

KINETIC STUDY OF n-HEPTANE HYDROCRACKING OVER HZSM-5 AND Pt-HZSM-5 CATALYSTS

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ABSTRACT

A kinetic study of the n-heptane transformation has been carried out on HZSM-5 and on Pt-HZSM-5 under low pressure (1 bar, p_{H_2}/p_{nC_7} from 10 to 35) and under high pressure (30 bar, p_{H_2}/p_{nC_7} from 4 to 15). There are fundamental differences in the distribution of the products in each case. On HZSM-5, cracking is the main reaction; under low pressure the light products are formed by scission of C_7 carbenium ions and under high pressure by scission of bimolecular intermediates. On Pt-HZSM-5 n-heptane is isomerized into methylhexanes and cracked into isobutane and propane. The formation of these light alkanes results from the scission of tertiary carbenium ions with a 2-methylhexane skeleton. The high rate of this scission is a peculiarity of the porous network of the ZSM-5 zeolite. Moreover the change in reaction rate with n-heptane pressure can only be explained by a concentration effect in the zeolite pores.

INTRODUCTION

The hydroisomerization and hydrocracking of n-alkanes on Pt-HY catalysts have been the subject of numerous studies and we now know the factors which determine the activity, the selectivity and the stability of these catalysts [1-7]. The catalysts in which the noble metal is deposited on a shape-selective zeolite have been studied in much less detail. The main work in this field is that of Weitkamp et al on the transformation of C_9-C_{16} n-alkanes on Pt-HZSM-5 which reveals a variety of shape-selectivity effects [8]. However, no kinetic study has been carried out on these catalysts.

In the kinetic study of the n-heptane transformation on Pt-HZSM-5 and on HZSM-5 reported here, a large range of operating conditions has been explored: p_{H_2} from 1 to 45 bar, p_{nC_7} from 0.03 to 7 bar, T from 250°C to 380°C. We shall try to define the factors which govern the activity and the selectivity of these catalysts.

EXPERIMENTAL

Catalysts. HZSM-5 (Si/Al = 40) synthesized according to Mobil Patents [10] was used in extrudates: HZSM-5 (30 wt %) in an alumina binder (70 wt %). Two samples of Pt-HZSM-5 containing respectively 0.4 wt % Pt (0.4 Pt-HZSM-5) and 1 % (1 Pt-HZSM-5).

were prepared by competitive ion exchange of extrudates with a 1/200 Pt(NH₃)₄ Cl₂/NH₄NO₃ solution. The conditions of calcination under dry air (300°C) and reduction under hydrogen (500°C) are those previously defined as leading to the best dispersion of platinum (H/Pt = 0.7) [11].

Reactions. n-Heptane hydrocracking was studied in dynamic reactors working respectively under normal pressure and under high pressure. The reaction mixtures were analyzed on line using a 100 m Squalane Scot capillary column.

RESULTS

1. Activity and selectivity. The total activities of the three catalysts determined at 260°C, total pressure $P_T = 30$ bars, $p_{H_2}/p_{nC_7} = 9$, are very close. However the influence of P_T (for $p_{H_2}/p_{nC_7} = 9$) on the reaction rates is clearly less significant for the bifunctional catalysts : thus under normal pressure the activity of Pt-HZSM-5 is about 25 times higher than that of HZSM-5. The influence of temperature however is more pronounced on the two Pt-HZSM-5 samples : the apparent activation energy is equal to 36 kcal mole⁻¹ whereas on ZSM-5 it is only 21.5 kcal mole⁻¹.

The selectivities of the HZSM-5 and of the Pt-HZSM-5 catalysts are different (tables 1 and 2) : if the formation of light products is always the main reaction, the isomerization of n-heptane is less significant on HZSM-5 than on Pt-HZSM-5 (table 2). On HZSM-5, C₈-C₁₁ alkanes (mainly linear or monobranched) are formed under high pressure. Under normal pressure, these alkanes are no longer observed and the isomerization/cracking rate ratio (I/C) is very small (table 2).

Table 1

Distribution of the products of n-heptane isomerization at 260°C
 $p_{H_2} = 27$ bar, $p_{nC_7} = 3$ bar for a conversion equal to about 5 %.

