Catalysis Letters 3 (1989) 53–58

COMPOSITION AND CATALYTIC PROPERTIES IN CINNAMALDEHYDE HYDROGENATION OF CHARCOAL-SUPPORTED, PLATINUM CATALYSTS MODIFIED BY $FeCl_2$ ADDITIVES

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Received 30 January 1989; accepted 2 June 1989

The activity and selectivity of platinum for the liquid-phase hydrogenation of cinnamaldehyde into cinnamyl alcohol are improved by adding $FeCl_2$ to the reaction medium. Analytical microscopy shows that iron is deposited on Pt-particles. The reaction data are interpreted in terms of a dual-site mechanism.

1. Introduction

The liquid phase hydrogenation of unsaturated aldehydes to unsaturated alcohols can be performed with good selectivity on supported or unsupported platinum catalysts provided metallic salts are added to the reaction medium [1]. The beneficial role of iron chloride to improve platinum selectivity is well known from the early work of Tuley and Adams [2], and a number of other metallic salts have been used [3]. However, the mode of action of these additives remains obscure. Thus one does not know if the metal additives are fixed on the base metal, and there is doubt concerning their oxidation state. This work is intended to study the catalytic properties in cinnamaldehyde hydrogenation of a charcoal-supported platinum catalyst modified by $FeCl_2$ additives in solution in relation to the composition of the metal particles controlled by high-spatial resolution, analytical electron microscopy.

2. Experimental

The active charcoal (CECA 50S, 1400 m^2g^{-1}), purified by washing with hot hydrochloric acid, was oxidized by sodium hypochlorite solution (15% active chlorine) at 300 K for 24 h. The acidic groups thus created were ion-exchanged by stirring the support for 15 h in oxygen-free ammonia solutions of $Pt(NH_3)_4^{2+}$, $2OH^-$ previously obtained by treatment of $Pt(NH_3)_4Cl_2$ on an ion-exchange resin. The suspension was filtered, thoroughly washed with water and dried overnight in nitrogen atmosphere at 373 K. The final Pt/C catalyst loaded with 4 wt% platinum was obtained by heating the ion-exchanged charcoal under flowing hydrogen from 298 to 573 K at 1 K min^{-1} and kept at this temperature for 2 hours. The Pt/C catalyst (0.4 g) was stirred in a mixture of 37.5 ml of isopropanol, 2.5 ml of CH_3COONa, 0.1 M and 10 ml of an aqueous solution of $FeCl_2$ in the required amount. The slurry was heated at 373 K for 2 h in an autoclave pressurized with 40 bars of hydrogen. After this pretreatment, the temperature was regulated at 333 K and 0.1 mol of cinnamaldehyde was transferred without contact with air from a reservoir under hydrogen atmosphere to the autoclave under hydrogen atmosphere. After pressurization at 40 bars, the mixture was stirred at 1500 rpm. The reaction rate and product distribution were followed by gas chromatography analysis of samples taken from the reaction mixture at specific time intervals.

The size and distribution of platinum particles on the support were studied by transmission electron microscopy (TEM) using a Jeol 100 CX microscope. The charcoal grains were embedded in an epoxy resin and cut into thin slices with an ultramicrotome so that the distribution of particles in the microporous grains could be established. The composition of the metal particles was determined by energy dispersive X-ray emission (EDX) with a spectrometer attached to a field-emission gun, scanning transmission electron microscope (FEG-STEM) VG HB 501. The spatial resolution of analysis is as high as 1.5 nm so that the composition of individual particles at different location in a charcoal grain can be measured.

3. Results and discussion

MORPHOLOGY AND COMPOSITION

Figure 1 is a high magnification TEM view taken through an ultramicrotome cut of the Pt/C, 0.2 Fe catalyst taken out of the autoclave after cinnamaldehyde hydrogenation. The metal particles are distributed homogeneously throughout the charcoal grain since the concentrations of particles are similar near the edge and near the center of the cut. The particles are in the size range 1.5 to 5 nm. The sizes are homogeneous in a given grain. The composition of micro or nanodomains on the catalyst has been studied by quantitative EDX analysis with the FEG-STEM. When the measurements were performed on comparatively large areas on the charcoal grains (typically 1–10 μm^2) the Fe/Pt ratios are in good agreement with the nominal ratio Fe/Pt = 0.2 which means that on a micrometer-large scale the composition is homogeneous. EDX measurements carried out on individual metal particles indicate that platinum is always associated with iron. The Fe/Pt ratios measured on different particles in different charcoal grains vary from 0.05 to 0.3 however most of the values were found in the 0.1–0.2 range.

