial Research Institute of Kyushu) for supplying the swellable fluor-mica and stimulating discussions, JGC Co., Ltd. for obtaining the MAS ^{29}Si NMR spectra, and the Nippon Sheet Glass Foundation for Materials Science and the Ministry of

Education, Science and Culture (Grant-in-Aid for Science Research, No. 02805100) for financial support of this work.

Received, 13th March 1991; Com. 1/01203G

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