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On the Role of Product Isomerization for Shape Selective Toluene Methylation over HZSM5

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The dependence of the reaction rates and selectivities in toluene methylation over zeolite HZSM5 upon the concentration and type of adsorbed surface species are reported. Rather low selectivity to *p*-xylene was found at 473 K, while high selectivity was observed at 573 K. Under reaction conditions which lead to low selectivity to *p*-xylene (e.g., at 473 K) the reaction can be described best as a network of parallel alkylation reactions. Under reaction conditions which lead to high selectivity to *p*-xylene the steady state concentration of the bulkier isomers in the adsorbed phase was so high that the secondary reaction, the isomerization of the formed xylenes, in the HZSM5 pores was faster than the rate of alkylation. Thus, we conclude that for shape selective methylation of toluene to *p*-xylene the rate of isomerization has to exceed the rate of alkylation. High concentrations of adsorbed molecules or coke precursors in the zeolite which certainly increase the spatial constraints of the reacting molecules do not suffice to achieve high *p*-selectivity. This indicates that transition state selectivity does not play a major role for the product selectivities in the methylation reactions studied.

INTRODUCTION

Shape selective synthesis of substituted aromatic molecules over medium pore zeolites are economically interesting reactions, which stimulated quite a number of investigations (e.g., 1–9). Despite this interest, the reasons for the high selectivity to *para*-substituted products over some molecular sieve catalysts were not unequivocally explained.

Usually, the proposed mechanisms were deduced from detailed kinetic measurements, which only allowed indirect conclusions (with respect to the proposed mechanism). This is well reflected in the quite controversial discussion documented in the literature (e.g., 1–10). Open questions in this respect remained the role of the acid strength of the catalytically active site (especially with transition metal ions present in the catalyst (10, 11)), the subtle role of the steric constraints in the pores of the molecular sieves and the role of diffusion and secondary isomerization in enhancing the selectivity to molecules with the highest diffusivity (i.e., *p*-xylene) (3).

For toluene methylation, the commonly accepted reaction scheme (1) suggests that an activated form of methanol (i.e., the methoxonium ion or the surface methoxy group) reacts with weakly adsorbed toluene. The two models to explain the high selectivity to *p*-xylene found with MFI type molecular sieve catalysts propose either restrictions for the transition state to form *m*- and *o*-xylene (1, 12, 13) and/or diffusional constraints of the bulkier isomers (4, 7, 14). In a previous contribution (15), we showed that both proposals are not ideally fulfilled. The product distribution in toluene methylation is neither controlled by the size of the transition state to the various xylenes, nor does one observe the xylene isomers in their equilibrium concentration in the catalyst pores (the product selectivity would then only be determined by their different rates of diffusion).

For xylene isomerization, previous measurements indicated that the monomolecular methyl shift mechanism prevails over HZSM5 catalysts (3, 4, 16, 17). For *m*-xylene isomerization, we were able to show unequivocally that the product composition is controlled by transition state selectivity (16). In contrast, the selectivities in the isomerization of *o*- and *p*-xylene are controlled by the secondary isomerization of the primary product, *m*-xylene, which reaches quite high concentrations in the zeolite pores due to the diffusional constraints in the channels of zeolite HZSM5 (16).

In the present paper we extend the experiments of toluene methylation (15) and xylene isomerization (16) over HZSM5 to a semiquantitative kinetic assessment of the role of xylene isomerization for the selectivity in toluene methylation. We will use time resolved IR spectroscopy quantitatively to derive *in situ* the surface coverage of the reacting species.

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EXPERIMENTAL

For all investigations, zeolite HZSM5 with a crystall diameter in the range of 1 μm was used. The zeolite powder (provided in the ammonium exchanged form), was converted to the protonic form by heating in He flow (20 ml/min) up to 773 K with a heating rate of 10 K/min.

For the IR measurements, the zeolite was pressed into self supporting wafers. These wafers were analyzed *in situ* during all treatments by means of transmission absorption IR spectroscopy using a BRUKER IFS 88 FTIR spectrometer (typical resolution 4 cm^{-1}). The IR cell was constructed as a continuously stirred tank reactor (volume 1.5 cm^3), equipped with 1/16-in. gas in- and outlet tubings and CaF_2 windows. The partial pressures of the reactants were 16-mbar xylene in the xylene isomerization experiments and 42-mbar toluene and 14-mbar methanol in the alkylation experiments.

