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Shape Selective Property of Alumina-pillared Montmorillonite with Different Lateral Distances in m-Xylene Conversion

Toshiaki MORI* and Kenzi SUZUKI
Government Industrial Research Institute, Nagoya,
Hirate-cho, Kita-ku, Nagoya 462

In m-xylene conversion on alumina-pillared montmorillonite, the selectivity of disproportionation increased with increasing lateral distance, while isomerization was predominant for the small lateral distance. The observed results suggest that the shape selectivity operates in the reaction.

In heterogeneous catalysis, the selective synthesis of a desirable product is important from the industrial aspect. When the pore size of a porous catalyst is decreased to be as small as the dimension of many simple molecules, the shape selectivity is expected on the porous catalyst, i.e., reactions are controlled strictly by the size of a reacting or producing molecule and also by that of an intermediate species appearing in the transition state. Zeolite is a typical porous catalyst exhibiting the shape selectivity.[1,2)]

A new zeolite-type porous material has been prepared by pillaring an expandable smectite with cationic oligomers of hydroxy metal.[3,4)] The pore structure of the pillared smectite is characterized by the parallel silicate layers to be two-dimensional. Since the pore size is also comparable with the dimension of simple molecules but slightly larger than that of zeolite, ca. 0.9 nm, a different type of shape selectivity is expected on the pillared smectite.[5-7)]

In addition to the distance between the silicate layers or the interlayer distance, the distance between pillars or the lateral distance also characterizes the pore structure of the pillared smectite. By using Na-montmorillonite with its controlled cation exchange capacity (CEC), we prepared the alumina-pillared montmorillonite having different lateral distances.[8)] The effect of the lateral distance on a reaction must be a stimulating subject from the viewpoint of shape selectivity. In this letter, we wish to report the typical results.

Controlling the CEC of a starting Na-montmorillonite and pillaring the resultant montmorillonite with alumina were made in the manner previously described.8) X-ray diffraction patterns are shown in Fig. 1. As a result of pillaring, the 001 reflection appears at 2θ = 5°.9) Table 1 lists the interlayer distance determined from the X-ray diffraction. The interlayer distance is virtually the same irrespective of the CEC of the starting Na-montmorillonite.9) Table 1 also summarizes the surface area and the Al_2O_3/SiO_2 weight ratio determined by X-ray fluorescence. The observed high surface area provides another evidence for pillaring. The Al_2O_3/SiO_2 weight ratio varies with CEC, which indicates that the amount of alumina introduced as pillars should be altered. The fact that the amount of alumina introduced is altered leaving the interlayer distance unchanged leads us to conclude that the number of alumina pillars is different and therefore the lateral distance is varied among alumina-pillared montmorillonites: the lateral distance decreases with increasing number of alumina pillars.

