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The bifunctional conversion of cyclooctane. A suitable reaction to test shape-selective effects in high-silica zeolites.

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INTRODUCTION

It was reported earlier ¹ that the bifunctional conversion of n-paraffines into feed isomers or hydro-cracked products was distinctly different over wide pore zeolites of the faujasite-type compared to those of the Pentasil-type. It was also established ¹ that the rate of conversion of n-decane into its monomethyl branched feed isomers was determined by the pore structure in case of the Pentasil-zeolites. Branching at the paraffin-end was found to be favored in MFI-zeolites (ZSM-5) while in MEL-structures (ZSM-11) the pore intersections allowed also methyl-branching in the 3-position. This clearly indicates that the structure of the pores in medium or small pore zeolites can determine the product selectivity. Vice versa a well-chosen catalytic test reaction may give useful information on the dimensions and geometry of the zeolite pores.

It was therefore the aim of the present work to select a suitable probe molecule, the catalytic conversion of which will give useful information on the dimensions and geometry of zeolite pores in general and on the occurrence of transition state shape selectivity. More particularly, in the present work it is reported how cyclooctane is converted on Pt-loaded acid zeolites. Small amounts of

Pt are added in order to ensure constant activity in time and to avoid perturbation of the measurements by differences in rate of deactivation. Three zeolite structures (FAU, MFI and MEL) with identical chemical composition are compared.

EXPERIMENTAL

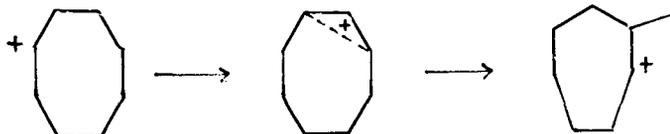
The acid forms of HZSM-5 and HZSM-11 had a Si/Al ratio of 60. Ultrastable Y-zeolite was treated with SiCl_4 and had the same chemical composition (FAU^{*}). These samples were impregnated with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ so as to obtain 1 % by weight loading with the metal.

The reaction with cyclooctane was carried out at atmospheric pressure in a continuous flow-reactor at a WHSV of 0.5 h^{-1} . Analysis of the reaction products was done on-line with high-resolution capillary gas-chromatography.

RESULTS AND DISCUSSION

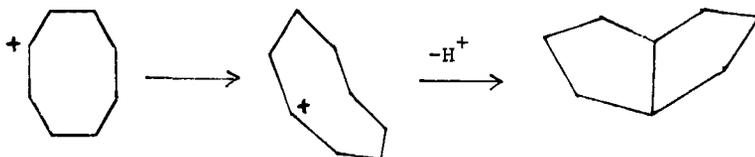
The activity sequence MEL > MFI > FAU^{*} for cyclooctane conversion (Fig. 1) is different from the one obtained for n-decane on the same samples : MFI > MEL > FAU^{*}. Comparison with the acid strength distribution measurements ¹ shows that for the present reaction only acid sites of intermediate strength are needed. The same figure indicates that the catalysts show stable behavior in the temperature range investigated. Just as for the case of n-paraffin conversion, feed isomerization and cracking (Fig. 2) are consecutive phenomena.

When the individual product yield is plotted against cyclooctane conversion (Figs. 3 - 5), it was found that ethylcyclohexane, methylcycloheptane and bis[330]cyclooctane are primary products. Methylcycloheptane may be formed via protonated cyclopropane intermediates, just as in the case of the ethylcyclohexane conversion ²:

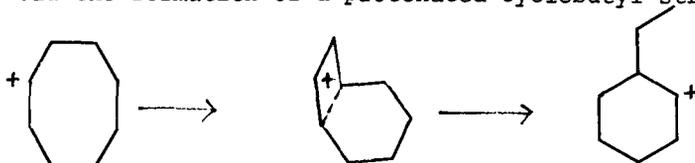


It is stabilized in the pentasil-type structures, more particularly in MEL.

