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CHEMIOSELECTIVITY IN THE CATALYTIC HYDROGENATION OF CINNAMALDEHYDE.
EFFECT OF METAL PARTICLE MORPHOLOGY

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The selectivity of platinum and rhodium catalysts for the hydrogenation of cinnamaldehyde into cinnamyl alcohol is much higher on large, facetted metal particles them on small (< 3 nm) particles. This is attributed to a steric effect of the phenyl group which hampers the molecule to adsorb parallel to the flat metal surface thus favouring the adsorption and hydrogenation of the carbonyl group with respect to the C = C double bond.

1. Introduction

In previous work on cinnamaldehyde hydrogenation we have shown that different factors can enhance the selectivity to unsaturated alcohol. Thus on bimetallic platinum catalysts, the presence of electropositive metal atoms on the surface of platinum favours the adsorption and activation of the carbonyl group [1]. Graphite-supported catalysts were found much more selective than charcoal-supported ones [2]. This was attributed to an electron transfer from graphite to metal which decreases the probability for the activation of the C = C bond. A high selectivity to cinnamyl alcohol was observed on Y-type zeolite containing encaged metal particles because shape-selectivity effects in the zeolite micropores impose a tip-on adsorption of the molecule via the C = O group on the metal [3].

Geometric effects depending both on the morphology of the metal particles and on the steric configuration of α, β unsaturated aldehydes molecules are also expected to modify the selectivity. Thus it has been reported that large platinum [2] or cobalt [4] particles give a higher selectivity to cinnamyl alcohol than smaller ones. This work was intended to give new evidences of particle morphology effects in cinnamaldehyde hydrogenation and to propose an interpretation in terms of steric constraints for the adsorption of the molecule on a flat surface.

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2. Experimental

Platinum and rhodium catalysts were prepared by ion-exchange with $Pt(NH_2)_4^{2+}$ and $Rh(NH_3)_5Cl^{2+}$ cations of a high surface area graphite (Lonza HSAG 12, 300 m^2 g^{-1}) previously oxidized by NaClO treatment as previously described [2]. Catalysts Pt/G1 (3.6 wt% Pt) and Rh/G1 (3.4 wt% Rh) were obtained by reduction under flowing hydrogen at 573 K for 2 h of the ion-exchanged graphites. Catalysts Pt/G2 and Rh/G2 were prepared by heating Pt/G1 and Ru/G1 respectively at 773 K under hydrogen and at 1173 K under vacuum. The Pt/Al_2O_3 catalyst (1 wt% Pt) was prepared by a metal loading technique based on successive platinum atom depositions on small particles by surface, oxido-reduction reactions [5]. A Pt-Adams catalyst obtained from commercial source was reduced in liquid phase under standard pretreatment conditions before reaction either at 333 K (PtAd1) or at 373 K (PtAd2).

Pretreatment consisted in heating at 333 or 373 K under 4 MPa H_2-pressure, a slurry of the catalyst (400 mg) in a mixture of isopropanol (37.5 cm^3) water (10 cm^3) and sodium acetate (2.5 cm^3, 0.1 M). After two hours of pretreatment, cinnamaldehyde (0.1 mol) was introduced under H_2-pressure in the reactor and reaction was started by stirring the slurry (1500 rpm) at 333 K under 4 MPa H_2-pressure. The product distribution was followed by gas chromatography analysis of samples taken from the reaction mixture at specific time intervals.

The particle morphology was studied after reaction. The catalyst was filtered, washed with alcohol, ultrasonically dispersed in alcohol and deposited or a carbon-coated copper grid for transmission electron microscopic (TEM) examination with a JEOL 100 CX electron microscope.

