JOURNAL OF CATALYSIS 65, 166–173 (1980)

Influence of Retardation Caused by Partially Oxidized Adsorbate upon the Oxidation State of Copper Catalyst and Its Performance for Selective Propylene Oxidation

T. INUI, T. UEDA, AND M. SUEHIRO

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

Received January 12, 1979; revised January 21, 1980

Propylene oxidation over a supported copper catalyst was studied by simultaneous measurements of the catalytic activity and the solid-state properties by means of a microthermogravimetric analyzer combined with a flow device. Initially adsorbed acrolein strongly retarded the consecutive oxidation of successively formed acrolein and allowed consistent stabilization of a copper-rich cuprous oxide state. The most active and stable solid phase for highly selective acrolein formation in the working state was the copper-rich cuprous oxide state such as $Cu_{2.17}O$. The state was found to be determined by the balance between the proceeding of copper oxidation and the keeping in check of the oxidation by the retardation due to adsorbate.

INTRODUCTION

Cuprous oxide is well known as an active catalytic species for the selective oxidation of propylene to acrolein (*1*, *2*). Although for the partial oxidation of propylene cuprous oxide has been replaced in industry by composite catalysts of the bismuth–molybdate type, the study of copper or copper oxide catalysts for investigating the principle of selectivity in oxidation remains a most interesting and intriguing topic (*3*–*8*). Hitherto, it has been qualitatively known that copper or cuprous oxide catalysts form a mixture of $CuO–Cu_2O–Cu$ according to the reaction conditions of propylene oxidation; the performance is controlled by this composition, and the state containing a large amount of Cu_2O gives the best result for acrolein formation (*3*, *9*, *13*). However, the optimum Cu_2O content has not been agreed upon in these reports. Furthermore, it is also known that metallic copper forms with increasing propylene concentration and decreasing selectivity to acrolein (*10*, *12*). When oxygen concentration or the O_2/C_3H_6 ratio is increased, deactivation of the catalyst occurs (*12*). In spite of these observations, many ambiguities still remain concerning the precise relationship between the oxidation state of copper and the catalyst performance.

The purpose of this work was to define the factors controlling the oxidation state of copper and to obtain a more accurate relationship between the oxidation state and the catalytic performance over a wide range of reaction conditions.

EXPERIMENTAL

Catalyst

A porous $SiO_2–Al_2O_3$ calcined at 1500°C, 28% porosity, 20–30 mesh, was impregnated with a solution of the ammonium complex of cupric nitrate. After drying and thermal decomposition in air, it was reduced completely in flowing hydrogen while the temperature was raised at a constant rate from 20 to 400°C for 2 hr, and then treated at 800°C for a period of 30 min in the same gas flow. The content of reduced copper was 9.7%. The BET surface area of the support was measured as 1.6 m^2/g by the one-point method (*14*) using

0021-9517/80/090166-08$02.00/0

the continuous-flow technique (15). The surface area of the supported metal was determined to be 17.4 m^2/g Cu by measuring the rapid CO chemisorption at room temperature (27°C) with CO partial pressure of 0.05 atm according to Scholten and van Montfoort (16). The mean diameter of supported copper crystallites was 40 nm, assuming them to be spherical. This catalyst gave quite high selectivity, ca. 80%, for acrolein formation with suitable conditions using water vapor (17).

Apparatus and Reaction Method

A Shimadzu microthermogravimetric analyzer (TG) with a gas flow control and gas-purification system was used. Its tolerance was 1 μg regardless of gas flow below 200 cm^3/min. A 0.019-cm^3 portion of the catalyst sample was situated in the sample pan suspended in the center of a transparent quartz tube of 13 mm diameter. The pan had a diameter of 5.8 mm and a depth of 1.6 mm. The sample was reduced completely *in situ* before use at 350°C with 6% H_2–94% N_2. A new catalyst of the same lot was provided for each test to eliminate any effect of hysteresis upon the catalyst performance, owing to contact with different reaction conditions. The reaction-gas mixtures were introduced under conditions within 200 to 500°C and 21 to 141 cm^3/min. A small portion of propylene combustion, due to catalysis of the platinum sash-wire and the sample pan in the heating zone of the reactor tube, was corrected by a blank test corresponding to each reaction condition.

