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Transformation of *m*-Xylene over Al-Pillared Clays and Ultrastable Zeolite Y

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The reaction of *m*-xylene has been carried out at 623 K over Al-pillared beidellite and montmorillonite, and over ultrastable zeolite Y (USY) as a reference catalyst. These microporous acidic solids exhibit similar open porosities and, therefore, the activity toward disproportionation and/or isomerization is not primarily ruled by geometrical limitations but merely reflects the relative amount and strength of the acid sites, strong Brønsted acid sites being required for disproportionation and weaker ones for isomerization. In terms of overall conversion and disproportionation selectivity, USY is more active than the pillared clays. This is due to a higher content of strong acid sites and to the greater micropore volume of USY. Al-pillared beidellite is more active than Al-pillared montmorillonite, which is interpreted in terms of framework substitution differences between the two clays. The OH/Al molar ratio of the starting pillaring solution does not confer to the pillared materials any significant effect on their catalytic performances. Deactivation is observed for all the catalysts, and there is some evidence that the stronger sites would deactivate first. © 1994 Academic Press, Inc.

INTRODUCTION

Aluminium-pillared clays exhibiting basal spacings near 1.8 nm (0.8-nm pillar height) are currently compared with 12-membered ring zeolites (large pore), principally Y faujasite, for their similar pore dimensions (1). However, one of the main differences between these two types of microporous solids resides in their respective acidic properties. Indeed, it is now well established that in Al-pillared clays, the Lewis acidity associated with the interlayered pillars prevails over the Brønsted acidity, as evidenced, e.g., by IR spectroscopy of adsorbed pyridine, whereas in HY zeolites, the acidity is principally protonic. It has also been shown that in cracking reactions, the most investigated area of their possible applications, pillared clays generally deactivate more rapidly than Y zeolites and can hardly be regenerated.

However, in other proton-catalyzed reactions which require less severe conditions of temperature and acid strength, the performances of pillared clays may support comparison with zeolites, particularly the Y type. This is the case, for instance, in the bifunctional hydroisomerization of *n*-alkanes on Pt-impregnated pillared clays (2). The type of clay is also of importance with respect to the development and stability of the Brønsted acidity. Recently, the catalytic properties of Al-pillared beidellite and Al-pillared montmorillonite, prepared in a similar manner, were compared in the conversion of *n*-heptane and in cumene dealkylation. In both reactions, Al-pillared beidellite was found to be more active than Al-pillared montmorillonite (3). In *n*-C_7 hydroisomerization, the selectivities in C_7 isomers were significantly higher over pillared beidellite than over ultrastable zeolite Y (USY), the maximum yields of isomers being 78 and 55% for pillared beidellite and USY, respectively. Similar results were obtained with *n*-C_{10} (to be published).

The catalytic properties of Al-pillared bentonite have been also evaluated in the alkylation of toluene with ethylene (4). This catalyst achieved higher conversions than a rare-earth-exchanged Y zeolite. The selectivities in ethyl toluene were also higher over the pillared clay as less disproportionation of toluene occurred. Shape selectivity was absent and deactivation through coke deposition was noted.

Disproportionation of 1,2,4-trimethylbenzene over Al-pillared montmorillonite has been investigated by Kikuchi *et al.* (5, 6) and Kojima *et al.* (7). Durene (1,2,4,5-tetramethyl benzene (TeMB)) was selectively formed. The former authors advocated space restrictions in the pillared material to favour transitional diphenylmethane-like species with the smallest cross-sectional dimension, namely those leading to 1,2,4,5-TeMB, though this interpretation was questioned by Kojima *et al.* (7). Comparing the disproportionation of the trimethylbenzenes over pil-

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lared clays and HY, Kikuchi *et al.* (6) observed higher selectivities for disproportionation against isomerization of every trimethylbenzene (TMB) isomer over pillared clays than over HY. Matsuda *et al.* (8) further showed that the selectivity for 1,2,4,5-TeMB from 1,2,4-TMB disproportionation over pillared clays could be markedly enhanced when the contribution of the Brønsted acidity was reduced, either by a thermal treatment or as a consequence of a more rapid deactivation of the Brønsted sites by coke deposition.

