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Effect of the support and added oxides on the bistability observed in the oxidative dehydrogenation of 2-propanol over copper-supported catalysts

A. Gil *, P. Ruiz, B. Delmon

Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2 / 17, Louvain-la-Neuve 1348, Belgium

Abstract

A bistability phenomenon has been observed in the oxidative dehydrogenation of 2-propanol over supported copper catalysts. Cu/Al_2O_3 and Cu/CeO_2 have been prepared by room temperature adsorption of the copper amino complex on the supports. The comparison of the hysteresis observed when the partial pressure of oxygen is varied, indicates that there is an important effect of the support. This effect is explained by the variation in specific surface areas of the supports and in their reducibilities. The possible influence of a second phase (α-Sb_2O_4, SnO_2, Bi_2O_3 and NiO) added to the copper catalysts has also been studied.

Keywords: Oxidative dehydrogenation; 2-Propanol oxidative dehydrogenation; Bistability; Copper-supported catalysts; Hysteresis loops

1. Introduction

Bistability phenomena and oscillatory behaviour in heterogeneous catalysis have attracted considerable attention in the last years [1–5]. These phenomena have been observed in various catalytic systems. Thus, they have been explained on the basis of various kinetic mechanisms. Most interpretations assume a change of composition or structure of the catalyst surface. The present study concerns phenomena observed with copper-supported catalysts. Greger et al. [6] have shown the existence of a bistability when a Cu/Al_2O_3 catalyst was used in propene oxidation. The acrolein and CO_2 production rates exhibited hysteresis loops. The authors suggested that the bistability was due to a re-oxidation of CuO_2 to CuO under non-equilibrium conditions. Amariglio et al. [7] confirmed these results, using pure copper oxide as catalyst. The dehydrogenation of 2-propanol is a very interesting model reaction catalysed by copper. In the absence of oxygen, 2-propanol is dehydrogenated into acetone. In the presence of oxygen, another reaction takes place, namely the oxidative dehydrogenation (production of acetone and water) [8]. This last reaction depends of the partial pressure of oxygen. This can be related to the oxidation state of copper.

In a previous work [9], we reported results concerning the dehydrogenation of 2-propanol

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* Corresponding author. Present address: Departamento de Química Aplicada, Universidad Pública de Navarra, Campus de Arrosadía, Pamplona 31006, Spain.

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over unsupported copper catalysts. We observed hysteresis loops when the oxygen pressure was modified. This phenomenon had been explained by the oxidation and reduction of copper under the conditions of the catalytic test. The idea of the present work was to investigate whether a support known for storing oxygen, namely CeO_2 would influence the oxidation and reduction of Cu in a different way when compared to Al_2O_3. The reason was that many cases are now known in which a phase distinct from that possessing the catalytic activity can control the catalytic activity, because it produces spillover species [10]. This phenomenon is the basis of the remote control concept. We hoped that the phenomena observed in the oxidative dehydrogenation of 2-propanol at 150°C could clarify several effects observed in oxidation reactions at higher temperatures. Along the same idea, possible influence of various oxides simply mixed with the catalysts (α-Sb_2O_4, SnO_2, Bi_2O_3 and NiO) has also been investigated.

2. Experimental

The catalysts were prepared by room temperature adsorption of the amino complex of copper on the supports. The copper amino complex was prepared from a solution of copper(II) acetate monohydrate (Aldrich, 98%). The concentrations were adjusted to obtain catalysts with ca. 5 wt% copper content. Al_2O_3 (Procatalyse, specific surface area = 234 m^2/g and specific pore volume = 0.67 ml/g) and CeO_2 (Janssen Chimica, 99.9%; specific surface area = 19 m^2/g and specific pore volume = 0.05 ml/g) were used as supports. The pH reached by the preparation mixture was 13. After 24 h, the solids were filtered and washed. The catalysts were dried at 110°C for 14 h and calcined at 300°C for 4 h. The copper content was 0.4 and 2.7 wt% for Cu/CeO_2 and Cu/Al_2O_3, respectively. Using these values, the copper content calculated as copper per specific surface area, was almost identical.

