On the Behavior of O_2^- and O^- Radicals over V_2O_5-SiO_2 Catalyst

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The behavior of oxygen, O_2^- and O^- radicals adsorbed on the partially reduced V_2O_5–SiO_2 catalysts has been investigated. Oxygen is adsorbed mainly in a molecular state at room temperature, the sum of amounts of paramagnetic adsorbed species O_2^- and O^- being less than 10% of total amount of adsorbed oxygen. High degree of reduction, high content of V_2O_5 and low pressure of oxygen at adsorption equilibrium are favorable for the formation of O^- radical. It was confirmed by the quantitative analysis of reaction products and the adsorbed species that O_2^-, not O^-, is the active species in the oxidation of propylene at room temperature. A mechanism involving an intermediate of an epoxide structure was proposed.

In the last decade, many works have been carried out mainly by ESR technique on the formation of O_2^- and/or O^- on the surface of partially reduced metal oxide. It has been established that O^- is very reactive to carbon monoxide, while O_2^- seems to be unreactive to such gases as hydrogen and carbon monoxide at room temperature.[1] In most works, zinc oxide and titanium oxide were chosen as adsorbents, which exhibit poor activity for the oxidation of hydrocarbons. No reports seem to have been given on the oxidation of hydrocarbons by O_2^- or O^- over these oxides.

Schvets *et al.*[2] and Tarama *et al.*[3] found that O_2^- and/or O^- were formed on partially reduced vanadium oxide used as a commercial catalyst for oxidation, when the oxide was supported on silica. Kazansky *et al.* have established the high reactivity of O^- to carbon monoxide and claimed that O_2^- is inactive in oxidation reactions.[4]

In a previous paper[5] a report was given on the stability and reactivity of O_2^-. It was found that propylene is oxidized to propionaldehyde by adsorbed oxygen species over this catalyst, a hypothesis being proposed that O_2^- is the active species in the reaction. Kazansky *et al.* reported that O^- was formed on the reduced vanadium oxide[4] but they gave no favorable conditions for its formation, and this could not be confirmed in the previous work. The first aim of the present work is the establishment of favorable conditions for the formation of O^-. The second aim is clarification of the active species in the oxidation of hydrocarbons. A large amount of diamagnetic oxygen species are coexistent on the surface.[5] The possibility of participation of these species can not be excluded from ESR investigation only. We attempted to solve the problem by investigation of the quantitative correlation between the amount of products and oxygen species.

Experimental

Materials. Carrier (SiO_2); Silica gel obtained from ethyl orthosilicate hydrolyzed in a water–ethanol mixture at boiling point was calcined at 500 °C for 5 hr in a dry stream of air and was ground to powder of less than 100 mesh.

Catalysts (V_2O_5–SiO_2): Silica gel impregnated with 0.3 M ammonia solution containing ammonium metavanadate was dried and calcined at 500 °C for 10 hr in dry stream of air. The amounts of vanadium oxide (V_2O_5) supported on SiO_2 were 2 and 5 wt%.

Gases: Commercial oxygen and propylene were used. Carbon monoxide was obtained by the decomposition of sodium formate. All gases were purified by vacuum distillation at a low temperature.

Apparatus and Procedure. Measurements of oxygen adsorption were carried out by the usual volumetric method. ESR spectra were recorded with a JES-3BSX type ESR spectrometer (X-band). Amounts of O_2^- were determined by means of a TE105 cavity using DPPH as a standard. Amounts of O^- were estimated from the amount of CO_2 produced by its reaction with CO at room temperature. The reaction of propylene with adsorbed oxygen was carried out in a similar manner to that described previously.[5] The reaction mixtures were recovered with a liquid N_2 trap and analyzed by a gas chromatograph with 3m column (PEG 1500 20% Celite) at 80 °C. Partial reduction of catalysts was carried out at 420 °C for a given time with CO. The degree of reduction was calculated from the amount of CO_2 produced and given in terms of the percentage of V^{4+} produced to the total V ions.

