New Acidic Pillared Clay Catalysts prepared from Fluor-tetrasilicic Mica

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The pillared clay prepared from fluor-tetrasilicic mica becomes acidic, and its catalytic activity for toluene alkylation by methanol is greatly enhanced, by La^{3+} ion modification.

Recently pillared clays have been actively studied as solid acid catalysts. The clay minerals of the smectite group with a layer charge ranging from 0.2—0.6 e per Si_4O_{10} unit are usually employed as the starting material.[1] However, clay minerals of the mica group such as muscovite and phlogopite with a layer charge of 1e per Si_4O_{10} unit are never used because of their lack of swelling ability. But fluor-tetrasilicic mica[2] (TSM) $[Na(Mg_{5/2})^{oct.}(Si_4)^{tet.}O_{10}F_2]$ is a unique synthetic mica with free swelling properties.† Employing such a mica as a starting material, Al-pillared TSM (PTSM) with a surface area as large as that of Al-pillared montmorillonite (PM) was obtained,[3] but it had a very low activity for toluene alkylation by methanol. Nevertheless, by making use of the large cation exchange capacity (C.E.C.; about 200 m equiv./100 g) of the parent TSM, it should be possible to modify the exchangeable cation sites of the catalyst and so increase its catalytic activity. Here we present a synthesis of such an acidic form of pillared TSM and an account of its catalytic activity.

The La^{3+} modified Al-pillared clay catalysts (La^{3+}-PTSM) were prepared as follows. The interlayer Na^+ ion of TSM was exchanged with La^{3+} by using $La(NO_3)_3$ and then calcined at 473—773 K for 3 h (Table 1, Calc. 1). Then 1.2 g of the clay was dispersed in a mixture of acetone and water (50 ml each), and 150 ml of Al hydroxy cluster cation solution was added to the clay-dispersed solution followed by stirring for 12 h. After washing and drying, the products were calcined in air (Table 1, Calc. 2) and used for the test reaction. Other cation modified catalysts were also prepared by a similar procedure. Non-modified pillared TSM (PTSM), a reference catalyst was also prepared.[3] The toluene alkylation by methanol was carried out in a conventional continuous flow system under atmospheric pressure.[3]

Table 1 shows the catalytic activities of modified and non-modified pillared catalysts along with the basal spacings and surface areas. Non-modified pillared TSM (PTSM) managed only a 0.1% conversion for toluene alkylation despite having a basal spacing of 18 Å. After modification, activities were greatly enhanced (from 0.1% conversion to 2—8% conversion), keeping similar basal spacings (17—18 Å) as for PTSM, except in the case of Al^{3+} modification. Both La^{3+}-PTSM and Ce^{3+}-PTSM exhibited Langmuir-type isotherms for N_2 adsorption at 78 K and the specific surface areas obtained by the Langmuir plots were 160—240 $m^2\,g^{-1}$ as shown in Table 1. However, Al^{3+}-PTSM exhibited a B.E.T.-type isotherm with a very small surface area (22 $m^2\,g^{-1}$). Thus, the useful cation species for modification were Ce^{3+} and La^{3+}, especially La^{3+}, but Al^{3+} was inadequate. It was also found that the activity of La^{3+}-PTSM varied depending upon the

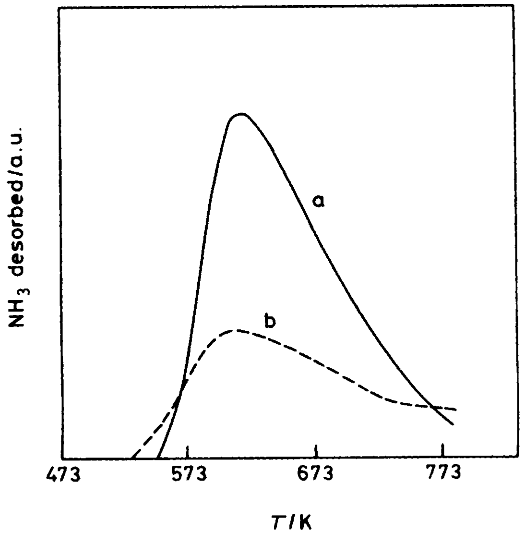

Figure 1. TPD profiles of NH_3 from La^{3+}-PTSM and PTSM. a = La^{3+}-PTSM, b = PTSM.

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† The TSM used was supplied by Topy Ind.

Table 1. Catalytic activities[a] of various catalysts for toluene alkylation by methanol.

Catalyst	Calcination condition Calc. 1	Calc. 2	$d(001)$ /Å	Surface area[b] /m^2 g^{-1}	% Toluene conv.	% Xylene selec.	% *p*-Xylene fraction
PTSM	—	673 K, 4 h	18.4	197	0.11	100	27.1
Al^{3+}-PTSM	673 K, 3 h	673 K, 4 h	9.8	22.0	0.06	100	—
Ce^{3+}-PTSM	673 K, 3 h	673 K, 4 h	17.0	182	1.8	83.6	36.0
La^{3+}-PTSM	673 K, 3 h	673 K, 4 h	17.0	163	3.2	88.7	35.0
La^{3+}-PTSM	573 K, 3 h	none[c]	17.7	242	7.6	77.5	40.1
PM	—	673 K, 4 h	17.3	228	11.6	73.6	43.2

[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 activity for 1 h after feeding of reactants. [b] Measured after evacuation at 573 K for 1 h. [c] Pre-treated at 623 K for 1 h under N_2 gas flow before reaction.

temperature of Calc. 1. When the calcination temperature was <473 K, toluene conversion did not rise over 1.3%. The highest activity was obtained when Calc. 1 was done at 573 K and Calc. 2 was omitted (in this case, the catalyst had undergone thermal treatment under nitrogen flow at 623 K for 1 h before reaction). This activity reached more than half of the activity of PM (11.6%) prepared according to conventional methods.

Along with the activity enhancement, an increase of the *p*-form fraction among the xylenes produced was observed. Although the fraction (27.1%) of the non-modified catalyst was close to the thermodynamic equilibrium fraction (23.7% at 623 K), the fraction of La^{3+}-PTSM which showed the highest activity (7.6%) reached 40.1%, which was comparable to that of PM (43.2%). Based on the information about basal spacings, the shape of isotherms, and surface areas, La^{3+}-PTSM is thought to have a microporous structure and its high *p*-xylene selectivity is brought about by this pore structure for the same reason as in the case of PM.[3]

Further, the acidity increase on modification was proved by temperature programmed desorption (TPD) of NH_3 (Figure 1). The amount of desorbed NH_3 (calculations based on the peak area of TPD) was 49 μ mol g^{-1} for PTSM and 182 μ mol g^{-1} for La^{3+}-PTSM (Calc. 1 at 573 K, Calc. 2 was omitted). As mentioned before, the temperature of Calc. 1 is one of the most important factors determining the catalytic activity of La^{3+}-PTSM. Mozas *et al.* reported that La^{3+} exchanged montmorillonite caused a reduction in C.E.C. when it was heated above 433 K.[4] This implies that some of the La^{3+} ions were converted to a non-exchangeable form by the thermal treatment. The existence of this non-exchangeable La^{3+} ion in our catalyst system was also confirmed by means of fluorescent *X*-ray spectroscopy. Therefore, it can be concluded that this acidity enhancement was caused by interlayer lanthanum ions strongly attached to cation exchanged sites on the silicate surface.

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