In order for both copper catalysts to be stabilised, the samples were subjected to a cyclic variation of conditions, namely several consecutive hysteresis loops. Catalysts were subjected to reduction, before the first and after all the consecutive hysteresis loops (conditions indicated below).

Mechanical mixtures with various oxides (50–50 wt%) were prepared by dispersing under agitation the already stabilised and reduced catalysts together with selected oxide powders (α-Sb_2O_4, SnO_2, Bi_2O_3 or NiO) in *n*-pentane (Aldrich, 98%GC). This operation was followed by evaporation of *n*-pentane at room temperature under reduced pressure and drying at 110°C. To allow perfect comparison, the pure copper catalysts after the consecutive hysteresis loops and the pure oxides were subjected to the same treatment with *n*-pentane and drying. The 2-propanol feed (Aldrich, 99 + %) was purified with activated molecular sieves and stored in a thermostated gas saturator at 38°C. The He (99.995%, Air Liquide) flow rate coming into the saturator was controlled by means of a Brooks 5850 TR mass flow controller. The amount of copper catalyst present in the mechanical mixture for the catalytic test was the same that when the catalytic test was carried out with the copper catalyst alone. Prior to reaction, the catalysts (200–316 μm) were again reduced under the standard conditions, namely at atmospheric pressure for 1 h at 200°C with 60 $cm^3/min\ g_{Cu}$ of H_2 (99.9%, Air Liquide, treated with a Chrompack clean-oxygen filter).

Catalytic measurements were carried out in a small laboratory U-shaped glass reactor at 150°C and nearly atmospheric pressure. The oxygen pressure in the feed was varied and the ratio W/F_{Ao} (0.07 and 0.17 g_{CuO} h/mol 2-propanol for Cu/Al_2O_3 and for Cu/CeO_2, respectively) was kept constant for all experiments. Each experimental point was measured after 20 min of reaction in the conditions and the experiment was stopped when no reaction could be detected any more. For the recovery of reaction, it was necessary to wait 1 h for each oxygen pressure to reach the new steady state. The reactants and the products were analysed by on line gas chromatography (Hewlett Packard 5880 A) with a ParaPLOT Q column (25 m × 0.32 mm, df = 10 μm; 150°C). The main product of reaction is acetone. In presence of oxygen in the feed, some water is detected. The results presented here were verified using new preparations of catalysts and mechanical mixtures. The reproducibility of the results was found to be better than 10%.

The catalyst samples were characterised before and after the catalytic tests by XPS using a Surface Science Instruments, SSI-XPS. The excitation radiation was Mg K_α (1253.6 eV). Binding energies were calculated taking as reference the C 1s (284.8 eV) peak of carbon contamination.

3. Results

3.1. Copper-supported catalysts

The evolution of the conversion of 2-propanol as a function of the oxygen pressure is presented in Fig. 1 in the case of Cu/CeO_2. After reduction of the catalyst, the conversion at $P_0 = 0$ corresponds to simple dehydrogenation of 2-propanol. When oxygen is introduced in the reactant mixture, the oxidative dehydrogenation of 2-propanol also takes place. For a certain value of the oxygen partial pressure ('higher critical pressure'), the catalyst almost completely loses its activity. The oxygen partial pressure is then decreased. At a certain value ('lower critical pressure'), the conversion increases considerably, although the initial activity is not completely recovered. The whole experiment, consisting in first increasing and finally decreasing the oxygen partial pressure thus show a hysteresis. This has been explained by a transition between Cu(0) and Cu(I) [9]. Consecutive hysteresis loops are also presented in Fig. 1. Between these loops, the catalyst was treated by reduction, as described in the experimental section. No modification of the critical oxygen pressures was observed, only a change in the initial value of the conversion. The same behaviour is observed for the Cu/Al_2O_3 catalyst.