3. Results and discussion

MORPHOLOGY OF THE CATALYSTS

Figure 1a is a TEM view of Rh/G1 taken through a thin slab of graphite. Rhodium particles are in the size range of 2–3 nm. They are selectively located on graphite steps as noticed previously for Pt/G1 [2]. This is because these catalysts prepared by ion exchange of oxidized graphites have acidic sites at the extremities of the basal planes acting as exchange sites for the metal precursor and as anchoring sites for the metal particles after reduction. Figure 1b gives a TEM view of Rh/G2 obtained by heating Rh/G1 at 1173 K. The particles are now in the size range 3–9 nm, they are facetted some of them with an hexagonal outline. This change in morphology is similar to that observed previously [2] upon heating Pt/G1 at 1173 K to obtain Pt/G2.

Figure 1c and 1d are the TEM images of PtAd1 and PtAd2 respectively. In the former, the metal is under the form of large agglomerates of 2–5 nm crystallite

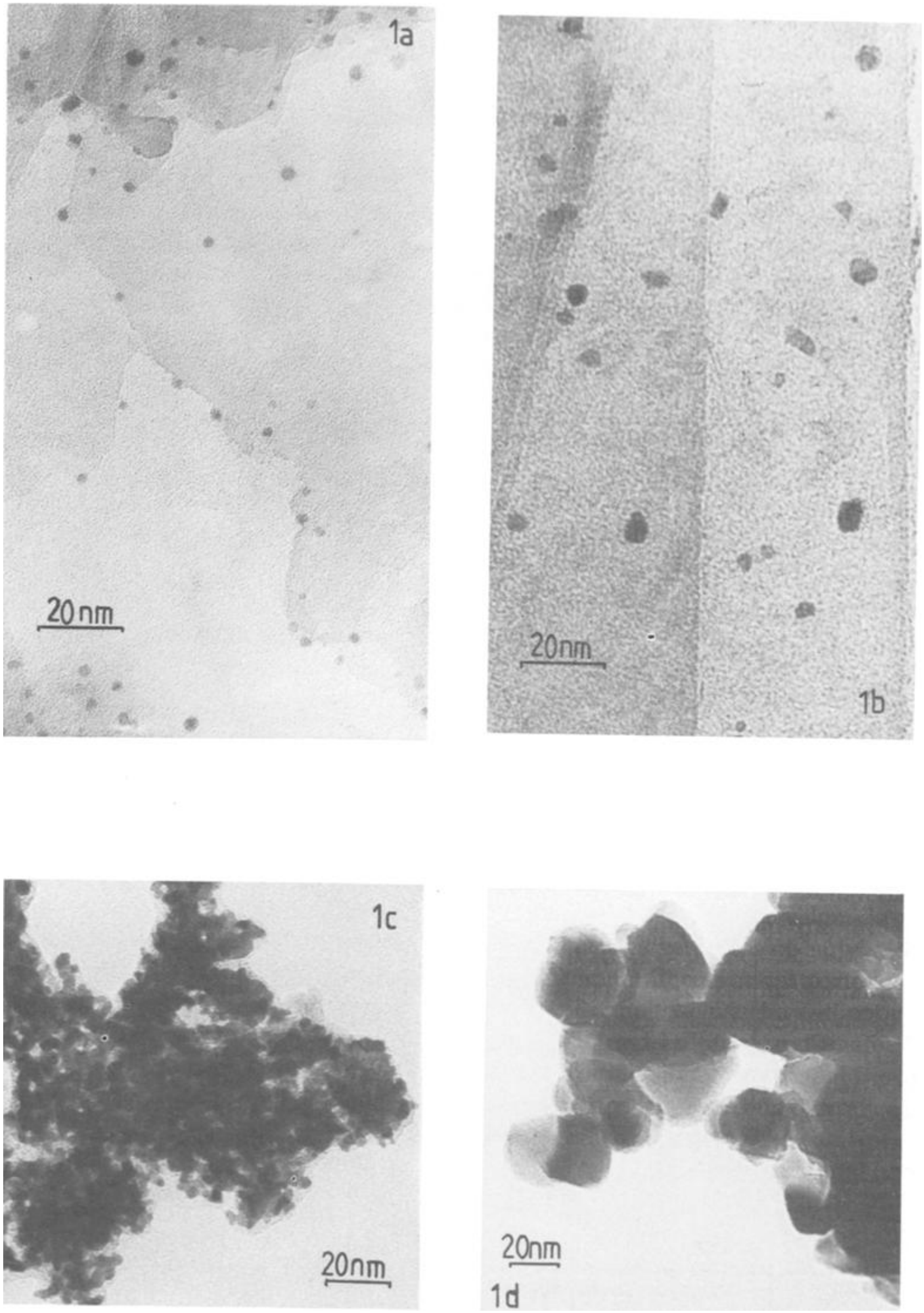

Fig. 1. TEM views taken with a JEOL 100 CX microscope. (a) Rh/G1, (b) Rh/G2, (c) PtAd1, (d) PtAd2.

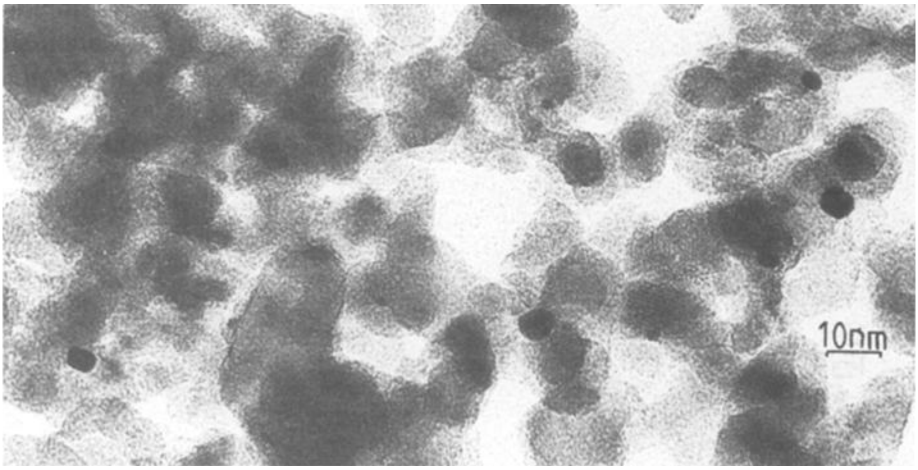

Fig. 2. TEM view of Pt/Al_2O_3 catalyst.

