JOURNAL OF CATALYSIS **146**, 579–582 (1994)

NOTE

Aromatisation of *n*-Octane over Pt-Based Catalysts: Influence of the Support on the Product Distribution among C_8 Aromatics

The cyclisation of C_6–C_8 linear alkanes is an important reaction from both industrial and fundamental viewpoints (1, 2). This reaction, which has been intensively studied (3–5), is catalyzed by monofunctional dehydrogenation catalysts and by bifunctional dehydrogenation-acid catalysts. Over bifunctional catalysts under reforming conditions the aromatisation of C_6–C_8 alkanes occurs via a C_5 or C_6 ring closure as reported by different authors (5, 6), C_5 ring closure on the metallic centers being followed by C_5–C_6 ring expansion on the acid centers (6).

Restricting the problem to the C_8 cyclisation over metal (Pt) deposited on a nonacidic support (monofunctional catalyst) namely Pt/alumina, Davis and Venuto (1) showed that at least 80% of the C_8 aromatics formed could be accounted for by a six-ring closure. There is no report in the literature on the possible role of the support on the selectivity of such a cyclisation reaction but it is known that a medium pore zeolite such as silicalite (MFI) can influence the xylene distribution. We therefore decided to compare the catalytic properties of Pt/SiO_2 and Pt/silicalite in the *n*-octane cyclisation.

Platinum was deposited on SiO_2 (Degussa Aerosil, 200 m^2/g, nonporous material, composed of small spheres 15 nm in diameter) and also on silicalite. Following the patent literature (7), silicalite was prepared via hydrothermal synthesis using sodium silicate dissolved in hydrochloric acid and tetrapropylammonium hydroxide (TPAOH from Aldrich). It was checked by using XRD that the solid was highly crystalline; the porosity of this material is due to pores of elliptical cross-section (0.53 × 0.56 nm) (8), and the individual grains have 1 to 2 μm length.

SiO_2 and silicalite supports were loaded with Pt using the ion exchange/impregnation technique. The required amount of Pt $(NH_3)_4(OH)_2$ solution was diluted with water in order to have 50 cm^3 of solution. Next, 1 g of support was added to the Pt solution under stirring at 70°C. After 10 hr the solution was removed by evaporation and the solid was dried at 100°C in air. Platinum loading was measured by elemental analysis. Platinum loading on silica and silicalite were 0.3 and 0.5 wt.%, respectively.

After preparation, the solids were heated in a flow of O_2 from room temperature to 300°C (ramping 0.5°C/min) and kept at this temperature for 1 hr; then O_2 was flushed out with N_2 before replacing with a flow of H_2 and raising the temperature from 300 to 500°C (ramping 2°C/min). The platinum particle sizes determined by transmission electron microscopy ranged from 0.7 to 1 nm for both supports.

The catalytic test was performed using a dynamic microreactor, with a catalyst weight of 0.01 g and flow rate of 1 to 4 liter/hr. The pressure of *n*-octane, 2-methyl heptane (2-MHp), or 3-methyheptane (3-MHp) was fixed at 0.5 kPa, and H_2 at 100.5 kPa. The reaction temperature was fixed at 500°C. Preliminary experiments (not reported here) have shown that the rates measured were independent of the contact time and that flowing continuously the reactant over the catalyst causes a deactivation. In order to avoid strong deactivation, the hydrocarbon + H_2 mixture was reacted for 2 min and then the sample was flushed with H_2 before reacting with the next pulse. The results so obtained were close to those obtained (first experimental point) using a continuous flow of reactant.

In another series of experiments, the dehydrogenation of ethylcyclohexane (ECHX), 1,2-dimethylcyclohexane (DMCHX) *cis–trans* mixture, 1,3-dimethylcyclohexane (DMCHX) *cis–trans* mixture, and 1,4-DMCHX (*cis–trans* mixture) was measured. In all cases, a mixture of H_2 (p = 100.5 kPa) and hydrocarbon (p = 0.5 kPa) was used. All these reactants were from Aldrich. Finally, the dehydrogenation of *n*-butane was studied, keeping the pressure of the hydrocarbon fixed at 101 kPa. Experimental conditions (contact time) were chosen in such a way as to have low conversion (1%). Reactant and products were analyzed on line with a F.I.D. gas chromatograph equipped with Bentone and Unibeds columns (Alltech, France).