The effluent gas was analyzed by a sensitive FID-TCD type gas chromatograph (Yanagimoto GC-80) every few minutes. Propylene and CO_2, O_2, and possible organic products such as acrolein, acetaldehyde, propionaldehyde, and acetone were analyzed using three types of columns, Porapak Q, MS-5A, and 30% polyethylene glycol 6000/Celite 545, respectively.

The overall oxidation state of the bulk copper, y in CuO_y, was obtained from the weight gain measured by the micro-TG. The calculated weight gain from adsorbates other than oxygen, such as organic compounds and CO_2, was less than 0.9%, and was negligible for the estimation of the y value. This was calculated following oxidation and successive hydrogenation at 400°C, of 30-min duration, using a 50-fold amount of catalyst at flow conditions similar to those of the micro-TG but using a tubular reactor.

Morphological observation of the catalyst surface before and after use for the propylene oxidation was studied by scanning electron microscopy, using Hitachi HFS and JEOL JSM-T20 instruments.

RESULTS AND DISCUSSION

Transient and Steady-State Reaction

A typical example of the transient and steady states in propylene oxidation starting from the reduced state of copper is shown in Fig. 1 together with reaction

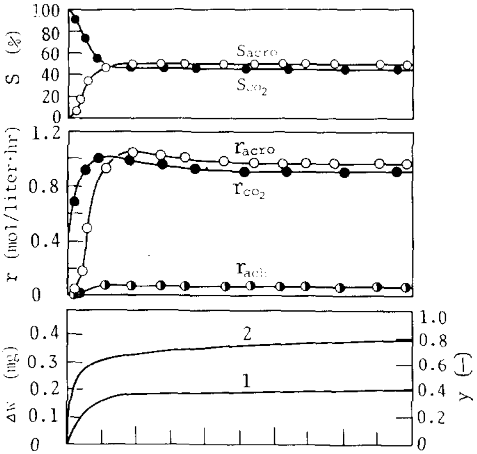

FIG. 1. Changes of weight and of catalyst performance with time for propylene oxidation starting from the reduced state of the catalyst. 1. Propylene oxidation; 2. oxygen treatment with 5% O_2–95% N_2; gas composition, 25% C_3H_6, 5% O_2, 2% H_2O, and 68% N_2; flow rate, 33 cm^3/min; temp., 300°C. S_{acro} and S_{CO_2} are selectivities of acrolein and CO_2, and r_{acro}, r_{CO_2}, r_{ach} are formation rates of acrolein, CO_2, and acetaldehyde, respectively.

conditions. In the early stage near $y = 0$, almost complete oxidation of propylene was observed as shown by the curves of selectivity for CO_2 formation (S_{CO_2}) and rate of CO_2 formation (r_{CO_2}). However, S_{CO_2} decreased with increase of y. On the contrary, acrolein formation (S_{acro} and r_{acro}) increased. Both the rates (r_{CO_2} and r_{acro}) and oxidation state attained steady states within 20 min.

In the reaction-gas stream, the weight increase of the catalyst (Δw) occurred linearly during the first few minutes, then decreased gradually and almost stopped after 20 min. On the other hand, the oxygen uptake of the catalyst in 5% O_2–95% N_2 gas stream proceeded rapidly for the first 10 min, and at that time Δw was ca. twice that found with propylene oxidation. Further, in this case, the slow oxygen uptake continued for more than 2 hr. It was considered whether or not this difference was due to the oxygen consumed on the catalyst surface with propylene oxidation. Assuming that Δw within the first 2 min was proportional to time (t), the increasing rate of Δw, $\{d(\Delta w)/dt\}$ expressed in milligarams per minute, was 0.029 for propylene oxidation, and was 0.103 for the oxygen treatment. The oxygen consumption rate for propylene oxidation was 0.031 in the same units, which was calculated from formation rates of the products at $t = 2$ in Fig. 1. So, the overall amount of oxygen converted for the propylene oxidation in first 2 min becomes 0.060, which is only about 60% of that in the oxygen treatment. Consequently, it is indicated that the increasing rate of catalyst weight in the propylene oxidation was strongly retarded from its initial rate by the action of adsorbate such as acrolein, as observed by Aso *et al.* (*8*).