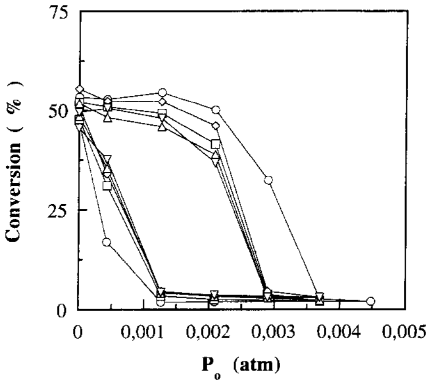

Fig. 1. Consecutive hysteresis loops for Cu/CeO_2 catalyst. (Symbols ○, □, ◇, △, ▽, correspond to the order of the consecutive hysteresis loops). The catalyst was reduced after each loop.

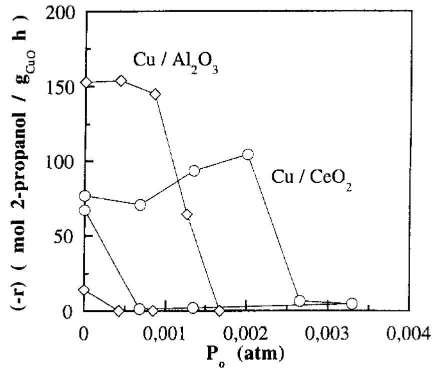

Fig. 2. Comparison of the hysteresis loops for Cu/Al_2O_3 and Cu/CeO_2 catalysts measured each after 5 consecutive hysteresis loops and treatment with *n*-pentane. ○, Cu/Al_2O_3; □, Cu/CeO_2.

A comparison of the hysteresis loops of the two catalysts, Cu/Al_2O_3 and Cu/CeO_2, after five consecutive hysteresis loops and treatment with *n*-pentane, is presented in Fig. 2. Differences are observed between Cu/Al_2O_3 and Cu/CeO_2. They concern the initial activity, the critical oxygen pressures and the recovery of activity.

The $Cu2p_{3/2}$ photoelectron spectra concerning Cu/Al_2O_3 and Cu/CeO_2 indicated no chemical shifts between the samples before and after catalytic reaction. Only reduced copper could be observed in both spectra. For both samples, the apparent copper content obtained by XPS was different from that obtained by chemical analysis (0.7 and 0.8 wt% for Cu/Al_2O_3, and 4.3 and 3.2 wt% for Cu/CeO_2, by XPS before and after catalytic test, respectively. These values are higher than those obtained by chemical analysis, namely 2.7 wt% for Cu/Al_2O_3 and 0.4 wt% for Cu/CeO_2).

3.2. Mechanical mixtures

The hysteresis loops obtained for the Cu/CeO_2 and Cu/Al_2O_3 catalysts and mechanical mixtures of these catalysts with various oxides (α-Sb_2O_4, Bi_2O_3, SnO_2 and NiO) have been compared. The results obtained in the presence of a second oxide indicate, in almost all the cases, no modification of the hysteresis loops. The behaviour of the mechanical mixtures obtained with α-Sb_2O_4 and Bi_2O_3 for the Cu/CeO_2 catalyst and with α-Sb_2O_4, Bi_2O_3 and SnO_2 for the Cu/Al_2O_3 catalyst are similar to those of Cu/CeO_2 and Cu/Al_2O_3 catalysts, but modifications can be observed in the hysteresis loops obtained with the mechanical mixtures with SnO_2 or NiO and the Cu/CeO_2 catalyst and NiO and the Cu/Al_2O_3 catalyst. The corresponding results are presented in Fig. 3 and Fig. 4, respectively.

The XPS results concerning the catalysts prepared by mechanical mixing indicated no chemical shift, except for the catalyst that contained nickel oxide. This chemical shift should probably be attributed to the presence of the metallic nickel and its influence on copper.

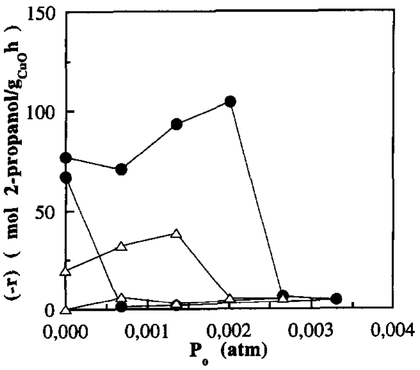

Fig. 3. Comparison of the hysteresis loops obtained for SnO_2 mechanical mixtures with Cu/CeO_2. ●, Cu/CeO_2; △, SnO_2 + Cu/CeO_2.