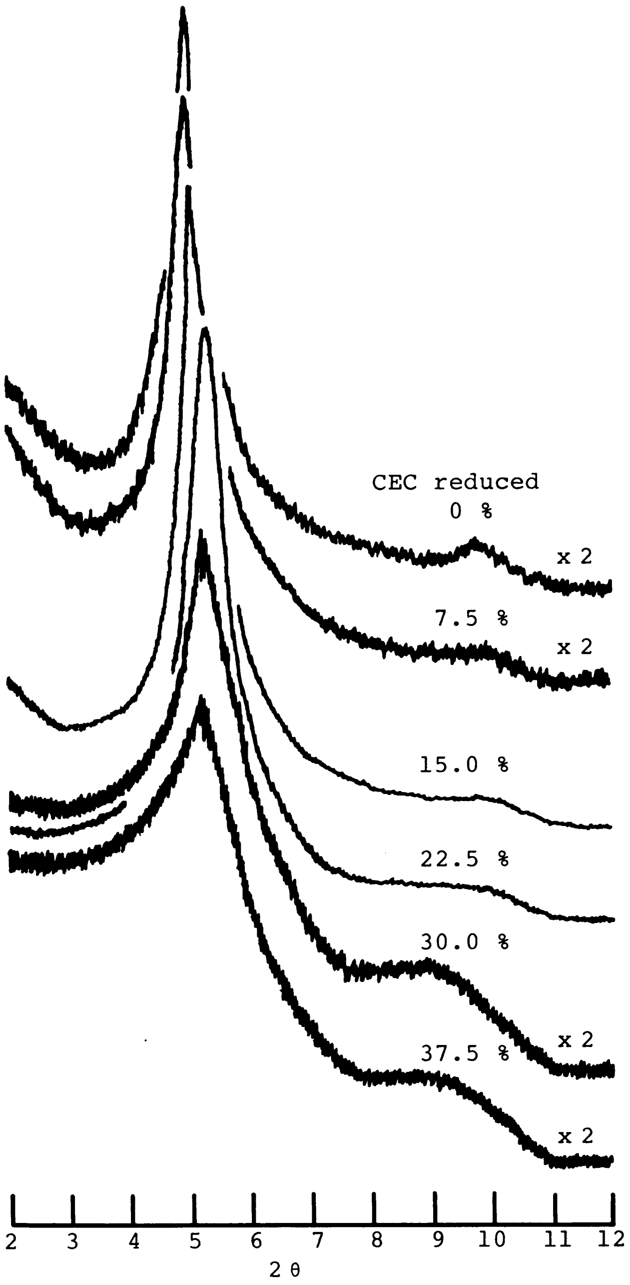

Fig. 1. X-Ray diffraction patterns of alumina-pillared montmorillonites.

Table 1 summarizes the results of m-xylene conversion. Isomerization to other isomers and disproportionation to toluene and trimethylbenzenes are main reactions. Benzene and ethylbenzene were also produced as minor products. For both reactions, the catalytic activity of the pillared montmorillonite decreases with decreasing number of alumina pillars. It is known that both reactions are acid-catalyzed one.

Table 1. Interlayer distance, surface area, Al_2O_3/SiO_2 weight ratio, and catalytic activity for m-xylene conversion of alumina-pillared montmorillonite, the lateral distance of which is varied

CEC reduced[a]	Interlayer distance	Surface area	Al_2O_3/SiO_2 wt.ratio[b]	Catalytic activity[c]			TMB isomer (mol%)		
%	nm	m^2g^{-1}	(-)	Iso.	Dispro.	I./D.[d]	1,3,5	1,2,4	1,2,3
0	0.78	344	0.590	14.35	5.79	2.48	22.0	68.2	9.81
7.5	0.79	334	0.588	11.86	4.84	2.45	21.8	68.3	9.90
15.0	0.76	336	0.579	8.39	4.77	1.76	29.8	61.7	8.50
22.5	0.74	346	0.556	5.64	4.38	1.29	29.8	64.0	6.21
30.0	0.74	281	0.486	2.98	3.01	0.99	34.5	60.6	4.93
37.5	0.74	259	0.473	3.21	2.52	1.27	34.7	60.3	5.00

a) Calculated CEC reduced by the method identical to that in Ref. 8.

b) The ratio for the original clay, the CEC of which is not reduced, is 0.351.

c) Reaction temperature = 628 K, WHSV = 2.0, He/m-xylene molar ratio = 2.8. Conversions are for the reaction after 30 min.

d) The isomerization/disproportionation activity ratio.

It is also reported that acid sites are formed not only on the silicate layers but also on the alumina pillars on alumina-pillared smectite.[10,11] Indeed, it was found that pyridine was adsorbed much more on the pillared montmorillonite having a large number of alumina pillars. These may rationalize the observed catalytic activities increasing with the number of alumina pillars.

The more interesting feature in m-xylene conversion is the selectivity varying with the number of alumina pillars, which is not explained by the difference in the conversion level. Although both reactions are enhanced with increasing number of alumina pillars, the enhancement is less pronounced for disproportionation than for isomerization. As a consequence, while isomerization is predominant on pillared the montmorillonite having a large number of alumina pillars, the selectivity of disproportionation increases with decreasing number of alumina pillars.

Concerning the reaction of alkylbenzene on a solid acid catalyst, it is accepted that while isomerization proceeds via intramolecular 1,2-methyl shifts,[12] disproportionation proceeds via the formation of a relatively large bi-molecular intermediate.7,13) According to these mechanisms, the disproportionation of m-xylene must require a larger space than the isomerization. As concluded above, the pillared montmorillonite with a larger number of alumina pillars has a smaller lateral distance and therefore has a smaller interlayer space. The formation of the bulky intermediate for disproportionation may be limited more severely in the small interlayer space than the formation of the intermediate for isomerization, to which the observed selectivity variation is ascribable. It is, therefore, concluded that the shape selectivity, classified as the restricted transition state-type selectivity,2) operates in m-xylene conversion on alumina-pillared montmorillonite with different lateral distances, i.e., the reaction is controlled by the size of the intermediate species appearing in the transition state.

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