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Reply to Comments on "Molecular Traffic Control in Zeolite ZSM-5"

The Letter by Lowe, Whan, and Spencer (*1*) raises a number of interesting questions on the molecular traffic control (MTC) effect which we believe can operate in materials containing two types of intersecting channels (*2*). These comments are well appreciated and prompt the following remarks.

It is indeed correct that the conversion of methanol to water and gasoline-type hydrocarbons is accompanied by an increase in the total number of molecules (inclusive of water), the water molecules being able to diffuse in the zeolite channels which show the highest shape-selective constraints, i.e., the sinusoidal channels with nearly circular pore opening. It is hence correct to state that, in principle, "complete absence of counterdiffusion in the smaller channels of ZSM-5 . . . is improbable" when considering the methanol conversion. If, however, one considers the occurrence of the latter reaction over a macroscopic ZSM-5 catalytic bed, i.e., when we believe that MTC will be best appreciated, one should not overlook the fact that methanol will be quickly dehydrated to dimethyl ether in the inlet region of the catalytic bed and that the water produced will not be largely readsorbed in zeolite crystallites further inside the bed due to the hydrophobicity of the ZSM-5 zeolite (*3*). The same should also hold for the subsequent conversion of dimethyl ether to light-molecular-weight olefins which are primary reaction products (*4*, *5*). These are oligomerized and aromatized in the inner and outlet regions of the catalytic bed where, in agreement with Lowe *et al.*, we feel that MTC will indeed take place.

Although our chosen example (*2*) was the methanol-to-hydrocarbons conversion reaction, it should be clear from such statements as "the conversion reaction . . . decrease(s) the total number of molecules" or from the overall use of "reactant molecules" (and not methanol) that we were not referring exclusively to the methanol-to-hydrocarbons conversion but that we were actually considering also the oligomerization of the primary olefins stemming from the early steps of the methanol conversion, as can be seen from another publication describing an integrated scheme for the methanol-to-hydrocarbons conversion in which we specifically refer to "light reactants" (*6*). Our initial statement may have been ambiguous and so we do acknowledge the comments which were made.

We believe, at present, that the MTC shape-selective effect could be of rather wide occurrence: it may occur indeed when diffusional pathways will be differentiated or impeded in a molecular sieve (zeolite) structure because of pore size dimensions imposed by the framework itself or altered by various chemical treatments such as ion exchange, partial coking, or the use of "chemical" modifiers (incorporation of P, Sb, etc.), provided that (some of) the reactant molecules and (some of) the product molecules have different steric requirements with respect to the particular shape-selective catalyst being used. It should happen whenever reactants reach the catalytic sites through diffusion pathways that are less readily accessible to the reaction products which are desorbing (although still possibly suffering side reactions), and vice versa.

Although no definite proof exists at

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present for the MTC effect, the latter is a novel concept which may help in the understanding of various observations such as the remarkable activity of ZSM-5-based catalysts in the alkylation of benzene by ethylene (*7*), the higher methanol to *p*-xylene alkylation activity of ZSM-11 when compared to ZSM-5 zeolite (although local site kinetics constraints may also operate) (*8*), the improved toluene alkylation activity (by methanol, to *p*-xylene mainly) of Na-exchanged ZSM-5-type catalysts (*9*), and the selective and efficient reaction of 1,4-disubstituted aromatic compounds on ZSM-5 zeolite-based catalysts (*10*).

It is indeed correct that "reverse molecular traffic control" should also be observed. For example, the excellent dewaxing activity of ZSM-5-based catalysts (*11*) could partly result from this property. Another limiting case could relate to the isomerization of xylenes in which *p*-xylene diffuses away preferentially from the catalytic sites (*12*).

Finally, it may not have been clear from our original note (*2*) that the effective length of the linear elliptical channels (per unit cell) was evaluated with taking into account the additional space available at the channel intersections (*13*) as, however, mentioned elsewhere (*6*). Such an "effective length" will be somewhat sensitive to the probe molecule which is used and to intermolecular interactions regulating the ordering of the molecules in the pores, as well as to the actual free volume at the channel intersections which should depend on chemical modifications of the zeolite as mentioned earlier. Accounting for this additional space is principally equivalent to recognizing that molecules can somewhat enter the sinusoidal channels even if they have a definite preference for the linear channels and that they can possibly relocate from one linear channel to the next one through such openings (in the particular case of zeolite ZSM-5). As with other molecular shape-selective effects (*12*), molecular traffic control would be expected to act in combination or in addition to others.

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