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# LETTERS TO THE EDITORS

## An Investigation of the Postulate of "Molecular Traffic Control" in Zeolite ZSM-5

In a recent note, Derouane and Gabelica (*1*) have suggested that a novel type of shape selectivity may operate in reactions catalysed by the zeolite ZSM-5.

The ZSM-5 framework contains two types of intersecting channels, both of which have ten-membered ring openings. One channel system runs parallel to the *a* axis of the orthorhombic unit cell; it is sinusoidal and has near-circular (0.54 to 0.56 nm) openings. The other channels are straight, parallel to the *b* axis, and have elliptical openings (0.52 to 0.58 nm (*2, 3*)).

On the basis of saturation adsorption capacity measurements, and calculations of the lengths of the channel systems, Derouane and Gabelica (*1*) have proposed that some adsorbates, such as 3-methylpentane, toluene, and *p*-xylene, are confined to the straight channels, whereas others, such as *n*-pentane and *n*-hexane can use all the available pore space. They then go on to suggest that this may lead to a shape selectivity factor in zeolite catalysis over ZSM-5 which they call "molecular traffic control." This refers to a situation in which it is envisaged that reactants preferentially enter the catalyst through one channel system, react at sites near the channel intersections, and products diffuse out via the other channels. It is proposed that this allows reactants to be supplied to and products cleared from the catalytic sites quickly, and without mutual interference.

Although the theory is primarily concerned with examining the dynamic situation within a working ZSM-5 catalyst, it has consequences which should be apparent in other situations. Indeed, the equilibrium saturation adsorption capacity data which were used to support the theory make this clear.

If the detailed proposals of Derouane and Gabelica are correct, it appears that a sample of ZSM-5 which is already saturated with an adsorbate which can only use the straight channels (such as toluene, or 3-methylpentane) should still rapidly adsorb a second adsorbate like *n*-pentane, which can utilise all the channel space, whereas the zeolite saturated with *n*-pentane first, should take up little or no further adsorbate if toluene were subsequently introduced. It is these consequences of the theory which the present experiments were designed to test.

An analysed sample of ZSM-5 in the hydrogen form was kindly supplied by Dr. D. M. Bibby, Chemistry Division, D.S.I.R., Petone, New Zealand. It had a unit cell composition of $Na_{0.1}H_{4.4}Al_{4.5}Si_{91.5}O_{192} \cdot xH_2O$. X-Ray examination showed only peaks characteristic of ZSM-5.

Adsorption was measured gravimetrically at 298 K with a CI Electronics Microforce, type 3B, electrobalance. The adsorption capacities found with the single adsorbates *n*-pentane, toluene, and 3-methylpentane are compared to those already reported in the literature in Table 1. The adsorption measured in this work is very similar to that reported in Ref. (*4*), but rather less than that in Refs. (*1, 5*). However, the relative amounts of *n*-pentane and 3-methylpentane adsorbed in this work and in Ref. (*1*) are similar. The rates of adsorption followed kinetic curves like those shown in Fig. 3 of the paper by Anderson *et al.* (*4*).

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TABLE 1

Adsorption of Hydrocarbons by ZSM-5

| Hydrocarbon | Adsorption (mmol $g^{-1}$) | Ref. |
|---|---|---|
| *n*-Pentane | 1.46 | This work |
| | 1.69 | (*1*) |
| | 1.72 | (*5*) |
| 3-Methylpentane | 1.00 | This work |
| | 1.17 | (*1*) |
| | 0.98 | (*4*) |
| Toluene | 1.03 | This work |
| | 1.07 | (*4*) |

*Note.* Adsorption at $p/p^0 = 0.5$ and 298 K.

When adsorption experiments were performed on the zeolite which had already been presaturated with a different adsorbate, no significant difference in behaviour was found, irrespective of whether the presorbed material was supposed to utilise all the pore space or not. In each case, the additional uptake observed was close to what might be expected if both adsorbates had access to the complete channel system. 3-Methylpentane and toluene behaved in the same way, so that no special behaviour can be attributed to the aromatic molecule in these experiments.

The results for the extent of adsorption after no further change was observed are shown in Table 2, in which the prediction from molecular traffic control (MTC) theory is also listed.

