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 than 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$_2$)$_2$$^+$ and Rh(NH$_3$)$_3$Cl$^+$ 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$_2$O$_3$ 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 on 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