Results and Discussion

Adsorption of Oxygen. Adsorption isotherms* of oxygen on partially reduced V_2O_5(5 wt%)–SiO_2 cata-

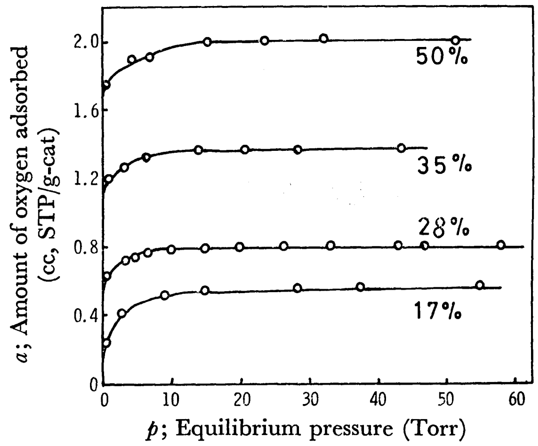

Fig. 1. Adsorption isotherms of oxygen on partially reduced V_2O_5(5 wt%)–SiO_2 (%; reduction degree)

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* V_2O_5–SiO_2 catalyst before reduction adsorbed a small amount of oxygen at room temperature. The adsorbed amount of oxygen on partially reduced catalysts was corrected by subtracting the amount.

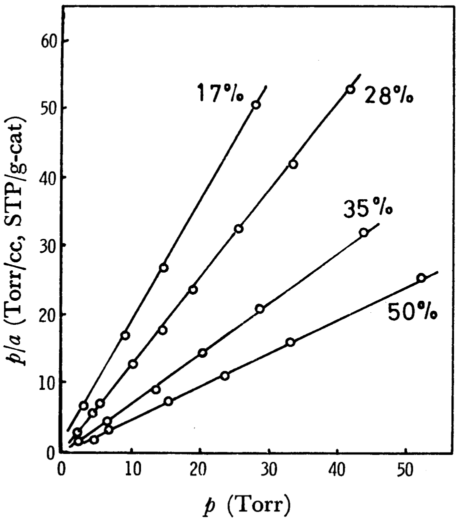


Fig. 2. Langmuir plot for oxygen adsorption isotherm (%; degree of reduction)

Table 1. Variation of a_s/V^{4+} by reduction

Degree of reduction (%)	16.7	20.0	22.1	28.5	34.7	49.6	50.1
a_s/V^{4+} (%)	26.9	23.6	27.1	22.7	32.2	25.8	33.7

a_s: Saturated adsorption amount of oxygen (mol/g-cat)
V^{4+}: Amount of V^{4+} produced by reduction (mol/g-cat)

lysts at room temperature are shown in Fig. 1. Since the Langmuir equation for non-dissociative adsorption fits the isotherms (Fig. 2), oxygen should be mainly adsorbed in a molecular state on these catalysts at room temperature. The saturated amount of adsorption of oxygen (a_S) increases with the increase in the reduction degree of the catalyst and the ratio of a_S to V^{4+} produced by reduction falls in the range 23—34% (Table 1).

ESR Spectra of Adsorbed Oxygen. Figure 3 shows the ESR spectrum of oxygen radical species adsorbed on the 17% reduced V_2O_5(5 wt%)–SiO_2 catalyst at room temperature. This spectrum with hfs of $A_{//}$= 9.3 G and $A_{\perp}$=5.8 G at $g_{//}$=2.022 and $g_{\perp}$=2.004 can be assigned to O_2^- radical.[2,3] Figures 4 and 5 show the ESR spectra of oxygen radical species adsorbed on the 22 and 51% reduced V_2O_5(5 wt%)–SiO_2 catalyst, respectively. In these spectra, a new signal (marked by arrows) is superimposed on the O_2^- signal. The new signal g=2.027, A=13 G corresponds to that assigned to the O^- radical by Kazansky.[4]

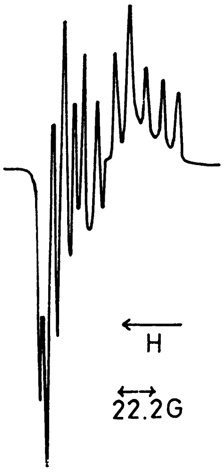


Fig. 3. ESR spectrum of oxygen adsorbed on 17% reduced V_2O_5 (5 wt%)–SiO_2.

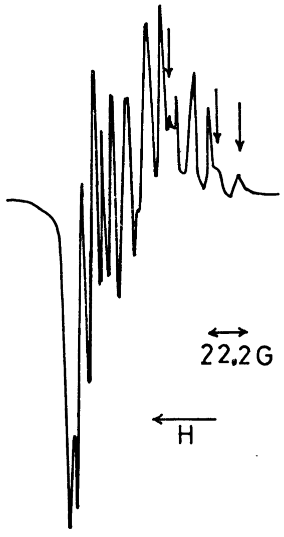


Fig. 4. ESR spectrum of oxygen adsorbed on 22% reduced V_2O_5 (5 wt%)–SiO_2.

