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Spectroscopic Studies of Catalysis by Vanadium Pentoxide

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The role of the V=O bond in V_2O_5 in the adsorption of several gases was studied by measuring the electron spin resonance (ESR) and the infrared (IR) spectra. The ESR spectra of V_2O_5 supported on γ-Al_2O_3 were similar to those of $VOSO_4$ on γ-Al_2O_3. When such electron-donating gases as CO, SO_2 and C_2H_4 were adsorbed on this V_2O_5 - γ-Al_2O_3, the signal intensity of ESR increased and the splitting of the h.f.s. became clear. Upon treatment with an electron-accepting gas such as O_2, a reverse change was observed. In the case of V_2O_5 supported on SiO_2, similar ESR spectra were observed by the adsorption of CO after a mild reduction. The IR spectra of V_2O_5 have a sharp absorption peak at 1023 cm^{-1} due to the stretching vibration of the $(V=O)^{3+}$ bond; this peak became broader by adsorption of such gases as CO and SO_2. Simultaneously, the center of the peak shifted to the red region and a weak hump appeared at 980—990 cm^{-1}, probably due to $(V=O)^{2+}$. These results of the ESR and IR measurements reveal that these electron-donating gases are adsorbed on the $(V=O)^{3+}$ bonds on the surface of V_2O_5, and that the increase in electron densities in the adsorption sites results from adsorption of these gases. Furthermore, the role of this $(V=O)^{3+}$ bond in oxidation reaction was also discussed.

Vanadium pentoxide is a well-known oxidation catalyst. There are fairly many works attempting to elucidate the catalytic action of this catalyst by kinetical studies or by studies of its physicochemical properties.

The present authors¹⁾ themselves previously reported a study of some physico-chemical properties of V_2O_5 and emphasized the importance of the role of the V=O bond, at the 3rd International Congress on Catalysis.

In the present work, the role of this V=O bond in the adsorption of several gases was studied by measuring the electron spin resonance (ESR) and the infrared (IR) spectra.

Recently, van Reijen and Cossee²⁾ studied the state of V^{4+} ions in V_2O_5 supported on SiO_2 and Al_2O_3 by the ESR method and reported the existence of $(VO_4)^{4-}$ or $(VO)^{2+}$. Ioffe *et al.*³⁾ studied the change in the IR spectra of V_2O_5 by doping of MoO_3, CoO_2 or P_2O_5 and by treatment with a mixture of benzene and O_2. But these papers were not very helpful for our purpose of elucidating the role of the V=O bond in the gas adsorption.

The present authors' results reveal that the $(V=O)^{3+}$ bond on the surface of V_2O_5 plays an important role as the adsorption site for the electron-donating gas and also as a reaction site for the oxidation reaction.

Experimental

Apparatus and Procedures. The ESR absorption measurements were made on a JES-3BSX-type, X-band spectrometer manufactured by the Japan Electron Optics Co. The cavity input power was 10 mW, and the modulation width was 10 gauss. DPPH was used as the standard for the measurement of the intensity of the ESR signal.

The samples for ESR measurement were evacuated for 3 hr at 350°C and 10^{-6} Torr in a glass reactor which had a quartz tube for ESR measurement as a side arm and which was joined to a vacuum line. After various treatments, the samples were moved to the side tube and the ESR absorptions were measured at room temperature.

The infrared absorption measurements were carried out with an IR-S-type spectrometer manufactured by the Japan Spectroscopic Co. The samples dispersed on a NaCl disk were placed in the center of a specially devised *in situ* cell and the IR absorptions were measured under various atmospheres and temperatures.

The adsorbed amounts of gases were measured by the usual volumetric method.

The catalytic activities for CO oxidation with air were determined by a flow method described previously¹⁾ at 350°C. The gas flow rate was 7.5 cc (NTP)/min for 500 mg of the catalyst, and the ratio of CO to air was kept at 1 : 4.

Materials. Several kinds of V_2O_5 catalysts were used. The unsupported V_2O_5-powders used mainly for the IR measurements were prepared from commercial extra-pure-grade V_2O_5 by grinding it to powder. This sample contained about 0.7 atom% of V^{4+}.

