Evidence for a Bimolecular Isomerization of Xylenes on Some Large Pore Zeolites

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Use of deuteriated p-xylene as reactant shows that alkyl isomerization takes place by both uni- and bi-molecular mechanisms on faujasite and mordenite, but only by a unimolecular 1,2-methyl shift on β-zeolite.

The isomerization of xylenes and ethylbenzene is carried out industrially using zeolites as catalysts. Besides its technological interest the isomerization of xylenes has been proposed as a test reaction for zeolites and zeolite-like materials.[1-3] The influence of site density, acid strength and size and shape of the channels can be followed from the relative rate for isomerization and transalkylation reactions, para- to ortho-xylene ratio, and product distribution in the trimethylbenzene isomers.[2] When the isomerization of xylenes is used as a test reaction, it is always assumed that the alkyl isomerization

takes place by a unimolecular process involving a 1,2-methyl shift, while the transalkylation of a methyl group to give toluene and trimethylbenzene is a bimolecular one. Based on this assumption, the ratio of isomerization to transalkylation is generally used as a basis for discussions on the framework Al density. We now report that on some large pore zeolites, even at low levels of conversion, part of the xylene isomer products are formed not only by a unimolecular 1,2-methyl shift but also by a bimolecular mechanism. The influence of zeolite composition and structure on the importance of this mechanism is discussed.

A series of ultrastable (HYD) faujasites was prepared by dealumination of NaY samples (SK-40, Union Carbide) using $SiCl_4$ and following the procedure reported in the literature.[4] Mordenite (Norton-100) was treated at 353 K with 1 mol dm^{-3} HCl solution. β-Zeolite was synthesized following the procedure described previously.[5] The β-zeolite was activated by heating the sample first in a stream of N_2 up to 773 K followed by calcination at 823 K in an air stream. The resultant samples were twice NH_4^+ exchanged, and calcined at 823 K.

All experiments were conducted in a conventional fixed-bed glass tubular reactor, heated electrically and equipped with a minipump for feeding the liquid hydrocarbon and a fine metering valve to regulate the nitrogen flow. The hydrocarbon partial pressure was always 2.0×10^4 N m^{-2}. The reaction products were separated by gas chromatography and identified by an ion trap detector. The identification was also carried out in an AEI MS30 mass spectrometer under the following conditions: ion source temperature 150 °C; filament current 100 mA, accelerating voltage 70 eV; mass span 103 to 120; variable sensitivity depending on the concentration of each isomer in the mixture. We found in all cases that the distribution of deuteriated species of each of the xylenes changed along its corresponding chromatographic peak. It was then necessary to record 30 or more mass spectra in each chromatographic peak in order to obtain a good measurement of the true raw mass peak heights. The accuracy of this procedure was checked using known mixtures of $p\text{-}C_8H_4D_6$ and $p\text{-}C_8H_{10}$. After this, the corrected mass peak heights were calculated following the usual correction to allow for naturally occurring carbon-13 and deuterium and for fragmentation of the molecules on the assumption that the energy required to break a C–H and C–D bond is the same, independent of the deuterium content in the molecule.
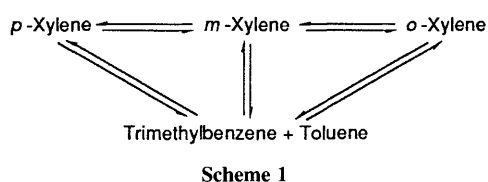
When p-xylene is fed as reactant, m-xylene, formed as a true primary product, can keep reacting inside the pores before desorption from the zeolite, to give o-xylene which appears as a primary product. Together with the xylene isomers, trimethylbenzenes are also formed, arising from the transalkylation of a methyl group from one molecule of xylene to another to give trimethylbenzene and toluene (Scheme 1).

Since the m-xylene which is formed, even if it is present in very low concentration, can further isomerize, there is also the possibility for transalkylation of the trimethylbenzene and toluene with a xylene molecule giving a xylene which can be different from the reactant. Indeed, Lanewala and Bolton[6] presented the possibility that xylene isomerization on faujasite zeolites occurred through a bimolecular reaction involving trimethylbenzenes as intermediates.

