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Enhancing the catalytic performance of Pt/ZnO in the vapour phase hydrogenation of crotonaldehyde by the addition of Cr to the support

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Abstract

An impressive enhancement of the catalytic performance of platinum in the vapour phase selective hydrogenation of crotonaldehyde (2-butenal) has been achieved by modifying a ZnO support by addition of Cr(III) cations. The addition of chromium enhances the structural properties of the support (larger surface area) and increases its reducibility. The presence of chromium in the support enhanced the catalytic activity and the selectivity towards the unsaturated aldehyde in such a way that the Pt/Cr–ZnO catalyst showed the best results (in terms of yield and stability) published until now. The improved behaviour of this catalyst has been explained on the basis of the high support reducibility and a proper metal-support interaction.

Keywords: Crotonaldehyde hydrogenation; ZnO support; Pt catalysts

1. Introduction

The selective hydrogenation of the carbonyl bond in α,β-unsaturated aldehydes with supported metal catalysts is still a challenge in heterogeneous catalysts. As an example, the use of monometallic platinum catalysts mainly leads to the formation of the saturated aldehyde, which is the most favoured product from the thermodynamic and kinetic points of view [1]. Therefore, the promotion of the metal is necessary in order to increase the selectivity toward the formation of the desired unsaturated alcohol.

It is widely reported that some oxide supports can provide the desired promotion of platinum [2]. In these cases, the possible interaction of platinum with the partially reduced oxide [3–7], or even with the metal [8,9], formed upon a reduction treatment has been proposed to be responsible for the improved selectivity. When platinum is supported on ZnO, the onset of electronic and ensemble effects is well known [10]. The electronic effects are due to free electrons produced upon the partial reduction of ZnO to Zn, these free electrons being donated to Pt. The resulting increase in electron density of Pt enhances its catalytic properties [11]. The reducibility of ZnO can be increased through valence induction by doping the oxide support with cations having a formal charge greater than 2. The addition to the support of an appropriate doping cation in the proper amount can also increase the BET surface area by suppressing the ZnO crystal growth [11]. This communication reports the effect of the addition of Cr(III) to ZnO on the catalytic behaviour of supported platinum in the vapour phase hydrogenation of crotonaldehyde. Very interesting results have been found in terms of activity and selectivity towards the hydrogenation of the carbonyl bond. The yield to crotyl alcohol obtained in this work is 20 times larger than the best results reported up to now in the free literature [12,13].

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2. Experimental

The supports were prepared by a homogeneous co-precipitation method. An aqueous solution (pH 9) of $Zn(NO_3)_2 \cdot H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and $CO(NH_2)_2$ was gently heated up to 465 K. The precipitate formed was centrifuged and calcined in air at 773 K. Two supports were prepared: pure ZnO and Cr-doped ZnO (Cr–ZnO) (Cr/Zn atomic ratio of 0.12), which were characterized by X-Ray diffraction, Raman spectroscopy and N_2 adsorption at 77 K. For the preparation of the catalysts, the supports were immersed into an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and stirred for 24 h. Then, the excess of solvent was removed by evaporation, and the obtained solids were calcined in air at 773 K for 2 h. The platinum content in both samples was 0.34 wt.%. The catalysts obtained were labelled as Pt/ZnO and Pt/Cr–ZnO, and were characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) after being reduced *in situ* at two temperatures (473 K and 623 K). The catalytic behaviour in the vapour phase hydrogenation of crotonaldehyde (2-butenal) was tested in a microflow reactor at atmospheric pressure under differential conditions. Before the determination of their catalytic behaviour, the catalysts were reduced *in situ* at the two temperatures noted above, under flowing hydrogen (50 ml min^{-1}), and then cooled to the reaction temperature. Finally, they were contacted with a reaction mixture (total flow: 50 cm^3 min^{-1}; H_2/aldehyde ratio of 26) of hydrogen and crotonaldehyde (Fluka, >99.5%). The concentration of reactants and products was determined by online GC with a Carbowax 20 M 58/90 semicapillary column.