In order to characterize the adsorbed species in the zeolite pores during the reaction, IR spectra of the catalyst were recorded after contacting the activated zeolite with a carrier gas stream containing the reactant (pressure transient response). The reactions were monitored for 1 hr. The time resolution was either 2 min for the whole time on stream or, for better monitoring the transient uptake, initially 30 sec, then 5 min. The surface concentrations of the adsorbed species were derived from the integrated areas of the ring vibration bands of the aromatic molecules (in combination with gravimetric measurements, for details see Ref. (15)). Simultaneously, samples of the effluent

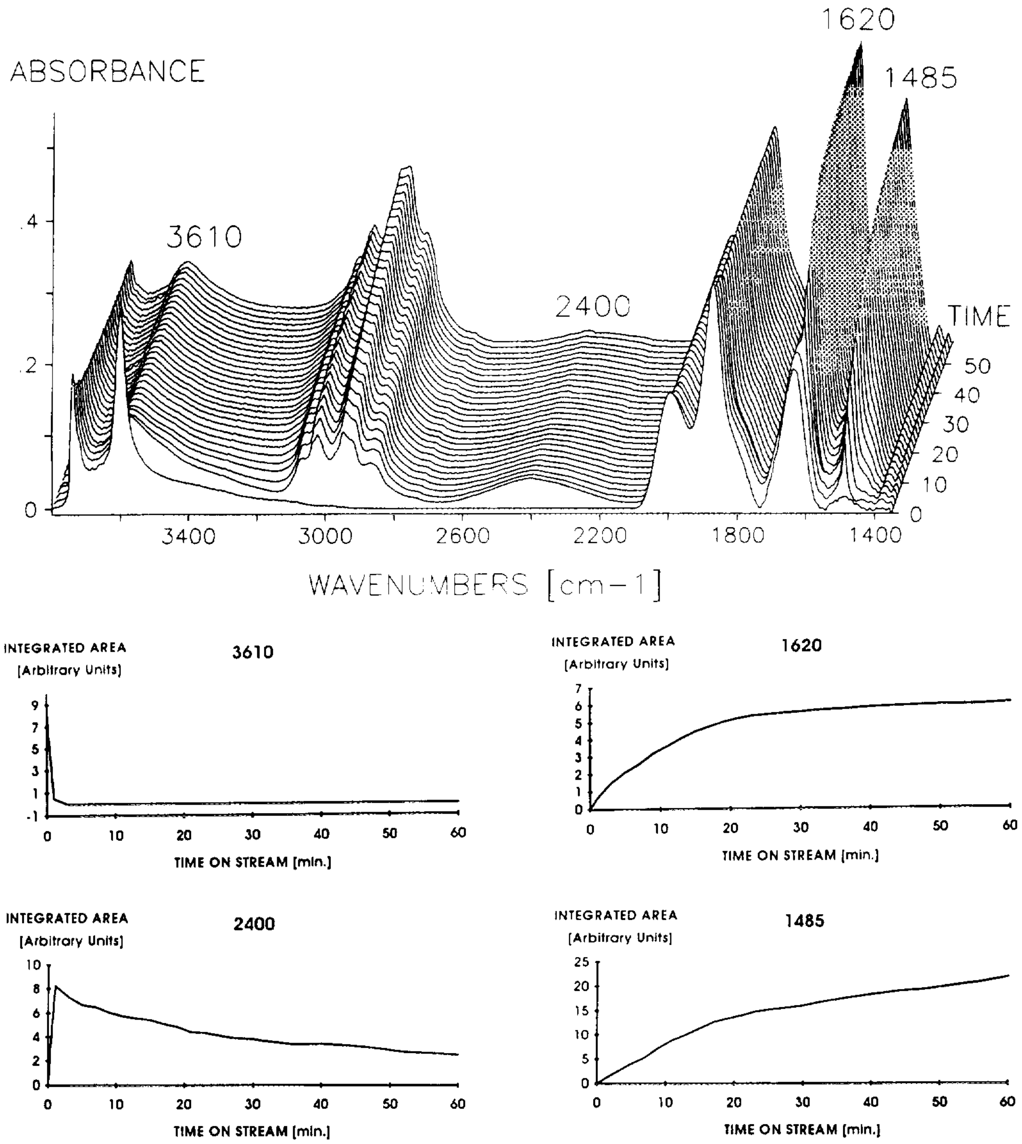

FIG. 1. (top) IR spectra recorded during the methylation of toluene at 473 K. (bottom) The integrated areas of the marked bands as a function of time on stream are given in separate plots.