Catalysts	2mC ₆	3mC ₆	3eC ₅	2,3dmC ₅	2,4dmC ₅	2,2dmC ₅	Other
H ZSM-5	46.2	35.1	4.5	8.3	3.3	2.6	0
0.4 PtHZSM-5	65.7	31.6	1.0	0.6	0.8	0.3	0
1 PtHZSM-5	66.1	32.0	0.9	0.4	0.6	0	0
Equilibrium (9)	21.7	19.8	2.4	28.1	6.5	10.5	11.0

The distribution of isomers and light products differs on HZSM-5 and on Pt-HZSM-5 (tables 1 and 2) :

- thus on the Pt-HZSM-5 catalysts at low conversion the n-heptane isomers are made up of 2- and 3-methylhexanes for 97 % and for more than 95 % at 50 % conversion whereas on HZSM-5 they constitute only 80 % of the n-heptane isomers at low conversion and less than 75 % at 50 % conversion. On all these catalysts the other isomers

formed are, in order of importance 2,3-dimethylpentane, 3-ethylpentane, 2,4-dimethylpentane and 2,2-dimethylpentane (3,3-dimethylpentane and 2,2,3-trimethylpentane are not found). On Pt-HZSM-5 catalysts, 2-methylhexane is clearly favored at low conversion : the rate ratio of the formation of 2- and 3-methylhexanes is 2.1 for a conversion of 5 % (table 1) ; this ratio approaches its equilibrium value (about 1.2) at very high conversion rates. On HZSM-5, methylhexanes are initially formed in a ratio close to that of equilibrium (1.3 for a 5 % conversion) : curiously this ratio decreases as the conversion rate rises, dropping well below its equilibrium value, e.g. 0.85 for a conversion of about 50 %.

- On Pt-HZSM-5 catalysts, propane and isobutane (in equimolar quantities) are practically the only cracking products, whatever the degree of conversion or the n-heptane pressure (table 2). On HZSM-5, C₃ to C₆ olefinic and saturated hydrocarbons are formed. The iso/n ratio is equal to 1 for C₄ and less than 1 for C₅ and C₆ products. The lower the n-heptane pressure, the higher the quantities of olefins, C₃ and C₄ (table 2).

Table 2

Distribution of the products of n-heptane transformation at 260°C for a conversion equal to about 5 %. I = Isomerization, C = Cracking.

	P _T	PnC ₇	C ₂	C ₃	iC ₄	nC ₄	iC ₅	nC ₅	iC ₆	nC ₆	iC ₄ ⁼ /iC ₄	I/C
HZSM-5	30	3	0.3	23.1	20.3	20.4	9.0	14.0	5.8	7.1	0.1	0.15
0.4 PthZSM-5	30	3	0	50.8	47.7	1.0	0.1	0.3	0	0.1	0	0.55
1 PthZSM-5	30	3	0	50.5	48.4	0.8	0.1	0.2	0	0	0	0.65
HZSM-5	1	0.03	0	41.6	23.9	19.1	2.6	10.5	0.85	1.85	0.75	0.03
1 PthZSM-5	1	0.03	0	51.7	47.8	0.4	0	0.05	0	0.1	0	0.45

2. Influence of hydrogen and n-heptane pressure on the reaction rate. On HZSM-5 the reaction rate increases proportionally to n-heptane pressure for low values (< 0.1 bar) and with an order value of 0.6-0.8 for high values (> 10 bar) ; it does not depend on hydrogen pressure (Fig. 1 and 2). On the other hand, on the Pt-HZSM-5 catalysts, the rate is inversely proportional to hydrogen pressure (order value ≈ -1) ; it increases with n-heptane pressure for low values, but remains practically constant for high values.

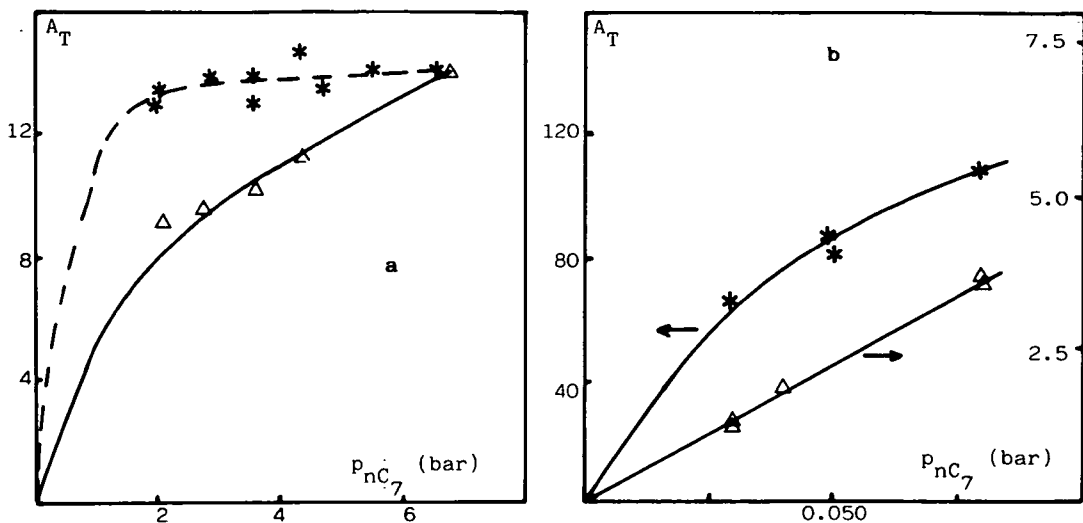


Fig. 1. Influence of n-heptane pressure on the total activities A_T (10^{-3} mole $h^{-1} g^{-1}$) on HZSM-5 (Δ) and on Pt-HZSM-5 ($*$) under high pressure (a) and low pressure (b).

