JOURNAL OF CATALYSIS 37, 523–530 (1975)

The Catalytic Deoxidation Reaction of Propylene Oxide on Copper Oxide

TOYOSABURO TAKEUCHI AND YOSHISATO TEZUKA

Faculty of Literature and Science[1] *and College of Liberal Arts,*[2]
Toyama University, Toyama-shi, Japan

Received August 29, 1972; revised November 8, 1974

The reaction mechanism in the catalytic formation of propylene from propylene oxide on copper oxide was investigated by using various copper oxides and reduced copper. The amount of propylene produced in the initial stage of the reaction on reduced copper was greater than that produced on copper oxide. The addition of oxygen to propylene oxide promoted catalytic formations of both propylene and carbon dioxide. The formation of these products was strongly curtailed by adding potassium iodide to the catalyst. These findings and results reported elsewhere on the exchange of oxygen between propylene oxide and copper oxide suggest that two different mechanisms, the redox cycle mechanism and the peroxide mechanism, proceed in parallel in the stational state of the reaction which produces propylene.

INTRODUCTION

Several years ago, we found in a study of the catalytic reaction of propylene oxide on copper oxide, that propylene was produced together with carbon dioxide and water (*1*). This result indicates that the oxidation and deoxidation reactions occurred in parallel. This report deals with the study of the reaction mechanism in the formation of propylene on the copper oxide catalyst. Various oxides, CuO, Cu_2O, the mixture of CuO and Cu_2O and reduced copper were used as catalysts in order to clarify the surface structure of the catalyst during the reaction.

EXPERIMENTAL METHODS

The reactions were carried out by means of a flow system using the apparatus shown in Fig. 1. A is the reaction tube and B is the reservoir of propylene oxide. C is the tube of calcium chloride used to dry the air, the nitrogen, and the oxygen, which were used for the reaction. D is the trap cooled by the dry ice. E is the soap-film meter, which was used for the measurement of the flow rate. F is the outlet for gas chromatography. Two kinds of reaction tubes with different dimensions were used. The diameter of one of the reaction tubes, V_1, was 8 mm, and the length of the tube was 280 mm. The diameter of the other tube, V_2, was 4 mm and its length was 100 mm. This smaller tube was only used to study the reaction products on the catalyst at the initial stage. In each experiment, 1 g of catalyst was packed in the middle of each tube. Air which had been dried with calcium chloride and diluted with various amount of nitrogen was passed through the reservoir of propylene oxide, which was kept at 0°C. The flow rate of the mixture of propylene oxide and air in both reaction tubes was always kept at 60 ml/min.

The poisoning effect of potassium iodide on the catalytic activity for the reaction was investigated using the same apparatus

---

[1] T. T.

[2] Y. T.

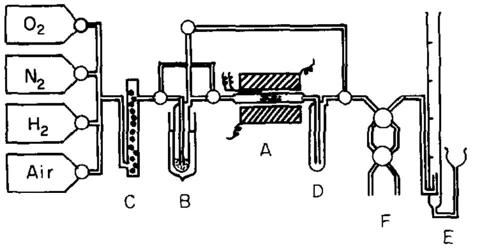


FIG. 1. Apparatus.

described above. The catalysts used in this case were prepared by immersing the cupric oxide in solutions of different concentrations of potassium iodide at room temperature. The catalyst was then removed from each solution after 4 hr and was dried in air at 450°C for 2 hr.

The cupric oxide used was of stick-like form. It was furnished by Wako Pure Chemical Co. Its purity was 99.9%. The cuprous oxide and the metallic copper were furnished by Nakarai Chemical Co. Both were in granular form and the purity was 99.9%. The metallic copper was used after it was reduced by a hydrogen stream at 400°C until no water was detected in the trap cooled by liquid nitrogen during the reaction. The mixture of cupric oxide and cuprous oxide was of the stick-like form. It was Merck reagent for elementary analysis. The propylene oxide and potassium iodide used were furnished by Wako Pure Chemical Co. They were of extra-pure quality and were used without further purification.