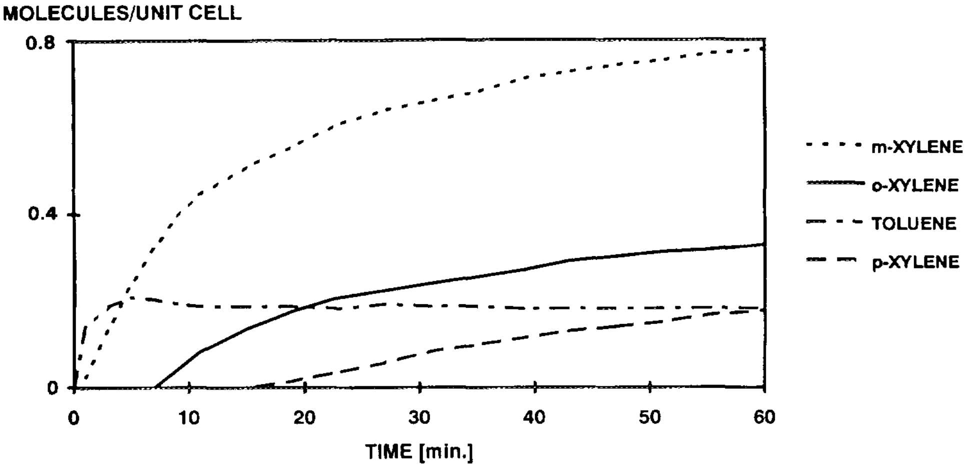

FIG. 2. Surface concentrations of the aromatic molecules during the toluene methylation at 473 K as a function of time on stream.

gas stream were collected into the 16 loops of a VALCO multiport valve and subsequently analyzed by means of gas chromatography (HP 5890 II, capillary column DBWAX, 30 m, FID, He as carrier gas). This experimental setup allowed the simultaneous analysis of the products inside the zeolite pores (IR spectroscopy) and in the gas phase (gc).

RESULTS

The product selectivities and surface species under steady state conditions for the methylation of toluene and a detailed study on the transport, adsorption, and reaction behavior of the xylenes over zeolite HZSM5 were reported previously (13, 14). Only the results necessary to understand the reaction network of alkylation and secondary xylene isomerization under conditions of low and high *p*-selectivity will be summarized in this contribution. The emphasis will be on the quantitative analysis of the transient behavior after contacting the activated catalyst with the reactants under reaction conditions, that favor high and low selectivity to *p*-xylene.

ALKYLATION

Methanol is adsorbed on the Brönsted acid sites (SiOHAl groups) of zeolite HZSM5 in the form of methoxonium ions or, at higher temperatures, as methoxy groups. Toluene and the other aromatic molecules interact with these sites or with the reactive surface species of methanol via hydrogen bonding (18).

The difference IR spectra recorded during the methylation of toluene (i.e., the IR spectra of HZSM5 in contact with the reactants minus the IR spectrum of the activated HZSM5) at 473 K as a function of time on stream are shown in Fig. 1. The surface concentrations of the aromatic molecules as estimated from the quantitative analysis of the IR spectra are compiled in Fig. 2 (following the procedures outlined previously (15)). The gas phase concentrations of the aromatic molecules at the reactor

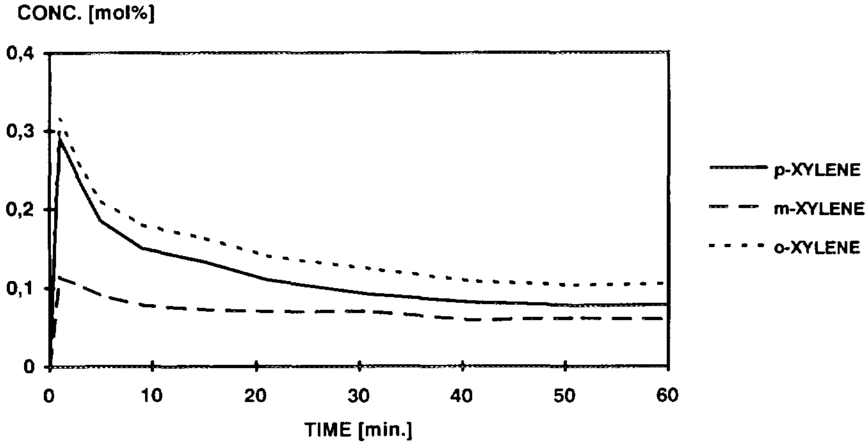

FIG. 3. Gas phase concentrations of the aromatic molecules during toluene methylation at 473 K as a function of time on stream.