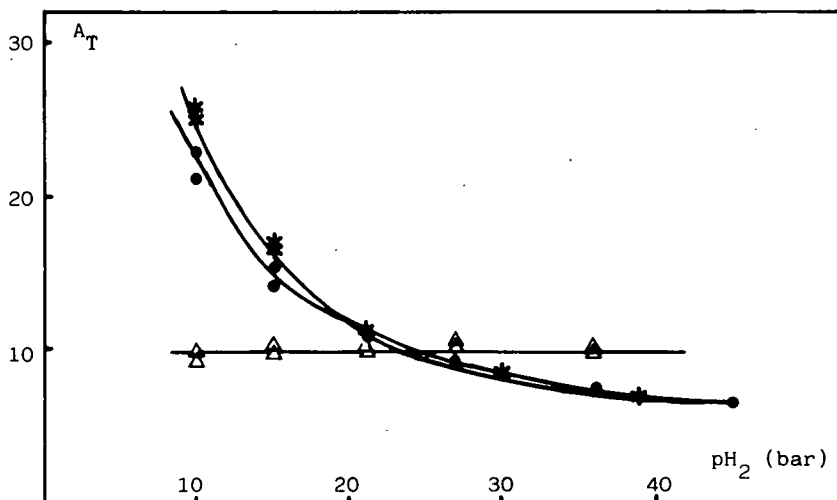


Fig. 2. Influence of hydrogen pressure on the total activities A_T (10^{-3} mole $h^{-1} g^{-1}$) over HZSM-5 (Δ), 0.4 Pt-HZSM-5 (\bullet) and 1 Pt-HZSM-5 ($*$).

DISCUSSION

On catalysts made up of a noble metal deposited on an acid support, three modes of alkane transformation can be found : the first involves only the metallic sites,

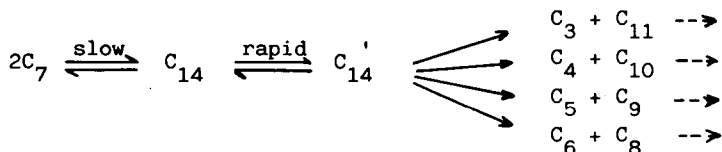
the second only the acid sites and the third successively the metallic and the acid sites (bifunctional mechanism). The relative significance of these three mechanisms depends essentially on the acid strength of the carrier and on the operating conditions [12, 13]. On Pt-HZSM-5 catalysts, C₁ and C₂ hydrocarbons are not formed and transformation on metallic sites (hydrogenolysis...) is probably very slow. The second reactional mode can also be excluded since Pt-HZSM-5 and HZSM-5 behave in a completely different way. On the other hand the absence of the bulkier isomers in the products : 3,3-dimethylpentane and 2,2,3-trimethylpentane suggests that the n-heptane transformation occurs inside the ZSM-5 porous system.

1. Factors governing product distribution. On HZSM-5, as on the majority of acid catalysts, cracking is the main reaction. Selectivity depends on n-heptane pressure :

- at low pressure, C₃ and C₄ hydrocarbons (the products expected from a simple scission) constitute more than 80 % of the cracking products and they are formed in equimolar amounts. Their formation can be explained by the scission of mono or bi-branched C₇ carbenium ions formed by rapid isomerization of the linear C₇ carbenium ions (nC₇⁺). The formation of these nC₇⁺ carbocations by hydride transfer from n-heptane to a preadsorbed carbenium ion is very likely the limiting step of this reaction.

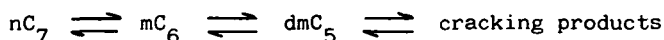


- At high pressure, C₃ hydrocarbons constitute only 20 % of the cracking products, the formation of C₄, C₅ and C₆ alkanes being highly favoured. Moreover alkanes with more than 7 carbons and n-heptane isomers are formed. All these products can be explained by the reactional scheme proposed for butane disproportionation on mordenite [14]: formation of bimolecular intermediates followed by their rearrangement and scission.

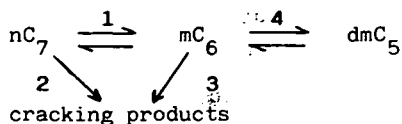


The formation of the bimolecular intermediates (C₁₄ ions carbenium) would be the kinetically limiting reaction [14]. This formation is probably favored by the very high concentration of n-heptane in the vicinity of the active sites as a result of the physical adsorption in the narrow pores of the HZSM-5 zeolite.

