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In Situ IR Spectroscopic Study of the Surface Species during Methylation of Toluene over HZSM-5

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The alkylation of toluene with methanol over HZSM-5 zeolites was studied in a continuously stirred tank reactor equipped with CaF_2 windows, which allows the monitoring of the catalyst and the adsorption complexes under reaction conditions by means of IR spectroscopy. The reactor effluent was analyzed by means of gas chromatography. The experiments were carried out in a continuous flow mode between 373 and 673 K. The selectivity to *p*-xylene changed in this temperature interval from 30% (at 473 K) to 55% (at 673 K). In contrast to these observations, the products adsorbed in the HZSM-5 pores were mainly *m*- and *o*-xylene as well as trimethylbenzenes. The results suggest that a subtle balance between the intrinsic rate of alkylation, the rate of isomerization, and the rate of diffusion of the products determines the selectivity observed. © 1991 Academic Press, Inc.

INTRODUCTION

The selectivity in alkylation of toluene with methanol over medium-pore zeolites has been proposed to be controlled either by the transport limitations in the molecular sieve channels (*1–6*) or by restrictions on the transition state (*4, 7, 8*). The kinetic analysis of the data of Kaeding *et al.* (*4, 5*) suggested that the transition state to form the bulkier *m*- and *o*-xylene molecules is more difficult to achieve than that during the *p*-xylene formation. Suppression of subsequent isomerization of the primary product by deactivation of acidic sites and hindered transport of the more bulky isomers (*o*- and *m*-xylene) increase the observed selectivity, when the catalyst is modified.

An excellent mathematical treatment of this problem has been published by Wei (*3*), which supports the proposal that the selectivity is mainly dependent upon the concentrations of acid sites and the diameter of the zeolite channels that imposes diffusional constraints upon more bulky isomers. Two scenarios can be derived from these models: (i) if only the diffusion of the products determines the selectivity of the alkylation, we would expect to observe xylenes adsorbed in the zeolite in concentrations according to the thermodynamic equilibrium irrespective of the observed gas phase selectivity; (ii) if only the formation of the products (transition state selectivity) controls the selectivity, the concentrations of the adsorbed products should be in the appropriate proportions to the concentrations observed by analyzing the effluent gas stream.

In order to differentiate between these proposals, we report here first results of an experiment analyzing the concentration of molecules within the zeolite pores by means of IR spectroscopy during the methylation of toluene. The catalytic activities and selectivities are determined by gas chromatography.

EXPERIMENTAL

Material

Zeolite HZSM-5 with a Si/Al ratio of 35.5 (corresponding to 2.6 Al atoms per unit cell) was used for all experiments investigated. The sample was provided from Mobil Corp. in the ammonium-exchanged form and was

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converted to HZSM-5 by heating the zeolite in He flow (about 20 ml/min) with a rate of 10 K/min up to 773 K.

FTIR Spectroscopy

For the IR measurements the zeolite was pressed into self-supporting wafers and placed with the sample holder in the center of the IR cell furnace. The sample was analyzed *in situ* during all treatments by means of transmission absorption IR spectroscopy using a Bruker IFS 88 FTIR spectrometer (resolution 4 cm^{-1}).

The IR cell was a continuously stirred tank reactor with a volume of 1.5 cm^3, equipped with $\frac{1}{16}$ -in. gas in- and outlet tubing and CaF_2 windows. The effluent gas stream was sampled in 16 sample loops of a multiport valve and subsequently analyzed by means of gas chromatography (HP 5890 II). The experiments were carried out in continuous flow mode in a temperature interval from 373 to 673 K. For all experiments reported, the partial pressures of helium, toluene, and methanol were 0.943, 0.043, and 0.014 bar, respectively.