The amount of adsorbate, which was determined by the redox analysis mentioned under experimental, was 0.49 cm^3 as C_3H_6 per gram copper. This value corresponds to a surface coverage of 0.2, assuming the area occupied by one adsorbed propylene molecule (s) to be 25.6 Å^2, as calculated with the usual equation $s = 2(3)^{1/2}\{M/(4(2)^{1/2}N_A \cdot d)\}^{2/3}$ using the data of molecular weight (M), Avogadro's number (N_A), and density (d).

Effect of the Initial State of Catalyst on the Steady State

The facts described above showed that the oxidation of the copper was markedly retarded, even in the early stage of the propylene oxidation, due to small amount of adsorbate. This suggested that the state of the catalyst at the start of the reaction had an effect on the catalyst performance at the steady state. To make this point clear, several catalysts having initially different states of oxidation were provided for the propylene oxidation. The results are summarized in Table 1.

The time required to attain the steady-state reaction from start-up in each of the initial oxidation states (y_0) of the catalyst was nearly equal to that shown in Fig. 1. The y at the steady state, when the reaction started from the completely reduced state of the catalyst (case 1, $y_0 = 0$), was 0.41. This value was the smallest in Table 1, and the greatest formation rate of acrolein and its selectivity were shown in this case. On the other hand, when the reaction started from the complete oxidized state of the catalyst (case 5), y was scarcely reduced and the catalyst gave the maximum combustion rate and minimum acrolein formation. Partially oxidized (case 2) or reduced (cases 3 and 4) catalysts always gave greater values for y and y_0, even when the reaction started from a y_0 which was equal to the y of case 1.

The reason for these facts was considered to be that the concentration of the products was small at the early stage, and oxidation of copper metal proceeded until the adsorption of the adsorbates attained equilibrium.

In conclusion, the y at the steady state strongly depended on the initial oxidation or reduction state of the catalyst metal, and

TABLE 1

Performance Parameters for Propylene Oxidation Starting from Various Oxidation States of the Catalyst

Exp. No.	Initial state of the catalyst	y_0	y	Rate and selectivity at the steady state							
				r_{acro} (mol/liter · hr)	S_{acro} (%)	r_{ach} (mol/liter · hr)	S_{ach} (%)	r_{CO_2} (mol/liter · hr)	S_{CO_2} (%)	$r_{C_3H_6}$[a] (mol/liter · hr)	r_{O_2}[a] (mol/liter · hr)
(1)[b]	R	0.00	0.41	0.96	51.6	0.065	3.5	0.82	44.1	1.86	4.69
(2)	R → O	0.38	0.50	0.61	39.2	0.047	3.0	0.90	57.8	1.56	4.68
(3)	O → R	0.38	0.59	0.74	39.5	0.067	3.6	1.07	60.5	1.88	5.90
(4)	O → R	0.69	0.78	0.35	20.7	0.040	2.4	1.30	76.9	1.69	6.22
(5)	O	1.00	0.98	0.12	7.3	0.026	1.7	1.51	91.0	1.66	6.93

Note. Test conditions are the same as in Fig. 1. R, completely reduced state (Cu); O, completely oxidized state (CuO); R → O, reduced catalyst was oxidized by O_2 until the y_0 listed; O → R, oxidized catalyst was reduced by H_2 until the y_0 listed; y_0, initial y. acro = acrolein; ach = acetaldehyde.

[a] Consumption rate.

[b] Small amount of propionaldehyde (S = 0.6%) and acetone (S = 0.2%) formed in this case.

the optimum result for acrolein formation was obtained with $y \approx 0.4$.

Retardative Behavior of Adsorbates

The strong retardative action of small amounts of adsorbate was further investigated by varying the reaction-gas composition and temperature over a wide range after previously setting y at a certain level (Fig. 2).

After taking a constant y (0.41) with the reductive gas as well as the conditions in Fig. 1, the inlet gas composition was varied stepwise into an oxidative one, with increasing oxygen or decreasing propylene. Rate values (r) immediately showed a variation corresponding to the gas composition; however, y remained constant even with a very oxidative gas, such as the composition f.

Taking into account both the time for the initial change of y and for the change in the oxygen treatment, the interval for each condition in Fig. 2 provided enough time for change to occur if retardation did not exist. Moreover, in another experiment, even when the reaction time for condition f was extended by 120 min, no change occurred in the effluent gas composition or in y.