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1) K. Tarama, S. Teranishi, S. Yoshida and N. Tamura, Proc. 3rd Int. Cong. Catalysis, Amsterdam (1965), p. 282.

2) L. van Reijen and P. Cossee, *Discussions Faraday Soc.*, **41**, 277 (1966).

3) B. E. Zaitsev, S. I. Ezhkova and I. I. Ioffe, *Kinetika i Kataliz*, **7**, 755 (1966).

The V_2O_5-samples supported on γ-Al_2O_3 and SiO_2 were prepared by impregnation with an aqueous solution of extra-pure NH_4VO_3, followed by drying at 100°C and calcination at 450°C for 6 hr in a dry-air stream.

The γ-Al_2O_3 was a commercial product of the highest purity from the Sumitomo Chemical Ind. Co. The SiO_2 was prepared from ethyl silicate which had been carefully purified by distillation.

The surface areas of these samples are given in Table 1.

TABLE 1. THE B.E.T. SURFACE AREAS OF THE SUPPORTED CATALYSTS

V_2O_5 Content (wt%)	Surface area (m^2/g)
1 (on γ-Al_2O_3)	170
3 (on γ-Al_2O_3)	180
5 (on γ-Al_2O_3)	180
20 (on γ-Al_2O_3)	170
5 (on SiO_2)	280

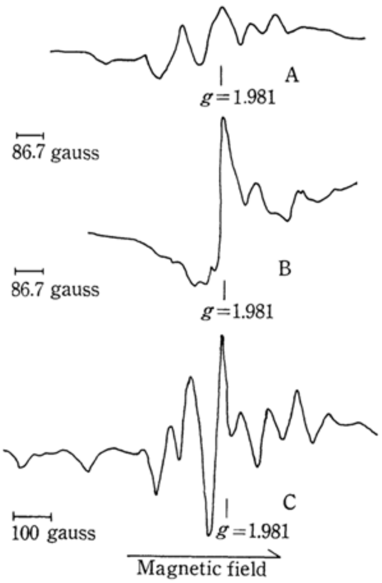

Fig. 1. ESR spectra of V_2O_5 - γ-Al_2O_3 after evacuation for 3 hr at 350°C.
A: $V_2O_5(5\%)$ - γ-Al_2O_3
B: $V_2O_5(50\%)$ - γ-Al_2O_3
C: $VOSO_4(0.6\%)$ - γ-Al_2O_3

Results

ESR Spectra of V_2O_5 Dispersed on γ-Al_2O_3. Figures 1-A and B show the ESR absorption spectra of the samples of 5 wt% and 50 wt% V_2O_5 respectively supported on γ-Al_2O_3. These spectra, with the h.f.s., were similar to that of $VOSO_4$ (0.6 wt%) on γ-Al_2O_3 (Fig. 1-C). The average h.f.s. coupling constants are 100 and 85 gauss for 5% V_2O_5-γ-Al_2O_3 and $VOSO_4$-γ-Al_2O_3 respectively. These spectra with h.f.s. were identified as those of $(V{=}O)^{2+}$.

When CO, SO_2 or C_2H_4 was adsorbed on this 5% V_2O_5 - γ-Al_2O_3 at room temperature and at 150°C, the signal intensities of the ESR spectra increased, as is shown in Table 2; the splitting of the h.f.s. also became clear, as Figs. 2-A, B and C show. The adsorbed amounts of CO, SO_2, and C_2H_4 (at room temperature, 200 Torr) were 0.5, 18 and 6 cc/g-cat respectively. The evacuation of gas at room temperature caused a decrease in the signal intensity, but this change was partially irreversible.