In order to characterize the surface species in the zeolite pores during the methylation of toluene, IR spectra of the catalyst were recorded (with a time resolution of 120 s) as the activated HZSM-5 was contacted with He containing toluene and methanol for 60 min at constant temperature. After 60 min time on stream, the feed was switched to pure He for 30 min at the same temperature. Thus, all molecules with a mean residence time smaller than 30 min (i.e., those that are more likely to contribute to the products) should desorb from the zeolite pores.

Thermogravimetry and Determination of the Molar Extinction Coefficients

The surface concentrations of each reactant and product at HZSM-5 and SiO_2 were determined gravimetrically using a Cahn RG microbalance. Additional adsorption experiments for each substance were performed under the same experimental conditions (at 308 K, 10^{-2} to 1 mbar and at 373 K, 1 mbar) in the IR cell. The uptakes were correlated with the normalized intensities (integrated areas) of one or more characteristic IR bands of these substances (see Table 1). A clearly defined relationship of the intensity of the IR band from the amount adsorbed per unit cell was found for all species. The determined molar extinction coefficients (see Table 1) were used for a semiquantitative analysis of the IR spectra recorded during the reaction. Since the bands of the CH stretching vibrations are very similar for all the aromatic compounds of interest, the characteristic bands of the ring vibrations were used for identification of the products. The intensities of the bands of the gas phase spectra were found to be significantly lower than the intensities of the adsorbed species. The contribution of the gas phase to the IR spectra was thus not considered.

RESULTS

The concentrations of the aromatic reactants and products in the effluent gas stream and in the zeolite pores after 1 h time on stream are compiled in Tables 2 and 3. The difference between the IR spectrum of the zeolite in contact with the reactants for 60 min at 373 K and the IR spectrum of the activated zeolite is shown in Fig. 1(A). In this mode of presentation, bands that increased in intensity upon adsorption of the reactants point upward and bands that decreased point downward.

After the reactants were introduced into the IR cell, the bands of hydroxyl stretching vibrations of HZSM-5 at 3745 cm^{-1} (attributed to SiOH groups (*9*)) and at 3610 cm^{-1} (attributed to SiOHAl groups (*10, 11*)) decreased in intensity compared to the activated sample. New bands appeared at approximately 3600 and 3560 cm^{-1}. These were previously assigned to silanol groups interacting with toluene (3600 cm^{-1}) and to OH groups of methoxonium ions (i.e., methanol molecules protonated at the strong Brønsted acid sites (*12, 16*)) interacting with

TABLE 1

Absorption Maxima of the Characteristic IR Bands of the Aromatic Compounds that Were Used for the Semiquantitative Analysis and the Estimation of the Extinction Coefficients (T = 373 K, $P_{\text{adsorptive}}$ = 1 mbar, Adsorbent = Aerosil 300)

Substance	IR Band	$I_{\text{norm}}{}^{a}/m_{\text{ads}}{}^{b}$
Toluene	1496 cm^{-1}	440
p-Xylene	1520 cm^{-1}	489
m-Xylene	1610 cm^{-1}	400
o-Xylene	1496 + 1466 cm^{-1}	721
1,2,3-Trimethylbenzene	1474 + 1447 cm^{-1}	792
1,2,4-Trimethylbenzene	1506 cm^{-1}	638
1,3,5-Trimethylbenzene	1606 cm^{-1}	363

[a] The intensities of the IR bands were normalized for the sample thickness by comparing intensities with the intensities of the lattice vibrations of the zeolite.

[b] The gravimetrically determined amount of adsorbed substance [mol/g catalyst].

the aromatic ring of toluene (3460 cm^{-1}). The schematic representation of this coadsorption complex can be seen in Fig. 2. A detailed description of the complex is given in Ref. (*13*). Bands of CH stretching vibrations were observed at 3086, 3060, 3030, 2925, 2877 (attributed to toluene (*14, 15*)), 2958, and 2856 cm^{-1} (attributed to methanol (*12, 16, 17*)). The broad absorption band between 1700 and 1500 cm^{-1} was assigned to the OH deformation vibration of the $CH_3OH_2^+$ ion (*12, 16*). Ring vibrations of toluene were observed at 1604 and 1495 cm^{-1} (*14, 15*). Reaction products were neither detected in the gas phase nor adsorbed in the zeolite pores.