On Pt-HZSM-5 catalysts isomerization accompanies the cracking of n-heptane. However, whereas on Pt-HY the n-heptane transformation occurs through the following successive scheme :

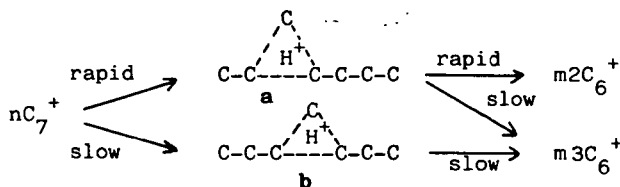


on Pt-HZSM-5 the reactional scheme is different, i.e. the cracking products are primary products (reaction 2) and isomerization to dimethylpentanes is very slow :



The cracking products being constituted of about 50 % of isobutane and 50 % of propane (table 2), evidently they cannot result from the scission of a carbenium ion with a n-heptane skeleton. The apparent reaction 2 can readily be explained using the classical bifunctional framework [6] if (i) the diffusion of the olefinic intermediates from one hydrogenating site to another is slow in comparison to their reaction on the acid sites or if (ii) these olefinic intermediates remain adsorbed on an acid site long enough to undergo, successively, isomerization and cracking. In both cases the cracking products result from the scission of a carbocation with a mono or bibranched skeleton.

On Pt-HZSM-5 2-methylhexane is clearly privileged in comparison to 3-methylhexane whereas statistically one would have expected the contrary [1]. Since these hydrocarbons diffuse at similar rates, this observation can only be explained by steric constraints in the formation and scission of protonated cyclopropanes [8] (intermediates of the transformation of n-heptane into methylhexanes). The privileged formation of 2-methylhexane found on Pt-HZSM-5 means that the reactions occurring through the protonated cyclopropane a are favored.



These steric constraints probably also explain why the transformation of methylhexanes into dimethylpentanes is very slow on Pt-HZSM-5. Indeed, this reaction also occurs through protonated cyclopropanes which are moreover bulkier than those invoked in the isomerization of n-heptane into methylhexanes. If such is the case, carbocations with a dimethylpentane skeleton will only be formed in small quanti-

The platinum content of the catalysts is sufficient to consider the reactions on the acid sites as kinetically limiting [11]. The formation of carbocations (step 2) is very rapid, and step 3 is very likely the limiting step in cracking and isomerization. At low conversion (neglecting the reverse reaction and the adsorption of products), the transformation rate of n-heptane can be written :

$$r = \frac{k_3 C_m K_1 K_2 C_{nC_7}}{p_{H_2} + K_1 K_2 C_{nC_7}}$$

where k_3 is the rate constant of step 3, C_m the concentration of Brönsted sites in the zeolite, K_1 and K_2 respectively the equilibrium constants of the dehydrogenation of n-heptane (reaction 1) and of carbenium ion formation (step 2) and C_{nC_7} the concentration of physisorbed n-heptane. This concentration can be linked to the pressure of n-heptane in gas phase (p_{nC_7}) by the Langmuir-Hinshelwood equation

$$C_{nC_7} = \frac{C_{(nC_7)m} K_L p_{nC_7}}{1 + K_L p_{nC_7}}$$

where (C_{nC_7})_m is the maximum concentration in zeolite pores and K_L the equilibrium constant of n-heptane physisorption.

$$r = \frac{k_3 C_m K_1 K_2 (C_{nC_7})_m K_L p_{nC_7}}{p_{H_2} + K_L p_{H_2} p_{nC_7} + K_1 K_2 (C_{nC_7})_m K_L p_{nC_7}} = \frac{a p_{nC_7}}{p_{H_2} + b p_{H_2} p_{nC_7} + c p_{nC_7}}$$

This equation accounts for our results : 1/r versus p_{H_2} and versus $1/p_{nC_7}$ are straight lines. The values of a, b, c are respectively : 3.5, 12.5, 14.

As expected, on HZSM-5 zeolite, the reaction rate does not depend on hydrogen pressure. Hydrocarbon order, equal to 1 at low pressure, remains close to this value under high pressure. This limited change can seem curious compared to the significant change observed on Pt-HZSM-5. But, as shown by the distribution of the products on HZSM-5, the reaction mechanism is not the same at low pressure (monomolecular intermediates) as it is at high pressure (bimolecular intermediates). The latter mechanism could give an alkane order value of 2, as has been observed in butane disproportionation on H mordenite [14]. The value in fact observed (0.7) is much lower, which could be explained, as on Pt-HZSM-5, by a condensation effect in the narrow pores of HZSM-5 zeolite.

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