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CHEMIOSELECTIVITY IN CINNAMALDEHYDE HYDROGENATION INDUCED BY SHAPE SELECTIVITY EFFECTS IN Pt-Y ZEOLITE CATALYSTS

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Platinum and rhodium particles encapsulated in Y-type zeolite are much more selective for the hydrogenation of cinnamaldehyde to cinnamyl alcohol than active charcoal-supported platinum and rhodium catalysts. The good selectivity is interpreted in terms of molecular constraints in the zeolite micropores which favour an end-on adsorption of the molecule via the C = O group on the encapsulated metal.

1. Introduction

Zeolite catalysts have been extensively used for their shape selectivity in reactions involving hydrocarbon conversion or hydrocarbon synthesis. Since the pioneering ideas of Venuto and Landis [1], they have been little used for the synthesis of fine chemicals. It was only recently that a number of selective catalytic reactions yielding functionalized organic compounds of high added value have been reported [2–4]. Still, most of these results deal with gas-phase, acid-catalysed reactions. Thus, there is, to our knowledge, no report on shape selective, metal catalysed hydrogenation on clusters selectively encapsulated in zeolite micropores.

This work was intended to take advantage of the geometric constraints in zeolite micropores, to hydrogenate selectively cinnamaldehyde (CAL) to cinnamyl alcohol (COL). Indeed, because of the size and of the rigidity of the CAL molecule, one can expect that the tip of the molecule, i.e. the carbonyl group, will adsorb selectively on metal clusters filling zeolite micropores. Two types of metal have been investigated, platinum which has a moderate selectivity to COL and rhodium which is quite unselective [5]. Zeolite Y has been chosen because its tridimensional system of large pores should favour molecular diffusion and

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because the metal dispersion and distribution in the porous lattice can be controlled by well documented treatments [6].

2. Experimental

The conditions of preparation yielding homogeneous platinum and rhodium clusters on zeolites have been thoroughly discussed in previous works [6]. We recall that NaY zeolite ion-exchanged with $(Pt(NH_3)_4)^{2+}$ or $(Rh(NH_3)_5Cl)^{2+}$ cations must be heated slowly (0.5 K/min) under flowing oxygen (1.5 l/min/g), from 300 to 573 K, before reducing under hydrogen at 573 K. Samples RhY and PtY1 were prepared in this way to obtain homogeneously distributed, nanometer-sized clusters. In contrast, PtY2 was obtained by heating directly the Pt-exchanged zeolite under H_2 at 573 K, a treatment which favours sintering of the metal [6]. The concentrations of platinum in calcinated PtY1, PtY2 and RhY zeolites are 11, 14 and 7 wt% respectively.

The size and distribution of metal particles in the zeolite microcrystals were determined by transmission electron microscopy (TEM). Zeolites were embedded in an epoxy resin and cut into thin slabs with an ultramicrotome for examination by transmission.

Batches of the catalysts (0.4 g) were introduced in a mixture of isopropanol (37.5 cm^3), water (10 cm^3) and sodium acetate (0.1 M, 2.5 cm^3). The suspension was stirred (1500 rpm) for 2 hours at 333 K in an autoclave under 40 bars H_2 pressure. After this pretreatment, 13.2 g of cinnamaldehyde ($C_6H_5{-}CH=CH{-}CHO$) were introduced under H_2 pressure and the reaction was carried out at 333 K under 40 bars of H_2 pressure. The product distribution was followed by repetitive samplings and gas chromatography analysis as a function of time.

3. Results and discussion

Figure 1a–c give TEM views taken on ultramicrotome cuts of RhY, PtY1 and PtY2 respectively. The particles in RhY are homogeneously distributed throughout the zeolite crystal, their sizes are in the range 1 ± 0.3 nm. The distribution of particles in PtY1 is also homogeneous with sizes in the range 1–2 nm (fig. 1b). The metal particles in PtY2 are still inside the zeolite crystals but they are much larger than the zeolite cages (average particle diameter 5 nm) and they form botryoidal agglomerates in the vicinity of the external surface.

