Nature of Oxygen Species Incorporated into Acrylaldehyde in Vapor-Phase Oxidation of Propylene over Supported Copper Catalyst

Masamichi AKIMOTO, Masao AKIYAMA, and Etsuro ECHIGOYA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received December 11, 1975)

The oxidation of propylene with Cu_2O as active phase for acrylaldehyde formation gave no acrylaldehyde in contrast to the fully oxidized CuO–SiC. However, CuO–SiC from which adsorbed oxygen species was eliminated gave rise to the formation of a negligible amount of acrylaldehyde. The presence of molecular oxygen species adsorbed on the CuO–SiC was shown by the desorption of oxygen and the isotopic mixing reaction of ^{16}O—^{18}O. The adsorbed oxygen (possibly molecular oxygen species) seems to be necessary as oxygen incorporated into acrylaldehyde. Agreement of the ratio of $^{18}O/^{16}O$ in acrylaldehyde formed by the oxidation with oxygen containing ^{18}O over $Cu_2{}^{16}O$ with that of $^{18}O/^{16}O$ in the reaction mixture supports the role of adsorbed oxygen species. The presence of O_2^- over Cu_2O during the course of oxidation was confirmed by the formation of furan and maleic anhydride in the co-oxidation with butadiene. The results were discussed in relation to the structure of the catalyst suitable for selective oxidation, the incorporation of oxygen atom *via* electronegative oxygen species adsorbed being proposed.

The vapor-phase oxidation of propylene to acrylaldehyde over copper(I) oxide has been investigated, some of the results being summarized.[1-3] Studies were mostly focused on the determination of intermediate hydrocarbon species *via* which acrylaldehyde is formed. The initial removal of a hydrogen atom from the methyl group to form an allylic intermediate was proposed by many workers.[4-6] However, not much attention has been paid to the form of oxygen species participating in the selective oxidation of propylene to acrylaldehyde. In this selective oxidation, oxygen plays two roles, *i.e.*, abstraction of hydrogen atoms and addition to the formed intermediate hydrocarbon species.

In general, the lattice oxygen of transition metal oxides is capable of hydrogen abstraction, differing with the type of metal-oxygen bond. However, the lattice oxygen is not always incorporated into selective oxidation products, as seen in the special role of double bond type lattice oxygen in the oxidation of butadiene to maleic anhydride.[7,8] Wood and co-workers[9] assumed in their semiconductivity studies on the oxidation of propylene over Cu_2O that electronegative oxygen species sorbed on the surface is the active species for acrylaldehyde formation. On the other hand, Callahan and Grasselli[10] showed that the lattice oxygen of copper oxide catalyst is involved in acrylaldehyde formation. The form of oxygen species incorporated into acrylaldehyde has not been sufficiently clarified. We have investigated the vapor-phase oxidation of propylene over supported copper catalyst as regards the nature of oxygen species incorporated into acrylaldehyde by means of X-ray analysis, oxygen isotope (^{18}O) and co-oxidation with butadiene or furan. The results were discussed in relation to the structure of the catalyst suitable for acrylaldehyde formation.

Experimental

Vapor-phase catalytic oxidation of propylene was performed using a conventional flow microreactor and a pulse reactor under atmospheric pressure. The microreactor was a Pyrex tube of inner diam 12 mm and length 300 mm with a concentric thermowell; the pulse reactor was a 4 mm inner diam U-type Pyrex tube. Heating was carried out with a cylindrical fluidized thermal bath. The catalyst was diluted with 30—50 mesh quartz, Raschig rings (2.5 $\times$ 2.5 mm) being used as a preheating medium.

As reacting substances, air, propylene (99% up), butadiene (99% up) and reagent grade furan were used. Nitrogen, hydrogen and helium were supplied from commercial cylinders. Gaseous oxygen containing ^{18}O (Japan-Isotope Association) was used. The air was purified by passing through silica gel and a soda-lime tower in order to remove water and CO_2. Helium was used as a carrier gas for oxidation by means of pulse technique. A trace amount of impurities such as oxygen existing in helium was removed by passing through a molecular sieve 13X column (4 mm inner diam, 1 m) cooled with liquid nitrogen.

