JOURNAL OF CATALYSIS 78, 275–280 (1982)

Hydroisomerization of *n*-Hexane on Platinum Zeolites

II. Comparison between the Reaction Mechanisms on Platinum/Y-Zeolite and on Platinum/Mordenite

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Received October 30, 1981; revised April 22, 1982

The transformation of *n*-hexane was carried out under hydrogen pressure, on platinum/mordenite and platinum/Y-zeolite with platinum areas ranging from 0 to 10–15 $m^2 g^{-1}$. For both series, as can be expected from the conventional bifunctional process, the isomerization activity is proportional to the platinum area for small platinum areas and almost independent of it for large platinum areas. However, the primary products of *n*-hexane and 3-methylpentane isomerization are notably different: the selectivity of platinum/Y-zeolite with a platinum area ≥ 0.5 $m^2 g^{-1}$ is typical of a bifunctional reaction with, as limiting step, the skeletal isomerization of intermediate olefins; that of platinum/mordenite, even with a platinum area equal to 15 $m^2 g^{-1}$, remains intermediate between those of platinum-free zeolites and large platinum area Y catalysts. These differences are clearly related to the higher activity of platinum/mordenite, to its lower hydrogenation activity as well as to diffusional limitations in the practically unidimensional porous structure of mordenite.

INTRODUCTION

A detailed kinetic study of *n*-hexane hydroisomerization on a platinum/Y-zeolite series (*1*) shows that this reaction occurs through the conventional bifunctional mechanism (*2*), i.e., the metal sites catalyze the formation of intermediate olefins and the acid sites their skeletal isomerization. These catalysts behave like amorphous bifunctional catalysts. However, some special features attributed to the stronger acidity of Y-zeolite have been revealed. The aim of this work is to account for the influence of the strength of the acid sites on the behavior of bifunctional catalysts by comparing the catalytic properties of platinum/mordenite with those of platinum/Y-zeolite. We chose mordenite, which is used in an industrial process for light alkane isomerization (Hysomer process from Union Carbide and Shell), since its acid sites are stronger than those of Y-zeolite (*3*).

Two series of experiments were carried out. First, in the conditions previously used with platinum/Y-zeolite (*1*), the kinetic characteristics of the *n*-hexane transformation were determined on platinum/mordenite samples with platinum contents varying from 0 to 10.2 wt%. Then, to define with greater accuracy the selectivity differences between the two series of catalysts, the isomerization of *n*-hexane and 3-methylpentane was studied on platinum-free zeolite and on 0.5 wt% platinum samples.

EXPERIMENTAL

Five platinum mordenite samples were prepared following an operating procedure slightly different from the one used for the preparation of the Pt/Y-zeolite (PtHY) catalysts (*1*), as follows.

(1) Preparation of a $(NH_4)_{0.997}Na_{0.003}$ mordenite by ion exchange (3 times at 20°C) of

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0021-9517/82/120275-06$02.00/0

the Norton Zeolon 100 Na(SiO_2/Al_2O_3 = 10) with ammonium nitrate solutions.

(2) Dilution of the zeolite in an alumina gel (67 wt% of alumina calculated on materials calcined at 800°C) and extrusion.

(3) Calcination in dry air at 500°C for 4 hr.

(4) Exchange by $Pt(NH_3)_4^{2+}$ in competition with NH_4^+ as described previously (*4*).

(5) Calcination in a very dry air flow at 500°C for 2 hr, then 8 hr under hydrogen pressure at 500°C.

The operating procedure for benzene hydrogenation and *n*-hexane transformation has been previously described (*1*).

RESULTS

Five catalyst samples of Pt/mordenite were prepared with platinum contents varying from 0 to the value obtained by zeolite exchange to saturation (10.2 wt%). The samples will be designated as PtHM followed by the mass platinum content of the *zeolite* in parentheses. Their physicochemical properties (BET surface area, platinum dispersion) were previously described (*5*).

The samples used for the catalytic study have a benzene hydrogenation activity which is not directly proportional to their metal surface area. The turnover number *N* increases with the platinum content of the catalysts, varying from 12×10^{-3} molecules transformed per second and per atom of platinum for PtHM(*0.5*) to $50–80 \times 10^{-3}$ molecules transformed per second and per atom of platinum for PtHM(*10.2*). These values are considerably lower than the ones found for PtHY catalysts for which *N* was equal to about 600×10^{-3} (*1*). This lower hydrogenation activity of the PtHM catalysts has already been noted in ethylene hydrogenation. It could be due to diffusional limitations in the mordenite channels (*6*).

n-Hexane transformation was carried out using the same operating procedure as with the PtHY catalysts (*1*), namely a preliminary aging phase and then determination of the kinetic characteristics under operating conditions such that the conversion is lower than 10%.