The reaction of *m*-xylene on zeolites, besides its industrial importance, is abundantly described in the literature not only because it provides information on the geometry of the zeolite channels (9), but also because it is considered as an appropriate reaction to give information on the acidic properties of solids. In a recent work, Martens *et al.* (10) showed that the 10- and 12-membered ring zeolites could be easily distinguished from each other according to the selectivity for disproportionation versus isomerization, whereas Ratnasamy *et al.* (11) and Giordano *et al.* (12) established for HY and dealuminated mordenites, respectively, that disproportionation requires stronger acid sites than isomerization.

The reaction of *m*-xylene has been investigated at 628 K by Mori and Suzuki (13) on Al-pillared montmorillonites wherein the number of pillars was varied by submitting the initial clay to Ni^{2+} treatments in order to decrease the layer charge.

In this work, *m*-xylene has been reacted over Al-pillared montmorillonite and beidellite, and an ultrastable Y zeolite. Since, because of their similar porosity, no particular differences in shape selectivity or transition state restriction should be observed, it may be expected that evidence for differences in acidity (especially acid strength) could be observed.

EXPERIMENTAL

Catalysts

A natural montmorillonite ($<2\mu$ fraction) from a Greek deposit with structural formula $[Si_{7.95}Al_{0.05}]^{IV}$ $[Al_{2.8}Fe_{0.60}Mg_{0.60}]^{VI}O_{20}(OH)_4Na_{0.65} \cdot nH_2O$, and a beidellite, with structural formula $[Si_{7.33}Al_{0.67}]^{IV}$ $[Al_4]^{VI}$ $O_{20}(OH)_4$ $Na_{0.67} \cdot nH_2O$, synthesized according to the procedure described earlier (14), were pillared with partially titrated aluminium solutions ($Al(NO_3)_3$, 0.2 *M*; NaOH, 0.5 *M*). The amount of Al in contact with the clay suspension (1 wt%) was 30 meq Al/g of clay. The OH/Al molar ratios of the pillaring solutions were 1.2, 1.6, 2.0, and 2.4. The pillared clays were washed by dialysis and freeze-dried. More details on the preparation have been reported elsewhere (14, 15). An ultrastable Y zeolite (USY, Si/Al = 5.0) supplied by Professor P. A. Jacobs (from the Centrum voor Oppervlaktescheikunde en Katalyse, Katholieke Universiteit Leuven), was taken as a reference catalyst.

Characterization of the Pillared Clays

- Basal spacings. The different pillared beidellites (AlPB) and montmorillonite (AlPM) showed, after calcination at 400°C for 4 h, similar basal spacings of 1.77 nm (0.8-nm pillar height) independently of the OH/Al molar ratio of the pillaring solution.
- Surface area and pore volume. The BET surface area (determined from the N_2 adsorption isotherms) of the samples calcined at 400°C were between 300 and 320 m^2/g for ALPB, and 220 m^2/g for AlPM. The total (meso + micro) pore volumes were 0.25 cm^3/g (micro: 0.12 cm^3/g) for AlPB and 0.21 cm^3/g (micro: 0.10 cm^3/g) for AlPM.
- Surface acidity. Both Lewis and Brønsted acidities were identified by IR spectroscopy of adsorbed pyridine. More detailed information has been reported in previous papers (2, 16).
- Catalytic evaluation. The catalytic tests were performed in a continuous flow microreactor operated at atmospheric pressure, by flowing the carrier gas (H_2, 20 ml/min) through a saturator containing *m*-xylene and kept at constant temperature. The catalyst (200 mg) was positioned in the quartz reactor between two layers of pure fine-sized quartz (0.2 mm). The catalyst was previously calcined at 400°C for 24 h under air flow. The WHSV of *m*-xylene was 1.37 h^{-1} and the reactions were carried out at 623 K. The analysis of the effluent was made on-stream by means of a 6-way sampling valve coupled with a 5880 HP gas chromatograph fitted with a WSCOT cpm Wax 51, 50-m-long, capillary column.