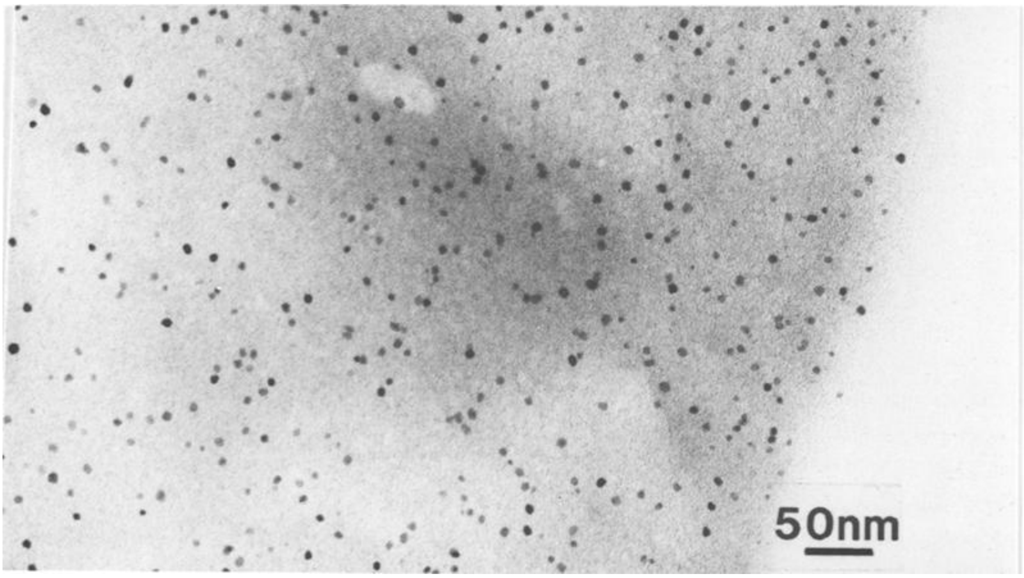


Fig. 1. TEM photograph taken through an ultramicrotome cut of Pt/C, 0.2 Fe catalyst after cinnamaldehyde hydrogenation.

In a given grain the particle sizes are homogeneous and the Fe/Pt ratios vary in a small range. The average Fe/Pt ratio is close to 0.12 which means that the particles are iron-deficient with respect to the nominal composition. Part of the iron is not associated with platinum, indeed some very large particles containing only iron were detected on the support.

These results prove that iron introduced in the autoclave under the form of a $FeCl_2$ solution is entirely deposited on the catalyst and more specifically on the platinum particles. Iron deposition is the result of an oxido-reduction process at the interface between the platinum surface and the solution. Indeed in an aqueous medium under hydrogen pressure the platinum takes the potential of the hydrogen electrode. Under the present treatment conditions in the autoclave ($pH = 7$, $P_{H_2} = 6$ MPa, $T = 373$ K) the potential of the hydrogen electrode is slightly lower than the reduction potential of Fe^{2+} ions so that they can be reduced by hydrogen dissociated on platinum. Since the process takes place at a temperature where the diffusion of iron atoms in the platinum lattice is unlikely, iron remains deposited as adatoms on the surface of platinum.

SELECTIVITY AND RATE OF CINNAMALDEHYDE HYDROGENATION

The initial rate of cinnamaldehyde (CAL) hydrogenation and the product distribution at different CAL conversion (cinnamyl alcohol: COL; hydrocinnamaldehyde: HCAL; hydrocinnamyl alcohol: HCOL) are given in table 1 for

Table 1
Selectivities to cinnamyl alcohol at different conversions [a]

Catalysts	Fe/Pt [b]	S^0	S^{25}	S^{50}	S^{75}
4% Pt/C	0	32	56	68	68
4% Pt/C + $FeCl_2$	0.1	64	82	88	88
4% Pt/C + $FeCl_2$	0.2	70	80	87	87
4% Pt/C + $FeCl_2$	0.3	69	76	83	85
4% Pt/C + $FeCl_2$	0.5	56	82	89	86

[a] S^0, S^{25}, S^{50}, S^{75} selectivities at 0, 25, 50 and 75% conversion.
[b] Fe/Pt nominal ratio.

different amounts of $FeCl_2$ additives introduced in the autoclave containing the slurry of 4 wt% Pt/C catalyst. The initial hydrogenation rate of CAL and the initial selectivity to COL are plotted in figs. 2a and b respectively as a function of the nominal Fe/Pt ratios.