outlet as a function of time on stream are given in Fig. 3. Immediately after contacting the zeolite with the reactants at 473 K, only toluene and methanol were found in the adsorbed phase. It should be noted that at this point all Brönsted acid sites were covered with reactant molecules. With time on stream, the accumulation of products, mainly *m*-xylene (characteristic bands at 1620 and 1485 cm^{-1}), in the pores was observed. IR bands characteristic for adsorbed *o*-xylene (1496 and 1466 cm^{-1}) and after approximately 20 min also for *p*-xylene (1520 cm^{-1}) were detected (see Fig. 2). Adsorption of the xylenes at the Brönsted acid sites lowered the concentration of methanol molecules bound to the acid sites (SiOHAl groups). It was found that the coverage of the methoxonium ions (characteristic band at 2400 cm^{-1}) decreased by more than 60% within 1 hr on stream. The concentration of toluene hardly changed during that period.

The main products in the effluent gas stream after short reaction times were *p*- and *o*-xylene, showing a ratio of *p*- : *m*- : *o*-xylene of 2.3 : 1 : 2.5 (see Fig. 3). The initial rate of toluene methylation was about 2×10^{-3} molecules · $[H^+]^{-1}$ · sec^{-1}. During 1 hr on stream, the rate decreased by approximately 60%. Note that the rate of *p*- and *o*-xylene formation decreased with a much higher rate than that of *m*-xylene, leading to a product distribution of *p*- : *m*- : *o*-xylene of 1.3 : 1 : 1.6 after 1 hr on stream. It should be pointed out that steady state was *not* reached at this point.

This indicates that for very short time on stream, the rate of formation of *o*- and *p*-xylene is controlled by the