The rate formation of bis[330]cyclooctanes (c + t) parallels the rate of isomerization to methylcycloheptane. The formation of a bicyclic molecule out of the cyclooctyl carbenium ion, requires that the ring is deformed to a chair-type form :



The direct formation of ethylcyclohexane without the formation of a primary carbenium ion, can only occur via the formation of a protonated cyclobutyl-structure :



The precursors of ethylcyclohexane and bis[330]cyclooctane from cyclooctane are therefore cyclooctyl cations deformed in a totally different manner, most probably under influence of the geometry of the zeolite pores. It is therefore straightforward that the transformation of cyclooctane will depend mainly upon the dimensions and structure of the zeolite pores.

REFERENCES

1. P.A. Jacobs, J. Martens, J. Weitkamp and H.K. Beyer, *Disc. Faraday Soc.*, 1982, 353.
2. M. Nitta and P.A. Jacobs, *Studies on Surface Science and Catalysis*, 5, 1980, 251.

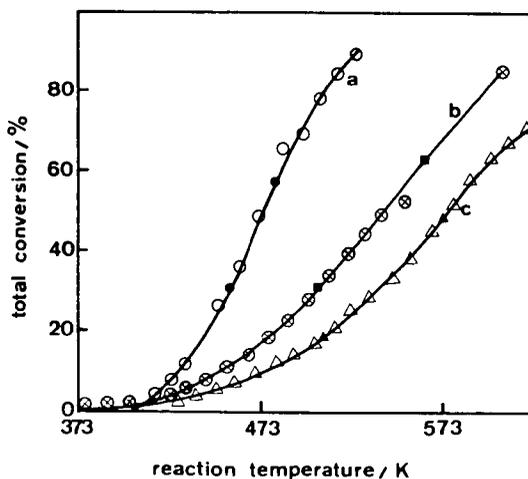


Figure 1

Total cyclooctane conversion in hydrogen over Pt-loaded acid a) MEL, b) MFI and c) FAU²⁺. Full points were obtained during a second cycle of temperature rise.

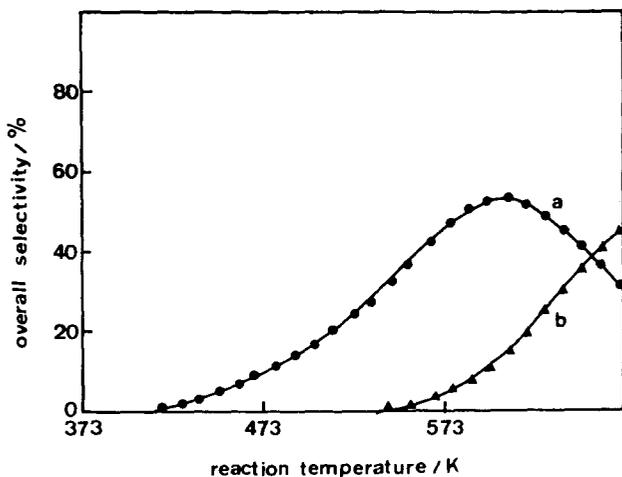


Figure 2

Overall selectivity of cyclooctane conversion over 1 Pt/H/MEL : a) feed isomers, and b) cracked products.

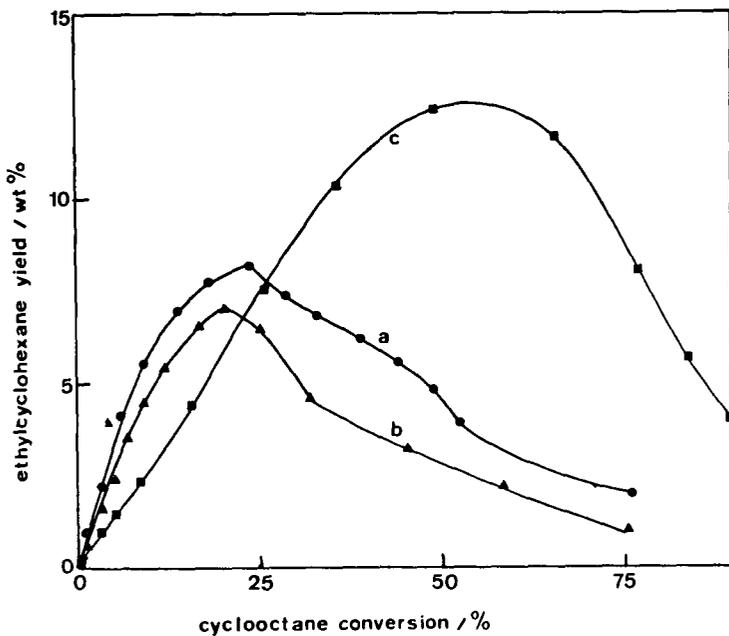


Figure 3

Yield of ethylcyclohexane from cyclooctane over FAU²⁺ (a), MFI (b), and MEL(c).