RESULTS

The variation of the conversion of *m*-xylene at 623 K with time-on-stream obtained for AlPBM, the AlPB's, and USY is shown in Fig. 1.

USY is substantially more active than the pillared clays. The 4 AlPB samples are more active than AlPM. All the catalysts deactivate with time.

Among the AlPB's, there is a slight difference according to the OH/Al molar ratio used in their preparation. AlPB (1.2) appears to deactivate to a slightly larger extent than the three other ones, which is particularly clear after several hours of reaction.

The conversion of *m*-xylene obtained over AlPM is similar to those reported by Mori and Suzuki (13).

m-Xylene on solid acids may undergo isomerization and/or disproportionation. Since the bimolecular disproportionation of xylenes requires stronger acid sites than the monomolecular isomerization (11), the relative importance of these two reactions may yield information on

FIG. 1. Overall conversion of *m*-xylene vs time-on-stream, for USY, Al-pillared beidellites (AlPB), and Al-pillared montmorillonite (AlPM). Reaction temperature, 623 K; WHSV, 1.37 g/g h. For the AlPB's, the numbers refer to the OH/Al molar ratios of the pillaring solutions.

the type and the relative strength and number of the acid sites. Besides, the variation of the isomerization/disproportionation (I/D) ratio with time-on-stream may provide, at least to a first approximation, indirect information on the relative stability and deactivation of the sites responsible for isomerization and for disproportionation.

The behavior of the different catalysts is illustrated in Fig. 2, where a clear distinction can be made. For USY, disproportionation prevails over isomerization, the fraction of the disproportionation products representing nearly 70% of the reaction products after 1 h of reaction, and about 50% after 25 h time-on-stream.

For the series of Al-pillared beidellites, the I/D ratio increases during the first 5–6 h and reaches a constant value (7.8) for longer times of reaction. Since the reaction was carried out at high conversions, extrapolation to initial conditions is somewhat meaningless. A distinction between the pillared samples according to the OH/Al ratio used in their preparation is hardly to be found: all the points are distributed along the experimental curve.

The variation of the I/D ratio for AlPM is very different from that of the pillared beidellites, with a steep and linear increase with reaction time. Note that the extrapolation to short time-on-stream (near initial conditions) would indicate high disproportionation activity.

If these data are presented in another way, it is possible to examine whether, during deactivation, the stronger acid sites which give rise to disproportionation are preferentially or not affected with respect to the weaker isomerisation sites. Figure 3 shows the changes in the yields of disproportionation products and of *m*-xylene isomers vs conversion, a higher conversion corresponding to a shorter time-on-stream. As in Fig. 2, three different cases may be distinguished. For USY, as conversion decreases (increasing deactivation) from 70 to 45%, the yields of the disproportionation products decrease linearly, while the yields of *o*- + *p*-xylene keep a constant value. At first sight, it would thus appear that the sites which produce disproportionation are those which first deactivate.

The four pillared beidellites behave similarly. Between 50 and 40% conversion (between 0.17 and 5 h time-on-stream), the decrease of the disproportionation products (D) is more rapid than the decrease of the *o*- + *p*-xylenes (I). Beyond 5 h of reaction, there is an almost linear decrease of the yields of both families of products with the diminution of the conversion. There is a factor of 7 between the slopes of the two linear portions.