CuO–SiC catalyst was prepared as follows. SiC (60—80 mesh) was calcined at 1000 °C for 4 h in a furnace. The precipitate obtained by the addition of an aqueous solution of Na_2CO_3 to the suspension of the calcined SiC in an aqueous solution of $Cu(NO_3)_2$ was thoroughly washed with water and then dried on a water-bath. The mass obtained was then calcined at 500 °C for 5 h in the air. The amount of CuO supported is 6.2 wt%, and the surface area is about 0.3 m^2/g. The catalyst was reduced with hydrogen current at 400 °C for 1.5 h prior to the experiment. Cu_2O was prepared according to two methods: (a) by the reduction of $Cu(AcO)_2$ with 1 N hydrazine in an aqueous media[11] (denoted by Cu_2O (I)); (b) by the addition of 10% aqueous solution of glucose to an aqueous mixture of $CuSO_4$, sodium potassium tartarate and NaOH at 100 °C[12] (denoted by Cu_2O(II)). The products were found to be pure by X-ray diffraction. The reduction of CuO–SiC was carried out by immersion into an aqueous solution of hydrazine at room temperature, the amount of nitrogen evolved being measured with a capillary glass tube.

The gaseous effluent from the reactor was analyzed by gas chromatography. PEG 20 M 20 wt% on Neopak 1A (acrylaldehyde, furan, acetaldehyde) and propylene carbonate 40 wt% on Celite 545 (CO_2) were used as separating columns. Maleic anhydride formed was absorbed in water followed by boiling of the solution in order to remove dissolved CO_2 and titration with an aqueous solution of NaOH. The structure of the catalyst was investigated by X-ray diffraction using nickel-filtered Cu $K\alpha$ radiation (30 kV, 20 mA). The isotopic mixture of gaseous oxygen or acrylaldehyde was analyzed by means of mass spectroscopy. Adsorption of

oxygen on the reduced catalyst was measured with a conventional volumetric apparatus.

Results

Active Phase for the Selective Oxidation. The oxidation of propylene (C_3' 28.0 vol%, O_2 5.0 vol%, and N_2 67.0 vol%) at W/F=0.934 g-catalyst h/g-mol became observable at 320 °C. Acrylaldehyde, CO_2 and a very small amount of CH_3CHO were formed. Above 370 °C, a gradual decrease in selectivity appeared. However, change in activity and selectivity was hardly observable at 350 °C during the course of oxidation. The selectivity is independent of the contact time below W/F=0.934 g-catalyst h/g-mol at 350 °C, as shown in Fig. 1. The steady state of the catalyst during oxidation under the reaction conditions was quenched by the introduction of helium (200 NTP ml/min) for 5 min to eliminate the reactant gas followed by a rapid decrease in temperature. X-Ray diffraction of the catalyst was observed at 2θ=36.3, 42.3, 61.4 (strong), and 38.8° (weak). The catalyst is composed of Cu_2O and a very small amount of CuO.

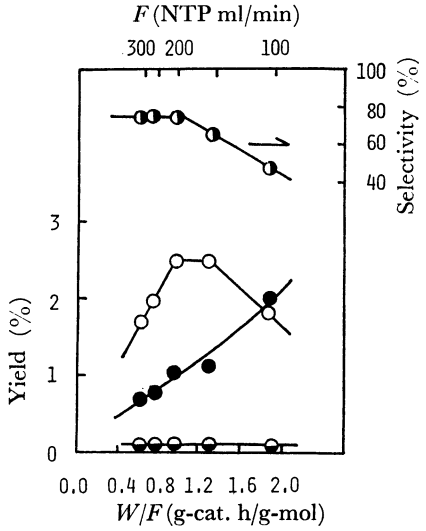

Fig. 1. Effect of the contact time on the oxidation of propylene.
Feed: C_3' 28.0 vol%, O_2 5.0 vol%, N_2 67.0 vol%.
Temp: 350 °C.
○: Yield of acrylaldehyde, ●: yield of CO_2, ◒: yield of acetaldehyde, ◑: selectivity to acrylaldehyde.