RESULTS

A transparent colorless liquid with a stimulative smell which suggests the existence of aldehydes and carboxylic acids was obtained, together with propylene and carbon dioxide, when propylene oxide was passed over the cupric oxide catalyst. During the reaction, the color of the catalyst gradually changed from black to reddish-brown, irrespective of the presence of oxygen gas in the reaction tube.

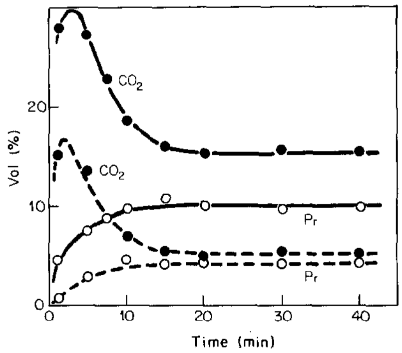


FIG. 2. Variation of reaction products given by propylene oxide on cupric oxide (450°).

(—) $P_{O_2}/P_{pro} = 0.8$; (---) $P_{O_2}/P_{pro} = 0.25$.

Two examples of the change in the gaseous products after the propylene oxide started to flow over the cupric oxide at 450°C with a different ratio of the propylene oxide and oxygen are shown in Fig. 2. The amount of carbon dioxide decreased markedly in the initial 15 min, and then became constant. On the contrary, the amount of propylene increased markedly in the initial period, and then became con-

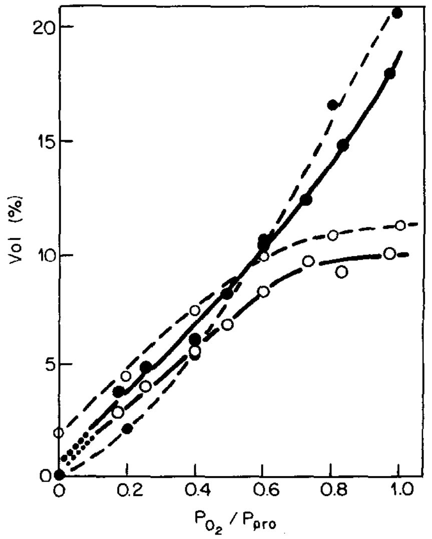


FIG. 3. Dependences of $r = P_{O_2}/P_{pro}$ upon the amounts of propylene and carbon dioxide on cupric oxide and reduced copper (450°C). CuO: (○—) Pr, (●—) CO_2; Cu: (○--) Pr, (●--) CO_2.

stant. Figure 3 shows the dependence of the ratio $r = P_{O_2}/P_{pro}$ upon the amount of propylene and of carbon dioxide produced on the cupric oxide and the reduced copper (metallic copper) catalysts 20 min after the reaction has started. In both cases, r was changed by the addition of nitrogen or oxygen to air, while keeping the temperature of the reservoir of propylene oxide 0°C. The r for pure air is given as 0.8. The amount of carbon dioxide produced on the reduced copper was nearly zero, when r was zero; but a considerable amount was obtained on cupric oxide. The reverse result was given for the amount of propylene. The amount of carbon dioxide increased in proportion to the wide region of r . The amount of propylene increased proportionately up to $r = 0.8$, then became constant.

Figures 4 and 5 show the dependence of the reaction temperature upon the amount of propylene and carbon dioxide produced by the cupric oxide catalyst 20 min after the reaction had started in two cases when the ratios were 0.5 and 0.8. These results show that the ratios of the amount of carbon dioxide and that of propylene P_{CO_2}/P_{pr} were practically constant, i.e., 1.0 and 1.5 irrespective of reaction temperature.