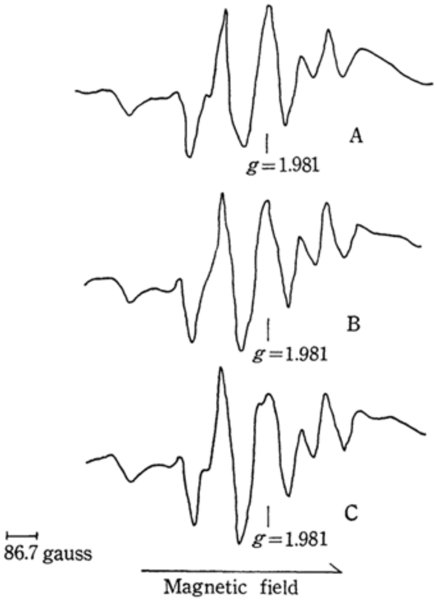

Fig. 2. ESR spectra of $V_2O_5(5\%)$ - γ-Al_2O_3.
A: SO_2 was adsorbed for 40 hr at 160 Torr and room temp.
B: C_2H_4 was adsorbed for 150 hr at 260 Torr and room temp.
C: CO was adsorbed for 150 hr at 226 Torr and room temp.

In the case of O_2 adsorption (200 Torr, 150°C, 1 hr), the relative signal intensity decreased to half of that of the starting sample. (The amount of O_2 adsorbed was 0.03 cc/g-cat.)

When O_2 (150 Torr) was introduced at room temperature after the adsorption of CO at 150°C, the relative signal intensity changed from 1.4 to 0.9, as is shown in Table 2 (VC-5, 6).

ESR Spectra of V_2O_5 Supported on SiO_2. In the case of V_2O_5 (5 wt%) supported on SiO_2, no signal of ESR absorption could be observed even after evacuation at 350°C. However, the ESR signal appeared after further reduction with CO at 350°C, as is shown in Fig. 3-A; furthermore, the h.f.s. with a characteristic feature of $(VO)^{2+}$ was observed in the ESR spectrum (Fig. 3-B) of this V_2O_5-SiO_2, which adsorbed CO at room temperature. van Reijen and Cossee[2] have reported

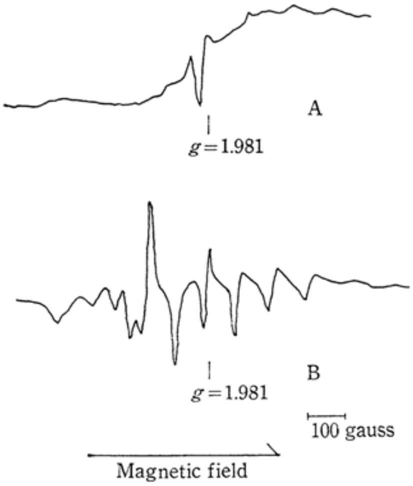

Fig. 3. ESR spectra of $V_2O_5(5\%)\text{-}SiO_2$.
A: The sample reduced by CO at 350°C.
B: CO was adsorbed at room temp. on the reduced sample.

a similar ESR spectrum of $V_2O_5\text{-}SiO_2$, one which was evacuated at 500°C and which was subsequently treated with H_2O at 20°C.

When C_2H_4 was adsorbed at room temperature and 150 Torr, a weak signal similar to that in Fig. 1-A appeared.

Infrared Absorption of V_2O_5 Adsorbing Some Gases. V_2O_5 gives infrared spectra composed of a sharp absorption at 1023 cm^{-1} and a broad one at 830 cm^{-1}. This sharp absorption band at 1023 cm^{-1} is assignable to the stretching vibration mode of the $(V{=}O)^{3+}$ bond by comparison with that of $VOCl_3$.[4,5] It has been reported that this sharp absorption shifts to a longer-wavelength region upon treatment with cyclohexane[4] or after the catalyst has been used for benzene oxidation.[3]

The changes in the absorption spectra by the adsorption of several gases were studied under mild conditions. Figures 4 and 5 show the changes in the spectra by the adsorption of SO_2 and CO respectively.