After the catalyst was purged with pure He for 30 min, the bands at 3600 cm^{-1} (attributed to SiOH in interaction with toluene) and all IR bands caused by vibrations of adsorbed toluene decreased in intensity, while the OH band of the silanol groups of the zeolite increased (see Fig. 1B and 1C). This indicates that toluene desorbed from SiOH groups. In contrast, the bands assigned to the adsorption complex at the strong Brønsted acid sites (methoxonium ions in interaction with the aromatic ring of toluene, see Fig. 2) were unaffected by this procedure.

The difference spectrum recorded after 60 min time on stream at 473 K shows the

TABLE 2

Concentration [mol%] of the Aromatic Reactants and Products in the Effluent Gas Stream[a] after 60 Min Time on Stream

Substance	373 K	473 K	573 K	673 K
Toluene	100	99.67	93.7	90.6
p-Xylene	0	0.08	3.3	4.5
m-Xylene	0	0.05	1.3	2.4
o-Xylene	0	0.09	1.0	1.3
1,2,3-Trimethylbenzene	0	0	0	0
1,2,4-Trimethylbenzene	0	0	0.7	1.2
1,3,5-Trimethylbenzene	0	0	0	0

[a] Only the concentrations higher than 0.05 mol% are tabulated.

TABLE 3

Estimation of the Concentration [mol%] (±20 Rel.%) of the Aromatic Reactants and Products in the Adsorbed Phase[a] after 1 h Time on Stream

Substance	373 K	473 K	573 K	673 K
Toluene	100	12	5	—
p-Xylene	—	8	—	—
m-Xylene	—	55	50	45
o-Xylene	—	25	20	17
1,2,3-Trimethylbenzene	—	—	10	15
1,2,4-Trimethylbenzene	—	—	5	8
1,3,5-Trimethylbenzene	—	—	10	15
			Coke	Coke

[a] (—) indicates concentrations of a reactant or product lower than 5 mol%.

wavenumbers and the intensities of the CH-stretching vibration bands to be comparable to the spectrum obtained (under otherwise identical experimental conditions) at 373 K. Only the intensity of the band at 2925 cm^{-1} (compared to the other CH stretching vibration bands of toluene) was higher. From the negative bands in the difference spectra at 3610 and 3745 cm^{-1} it was concluded that all Brønsted acid sites, but only a small fraction of the silanol groups, were in interaction with adsorbed molecules (see Fig. 3A). New IR absorption bands appeared in the spectrum in the spectral region of the ring vibrations that changed in intensity and shape with time on stream without reaching a steady state (see Fig. 3B). In the first spectrum (recorded after 1 min time on stream) the bands observed were attributed to the ring vibrations of toluene (1604 and 1495 cm^{-1}). With increasing time on stream new intense bands appeared and overlapped with the toluene bands resulting in two somewhat broad bands with maxima at 1620 and 1485 cm^{-1}. The band at 1485 cm^{-1} broadened further with time on stream, because it over-

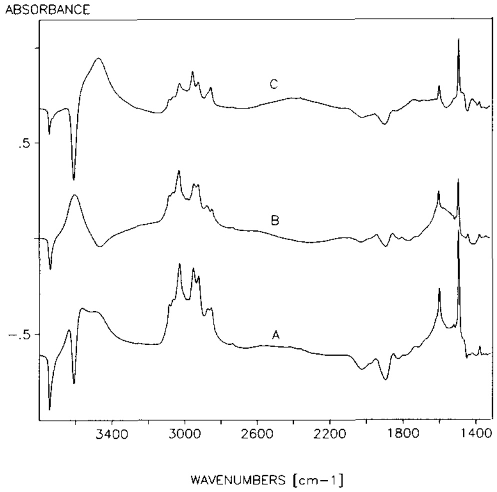

FIG. 1. (A) Difference between the IR spectrum of HZSM-5 in contact with the reactants at 373 K for 60 min and the activated HZSM-5. (C) Difference between the IR spectrum of HZSM-5 purged with He for 30 min at 373 K after (A) and the activated HZSM-5. (B) Difference spectrum between (A) and (C); corresponds to the desorbed species.