Figures 6 and 7 show the results of the reactions on various copper oxides and the reduced copper catalysts. In the case of Fig. 6, propylene oxide was passed over each catalyst without oxygen gas. It was mixed with helium in ratio, P_{pro}/P_{He}, of 0.2. In the case of Fig. 7, air was mixed with the propylene oxide at the ratio of P_{O_2}/P_{pro} of 0.8. Figure 6 indicates that the amount of carbon dioxide produced in the initial stage was in order of CuO, Cu_2O and Cu, but it decreased rapidly to a constant value after 30 min. The following order which is similar to the case of carbon dioxide was obtained for the amount of propylene in the initial stage of the reaction.

$$CuO > Cu_2O + CuO > Cu_2O > Cu.$$

These results indicate that the addition of oxygen to propylene oxide did not change

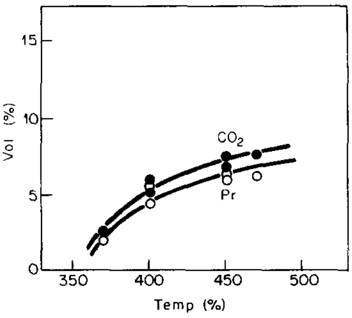


FIG. 4. Dependence of the reaction temperature upon the amount of propylene and carbon dioxide (cupric oxide, $P_{O_2}/P_{pro} = 0.5$).

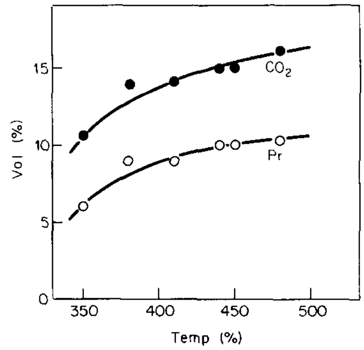


FIG. 5. Dependence of the reaction temperature upon the amounts of propylene and carbon dioxide (cupric oxide, $P_{O_2}/P_{pro} = 0.8$).

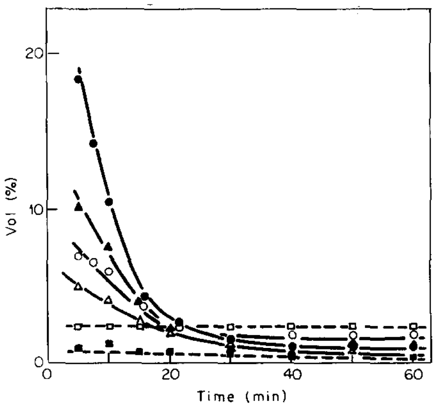


FIG. 6. Variation of reaction products on various copper oxides ($P_{pro}/P_{He} = 0.2$). CuO: (●—) CO_2, (○—) Pr; Cu_2O: (▲—) CO_2, (△—) Pr; Cu: (■--) CO_2, (□--) Pr.

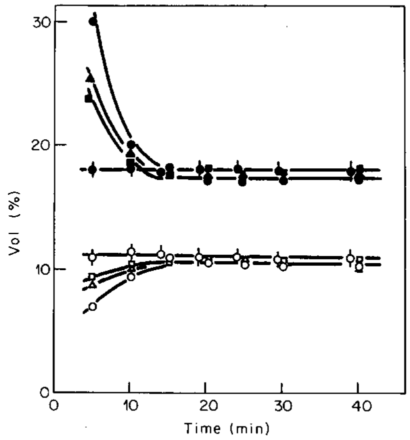


FIG. 7. Variation of reaction products on various copper oxides ($P_{O_2}/P_{pro} = 0.8$). CuO: (●—) CO_2, (○—) Pr; $CuO\text{-}Cu_2O$: (▲—) CO_2, (△—) Pr; Cu_2O: (■—) CO_2, (□—) Pr; Cu: (●—) CO_2, (⌽—) Pr.

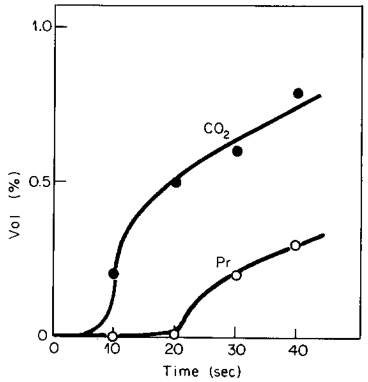


FIG. 9. Variation of reaction products during the initial 1 min on cupric oxide ($P_{pro}/P_{He} = 0.2$).

the order of the activity in the initial stage, though the time necessary for arrival at the stationary state became short, ca. 1/2.