with a spongious texture whereas in PtAd2 large facetted particles in the size range 20–200 nm are observed. This indicates that an extensive sintering and recrystallisation of platinum occurs when the catalyst is pretreated at 373 K. Figure 2 is a view of Pt/Al_2O_3 prepared by multi-steps metal loading, most of the particles are in the range 4–6 nm with a facetted outline.

SELECTIVITY OF CINNAMALDEHYDE HYDROGENATION

Yields of cinnamyl alcohol (COL), hydrocinnamyl aldehyde (HCAL) and hydrocinnamyl alcohol (HCOL) as function of cinnamaldehyde (CAL) conversion are given in fig. 3a–d for Rh/G1, Rh/G2, Pt/Al_2O_3 and $PtAd_2$. Table 1

Table 1
Characteristics and selectivities to cinnamyl alcohol of catalysts at different conversions.

Catalysts	D [a] (nm)	X [b] (wt%)	T [c] (K)	S^0	S^{25}	S^{50}	S^{75}
Rh/G1	2–3(2.5)	3.4	373	12	14	18	20
Rh/G2	3–9(7)	3.4	373	32	36	42	45
Pt/G1 [d]	1–15(1.3)	3.6	333	72	78	83	
Pt/G2 [d]	3–6(5)	3.6	333	91	96	98	
Pt/Al_2O_3	4–6	1.0	373	74	76	72	
PtAd1	2–6	100	333	73	74	81	
PtAd2	20–200	100	373	90	90	93	

[a] particle size, average values in parentheses.
[b] wt% metal in the catalyst.
[c] temperature of pretreatment in liquid phase before reaction.
[d] from ref. [2].

