Chem. Mater. **1999,** *11,* 875−878

Permeation of Aromatic Isomer Vapors through Oriented MFI-Type Membranes Made by Secondary Growth

George Xomeritakis and Michael Tsapatsis*

Department of Chemical Engineering University of Massachusetts, Amherst, Massachusetts 01003-3110

Received December 18, 1998
Revised Manuscript Received February 4, 1999

Zeolite membranes that possess well-defined pores of molecular dimensions as well as good thermal, chemical, and mechanical stability have potential for new separation applications in the petrochemical industry. Recent laboratory-scale efforts aimed at the development of zeolite membranes more frequently involved MFI (silicalite-1 and ZSM-5) since this zeolite has a pore channel system (sinusoidal channels of circular cross section 5.4 Å interconnected with straight channels of elliptical cross section 5.1 Å × 5.7 Å) with dimensions near the sizes of many industrially important organic molecules.[1] Preparation of supported MFI-type membranes has been more commonly implemented by in situ crystallization where a porous support is brought in contact with a precursor solution or gel under hydrothermal conditions.[2] In this approach, appropriate conditions should be identified so that zeolite crystals nucleate and grow on the surface of the support in an interlocking fashion with minimal nonselective interzeolitic porosity. Indeed, several groups were able to demonstrate synthesis of high-quality MFI-type membranes on different types of porous supports with gas/vapor permeation properties characteristic of those expected for a zeolite membrane.[2−8]

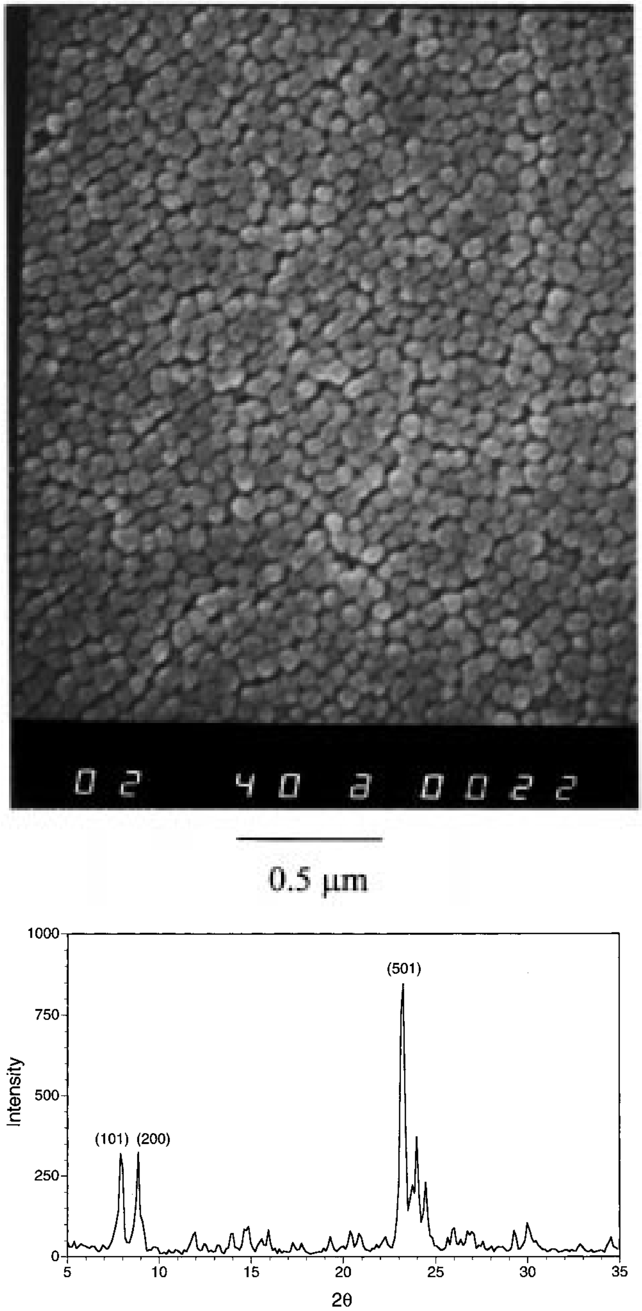

Figure 1. (a) SEM top view of silicalite-1 seeds coated on an α-Al_2O_3 support, (b) XRD pattern of silicalite-1 seeds.