By using as reactant a mixture of deuteriated and normal p-xylene it is possible to distinguish between uni- and bi-molecular mechanisms for xylene isomerization. Then, if all isomers are only formed by a unimolecular 1,2-methyl shift all isomers will have molecular weights of 106 and 112 corresponding to structures (A) and (B). However, if xylene isomerization also takes place by a bimolecular trans-alkylation mechanism, products (C) with M 109 will also be present.

Results in Table 1 clearly show that in the case of faujasite, more than 20% of the xylene isomers are formed by a bimolecular mechanism. On this zeolite, the relative proportion of uni- to bi-molecular isomerization depends on the Al content of the zeolite, the bimolecular contribution being smaller when the framework Al content is smaller. By quantifying the proportion of xylenes with intermediate masses, i.e. 107, 108, 110 and 111, it is clear that practically none of the 109 product comes from deuterium scrambling due to isotopic exchange.

It is apparent that the intermediate complex for the bimolecular isomerization will need a bigger void space to be formed than the intermediate for the 1,2-methyl shift. If this is so, there is no doubt that the structure of the zeolite will also control the relative proportion of bi- to uni-molecular isomerization mechanisms. Results from Table 1 show that a mordenite gives something like three times less bimolecular isomerization, while on β-zeolite practically all isomerization occurs by a 1,2-methyl shift. This can be understood by considering that, while disproportionation between two mol-
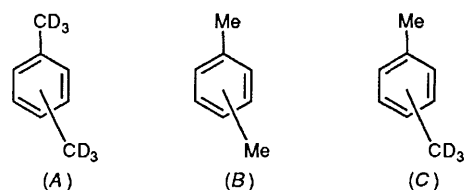

Scheme 1

(A) (B) (C)

Table 1 Results obtained in the isomerization of a mixture of deuteriated p-xylene $[C_6H_4(CD_3)_2]$ (30%) and normal p-xylene $[C_6H_4Me_2]$ (70%) using different zeolites at 200 °C

Zeolite	Framework Al/(Al + Si)	Cryst.(%)	W/g	Feed/ mol h^{-1}	τ/g h mol^{-1}	Conv.(%)	X^b	Selec. to TMB (%)^c
HYD-1	0.189	90	0.29	0.13	2.23	6.0	22.0	19
HYD-2	0.115	85	0.30	0.13	2.31	8.5	21.0	22
HYD-3	0.033	90	0.34	0.13	2.62	5.5	2.5	17
Mordenite	0.125	95	0.53	0.27	1.96	4.5	6.8	25
β	0.107	75	0.26	0.13	2.00	5.0	0.0	7
Amorphous Silica– alumina^a	0.130		0.30	0.09	3.33	5.6	0.0	14

^{a} Results obtained at 400 °C and 3.33×10^4 N m^{-2} xylene partial pressure. ^{b} $X = 100 \times m_{109}/(m_{106} + m_{109} + m_{112})$. ^{c} TMB = trimethylbenzene.

ecules of xylene is sterically prevented in the narrow sinusoidal channels, giving therefore a high isomerization to transalkylation ratio, the transalkylation between a molecule of xylene and a molecule of trimethylbenzene is clearly restricted in both the rectilinear and the sinusoidal channels.[7]

It should be noted that no bimolecular isomerization was detected on amorphous silica–alumina. This indicates that the cavities of the zeolite strongly favour the bimolecular reaction. Owing to diffusional constraints within the zeolite, secondary reactions such as the transalkylation between trimethylbenzenes and xylenes appear as a primary reaction, allowing the bimolecular isomerization mechanism to be observed even at low levels of conversion on zeolites, but not on an amorphous silica–alumina which contains meso- and macro-pores. Secondly, the space confination and the proximity imposed on the molecules inside the cavities of the zeolites can favour bimolecular with respect to unimolecular reactions.

It can be concluded that in order to observe the bimolecular isomerization mechanism one needs to have micro cavities, but these should be big enough to be able to accommodate a molecule of trimethylbenzene and another of xylene in the intermediate complex.

From this study, it becomes apparent that if xylene isomerization is to be used as a test reaction, it cannot be assumed, in some 12MR zeolites, that all isomers are formed by a unimolecular reaction. This observation has clear implications on the kinetic models to be used, the activation energies and turnover frequencies calculated, and finally on all the hypotheses on the influence of the framework Al density on product distribution.

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