The results obtained are reported in the following sections.

(*a*) *n-Octane Conversion on Pt/SiO_2 and Pt/Silicalite*

In a first series of experiments, pulses of *n*-octane were reacted with Pt/SiO_2 in order to establish how the catalytic properties were modified with the number of pulses. In

021-9517/94 $6.00

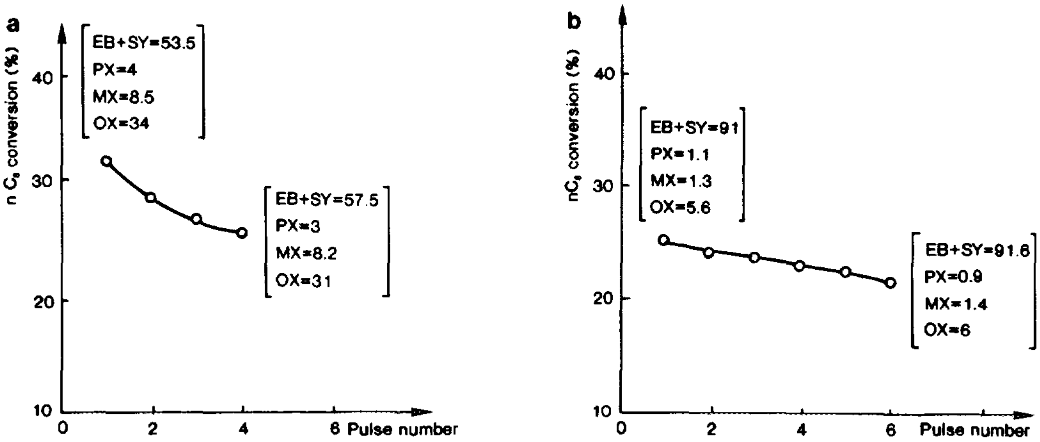


FIG. 1. (a) Pt/SiO_2. Change in the *n*-octane conversion as a function of the number of pulses. Numbers in brackets indicate C_8 aromatic distribution for the first and last pulses. (b) Pt/silicalite—as for Fig. 1a, except that six pulses have been reacted.

Fig. 1 the total *n*-octane conversion is plotted as a function of the pulse number, and it appears that there is only a slight decrease in the conversion with the number of pulses. In addition, the distribution of the C_8 aromatics as indicated in Fig. 1a for the first pulse and the fourth does not change very much. Similar results obtained on Pt/silicalite are reported in Fig. 1b. It appears that for both solids the catalytic properties (conversion, C_8 distribution) are not strongly modified with the number of pulses.

In Table 1, we have reported the rate of *n*-octane conversion and the selectivity in C_8 aromatics for the two solids under study. It is observed that the rates of *n*-octane transformation are of the same order of magnitude for the two catalysts and that it is the C_8 aromatic distribution which is strongly dependent on the nature of the support, the silicalite support favouring the formation of ethylbenzene (EB) and styrene (SY).

In order to gain more information on the causes of the shift in selectivity as a function of the nature of the support, 2-MHp and 3-MHp were used as reactants, and the results are reported in Table 2. It appears that the rate of the C_8 aromatic formation on Pt/SiO_2 is not really dependent on the nature of the C_8 reactant. By contrast, for Pt/silicalite this rate is definitely the highest for *n*-octane, 2-MHp having the lowest rate and 3-MHp being in between. For *n*-octane, the rate is not dependent dramatically on the nature of the solid (1.1 mmole hr^{-1} g^{-1} for Pt/SiO_2 compared to 1 for Pt/silicalite). The C_8 aromatic distribution is, as expected, changing with the C_8 alkane, and it has to be noted that this C_8 aromatic distribution is very different on the two catalysts. Since we suspected that the diffusion of the products could play a role in the C_8 aromatic distribution (see discussion below) we have used another test reaction (dehydrogenation) in order to gain more information on these solids.

