CHEMISTRY LETTERS, pp. 759-760, 1979. Published by the Chemical Society of Japan

SEPARATION OF 2-METHYLPENTANE AND 2,2-DIMETHYLBUTANE BY MEANS OF SHAPE-SELECTIVE ADSORPTION INTO MODIFIED H-MORDENITE

Seitaro NAMBA, Atsushi YOSHIMURA, and Tatsuaki YASHIMA
Department of Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

A competitive adsorption of 2-methylpentane and 2,2-dimethylbutane into various zeolites were carried out in a 1,3,5-trimethylbenzene solution at 273 K. Partially exchanged H-mordenite by Sr^{2+} or Ba^{2+} and a new type zeolite (H-ZSM-5) could adsorb only 2-methylpentane. We succeeded in the complete separation of 2-methylpentane and 2,2-dimethylbutane.

We are reporting that a complete separation of 2-methylpentane and 2,2-dimethylbutane by means of a selective adsorption into some modified H-mordenites.

It has been well-known that normal paraffins can be separated from the other paraffins by a selective adsorption into Ca-A zeolite1). On the other hand, nobody has succeeded in a separation of paraffins with a quaternary carbon from the other paraffins in a competitive adsorption into any types of zeolite.

It has been known that the effective pore dimension of H-mordenite (H-M) can be adjusted by a partially exchanged cation with a suitable ionic radius2-4). In the previous paper, we have reported that in the selective cracking of octanes (octane, 3-methylheptane, and 2,2,4-trimethylpentane) over partially exchanged H-M catalysts by various alkaline earth cations, the relative reactivity of 2,2,4-trimethylpentane, having a quaternary carbon, decreases with increasing the ionic radius of exchanged cation, while the relative reactivity of 3-methylheptane, having a tertiary carbon, whose molecular size is smaller than that of 2,2,4-trimethylpentane, scarcely decreases4). So, we expected that a paraffin with a quaternary carbon could be separated from a paraffin with a tertiary carbon and without a quaternary carbon by using such modified H-M.

2-Methylpentane (2-MP) and 2,2-dimethylbutane (2,2-DMB), whose molecular sizes are 0.56 and 0.70 nm, respectively5), were chosen as adsorbates and the competitive adsorption in a liquid phase was carried out at 273 K by using 1,3,5-trimethylbenzene, whose molecular size was 0.86 nm6), as a solvent. The concentration of each adsorbate was 2.0 wt%. The preparation and pretreatment of the adsorbent were described in Ref. 4. The amount of adsorption was determined by a gas chromatographic analysis of the liquid phase.

Fig. 1 shows the time course in the competitive adsorption of 2-MP and 2,2-DMB into H(96)-M (the number in parenthese indicates percentage degree of cation exchange). 2-MP, having a smaller molecular size than 2,2-DMB, was adsorbed more easily than 2,2-DMB. The equilibrium state was obtained over 35 hours of adsorption time at 273 K.

In Table 1, the amounts of 2-MP and 2,2-DMB adsorbed into various mordenites, H-Y zeolite, and H-ZSM-5 zeolite at equilibrium state are summerized. In the case of partially exchanged H-M by the alkaline earth cations, the larger ionic radius provided the higher selectivity, that is, Sr(18)-H-M or Ba(24)-H-M did not adsorb 2,2-DMB, while H-M or Ca(21)-H-M adsorbed a small amount of 2,2-DMB. In the case of Ba-H-M, the degree of cation exchange affected the selectivity at low degree of cation exchange. However, above 24 % of degree of cation exchange the complete selectivity was obtained.

The adsorption of neither 2-MP nor 2,2-DMB into H-Y zeolite could be observed, probably because H-Y, whose effective pore dimension was large enough for 1,3,5-trimethylbenzene to diffuse into, could adsorb the solvent rather than 2-MP or 2,2-DMB. The new type zeolite, H-ZSM-5, was also examined. It has a high selectivity, that is, it adsorbed 2-MP and did not adsorb 2,2-DMB. The amount of 2-MP adsorbed into H-ZSM-5 was a little more than those into the modified mordenites.

Thus, in the competitive adsorption of 2-MP and 2,2-DMB, Sr-H-M, Ba-H-M, and H-ZSM-5 can adsorb 2-MP, while they cannot adsorb 2,2-DMB, which have a quaternary carbon. Accordingly, we succeed in the complete separation of 2-MP and 2,2-DMB.

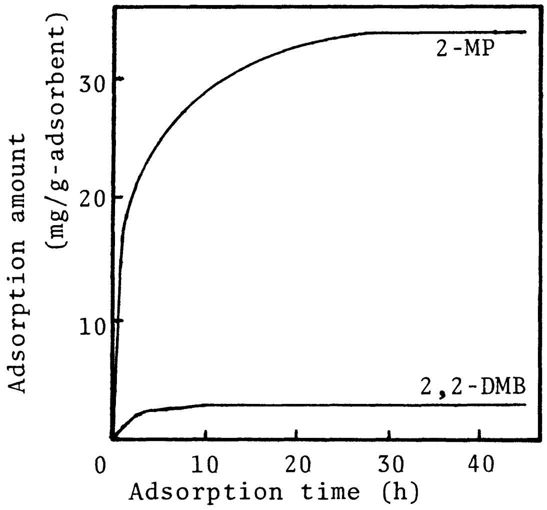

Fig. 1. Competitive Adsorption of 2-MP and 2,2-DMB into H-M

Table 1. Competitive Adsorption of 2-MP and 2,2-DMB into Various Zeolites

Adsorbent	Ionic radius (nm)	Adsorption amount (mg/g-adsorbent)	
		2-MP	2,2-DMB
H(96)-M	—	33.8	3.0
Ca(21)-H(75)-M	0.99	34.0	2.9
Sr(18)-H(78)-M	1.16	29.2	0
Ba(10)-H(86)-M	1.36	25.3	2.1
Ba(24)-H(72)-M	1.36	27.5	0
Ba(34)-H(62)-M	1.36	29.2	0
H(79)-Y	—	—	—
H(100)-ZSM-5	—	38.2	0

Reference

1) P.E.Everly,Jr., "Zeolite Chemistry and Catalysis," ACS Monograph 171, ed by J. A.Rabo, American Chemical Society, Washington D.C. (1976), Chap. 7.
2) T.Yashima, O.Iwase, and N.Hara, Chem. Lett., 1975, 1215.
3) S.Namba, O.Iwase, N.Takahashi, T.Yashima, and N.Hara, J.Catal., 56, 445 (1979).
4) S.Namba and T.Yashima, Chem, Lett., 1978, 1261.
5) D.W.Breck, "Zeolite Molecular Sieves," John Wiley & Sons Inc., New York (1974), p. 636.
6) S.M.Csicsery, J. Catal., 19, 394 (1970).

(Received May 9, 1979)