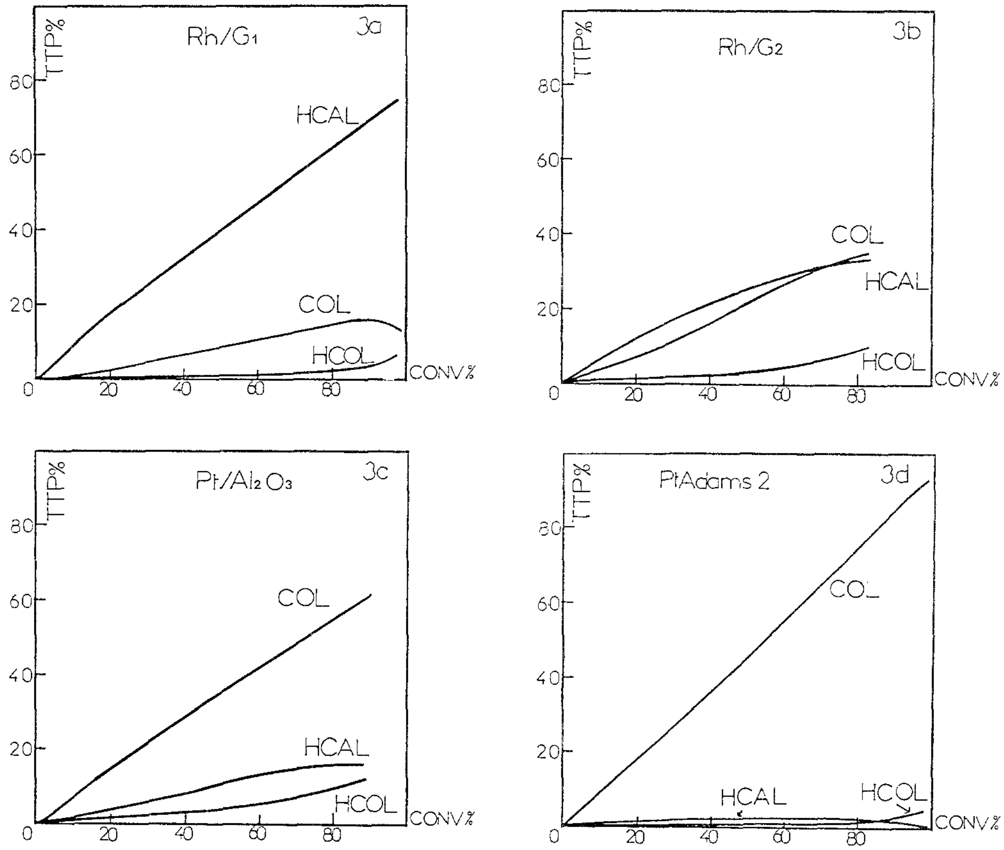

Fig. 3. Distribution of reaction products vs-conversion (a) Rh/G1, (b) Rh/G2, (c) Pt/Al_2O_3, (d) PtAd2.

gives the selectivity to COL at different conversions for all the catalysts investigated.