(*b*) *Dehydrogenation of ECHX, 1,2-DMCHX, 1,3-DMCHX, and 1,4-DMCHX on Pt/SiO_2 and Pt/Silicalite*

These dehydrogenation reactions were performed by flowing 0.5 kPa of hydrocarbon and 100.5 kPa of H_2. For each reactant, it has been checked by changing the contact time that the dehydrogenation rate was constant as previously. The pulse technique was used in order to minimize the deactivation with time on stream. In Table 3, the data obtained at 400°C for Pt/SiO_2 and at 500°C for Pt/silicalite are reported. Since the Pt/SiO_2 catalyst was much more active than Pt/silicalite, it has not been possible to work at the same temperature for both solids. Table 3 shows how much Pt/SiO_2 is more active than Pt/silicalite for these dehydrogenation reactions. For a temperature of 100°C lower than that used for Pt/silicalite, Pt/SiO_2 has a rate which is still four times higher. For Pt silicalite, the order of reactivity is in the sequence ECHX = 1,4-DMCHX > 1,3-DMCHX = 1,2-DMCHX.

(*c*) *Dehydrogenation of n-Butane*

The difference in reactivity for the solids in dehydrogenation seen above is very large compared to that observed for the *n*-octane transformation. Therefore the de-

TABLE 1

Rate of *n*-C_8 Transformation and C_8 Aromatic Selectivity on Pt/SiO_2 and Pt/Silicalite

Catalyst	Rate[a] of *n*-octane transformation (1st pulse)	Selectivity (C basis) of C_8 aromatics (%)
0.3% Pt/SiO_2	2.0	54.8
0.5% Pt/silicalite	2.5	40.0

[a] mmole hr^{-1} g $catalyst^{-1}$.

TABLE 2

Rate of the C_8 Alkane Transformation into C_8 Aromatics and C_8 Aromatic Distribution as a Function of the Nature of the Alkane for Pt/SiO_2 and Pt/Silicalite Catalysts

Catalyst	Reactant	Rate (mmole hr^{-1} g^{-1})	C_8 aromatic distribution (%)			
			E_B+SY	PX	MX	OX
0.3% Pt/SiO_2	*n*-octane	1.1	52.5	4.0	8.5	34.0
	2-MHp	1.1	8.3	12.1	75.8	3.8
	3-MHp	1.1	30.8	37.0	8.5	23.7
0.5% Pt/silicalite	*n*-octane	1	91.0	1.1	1.3	5.6
	2-MHp	0.3	58.0	13.0	26.9	1.6
	3-MHp	0.6	68.8	25.7	0	5.5

Note. T = 500°C; P_{alkane} = 0.5 kPa; P_{H_2} = 100.5 kPa; catalyst weight = 10 mg; flow rate = 2 liters/hr.

hydrogenation of a short alkane (*n*-butane) has been performed on both solids at 500°C. The results (Table 4) indicate that both the solids have nearly the same activity for the dehydrogenation of *n*-butane.

Before discussing the results on *n*-octane cyclisation it is easier to examine the results obtained for the dehydrogenations. For *n*-butane both solids produce a similar dehydrogenation rate. This result is expected since on the two supports the particles of platinum have the same diameter (7–10 Å) as observed by TEM. By contrast, the dehydrogenation of the different C_8 cyclo-alkanes is much faster on Pt/SiO_2 than on Pt/silicalite. The most probable explanation is that the dehydrogenation rate over Pt/silicalite is limited by the diffusion of the reactant and the products. So, in the zeolite grain, the particles of Pt which are located near the external surface of the grain are active, the others having a negligible activity. The observation that the dehydrogenation rate of ECHX is equivalent to that of 1,4-DMCHX is in agreement with this explanation since it is known that in the MFI structure, ethylbenzene and p-xylene (Px) have similar diffusivities (9). The same explanation is valid for 1,3-DMCHX and 1,2-DMCHX since it is also known (10) that o-xylene (OX) and m-xylene (MX) have a smaller diffusivity than p-xylene or ethylbenzene.

