JOURNAL OF CATALYSIS **159,** 496–499 (1996)
ARTICLE NO. 0114

NOTE

Bistability in the Oxidative Dehydrogenation of 2-propanol over Copper Catalysts

Bistability phenomena and oscillatory behavior in heterogeneous catalysis have attracted considerable attention in recent years (1–5).

Oscillatory phenomena and/or bistability have been observed in catalytic systems including Pt, Pd, Cu, or Ni in the oxidation of hydrogen (3, 4, 6–8), carbon monoxide (5, 9–11), ethylene (12, 13), a mixture of CO and 1-butene (14), propene (15, 16), nitrous oxide reduction by carbon monoxide (17), etc. Several kinetic mechanisms have been proposed to account for these phenomena. It seems that most interpretations assume a change of composition or structure of the catalyst surface. The present study concerns phenomena observed with copper catalysts. Greger *et al.* (18) have shown a bistability when a Cu/Al_2O_3 catalyst was used in propene oxidation. In this study, the acrolein and CO_2 production rates exhibited hysteresis loops. The authors suggested that the bistability was due to a reoxidation of Cu_2O to CuO under nonequilibrium conditions. Amariglio *et al.* (16) confirmed these results, using pure copper oxide as catalyst.

The aim of the present work is to show, contrary to the conclusions of Thomas *et al.* (19), that a bistability is also observed in 2-propanol dehydrogenation over copper catalysts in the presence of oxygen. These authors have indicated that this reaction, when conducted under isothermal conditions, was completely inhibited for oxygen pressures p_O exceeding a critical value that we call p_h (h for high). But the authors mentioned that the deactivation was irreversible, namely that the activity was not recovered when p_O was decreased back to lower values. We found that copper catalysts recover part of their activity when p_O is lowered below a critical value p_l (l for low). The phenomenon can be reproduced several times in the same catalyst conditions giving hysteresis loops. Although the experiments were carried out in isothermal conditions, it could have been argued that the bistability has to be attributed to the exothermicity of the reaction. For that, we made experiments with powders as diluent. The presence of an inert second phase such as silicon carbide or Co_3O_4 does not alter the hysteresis loops. There is thus a bistability in the region $p_l < p_O < p_h$ (this pressure interval depends on the catalyst nature): activity depends on the direction of change of p_O for reaching a given value in the range of bistability. We show that this phenomenon is due to the oxidation and/or reduction of CuO in the conditions of the catalytic test.

Copper oxide was prepared by dissolution and precipitation of basic copper carbonate (Janssen Chimica p.a.) in an ammoniacal solution. After filtration, the precipitate was dried and calcined for 20 h at 773 K.

A mechanical mixture was prepared by dispersing together CuO and either Co_3O_4 (BDH Chemicals Ltd. p.a.) or silicon carbide (Prolabo, particle size 340 μm) powders in *n*-pentane (Aldrich, 98% GC) under agitation at 6000 rpm for 10 min. This operation was followed by evaporation of the *n*-pentane at room temperature under reduced pressure and drying at 383 K. To allow perfect comparison, the pure oxides were subjected to the same succession of treatments with *n*-pentane and drying as the mixture. The composition of the mixtures was 50–50 wt%. The samples were made from the powders by pressing at 10 ton cm^{-2}, gently grinding the pellet and taking the fraction between 200 and 315 μm.

The 2-propanol feed (Aldrich, 99 + %) was purified with activated molecular sieves and stored in a thermostated gas saturator at 311 K. The He (99.995%, Air Liquide) flow rate coming into the saturator was controlled by means of a Brooks 5850 TR mass flow controller. Prior to reaction, the catalysts (0.1 g) were reduced at atmospheric pressure for 1 h at 473 K with 60 ml min^{-1} of H_2 (99.9%, Air Liquide, treated with a Chrompack clean-oxygen filter). Catalytic measurements were carried out in a fixed-bed reactor at 423 K and at atmospheric pressure. The amount of copper catalyst present in the mechanical mixture for the catalytic test was the same as when the catalytic test was carried out with the copper catalyst alone. The oxygen pressure in the feed was varied from 0 to 1500 Pa and it was controlled by means of a Bronkhorst Hi-Tec model F-201C mass flow controller. The ratio O_2/2-propanol in the feed was varied from 0 to 0.125. The W/F_{Ao} ratio (4.57 g_{CuO} h/mol 2-propanol) was kept constant for all experiments. The reactants and products were analyzed by on-line gas chromatography (Hewlett Packard 5880 A) with a ParaPLOT Q column (25 m × 0.32 mm, df = 10 μm; 423 K). The reproducibility of the results has been verified.