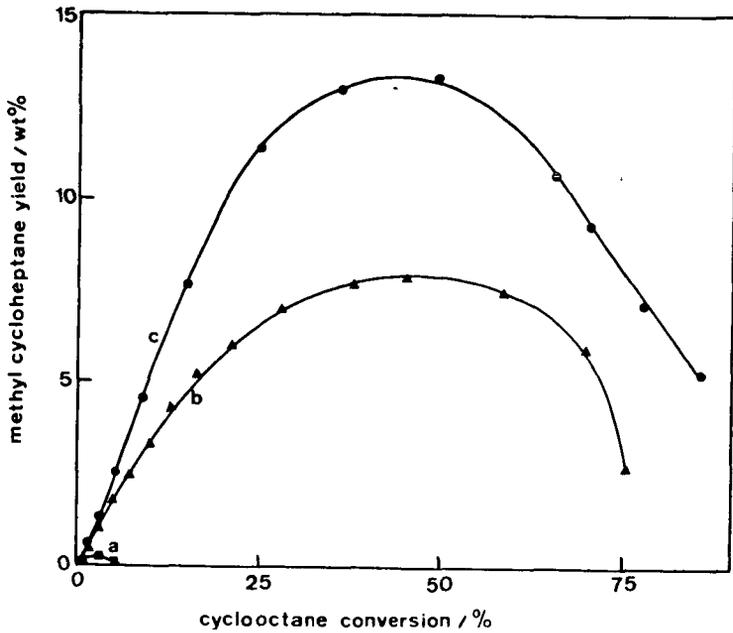


Figure 4

Yield of methylcycloheptane from cyclooctane on a) FAU[®],
b) MFI, and c) MEL - zeolites.

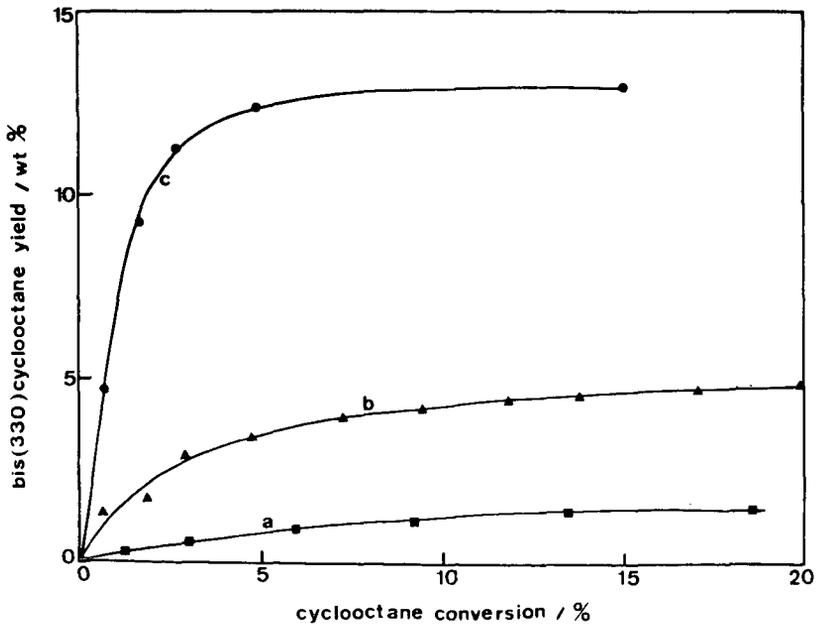


Figure 5

Yield of bis[330]cyclooctane from cyclooctane over a)
FAU[®], b) MFI, and c) MEL - zeolites.