Evidence for *X*-Ray-amorphous Zeolites

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Summary *X*-Ray-amorphous zeolites have been prepared which exhibit i.r. and catalytic properties typical for ZSM-5 materials and therefore must contain ZSM-5 crystals of less than 8 nm size in an amorphous matrix.

ZSM-5 ZEOLITES have been used to prepare some unique catalysts for a variety of processes.[1,2] It has been shown that these zeolites may be modified in various ways to monitor reaction selectivity.[2] One way of doing so depends on the variation of the crystal size.[3]

In an effort to reduce the crystal size of these zeolites, a family of ZSM-5 materials has been discovered which is amorphous when studied by *X*-ray diffraction (XRA/ZSM-5). The zeolites were prepared by interrupting the crystallisation during the synthesis. Experimental evidence is presented which indicates that the material contains very small zeolite nuclei, with sizes below the *X*-ray detection limit. The catalytic properties of the material in the bifunctional hydroconversion of n-decane, *i.e.* in the hydroisomerization–hydrocracking reaction of n-decane over Pt-loaded acid zeolite, reflect mainly the action of these crystal nuclei.

The procedure used for the synthesis of ZSM-5 has been published earlier.[4] A mixture with the following molar chemical composition: $(NPr^n{}_4OH)_{125}(Na_2O)(Al_2O_3)(SiO_2)_{200}(H_2O)_{5500}$ was allowed to react at 433 K. Crystallization times varied between 0·25 and 10 days. The materials were then air-dried, calcined at 550 °C, and ammonium exchanged. Crystallinity was studied by both i.r. spectroscopy and *X*-ray diffraction using a highly crystalline laboratory preparation as the 100% standard. For i.r. crystallinity the absorbance of a typical ZSM-5 skeleton vibration[5] at 550 cm^{-1} was followed. This band has been assigned to highly distorted double six-rings, present in the ZSM-5 structure.[5] The KBr pellet technique was used with KCN as internal standard (reference peak at 2200 cm^{-1}). For *X*-ray crystallinity, the sum of the area of the typical diffraction peaks between $2\theta = 22°$ and $2\theta = 25°$ (Cu-K_α radiation) was calculated.

The variation of crystallinity for different synthesis times is given in the Figure. A sigmoid plot is obtained for the changes in the *X*-ray crystallinity. This indicates that an induction–nucleation period and a growth period occur successively. The curve for the i.r. crystallinity shows a totally different behaviour. It is clear that for the shorter synthesis times, *X*-ray-amorphous materials with fairly high i.r. crystallinity are formed. Using the Scherrer formula,[6] it is calculated that in order to observe an *X*-ray diffraction peak at $2\theta = 10°$ with a half-band-width of 1°, crystallite sizes of 8·0 nm are needed. In other words, the XRA/ZSM-5 materials must have crystals which contain less than 4 unit cells. Scanning electron micrographs only show ill defined amorphous agglomerates without any trace of crystalline material. In this respect, the existence of amorphous zeolites of type A has recently been reported.[7]

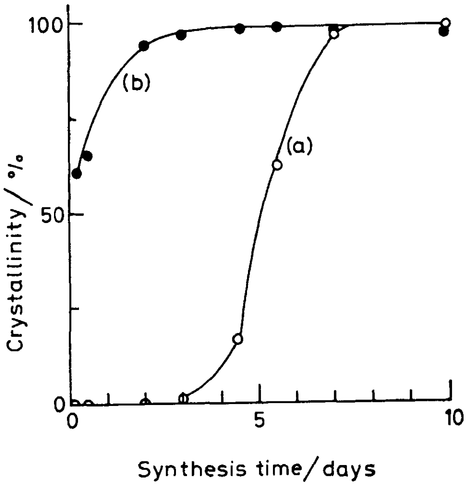

FIGURE. Change of the crystallinity of ZSM-5 materials with synthesis time: (a) *X*-ray crystallinity derived from peak summation between $2\theta = 22$ and 25°; (b) i.r. crystallinity using the 550 cm^{-1} skeleton vibration in a KBr pellet technique with the 2200 cm^{-1} vibration of KCN as internal standard.

In the Table are given the catalytic properties of the XRA/ZSM-5 materials, and a comparison with a crystalline HZSM-5 zeolite and USY† zeolite. It is known that the bifunctional behaviour of Pt/HZSM-5 and Pt/USY zeolite[8] is totally different in the hydroconversion of n-decane. As a result of a branching mechanism *via* protonated cyclopropanes, the yield of 2-methylnonane is always below that for thermodynamic equilibrium for open structures such as zeolite Y.[8] In the case of HZSM-5, however, this isomer is highly preferred. This is attributed to a particularly good fit of the shape and size of 2-methylnonane to the zeolite pore. In contrast with the yield of the other methyl isomers (3-, 4-, and 5-methylnonane), the 2-methylnonane yield is much greater than that for thermodynamic equilibrium.[8] Taking this into account, the Table shows that: (i) the XRA/ZSM-5 zeolites are fairly active materials in the present reaction; the activity is definitely not due to the amorphous matrix in which the small crystals are imbedded; (ii) the XRA/ZSM-5 zeolites exhibit bifunctional characteristics very similar to those of crystalline ZSM-5. Indeed, the yield of the 2-methylnonane isomer is always much greater than the thermodynamically expected value, while for the Y zeolite and the silico-alumina the opposite is true at low total conversions and for the reasons explained earlier.

TABLE. Hydroconversion of n-decane[a] at 200 °C over Pt-loaded[b] *X*-ray-amorphous ZSM-5 materials.

Catalyst	I.r. crystallinity/%	Conv./%	Hydroisomerization of feed/%	2-Methylnonane in feed isomers[c]/%
XRA/ZSM-5	61	8·0	3·0	36·0
	66	8·2	3·5	38·0
	94	8·6	5·0	43·0
	97	9·2	4·9	44·0
ZSM-5[d]		35·0	3·0	50·0
USY[e]		15·0	15·0	25·0
silica-alumina[f]		0·5	0·4	16·0

[a] Feed rate: 1500 kg s mol^{-1}; H_2:hydrocarbon ratio: 19:1; total pressure: 1 bar. [b] 1% by weight. [c] Thermodynamic yield: 30·1%. [d] Crystal size: 4 × 6 μm. [e] Stabilized Y zeolite (ref. 8). [f] Si/Al: 7, prepared by coprecipitation, with surface area 450 m^2/g.

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† USY is the ultrastable form of zeolite Y produced by steam treatment.

In conclusion, the present note shows that: (i) *X*-ray diffraction should be used with caution for crystal sizes below about 8 nm; in contrast, i.r. vibrations of the skeleton are intense for agglomerates of even a few unit cells; (ii) the very small crystals exhibit the shape-selective properties of ZSM-**5** materials in the case of the hydroconversion of long-chain paraffins.

The selectivity of these materials for other catalytic reactions and their catalytic stability is now being compared with that of the *X*-ray-crystalline ZSM-**5** structures.

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