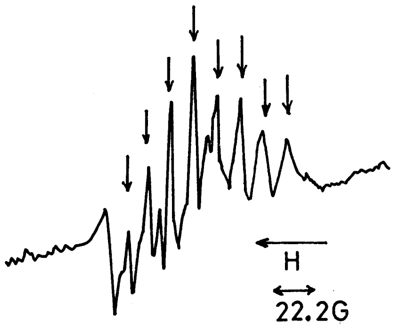


Fig. 5. ESR spectrum of oxygen adsorbed on 51% reduced V_2O_5 (5 wt%)–SiO_2.

The signal assignable to the O^- radical was detected on catalysts more highly reduced than 20% for V_2O_5-(5 wt%)–SiO_2 and 30% for V_2O_5(2 wt%)–SiO_2, the ratio of O^-/O_2^- increasing with the increase in the reduction degree of catalysts (Fig. 6).

The influence of adsorption pressure of oxygen on the formation of oxygen radical species was investigated, the results being given in Table 2. Increase in the pressure of oxygen resulted in the increase in relative signal intensity of O_2^- and decrease in that of O^-, regardless of degree of reduction of the catalysts. This evidently shows that high degree of reduction, high content of V_2O_5 and low pressure of oxygen at equilibrium are favorable for the formation of O^- radicals.**

Both signals of O_2^- and O^- radicals are stable *in*

** In the former study,[5] the O^- radical was not detected for the catalyst of 1—45% reduction, which seems to have been due to high oxygen pressure.

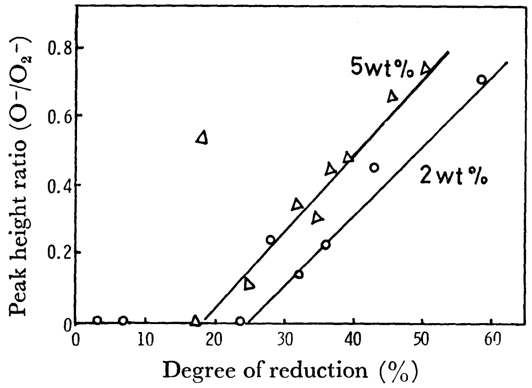


Fig. 6. Variation of O^-/O_2^- by reduction (wt%; V_2O_5 content in catalyst)

TABLE 2. RELATIVE INTENSITY OF O_2^- AND O^-

Catalyst	Equilibrium pressure p (Torr)	Amount of oxygen adsorbed 10^{-6} mol/g-cat	a/V^{4+}	Relative intensity of ESR signal O_2^-	Relative intensity of ESR signal O^-	O^-/O_2^-
50% reduced V_2O_5(5 wt%)-SiO_2	<0.1	63.1	22.8	29	20	0.69
	2.1	76.5	27.6	49	15	0.31
	7.5	78.0	28.2	43	11	0.26
	15.2	91.3	33.2	49	7.4	0.15
	25.3	92.7	33.7	52	4.6	0.09
35% reduced V_2O_5(5 wt%)-SiO_2	<0.1	53.8	27.6	20	6.0	0.30
	4.4	57.3	29.4	24	4.0	0.17
	10.6	60.0	30.1	29	2.0	0.07
	17.4	62.8	32.2	29	1.2	0.04

vacuo at room temperature even after 16 hr, but heating for 15 min at 150 °C caused a decrease of O_2^- by 80% and O^- by 30%. This shows that O^- is more stable than O_2^- at high temperatures in agreement with the result of Shvets *et al.*[6]

Quantitative Measurement of O_2^- and O^-. 17% reduced V_2O_5(5 wt%)-SiO_2 catalyst adsorbed 2.6×10^{-5} mol oxygen/g-cat at room temperature. The amount of O_2^- on this catalyst was determined to be 1.6×10^{-6} g ion/g-cat by the ESR method. On the other hand, both ESR signals of O_2^- and O^- were observed for 20% reduced V_2O_5(5 wt%)-SiO_2 catalyst adsorbing 2.62×10^{-5} mol oxygen/g-cat, the ratio of O^- to O_2^- being 0.59 from the relative signal intensity. Addition of CO at room temperature caused instantaneous disappearance of the ESR signal of O^- and formation of CO_2, as reported by Kazansky *et al.*[4] It was confirmed that the ESR signal intensity of O_2^- radical is not affected by either the addition of CO or the recovery of the resulting CO_2. This can be utilized for the evaluation of the amount of O^- by measuring the amount of CO_2 produced by reaction of O^- with CO. The amount of O^- radical adsorbed on 20% reduced V_2O_5(5 wt%)-SiO_2 was evaluated to be 9.6×10^{-7} g-ion/g-cat. The amount of O_2^- calculated from these values of O^- and O^-/O_2^- was 1.6×10^{-6} g-ion/g-cat. Thus, the values from the two different methods agree. In the following experiments, the amounts of O_2^- and O^- were estimated by the latter method.