The distributions of products as a function of time and as a function of conversion are given in figs. 2a,b, 3a,b, and 4a,b respectively. Table 1 gives the distribution of products at 0, 25, 50 and 75% conversion. Results obtained previously [7,8] on platinum and rhodium catalysts supported on active charcoal are given for comparison. It is noteworthy that, for all the catalysts, cinnamyl

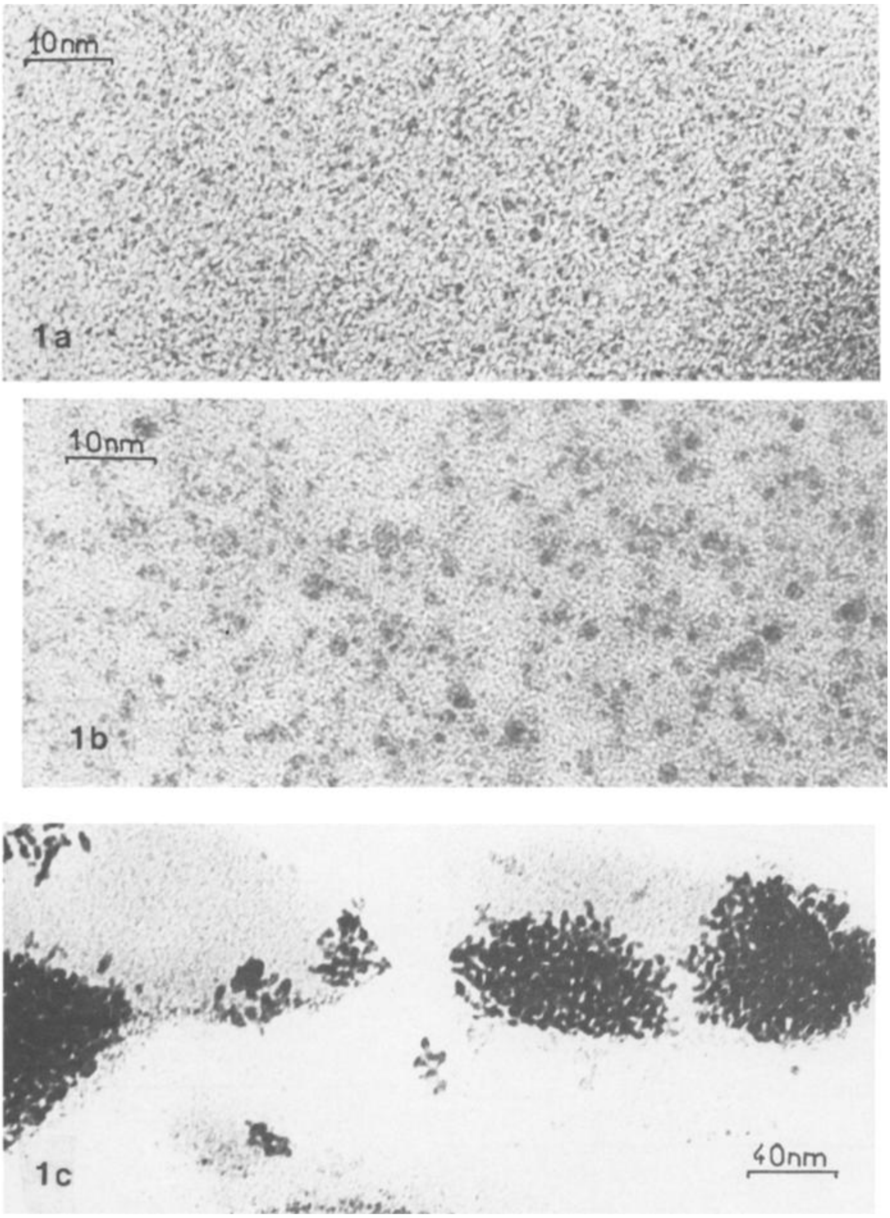

Fig. 1. TEM photographs taken through ultramicrotome sections of zeolites (a) RhY; (b) PtY1; (c) PtY2.

alcohol (COL) is detected in the liquid phase after a substantial period of time: 20, 45 and 110 minutes for PtY2, PtY1 and RhY respectively (fig. 2a–4a). Such a delay was never observed on non-zeolitic support [7,8].

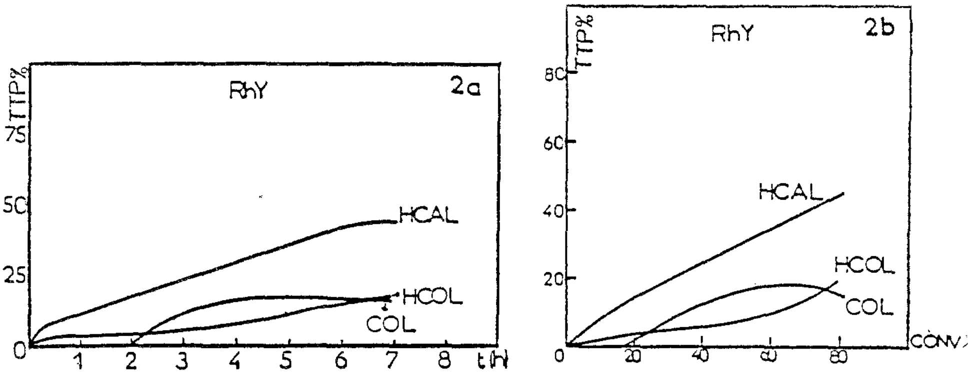

Fig. 2. Distribution of products in cinnamaldehyde hydrogenation on RhY catalyst (COL: cinnamyl alcohol; HCOL: hydrocinnamyl alcohol; HCAL: hydrocinnamyl aldehyde) (a) yields vs. time; (b) yields vs. CAL conversion.