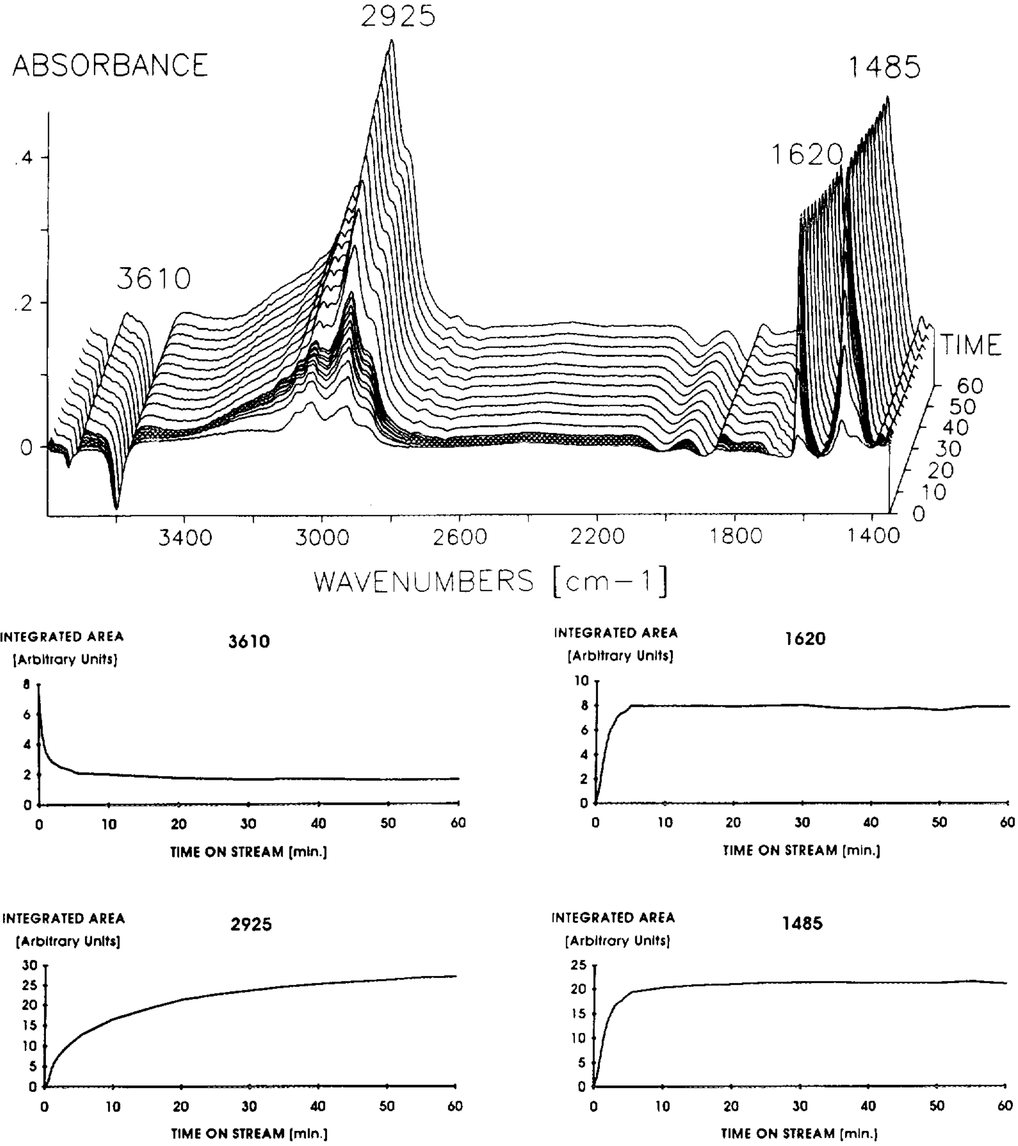

FIG. 4. (top) Difference IR spectra recorded during the methylation of toluene at 573 K. (bottom) The integrated areas of the marked bands as a function of time on stream are given in separate plots.

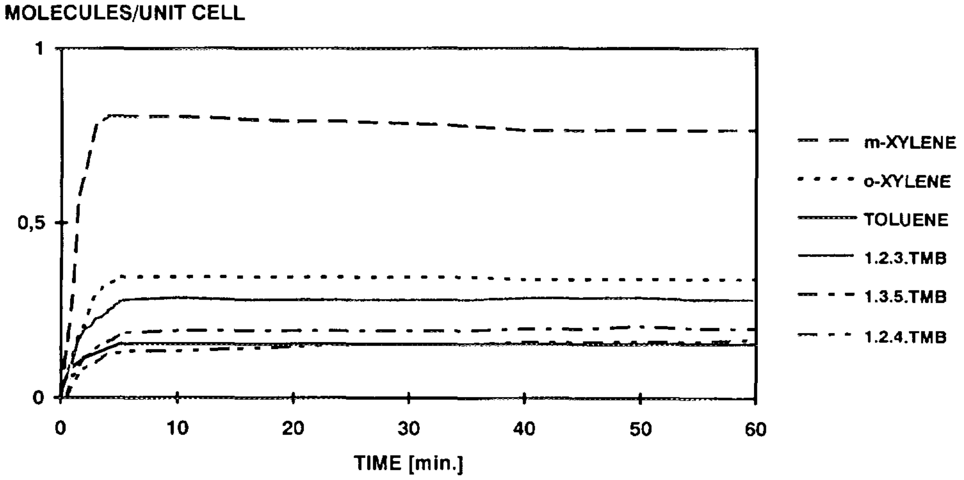

FIG. 5. Surface concentrations of the aromatic molecules during the toluene methylation at 573 K as a function of time on stream.

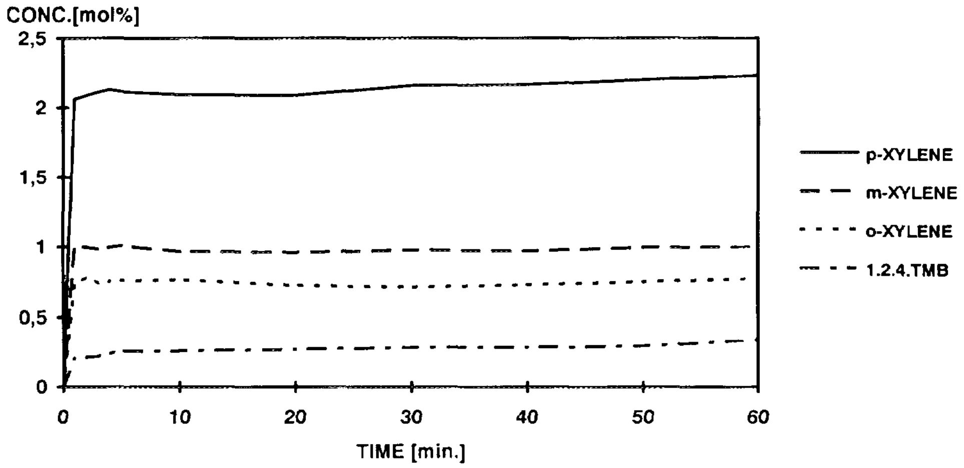

FIG. 6. Gas phase concentrations of the aromatic molecules during the toluene methylation at 573 K as a function of time on stream.