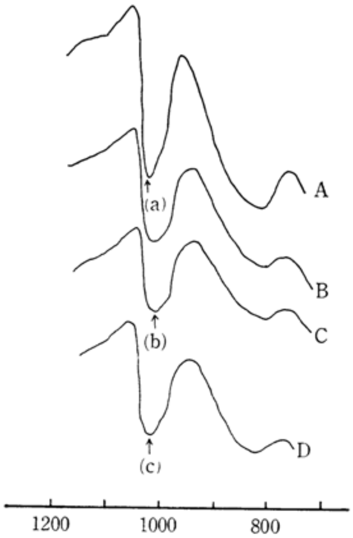

Fig. 4. IR spectra of V_2O_5 treated by SO_2 and O_2.
A: V_2O_5 untreated.
B: V_2O_5 treated by SO_2 at 226 Torr and 24°C for 16 hr.
C: V_2O_5 treated by SO_2 at 226 Torr and 50°C for 3 hr after B.
D: V_2O_5 treated by O_2 at 342 Torr and 75°C after evacuation of SO_2.
(a) 1023 cm^{-1}, (b) 1005 cm^{-1}, (c) 1013 cm^{-1}

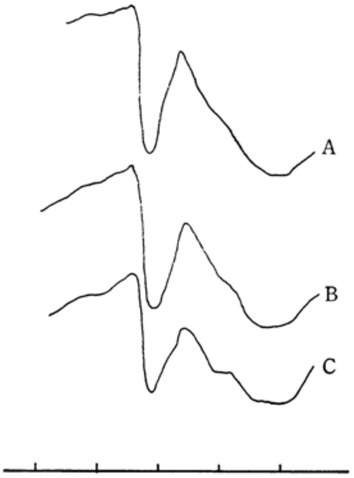

Fig. 5. IR spectra of V_2O_5 treated by CO.
A: V_2O_5 untreated.
B: V_2O_5 treated by CO at 157 Torr and 100°C for 1 hr.
C: V_2O_5 treated by CO at 157 Torr and 140°C for 3 hr after B.

By the adsorption of SO_2, the absorption band due to the $(V{=}O)^{3+}$ bond became broader and the center of the absorption peak shifted from 1023 cm^{-1} to 1005 cm,$^{-1}$ and, furthermore, a weak shoulder appeared at 980—990 cm^{-1} as is shown in curves A, B and C of Fig. 4. Almost all these changes in the IR spectra remained even after evacuation for 2 hr at 110°C, but when O_2 was introduced into the cell at 75°C, the center of the absorption band returned from 1005 cm^{-1} to 1013 cm^{-1}, as is shown in curve D of Fig. 4. On the other hand, the broad absorption band at 830 cm^{-1} was almost unchanged by this treatment. When a V_2O_5 sample, freshly prepared, was

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[4] K. Tarama, S. Teranishi and S. Yoshida, *Shokubai,* **6,** 299 (1964).

[5] L. Frederickson and D. Hausen, *Anal. Chem.,* **35,** 818 (1963).

TABLE 2. THE CHANGES OF ESR SIGNAL INTENSITIES BY TREATMENT WITH SOME GASES

Sample	Condition of treatment with gases				Relative intensity
	Gas	Pressure	Temperature	Duration	
V-O	evacuation for 3 hr at 350°C*				1.0
VC-1	CO	3.9 Torr	room temp.	84 hr	1.3
VC-2	CO	98 Torr	room temp.	55 hr	1.5
VC-3	CO	226 Torr	room temp.	84 hr	2.0
VC-4	VC-3 evacuated for 8 hr at room temp.				1.8
VC-5	CO	17 Torr	150°C	17 hr	1.4
VC-6	VC-5 treated with O_2 (150 Torr) at room temp.				0.9
VC-7	VC-6 kept for 3 hr at 150°C				0.8
VC-8	CO	110 Torr	150°C	17 hr	1.9
VC-9	VC-8 evacuated for 3 hr at room temp.				1.6
VS-1	SO_2	15.2 Torr	room temp.	7 hr	1.2
VS-2	SO_2	163 Torr	room temp.	7 hr	1.6
VS-3	SO_2	300 Torr	room temp.	14 hr	1.4
VS-4	VS-3 evacuated for 8 hr at room temp.				1.2
VE-1	C_2H_4	28.2 Torr	room temp.	192 hr	1.8
VE-2	VE-1 evacuated for 15 hr at room temp.				1.6
VE-3	C_2H_4	260 Torr	room temp.	168 hr	2.1
VE-4	VE-3 evacuated for 15 hr at room temp.				1.6

* The starting samples are V_2O_5(5 wt%) - γ-Alumina evacuated for 3 hr at 350°C in all cases and signal intensity of this sample is adopted as standard.

treated by O_2 at 100°C, no change in the spectra could be observed.

