

TiO₂-carbon xerogel composites as supports in the preparation of Pt catalysts for selective hydrogenation

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Introduction

In the last decades, considerable efforts have been devoted to the development of heterogeneous catalysts able to perform efficient selective hydrogenation of the carbonyl function in α,β -unsaturated aldehydes, to yield the corresponding unsaturated alcohols, which are important intermediates in organic synthesis of fine chemicals for several industries, such as flavor, fragrance and pharmaceutical. Unfortunately, high selectivities towards these alcohols are difficult to achieve, since thermodynamics favors the hydrogenation of the C=C over the C=O bond and due to kinetic reasons, as the reactivity of the olefinic bond is higher than that of the carbonyl. To increase selectivity, the thermodynamic constraint must be reduced, e.g. by a preferential adsorption of the carbonyl function at the catalyst surface. Pt supported on TiO₂ seems to be able to promote the hydrogenation of the carbonyl group due to a Strong Metal Support Interaction (SMSI) effect [1], resulting from the partial coverage of Pt particles with reduced TiO_x. This is achieved during high temperature reduction treatment, creating active sites at the metal-support interface, which can selectively hydrogenate the C=O function. Other supports with some semiconductor properties, but with a different nature, such as carbon nanotubes, gave interesting results for the selective hydrogenation of cinnamaldehyde [2]. Motivated by these findings, we studied the effect of incorporating carbon xerogels in a TiO₂ matrix, and used the resultant materials as supports in the preparation of Pt catalysts. The activity and selectivity of the developed catalysts was assessed in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

Experimental

The preparation of TiO₂-carbon xerogel (TiO₂-CX) composites involved a similar procedure described elsewhere for the preparation of TiO₂-MWCNT composites from alkoxide precursors, according to an acid catalyzed sol-gel method [3]. Carbon xerogels in different amounts, and with varying surface chemistry, were incorporated during the sol-gel procedure. Platinum catalysts, containing 5wt.% metal loading, supported on the TiO₂-CX composites, were then prepared by the photochemical deposition method.

Hydrogenation of cinnamaldehyde was carried out in a 100 mL well-stirred stainless steel reactor at 363 K and 10 bar of H₂ pressure. Product analysis was performed in a DANI GC 1000 gas chromatograph, equipped with a flame ionization detector.

Results and discussion

High Resolution Transmission Electron Microscopy observations of the Pt catalysts supported on the TiO₂-CX composites, regardless of the carbon xerogel used, show that a thin layer of amorphous carbon covers the TiO₂ particles, acting as an adhesive agent of the TiO₂ and Pt particles. The Pt particles were observed to form strong interfaces with the TiO₂-CX supports.

The catalytic results obtained are shown in Table 1, where are indicated the reaction time needed to achieve 50% cinnamaldehyde (CAL) conversion and the selectivities towards cinnamyl alcohol (S_{COL}), hydrocinnamaldehyde (S_{HCAL}) and hydrocinnamyl alcohol (S_{HCOL}).

Table 1. Catalytic results obtained for the hydrogenation of CAL at 363 K and 10 bar, using the Pt/TiO₂-carbon xerogel and Pt/TiO₂ catalysts (results measured at 50% conversion)

Catalyst	time (min)	S_{COL} (%)	S_{HCAL} (%)	S_{HCOL} (%)
Pt/TiO ₂	7	82	5	13
Pt/TiO ₂ -1wt.% CX	25	84	5	11
Pt/TiO ₂ -1wt% CX O ₂ oxidized	27	85	5	10
Pt/TiO ₂ -1wt% CX nitric acid oxidized	28	85	4	11
Pt/TiO ₂ -5wt.% CX O ₂ oxidized	56	80	7	13

Analysis of Table 1 shows that all tested catalysts are very selective towards the formation of COL, values between 80 and 85% being obtained. There are however slight differences depending on the amount of carbon xerogel incorporated in the composite support. When 1wt.% of carbon xerogel is incorporated, regardless of the carbon xerogel nature, the selectivity towards the formation of COL is slightly increased when compared with that found when using the Pt/TiO₂ catalyst. This is due to the enhanced SMSI effect, resulting in improved catalytic properties at the metal-support interface (active sites responsible for catalytic selectivity). This increase in selectivity is followed by a decrease in catalytic activity, since, as carbon xerogel acts in the catalyst as an adhesive agent, it will partially cover and decrease the number of available active sites (at the metal surface and metal-support interface) for cinnamaldehyde adsorption. When the amount of incorporated carbon xerogel is increased to 5wt.%, the coverage effect is more pronounced, a high reduction of activity being observed, followed by a slight reduction in the selectivity to COL formation.

Conclusions

Pt catalysts supported by photodeposition on TiO₂-carbon xerogel composites prepared by sol-gel techniques (5wt.% Pt) were found to be very selective in the liquid-phase hydrogenation of cinnamaldehyde to cinnamyl alcohol. The incorporation of carbon xerogel in TiO₂ was beneficial to improve the catalytic properties of the resulting material, which is probably explained in terms of a SMSI effect, due to the strong interface interaction of the Pt with the support.

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References

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