The reaction data on graphite-supported rhodium catalysts (fig. 3a, b, table 1) show that they give a low selectivity to COL. This is because rhodium is known to be highly active for the hydrogenation of $C=C$ double bonds. However, the interesting result is that Rh/G2 is much more selective than Rh/G1. Since the composition, the pretreatment conditions and the reaction conditions are identical for the two catalysts, the higher selectivity of Rh/G2 is attributed to the difference in particle morphology namely the presence of 7 nm-large, facetted particles in Rh/G2 compared to 2–3 nm particles in RhG1. Similar trends are observed for platinum catalysts, the 4–6 nm facetted Pt-particles in Pt/G2 are more selective than the 1–2 nm Pt-particles in Pt/G1 (table 1) and the large 20–200 nm crystals in PtAd2 more selective than the agglomerates of small crystallites in PtAd1 (table 1). The selectivities of Pt/G2 and PtAd2 are noteworthy ($S^0 = 91$, $S^{50} = 98$ and $S^0 = 93$, $S^{50} = 93$ respectively), such high selectivities are usually obtained only after promotion of platinum with metal salts [1,6] or on bimetallic catalysts [2,7]. Finally, the alumina-supported Pt-catalyst gives a reasonably good selectivity (fig. 3d, table 1) in spite of the fact that alumina is not a suitable support to obtain good selectivities to unsaturated alcohols in α, β unsaturated aldehyde hydrogenations [6]. This can also be attributed to the facetted morphology of the Pt-particles prepared by a technique which avoid the presence of small particles by making them grow by successive deposition of metal atoms [5].

All the results reported above point to the same conclusion namely that metal particles exhibiting large faces, at least compared to the dimension of the CAL molecule, are more selective than particles too small (< 2–3 nm) to present extended faces. This can be attributed to the different steric constraints experienced by the CAL molecule when it adsorbs on a flat or on a curved (stepped) metal surface. Indeed the planar CAL molecule is expected to adsorb on metal particles with its plane parallel to the metal surface. As the molecule approaches a flat surface, the phenyl group restrains a parallel landing of the molecule. Theoretical calculations show that to be associatively adsorbed on a metal surface, benzene or toluene [8,9] should pass an energy barrier culminating when these molecules are at 2.8 Å from the surface but which exerts a repulsive effect at distances larger than 3 Å. Since the phenyl group is never hydrogenated under the present reaction conditions it can be concluded that either it does not adsorb on the metal or if it adsorbs, the molecule remains bonded to the surface as a spectator ligand. Therefore, the reacting molecules in the adsorbed state should be tilted with respect to the plane of the flat surface, the phenyl group lying at 0.3 nm above the surface as illustrated in the scheme given in fig. 4. Simple molecular models show that the C = C bond remains comparatively far from the surface whereas there is no steric hindrance for the adsorption of the carbonyl group which can be activated and hydrogenated more easily than the C = C bond thus accounting for the high COL selectivity of Rh/G2, Pt/G2 and PtAd2 catalysts.

In contrast there is no steric constraint for the approach and adsorption of both the C = C and the C = O bonds on particles smaller than 2–3 nm because the phenyl group lies well above (aside) the metal surface as suggested by the scheme given in fig. 4. This accounts for the very low selectivity of Rh/G1 where the C = C bond is hydrogenated much more rapidly than the C = O bond as

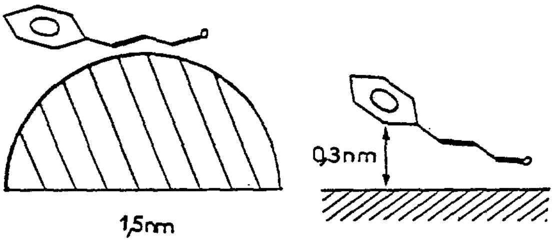

Fig. 4. Scheme of cinnamaldehyde adsorption on a small metal particle and on a flat metal surface.

expected for a rhodium catalyst. Thus the rate of C = C bond hydrogenation is ten times faster on Rh/G1 than on Rh/G2 because of the absence of steric effect.

4. Conclusion

This study provides an interesting example of chemioselectivity favoured by a combination of two complementary geometric effects: the morphology of the metal surface (molecular receptor) and the configuration of the cinnamaldehyde molecule (organic substrate). Indeed the selectivity to unsaturated alcohol is due to the presence of the phenyl group which, on a flat metal surface, imposes a tilt of the molecule favouring its adsorption via the carbonyl group. As in the case of cinnamaldehyde hydrogenation on zeolite-supported metals [3], this is a simple supramolecular catalytic system where the compatibility between the molecular receptor and the organic substrate determines the selectivity.

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