The change induced by the adsorption of CO was the same as that in the case of SO_2, but effect was smaller and a new peak, at 910 cm^{-1}, appeared at 140°C, as is shown in Fig. 5. This peak probably belongs to the absorption band of V_2O_4.[5] Therefore, the appearance of this peak suggests that V_2O_5 was partially reduced to V_2O_4 by CO-treatment at 140°C. In the case of C_2H_4, no change in the IR spectra could be observed upon the treatment at 25°C, but a partial reduction of V_2O_5 to V_2O_4 was observed at 80°C, as in the case of CO.

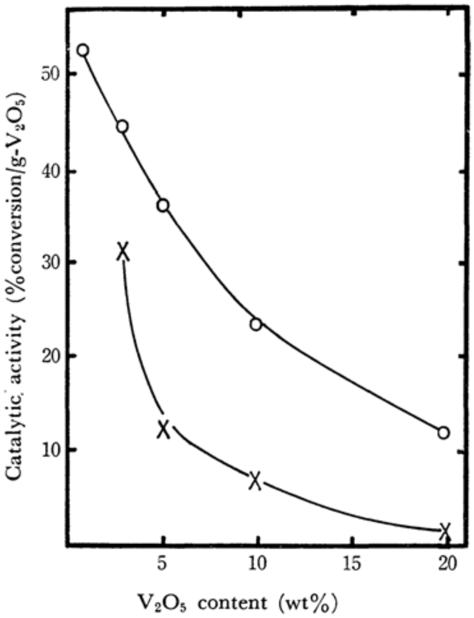

Fig. 6. Catalytic activity for CO-oxidation of supported V_2O_5.
○ and × marks stand for the catalysts supported on γ-Al_2O_3 and SiO_2 respectively.

These results indicate that the reducing power of these gases increases in the order of SO_2, CO and C_2H_4 under these experimental conditions.

Oxidation of CO with Air. Because a linear relation between the conversion (α, %) of CO to CO_2 and the contact time was observed up to 30% conversion, the values of α at the same contact time were adopted as the measure of the activity.

The activities of V_2O_5 on γ-Al_2O_3 of various concentrations and V_2O_5 on SiO_2 are shown in Fig. 6. The relative activities per gram of V_2O_5 in the catalysts decreased with the increase in the concentration of V_2O_5. This indicates that the number of effective sites of V_2O_5 is increased by dispersion on carriers.

TABLE 3. REDUCTION OF CATALYST BY CO AT 350°C FOR 1 HR (P_{CO}: 150 Torr)

Catalyst	Produced CO_2 cc(NTP)/g-cat.	Reduction % (V^{4+}/V^{5+} initial)
V_2O_5(5%) on γ-Al_2O_3	4.1	65
V_2O_5(5%) on SiO_2	0.55	9

TABLE 4. THE ADSORPTION SITE ON THE METAL OXIDE OR SULFIDE OF SEMICONDUCTOR

Adsorbent (catalyst)	Adsorbate (gas)	Adsorption site in surface (example)
n-Type semiconductor (example, V_2O_5)	Electron donor	Metal ion at normal lattice point (V^{5+})
	Electron acceptor	Metal ion adjacent to defect of anion (V^{4+})
p-Type semiconductor (example, NiO)	Electron donor	Metal ion adjacent to excess anion (Ni^{3+})
	Electron acceptor	Metal ion at normal lattice point (Ni^{2+})

V_2O_5 - γ-Al_2O_3 catalysts are more active than the V_2O_5-SiO_2 catalyst. These activities are closely correlated with the reducibilities of these catalysts by CO at 350°C, as is shown in Table 3.