The catalyst samples were characterized before and after the catalytic tests by X-ray diffraction (XRD) and XPS

0021-9517/96 $18.00

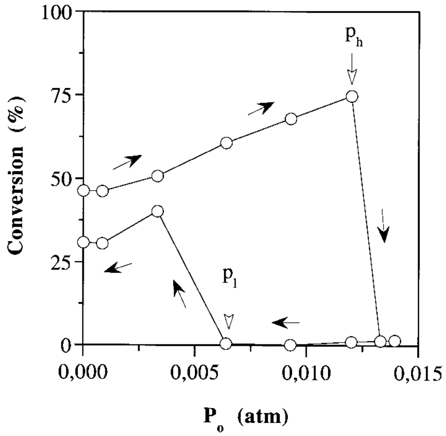

FIG. 1. Variation of the conversion of 2-propanol to acetone as a function of the pressure of oxygen for a pure CuO catalyst. Arrows indicate the direction along which the loop is gone over. Dehydrogenation of 2-propanol was carried out at 1 atm and 423 K. $W/F_{Ao} = 4.57$ g_{CuO} h/2-propanol.

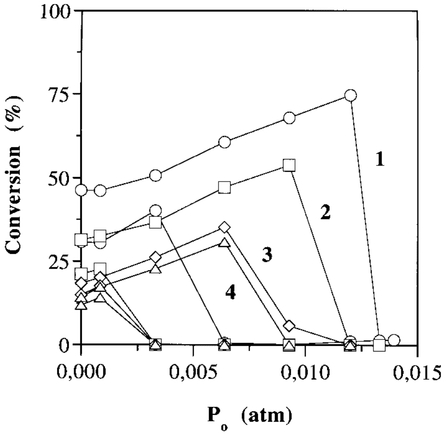

FIG. 2. Consecutive hysteresis loops for CuO catalyst. Numbers indicate the order in which the loops were recorded. The catalyst was reduced before the first loop, but no reduction took place before loops 2, 3, or 4. Dehydrogenation of 2-propanol was carried out at 1 atm and 423 K. $W/F_{Ao} = 4.57$ g_{CuO} h/2-propanol.

analyses. No particular precautions were taken for XRD and XPS analyses in used samples.

X-ray diffraction was carried out in a Siemens D-5000 powder diffractometer using Ni-filtered Cu*Kα* radiation ($\lambda = 1.5404$ Å).

XPS analyses were performed on a Surface Science Instruments, SSI-XPS. The excitation radiation was Mg *Kα* (1253.6 eV). Binding energies were calculated taking as reference the C 1*s* (284.8 eV) peak of carbon contamination. The method for determining the oxidation state of copper using photoelectron spectroscopy will be indicated in the section reporting the corresponding results. More details are given elsewhere (20).

The evolution of the conversion of 2-propanol as a function of the oxygen pressure, with the pure copper catalyst, is presented in Fig. 1. After reduction of the initial CuO, the conversion at $p_O = 0$ corresponds to simple dehydrogenation of 2-propanol. When oxygen is introduced in the reactant mixture, the oxidative dehydrogenation of 2-propanol also takes place and the conversion increases. For a certain value of oxygen partial pressure (p_h), the catalyst loses almost completely its activity. The oxygen partial pressure is then decreased. At a certain value (p_l), the conversion increases considerably, although the initial activity is not completely recovered.

The consecutive hysteresis loops observed for the CuO catalyst are presented in Fig. 2. Between these loops, the catalyst was not treated by reduction. As can be seen in Fig. 2, the p_h and p_l values and the conversion change for such hysteresis loops. However, if reduction at 473 K was carried out, hysteresis loops similar to the first ones were obtained.

