Micropore Structure of Zeolite MCM-22 as determined by the Decane Catalytic Test Reaction

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According to the decane catalytic test reaction, the pore architecture of zeolite MCM-22, with unknown topology, contains two micropore systems circumscribed by 10- and 12-rings; the 12-ring channel system is monodimensional and has no connections with the 10-ring pores, where the strongest acid sites are located.

MCM-22 is a high-silica zeolite.[1] Although the crystallographic structure of MCM-22 has not yet been reported, it is denoted in the patent literature as a medium-pore zeolite possessing valuable catalytic properties for several hydrocarbon conversion reactions.[2]

A sample of zeolite MCM-22 was synthesized following example 1 of a patent assigned to Mobil,[3] converted into its acid form and loaded with a trace amount of noble metal. The transformation, activation and catalytic testing procedure were reported earlier for other zeolite samples.[4] In the conversion of decane, H-MCM-22 on a weight basis exhibits a catalytic activity comparable to zeolite H-beta and is more active than ultrastable Y zeolite (USY).

Catalytic test reactions, and the isomerization and hydrocracking of decane in particular, are powerful tools for determining microvoid structures of unknown zeolites.[5–6] They are based on a comparison of reaction selectivities obtained on the zeolite with unknown structure and on reference zeolites with known structures and micropores. Catalytic test reactions allow us to probe the micropore architecture around the active sites, which is relevant when more than one type of cage or channel are present.

In a first criterion of the decane test reaction the content of ethyloctanes in the monobranched isomerization products from decane is considered, and this at 5% isomerization of the feed. The formation of these bulky molecules is a very sensitive probe for the existence of 10-ring windows.[5] In zeolites with 10-ring windows, the formation of ethylbranched isodecanes is suppressed (Fig. 1). On MCM-22 only traces of ethyloctanes are formed. It is concluded that MCM-22 zeolite contains channels with 10-ring apertures.

The second criterion of the decane test is the refined constraint index, CI*.[5] The value of CI* corresponds to the ratio of reaction selectivities of 2-methylnonane to 5-methylnonane. MCM-22 exhibits a CI* value of 4.6 and is comparable to ZSM-11 and SAPO-11 in this respect. A CI* index with a value higher than 2.7 is characteristic of 10-ring zeolites.[6]

4-Propylheptane is the bulkiest isomer of decane. On MCM-22, trace amounts of this product (0.6% of total isomers) are found at 75% conversion. High selectivities for 2,7-dimethyloctane in the dibranched isomer fraction are typical for 10-ring zeolites.[6] At a 5% yield of dibranched isodecanes, 2,7-dimethyloctane represents 20.5% of this fraction. These two criteria classify MCM-22 as one of the more open structures among the 10-ring zeolites.[6]

Consecutive branching rearrangements of the decane molecules give rise to the formation of mono-, di- and tri-branched isodecanes, which become progressively more bulky in nature. The suppression of the second and further branching steps reflects the existence of steric constraints imposed by the architecture of the pore system. 10-Ring zeolites produce a much lower amount of dibranched isomers and can this way be distinguished from 12-ring zeolites. MCM-22 shows a high selectivity for dibranching which significantly exceeds values obtained for the known 10-ring zeolites (Fig. 2).

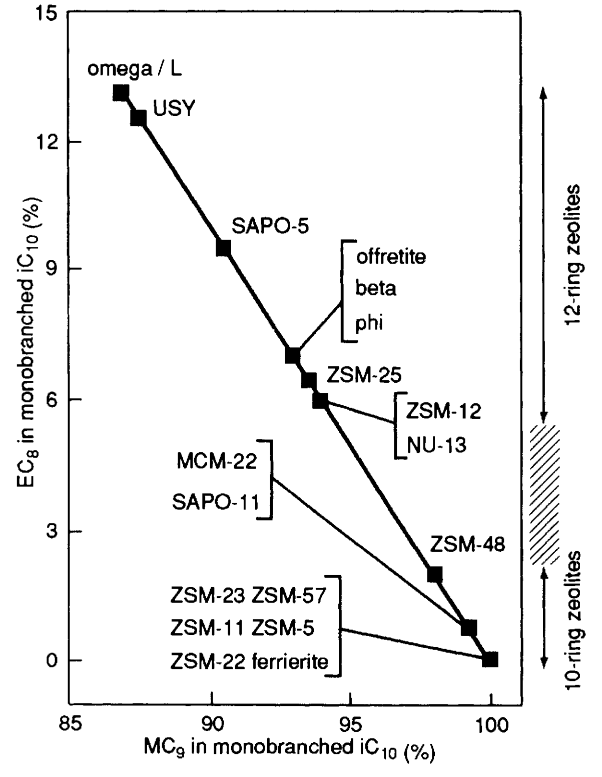

Fig. 1 Contents of ethyloctanes (EC_8) versus methylnonanes (MC_9) in monobranched decane isomers at 5% isomerization