Kinetic Characteristics of n-Hexane Transformation on PtHM Catalysts

The variation of the isomerization and of the cracking rate against the platinum content, the platinum surface area (Figs. 1 and 2), or the hydrogenation activities of the samples, is identical to that observed for PtHY catalysts: the isomerization rate increases strongly with the platinum content, passes through a maximum, then decreases (*5*). The cracking rate decreases when a small amount of platinum is introduced in the zeolite; for high platinum contents, it is proportional to the content.

As on PtHY catalysts, the composition of light products depends to a large extent on the platinum content of the samples. On low platinum content catalysts, there are five times less C_1 and C_2 molecules than C_5 and C_4 molecules, whereas only 1.3 times less on PtHM(*10.2*). The $(C_1 + C_2)/C_3$ molar ratio, equal to 0.25 on PtHM(*0*) and PtHM(*0.015*), increases with the platinum content: it is 0.8 for PtHM(*3.9*) and 0.9 for PtHM(*10.2*) (*5*). However, on PtHM catalysts, the change with platinum content of the cracking selectivity is much more gradual than on PtHY catalysts (*1*).

For isomerization, the apparent activa-

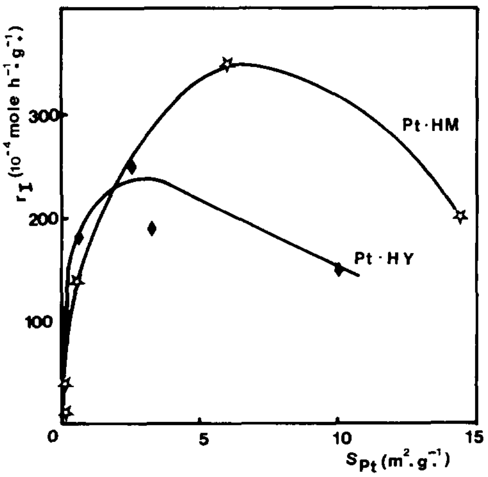

FIG. 1. *n*-Hexane isomerization at 250°C on platinum/mordenite and platinum/Y-zeolite: isomerization rate (r_I) against the metal surface area (S_{Pt}).

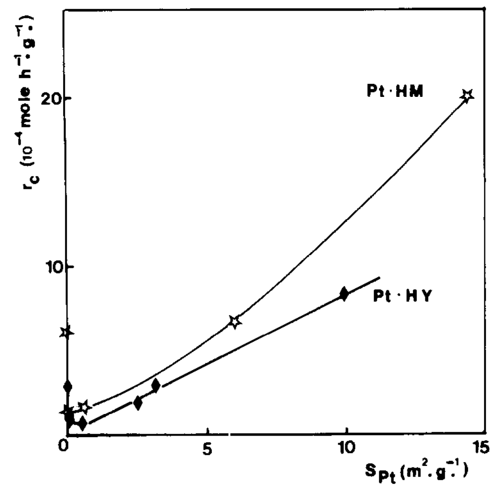

FIG. 2. *n*-Hexane cracking at 250°C on platinum/mordenite and platinum/Y-zeolite: cracking rate (r_C) against the metal surface area (S_{pt}).

tion energy and the selectivity change with the platinum content (or the platinum surface area) in the same manner as on PtHY catalysts, but much more slowly: the 2,3-dimethylbutane content in the 2,3-dimethylbutane–methylpentane mixture, equal to its equilibrium value on PtHM(*0*) and on PtHM(*0.015*), decreases with the platinum content as on PtHY catalysts. However, even on PtHM(*10.2*) this content remains equal to 40% of its equilibrium value while on PtHY with a platinum content ≥0.5% it is formed at only 10% of its equilibrium value. The 2,2-dimethylbutane content remains also considerably higher, i.e., 10% of its equilibrium value compared with 2% on PtHY.

Isomerization of n-Hexane and 3-Methylpentane on PtHM and PtHY Catalysts (with 0 and 0.5 wt% Pt)

On both catalysts, 3-methylpentane is transformed faster than *n*-hexane (7.5 to 12.5 times). Tables 1 and 2 compare the distribution of their isomerization products with the equilibrium mixture. The selectivities of platinum-free zeolites are very similar: *n*-hexane leads to an equilibrated mixture of methylpentanes and 2,3-dimethylbutane, while 3-methylpentane is isomerized very slowly into 2,2-dimethylbutane, slowly into *n*-hexane, and rapidly into 2-methylpentane and 2,3-dimethylbutane (Table 1). The selectivities of PtHM(*0.5*) and PtHY(*0.5*) are quite different: the selectivity of PtHM(*0.5*) is very similar to that of platinum-free zeolites whereas on PtHY(*0.5*) *n*-hexane leads mainly to the methylpentane equilibrium mixture and 3-methylpentane to 2-methylpentane (Table 2).