In the first instance, an abrupt increase of y occurred 10 min after the gas changed into

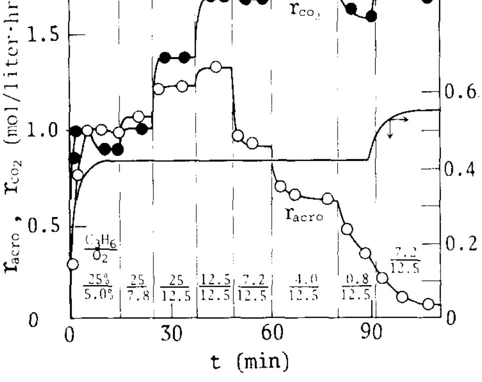

FIG. 2. Responses of the oxidation state of copper (y in CuO_y) and rates (r) to changes in gas composition.

an extremely oxidative form, with propylene concentration decreasing to a very low level, as shown in g. It was considered that at this time the adsorbates were burned off, and their retardative effect for the oxidation of catalyst metal ceased. After that (period h), the gas composition was restored to that used in e. y attained a new level, 0.55, which was constant. However, r_{acro} was quite different from that previously in e, and had a very small value. The temperature was then raised at a constant rate to 400°C for 100 min; nevertheless, y did not change within the accuracy of the apparatus. Thus, once y had been fixed, it remained constant over a wide range of reaction conditions. On the basis of these facts the action of the adsorbates was deduced to be as follows:

(1) The adsorbates not only strongly retarded the oxidation and reduction of the catalyst metal, but also played an important role in controlling the selectivity to the partial oxidation product (acrolein) by retarding the rate of successive oxidation.

(2) Active sites, which are regenerated repeatedly by redox cycles (*17–19*), occupy only an extremely small portion of the catalyst surface because rates changed rapidly with changes of gas composition over a surface with quite constant y. This further suggests that the adsorbed oxygen and not the lattice oxygen is of significance.

(3) In particular, the complete-combustion activity is determined directly by the equilibrium bulk composition of copper and copper oxide mixtures.

Temperature Dependence of Catalyst Performance

Propylene oxidations were carried out in the same manner as was illustrated in Fig. 1, at several different reaction temperatures ranging from 200 to 500°C. The reaction parameters for each steady state are plotted in Fig. 3.

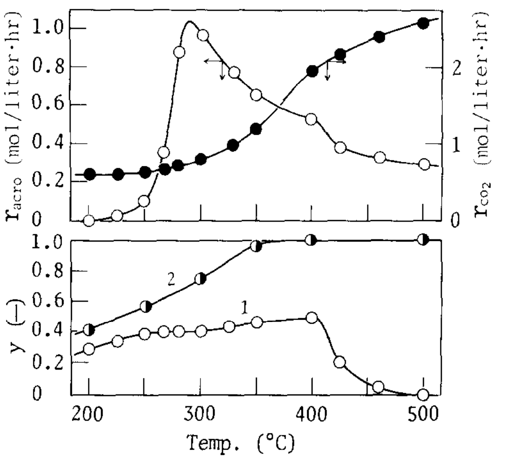

FIG. 3. Changes in the values of y and r at the steady state over a wide range of reaction temperatures. Each point was determined after an interval of 70 min after starting from the completely reduced state of the catalyst. 1. Propylene oxidation; 2. oxygen treatment with 5% O_2–95% N_2.

The temperature dependence of y was minor below 400°C, when compared with the oxygen-treatment case. y abruptly decreased above 400°C, and maintained a perfectly reduced state to 500°C. The rates, r_{acro} and r_{CO_2}, showed quite different dependences. r_{acro} was very small in the lower-temperature range, and after an exponential increase with rising temperature, decreased gradually after the maximum value. In contrast to this, r_{CO_2} increased monotonically with an S-shaped dependence. Consequently, S_{acro} varied in the same manner as r_{acro}. Similar results were obtained when an oxygen-rich gas, such as one with 15% or 25% O_2 was used. The y values below 400°C in these cases were 0.47 and 0.57, respectively.

From these results it was recognized that y depended on the concentration of acrolein formed (C_{acro}) according to the adsorbed concentration of acrolein. When C_{acro} was large, the retardation of oxidation or reduction of the catalyst was strong, and the composition of the copper–oxide system remained stable. Also, the combustion of propylene was relatively small.

