Communication

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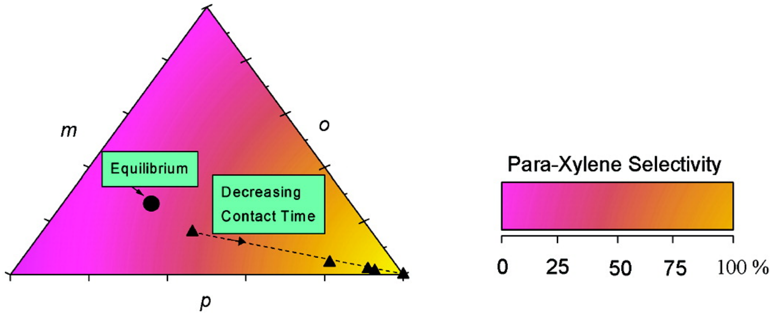

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Enhanced *para*-Xylene Selectivity in the Toluene Alkylation Reaction at Ultralow Contact Time

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We are able to achieve close to 100% *para*-xylene selectivity by operating the catalyzed gas-phase methylation of toluene at high space velocity. The near-perfect selectivity is the direct result of low contact time between the gas stream and the catalyst, which avoids re-isomerization of *para*-xylene once it has been formed within the internal structure of the zeolite catalyst.

para-Xylene is a key intermediate in the synthesis of terephthalic acid and terephthalates, which are used to make polyesters. Of the competing routes to xylene, toluene methylation could ultimately prevail, if the para selectivity of the process can be pushed well above 90% while the price of methanol declines as expected. Despite several phases of catalyst improvement over the last 30 years, however, the highest selectivities reported generally lie between 80 and 90%.[1] When methanol and toluene are passed through a heated bed of ZSM-5 microporous aluminosilicate zeolite, an equilibrium mixture of xylene isomers is formed. At temperatures between 350 and 650 °C, the mixture is approximately 23% *para*-xylene, 51% *meta*-xylene, and 26% *ortho*-xylene.[2] Non-equilibrium operation, for example by zeolite modification, typically leads to increased *para*-xylene yields. Techniques used routinely include (i) addition of an oxide, such as MgO, B_2O_3, or P_2O_5,[3] (ii) pre-coking by high-temperature anaerobic treatment with a carbonaceous material,[2] (iii) silanization,[4] and (iv) steaming.[5] Each treatment is thought to reduce the Brønsted acidity of the zeolite, so that isomerization is suppressed, causing an inversion in the isomerization/alkylation ratio (which is 10/1 in unmodified ZSM-5[6]). By constraining the channels and intersections inside the zeolite, the modifiers also suppress the formation of the ortho and meta isomers and enhance the relative rate of diffusion of *para*-xylene, though usually at the expense of toluene conversion.[2,3,7] Further modification of the zeolite can be achieved online, by operating the methylation reaction at relatively high temperature (>500 °C) and at low contact time.[8] These conditions promote coking,[9,10] which can result in additional improvement in para selectivity, but a consequence of this is loss of toluene conversion and poor methanol utilization in the formation of xylene.[2,10]

We have studied the alkylation of toluene using ZSM-5 ($SiO_2/Al_2O_3 = 80/1$), modified by the addition of 10% (by weight) of either Mg or B, which is present as the oxide in the final catalyst. In both cases, an aqueous precursor (magnesium nitrate; boric acid) was used to impregnate the zeolite, which was then dried (120 °C, 2 h) and calcined (500 °C, 2 h) to form the oxide on the external and internal surfaces.

The modified zeolites were tested under conditions designed to simulate the first stage of a known manufacturing route,[11] in which a large excess of toluene is used to limit methanol condensation to dimethyl ether, and steam is added to inhibit methanol dehydration to ethylene. Under these initial conditions, the yield of *para*-xylene did not greatly exceed the equilibrium level. However, we were able to increase the para selectivity, for a fixed toluene/methanol/steam ratio, by (a) proportionally increasing the feed rate of each component, (b) adding a gas-phase diluent such as hydrogen or nitrogen to the feed (see Figure 1), (c) reducing the catalyst charge while keeping the bed size constant (by adding cordierite as an inert solid diluent), or (d) coating a smaller charge of catalyst on a ceramic foam substrate. The common effect in each instance was to lower the contact time between the catalyst charge and the reactants, as calculated by dividing the active catalyst volume by the total feed rate (see example in Supporting Information). We were not able to increase the para selectivity of unmodified HZSM-5 much above the equilibrium level in the same way.

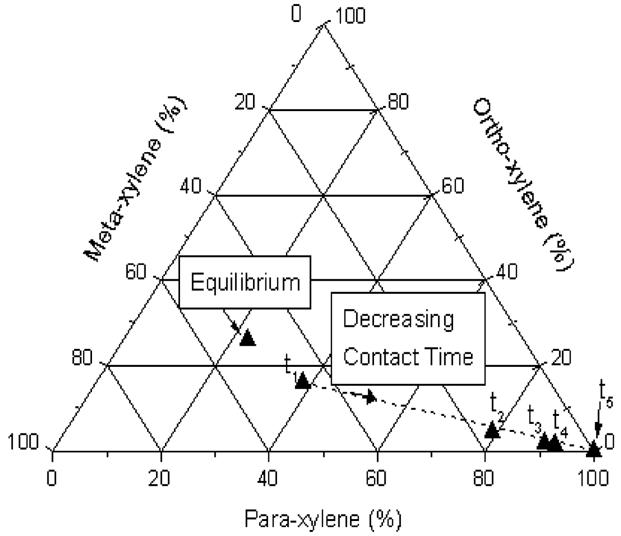

Figure 1. Ternary xylene isomer plot illustrating the beneficial effect on *para*-xylene selectivity by operating at ultralow contact time. MgO−ZSM-5 catalyst at 440 °C and molar feed = 44.4% $C_6H_5CH_3$, 5.6% CH_3OH, 50% H_2O, and variable H_2 to alter contact time. $t_1 = 2.54$ s, $t_2 = 1.1$ s, $t_3 = 0.86$ s, $t_4 = 0.63$ s, $t_5 = 0.17$ s. Toluene conversion was typically between 10 and 12%.