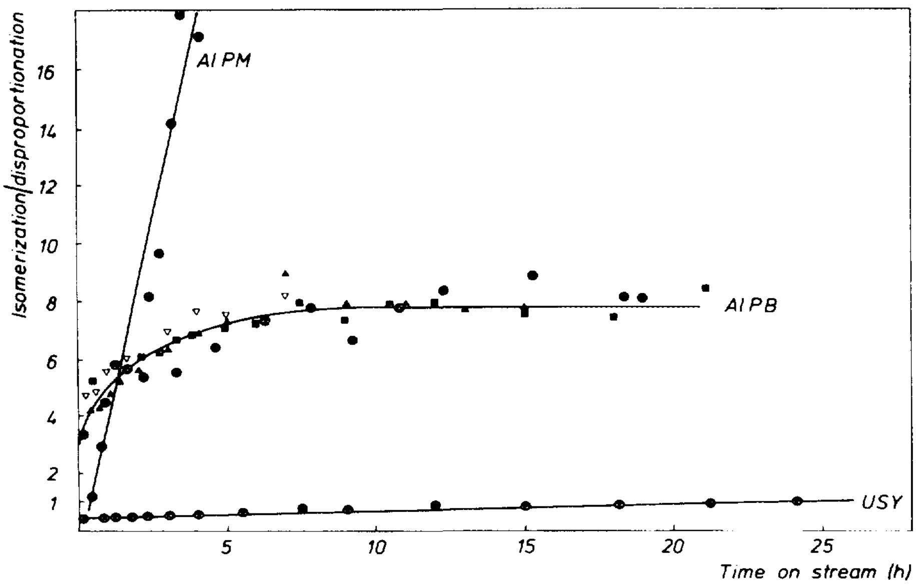

FIG. 2. Isomerization/disproportionation products vs time-on-stream.

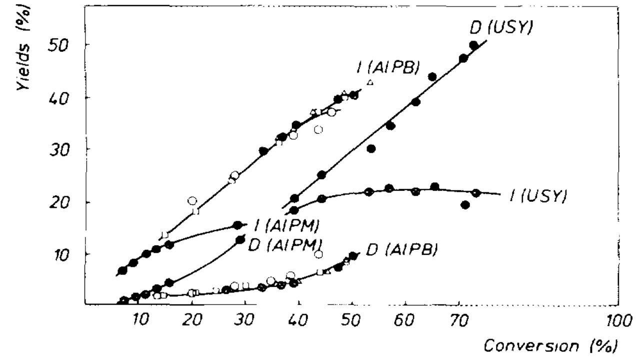

FIG. 3. Yields of the xylene isomers (*o* + *p*) (I) and of the trimethylbenzenes (D) as a function of conversion of *m*-xylene.

In the case of AlPM also, the disproportionation products decrease more rapidly than the *m*-xylene isomers as deactivation proceeds, up to about 10% conversion, i.e., 2 h of reaction. Beyond that time, the reverse is observed.

Distribution of the Disproportionation Products

For USY, which exhibits a higher disproportionation activity, the composition of the trimethylbenzenes does not significantly change with time-on-stream. The main variation is noted within the first hour of reaction. The composition of the TMBs, expressed in %, are given in Table 1. The mean composition (excepting the values obtained at 0.12 h of reaction) is also indicated.

In the case of the pillared clays, the three TMB isomers are produced only during the first hour of reaction. Beyond that time, 1,2,3-TMB is no longer formed, at least in detectable amounts.

For AlPM, the distribution is slightly different, and after 1 h of reaction, disproportionation products are no longer detected. As shown in this table, the distribution of the TMB isomers does not much depart from the values at thermodynamic equilibrium.

The 1,2,3/1,3,5 ratio obtained for USY after 0.12 h reaction is near the value reported by Martens *et al.* (10) for HY (0.28) at low yield of disproportionation.

As shown in Table 2, the balance between toluene and the trimethylbenzenes produced under the reaction conditions adopted was respected in the case of the pillared clays. For USY, the TMB isomers exceed toluene; for this catalyst, benzene was also observed, probably due to the partial disproportionation of toluene. This observation is consistent with the presence of stronger Brønsted sites of the zeolite as compared with the pillared clays.

Overall Isomerization Selectivities

The selectivities in isomerization, expressed as the ratio I/(I + D), were compared at 40% conversion of *m*-xylene.