It was considered that above 400°C, with increasing combustion, C_{acro} decreased due to successive oxidation, and was unable to check reduction of the metal oxide. Reduction predominates in the high-temperature range in spite of the large oxidation rate of copper. As in the combustion of propylene, 1 mole of adsorbed oxygen was consumed at once by 4.5 moles of propylene; it may mean that the gas composition in contact with the catalyst surface becomes extremely reductive at high temperature.

Gas-Composition Dependence of Catalyst Performance

At the optimum temperature for S_{acro} obtained above, both the concentrations of oxygen and propylene were varied widely. As shown in Fig. 4, y increased monotonically with oxygen concentration. However, it decreased with an inverse-sigmoid-shaped dependence with propylene concentration. The latter type of retardation has often been observed in catalytic oxidation reaction with an inhibitor (*20, 21*). The retardative action of adsorbates mentioned above may also be relevant in this case.

To summarize the correspondence between gas composition and catalytic performance, gas compositions tested were plotted in O_2–C_3H_6 coordinates, and contour curves for r_{acro} and S_{acro} were drawn (Fig. 5). Both the contour curves showed symmetrical patterns with the centerline of $C_3H_6/O_2 = 3.5$. Better catalytic performances were observed with higher concentrations of both propylene and oxygen. The optimum results were obtained at more than 50% propylene and more than 17% oxygen, where y was held at 0.46 constantly. Another expression for $y = 0.46$ is $Cu_{2.17}O$ or slightly copper-rich cuprous oxide.

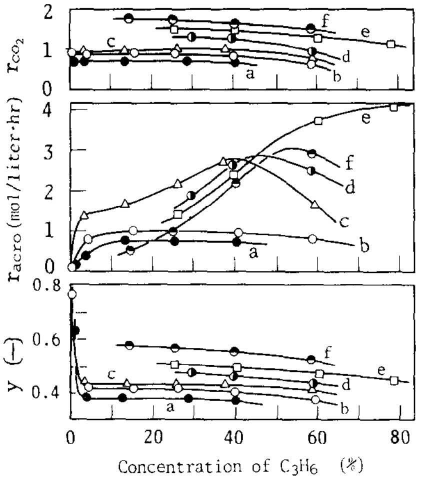

FIG. 4. Effect of propylene concentration on y and r at the steady state. Temp., 300°C; flow rate, 33 cm^3/min. Concentration of O_2 in percent: a, 2.4; b. 5.0; c, 11; d, 15; e, 19; f, 25.

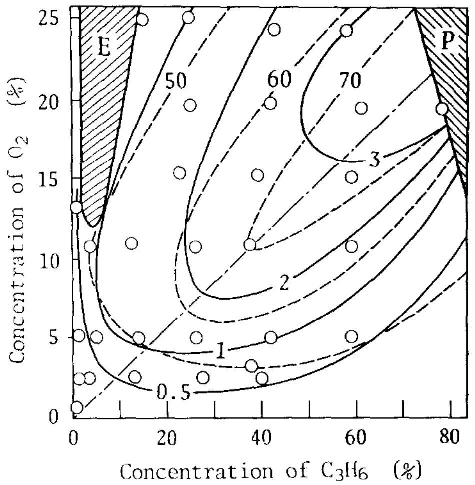

FIG. 5. Contour curves of r_{acro} and S_{acro} as functions of the concentration of propylene and oxygen. Data in Fig. 4 were used. E, explosive composition; P, outer region of 1 atm; solid line, r_{acro}; broken line, S_{acro}; dot-dashed line, ratio of C_3H_6/O_2 is 3.5; numerals stand for r_{acro} (mol/liter · hr) or S_{acro} (%) of contour line.