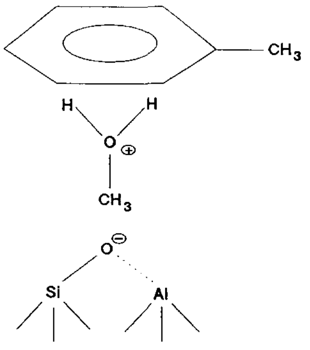

FIG. 2. Schematic representation of the coadsorption complex of toluene and methanol at the strong Brønsted acid sites.

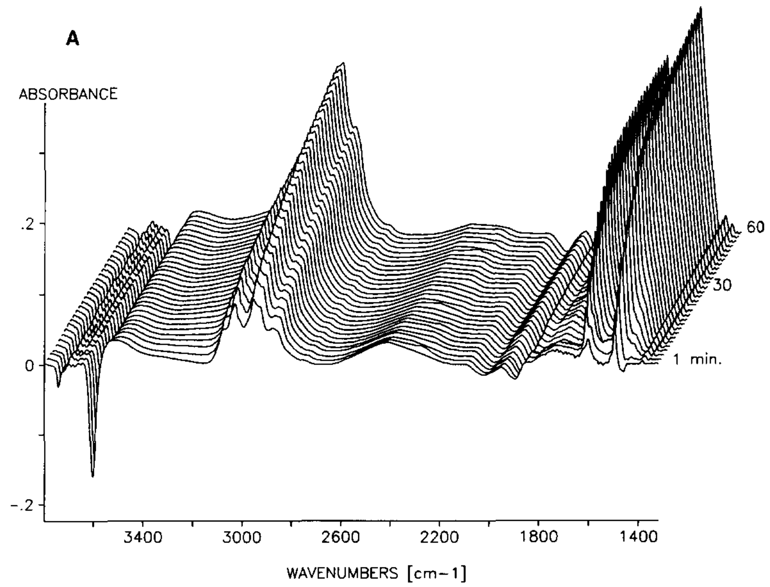

FIG. 3. (A) Changes of the difference IR spectra recorded during the reaction at 473 K as a function of the time on stream. (B) Changes of the bands of the ring vibrations of reactants and products adsorbed on HZSM-5 at 473 K as a function of the time on stream.

lapped with new bands (maxima at 1466 and 1496 cm^{-1}) arising in the spectra. After 30 min an additional shoulder was observed at 1520 cm^{-1}, which increased slightly with time. The new IR bands were attributed to reaction products, mainly *m*-xylene (1620 and 1485 cm^{-1}) and *o*-xylene (1466 and 1496 cm^{-1}), and the shoulder at 1520 cm^{-1} was attributed to a ring vibration of *p*-xylene.

Analysis of the gas phase indicated that steady state was not reached after 1 h time on stream and that the rate of formation of xylene isomers continuously decreased in this period.

Subsequent to purging the catalyst with pure He for 30 min, the bands attributed to toluene, methanol, and *p*-xylene decreased in intensity, while those of the bulkier xylenes hardly changed. Thus we conclude that *m*- and *o*-xylenes, which were formed by alkylation of toluene, were adsorbed at the strong Brønsted acid sites and could not desorb or desorbed very slowly from the pores at 473 K.