Figures 2a and 2b show that both the initial rate and the initial selectivity increase in the presence of $FeCl_2$ additives with an optimum amount close to

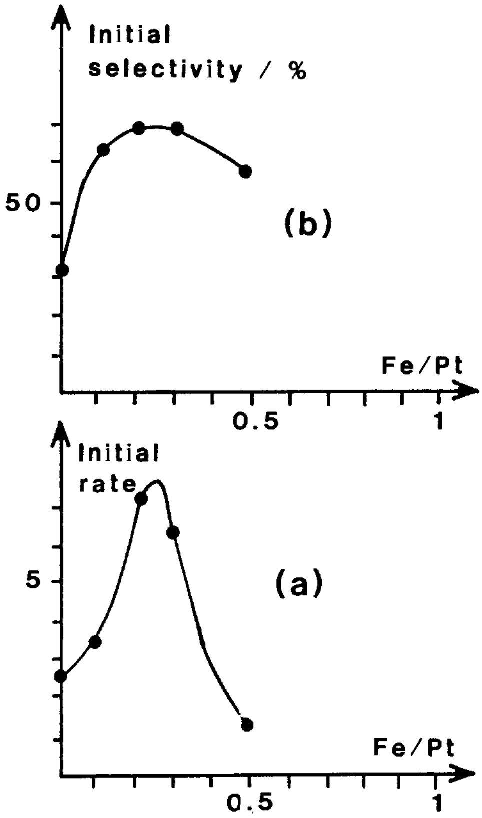
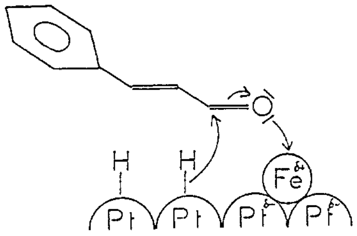


Fig. 2. (a) initial rate of cinnamaldehyde hydrogenation (10^{-3} mol min^{-1} g^{-1} (cata); (b) initial selectivity to cinnamyl alcohol.

Fe/Pt = 0.2. A maximum of CAL rate was also observed for the same Fe/Pt ratio in the case of a Pt-Fe/charcoal catalyst prepared by coimpregnation and high temperature H_2-reduction [5].

Therefore, iron atoms associated with platinum in the same particle, as shown by analytical electron microscopy, favors the hydrogenation of the C=O group and thus, the overall rate of CAL hydrogenation and the selectivity to COL. We suggest the following interpretation. The iron adatoms on the surface of platinum particles are positively charged either because they are incompletely reduced or because there is an electron exchange from iron atoms to platinum atoms as iron is much more electropositive than platinum. Accordingly, in the case of the Pt-Fe/charcoal catalysts [5], an increase in the electron density of platinum was detected both by XANES [6] and by the change in the relative adsorption coefficients of toluene and benzene [7]. The electron deficient iron adatom can act as an adsorption site for the C=O group of the cinnamaldehyde molecule via donation of electrons from one of the unshared electron pairs of the oxygen atom. The first step of the hydrogenation of the CO bond with hydrogen atoms adsorbed on nearby platinum atoms is tentatively described by the following scheme 1.



Scheme 1

Note that the selectivity of the Pt/charcoal catalyst promoted with iron is also improved by a lower rate of hydrogenation of the C=C bond. This could be due to the higher charge density on platinum, which decreases the probability of the activation of the C=C bond involving as a first step an electron donation of π-electron to the metal. A similar interpretation was used to explain why graphite-supported platinum has a much better selectivity than charcoal-supported platinum [7].

As expected for a bimetallic catalyst where each of the component plays a specific role in the reaction mechanism, there is an optimum activity for a given proportion of the two components on the surface. In the present system the maximum is found near a nominal composition Fe/Pt = 0.2 but STEM-EDX measurements have shown that the real average composition of individual particles was Fe/Pt = 0.12. This corresponds to less than a monolayer of iron atoms in close packing on the surface of the particles in the 1–5 nm range. Any increase in the number of iron atoms results in a lower activity either because there are too many iron-covered platinum atoms which are unable to dissociate hydrogen as in the Pt-Mo catalysts studied previously [8,9] or because the CAL molecule could not approach the surface close enough for the mechanism of hydrogenation of the C=O group described above to be operative.

4. Conclusion

This study confirms early findings on the promoting effect of $FeCl_2$ on platinum activity and selectivity in cinnamaldehyde hydrogenation to cinnamyl alcohol. It has been shown that part of the iron atoms are deposited on the surface of charcoal-supported platinum particles as a result of an oxido-reduction reaction between adsorbed hydrogen on the surface and Fe^{2+} ions in solution. The bimetallic catalyst system thus obtained behaves like Pt-Fe alloys prepared by high-temperature reduction of co-impregnated charcoal i.e. there is a volcano-type curve for both the activity and selectivity as a function of the iron content. This is interpreted by a dual-site mechanism whereby electron acceptor $Fe^{\delta+}$ species at the surface of platinum act as adsorption sites for the cinnamaldehyde molecule via the oxygen atom. The C=O bond thus activated is hydrogenated by hydrogen dissociated on nearby Pt atoms which also maintains the iron in a low oxidation state.

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