Figures 8 and 9 show the change of the reaction products during the initial 1 min; that is, soon after propylene oxide had begun to flow over the reduced copper and the cupric oxide catalysts. In these studies the reaction tube, V_2, was used in order to make the dead volume of the reaction tube smaller and to make the error in the measurement of the reaction products smaller than in V_1. These figures indicate that in the reaction on the reduced copper, propylene was produced 10 sec after the propylene oxide had passed the reaction tube; however, no carbon dioxide was produced. On the contrary, carbon dioxide was produced on the cupric oxide within the initial 10 sec; however, no propylene was produced.

Figure 10 shows the influence of potassium iodide treatment of the catalyst upon the catalytic activity using 10% potassium iodide solution. The formation of both propylene and carbon dioxide was strongly curtailed by potassium iodide. The prevention of propylene formation was practically complete, the production of carbon dioxide was reduced by 50%. The prevention sud-

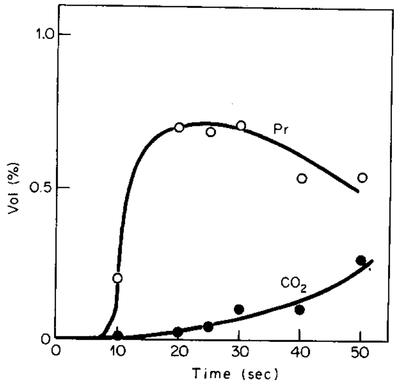


FIG. 8. Variation of reaction products during the initial one minute on reduced copper ($P_{pro}/P_{He} = 0.2$).

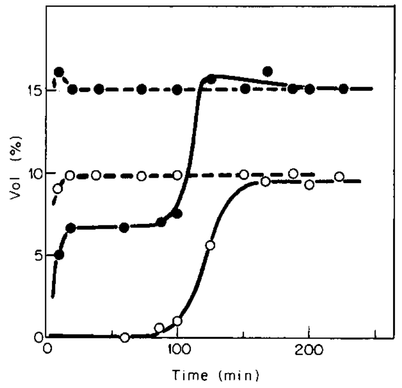


FIG. 10. Variation of reaction products with time on copper oxide treated by the solution of 10% potassium iodide (450°C, $P_{O_2}/P_{pro} = 0.8$). KI-CuO: (●—) CO_2, (○—) Pr; CuO: (●--) CO_2, (○--) Pr.

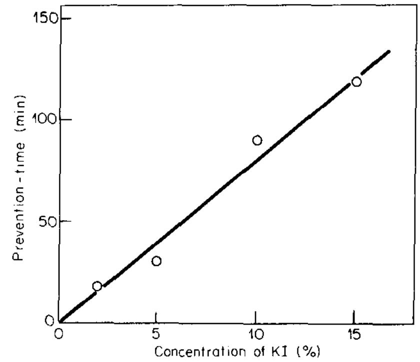
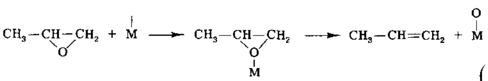


FIG. 11. Relation between the prevention-times and the concentration of potassium iodide.

denly ceased after a period of time proportionate to the concentration of potassium iodide, as is shown in Fig. 11. To determine whether the recommencement of both deoxidation and oxidation reactions depends upon the disappearence of potassium iodide on the surface of the catalyst, due to evaporation, or whether it is caused by the dissolution of potassium iodide, a starch reaction was carried out for the liquid products which had been collected in a trap cooled by dry ice. Surprisingly no change in the color of the testing solution was observed.