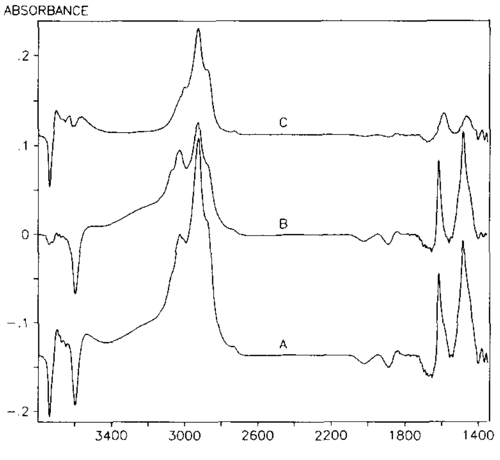

FIG. 4. (A) Difference between the IR spectrum of HZSM-5 in contact with the reactants at 573 K for 60 min and the activated HZSM-5. (C) Difference between the IR spectrum of HZSM-5 purged with He for 30 min at 573 K after (A) and the activated HZSM-5. (B) Difference spectrum between (A) and (C); corresponds to the desorbed species.

At 573 K, the difference IR spectrum (see Fig. 4 A) recorded after 60 min time on stream, showed well-resolved bands at 3030 cm^{-1} (with a shoulder at 3060 cm^{-1}), 2925 cm^{-1} (very intense, with a shoulder at 2877 cm^{-1}), and overlapping bands with absorption maxima at 1620 and 1485 cm^{-1}. The negative bands at 3745 and 3610 cm^{-1} indicate that the adsorbed molecules interact with both the silanol groups and the strong Brønsted acid sites. Most bands reached constant intensity after 5 min time on stream. Only the band at 2925 cm^{-1} increased further in intensity without reaching a steady state within 60 min. It should be noted that this band is characteristic of CH_2 groups (*18*) indicating oligomerization and/or formation of higher linear hydrocarbons from methanol. Because this band showed the highest absorption in the difference IR spectrum of the catalyst after purging with He for 30 min, it was attributed to hydrocarbons that were strongly adsorbed at the silanol groups and did not contribute to the alkylation reaction (see Fig. 4C). The other species, which were adsorbed at the Brønsted acid sites, were identified by a qualitative and semiquantitative analysis of the overlapping bands of the ring vibrations. It was found that approximately 50% *m*-xylene (1485 and 1620 cm^{-1}) and 25% *o*-xylene (1496 and 1466 cm^{-1}) were adsorbed in the pores; additionally 1,2,3-trimethylbenzene (1474 and 1447 cm^{-1}) and 1,3,5-trimethylbenzene (1606 cm^{-1}) were detected in concentrations of about 10% and 1,2,4-trimethylbenzene (1506 cm^{-1}) in lower concentrations. Bands characteristic for *p*-xylene (1520 cm^{-1}) were below the detection limit. In contrast, the analysis of the gas phase showed that at 573 K the products were *p*-xylene (52%), *m*-xylene (21%), *o*-xylene (16%), and 1,2,4-trimethylbenzene (11%) at a conversion of toluene of 6–7%. In contrast to the measurements at 473 K, the concentrations of the products in the gas phase and therefore the observed *p*-selectivity did not change with increasing time on stream at 573 K.

After switching to pure He, the bands of the ring vibrations (with maxima at 1620 and 1485 cm^{-1}) and all bands caused by CH stretching vibrations decreased in intensity (see Fig. 4B and 4C), while the intensity of the OH groups of the acid sites (3610 cm^{-1}) increased. After this treatment the most intense bands were found at 2925 cm^{-1}, 1585 and 1460 cm^{-1} and were attributed to hydrocarbons adsorbed at SiOH groups (3745 cm^{-1}). We propose that this species is a linear form of coke or a linear coke precursor (*18*). As we have no evidence on the specific concentrations of adsorbed coke or coke precursors, these species are not included in the concentrations of Table 2.