TABLE 3

Dehydrogenation of 1,2-DMCHX, 1,3-DMCHX, 1,4-DMCHX (*cis–trans* mixture), and Ethylcyclohexane over Pt Silicalite at 500°C and on Pt/SiO_2 at 400°C

Catalyst	Rate[a]			
	1,2 DMCHX	1,3 DMCHX	1,4 DMCHX	Ethylcyclohexane
Pt/Silicalite	3.6	3.6	5.6	5.4
Pt/SiO_2[b]	19.8[c]	20.2[c]	20.0[c]	25.0[c]

[a] Rate in mmole hr^{-1} g catalyst^{-1}.

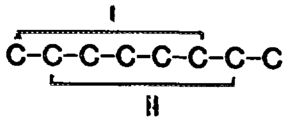
[b] The conversion was 100% at 500°C; rates have been measured at 400°C.

[c] A deactivation is observed and so the rates are a little underestimated, and consequently it is not possible to classify the reactivity of the different isomers.

For Pt/SiO_2, we have not established the true whole sequence of reactivity for the different C_8 cyclo-alkanes since a deactivation has been observed and this has been well reported in the literature (11, 12).

It appears from this that the low activity for the Pt/silicalite as compared to that of Pt/SiO_2 could be attributed to the limitation by diffusion of reactants and products. The results obtained for the dehydrogenation of *n*-butane confirm this hypothesis since both the solids have nearly the same activity and since for such a molecule no diffusional effect is expected.

We now discuss the cyclisation of the C_8 compounds. *n*-octane can be cyclised via



where I → EB and II → OX. For 2-MHp

and 3-MHp

For Pt and PtSn on nonacidic supports (13–15) it has been shown that *n*-octane is transformed into a nearly 50% EB/OX mixture, 2-MHp giving MX and 3-MHp giving a ratio of about 1/1/1/ of EB/OX/PX.

The results we have obtained on Pt/SiO_2 are in good agreement with those reported in these papers (13, 14): for *n*-octane (Table 2) small quantities of PX and MX are observed. As suggested in Ref. (15) MX could result from the isomerisation of *n*-C_8 into 2-MHp, PX being formed via cyclisation of 3-MHp coming from the isomerisation of 2-MHp. For the MHp (2-MHp and 3-MHp) the aromatic distribution is as expected (1). For 2-MHp, MX is the major product, PX, EB, and MX being secondary products coming from the isomerisation of 2-MHp into 3-MHp. For 3-MHp, the three major products, as expected, are

TABLE 4

Rate of n-Butane Dehydrogenation over Pt/SiO_2 and Pt Silicalite at 500°C $P_{C_4H_{10}} = 101$ kPa

Catalyst	Dehydrogenation rate (mmole hr^{-1} g $catalyst^{-1}$)
Pt/SiO_2	42.2
Pt/silicalite	30.0

Note. The rates have been measured after 2 min on stream.

PX, EB, and OX, MX being formed via cyclisation of the 2-MHp which could be an isomerisation product (3MHp → 2 MHp → MX).

Since similar results have been reported and discussed earlier, we emphasize only the change in C_8 distribution as a function of the nature of the support. Table 2 indicates that the rate of n-octane transformation is of the same order of magnitude for both solids, but that of 2-MHp and 3-MHp is definitely lower on Pt/silicalite. Concerning n-C_8 transformation into aromatics, it appears that EB + SY (styrene coming from the dehydrogenation of EB) selectivity is greatly enhanced compared to Pt/SiO_2. Two possible explanations can be considered, namely (i) diffusion and steric effect and/or (ii) change in the properties of Pt due to the change of the support.