Our group has proposed an alternative approach for synthesis of zeolite films and membranes which consists of applying layers of nanosized zeolite seed crystals on suitable supports followed by secondary growth of these crystals to a continuous film or membrane on the support surface.[9−13] The elimination of the nucleation step, due to the presence of seed crystals on the support surface, provides improved flexibility for crystal growth and control of film microstructure as well as enhanced reproducibility and scaleability.[12] This simple and general processing scheme has been applied for the synthesis of continuous films of various zeolite types such as LTL, MFI, and LTA. In the case of MFI, we have recently reported successful growth of self-supported or ceramic-supported membranes from seeds of particle size ~100 nm. These membranes exhibited single-component or mixture selectivities as high as 30 for H_2:N_2, 10 for CO_2:CH_4, 3 for O_2:N_2,[13] and 60 for n-C_4H_{10}:i-C_4H_{10}.[14]

A challenging but potentially rewarding application of MFI-type membranes is the continuous separation

---

* Corresponding author. E-mail: tsapatsi@ecs.umass.edu

[1] Funke, H. H.; Argo, A. M.; Falconer, J. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **1997**, *36*, 137.

[2] Yan, Y.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652.

[3] Geus, E. R.; van Bekkum, H.; Bakker, W. J. W.; Moulijn, J. A. *Microp. Mater.* **1993**, *1*, 131.

[4] Vroon, Z. A. E. P.; Keizer, K.; Gilde, M. J.; Verweij, H.; Burggraaf, A. J. *J. Membr. Sci.* **1996**, *113*, 293.

[5] Kusakabe, K.; Yoneshige, S.; Murata, A.; Morooka, S. *J. Membr. Sci.* **1996**, *116*, 39.

[6] Bakker, W. J. W.; Kapteijn, F.; Poppe J.; Moulijn, J. A. *J. Membr. Sci.* **1996**, *117*, 57.

[7] Coronas, J.; Falconer, J. L.; Noble, R. D *AIChE J.* **1997**, *43*, 1797.

[8] Vroon, Z. A. E. P.; Keizer, K.; Burggraaf, A. J.; Verweij, H. *J. Membr. Sci.* **1998**, *144*, 65.

[9] Lovallo, M.; Tsapatsis, M.; Okubo, T. *Chem. Mater.* **1996**, *8*, 1579.

[10] Boudreau, L. C.; Tsapatsis, M. *Chem.Mater.* **1997**, *8*, 1705.

[11] Lovallo, M. C.; Tsapatsis, M. *AIChE J.* **1996**, *42*, 3020.

[12] Gouzinis, A.; Tsapatsis, M. *Chem. Mater.* **1998**, *10*, 2497.

[13] Lovallo, M. C.; Gouzinis, A.; Tsapatsis, M. *AIChE J.* **1998**, *44*, 1903.