Table 1. Oxidation of propylene with various copper oxides using a pulse method[a)]

Oxidant	Pulse No.	Yield (%) Acrylaldehyde	Yield (%) CO_2	Selectivity (%) Acrylaldehyde
Cu_2O(I) 0.040 g	1	0.00	0.30	0.00
	2	0.00	0.21	0.00
	3	0.00	0.19	0.00
Cu_2O(II) 0.040 g	1	0.00	0.28	0.00
	2	0.00	0.18	0.00
	3	0.00	0.18	0.00
CuO-SiC 0.50 g	1	1.01	5.76	14.9
	2	0.11	0.86	11.3
	3	0.00	0.93	0.00
CuO-SiC 0.50 g treated with hydrazine	1	0.06	4.28	1.38
	2	0.00	0.55	0.00
	3	0.00	0.36	0.00

a) Temp: 350 °C, carrier gas: He 45 NTPml/min, pulse: C_3' 5.69 NTPml.

Oxidation of Propylene with Copper Oxides. The oxidation of propylene with various copper oxides was carried out by the pulse method. Only propylene was successively injected over the oxides (Table 1). In the case of Cu_2O (I) and Cu_2O (II), no formation of acrylaldehyde was observed even on the first injection in contrast to the case of CO_2. Use of 0.20 g Cu_2O (I) also gave the same result. In contrast, acrylaldehyde was formed in the first and second injections onto CuO–SiC which was prepared by reduction with hydrogen at 400 °C for 1.5 h followed by oxidation with air current at 350 °C. The amount of oxygen participating in acrylaldehyde formation and complete oxidation up to the second injection is 0.128 and 3.390 NTP ml/g-catalyst, respectively. However, when the CuO–SiC had been treated with 1 N NH_2–NH_2 at room temperature with evolution of 0.80 NTP ml N_2/g-catalyst, only a trace amount of acrylaldehyde was formed. X-Ray diffraction of this treated catalyst was observed at 2θ=35.7, 38.8, and 48.9° (strong). Thus the product is CuO.

Reduction of the Catalyst and Adsorption of Oxygen. Reduction of CuO–SiC with an aqueous solution of hydrazine (0.1 N) and adsorption of gaseous oxygen on the reduced one were performed in order to clarify the form of oxygen removed by treatment with the hydrazine solution. The hydrazine solution was heated at 80—90 °C for 10 min followed by cooling to room temperature. The solution was stirred for about 1 h until scarcely any evolution of nitrogen gas was observed. CuO–SiC catalyst was then introduced into the hydrazine solution and the amount of nitrogen evolved was determined (Fig. 2). CuO–SiC was prepared by the oxidation of the reduced catalyst with air current at 350 °C. An inflection point appears at 0.33 NTP ml N_2/g-catalyst (Fig. 2). No

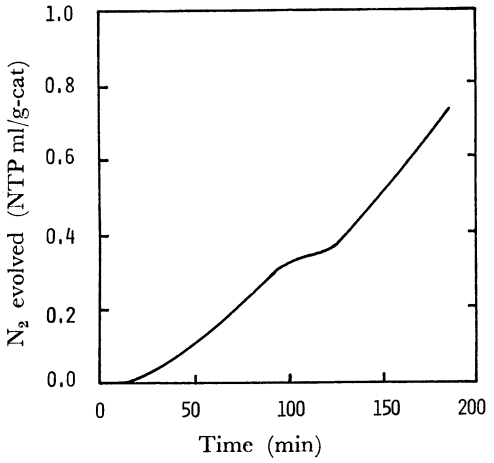

Fig. 2. Reduction of CuO-SiC catalyst with an aqueous solution of hydrazine.
CuO-SiC: 0.50 g, hydrazine: 0.1 N, temp: 18 °C.

definite inflection point was observed in the case of 1 N hydrazine. Adsorption of gaseous oxygen on the reduced catalyst was quantitatively studied. CuO–SiC reduced similarly was evacuated for 1 h at room temperature and again for 1 h at 250 °C. After determination of the dead volume of the adsorption apparatus, gaseous oxygen was introduced at room temperature and the catalyst was treated at 350 °C for 1 h. The amount of oxygen adsorbed was measured by observing the pressure drop of oxygen. When the amount of nitrogen evolved by the reduction was 0.30 or 0.60 NTP ml/g-catalyst, that of oxygen adsorbed was 0.32 or 0.63 NTP ml/g-catalyst at oxygen pressure of 137.6 or 133.6 Torr, respectively.