The results we have obtained by studying the dehydrogenation of ECHX and 1–3 DMCHX fit well with the first explanation. It is expected that n-octane should give EB and OX (see Pt/SiO_2). If the diffusion of OX is the rate-controlling step on Pt/silicate, one can expect to observe an increase in the EB selectivity since it is known that EB diffuses more rapidly than OX in silicalite. The traces of PX and MX we observed during n-C_8 cyclisation could come from a secondary reaction, namely cyclisation of 2-MHp and 3-MHp, the expected n-octane isomers. It is of interest to observe that the rate of 2-MHp is three times lower than that of n-octane : 2-MHp gives MX as a primary product, and it is known that MX diffuses much less rapidly than EB or PX. It is therefore expected to have a lower rate for the 2-MHp cyclisation as compared with that of n-octane or 3-MHp. 2-MHp cyclisation gives an EB selectivity higher than that of PX, a result which is not expected since both EB and PX are known to diffuse at nearly equal rates in the MFI channels. The results obtained with 3-MHp, for which 68.8% of EB is obtained compared to 25.7% for PX, clearly indicate that the diffusion factors are not the only explanation which has to be considered. It is known that PX and EB diffuse at similar rates in the MFI structure. Our results on the 1,4-DMCHX and ECHX dehydrogenation confirm this finding. For 3-MHp nearly equal rates are expected for EB, PX, and OX formation. EB and PX have the same diffusion factor in the silicalite pores. Hence one has to assume that due to the steric effect of the methyl groups and the pore size of the silicalite, the less bulky intermediate is favoured, and consequently the EB selectivity is larger than that of PX.

To sum up, it has been established that on the nonacidic supports, SiO_2 and silicalite, Pt exhibits different properties for n-octane cyclisation, the silicalite support favouring EB formation, as shown by using MHp isomers (2-MHp and 3-MHp). This high EB selectivity could be explained by considering the two factors:

—diffusion of the products into the silicalite channels (most important factor).

—size of the intermediate (secondary factor).

ACKNOWLEDGMENT

This work was funded by CEFIPRA (Centre Franco Indien Pour la Recherche Avancée), Indo French Center for the Promotion of Advanced Research (IFCPAR) New Delhi, under Project 506-1.

REFERENCES

1. Davis, B. H., and Venuto, P., *J. Catal.* **15,** 363 (1969).
2. Callender, W., Brandenberger, S. G., and Meerbott, W. K., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach 1972" (J. W. Hightower, Ed.), p. 1265. North-Holland, Amsterdam, 1973.
3. Christoffel, E. G., and Paál, Z., *J. Catal.* **73,** 30 (1982), and references therein.
4. Sharan, K. M., *Catal. Rev.—Sci. Eng.* **26,** 142 (1984).
5. Pines, H., and Gotschel, C. T., *J. Org. Chem.* **30,** 3548 (1965).
6. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 184. McGraw–Hill, New York, 1979.
7. Grose, R. W., and Flanigen, E. M., U.S. Patent 4, 061, 724 (1977).
8. Meier, W. M., and Olson, R. D. (Eds), "Atlas of Zeolites Structure Types," p. 10. Butterworth–Heinemann, London, 1992.
9. Le Van Mao, R., Ragaini, V., Leofanti, G., and Foris, R., *J. Catal.* **81,** 416 (1983).
10. Ruthven, D. M., Eic, M., and Richard, E., *Zeolites* **11,** 647 (1991).
11. Hishida, T., Uchijima, T., and Yoneda, Y., *J. Catal.* **11,** 71 (1968).
12. Ritchie, A. W., and Nixon, A. C., Prepr. *Am. Chem. Soc., Div. Pet. Chem.* **11,** 93 (1966).
13. Davis, B. H., Westfall, G. A., Watkins, J., and Pezzanite, J., *J. Catal.* **42,** 247 (1976).
14. Davis, B. H., *J. Catal.* **42,** 376 (1976).
15. Davis, B. H., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, P. Tétényi, Eds.), p. 889. Akademiai Kiado, Budapest, 1993.

P. Mériaudeau*,[1]
A. Thangaraj*
C. Naccache*
S. Narayanan†

* *Institute de Recherches sur la Catalyse (CNRS)*
2 Avenue Albert Einstein
69626 Villeurbanne Cédex, France

† *Catalysis Section*
Indian Institute of Chemical Technology
Hyderabad 500007, India

Received June 7, 1991; revised October 4, 1993

---

[1] To whom correspondence should be addressed.