DISCUSSION

The reaction mechanism of the catalytic deoxidation of propylene oxide may be assumed to include a step in which the oxygen atom of the reactant transfers to the catalyst. The acceptance of the oxygen atom would be easier for metal than for metal oxide. Figure 8 indicates that the reaction product in the initial stage on the reduced copper contained a conspicuous amount of propylene but did not contain carbon dioxide. This fact reveals that the metallic copper attracts the oxygen atom of propylene oxide as the following mechanism



$$CH_3{-}CH{-}CH_2(O) + M \longrightarrow CH_3{-}CH{-}CH_2(O{-}M) \longrightarrow CH_3{-}CH{=}CH_2 + M{-}O \qquad (1)$$

where M denotes a metal atom. Carbon dioxide is produced with the oxygen which is fixed on the surface of the catalyst, and the oxidation reaction begins after the oxygen on the surface attains a certain concentration. Figure 9 indicates that propylene was not produced, though a conspicuous amount of carbon dioxide was produced. This finding reveals that the deoxidation of propylene oxide took place after the removal of a certain amount of oxygen from the catalyst.

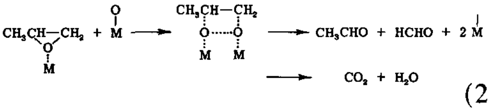
The total number of oxygen atoms which had been accumulated on the surface of 1 g of the reduced copper during the deoxidation of propylene oxide before the initiation of the oxidation reaction, N_O, is given as 1.9×10^{18}/g from Fig. 8, and the total number of copper atoms of the surface, N_{Cu} is given as 8×10^{18}/g. The surface area of the reduced copper was 0.5 m^2/g. The coverage of the oxygen atoms on the reduced copper, N_O/N_{Cu}, is given as 0.24. In the case of the reaction on copper oxide, the total number of metal copper atoms produced by the oxidation of propylene oxide before the initiation of propylene formation, N_{Cu}, is 3.5×10^{18}/g, and the total number of copper atoms on the oxide surface, N_{CuO}, is 12.8×10^{18}/g. The surface area of cupric oxide is 0.8 m^2/g. Therefore, the ratio N_{Cu}/N_{CuO} is given as 0.27, which is very similar to the value of the N_O/N_{Cu}. These results indicate that a dimension of the group of sites corresponding to at least 1/4 of the surface was necessary for both reactions to occur in parallel.

The pattern of the X-ray diffraction of the cupric oxide showed that the oxide was gradually reduced to the mixture of metallic copper and cuprous copper and then to the metallic copper, as the reaction approached a stationary state. This finding confirms that the deoxidation and the oxidation reactions proceed on the surface of metallic copper. The same conclusion had been proposed by Isaev *et al* (*2*) on the oxidation reaction of propylene.

The similar results at the stationary state of the reaction with four catalysts, cupric oxide, mixture of cupric oxide and cuprous oxide, cuprous oxide, and reduced copper, indicate that the surface of these catalysts became structurally similar during the reaction.

It has been proposed that the activity of a catalyst is affected by the kind of single crystals (*3*) as well as lattice imperfections (*4–6*). Kummer (*7*) found that the rate of oxidation of ethylene on silver varied with different crystal faces at the beginning of the reaction, but, it became the same due to the sintering of the surface. Gwathmey and Cunningham (*3*) found that the rates of oxidation of hydrogen on copper varied with their faces and the reaction time. Swanson and Uhlig (*8*) reported that the rate of oxidation of a single crystal of copper was greatly affected by pretreatment with gas, such as hydrogen and nitrogen. The nature of the surface for the reaction is very complicated, as mentioned above. However, if it is assumed that a special face was preferentially concerned in the initiation of the redox reaction in this study and that equal areas of the typical three faces, (100), (110) and (111), are present on the surface of the reduced copper and cupric oxide, $N_O/N_{Cu} = 0.24$ and $N_{Cu}/N_{CuO} = 0.27$ values at the initiation of the reaction become very large, about 3/4 of the special face.