surface reaction (i.e., that initially the rate of diffusion of *p*- and *o*-xylene is higher than their rate of formation). In contrast, the lower initial concentration of *m*-xylene in the effluent gas stream and the continuous increase of the surface concentration of *m*-xylene are attributed to the higher rate of the alkylation in comparison to the rate of *m*-xylene diffusion. The overall rate of toluene methylation decreased as function of time on stream (see Fig. 3), because the increasing concentration of adsorbed product molecules (mainly *m*-xylene) blocked catalytically active Brönsted acid sites and impeded the methylation reaction.

The difference IR spectra recorded during the methylation of toluene at 573 K are plotted in Fig. 4. The surface concentrations of the aromatic reactants and products and the gas phase selectivities as a function of time on stream are given in Figs. 5 and 6, respectively. At 573 K, steady state with respect to the surface concentrations of formed xylenes was reached within a few minutes on stream. The main product adsorbed at the acid sites was *m*-xylene. Lower concentrations of *o*-xylene, 1,2,3- and 1,3,5-trimethylbenzene (and to a lower extent 1,2,4-trimethylbenzene) were also detected in the adsorbed phase. The concentration of *p*-xylene in the zeolite pores was below the detection limit (see Fig. 5). The presence of 1,2,4-trimethylbenzene in the adsorbed phase as well as in the gas phase indicates that the isomerization of the trimethylbenzenes was faster and the rate of dealkylation slower than the rate of diffusion of 1,2,4-trimethylbenzene. The overall reaction rate of the methylation of toluene, 1.10^{-2} molecules $\cdot$ $[H^+]^{-1}$ $\cdot$ sec^{-1}, was constant over one hour on stream. The analysis of the xylenes in the effluent gas stream revealed a *p*-selectivity higher than 50% which was also constant over the whole reaction time (see Fig. 6).

With increasing reaction time substantial concentrations of coke precursors were adsorbed on the terminal silanol groups. From the bands of the CH stretching vibrations (main band at 2925 cm^{-1}) we conclude that the surface species formed has rather the character of linear aliphatic hydrocarbon chains. These species did not affect the concentration of free SiOHAl groups, the reaction rate and the selectivity of *p*-xylene (see Figs. 4–6). Thus, we tentatively conclude that the coke precursor was *not* adsorbed inside the zeolite pores.

XYLENE ISOMERIZATION

The diffusion constants of *p*- : *m*- : *o*-xylene in zeolite HZSM5 (as determined from the adsorption kinetics) have a ratio of 1000 : 10 : 1 (1, 4, 16). For the isomerization, the reaction rates for all three xylene isomers were found to be equal at low reaction temperatures (473 K). As the adsorption constants were approximately equal for all three isomers and the rates of transport varied over 3 orders of magnitudes, this indicates that the surface reaction is the rate determining step. The rate of isomerization at steady state was 1.2×10^{-3} molecules · $[H^+]^{-1}$ sec^{-1}, corresponding to a rate constant of 2.4×10^{-3} molecules/site occupied · sec. Note that this value is the true rate constant k for the isomerization. The rates r_{iso} can thus be perfectly described in the form $r_{iso} = k_{iso} \cdot \Theta_{xyl} \cdot C_{site} \cdot m_{cat}$, where k_{iso} denotes the rate constant, Θ_{xyl} the coverage of the xylene isomer, C_{site} the concentration of the catalytically active sites, and m_{cat} the mass of the catalyst. At higher reaction temperatures (573 K), the rates of isomerization were different for the three xylene isomers. For *p*-xylene the highest TOF (8.8×10^{-3} molecules · $[H^+]^{-1}$ · sec^{-1}) was determined, for o-xylene it was about 6.7 and for *m*-xylene 5.4×10^{-3} molecules · $[H^+]^{-1}$ · sec^{-1}. The rate constants (k = TOF/coverage), however, were again equal for the three isomers (1.4×10^{-1} molecules · $[H^+]^{-1}$ · sec^{-1}). Thus, we conclude that the difference in the diffusion rates caused the different surface coverages, i.e., leading to different catalyst efficiencies for the three xylene isomers.