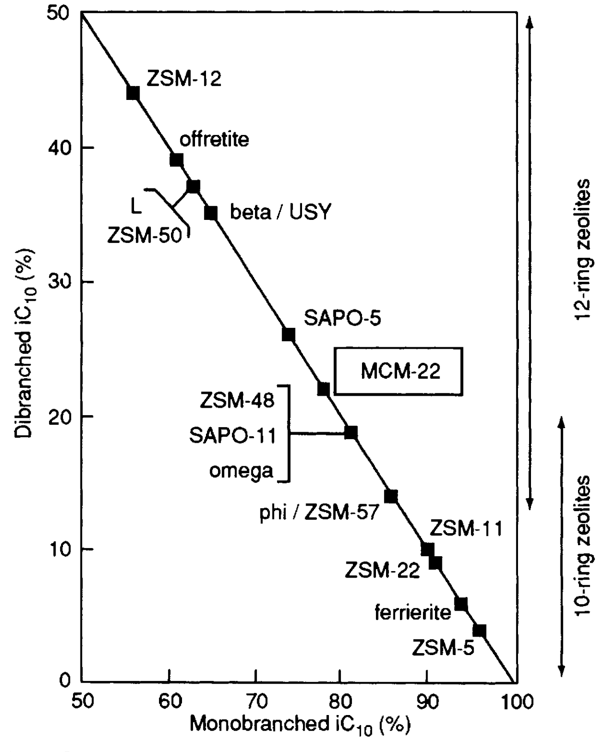

Fig. 2 Content of dibranched and monobranched isodecanes in the decane isomers at maximum isomerization yield

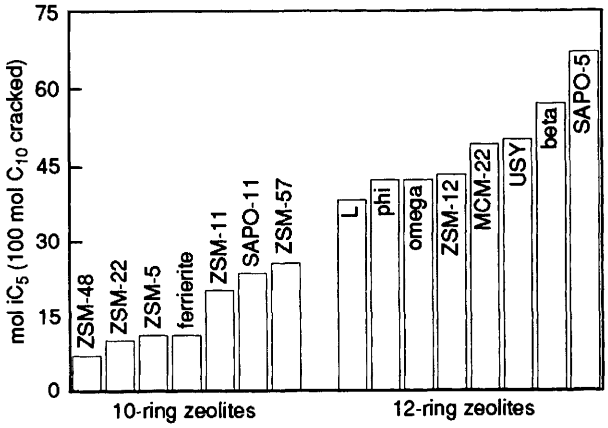

Fig. 3 Molar yield of isopentane (iC_5) at 35% cracking

The more the feed hydrocarbon undergoes branching rearrangements before cleavage, the higher will be the yield of branched cracked products. The molar yield of isopentane (iC_5) (moles of iC_5 formed per 100 mole of decane cracked) is correlated with the pore size.[5] MCM-22 produces an amount of iC_5 that is unusually high for a 10-ring zeolite (Fig. 3). The high quantity of iC_5 in the reaction products, similar to that found *e.g.* on USY zeolite, suggests a classification among the 12-ring zeolites.

The only way to reconcile the results from the different criteria is to accept that two types of channel systems are present. Monobranching should occur in channels with 10-ring openings, while further transformation of monobranched isomers *via* branching and cracking, should occur in 12-ring channels. The most active sites should be located inside the 10-ring channel system, as monobranching of *n*-alkanes is the primary reaction step[7] and the monobranched products reflect the 10-ring properties. At higher reaction severity, further branching and cracking which are suppressed in the 10-ring pores for steric reasons, should occur on less active sites in the 12-ring channels. The decane test therefore seems to indicate that MCM-22 contains two discrete acid strengths in the 10- and 12-rings, respectively.

The dimensionality of a micropore system is revealed by the dimensionality index (DI), proposed by Olken and Garces.[8] For the decane test reaction the DI index is derived from the molar distribution of the cracked products at 35% cracking conversion. Asymmetric molar product distributions, skewing towards C_3 and C_4 products, give rise to high DI values.[6] These are typically observed in monodimensional micropore systems. The explanation is that primary fragments from cracking undergo secondary cracking due to the severe counterdiffusion in this type of pore.[6] In zeolite structures having pores with 10-ring or larger windows interconnected in 2 or 3 dimensions, the value of the DI index is always below 5.[6] Since the DI value of MCM-22 amounts to 12, it is concluded that the 12-ring pores in MCM-22 in which cracking occurs are monodimensional.

In conclusion, the decane test reaction clearly shows that the pore architecture of zeolite MCM-22 is more complex than that of a medium pore zeolite. Comparison of several sets of product selectivites, from a *n*-decane conversion reaction on this unknown zeolite, with the corresponding values for known structures, advances evidence for a channel system with 10- and 12-membered rings and with monodimensionality. Protons are present in both sets of rings, the stronger ones being located in the smaller rings.

SSZ-25[9] and PSH-3[10] zeolites have X-ray patterns that are similar to those of MCM-22. These zeolites should have a comparable pore architecture.

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