

Molecular Design, Function, and Commercial Application of Shape Selective Catalysts for the Petrochemical Industry

Jeffrey S. Beck

Corporate Strategic Research, ExxonMobil Research and Engineering,
1545 Route 22 East, Annandale, NJ 08801
Jeffrey.S.Beck@ExxonMobil.com

Introduction

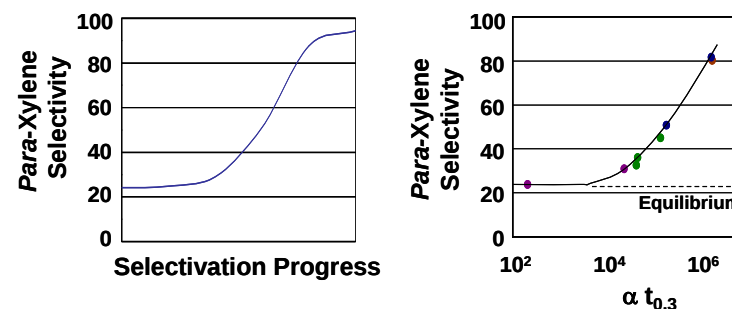
Over the past 35 years, shape selective molecular sieves have revolutionized the petrochemical industry, enabling the world scale production of high purity aromatics, olefins, and specialty petrochemicals from low cost feedstocks [1,2]. Control of both reaction mechanism/kinetics, and molecular diffusion, is critical for effectively catalyzing these selective transformations. In the work described here, we demonstrate the ability to predictably and precisely tailor both the active site and molecular transport within the sieve, making tunable “nano-reactors” for the shape-selective production of important polymer precursors such as *para*-xylene.

Results and Discussion

We have developed an arsenal of techniques for both *in-situ* and *ex-situ* treatment of zeolites, enabling differentiation of molecules with size differences of 0.2 Å, such as *para*- and *meta*-xylene. These treatments also allow us to tailor reactivity as desired - extremes include eliminating undesirable surface reactivity, and providing an open cage which nearly eliminates secondary reactivity.

The centerpiece of this work is the design of a permanently selectivated ZSM-5 catalyst for selective toluene disproportionation (STDP). The catalyst is prepared via a multi-step, *ex-situ* selectivation procedure. Characterization results, including measurement of diffusivity, acidity, catalytic performance in STDP, NMR, and microscopy techniques, help in monitoring the selectivation procedure; results for the fully selectivated catalyst include an increase in *para*-xylene selectivity to > 98% versus the bulkier *meta*- and *ortho*-xylene isomers (Figure 1a), and an increase in diffusional resistance of over 5,000 versus the untreated material example. These results allow us to construct a model based on a Pseudo-Thiele Modulus (Figure 1b) for the selectivation procedure, which correlates well with the observed *para*-xylene selectivity. These effects can be best understood via a simple model to help understand why these catalysts are so selective (Figure 2) [3].

The specificity with which the selectivation barrier is applied results in advantageous catalytic performance. Kinetic studies find that both the intrinsically high *para*-xylene selectivity in TDP, and the exhaustive titration of surface active sites, are responsible for the product slates observed. Post-synthetic activity modification allows for ultimate tailoring of the modified sieve for the applications of interest, including TDP (PxMax), xylene isomerization (XyMax), and *para*-diethylbenzene and *para*-ethyltoluene synthesis.



Figures 1a (left) and 1b (right). Increase in *para*-xylene selectivity as a function of Selection Progress (1a) and Pseudo-Thiele Modulus (1b).

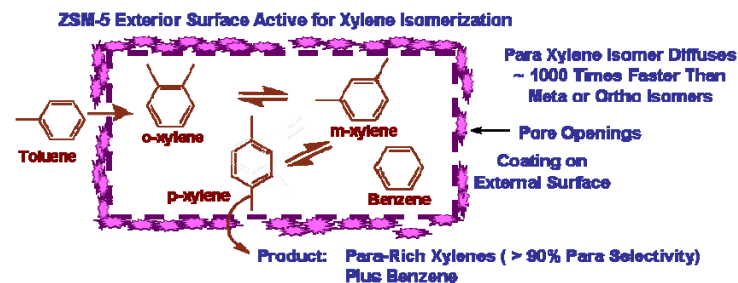


Figure 2. Model for enhanced *para*-xylene selectivity in selectivated catalyst.

Significance

Since the first use of PxMax at Mobil's Chalmette Refinery in 1996, there are over 20 commercial PxMax and XyMax units. This technology significantly lowers the cost of producing one of the world's most widely used polymers while generating less waste and less energy than previous methods, which, in turn, lowers CO₂ emissions. As the polyester market is expected to grow, the demand for use of 'selectivated' *para*-xylene technologies is expected to continue.

References

1. Stern, D. L., Brown, S. H., and Beck, J. S. in "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knozinger, F. Schuth, and J. Weitkamp, ed) Vol. 7, p. 3168. Wiley-VCH, Weinheim, 2008.
2. Clark, M. E., Smith, C. M., Stern, D. L., and Beck, J. S. in "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knozinger, F. Schuth, and J. Weitkamp, ed) Vol. 7, p. 3153. Wiley-VCH, Weinheim, 2008.
3. Olson, D. H. and Haag, ACS Symp Ser **248**, 275 (1984).