In all the experiments, the observed weight changes due to adsorption had become very slow after 20 min contact time.

TABLE 2

Adsorption in the Presaturation Experiments

| Presaturation | | Second adsorption | | Predicted percentage second adsorption | |
|---|---|---|---|---|---|
| Hydrocarbon | Percentage[a] | Hydrocarbon | Percentage,[b] no presaturation value | MTC theory[c] | Simple volume filling[d] |
| *n*-Pentane | 82.4 (86.5) | Toluene | 21.1 (20.1) | 17.6 | 17.6 |
| *n*-Pentane | 87.3 (91.7) | 3-Methylpentane | 10.5 (7.8) | 12.7 | 12.7 |
| Toluene | 88.7 (84.3) | *n*-Pentane | 10.9 (10.4) | 39.1 | 11.3 |
| 3-Methylpentane | 94.8 (80.5) | *n*-Pentane | 7.7 (7.8) | 34.9 | 5.2 |
| *n*-Pentane | 80.4[e] (137)[e] | Toluene | 13.9[e] (28.9)[e] | | 18.6 |
| Toluene | 100.0[e] (210)[e] | *n*-Pentane | 8.6[e] (13.8)[e] | | 0 |

[a] Expressed as percentage of $p/p^0 = 0.5$ value. Figures in parentheses are specific uptakes/mg $g^{-1}$.

[b] Expressed as percentage adsorption which would have occurred if no presaturation had been used. Figures in parentheses are specific uptakes/mg $g^{-1}$.

[c] Worked out on the basis that the straight channels constitute 67% of the adsorption space.

[d] Treating all pore volume as equally accessible to either adsorbate.

[e] Results on NaY. All others on ZSM-5.

This, of course, is not to deny that further changes might occur, corresponding to the slow equilibration of the mixed adsorbate in the adsorption space, but it does strongly suggest that volume filling is essentially complete at this time. In the far more complete study of the uptake of mixed benzene and *n*-heptane vapours by NaX at 85°C by Kärger *et al.* (*6*), it was observed that composition and weight changes occurred for more than 6 h. However, the volume uptake, estimated from the amount, and not of molar volumes of the pure liquid adsorbates, changed very little after the first 20 min.

The second adsorbate always adsorbed rather more slowly than it would have done in the absence of presaturation, but there was no great difference, for example, in the decreased rate of toluene adsorption following *n*-pentane presaturation, and *n*-pentane adsorption following toluene presaturation. Some of these results are shown in Fig. 1. Experiments with a sample of NaY, in which no molecular traffic control effects would be expected, gave very similar results to those with ZSM-5.

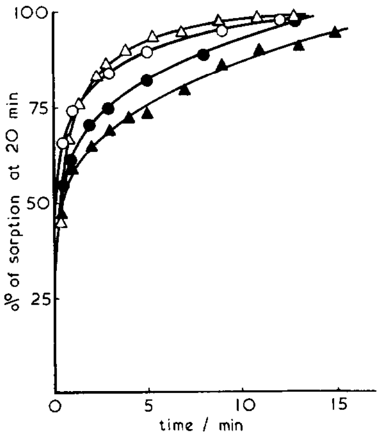

FIG. 1. Sorption as a function of time at 298 K. ○, Toluene on outgassed zeolite; ●, toluene on zeolite 82.4% presaturated with *n*-pentane; △, *n*-pentane on outgassed zeolite; ▲, *n*-pentane on zeolite 88.7% presaturated with toluene.

This work thus lends no support to the existence of a molecular traffic control effect. It may perhaps be suggested that the rather striking adsorption capacity results could reflect the difficulty in obtaining efficient molecular packing in the pore space. Even in the very large cavities of zeolite X, effects such as this occur. For example, the saturation adsorption capacities for cyclohexane and cyclopentane differ by about 25%, when expressed in terms of the volumes of the corresponding bulk liquids (*7*). The maximum variation observed on a single sample of ZSM-5 in this work, or in Refs. (*1*, *4*, *5*), is 54%, between *n*-pentane and toluene. This larger difference may reflect the greater restrictions imposed on packing in a pore space which is only a little bigger than the molecules to be accommodated. Such packing problems have already been discussed and documented, and earlier work has been summarised by Breck (*8*).

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