Isotopic Mixing Reaction of ^{18}O—^{16}O. $Cu^{16}O$–SiC was evacuated at 350 °C for 1.5 h in a vessel and then a mixture of oxygen ($^{18}O^{16}O$ 36.58, $^{16}O^{16}O$ 63.42 mol %) was introduced under 54 Torr at 20 °C. The isotopic mixing reaction was carried out at 198 °C. The gaseous oxygen was withdrawn to a small glass tube (*ca.* 1 ml) during the course of the reaction and was diluted with helium to *ca.* 5% O_2 followed by the analysis. Hardly any formation of $^{18}O^{18}O$ or change in the composition of the gaseous phase was observed (Fig. 3).

On the other hand, CuO–SiC (13.3 g) was evacuated at 525 °C under 10^{-5} Torr for 2 h. Oxygen was then adsorbed at 155 °C under $P_{O_2}=150$ Torr for 3 h. The oxygen pressure was then kept at room temperature overnight. After pumping out gaseous oxygen at room temperature, the temperature was raised and after 1 h, the amount of oxygen desorbed was determined by measuring the oxygen pressure. The amount was 0.007, 0.017, or 0.019 NTP ml/g-catalyst at 203, 350, or 448 °C, respectively.

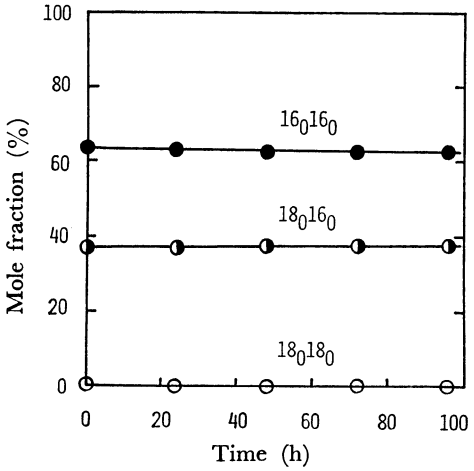

Fig. 3. Isotopic mixing reaction of ^{18}O—^{16}O over CuO–SiC catalyst.
Cat.: CuO-SiC 13.3 g, temp: 198 °C.

Oxidation of Propylene with $^{18}O_2$ over $Cu_2{}^{16}O$. A pulse containing propylene and heavy oxygen was injected over $Cu_2{}^{16}O$ (I) at 350 °C and the acrylaldehyde formed was separated with a gas chromatographic column coupled with the outlet of the pulse reactor. Injection was repeated several times using new $Cu_2{}^{16}O$ (I) at each injection, and the content of ^{18}O in acrylaldehyde collected was determined (Table 2). For the sake of comparison, the result obtained by using $^{16}O_2$ is given in the Table. The relative intensity of the species was $I_{58}/I_{56}=0.213$ or $I_{57}/I_{55}=0.218$, the average being 0.215. The values were in good agreement with that of $^{18}O/^{16}O$ in the pulse.

Co-oxidation of Propylene with Furan or Butadiene over Cu_2O. In order to investigate the form of oxygen species present on Cu_2O during the course of oxidation of propylene, co-oxidation with furan or butadiene was performed with reference to the formation of maleic anhydride and furan. Oxidation of propylene was first carried out for 2 h and then furan or butadiene was supplied. The concentration of furan or butadiene in the feed was kept very low, 1.5—3.0 vol%, as com-

Table 2. Oxidation of propylene with oxygen containing ^{18}O over $Cu_2{}^{16}O$ using a pulse method[a]

m/e	Species	Intensity of mass spectra $^{16}O_2$[b]	Intensity of mass spectra $^{16}O-{}^{18}O$[c]	
55	$CH_2=CH-C^{16}O$	72	64	$I_{58}/I_{56}=0.213$
56	$CH_2=CH-CH^{16}O$	106	94	
57	$CH_2=CH-C^{18}O$	0	14	$I_{57}/I_{55}=0.218$
58	$CH_2=CH-CH^{18}O$	0	20	

a) Temp: 350 °C, carrier gas: He 45 NTPml/min, cat.: $Cu_2{}^{16}O$(I) 0.040 g, pulse: 5.69 NTPml, C_3' 28.0 vol%, O_2 5.0 vol%, N_2 67.0 vol%. Composition of the oxygen in the pulse: b) $^{18}O/^{16}O=0.000$. c) $^{18}O/^{16}O=0.216$.