All the pillared beidellites exhibit similar selectivities, with a value between 0.85 and 0.89. USY, more active in disproportionation than the pillared clays, is of course, less selective in isomerization, with a value of 0.46.

For AlPM, the highest overall conversion is 28% at the early stage of the reaction and therefore a comparative figure cannot be given. However, when compared with the results obtained by Mori and Suzuki (13) on Al-pillared montmorillonites, after 30 min reaction, this ratio is 0.66, which is in good agreement with 0.71 calculated from the data of Mori and Suzuki.

Selectivities in m-Xylene Isomerization

At thermodynamic equilibrium, the *para/ortho* (*p/o*) ratio at 623 K is 1.09 : 1 (10).

It was observed that for the pillared clays (montmorillonite and beidellite), the *p/o* ratio did not change

TABLE 1

Catalyst	Time-on-stream (h)	Overall conversion (%)	Distribution of TMB (%)			TMB ratio 1,2,3/1,3,5
			1,2,4	1,3,5	1,2,3	
USY	0.12	71	64.5	28.5	7	0.24
	0.82	73	64.5	25.8	9.7	0.38
	25.70	38.2	65.0	25.9	9.1	0.35
(x)			64.9 ± 0.6	26.1 ± 0.8	9 ± 0.5	0.34
AlPM	0.38	28.7	67.2	22.0	10.8	0.49
AlPB(1.2)	1.00	47.3	64.5	26.9	8.6	0.32
AlPB(1.6)	0.7	49.6	65.2	26.2	8.6	0.33
AlPB(2.0)	0.83	46.1	65.7	25.9	8.4	0.32
(xx)			68	24	8	0.33

Note. (x), mean distribution over 25 h of reaction; (xx), distribution at thermodynamic equilibrium (623 K) from Ref. (10).

TABLE 2

Yields of Toluene and TMB Isomers in the Reaction Products (in %) vs Conversion for USY and AlPB (OH/Al + 2.4)

USY			AlPB (OH/Al = 2.4)		
Conversion (%)	Toluene (%)	TMB isomers (%)	Conversion (%)	Toluene (%)	TMB isomers (%)
73.30	19.75	30.65	48.65	4.40	4.17
70.95	18.59	29.51	47.46	3.63	3.05
68.31	16.52	28.05	46.47	3.45	3.41
65.39	15.69	27.41	45.48	3.27	3.05
61.67	14.73	24.35	42.62	2.69	2.65
57.44	13.09	21.64	40.27	2.34	2.30
52.89	11.00	18.83	38.92	2.29	2.17
50.85	11.11	17.74	36.01	2.00	1.90
44.92	9.83	15.69			
42.64	8.88	14.55			
38.20	8.20	11.42			

throughout the reaction duration, with a mean value of 1.05 : 1. For USY, a slight increase of this ratio was noticed, going from 0.87 : 1 in the initial period of reaction, to 0.96 : 1 after 25 h time-on-stream, thus slightly but significantly lower than for the pillared clays. As *p*-xylene undergoes disproportionation faster than either of the other isomers over acid catalysts, this slight increase of the *p*/*o* ratio might be due to a kinetic effect.

DISCUSSION

AlPB vs AlPM

The higher activity of Al-pillared beidellites as compared with Al-pillared montmorillonites, also found in previous work (2,3,15), cannot be attributed to differences in their respective textural characteristics. Indeed, both types of pillared clays, prepared under similar conditions, exhibit identical basal spacings, almost equal amounts of Al fixed as pillars in their interlamellar regions (~2 mmol/g), similar residual cation exchange capacities (20–25 meq/100 g) and micropore volumes. The major difference, shown by IR spectroscopy of adsorbed pyridine and ammonia adsorption measurements, concerns their respective proton contents and relative stability (2). As inferred from the relative losses of intensity of the pyridinium band at 1540 cm^{-1} upon outgassing at increasing temperatures, AlPM has a lower proton content than AlPB, and these Brønsted acid sites are also more sensitive to thermal treatment than in AlPB. A factor of 2.4 in the integrated intensity (absorbance × $\text{cm}^{-1} \times \text{g}^{-1}$) of the pyridinium band in favor of pillared beidellite was observed on samples calcined at 350°C prior to pyridine adsorption and subsequent outgassing at 500°C. This factor was still higher (~12.5) when precalcination was carried out at 500°C.