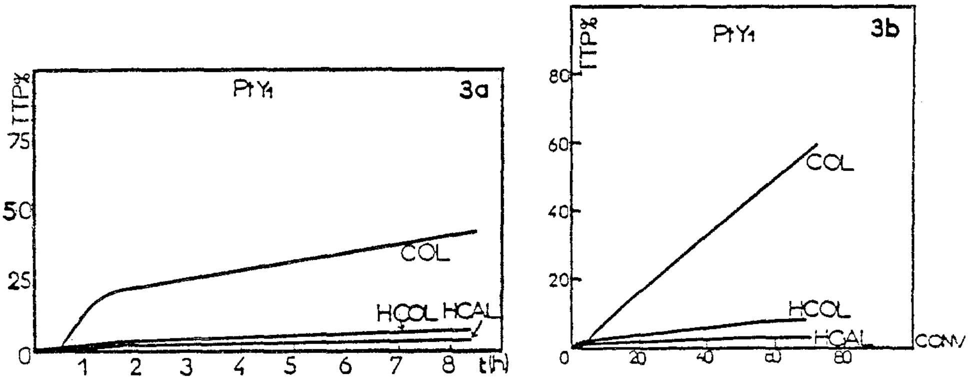

Fig. 3. Distribution of products on PtY1 catalyst (a) yield vs. time; (b) yield vs. CAL conversion.

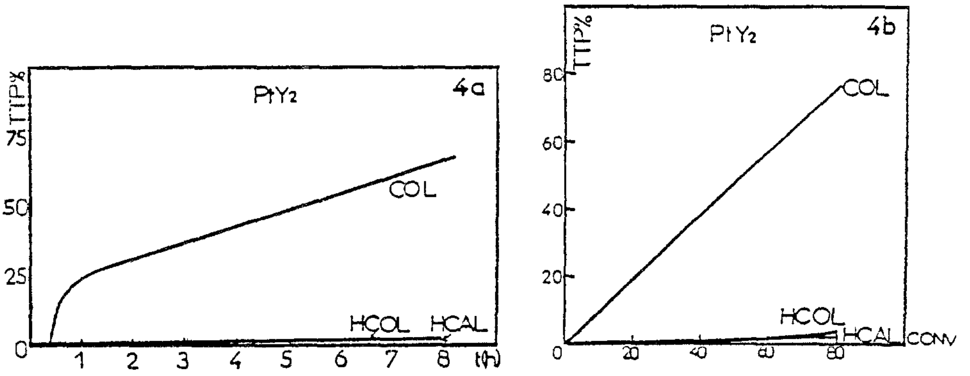

Fig. 4. Distribution of products on PtY2 catalyst (a) yield vs. time; (b) yield vs. CAL conversion.

Table 1
Selectivities to cinnamyl alcohol at different conversions

Catalysts	S^{0}	S^{25}	S^{50}	S^{75}
PtY1	0	74	82	82
PtY2	0	97	97	96
RhY	0	16	30	22
Pt/C [a]	0	33	55	
Rh/C [a]	0	0	5	

[a] From ref. [8].

The most interesting result of this study is the very high selectivity to unsaturated alcohol obtained on metal clusters encapsulated in zeolites. Thus at 25% CAL conversion, the selectivities to COL on PtY1 and PtY2 are 74 and 97% respectively compared to only 33% on Pt/C catalyst (table 1). Such high selectivities are usually obtained after promotion of platinum with metal salts [5] or on bimetallic catalysts [9–11]. Similarly, the 30% selectivity observed on RhY at 50% conversion is unexpected for rhodium which is known to be unselective. Indeed, a 5% selectivity is measured on Rh/C catalyst (table 1). In the three catalysts investigated, the hydrogenation of the C = O bond is highly favored with respect to the hydrogenation of the C = C bond because of molecular constraints (shape selectivity) in the zeolite pores. As illustrated in fig. 5, because of its rigidity and dimension, the CAL molecule can adsorb only end-on, i.e. via the C = O group, across the twelve-membered oxygen ring, on metal clusters located in the zeolite supercages of PtY1 and RhY. This shape selectivity operates also when the particles are larger than the supercages provided they are still encapsulated in the zeolite crystal as in PtY2. Indeed the approach of the molecules to the metal surface is still constrained by the micropores which orientate the molecule end-on, thus hampering the adsorption and activation of the C = C bond.