10.1021/cm9811343 CCC: $18.00

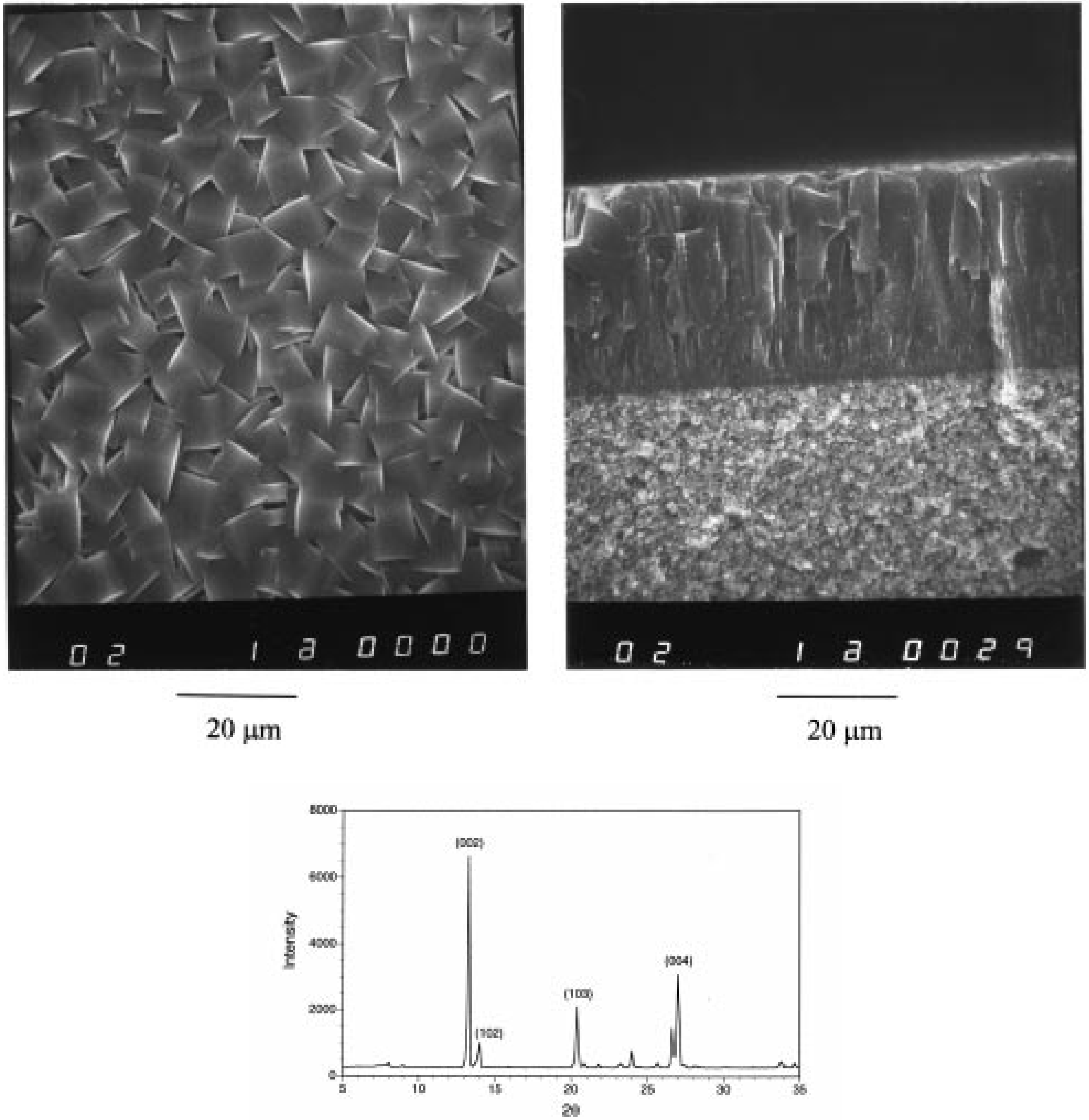

Figure 2. (a) SEM view of surface of MFI membrane made by two growths, (b) cross section of MFI membrane made by two growths, and (c) XRD pattern of MFI membrane surface.

of *p*-xylene (kinetic diameter 5.8 Å) from mixtures of its other two bulkier isomers, *m*-xylene and *o*-xylene (kinetic diameter 6.8 Å).[15] Successful membrane separation of xylene isomers has not been extensively documented so far. An earlier report showed that single-component *p*-xylene permeated 20 times faster than *o*-xylene at 100 °C through a tubular MFI-type membrane made by in situ growth technique.[16] However, no separation was possible from binary mixtures of the two isomers. It was found that both components permeated at a rate equivalent to that of the slower isomer, an effect described as single-file transport. Only recently, researchers at the University of Twente demonstrated separation of *p*-xylene from *o*-xylene with planar, randomly oriented MFI-type membranes made by in situ growth.[17] In view of the limited literature data on separation of xylene isomers by MFI-type membranes and the recent advances in reproducible synthesis of high-quality MFI-type membranes by secondary growth in our laboratory, a systematic investigation of xylene isomers permeation through our membranes is under

---

(14) Xomeritakis, G.; Gouzinis, A.; Nair, S.; Okubo, T.; He, M.; Overney, R.; Tsapatsis, M. *Che. Eng. Sci.* In press.