The amounts of ammonia adsorbed at 350°C were 190, 340, and 460 μmol/g for, respectively, AlPM, AlPB, and USY.

The difference of the proton content and stability was related, as proposed earlier (3), to the nature of the clay, and more precisely, to the lattice substitutions which in montmorillonite or bentonite clays mainly occur within the octahedral layers, whereas they take place principally in the tetrahedral layers in beidellites. Protons generated during the pillaring process will be trapped by the tetrahedral layer in beidellite, as a result of Si–O–Al bond opening and formation of SiOH · · · Al groups shown by an IR OH stretching band at 3440 cm^{-1}. This band disappears upon pyridine adsorption. In montmorillonite-type clays, such acid sites are not formed and the protons generated during the pillaring step will merely migrate toward the more labile octahedral layers. Therefore, the proton sites in pillared beidellite are stronger and directly accessible to the reacting molecules, whereas in montmorillonite they are less accessible due to the screening effect of the silicon tetrahedral layer.

This interpretation is consistent with the one proposed by Davidtz (17), who established, for the dehydration reaction of *tert*-butanol, a quantitative relationship between the activity of H-exchanged 2 : 1 (unpillared) clays and their tetrahedral exchange site density, i.e., the amount of tetrahedral substitutions. A similar relation was recently established for a series of Al-pillared clays with different degrees of tetrahedral substitutions, using the n-C_{10} hydroisomerization–hydrocracking reaction (article in preparation).

Al-pillared saponite (a synthetic trioctahedral clay with Al for Si substitution in the tetrahedral layers) was also found to be more active than Al-pillared montmorillonite in the alkylation of toluene with methanol (18), and in the hydroisomerization reaction of *n*-heptane (unpublished result).

Catalytic Sites

Evidence is provided in the literature that both isomerisation and disproportionation of *m*-xylene are catalyzed by Brønsted acid sites, disproportionation requiring stronger sites than isomerization (11, 19–22). Lewis sites do not appear to be involved either in isomerization, as observed by Ward and Hansford (23), or in disproportionation, as Lewis–Brønsted pairs, as was proposed by Csicsery and Hickson (24) and Poutsma (25), but recently contradicted by Martens *et al.* (10). In pillared clays, Lewis acidity associated with the Al pillars prevails over Brønsted acidity, as shown by IR spectroscopy of adsorbed pyridine (2, 3, 8, 26–28). Since both AlPB and

AlPM contain nearly the same number of pillars, one would expect similar catalytic activities if Lewis sites were involved in the transformation of *m*-xylene. Isomerisation may occur on strong (29) as well as on weak protonic sites (30). According to Guisnet (31), the D/I ratio obtained for HY zeolite is not related to the strength of the proton sites but merely to their density, pairs of adjacent sites being required for the bimolecular disproportionation. On the contrary, strong, isolated Brønsted sites were invoked by Martens *et al.* (10) to account for the high disproportionation activity of ZSM-12 with Si/Al = 150 as compared with HY zeolite.

In spite of these conflicting interpretations, the higher activity of USY is attributed to its higher proton content and micropore volume (about twice that of pillared clays) and its higher disproportionation activity, assuming that porosity effects may be neglected (32), would reflect a greater proportion of strong sites than in the pillared clays, which, as proposed by Breck and Skeels (33) and Ratnasamy *et al.* (11), could be associated with extraframework Al indicated by solid-state MAS-NMR (34). Such strong sites could be responsible as well for the poor balance between toluene and the trimethylbenzenes.