Although the long-term durability of B_2O_3−ZSM-5 was limited by a very slow loss of boron, it was possible to make direct comparisons between its performance and that of MgO−ZSM-5 even after one week of testing. For a toluene/methanol mole ratio of 8/1, the maximum possible toluene conversion by methylation alone is 12.5%, which was achieved by B_2O_3−ZSM-5 with 99.9% para selectivity at a contact time of 0.4 s. The contact time had to be decreased by half again before MgO−ZSM-5 matched this performance (Figure 1).

Our observation that para selectivity increases in a linear manner with decreasing contact time contradicts previously accepted opinion in this area, namely that the selectivity of ZSM-5 based catalysts is largely insensitive to contact time (a view reinforced by a neural

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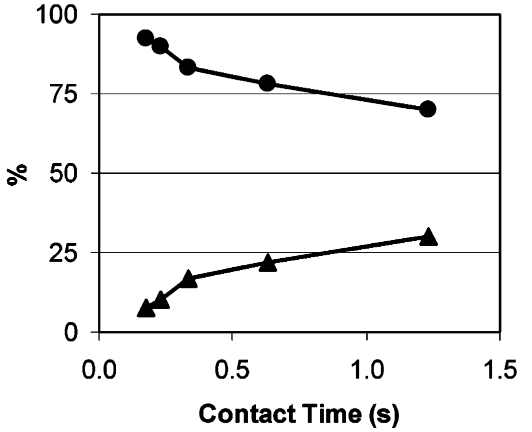
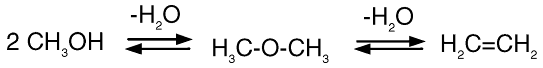


Figure 2. *para*-Xylene isomerization using a MgO−ZSM-5 (80) catalyst (● *para*-xylene and ▲ *ortho*- and *meta*-xylene). 440 °C and molar feed = 44.4% $C_6H_4(CH_3)_2$, 5.6% CH_3OH, 50% H_2O, and variable H_2 to alter contact time.

Scheme 1. Side Reactions of Methanol



$$2\ CH_3OH \overset{-H_2O}{\rightleftharpoons} H_3C\text{-}O\text{-}CH_3 \overset{-H_2O}{\rightleftharpoons} H_2C{=}CH_2$$

network analysis of a large number of publications[1]). However, interpretation of the results of previous studies is often complicated by the fact that toluene methylation can be accompanied by side reactions, such as the dehydration of methanol to form ethylene (Scheme 1), which in turn can lead to coke formation on the internal and external catalyst sites. The conditions we used (440 °C; high steam content in feed) lay outside those normally associated with either dehydration or coke formation. Significantly, in our experiments, there was no induction phase at each new contact time and no hysteresis between selectivity trends measured during different cycles. Because the changes in para selectivity cannot be attributed to online modification of our catalysts by coke or its precursors, the underlying effect must be associated with the contact time between the catalyst and the gas phase.

Wei[12] has proposed a mathematical model for toluene alkylation, which correlates para selectivity with the Thiele modulus (essentially the ratio of the alkylation rate to the isomerization rate). High values of the Thiele modulus can result from strong diffusional or kinetic control of the isomerization reaction and lead to high *para*-xylene selectivity. Traditionally, this has been achieved by chemical modification of the zeolite (by Mg, P[3], or coke[2]), which causes site blocking and narrowing of the channels.

Our proposed model for toluene methylation is consistent with Wei's by assuming the preferential diffusion of *para*-xylene through the channel structure of modified zeolites. However, as the product emerges it can come into contact with unconstrained (and in some cases unmodified) sites, where isomerization can occur. As the gas velocity through the bed is raised, and the contact time lowered, the incidence of readsorption and hence isomerization of *para*-xylene on the external sites is reduced; that is, the Thiele modulus is increased. To test this model, we examined the effect of contact time on the isomerization of *para*-xylene by our catalysts in the presence of methanol, steam, and hydrogen at our normal operating temperature. As Figure 2 confirms, the probability of isomerization decreases as contact time is lowered, and this trend becomes even more pronounced at very low contact times (below about 0.3 s in the case of MgO−ZSM-5).

Up until now, academic and patent literature in the field of toluene methylation has indicated a tradeoff between selectivity and activity. This has led to an emphasis on catalyst design and modification as potential routes to achieving complete conversion with 100% para selectivity. For example, reaction models predict that the ideal zeolite catalyst should have an internal/external site ratio of 10/1 or more.[13] Our results show that, through a combination of noncoking conditions and ultralow contact time, even nonoptimized catalysts can be made to perform exceptionally.

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Supporting Information Available: Example calculation of contact time in the toluene alkylation reaction and experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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