(15) Hudek, P.; Bobok, D.; Smieskova, A.; Zidek, Z. *Adsorpt. Sci. Technol.* **1996**, *13*, 495

(16) Baertsch, C. D.; Funke, H. H.; Falconer, J. L.; Noble, R. D *J. Phys. Chem.* **1996**, *100*, 7676.

(17) Keizer, K.; Burggraaf, A. J.; Vroon, Z. A. E. P.; Verweij, H. *J. Membr. Sci.* **1998**, *147*, 159.

Table 1. Single-Component Permeation of Xylene Isomers through MFI Membrane M1

temp (°C)	permeation flux (mol m^{-2} s^{-1})		flux ratio para:ortho
	p-xylene[a]	o-xylene[b]	
100	2.13×10^{-5}	6.04×10^{-7}	35.3
150	2.17×10^{-5}	5.93×10^{-6}	3.7
200	2.14×10^{-5}	1.31×10^{-5}	1.6

[a] Feed partial pressure = 0.6 kPa. [b] Feed partial pressure = 0.5 kPa.

Table 2. Single-Component Permeation of Xylene Isomers through Different MFI Membrane Samples at 100 °C

sample	permeation flux (mol m^{-2} s^{-1})		flux ratio para:ortho
	p-xylene[a]	o-xylene[b]	
support	5.86×10^{-5}	4.51×10^{-5}	1.3
M1	2.13×10^{-5}	6.04×10^{-7}	35.3
M2	1.62×10^{-5}	4.14×10^{-7}	39.1
M3	1.45×10^{-5}	4.27×10^{-7}	34.0
M4	1.02×10^{-5}	2.58×10^{-7}	39.5

[a] Feed partial pressure = 0.6 kPa. [b] Feed partial pressure = 0.5 kPa.

Table 3. Effect of Feed Composition on Permeation of Xylene Isomers through MFI Membrane M4 at 100 °C

feed partial pressure (kPa)		permeation flux (mol m^{-2} s^{-1})		flux ratio para:ortho
p-xylene	o-xylene	p-xylene	o-xylene	
0.60		1.02×10^{-5}		39.5[a]
–	0.50		2.58×10^{-7}	
0.30	0.25	6.02×10^{-6}	1.58×10^{-6}	3.8
0.15	0.125	3.53×10^{-6}	6.32×10^{-7}	5.6
0.06	0.05	1.75×10^{-6}	1.94×10^{-7}	9.0
0.03	0.025	1.03×10^{-6}	7.92×10^{-8}	13.0
0.015	0.0125	7.84×10^{-7}	4.35×10^{-8}	18.0

[a] Ratio of single-component fluxes.

way and preliminary results are reported in this paper.

Zeolite membrane preparation was carried out on homemade α-Al_2O_3 support disks of 2 mm thickness, 22 mm diameter, and 0.15 μm pore size. One surface of the supports was polished with SiC paper to form a smooth surface for applying the seed layers by dip-coating in an aqueous suspension of silicalite-1 seed nanocrystals prepared as described elsewhere.[11] Figure 1 shows the SEM top view (a) and XRD pattern (b) of the silicalite-1 seeds coated on the support surface. The MFI membranes were prepared on the seed-coated support surface by two successive 24-h growths at 175 °C using a clear solution of composition 1:1:4.5:1000 KOH:TPABr:SiO_2:H_2O with TEOS as silica source. The SEM top view and cross section and XRD pattern of a representative MFI membrane prepared by two successive growths are shown in panels a, b, and c of Figure 2, respectively. We have previously established by SEM and XRD that MFI films made by secondary growth on glass slides consist of coffin-shaped MFI crystals oriented with their c-axis nearly parallel to the surface normal.[12,13] The SEM and XRD results presented here suggest that the MFI membranes made on porous α-Al_2O_3 supports have similar orientation and thickness in the range 25−40 μm. The Al content in the zeolite layers was below the detection limit of EDS and microprobe analysis, indicating a Si:Al ratio >800 for these membranes.