Note that the shape selective effects discussed above would not operate if the CAL molecules were able to enter supercages hosting very small clusters. Thus a cluster of six atoms or less would leave enough space for the molecule to enter the cage and adsorb laterally i.e. via the C = C bond. This could well happen in the

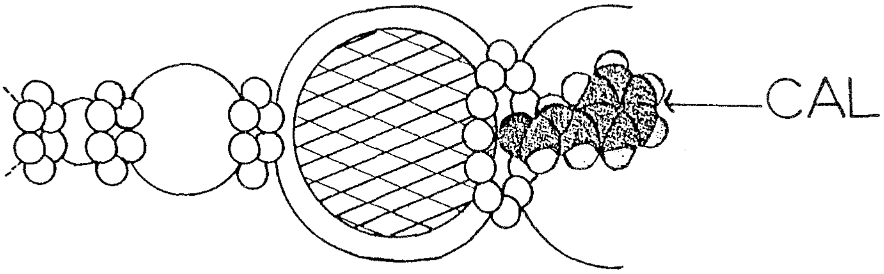

Fig. 5. Scheme showing a CAL molecule approaching a metal particle in adjacent supercage.

case of RhY zeolite and PtY1 zeolites where some clusters could be smaller than 0.7 nm thus escaping TEM detection. However in the case of rhodium which has a very high activity for C = C bond hydrogenation, HCAL could also be formed on the small fraction of rhodium possibly located on the external surface of the zeolite. Correlatively the almost quantitative yield in COL observed in PtY2 could be due to the absence of subnanometric clusters in zeolite cages.

4. Conclusion

This study shows that the chemioselectivity in cinnamaldehyde hydrogenation can be greatly improved by using metal clusters encapsulated in Y-type zeolites. The selectivities of platinum and rhodium to unsaturated alcohol are unusually high because geometric constraints in the pores impose an end-on adsorption on the metal and therefore a selective activation of the C = O bond.

This first attempt to tune the selectivity of liquid phase hydrogenation with metal zeolite catalysts is encouraging. Other problems of chemio-, regio- or stereoselectivity in organic synthesis can be addressed provided the molecular dimensions of the organic substrates are commensurate with the pores. Large-pore zeolites, or other solids with calibrated micropores containing encapsulated metal particles, are supramolecular catalytic systems of high potential interest.

References

[1] P.B. Venuto and P.S. Landis, Adv. Catal. 18 (1968) 259–371.

[2] W.F. Hölderich, in: *Proc. 7th Int. Zeolite Conf.*, Tokyo, 1986, eds. Murakami et al. (Kodanska, Tokyo, 1986) p. 709; Ibid, in: *Proc. 8th Int. Zeolite Conf.*, Amsterdam, 1989, eds. P.A. Jacobs and R.A. Van Santen (Elsevier, Amsterdam, 1989) pp. 69–93.

[3] H. Van Bekkum and H.W. Kouwenhoven, in: *Heterogeneous Catalysis and Fine Chemicals*, eds. M. Guisnet et al. (Elsevier, Amsterdam, 1988) pp. 45–59.

[4] D. Chiche, A. Fimiels, C. Gauthier and P. Geneste, Appl. Catal. 30 (1987) 365.

[5] P. Rylander, in: *Catalytic Hydrogenation in Organic Syntheses* (Academic Press, New York, 1979) pp. 74–80.

[6] P. Gallezot, in: *Proc. 6th Int. Zeolite Conf.*, Reno, 1983, eds. D. Olson and A. Bisio (Butterworths, Guildford, 1984) pp. 352–367 and references therein.

[7] D. Richard, P. Fouilloux and P. Gallezot, in: *Proc. 9th Int. Congr. on Catalysis*, eds. M.J. Phillips and M. Ternan, Vol. 3 (the Chemical Institute of Canada, Ottawa, 1988) pp. 1074–1081.

[8] A. Giroir-Fendler, D. Richard and P. Gallezot, in: *Heterogeneous Catalysis and Fine Chemicals*, eds. M. Guisnet et al. (Elsevier, Amsterdam, 1988) p. 171.

[9] D. Goupil, P. Fouilloux and R. Maurel, React. Kinet. Catal. Letters 35 (1987) 185.

[10] Z. Poltarzewski, S. Galvagno, R. Pietropaolo and P. Staiti, J. Catal. 102 (1986) 190.

[11] D. Richard, J. Ockelford, A. Giroir-Fendler and P. Gallezot, Cat. Lett. 3 (1989) 53.