Table 3. Co-oxidation of propylene with furan or butadiene over copper(I) oxide[a]

Temp (°C)	Furan or butadiene in feed(vol%)	Conversion of furan or butadiene(%)	Yield(%) Acrylaldehyde	CO_2	Furan	Maleic acid
352	0.00	—	1.17	0.37	0.00	0.00
352	Furan 1.55	9.38	0.35	1.01	—	0.23
375	Furan 1.55	11.7	0.47	1.75	—	0.19
378	Butadiene 3.00	5.21	1.30	1.79	0.54	0.07
400	Butadiene 3.05	6.03	1.15	2.66	0.52	0.12

a) Cat.: CuO-SiC 0.51 g, feed: C_3' 28.0 vol%, O_2 5.0 vol%, diluent N_2, $W/F=0.951$ g-catlyst h/g-mol, yield of CO_2 was calculated by propylene base.

pared with that of propylene, so that the catalyst would not change structurally. The formation of maleic anhydride or of furan and maleic anhydride in the cooxidation with furan or butadiene, respectively, is given in Table 3. The selectivity for maleic anhydride or furan and maleic anhydride formation was 1.6—2.5 or 10.6—11.7%, respectively.

Discussion

The catalyst consists of Cu_2O and a very small amount of CuO during the oxidation of propylene. Thus, Cu_2O is the active phase for acrylaldehyde formation in line with the results reported.[9,13,14] However, the oxidation of propylene with Cu_2O gave no acrylaldehyde in accordance with the result for the CuO–SiC reduced with hydrazine (Table 1). This supports strongly the view that the lattice oxygen of Cu_2O and CuO is not incorporated into acrylaldehyde though it can abstract hydrogen atom from propylene. In contrast, the formation of acrylaldehyde in the oxidation with fully oxidized CuO–SiC suggests an important role of oxygen species adsorbed on the catalyst in acrylaldehyde formation. However, if the lattice oxygen existing on the surface of CuO could be eliminated by treatment with the hydrazine solution, the important role of the lattice oxygen can not be denied.

An inflection point appears at 0.33 NTP ml N_2/g-catalyst in the reduction of CuO–SiC with an aqueous solution of hydrazine (Fig. 2). The amount of nitrogen evolved up to this point might be equivalent to that of oxygen adsorbed on the surface, and nitrogen evolved beyond this point is due to the reduction of lattice oxygen with hydrazine and the decomposition of hydrazine by contact with copper ions. Reliability of the reduction is strongly supported by the good agreement of the amount of nitrogen evolved in the reduction of CuO–SiC with hydrazine with that of oxygen adsorbed on the reduced catalysts at $P_{O_2}=134$—138 Torr. Thus, the amount of oxygen adsorbed on the surface of CuO–SiC is 0.33 NTP ml O_2/g-catalyst or 5.32 NTP ml/g-CuO. The fact that the amount of oxygen consumed for acrylaldehyde formation up to the second injection is 0.128 NTP ml/g-catalyst or 2.065 NTP ml/g-CuO and that only a trace of acrylaldehyde was formed by the oxidation with the CuO–SiC which had been treated with the hydrazine solution (N_2 0.80 NTP ml/g-catalyst evolved) offer further evidence for the very important role of the adsorbed oxygen species or the surface lattice oxygen in the selective oxidation. As lattice oxygen of metal oxide is expected to play the role of hydrogen abstraction,[15–17] the adsorbed oxygen species or the surface lattice oxygen might be necessary for acrylaldehyde formation as the oxygen species incorporated rather than that abstracting the hydrogen atom from hydrocarbon species.