For permeation experiments, the membrane disks were calcined for 5 h at 525 °C to remove the tetrapropylammonium template occluded in the zeolite pores during synthesis and subsequently sealed with the aid of Viton O-rings inside a custom-made stainless steel permeation cell fixed inside a box furnace. Single-component or binary feeds of xylene isomers were generated by passing helium through saturators maintained at room temperature and introduced continuously over the disk side with the zeolite layer. The feed was optionally diluted by a third helium stream. The permeate side of the disk was flushed with helium, and its composition was analyzed with the aid of a HP 5890 Series II gas chromatograph over a period of several hours until steady-state conditions were reached. The permeation flux of each xylene isomer was estimated by its molar fraction and the volumetric flow of the helium stream of the permeate side (5−20 cm^3/min) and the membrane surface area available for permeation (1.4 cm^2).

In a first series of experiments, single-component xylene permeation was studied for temperatures in the range 100−200 °C. Table 1 shows the p-xylene and o-xylene permeation flux data for membrane sample M1. The data indicate that the p-xylene permeation flux remains practically constant in the temperature range studied, whereas the o-xylene permeation flux increases by more than 20 times from 100 to 200 °C. In this way, the single-component flux ratio dropped from about 35 at 100 °C to 1.6 at 200 °C. These results indicate that with the membranes reported here potential separation of xylene isomer vapors cannot be realized at elevated temperatures.

The reproducibility of membrane permeation behavior was examined by single-component permeation measurements at 100 °C for different membrane samples, and the results are given in Table 2. For comparison, the permeation flux data of a plain support are also shown in the table. For all the samples studied, the permeation flux of p-xylene varies in the range 1.0−2.0 × 10^{-5} mol m^{-2} s^{-1} while the para:ortho single-component ratio varies in the range 34−40, suggesting consistent xylene permeation properties between membrane samples prepared under similar conditions. These flux values of each isomer could be reproduced within 5% by alternating the feed between p-xylene and o-xylene for several times. For membrane sample M4, the permeation flux of m-xylene and the para:meta single-component ratio were 3.0 × 10^{-7} mol m^{-2} s^{-1} and 33.8, respectively, indicating that both m-xylene and o-xylene permeate much slower than p-xylene in these MFI membranes. Under similar experimental conditions, no permeation of p-xylene could be detected after 48 h through an uncalcined membrane prepared by one growth (the detection limit of the permeation setup is 10^{-8} mol m^{-2} s^{-1}). This result indicates that (a) the MFI membranes are essentially defect-free, at least before calcination for template removal, and (b) leaking between the O-ring seals and the (microscopically rough) surface of the MFI membranes is negligible.

One of the most striking observations in this study is that in binary mixtures the permeation flux of o-xylene is a strong function of the partial pressure of p-xylene in the mixture. As shown in Table 3, o-xylene alone permeates much slower as compared to the case where *p*-xylene is also present at feed partial pressure ≥ 0.15 kPa (about 25% of the saturation pressure at 22 °C). For example, the permeation flux of *o*-xylene from a binary mixture with a feed partial pressure of each component 50% of its respective saturation pressure is 6 times higher than the flux of single-component *o*-xylene (feed partial pressure equal to saturation pressure), and the resulting binary para:ortho flux ratio is <4 as opposed to almost 40 for the single-component flux ratio. It is observed that the permeation flux of *o*-xylene is restored to its original value when the binary feed is replaced by a single-component *o*-xylene feed. Substantial separation of the two isomers (para:ortho flux ratio ≥ 9) was possible in the case of dilute feeds with *p*-xylene feed partial pressure ≤ 0.06 kPa. The permeation flux of *p*-xylene decreased monotonically with decreasing feed partial pressure and was insensitive to the presence of *o*-xylene in the mixture.