DISCUSSION

Isomerization Mechanisms

Isomerization activity and platinum surface area. The change with the platinum surface area in the isomerization activity of PtHM catalysts is similar to that observed

TABLE I

Distribution of Isomers Produced by Transformation of *n*-Hexane (a) and of 3-Methylpentane (b) at 300°C on PtHY(*0*) and on PtHM(*0*): Equilibrium Distribution (*7*)

	PtHY(*0*)		PtHM(*0*)		Equilibrium	
	a	b	a	b	a	b
n-Hexane		3.6		3.5		21.7
2-Methylpentane	51.9(53.1)	80.6(83.7)	49.8(53.0)	77.6(80.7)	36.7(50.0)	37.9(74.6)
3-Methylpentane	30.7(31.4)		28.1(29.9)		24.2(33.0)	
2,3-Dimethylbutane	15.1(15.5)	15.7(16.3)	16.1(17.1)	18.5(19.3)	12.5(17.0)	12.9(25.4)
2,2-Dimethylbutane	2.3	0.1	6	0.4	26.6	27.5
	100(100)	100(100)	100(100)	100(100)	100(100)	100(100)

TABLE 2

Distribution of Isomers Produced by Transformation of *n*-Hexane (a) and 3-Methylpentane (b) at 250°C on PtHY(*0.5*) and on PtHM(*0.5*): Equilibrium Distribution (*7*)

	PtHY(*0.5*)		PtHM(*0.5*)		Equilibrium	
	a	b	a	b	a	b
n-Hexane		2.6		3.0		18.4
2-Methylpentane	60 (60.6)	95.9(98.6)	48.7(51.3)	78.5(81.6)	34.2(49.4)	36.0(73.1)
3-Methylpentane	36.9(37.3)		31.9(33.6)		22.5(32.4)	
2,3-Dimethylbutane	2.0(2.1)	1.3(1.4)	14.4(15.1)	17.7(18.4)	12.5(18.2)	13.2(26.9)
2,2-Dimethylbutane	1.1	0.2	5.0	0.8	30.8	32.4
	100(100)	100(100)	100(100)	100(100)	100(100)	100(100)

with PtHY catalysts (*1*) and can be explained by the conventional bifunctional mechanism. The activity of small metal surface area catalysts depends very much on the area, i.e., at 250°C, it varies from about 6.10^{-4} mole hr^{-1} g^{-1} for PtHM(*0*) to 140×10^{-4} for PtHM(*0.5*) whose metal surface area is equal to 0.6 m^2 g^{-1}; the activity of large metal surface area catalysts is great and practically independent of the metal area.

On large platinum surface area catalysts, the limiting step is the skeletal isomerization of olefins on acid sites; the more acid the catalyst, the higher must be the activity. This is effectively what can be seen: the activity of PtHM catalysts is higher than that of PtHY catalysts (Fig. 1). On small platinum surface area catalysts, the limiting step is the reaction on the hydrogenation sites and the larger the metal surface area, the greater the activity. The hydrogenation activity of platinum being much smaller on PtHM than on PtHY catalysts, the initial slope of the isomerization activity curve plotted against the platinum area must be less acute for PtHM than for PtHY catalysts. Figure 1 shows that this is effectively the case.

Isomerization selectivity and platinum surface area. For both series of catalysts the isomerization selectivity changes with the platinum surface area in the same way but much more gradually in the PtHM than in the PtHY series. Thus, if the selectivities of PtHY(*0*) and PtHM(*0*) are identical (Table 1) that of PtHM catalysts (even with a platinum area equal to 14.5 m^2 g^{-1} (PtHM(*10.2*)) remains between the selectivity of platinum-free zeolites and that of all the PtHY catalysts with a platinum area ≥ 0.1 m^2 g^{-1}. The more reduced hydrogenation activity of PtHM catalysts cannot completely explain this. Indeed, PtHM(*10.2*) has a hydrogenation activity about 10 times higher than that of PtHY(*0.5*).