TABLE 3. AMOUNT OF ADSORBED SPECIES

Reduction degree %	V^{4+} $10^{-4}\times$ mol/g-cat	Amount of oxygen adsorbed $10^{-5}\times$ mol/g-cat	$\frac{O^-}{O_2^-}$	O^- $10^{-6}\times$ mol/g-cat	O_2^- $10^{-6}\times$ mol/g-cat	$\frac{\frac{1}{2}O^- + O_2^-}{a}$ %
17	1.12	2.60	—	–	1.6	6.2
20	1.20	2.62	0.59	0.95	1.6	7.91
35	2.0	6.13	0.04	0.13	3.	5.2
45	2.5	4.76	0.65	1.2	1.8	5.0
50	2.75	9.27	0.09	0.42	4.8	5.4

The amounts of V^{4+}, total adsorbed oxygen (a), O_2^- and O^- for several catalysts are given in Table 3. In all cases, the values of $[O_2^- + (1/2)O^-]/a$ are smaller than 10%. From the fact that paramagnetic adsorbed species are only a small part of total adsorbed oxygen and the Langmuir equation for non-dissociative adsorption fits the isotherms, a large part of oxygen seems to be adsorbed as a neutral molecule.

Reaction with Propylene. Some olefins are oxidized by adsorbed oxygen, accompanied by the simultaneous disappearance of O_2^- signal in ESR spectra.[5] Since large amounts of adsorbed oxygen besides O_2^- are existent together with O^- on the catalyst surface, it seems that the previous results can not exclude the possibility of oxidation of olefins by adsorbed oxygen species other than O_2^-. In order to specify the oxidative species unambiguously a correlation between amounts of consumed O_2^- and oxidation products of propylene was quantitatively investigated.

At room temperature, propylene was brought into contact with catalysts, on which O^- had been removed by CO treatment to exclude the possibility of oxidation by O^-. After 1 hr, the reaction mixture was recovered in a liquid N_2 trap. For the desorption of products, the catalyst was evacuated at 200 °C during the course of recovery (1 hr). The results of gas chromatographic analysis of reaction products are given in Table 4. The amounts of recovered oxidation products (p_{ox}) for the A-series experiments are in the same order as that of consumed O_2^-, the ratios of p_{ox} to O_2^- being nearly in the range 0.8—1. Case B shows the result for the 46.5% reduced V_2O_5(5 wt%)-SiO_2 catalyst, on which both O_2^- and O^- initially coexist and O^- mainly remains after heating at 150 °C for 15 min. Although both O^- and O_2^- rapidly diminish in contact with propylene, the amount of oxidation product is in the same order as that of O_2^- rather than that of O^-. This probably means that in spite of reaction of O^- with propylene, the oxidation products resists the desorption from catalyst surface,[7] where oxidation products of propylene on zinc oxide are too tightly adsorbed to remove and are recovered as CO_2 only at a higher temperature than 200 °C. The oxidation products (Table 4) can be regarded to result from the reaction of O_2^- but not from other oxygen species.

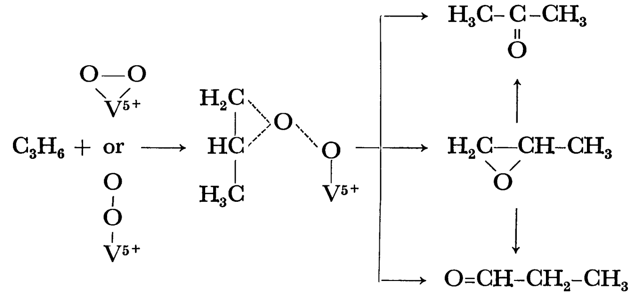
Propionaldehyde, acetaldehyde and acrolein were detected with small amounts of acetone and propylene oxide in the oxidation products. Since these products except acrolein are not expected from the allylic intermediate, it is suggested that low temperature oxidation