At 673 K, only low concentrations of reaction products in the catalyst pores were observed. Note that only 20% of all Brønsted acid sites were interacting with reactant or product molecules under this experimental conditions, while about 60% of the silanol groups were in interaction with adsorbed species. In contrast to the situation at 573 K the relative intensities of the bands of the ring vibrations were low compared to the intensity of the bands of the CH stretching vibrations. The main product adsorbed was characterized by IR bands at 2925, 1585, and 1460 cm^{-1} and this was in interaction with the silanol groups. The main product persisted purging with He for 30 min indicating the high stability of this species. At approximately 10 mol% conversion of toluene at 673 K, 55% *p*-selectivity of the xylenes was observed.

In order to check whether the concentrations of the adsorbed xylenes are primarily governed by differences in the adsorption constants, equilibrium mixtures of the xylenes were adsorbed at several temperatures. The results indicate that all three xylene isomers have approximately the same adsorption constant. At low temperatures (373 K), however, the equilibration takes a very long time.

DISCUSSION

At low temperatures (373 K) methylation of toluene did not occur. The IR spectra of Fig. 1A together with our previous experiments (*13*) suggest that methanol is adsorbed as methoxonium ion and interacts with its OH_2^+ group with the aromatic ring of a toluene molecule. This coadsorption complex is characterized by the appearance of a new perturbed OH band at 3460 cm^{-1} (see Fig. 2). As previously suggested (*13*), this adsorption complex might be a feasible precursor to the rate-determining step of the reaction. The high stability against removal by purging at 373 K may indicate that the complex is rather stable in flowing He. It should be emphasized, however, that persistence in purging for some time cannot be directly related to the residence time under reaction conditions, but allows estimation of the strength of the surface adsorbate bonds.

As the reaction temperature increased to 473 K, the surface concentration of the coadsorption complex between the adsorbed reactants decreased (see Fig. 3A). The IR spectra indicate that adsorbed products (mainly *m*-xylene—see Table 2) are present at 473 K in the zeolite pores. It is interesting to note that the molecules are adsorbed on the bridging hydroxyl groups. We consider this to be the consequence of the significantly higher partial pressure (fugacity) in the pores compared to the outside of the zeolite crystals at low temperatures. Thus, these aromatic molecules must face quite significant transport limitations in the ZSM-5 pores, which is in accordance with the proposals in the literature (e.g., (*3, 21*)).

m-Xylene and, to a lesser extent, *o*-xylene are enriched in the zeolite pores because their initial rate of formation is much higher than their rate of transport out of the pore system at temperatures as low as 473 K. A significant time on stream is needed to increase the pressure in the pores, so that the rate of formation equals the rate of transport out of the zeolite pores. It should be emphasized that not only the rate of diffusion of *m*- and *o*-xylene increased with time, but also the intrinsic rate of methylation decreased during that period. Therefore, the apparent rate of methylation to *m*- and *o*-

xylene is influenced by the concentration gradient between the inside and the outside of the crystal and the (individual) diffusion constants (*21*).

p-Xylene was found in the adsorbed phase only after long reaction times at 473 K, when high concentrations of adsorbed *m*-xylene block the pores and hinder the formed *p*-xylene molecules from leaving the zeolite particle. Therefore we conclude that for small time on stream the rate of formation of *p*-xylene is only controlled by the surface reaction. Again it can be seen that the adsorbed xylene molecules block the catalytically active sites and, thus, the reaction rate to *p*-xylene also decreased drastically with increasing time on stream.

At 573 K, not all of the acid sites were interacting with reactant or product molecules. In the zeolite pores high concentrations of *m*- and *o*-xylene and low concentrations of trimethylbenzenes were found. With increasing reaction time high concentrations of coke were adsorbed on the silanol groups. The concentration of free SiOHAl groups and the reaction rate were not affected by the coke formation. Also the *p*-selectivity of the products did not change upon coke formation. Thus we tentatively conclude that the coke was not inside the zeolite pores. IR spectra suggest that the coke is of a linear nature.