Callahan and Grasselli[10] found the formation of acrylaldehyde in the oxidation of propylene with fully oxidized CuO–SiC (0.4 wt% as CuO) at 300 °C by means of a pulse method and concluded that lattice oxygen is involved in the selective oxidation. According to our calculations based on the assumption that the volume of propylene was measured at 20 °C and 1 atm, only CO_2 and H_2O being formed by unselective oxidation, the amount of oxygen used for acrylaldehyde formation is 0.01 NTP ml/g-catalyst or 2.58 NTP ml/g-CuO. The latter value is comparable to the value previously obtained 2.065 NTP ml/g-CuO and is less than the amount of adsorbed oxygen species 5.32 NTP ml/g-CuO. Even taking account of the differences in the reaction temperature and the content of CuO supported, their result is explained by assuming the very important role of adsorbed oxygen species in acrylaldehyde formation.

Formation of acrylaldehyde in the reduction of metal oxide with propylene also takes place in the case of SnO_2, Sb_2O_4, Fe_2O_3–Sb_2O_4,[16,17] MoO_3, and bismuth molybdates.[17,18] Double bond type lattice oxygen Mo=O of MoO_3 is incorporated into furan and maleic anhydride formed in the oxidation of butadiene.[8] Incorporation of the lattice oxygen into acrylaldehyde in the oxidation of propylene over the catalysts containing MoO_3 is very likely to occur. This is supported by the formation of MoO_2 in the reduction of the catalysts with propylene.[17,18] In the case of other oxides which have no double bond type lattice oxygen, formation of acrylaldehyde might be attributed to the presence of adsorbed oxygen species or to the higher positive charge of the adsorbed hydrocarbon species. Formation of acrylaldehyde appeared with a rise in the acidity of Bi_2O_3 and SnO_2 catalysts by addition of P_2O_5.[19] However, this is not the case of the selective oxidation over Cu_2O since the amount of CuO was very small.

The form of oxygen species adsorbed on the CuO–SiC is discussed in the following. The fact that no change in the composition of gaseous oxygen was observed in the isotopic mixing reaction over the catalyst suggests non-dissociative adsorption of oxygen molecule on the surface (Fig. 3). The desorption of oxygen from the CuO–SiC with a rise in temperature provides further evidence for the existence of adsorbed oxygen species and the reversibility of some portion of oxygen adsorption. A part of adsorbed oxygen species seems to be present as diatomic species. Incorporation of the adsorbed oxygen species into acrylaldehyde was also supported in accordance with $^{18}O/^{16}O$ ratio in the formed acrylaldehyde with that in the pulse (Table 2). Oxygen species adsorbed on Cu_2O are negatively charged.[20,21] This strongly suggests formation of various oxygen species over Cu_2O during the course of oxidation of propylene as follows: O_2-(gas)$\rightarrow O_2^-\rightarrow O^-\rightarrow O^{2-}$ (lattice). We showed in our studies on the oxidation of butadiene[8] and furan[22] over supported molybdena and promoted anatase-type titania catalysts that oxygen atom of O_2^- is incorporated into maleic anhydride. Furan is an intermediate of maleic anhydride from butadiene.[23] Thus, formation of furan and maleic anhydride in the cooxidations (Table 3) gives strong evidence to the formation of O_2^- over Cu_2O during the course of oxidation of propylene. Enikeev *et al.*[21] proposed in their studies on the work function of Cu_2O upon the adsorption that adsorbed propylene and various products

have a partial positive charge in contrast with adsorbed oxygen species. Even if this positively charged hydrocarbon intermediate reacts with electronegative oxygen species such as O_2^-, there appears no special difficulty in these addition reactions.

The result given in Table 1 can not clarify whether lattice oxygen on the surface of CuO is incorporated into acrylaldehyde or not. However, the fact that CuO is not a selective phase in contrast with Cu_2O during the course of oxidation and that the catalyst consists of Cu_2O and a very small amount of CuO at the steady state suggests the incorporation of the adsorbed oxygen species rather than the surface lattice oxygen during the course of steady state oxidation. Formation of the electronegative oxygen species on CuO is very difficult in contrast with that on Cu_2O[9]. This possibly accounts for the great difference in selectivity during the oxidation of propylene over these copper oxides rather than the ability to perform hydrogen abstraction. Charge of the adsorbed oxygen species existing on the surface of CuO–SiC was not clarified. It is apparent that the oxygen species adsorbed on the surface acts as oxygen incorporated into acrylaldehyde in the pulse experiment. The results provide one possibility that acrylaldehyde can be formed even over CuO if lattice oxygen of this oxide could abstract hydrogen from propylene and electronegative oxygen species adsorbed could be present. This is the case of acrylaldehyde formation in the pulse experiment.

