Effect of Platinum on the Constraint Index of ZSM-5 Zeolite

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A significant increase of the ZSM-5 zeolite constraint index following the introduction of platinum is reported and is ascribed to the influence of olefins formed by alkane dehydrogenation on the cracking mechanism.

The ratio between the cracking rate constants of n-hexane and 3-methylpentane, measured during a competitive reaction, has been proposed as a means of characterizing intermediate pore-size zeolites such as ZSM-5.[1] At 400 °C, this ratio, called the constraint index (C.I.), was equal to about 4 on ZSM-5 whereas it was only 0.4 on Y zeolite. According to Haag *et al.*[2] this higher C.I. value is due to steric constraints affecting the first step of the alkane cracking, *i.e.* carbocation formation by hydride transfer from the alkane to a preadsorbed carbocation. In the case of 3-methylpentane the transition state of this bimolecular step is bulky and so formed with difficulty in the space available near the active centres.[2]

The C.I. of Pt-H-ZSM-5 was measured in the absence of hydrogen in order to avoid bifunctional catalysis. The C.I. found for Pt-H-ZSM-5 was significantly higher than for the corresponding H-ZSM-5. This is attributed to the fact that when platinum is present, traces of olefins are formed by dehydrogenation of the starting alkanes. These olefins provoke an increase in the cracking rate, which depends on the alkane structure.

The C.I. measured by competitive transformation of n-hexane and 3-methylpentane at 400 °C under nitrogen[1] is roughly 4 times greater on Pt-H-ZSM-5 with 0.43 wt % Pt than on pure H-ZSM-5 (Table 1). To confirm this result, the reactivities of n-hexane and of 3-methylpentane were compared during separate experiments. The constraint index C.I.′ = log (fraction of n-hexane remaining)/log (fraction of 3-methylpentane remaining) was again much higher on Pt-H-ZSM-5 than on H-ZSM-5 (Table 1). In both cases on Pt-H-ZSM-5 and H-ZSM-5, the main reaction was cracking but with Pt-H-ZSM-5 traces of C_6 olefins (0.5—1 mol %) were detected; moreover as can be seen from the experiments with

Table 1. Transformation of n-hexane and 3-methylpentane at 400 °C.

			n-Hexane		3-Methylpentane	
Catalysts	C.I.[a]	C.I.′	$A_{\mathrm{C}}{}^{c}$ (conv., %)	$A_{\mathrm{I}}{}^{c}$ (conv., %)	$A_{\mathrm{C}}{}^{c}$ (conv., %)	$A_{\mathrm{I}}{}^{c}$ (conv., %)
H-ZSM-5	4.0	2.7	6.7(20)	0	2.6(8)	0
Pt-H-ZSM-5	15.5	13.4	52.3(67)	3.9(5)	6.1(8)	0.5(0.7)

[a] C.I. = constraint index measured by competitive transformation of n-hexane and 3-methylpentane according to the procedure of Frilette *et al.*[1] [b] C.I.′ = constraint index measured by separate transformations of n-hexane and 3-methylpentane. [c] A_{C} and A_{I} = cracking and isomerization reactivities, respectively (10^{-3} mol h^{-1} g^{-1}).

Table 2. Transformation of n-hexane and 3-methylpentane over H-ZSM-5 at 350 °C.

Reactant	Cracking/mol %	Isomerization/mol %
n-Hexane	10.6	0
n-Hexane + n-hexene (1 mol %)	12.5	0.3
n-Hexane + n-hexene (5 mol %)	17.7	1.0
3-Methylpentane	2.0	0.7
3-Methylpentane + n-hexene (1 mol %)	2.7	0.9
3-Methylpentane + n-hexene (5 mol %)	6.6	1.2

pure n-hexane and 3-methylpentane (Table 1) a slow isomerization also occurs.

The increase in C.I. and C.I.′ on introduction of platinum could be explained by a decrease in the space available near the active centres. However, the rate of ion exchange of the protonic sites by platinum (16%) was insufficient to account for such a large increase in C.I. Moreover with a platinum dispersion equal to 54% determined by H_2–O_2 titration, we obtained for the platinum crystallites an average size of about 20 Å. Hence the greater part of the platinum was probably situated outside the zeolite channels. Lastly, an increase in the steric constraints should correspond to a decrease in the cracking activity whereas actually a very significant increase of this activity is observed (Table 1). This increase in the overall activity could be due to an increase in acidity. However it has been found that Pt-H-ZSM-5 and pure H-ZSM-5 have practically the same activity in *m*-xylene isomerization, a typical acid-catalysed reaction.[3]

The increase of the overall activity and of C.I. seem therefore to be due to another phenomenon, namely the formation on Pt-H-ZSM-5 of olefins resulting from the platinum-catalysed dehydrogenation of n-hexane and 3-methylpentane. It is known that olefins can increase the cracking rate of alkanes by increasing the number of chain initiators.[4,5] Thus, we found that the addition of hex-1-ene (1—5 mol %) to n-hexane or 3-methylpentane caused an increase in the H-ZSM-5 cracking and isomerization activities (Table 2). This effect is more pronounced for n-hexane than 3-methylpentane. Hence we suggest that this C.I. increase could be due to the fact that on Pt-H-ZSM-5, most of the chain initiators are probably C_6^+ cations whereas on H-ZSM-5 we have C_3^+ cations. This would cause more steric constraints in the transition state during the hydrogen transfer from the gaseous alkane to a preadsorbed cation.

In conclusion, this result shows that care should be taken in interpreting the C.I. of zeolite catalysts containing a dehydrogenation function.

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