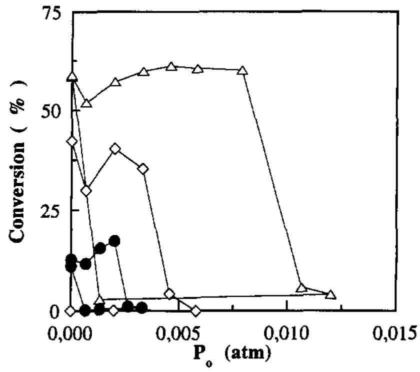

Fig. 4. Comparison of the hysteresis loops obtained for Cu/CeO_2 and NiO + Cu/CeO_2. ●, Cu/CeO_2; △, NiO + Cu/CeO_2; ◇, NiO.

4. Discussion

Before discussing the implication of the results, the validity of photoelectron spectra must be considered. It is indeed known that supported copper gets easily reduced during XPS experiments [11]. This makes difficult to conclude directly, if our results really indicate some modification in the oxidation state of copper between the beginning and the end of the hysteresis loops. The reducibility of copper during XPS measurements is sufficiently low to allow measurement. The results presented in our previous paper concerning unsupported catalysts [9] show that copper is reduced at the beginning of the loop and gets oxidized when the partial pressure of oxygen is higher.

Two factors play a role on the results presented here: the nature of the support, and the nature of the oxide mixed with the catalysts.

4.1. Effect of the support

Both catalysts (Cu/Al_2O_3 and Cu/CeO_2) show the same initial conversion (< 10%), but if the comparison is based on the rates of reaction of 2-propanol per gram of CuO and per hour, the Cu/Al_2O_3 shows an initial activity two times higher than that observed for Cu/CeO_2 (Fig. 2). If the overall specific surface area (support + metal) of the catalysts is taken into account this difference becomes considerable: the specific surface area is 28 times higher for Cu/Al_2O_3 than for Cu/CeO_2. Following these considerations, the differences in the initial activities can be mainly ascribed to a difference in specific surface areas.

Modifications in the higher critical oxygen pressure are also observed. As the oxygen pressure is increased, Cu/Al_2O_3 loses activity at lower pressures than Cu/CeO_2. Following results published earlier [9], the higher critical oxygen pressure corresponds to the oxidation of Cu(0) to Cu(I). The sensitivity to oxidation of metallic copper in Cu/Al_2O_3 and Cu/CeO_2 could be the explanation. This can be related to the dispersion of copper in both catalysts and/or to a possible interaction of CeO_2 with the copper.

A difference in the recovery of activity when the oxygen pressure decreases can also be observed. The interpretation of the recovery of oxidised copper catalysts had been that an initial removal of oxygen from the surface of Cu_2O possibly due to, or accompanied by reduction by 2-propanol could lead to the reduction of copper oxide [9].

In the case of the present work, a special influence of CeO_2 on the reducibility of the copper could explain both results [12].

4.2. *Effect of added oxides*

4.2.1. *Effect of NiO*

Two interesting effects are observed with the $NiO + Cu/CeO_2$ mixture. These are the increase of the upper critical oxygen pressure compared to those of Cu/CeO_2 and pure nickel oxide, and the high activity observed at this critical oxygen pressure. This high activity cannot be directly explained by the simple addition of the contributions of the two catalysts, because the metallic copper is normally oxidised at lower oxygen pressures. A possible explanation is that the initial activity is due only to metallic nickel. The low activity observed when the pure nickel oxide is tested could be due to the fact that nickel oxide is not totally reduced at a reduction temperature of 473 K [13]. It is possible that the presence of CeO_2 favours the reduction of pure nickel oxide (that would not be reduced under the conditions of the initial activation). This can explain both the higher upper critical oxygen pressure and the higher lower critical oxygen pressure observed with the mechanical mixture. This hypothesis is verified by XPS measurements. Before the catalytic test, the ratio of satellite/main peaks of $Ni2p_{3/2}$ is 3.1 and after the catalytic test it is 1.5. The literature indicates that the modification of the ratio satellite/main peaks and the chemical shift of the main peak are the best indicators of the presence of the metallic nickel [14]. The fact that the ratio of the satellite/main peaks of $Ni2p_{3/2}$, is lower for the used samples indicates the presence of metallic nickel after the test.