We have no experimental result showing which electronegative oxygen species of O_2^- or O^- is incorporated. No attention was paid to the direct incorporation of gaseous oxygen into acrylaldehyde since this mechanism could not explain the difference in selectivity during the course of oxidation over Cu_2O and CuO. Kugler and Kokes[24] presumed from IR that acrylaldehyde is formed by the reaction of O_2^- with the π-allyl. Cant and Hall[25] also proposed a very important role of diatomic oxygen species in the oxidation of propylene to acrylaldehyde over Rh or Ru–α-Al_2O_3. These observations are in line with ours and offer a greater possibility for preferential incorporation of the electronegative molecular oxygen species during the course of selective oxidation over Cu_2O. This is consistent with the fact that the amount of oxygen consumed for acrylaldehyde formation, which is equal to that of the adsorbed molecular oxygen used for the incorporation, is less than that of the adsorbed oxygen species (Table 1 and Fig. 2).

References

1) T. J. Jennings and F. S. Stone, "Advances in Catalysis," Vol. 9, Academic Press, New York (1957), p. 441.
2) L. Ya. Margolis, "Advances in Catalysis," Vol. 14, Academic Press, New York (1963), p. 429.
3) H. H. Voge and C. R. Adams, "Advances in Catalysis," Vol. 17, Academic Press, New York (1967), p. 151.
4) H. H. Voge, C. D. Wagner, and D. D. Stevenson, *J. Catal.*, **2**, 58 (1963).
5) C. R. Adams and T. J. Jennings, *J. Catal.*, **2**, 63 (1963).
6) C. R. Adams and T. J. Jennings, *J. Catal.*, **3**, 549 (1964).
7) M. Akimoto and E. Echigoya, *J. Catal.*, **29**, 191 (1973).
8) M. Akimoto and E. Echigoya, *J. Catal.*, **31**, 278 (1973).
9) B. J. Wood, H. Wise, and R. S. Yolles, *J. Catal.*, **15**, 355 (1969).
10) J. L. Callahan and R. K. Grasselli, *AIChE J.*, **9**, 755 (1963).
11) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 755.
12) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," 3rd ed., The Macmillan Company, New York (1951), p. 108.
13) O. V. Isaev, M. Ya. Kushnerev, and L. Ya. Margolis, *Proc. Acad. Sci. USSR, Phys. Chem. Sect. (Engl. Transl.)*, **119**, 129 (1958).
14) Y. B. Gorokhovatskii, I. I. Vovyanko, and M. Y. Rubanik, *Kinet. Catal. (Engl. Transl.)*, **7**, 65 (1966).
15) H. E. Swift, J. E. Bozik, and J. A. Ondrey, *J. Catal.*, **21**, 212 (1971).
16) V. Fattore, Z. A. Fuhrman, G. Manaro, and B. Notari, *J. Catal.*, **37**, 215 (1975).
17) V. Fattore, Z. A. Fuhrman, G. Manaro, and B. Notari, *J. Catal.*, **37**, 223 (1975).
18) M. Egashira, H. Sumie, T. Sakamoto, and T. Seiyama, *Kogyo Kagaku Zasshi*, **73**, 860 (1970).
19) T. Seiyama, M. Egashira, T. Sakamoto, and I. Aso, *J. Catal.*, **24**, 76 (1972).
20) W. E. Garner, T. J. Gray, and F. S. Stone, *Proc. R. Soc. London, Ser. A*, **197**, 294 (1949).
21) E. Kh. Enikeev, O. V. Isaev., and L. Ya. Margolis, *Kinet. Katal.* **1**, 431 (1960).
22) M. Akimoto and and E. Echigoya, *Trans. Faraday Soc.*, in press.
23) M. Akimoto and E. Echigoya, *Bull Chem. Soc. Jpn.*, **48**, 3518 (1975).
24) B. L. Kugler and R. J. Kokes, *J. Catal.*, **32**, 170 (1974).
25) N. W. Cant and W. K. Hall, *J. Catal.*, **22**, 310 (1971).