When *m*-xylene was used as reactant, the IR spectra suggest that this isomer is the main adsorbate. Bands which could be attributed to other isomers were *not* detected. This suggests that the diffusion of all products (*p*- and *o*-xylene) out of the zeolite is fast in comparison to their rate of formation. Thus, differences in diffusivities of the products cannot account for the selectivities observed. The increase in the reaction rate with time was found to be directly proportional to the increase in coverage as determined from the IR spectra. All acid sites which are capable of adsorbing *m*-xylene are therefore concluded to have the same catalytic activity. Furthermore, this shows that the reaction is of strict first order with respect to the surface concentration of the xylenes. For the isomerization of *m*-xylene, the product ratio *p*- to *o*-xylene was 2 for all reaction temperatures under investigation (473, 523, 573 K). We conclude, therefore, that the preferential formation of *p*-xylene is not due to a lower energy of activation, but rather due to differences in the transition entropies.

In *p*- and *o*-xylene isomerization, the analysis of the adsorbed phase showed that besides the reacting isomer, an accumulation of *m*-xylene in the pores occurred with increasing time on stream. This accumulation was accompanied by a decrease in the selectivity to *m*-xylene in the gas phase (see Fig. 7) which results from an increase in the rate of secondary isomerization of the primary product *m*-xylene to *p*- and *o*-xylene.

DISCUSSION

For both reactions, methylation of toluene and isomerization of the xylenes, all results suggest that the catalytic activity of all strong Brönsted acid sites (SiOHAl groups) is identical. These reactions are concluded to be of first order with respect to the surface concentration of methanol and xylenes.

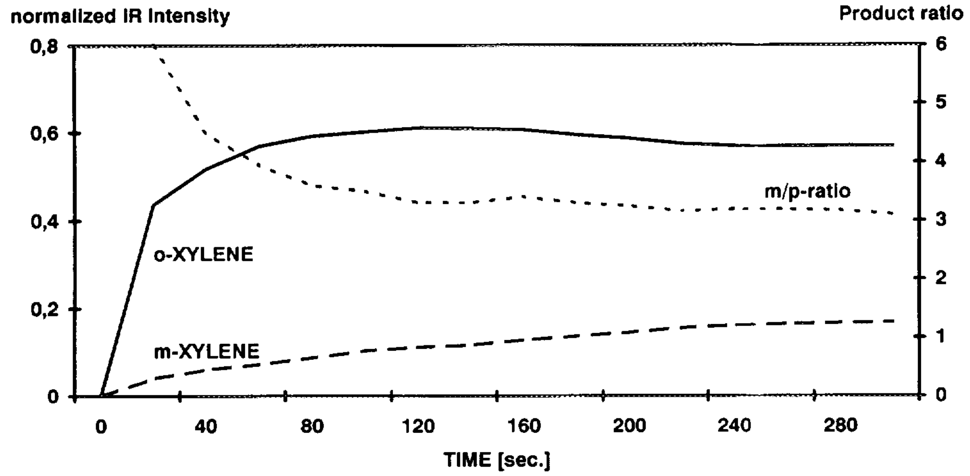

FIG. 7. *o*-Xylene isomerization at T = 473K. Surface concentrations of *o* and *m*-xylene and product ratio *m*/*p* in the gas phase as function of time on stream.

In the absence of reactant diffusion limitations the surface concentrations are determined by the adsorption constants, the reaction temperature and the reactant pressure. If the reaction becomes reactant diffusion limited, the slow transport into the zeolite pores leads to a decrease in the surface concentration of the reactant(s) at the catalytically active sites. This in return decreases the rate of reaction. Reactant diffusion limitation is found to be of high importance in the isomerization of *m*- and *o*-xylene. It should be strongly emphasized that the rate constants k = TOF/Θ (and the true energies of activation) were identical for all three xylene isomers at all temperatures investigated (see also Ref. (16), although the increase in rate with temperature was significantly lower for the isomerization of *m*- and of *o*-xylene than for the isomerization of *p*-xylene.