Textural differences between USY and pillared clays have also to be considered. In USY, with its higher micropore volume as compared with pillared clays, the bulky transitional diphenylmethyl species could more easily be accommodated in the supercages (~1.3 nm diameter). In pillared clays, space restrictions, advocated by Kikuchi *et al.* (9) and Ko *et al.* (35) in the disproportionation-isomerization of 1,2,3-trimethylbenzene, could hinder the formation of the intermediate compounds. However, there is up to now no clear vision on the size and geometry of the micropores in pillared materials. Indeed, contrary to zeolites with well-defined pore geometries, the values found in the literature, obtained by indirect measurements, are often conflicting because they are depending on several factors such as preparation conditions, type of parent clay, layer charge and pillar distribution, calcination temperature, etc. Pore distributions centered at 0.8 nm (extending beyond 1.1 nm) were recently reported by Michot and Pinnavaia (36), whereas Kojima *et al.* (7) quote that pore dimensions of pillared clays are larger than those of large pore zeolites. Therefore, the influence of this parameter on the catalytic results cannot be clearly established at the present time.

In pillared clays, the lower disproportionation activity would reflect a smaller proportion of strong sites. The lower proton content, besides bringing about possible concentration effects in the void volumes, and their weaker strength would favor the monomolecular isomerization. This is also consistent with the results obtained over dealuminated zeolites (37). The lower catalytic performances of AlPM as compared with AlPB is attributed to its lower number of protonic sites as well as to their strength and instability, as discussed above. It may also be noted that the distributions of the TMB isomers (Table 1) are close to those at thermodynamic equilibrium both for USY and the pillared clays, which seems to indicate that if spatial hindrances exist in the pillared clays, they have only a limited impact on the reaction.

The loss of activity with time noted for all the catalysts is not surprising for microporous acid solids. The relatively more rapid deactivation of AlPM as compared with AlPB may be explained by the differences in proton content and stability, and also, as it has been suggested (38), by lattice iron (absent in beidellite), although this effect still needs confirmation.

For USY (Fig. 3), the nearly constant isomer yields (I) and the linear decrease of the TMB yields (D) as conversion decreases (as deactivation proceeds) could indicate that the strong Brønsted sites deactivate first, in agreement with Machado *et al.* (39), the weaker isomerization sites being unaffected.

If pore blockage was the main cause of deactivation of USY, one would expect, according to Guisnet *et al.* (40), diffusion limitations of both reactant and products, and, hence, disproportionation and isomerization activities should both be affected. On the contrary, if site poisoning is involved, and this hypothesis has our preference, the stronger sites would be first eliminated, i.e., disproportionation activity should decrease more rapidly with increasing poisoning. That the weaker isomerization sites "escape" deactivation may signify that they are too weak to initiate coke formation or be interpreted in terms of the "hidden sites" concept proposed by Corma *et al.* (37), for dealuminated faujasites. In the pillared clays, where the Lewis sites (on the Al pillars), promoting polycondensation reactions (38), are easily accessible, both isomerization and disproportionation products decrease with increasing deactivation. According to Guisnet *et al.* (40), this would merely characterize a deactivation process through pore blockage.

CONCLUSIONS

The transformation of *m*-xylene follows the activity sequence USY > AlPB > AlPM. The higher disproportionation activity of USY with respect to the Al-pillared clays is indicative of a higher content of strong protonic sites.

The high activity of Al-pillared beidellite as compared with Al-pillared montmorillonite is clearly shown experimentally and accounted for by structural differences, namely, the location of their main isomorphous framework substitutions which, in turn, control the type, strength, and stability of the Brønsted sites. The OH/Al molar ratio of the pillaring solution does not appear to be of prime importance for the catalytic performances.

The distributions of the TMB isomers are similar for both types of catalysts and near the values expected at thermodynamic equilibrium. Although geometrical hindrances on the formation of the intermediate species as well as diffusional limitations cannot be ruled out, they appear to have only a secondary effect.

Over USY, the disproportionation activity decreases with time-on-stream (as deactivation proceeds), which is interpreted in terms of preferential poisoning of the stronger Brønsted sites.

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