When CuO is mixed with an inert powder that does not show catalytic activity, such as silicon carbide or Co_3O_4, similar but not the same hysteresis loops are observed as with pure CuO. The results obtained for the Co_3O_4/CuO mixtures are presented in Fig. 3. Similar results are obtained with other powders, such as SnO_2, α-Sb_2O_4, Cr_2O_3, and CeO_2.

In order to give an explanation to the observed phenomena, the catalyst was characterized in differents points of the hysteresis loop. For that, we selected the Co_3O_4/CuO mixture. The points where the catalysts were analyzed are represented by solid symbols in Fig. 3.

The Cu $2p_{3/2}$ photoelectron spectra and Cu_{LMM} Auger spectra are presented in Fig. 4. The relevant XPS and Auger information obtained is presented in Table 1. This table also reports the ratio of the satellite intensity to the main

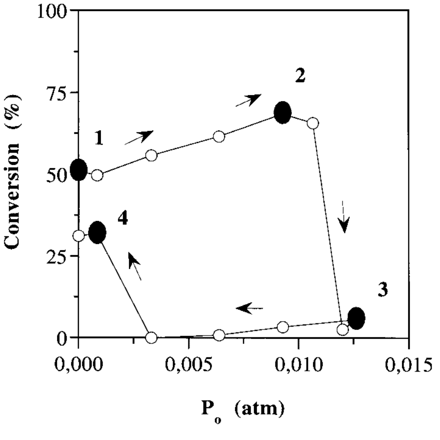

FIG. 3. Variation of the conversion of 2-propanol to acetone as a function of the pressure of oxygen for the Co_3O_4/CuO catalyst. The solid symbols indicate the points where the catalyst was analyzed. Dehydrogenation of 2-propanol was carried out at 1 atm and 423 K. $W/F_{Ao} = 4.57$ g_{CuO} h/2-propanol.

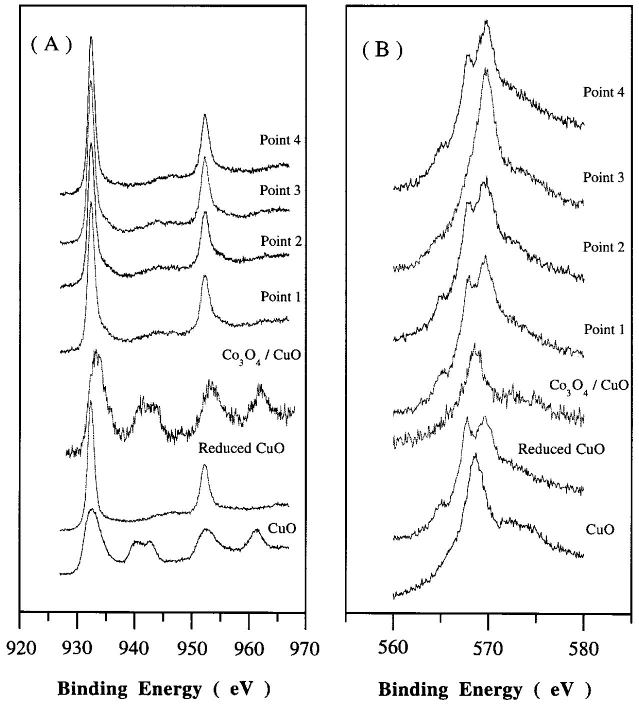

FIG. 4. XPS analysis (A) Cu $2p_{3/2}$ photoelectron spectra and (B) Cu_{LMM} Auger spectra of the samples corresponding to the points indicated in Fig. 3.