These results can be compared to the behaviour of the $NiO + Cu/Al_2O_3$ mechanical mixture. In this case, only the recovery of the activity when the oxygen pressure decreases is observed. Formation of metallic nickel after the catalytic test is also indicated by the observed decrease of the satellite/main ratio peaks of $Ni2p_{3/2}$ [14] (2.1 before and 0.6 after catalytic test). No increase in the initial activity near the critical oxygen pressure is observed.

This differentiation between Al_2O_3 and CeO_2 as supports can be explained by the reducibility of the support [15] and/or by the influence of the nature of the support on the mobility of hydrogen [12].

4.2.2. *Effect of SnO_2*

Another hypothesis concerning modification of hysteresis loops by foreign substances could be the role of oxygen spillover (facilitating oxidation of Cu), or that of reverse spillover (facilitating the removal of oxygen from Cu). This might be the case for $SnO_2 + Cu/CeO_2$ mixtures.

For this mixture, various explanations can be considered: the formation of a new phase, the effect of the support or the role of spillover oxygen. XPS analyses do not indicate any chemical shift in $SnO_2 + Cu/CeO_2$ mechanical mixture before nor after the catalytic test, in comparison with pure SnO_2 or Cu/CeO_2.

In the mixture, a possible inhibition of the reducibility of the copper by the presence of SnO_2 could explain the observed evolution in the conversion. According to this, a low initial activity, a decrease in the higher critical oxygen pressure and the absence of recovery of the activity when the oxygen pressure decreases should be observed for $SnO_2 + Cu/CeO_2$ mechanical mixture compared to Cu/CeO_2.

Another explanation could be the formation and migration of reduced species of the support onto the transition metal [16,17] leading to the decrease of the copper active surface. If this is the case, the phenomenon should be observed at high temperatures of reduction. The phenomenon could be favoured by the presence of SnO_2, but indeed this cannot explain the decrease of the higher critical oxygen pressure and the absence of recovery of the activity when the oxygen pressure decreases. An additional argument against this explanation is that no modification of the copper concentration at the surface is observed by XPS.

Another possibility could be an oxygen spillover effect from SnO_2 [10]. This effect can explain the decrease of the higher critical oxygen pressure and the absence of recovery of the activity when the oxygen pressure is decreased, but not the decrease of the initial activity, because oxygen is not present at that moment.

Then, for the $SnO_2 + Cu/CeO_2$ mixtures, apparently two factors should be considered in order to give a possible explanation. These are a possible inhibition of the influence of the support due to the presence of SnO_2 and an oxygen spillover effect from SnO_2. The initial activity can only be explained by the inhibition of the effect of the support.

5. Conclusions

It is shown that a bistability exists in the oxidative dehydrogenation of 2-propanol over supported copper catalysts. The comparison of the hysteresis loops detected when the partial pressure of oxygen is varied indicates that there is an important effect of the support in Cu/Al_2O_3 and Cu/CeO_2. This effect is explained by the specific surface areas of the supports and their reducibility.

The possible effect on the hysteresis loops of a second phase added to the copper catalysts has also been considered. Only the presence of SnO_2 or NiO in Cu/CeO_2 catalysts modifies their hysteresis loops. The modification is explained by an inhibition by SnO_2 of the influence of the support and/or an oxygen spillover effect from SnO_2, and the reduction of NiO by CeO_2. The absence of these phenomena when Al_2O_3 is the support, is due to the different reducibility of the two supports. The other oxides tested, namely α-Sb_2O_4 and Bi_2O_3, have no influence.

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