Although many studies on the reaction mechanisms of the catalytic oxidation reaction of propylene have been reported earlier (*9–13*) there have been few reports on the oxidation of propylene oxide. Our results in this study suggest that the oxidation of propylene oxide took place when propylene oxide adsorbed in the environment of the densely adsorbed oxygen. Studies of the oxidation of propylene on copper oxide have concluded that the abstraction of hydrogen followed by the formation of an allyl species (*11,12*) or by the formation of acetic acid and formic acid (*13*) takes place, and that the latter reaction relates to the formation of carbon dioxide. The formation of carbon dioxide and water from propylene oxide may be written in a similar manner (*13*)

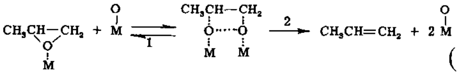


(2)

where $\overset{O}{\overset{|}{M}}$ shows the active oxygen adsorbed on metal atom.

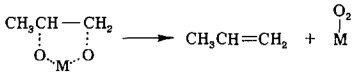
Figure 3 which shows the increase in the amount of propylene by the increase in the partial pressure of oxygen suggests that the redox cycle of the catalyst is promoted by an increase in the adsorbed oxygen. The adsorbed oxygen is removed not only by the oxidation reaction of propylene oxide but also by oxidation of the propylene produced in this reaction. The increase in the partial pressure of oxygen would promote this secondary oxidation reaction. For this reason, the amount of propylene produced becomes constant as the P_{O_2}/P_{pro} value increases, and the resulting curve is not linear.

There is very clear evidence that the deoxidation reaction of propylene oxide takes place with the aid of the adsorbed oxygen on copper oxide catalyst. That is, it was found earlier by the authors (*14*) that the exchange of oxygen between propylene oxide and copper oxide takes place at a lower temperature than that of the deoxidation reaction. This finding suggests that the oxygen of propylene oxide associates equally with that on the surface of the catalyst, in the following manner



(3)

It is assumed that propylene oxide adsorbs on the catalyst forming a peroxide with the adsorbed oxygen atom of the catalyst. The deoxidation of propylene oxide is a two-step process involving a prior equilibrium between propylene oxide and the adsorbed propylene oxide, followed by a rate-determining removal of oxygen from the peroxide by the catalyst. The reverse reaction of step 1, the oxygen scission of the intermediate complex results in the exchange reaction of the oxygen. If one intermediate associates with one site, as was proposed for the supported iridium catalyst by Cant and Hall (*15*), step 2 is written as



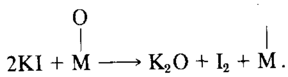
$$\underset{\text{O}\cdots\text{M}\cdots\text{O}}{\text{CH}_3\text{CH}-\text{CH}_2} \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \overset{\text{O}_2}{\overset{|}{\text{M}}} \quad (4)$$

It is concluded, therefore, that the deoxidation reaction proceeds by the parallel routes of (1) and (3) or (4).

The relation between the reactivity and the type of adsorbed oxygen is an important problem in catalytic oxidation reactions. Study of the X-ray diffraction concluded that the surface of the cupric oxide catalyst at the stationary state of the reaction had changed to the metallic form. This finding suggests that lattice oxygen was not involved in the catalytic reaction. In the case of the oxidation of ethylene on silver oxide, Hayes (*16*) took the view that O_2^- ion is responsible for the complete oxidation and O^- ion for the formation of the partial oxidation products. Smith (*17*) proposed the existence of O^- on cupric oxide; however, he could not confirm the O_2^- ion. Yoshida (*18*) proposed from the result of the study by means of ESR on the oxidation of ethylene and propylene on vanadium oxide that O_2^- is reactive. On the contrary, Naccache and Che (*19*) have shown that O^- reacts with ethylene faster than O_2^- using magnesium oxide. Schvets *et al.* (*20*) reported that the stability of O_2^- and O^- ions depends upon the reaction temperature. Since the following change is considered to occur between both ions

