

# COBALT CATALYSTS SUPPORTED ON ACTIVATED CARBONS WITH DIFFERENT SURFACE PROPERTIES

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## Introduction

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to unsaturated alcohols is a very important reaction in the field of fine chemicals production. It is not easy to find a catalyst which is selective in this reaction; indeed, the most common hydrogenation catalysts, such as Ni, Pd or Pt, preferentially hydrogenate the C=C bond, thus yielding the saturated aldehydes [1]. However, cobalt based catalysts have been reported to show a higher selectivity to unsaturated alcohols [2,3]. In the case of carbon-supported platinum-based catalysts, it has been recently reported that the catalytic behavior of platinum can be modified by support effects. Thus, the use of oxidized activated carbons as supports for platinum produces catalysts which yield a very high selectivity towards crotyl alcohol in the gas phase hydrogenation of crotonaldehyde (*trans*-2-butenal) [4]. This effect seems to be related with sites on the support created upon the reduction-desorption of the oxygen surface groups during the thermal pretreatments of the catalyst. This communication reports the preparation, characterization and catalytic behavior in the gas phase hydrogenation of crotonaldehyde of cobalt based catalysts supported on activated carbons with different surface properties.

## Experimental

Supports have been prepared from a parent activated carbon (AC1) by subjecting it to different treatments. AC1 was prepared from olive stones, by carbonization under a nitrogen flow (1223 K, 2h) and further activation with steam (1123 K, 3h). On one hand, it was subjected to an oxidizing treatment with H<sub>2</sub>O<sub>2</sub> 12 N to yield support AC1<sub>ox</sub>. On the other hand, support AC1 was washed with an aqueous hydrochloric acid solution to remove inorganic impurities, and then heat treated under nitrogen at 1273 K to remove the surface complexes (support AC2). The latter was also oxidized with H<sub>2</sub>O<sub>2</sub> to yield support AC2<sub>ox</sub>, a part of which was treated at 773 K under nitrogen to remove the less stable surface complexes (support AC2<sub>ox</sub>T). These supports were characterized by nitrogen adsorption at 77 K, temperature-programmed desorption, determination of their pH<sub>slurry</sub> and X-ray fluorescence. Cobalt catalysts were prepared by the incipient wetness method; thus,

the supports were impregnated with the minimum amount of aqueous solutions of cobalt (II) nitrate of the appropriate concentration to achieve a metal loading of 5 wt%. They were characterized by temperature-programmed desorption (TPD), temperature-programmed reduction (TPR) and hydrogen chemisorption, and their catalytic behavior in the gas phase hydrogenation of crotonaldehyde was studied, under differential conditions, after reduction at several temperatures.

## Results and discussion

Table 1 reports the pH<sub>slurry</sub> values for the five supports, as well as the amount of carbon monoxide and carbon dioxide evolved during TPD runs under an inert atmosphere. Both unoxidized supports, AC1 and AC2, show basic properties in solution; the introduction of oxygen surface groups upon oxidation with H<sub>2</sub>O<sub>2</sub> lowers the pH<sub>slurry</sub> of the samples due to the creation of acidic surface groups. Data in Table 1 also indicate the different surface composition of the supports, which is evident from the amount of CO and CO<sub>2</sub> evolved in TPD experiments as a result of the decomposition of the oxygen surface groups.

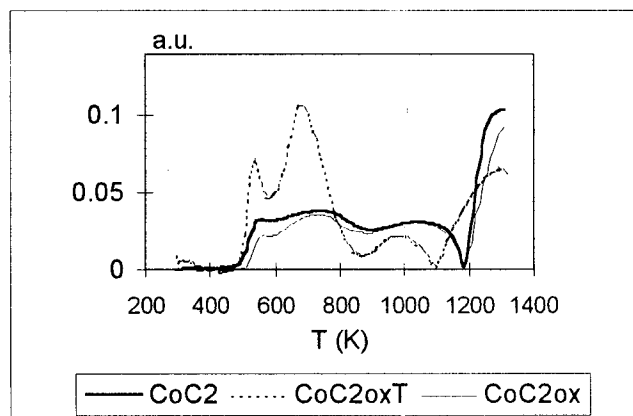
**Table 1.** Some surface characteristics of the supports.