The mixture permeation behavior in the case of our membranes (slow-permeating isomer accelerated in the presence of the fast-permeating isomer) is entirely different from that observed by Baertsch et al.[16] (fast-permeating isomer retarded in the presence of the slow-permeating isomer) or Keizer et al.[17] (no effect of the presence of either isomer on the flux of the fast- or slow-permeating one). An entirely different single-component permeation behavior was also observed by Shah and Liou,[18] who found that all three xylene isomers permeate at equivalent rates through a *c*-oriented MFI single-crystal membrane. In contrast, single-component permeation measurements with the membranes reported here indicate that *p*-xylene permeates at a rate more than 1 order of magnitude higher than the other two isomers.

The results reported here indicate that the *c*-oriented, high silica MFI-type membranes have potential for separating *p*-xylene from a mixture with its ortho and meta isomers. The presence of *p*-xylene in the membrane at high loading leads to changes in the membrane, resulting in enhancement of the permeation rate of *o*-xylene. Transient permeation and structural studies are currently under way in our laboratory in order to elucidate the effect of adsorbed *p*-xylene in the microstructure of the MFI membranes made by secondary growth. This behavior may be due to the flexibility of MFI, which is known to undergo structural transitions in the presence of organic molecules with a close fit to its framework.[19,20] Indeed, Karsli et al.[21] observed that the sorption rate of *o*-xylene in a fresh sample of silicalite-1 was extremely slow but increased drastically after the same sample underwent a *p*-xylene adsorption/desorption cycle. The results of these workers suggest that sorption of *p*-xylene induces (irreversible) structural modifications so that *o*-xylene can also penetrate the silicalite-1 lattice. Despite the apparent agreement between our results and those of Karsli et al. (although in our case the transition appears to be reversible), results of other workers indicate that MFI crystals can selectively adsorb *p*-xylene at high loading from mixtures with its ortho and meta isomers,[22,23] whereas a marked difference of single-component diffusion or uptake rates of *p*-xylene over its other two isomers is widely documented in the literature.[24−27]

Acknowledgment. Financial support for this work was provided by Amoco Corporation, NSF [CTS-9624613 (CAREER) and CTS-9512485 (ARI)] and NETI. M.T. is grateful to the David and Lucile Packard Foundation for a Fellowship in Science and Engineering. Finally, we acknowledge the W.M. Keck Polymer Morphology Laboratory for use of its electron microscopy facilities.

CM9811343

---

(18) Shah, D. B.; Liou, H. Y. *Zeolites* **1994**, *14*, 541.

(19) Mueller, J. A.; Conner, W. C. *J. Phys. Chem.* **1993**, *97*, 1451.

(20) van Koningsveld, H.; Tuinstra, F.; van Bekkum, H.; Jansen, J. C. *Acta Crystallgr.* **1989**, *B45*, 423.

(21) Karsli, H.; Culfaz, A.; Yucel, H. *Zeolites* **1992**, *12*, 728.

(22) Yan, T. Y. *Ind. Eng. Chem. Res.* **1989**, *28*, 572.

(23) Namba, S.; Kanai, Y.; Shoji, H.; Yashima, T. *Zeolites* **1984**, *4*, 77.

(24) Garcia, S. F.; Weisz, P. B. *J. Catal.* **1990**, *121*, 294.

(25) Ruthven, D. M.; Eic, M.; Richard, E. *Zeolites* **1991**, *11*, 647.

(26) Mirth, G.; Cejka, J.; Lercher, J. A. *J. Catal.* **1993**, *139*, 24.

(27) Choudhary, V. R.; Nayak, V. S.; Choudhary, T. V. *Ind. Eng. Chem. Res.* **1997**, *36*, 1812.