When the catalyst was put into contact with a gas flow having a C_3H_6/O_2 ratio > 2 and with 25 ± 5% O_2, the steady state was gained rapidly, and was stably maintained with high values of r_{acro} and S_{acro}. In these conditions, y did not exceed 0.5, and the same r_{acro} and S_{acro} were obtained repeatedly with the hydrogen-reduction treatment. As can be seen in Fig. 6b, which depicts the surface shape after these conditions applied, interparticle voids were largely filled up due to expansion following oxidation of the initially reduced copper particles shown in Fig. 6a. Nevertheless, copper particles on the support still re-

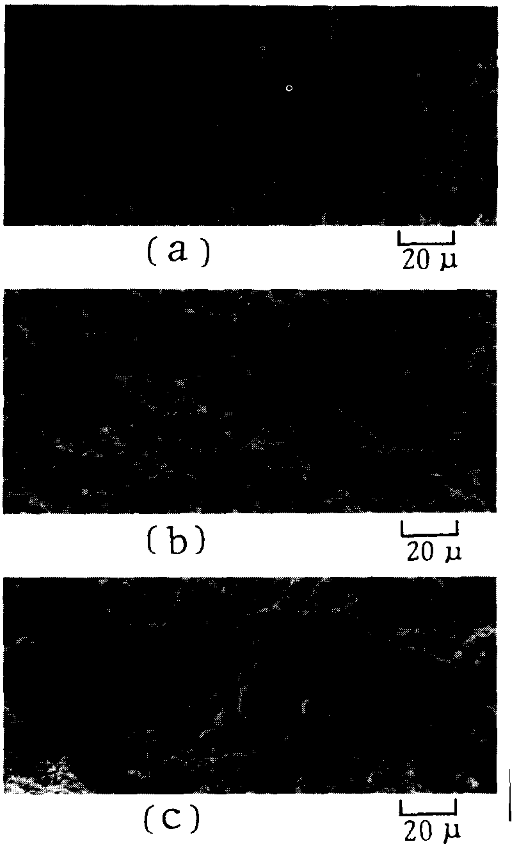

FIG. 6. Scanning electron micrographs of the catalyst surface before and after use for propylene oxidation. (a) Before use ($y = 0$); (b) after use with the gas of 26% C_3H_6, 5% O_2 at 300°C for 70 min ($y = 0.41$); (c) after use with the gas of 25% C_3H_6–25% O_2 at 300°C for 70 min ($y = 0.57$).

mained independent of each other, and no rearrangement or sintering was observed.

On the other hand, when the catalyst was contacted with a gas flow having a C_3H_6/O_2 ratio < 1 with 25% O_2, or less than 3% C_3H_6, both r_{acro} and S_{acro} were very small, y increased gradually beyond 0.55, and activity decreased. Under such conditions, permanent deterioration of the catalyst activity took place. The flat parts on the catalyst surface after use (Fig. 6c), were sintered copper particles in an oxide state which had the appearance of a river. Magnifying these one hundred times, whiskers, like those shown in Fig. 7b, were found in all parts. These whiskers were confirmed by electron-diffraction analysis and were similar to the whiskers of CuO (Fig. 7a) which grew when the catalyst was placed in a gas stream of low oxygen concentration (0.3 vol%) diluted with He at 450°C for 2 hr.

The river-like rearrangement seemed to indicate that propylene combustion occurred locally, and a high-temperature front due to the accumulation of combustion heat propagated successively and was accompanied by sintering, just like the spread of a fire. In effect, due to the local heat accumulation, these microscopic parts acquired conditions suitable for whisker growth, i.e., 400–450°C (*22*) and the diffusion of metallic