3. Results and discussion

The BET surface areas (N_2 adsorption at 77 K) were low for ZnO and Cr–ZnO supports (1 m^2 g^{-1} and 11 m^2 g^{-1}, respectively). The Cr–ZnO support presents larger surface area and smaller ZnO crystal size (19.1 nm) than the pure ZnO support (42.2 nm). On the other hand, the X-ray diffraction pattern shows the presence of a small amount of $ZnCr_2O_4$ spinel phase. The formation of this mixed oxide has also been assessed by Raman spectroscopy [14].

The temperature-programmed reduction (TPR) profiles are shown in Fig. 1. The profile corresponding to the Pt/ZnO catalysts shows a peak centred at 480 K, which can be assigned to the reduction of oxidized Pt species, together with a part of the ZnO support in close contact with the platinum particles. On the other hand, the TPR profile of the Pt/Cr–ZnO catalysts shows a sharp H_2 consumption peak, centred at 515 K, which it assigned to the reduction of support in close contact with platinum particles, together with a small shoulder at lower temperatures that may be due to the reduction of oxidized platinum species. Although the maximum rate of hydrogen consumption is produced at a higher temperature, the amount of hydrogen consumed (it has not been quantified) is much larger, this producing a larger amount of metallic Zn and free electrons in the support.

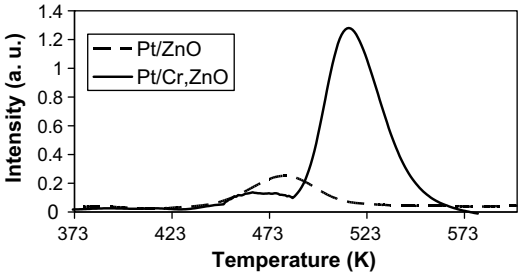

Fig. 1. Temperature-programmed reduction (TPR) profiles for both catalysts.

The *in situ* reduced catalysts (473 and 623 K) have been characterized by XPS. Table 1 shows the binding energies of the $Pt4f_{7/2}$ peaks, as well as the Pt/(Cr + Zn), Cl/Pt, and Cr/Zn atomic ratios. In both catalysts, and after both reduction treatments, the core-level spectra showed the presence of only one component at binding energy 71.2 ± 0.3 eV. While binding energies about 70.5–70.7 eV are characteristics of metallic platinum, [15,16] the shift of the of Pt 4f binding energy to higher values (71.2 eV) has been attributed to final state effects due to reduced screening of the photo hole after electron emission in small particles [17]. In fact, the presence of small particles has been observed by TEM. XPS also reveals an increased dechlorination of catalysts with increasing the reduction temperature. Furthermore, this increase in the reduction temperature does not produce important changes in the surface distribution of Cr or Pt species.

TEM micrographs of the catalysts were acquired after reduction at 623 K. The results show that good and homogeneous platinum dispersion was achieved in both catalysts. In order to evaluate the degree of dispersion of platinum on the support a set of high magnification images were analyzed. Thus, a great number of platinum particles were measured. The mean platinum particle size was 1.7 nm in Pt/ZnO, and 1.8 nm in Pt/Cr–ZnO. The good dispersion is attributed to the strong interaction between the platinum precursor (acid solution) and the supports (basic character).

Fig. 2 shows the evolution of the overall activity (micromoles of crotonaldehyde transformed per gram of platinum and per second) at 373 K, as a function of time on

Table 1
XPS characterization results

Catalysts	T_{red} (K)	Pt/(Cr + Zn)	Cl/Pt	Cr/Zn	B.E. Pt $4f_{7/2}$ (eV)
Pt/ZnO	473	0.059	1.35	0	71.3
	623	0.049	0.32	0	71.2
Pt/Cr–ZnO	473	0.051	3.9	0.18	71.3
	623	0.058	2.1	0.16	71.2