In the gas phase, *p*-xylene was found to be the main product. Again this was explained by a diffusion constant of p-xylene significantly higher than that of the other isomers (*5*, *6*, *20*, *22*). Thus, we conclude that under these experimental conditions *p*-xylene did not face any transport constraints. It should be emphasized that under these conditions the xylene isomers are not in thermodynamic equilibrium in the gas phase or in the zeolite pores. This can be illustrated (see Table 2 and 3) by the concentration of *p*-xylene, which was approximately 50 mol% in the gas phase at 573 K; but the IR spectroscopic analysis indicated concentrations in the adsorbed phase below the detection limit. The adsorption of the mixture of xylene isomers in equilibrium composition indicates that the high concentrations of *m*- and *o*-xylene are not due to higher relative adsorption constants of these isomers.

Although the overall concentration of molecules in the pores is much lower at 673 K than at 573 K, the differences in product concentrations between the zeolite pores and the gas phase were similar to those at 573 K. Only the bulkier xylenes were found in detectable concentrations in the zeolite pores although *p*-xylene was the main product in the gas phase. Similarly, 1,2,4-trimethylbenzene (*19*), the trimethylbenzene isomer with the smallest kinetic diameter, was detected in high concentrations in the product gas stream while the bulkier isomers, 1,2,3- and 1,3,5-trimethylbenzene were detected only in the adsorbed phase. This clearly indicates that the diffusion of the products out of the zeolite pores strongly affects the observed product distribution in the gas phase.

CONCLUSIONS

At low temperatures, prior to the onset of the reaction, a coadsorption complex between a methoxonium ion and toluene was identified. This is in accordance with experiments carried out at a significantly lower partial pressure of the reactants in vacuum (*13*). As the reaction temperature increased, the concentration and stability of this complex decreased. Instead, products (mainly the more bulky xylene isomers) were found to be adsorbed in the zeolite pores. The existence of high concentrations of adsorbed molecules indicates high partial pressures of the more bulky products inside the zeolite pores at low reaction temperatures. The high partial pressures are the result of the large initial difference between the rate of surface reaction and the rates of transport. In steady state the net rate of formation at low temperatures is equal to the rate of transport out of the pores. This situation is not achieved at temperatures below 523 K under our experimental conditions. At present, we cannot assess the role of isomerization at temperatures below 573 K. Because the concentration of *p*-xylene in the pores is very low, the rate of isomerization must be lower than the rate of diffusion of *p*-xylene out of HZSM-5.

Thus, the results described in this paper cannot be explained by either one of the two extreme explanations discussed in the literature (*1*–*8*) that suggest that the high selectivity to *p*-xylene is either (i) caused by the differences in the diffusion constants of the formed products (which are in thermodynamic equilibrium) or (ii) by constraints in the transition state. If the selectivity were caused only by transport limitations and the rate of isomerization were larger than the rate of diffusion of the products, then thermodynamic equilibrium would exist between the products in the interior of the zeolite and we would be able to detect products in concentrations equivalent to the thermodynamic equilibrium.

If the transport limitations were absent, however, we would expect to see comparable relative concentrations in the pores and outside of the zeolite crystals at steady state. The results presented here fulfill neither one of the two extreme requirements. Thus, we conclude that the rate of formation of *p*-xylene is mainly determined by the direct rate of formation of the xylenes (i.e., the surface reaction) and at elevated temperatures by the subsequent isomerization of the other isomers. The rates of reaction to *m*- and *o*-xylene are strongly influenced by the rate of diffusion, which depends upon the diffusion constants and the concentration gradients in the zeolite pores. At steady state, the intrinsic rates of *m*- and *o*-xylene formation at the active sites must, of course, be equal to the sum of the rates of transport out of the pores, of isomerization, and of the secondary alkylation/dealkylation. These latter reactions play small roles at temperatures below 573 K.

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