line. Oxidation states have been determined using Cu $2p_{3/2}$ binding energies, the associated shake-up satellites and the binding energy of the $CuL_3M_{4,5}M_{4,5}$ (LMM) Auger transition. The presence of a shake-up satellite at a binding energy higher than the main core level is characteristic of all Cu(II) compounds. This is the best indicator of the presence of this oxidation state (21–25), and for this reason, no spectrometric reference external for pure Cu(I) and Cu(0) was used. The Cu_{LMM} Auger line has been used to discriminate between Cu(I) and Cu(0) because both oxidation states show almost identical Cu $2p_{3/2}$ binding energies (21–25). The Cu_{LMM} Auger line for Cu(0) shows two peaks, contrary to the Cu(I) and Cu(II) oxidation states, which show only one peak. The Auger binding energies for the most appropriate reference compounds, Cu_2O and Cu metal, have been reported to be 570.0 and 568.1 eV (26). The XPS analyses, confirmed by XRD, show the presence of Cu(0) after the initial reduction of CuO (point 1, 569.4 and 567.7 eV Auger peaks). Copper remains in the metallic state (Cu(0)) until the initial oxygen pressure p_{h} is reached. At this point (point 2), the conversion drastically drops and the presence of Cu_2O is observed (point 3, 569.6 eV Auger peak). When the conversion is recovered the presence of Cu(0) is again observed (point 4, 569.6 and 567.6 eV Auger peaks). Our interpretation is that the recovery of the conversion can be caused by the initial removal of oxygen from the surface of Cu_2O and reduction by 2-propanol (27). It seems that the hydrogen produced by some dehydrogenation of 2-propanol can contribute to this reduction. This behavior was predicted by the theory of Wagner (28).

As can be seen in Fig. 4A, only the initial nonreduced pure CuO (lower curve) and copper in the nonreduced cobalt/copper oxides show the associated shake-up satellites to Cu $2p_{3/2}$ (941 and 944 eV). When pure CuO is reduced or when the analysis is carried out in the Co_3O_4/CuO sample at points 1–4 (see Fig. 3), this shake-up satellite is not observed. As can be seen in Fig. 4B in sample 3, only the presence of Cu(I) is observed in the Cu_{LMM} Auger spectrum (569.6 eV Auger peak). In the other samples CuO is also observed in addition. On the other hand, Table 1 shows that the binding energy of the cobalt remains unchanged when the dehydrogenation of 2-propanol has been carried out in the Co_3O_4/CuO catalyst. XPS gives another important

TABLE 1

XPS Analysis Results

Catalyst	Cu $2p_{3/2}$[a]	Cu $2p_{3/2}$(s)[a]	Cu $2p_{3/2}$(s)[a]	*s/m*[b]	Co/Cu[c]	Cu_{LMM}[a]	Co $2p_{3/2}$[a]	*s/m*[b]
CuO	933.2	940.9	943.4	0.47	0	568.3		
Reduced CuO	932.3	—	—	—	0	569.5–567.6		
Co_3O_4							780.2	—
Co_3O_4 (after reduction treatment)							779.7	0.17
Co_3O_4/CuO	933.5	941.1	943.6	0.50	0.3	568.6	779.7	—
Point 1	932.3	—	—	—	0.6	569.4–567.7	779.7	0.25
Point 2	932.2	—	—	—	0.8	569.5–567.9	780.0	0.22
Point 3	932.2	—	—	—	0.8	569.6	780.0	0.31
Point 4	932.2	—	—	—	1	569.6–567.6	780.0	0.36

Note. The spectra are shown in Fig. 2. The samples analyzed correspond to the points indicated in Fig. 3. The theoretical ratio of the mechanical mixture is 0.9.

[a] Binding energy (eV).

[b] Satellite/main ratio peaks.

[c] XPS atomic ratio (Co $2p_{3/2}$/Cu $2p_{3/2}$).

information. The progressive increase in the XPS Co/Cu atomic ratio in the series of samples 1 to 4 can suggest an important sintering of the copper particles in the oxidation and reduction processes occurring along the hysteresis loop. This sintering can explain the progressive reduction of the successive hysteresis loops from 1 to 4 (Fig. 2).

In summary, it is shown that a bistability exists in the oxidative dehydrogenation of 2-propanol over copper catalysts. A hysteresis loop is observed when the partial pressure of oxygen is varied. This phenomenon is due to a transition between Cu(0) and Cu(I). Copper Cu(0) gets oxidized above a critical oxygen pressure. An initial removal of oxygen from the surface of Cu_2O and a reduction by 2-propanol can reduce the copper oxide formed. Finally, the hydrogen produced by the dehydrogenation of 2-propanol can contribute to this reduction. This behavior is not modified by the presence of a second phase such as silicon carbide, Co_3O_4, SnO_2, α-Sb_2O_4, Cr_2O_3, or CeO_2.