If the rate constant of the surface reaction is higher than the rate constant of the transport of the products out of the pores, a considerable amount of the intermediate or products builds up in the pores (product diffusion limitation). Such effects were found in the case of toluene methylation. The accumulation of formed *m*-xylene and other bulky products was observed in the zeolite pores (15). It should be noted, however, that at low temperatures (473 K) the coverage of the bulky reaction products increase with time on stream and caused a decrease in the rate of methylation. Knowing the surface concentration of the xylenes during the toluene methylation and the rate constants for the isomerization of the xylenes (from separate experiments), the intrinsic rates for the secondary reaction, xylene isomerization was calculated. Under conditions (473 K), when the rate of isomerization is lower than the rate of alkylation, *o*- and *m*-xylene as well as other substituted aromatic molecules accumulate in the pores until the rate of formation equals the rate of transport out of the pores. As these products reach quite high concentrations in the pores, they will adsorb markedly on the catalytically active sites. The low rate of isomerization of *m*- and *o*-xylene in comparison to the rate of methylation leads to a steady decrease in the concentration of the active sites for further alkylation steps due to product inhibition. Therefore, the rate of formation of new xylene molecules is decreased. Blocking of the catalytically active SiAlOH groups affects the products with a higher diffusivity (e.g., *p*-xylene) more than those with a lower diffusivity, *m*-xylene (see Figs. 2 and 3). Consequently, the selectivity to *m*-xylene increases with time on stream. Because the surface concentration of reaction products and coke precursors increased with time on stream, we concluded that the increase in concentration of these species in the zeolite pores (which certainly increased the diffusional constraints for all diffusing molecules) does not suffice to enhance the selectivity to *p*-xylene.

At 573 K, the coverage of the strong Brönsted acid sites was lower than at 473 K, and the accumulation of xylenes or trimethylbenzenes in the MFI pores did neither decrease the surface coverage of the reactants nor the overall rate of reaction. Also the selectivity remained constant with time on stream. From the coverage of the primary products and the rate constants for the xylene isomerization, the reaction rates for the secondary isomerization were obtained. It was found that the high concentration of *m*-xylene in the ZSM5 pores caused the rate of isomerization to exceed the rate of toluene methylation. Because *m*-xylene isomerizes to approximately 66 mol% *p*-xylene and 34 mol% *o*-xylene (16) over HZSM5, the higher selectivity to *p*-xylene is well explained with the contribution of the secondary isomerization. This holds true not only for *m*-xylene, but also for the other products which face diffusional constraints, i.e., *o*-xylene and the trimethylbenzenes. *o*-Xylene, for example, reacts to *m*-xylene (1, 2 methyl shift mechanism (4, 17)) which in turn undergoes reactions as described above. Note that 1,2,4-trimethylbenzene was the only isomer observed in the products, but was found to have the lowest concentration in the zeolite pores. Under the reaction conditions of the present study, the rate of interconversion of the xylene and trimethylbenzene isomers was higher than the overall rate of methylation at 573 K. Because we did not observe benzene or other dealkylation and transalkylation products in the adsorbed phase or in the gas phase, it was concluded that the rate of dealkylation is significantly slower.

CONCLUSIONS

The selectivity of toluene methylation over HZSM5 was shown to depend critically upon the choice of the reactions parameters. Rather low selectivity to *p*-xylene was found at 473 K, while high *p*-selectivity was observed at 573 K. Highly selective methylation of toluene to *p*-xylene only occurred under reaction conditions, under which the rate of isomerization exceeded the rate of alkylation. The high rate of isomerization is concluded to be primarily the consequence of the accumulation of the bulky products *m*- and *o*-xylene in the pores. Under these conditions any increase of the diffusional constraints would increase the concentration of *o*- and *m*-xylene in the pores and, therefore, enhance the *p*-selectivity. Note that this has been achieved by external coating of the surface (19, 20, 21) or by adding functional groups in the interior (2, 12, 22, 23).

If the rate of isomerization is lower than the rate of the alkylation (e.g., at 473 K under our reaction conditions), the overall reaction can be described best as a network of parallel alkylation reactions resulting in low *p*-selectivity. High concentrations of adsorbed molecules or coke precursors in the zeolite do not help to increase the selectivity to *p*-xylene under those reaction conditions. Thus, transition state selectivity is concluded *not* to be the mechanism by which the high selectivity to *p*-xylene in the toluene methylation over HZSM5 is caused. The results presented here indicate that the secondary isomerization of xylene is indispensable for the high selectivity to *p*-substituted products in toluene alkylation.

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