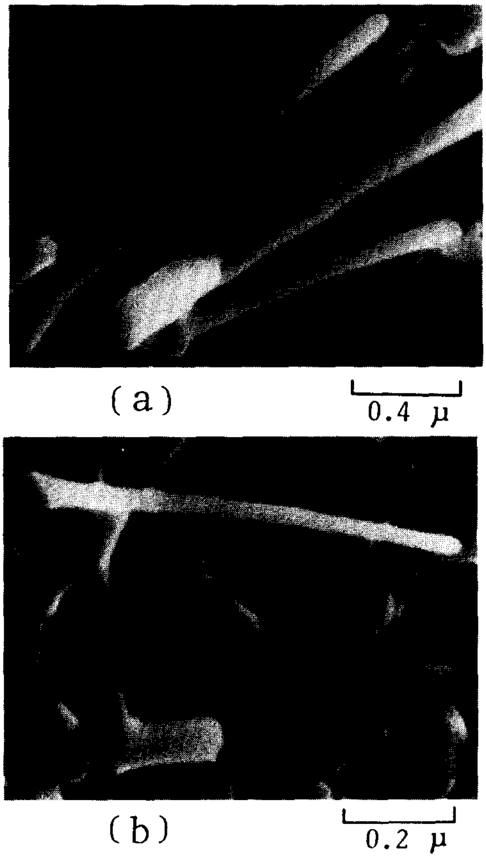

FIG. 7. Scanning electron micrographs of oxide whiskers grown on the surface of a supported copper catalyst. (a) After oxidation with a He stream containing 0.3% O_2 at 450°C for 2 hr; (b) after use for propylene oxidation. A part of the river-like feature in Fig. 6c was observed by further magnification by 100 times (120,000 ×).

ions toward the surface of particles was promoted (*22*). Consequently, it is considered that the rearrangement is also accelerated along with the whisker growth.

In conclusion, it has been shown that the concentration of adsorbed acrolein is determined by the initial oxidation or reduction state of the catalyst metal, and by the reaction conditions at the outset. Retardation due to the adsorbate strongly controls the oxidation state of the catalyst metal and catalytic performance, especially in selectivity for acrolein formation.

ACKNOWLEDGMENTS

The authors would like to thank Emeritus Professors Haruo Shingu and Kimio Tarama, and Professor Yoshinobu Takegami, of Kyoto University, for their helpful discussions and encouragements. The authors also thank Dr. Seishiro Nakamura, Akira Kubotsu of Kurare Co. Ltd., JEOL Co. Ltd., and Hitachi Co. Ltd. for cooperation in the electron-micrograph observations.

REFERENCES

1. Sampson, R. J., and Shooter, D., *Oxid. Combust. Rev.* **1**, 250 (1965).
2. Voge, H. H., and Adams, C. R., *Advan. Catal.* **17**, 174 (1967).
3. Wood, B. J., Wise, H., and Yolles, R. S., *J. Catal.* **15**, 355 (1969).
4. Adams, C. R., *Ing. Eng. Chem.* **61**, 31 (1969).
5. Holbrook, L. L., and Wise, H., *J. Catal.* **20**, 367 (1971).
6. Rosso, R. D., Mazzocchia, C., and Centola, P., *React. Kinet. Catal. Lett.* **9**, 23 (1978).
7. Davydov, A. A., Mikhaltchenko, V. G., Sokolovskii, V. D., and Boreskov, G. K., *J. Catal.* **55**, 299 (1978).
8. Aso, I., Nakao, M., Yamazoe, N., and Seiyama, T., *J. Catal.* **57**, 287 (1979).
9. Jsaev, O. V., and Kushnerev, M. Ya., *Dokl. Akad. Nauk SSSR* **124**, 858 (1959).
10. Popova, N. I., Belyaev, V. J., and Vermel, E. E., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* **2**, 926 (1959).
11. Kominami, N., *Kogyo Kagaku Zasshi* **65**, 1520 (1962).
12. Shingu, H., Okazaki, T., and Inui, T., *Shokubai* **6**, 32 (1964).
13. Gorokhovatskii, Y. B., Vovyanko, I. I., and Rubanik, M. Y., *Kinet. Catal.* **7**, 65 (1966). [English transl.]
14. Byck, H. T., Fidiam, J. F., and Spell, A., "Paper No. 49, Division of Colloid Chemistry, American Chemical Society Meeting," p. 12. Chicago, September, 1956.
15. Nelsen, F. M., and Eggertsen, F. T., *Anal. Chem.* **30**, 1387 (1958).
16. Scholten, J. J. F., and van Montfoort, A., *J. Catal.* **1**, 85 (1962).
17. Inui, T., Ueda, T., Suehiro, M., and Shingu, H., *J. Chem. Soc. Faraday Trans. I* **74**, 2490 (1978).
18. Kominami, N., *Kogyo Kagaku Zasshi* **65**, 1517 (1962).
19. Inui, T., and Mitsuhashi, K., *Nippon Kagaku Kaishi*, 1311 (1977).
20. Inui, T., Ueda, T., and Suehiro, M., *Nippon Kagaku Kaishi*, 934 (1977).
21. Inui, T., and Tanabe, Y., *J. Catal.* **52**, 375 (1978).
22. Inui, T., and Ueda, T., *Nippon Kagaku Kaishi*, 773 (1977).