Support	pH <sub>slurry</sub>	CO evolved (μmol/g)	CO <sub>2</sub> evolved (μmol/g)
AC1	10.0	980	980
AC1 <sub>ox</sub>	7.7	1840	1110
AC2	10.4	70	76
AC2 <sub>ox</sub> T	8.3	405	109
AC2 <sub>ox</sub>	7.7	490	240

The impregnation of the supports with aqueous solutions of cobalt (II) nitrate (pH: 4.9) also creates oxygen surface groups due to the oxidation of the carbon support with nitrate and/or nitric acid species. This will favor the support-metal precursor interaction, given that the pH<sub>slurry</sub> of the supports will approach that of the impregnating solution. In this way, it is important not only to know the surface properties

of the support (the  $\text{pH}_{\text{support}}$ , as an example), but also how it is affected by the impregnating solution and the metal precursor.

The interaction between the support and the metal precursor can be followed by analyzing the temperature-programmed reduction profiles of the resulting catalysts. Figure 1 shows the TPR profiles obtained with fresh samples prepared with the purified supports AC2 and related supports ( $\text{AC2}_{\text{ox}}$  and  $\text{AC2}_{\text{oxT}}$ ). In all cases hydrogen consumption is plotted, except for high temperatures (from 1100 K or 1200 K up), where hydrogen evolution is plotted. This hydrogen evolved at high temperature is a result of hydrogen desorbing from the metal surface and hydrogen desorbing from the support. It can be seen that similar profiles are obtained for  $\text{Co}/\text{AC2}$  and  $\text{Co}/\text{AC2}_{\text{ox}}$ , but that of  $\text{Co}/\text{AC2}_{\text{oxT}}$  is somewhat different. In all cases, three peaks of hydrogen consumption can be envisaged. The first of them, at about 550 K, is related to the reductive decomposition of the cobalt precursor attached to the surface of the support; the second one, at about 680 K, is probably due to the reduction of  $\text{CoO}$  and finally, the broad peak at about 1000 K may be due to the catalyzed gasification of the carbonaceous support to yield methane.



**Figure 1.** Temperature-programmed reduction profiles for fresh  $\text{Co}/\text{AC2}$ ,  $\text{Co}/\text{AC2}_{\text{ox}}$  and  $\text{Co}/\text{AC2}_{\text{oxT}}$  catalysts.

The catalytic behavior of the samples in the gas phase hydrogenation of crotonaldehyde has been evaluated after reducing the catalysts at 623, 723 and 773 K for 12 h under a hydrogen flow. Both the catalytic activity and the selectivity towards crotyl alcohol (hydrogenation of the  $\text{C}=\text{O}$  double

bond) decrease after reduction at 773 K. The loss of catalytic activity can be explained on the basis of an increase in the metal particle size by sintering; the decrease in selectivity may be due to an increase of the amount of metallic cobalt in the samples. It is well known that a certain amount of ionic  $\text{Co}^{\text{II}}$  species is needed for the catalyst to show some selectivity towards the unsaturated alcohols [5]. On the other hand, the catalytic behavior of the different samples becomes closer after reduction at 773 K.

Table 2 reports the results of catalytic activity and selectivity of the different samples after reduction at 723 K and for a reaction temperature of 333 K. The presence of oxygen surface groups on the support produces an increase in the total activity and in the selectivity towards the production of crotyl alcohol. The selectivity is much more enhanced in catalysts prepared with supports containing inorganic impurities, whereas the activity is hardly affected. Anyway, this behavior is somewhat softened when the reaction is carried out at a higher temperature, i.e., at a higher conversion degree. The higher selectivity of catalyst  $\text{Co}/\text{AC1}_{\text{ox}}$  could be due to the beneficial effects of both the oxygen surface groups on the support and inorganic impurities.

**Table 2.** Catalytic behavior of activated carbon supported cobalt catalysts after reduction at 723 K. Reaction temperature: 333 K.

Catalyst	Activity ( $\mu\text{mol/s/gCo}$ )	Selectivity (%)	Conv. (%)
$\text{Co}/\text{AC1}$	16	6	10
$\text{Co}/\text{AC1}_{\text{ox}}$	19	33	12
$\text{Co}/\text{AC2}$	15	7	14
$\text{Co}/\text{AC2}_{\text{oxT}}$	22	9	12
$\text{Co}/\text{AC2}_{\text{ox}}$	35	12	17

## References

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