$$O_2^- + e \rightleftharpoons 2O^-$$

it is difficult to decide clearly which type of oxygen played the catalytic role in this reaction. However, the disturbance of potassium iodide for both oxidation and deoxidation reactions can be explained in terms of the removal of the active oxygen of the surface by the reaction with potassium iodide. Uchijima *et al.* (*21*) measured the distribution power of excess oxygen of oxide catalysts by the potassium iodide method. They concluded that the oxygen which reacts with potassium iodide has a high oxidation power. Such active oxygen would be removed by potassium iodide from the surface of the catalyst. However, the iodide–starch reaction detected no potassium iodide in the liquid products. The removal of active oxygen on metal would be explained by the following reaction;



$$2\text{KI} + \overset{\text{O}}{\overset{|}{\text{M}}} \longrightarrow \text{K}_2\text{O} + \text{I}_2 + \overset{|}{\text{M}}.$$

The iodine produced by this reaction might be carried outside the reaction tube.

ACKNOWLEDGMENTS

The authors thank Mr. Tsuneo Yamazaki, Mr. Taizo Nakamura and Mr. Yoshio Toda for their assistance in these experiments.

REFERENCES

1. Takeuchi, T., Nakamura, T., and Tezuka, Y., *Jap. Chem. Soc. Meet., 19th, Prepr.* 1, p. 508 (1966).

2. Isaev, O. V., Kushnerev, M. Y., and Margolis, L. Y., *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* (English Transl.), **119,** 131 (1958).

3. Gwathmey, A. T., and Cunningham, R. E., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 10, p. 57. Academic Press, New York, 1958.

4. Vol'kenshtein, F. F., *Zh. Fiz. Khim.* **22,** 311 (1948); **23,** 917 (1949).

5. Uhara, I., Yanagimoto, S., Tani, K., Adachi, G., and Teratani, S., *J. Phys. Chem.* **66,** 2691 (1962).

6. Takeuchi, T., Miyatani, D., Okamoto, K., Takada, Y., and Takayasu, O., *Proc. Int. Congr. Catal., 5th, 1972* 555 (1973).

7. Kummer, J. T., *J. Phys. Chem.* **60,** 666 (1956).

8. Swanson, A. W., and Uhlig, H. H., *J. Electrochem. Soc.* **118,** 1325 (1971).

9. Voge, H. H., Wagner, C. D., and Stevenson, D. P., *J. Catal.* **2,** 58 (1963).

10. Adams, C. R., and Jennings, T. J., *J. Catal.* **2,** 63 (1963).

11. Adams, C. R., Voge, H. H., Morgon, C. D., and Armstrong, W. E., *J. Catal.* **3,** 379 (1964).

12. Sachtler, W. M. H., and Deboer, N. H., *Proc. Int. Congr. Catal., 3rd, 1964* 252 (1965).

13. Sampson, R. J., and Shooter, D., *in* "Oxidation and Combustion Reviews" (C. F. H. Tipper, Ed.), Vol. 1, p. 269. Elsevier, New York, 1965.

14. Tezuka, Y., Toda, Y., and Takeuchi, T., *Shokubai* **10,** Prepr. 48 (1968).

15. Cant, N. W., and Hall, W. K., *J. Catal.* **27,** 70 (1972).

16. Hayes, K. E., *Can. J. Chem.* **38,** 2256 (1960).

17. Smith, A. W., *Actes Int. Congr. Catal., 2nd, 1960* 1171 (1961).

18. Yoshida, S., *USA-Jap. Seminar Catalytic Sci.,* (Hawaii) Prepr. 361 (1971).

19. Naccache, C., and Che, M., *Proc. Int. Congr. Catal., 5th, 1972* 1389 (1973).

20. Schets, V. A., Vorotinthev, V. M., and Kasansky, V. B., *Kataliz* **10,** 356 (1969).

21. Uchijima, T., Takahashi, M., and Yoneda, Y., *J. Catal.* **9,** 403 (1967).