The selectivities of PtHM(*0.5*) and PtHY(*0.5*) which have similar platinum areas ($\simeq 0.5$ m^2 g^{-1}) are completely different (Table 2). The selectivity of PtHY(*0.5*) is that which can be expected from a conventional bifunctional process with, as limiting step, the skeletal olefin isomerization on acid sites. The selectivity of PtHM(*0.5*) is similar to that of acid catalysts such as PtHM(*0*), PtHY(*0*), or chlorinated alumina (*9*). Consequently, on PtHM(*0.5*) the reaction can occur by an acid mechanism. Platinum would have only the role of making the hydrogenation of coke precursors possible, thus limiting coking and catalyst deactivation (*9, 10*). Thus, after deactivation, the activity of platinum-containing catalysts would be higher than the platinum-free mordenite activity. A decrease in coking is effectively observed (*5*): PtHM(*0*) contains about 8% coke, PtHM(*0.5*) only 4%. It seems difficult, however, to account for the fact that the PtHM(*0.5*) activity is about 15 to 20 times greater than the PtHM(*0*) activity. A better explanation would be that, in addition to an acid reaction, there is on PtHM(*0.5*) a bifunctional *n*-hexane isomerization. This proposal has already been made for alkane isomerization on platinum/H-mordenite (*11*). On the portion of PtHM(*0.5*) carrying platinum crystallites, *n*-hexane should isomerize into 2- and 3-methylpentanes through the bifunctional mechanism. These products should rapidly isomerize into 2,3-dimethylbutane on acid sites distant from platinum crystallites; on these acid sites, *n*-hexane isomerization would be much slower than methylpentane isomerization as confirmed by the experiments on platinum-free mordenite. For this proposal to be accepted, one must assume that the part of mordenite with platinum and that without platinum work independently, the former by a bifunctional and the latter by an acid mechanism. The practically unidimensional porous structure of mordenite would be responsible for this particular behavior.

However, since the selectivity of a bifunctional isomerization, with as limiting step the reaction on platinum sites, is identical to that resulting from an acid reaction (*1*), this mechanism, which explains the proportionality between the isomerization activity and the platinum area on PtHM with a platinum content $\leq 0.5\%$, can account for the hexane isomerization on PtHM(*0.5*). Nevertheless, it cannot explain the selectivity of PtHM(*10.2*) for which the limiting step of the bifunctional process should be the acid reaction.

The selectivities of PtHM catalysts can also be explained if, in the bifunctional process, the migration of the intermediate olefins from one metal site to another metal site is slower than their isomerization on acid sites. In this case, the olefins have the possibility of reacting successively on several acid sites before being hydrogenated and 2,3-dimethylbutane will appear as a primary product of *n*-hexane isomerization as in an acid reaction. This proposal can account for the differences of behavior between the PtHY and PtHM series. These differences would be due to the greater reactivity of olefins on the stronger acid sites of mordenite; moreover, diffusional limitations larger in the narrow one-dimensional porous structure of mordenite than in the three-dimensional structure of Y-zeolite, can, especially in the presence of coke, limit the olefin migration.

Mechanism of Formation of Light Products

The changes of the cracking activity and selectivity of PtHM catalysts as a function of their metal surface area (Fig. 2) (or of their benzene hydrogenation activity) is very similar to that found on PtHY catalysts. Thus the mechanisms proposed on PtHY catalysts can explain the reaction on PtHM catalysts: a mechanism with carbonium ion intermediates on small metal surface area catalysts (platinum area $<0.5\ m^2\ g^{-1}$); a simple hydrogenolysis on large metal surface area catalysts.

For the same value of the platinum area, the activity of PtHM catalysts is greater than that of PtHY catalysts. In the case of small platinum area catalysts it is due to the higher acidity of mordenite. For large platinum area catalysts, the higher specific hydrogenolysis activity of platinum in platinum/mordenite confirms that this hydrogenolysis is a structure-sensitive reaction (*12*) catalyzed by specific sites whose concentration is greater on small crystallites than on large ones.

REFERENCES

1. Ribeiro, F., Marcilly, C., and Guisnet, M., *J. Catal.* **78,** 000 (1982).

2. Weisz, P. B., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 13, p. 137. Academic Press, New York, 1963.

3. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171, p. 437. American Chemical Society, Washington, 1976.

4. Ribeiro, F., and Marcilly, C., *Rev. Inst. Fr. Pét.* **34,** 405 (1979).
5. Ribeiro, F., Marcilly, C., Guisnet, M., Freund, E., and Dexpert, H., *in* "Catalysis by Zeolites" (B. Imelik *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 5, p. 319. Elsevier, Amsterdam, 1980.
6. Minachev, Kh., and Isakov, Y. I., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171, p. 552. American Chemical Society, Washington, 1976.
7. Douslin, D. R., American Petroleum Institute Research Project 62, Thermodynamics of Hydrocarbons from Petroleum, 1970.
8. Chevalier, F., Guisnet, M., and Maurel, R., Proc. Intern. Congr. Catalysis, 6th (London, 1976), p. 478. Chemical Society, London, 1977.
9. Guisnet, M., Garcia, J. J., Chevalier, F., and Maurel, R., *Bull. Soc. Chim.* 1657 (1976).
10. Chick, D. J., Katzer, J. R., and Gates, B. C., *in* "Molecular Sieves II" (J. R. Katzer, Ed.), ACS Symposium Series 40, p. 519. American Chemical Society, Washington, 1977.
11. Kouwenhoven, H. W., *in* "Molecular Sieves" (W. M. Meier and J. B. Uytterhoeven, Eds.), *Adv. Chem. Ser.* 121, p. 529. American Chemical Society, Washington, 1973.
12. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.