ACKNOWLEDGMENTS

The authors thank Professor P. Grange for valuable discussions and for critical reading of the manuscript. The financial support of the EU (Human Capital and Mobility Project ERBCHRX-CT93-0154) and the SPPS (Service de Programmation de la Politique Scientifique), Belgium, is also gratefully acknowledged.

REFERENCES

1. Sheintuch, M., and Schmitz, R. A., *Catal. Rev. Sci. Eng.* **15**, 107 (1977).
2. Slin'ko, M. G., and Slin'ko, M. M., *Catal. Rev. Sci. Eng.* **17**, 119 (1978).
3. Sheintuch, M., *J. Catal.* **96**, 326 (1985).
4. Razon, L. F., and Schmitz, R. A., *Catal. Rev. Sci. Eng.* **28**, 89 (1986).
5. Imbihl, R., Cox, M. P., and Ertl, G., *J. Chem. Phys.* **84**, 5196 (1986).
6. Zúñiga, J. E., and Luss, D., *J. Catal.* **53**, 312 (1978).
7. Eng, D., Stoukides, M., and McNally, T., *J. Catal.* **106**, 342 (1987).
8. Kurtanjek, Z., Sheintuch, M., and Luss, D., *J. Catal.* **66**, 11 (1980).
9. Varghese, A., Carberry, J. J., and Wolf, E. E., *J. Catal.* **55**, 76 (1978).
10. Lynch, D. T., Emig, G., and Wanke, S. E., *J. Catal.* **97**, 456 (1986).
11. Turner, G. E., Sales, B. C., and Maple, M. B., *Surf. Sci.* **103**, 54 (1981).
12. Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66**, 36 (1980).
13. Vayenas, C. G., Georgakis, C., Michaels, J., and Tormo, J., *J. Catal.* **67**, 348 (1981).
14. Cutlip, M. B., and Kenney, C. N., *ACS Symp. Ser.* **65**, 475 (1978).
15. Sheintuch, M., and Luss, D., *J. Catal.* **68**, 245 (1981).
16. Amariglio, A., Benali, O., and Amariglio, H., *J. Catal.* **118**, 164 (1989).
17. Sadhankar, R. R., Ye, J., and Lynch, D. T., *J. Catal.* **146**, 511 (1994).
18. Greger, M., Ihme, B., Kotter, M., and Riekert, L., *Ber. Bunsenges. Phys. Chem.* **88**, 427 (1984).
19. Thomas, E., Brahm, J., and Jottrand, R., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 353. Elsevier, Amsterdam, 1980.
20. Gil, A., Ruiz, P., and Delmon, B., *in* "2nd International Conference on Unsteady-State Processes in Catalysis, USPC-2, St Louis, MO, 1995," Paper A15.
21. Hierl, R., Knozinger, H., and Urbach, H. P., *J. Catal.* **69**, 475 (1981).
22. Panzer, G., Egert, B., and Schmidt, H. P., *Surf. Sci.* **151**, 400 (1985).
23. Wagner, C. D., Riggs, W. M., Davis, L. E., and Moulder, J. F., *in* "Handbook of X-ray Photoelectron Spectroscopy." Perkin–Elmer Corp., Physical Electronics Div., Eden Prairie, MN, 1979.
24. Barr, T. L., *J. Phys. Chem.* **82**, 1801 (1978).
25. Brundle, C. R., Peden, C. H. F., and Goodman, D. W., *J. Phys. Chem.* **92**, 5213 (1988).
26. Shapiro, E. S., Grünert, W., Joyner, R. W., and Baeva, G. N., *Catal. Lett.* **24**, 159 (1994).
27. Cunningham, J., Al-Sayyed, G. H., Cronin, J. A., Garcia Fierro, J. L., Heady, C., Hirschwald, W., Ilyas, M., and Tobin, J. P., *J. Catal.* **102**, 160 (1986).
28. Wagner, C., *Ber. Bunsenger. Phys. Chem.* **74**, 401 (1970).

A. Gil
P. Ruiz
B. Delmon

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

Received April 26, 1995