TABLE 4. PRODUCTS OF PROPYLENE OXIDATION ON V_2O_5 (5 wt%)-SiO_2 CATALYST

Expt. No.*)	10^{-6}mol/g-cat		Composition of product (%)						Oxygen containing product P_{ox}; $10^{-6}\times$ mol/g-cat	P_{ox}/O_2^- %
	O_2^-	O^-	C_3H_6	CH_3CHO	Propylene oxide	Propion-aldehyde	Acetone	Acroleine		
A-1	1.8	—[a]	99.3	0.16	—	0.55	—	—	1.78	99
A-2	3.1	—[a]	92.3	2.47	—	3.34	0.80	1.14	2.94	95
A-3	3.7	—[a]	96.1	1.16	—	2.69	—	—	2.95	80
A-4	4.8	—[a]	59.0	15.94	1.46	16.33	2.89	4.40	4.40	92
B[b]	0.36	0.97	99.2	0.36	—	0.34	0.13	—	0.165	47
C[c]	—	—	10.6	—	22.0	52.8	14.6	—	—	—

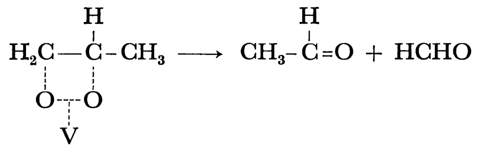
a) O^- was removed by reaction with CO. b) Catalyst adsorbing oxygen was heated at 150 °C for 15 min. c) 1.5×10^{-5} mol propylene oxide was introduced at room temperature on the 10% reduced V_2O_5(5 wt%)-SiO_2 and then evacuated. The reaction products were recovered by the same method as for Expt. A and B. *) Reduction degrees of catalysts in A-1, A-2, A-3, A-4 and B were 22.1, 34.7, 47.6, 50.1 and 46.5%, respectively.

of propylene with O_2^- radical occurs mainly through the intermediate of an epoxide structure as follows.



Propionaldehyde and acetone are also formed by the isomerization of propylene oxide on this catalyst. (Expt. No. C, Table 4).

The mechanism of formation of acetaldehyde is not clear, but the following mechanism might be partially cooperative with the above one.



$$\underset{\underset{V}{O-O}}{H_2C-\overset{H}{C}-CH_3} \longrightarrow CH_3-\overset{H}{C}=O + HCHO$$

However, we could not detect any formaldehyde in reaction products, nor could be elucidate the reaction products of O^- with propylene.

In conclusion, the respective amounts of total oxygen, O_2^- and O^- adsorbed on partially reduced V_2O_5-SiO_2 catalyst were quantitatively determined. It was confirmed that O_2^- on the catalyst oxidized propylene at room temperature by a mechanism involving the intermediate of an epoxide structure.

References

1) R. J. Kokes, *J. Phys. Chem.*, **66**, 99 (1962); M. Setaka and T. Kwan, This Bulletin, **38**, 1414 (1964), *J. Catal.*, **16**, 44 (1970); K. Sancier, *ibid.*, **5**, 314 (1966); J. Lunsford, *J. Chem. Phys.*, **44**, 1487 (1966); A. I. Maschenko, V. B. Kazansky, G. B. Parinsky, and V. M. Schpapov, *Kinet. Katal.*, **8**, 853, 1363 (1967).

2) V. A. Schvets, M. E. Sarichev, and V. B. Kazansky, *J. Catal.*, **11**, 378 (1968).

3) K. Tarama, S. Yoshida, S. Ishida, and Y. Doi, This Bulletin, **42**, 1161 (1969).

4) V. B. Kazansky, V. A. Shvets, M. Ya. Kon, V. V. Nikisha, and B. N. Shelimov, "Catalysis" Proc. the Fifth Int. Cong. Catalysis, Vol. 2, edited by J. W. Hightower, North-Holland Pub. Co., Amsterdam (1973), p. 1423, and *J. Catal.*, **25**, 123 (1972).

5) S. Yoshida, T. Matsuzaki, S. Ishida, and K. Tarama, "Catalysis" in Ref. 4, Vol. 2, p. 1049 (1972).

6) V. A. Shvets, V. M. Vorotinthev, and V. B. Kazansky, *Kinet. Katal.* **10**, 356 (1969).

7) Y. Kubokawa, T. Ono, T. Tomino, and N. Yano, This Bulletin, **43**, 291 (1970).