Discussion

The State of Vanadium Ions in V_2O_5 Dispersed on Carriers. The unsupported V_2O_5 powder gave a broad single ESR signal, and the line width (ΔH_{msl}) of this absorption signal became larger at a low temperature (ΔH_{msl}; 90 gauss at room temperature and 180 gauss at the temperature of liquid nitrogen), as has previously been reported.[1,6] In the case of V_2O_5 dispersed on γ-Al_2O_3, however, the h.f.s. of the ESR spectrum due to $(V=O)^{2+}$ was observed. The appearance of this h.f.s. by the dispersion of V_2O_5 on a carrier seems to result from the decrease in the delocalizability of the electron associated to $(V=O)^{2+}$. Therefore, it is clear that V(IV) ions in V_2O_5 on γ-Al_2O_3 are stabilized in the form of $(V=O)^{2+}$. However, $(V=O)^{2+}$ seems not to be in the isolated state, but to be stabilized as $(V=O)^{2+}$ in the thin layer of the micro crystal of V_2O_5 on γ-Al_2O_3 for the following reasons: a) Even the sample of V_2O_5 (50 wt%) on γ-Al_2O_3 gave ESR spectra with fairly well resolved h.f.s. (Fig. 1-B). In this sample, it is quite difficult to believe that $(V=O)^{2+}$ ions are isolated on the surfaces of carriers. b) The observed ESR signal for V_2O_5 (5 wt%) on γ-Al_2O_3 is similar to that of $VOSO_4$ in γ-Al_2O_3, but there is some difference in resolutions and in coupling constants between the h.f.s.'s of the two samples. Of course, the resolution of the spectrum depends on the concentration of the paramagentic species. Though the concentration of V(IV) ions is about 1% of the total vanadium in V_2O_5 (5%) on γ-Al_2O_3, and is thus so small that the interaction between paramagnetic species is negligible, the resolution of h.f.s. is not clear.

In the case of V_2O_5 on SiO_2, the state of V(IV) is not clear, either, no signal could be observed as has been reported above; the amount of V(IV) ions in this sample may be too small to be detected by the ESR method.

On the other hand, V(V) ions (the diamagnetic species) can not be detected by ESR measurement, and so their state in V_2O_5 is presumed indirectly from the change in the ESR signal and in the IR specta with gas adsorption or reduction.

The Adsorption Sites on V_2O_5. When electron-donating gases, such as CO, SO_2 and C_2H_4, were adsorbed on V_2O_5 supported on γ-Al_2O_3, the signal intensity of the ESR spectra increased and the splitting of the h.f.s. became clear. Even in the case of the sample supported on SiO_2, which gave no ESR signal after evacuation at 350°C, a weak signal with a h.f.s. identified as $(V=O)^{2+}$ appeared by the adsorption of these gases.

The growth of this signal intensity indicates an increase in $(V=O)^{2+}$. Therefore, it seems sure that these electron-donating gases are adsorbed on $(V=O)^{3+}$ bonds on the surface of a V_2O_5 crystal, and that an electron is transferred from adsorbed gas to an adsorption site, thus leading to the formation of $(V=O)^{2+}$.

On the other hand, the signal intensity became weak by O_2 adsorption. As O_2 is an electron-accepting gas, this shows that oxygen is adsorbed on $(V=O)^{2+}$ and that this adsorption site is converted to $(V=O)^{3+}$ by electron transfer.

The above model for gas adsorption is supported by the IR measurements, too. By the adsorption of CO or SO_2, the IR absorption band due to $(V=O)^{3+}$ bond broadened, the center of the peak shifted to the red region, and a weak hump, probably due to the $(V=O)^{2+}$ bond,[5] appeared at 980—990 cm^{-1}.

These changes in the IR spectra reflect the increase in the electron density in the V-ion of the $(V=O)^{3+}$ bond. The effect of the treatment with O_2 on the IR spectrum was the reverse of that with CO or SO_2.

From the results of these ESR and IR measuremenets, it can be concluded that the adsorption sites on V_2O_5 are $(V=O)^{3+}$ for such electron-donating gases as CO, SO_2 and C_2H_4 and $(V=O)^{2+}$ for such electron-accepting gases as O_2.

This conclusion is very probable in the light of the general rule previously proposed by one of authors[7] for the adsorption site on the metal oxide or sulfide of a semiconductor, as is shown in Table 4.

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[6] K. Tarama, S. Teranishi, S. Yoshida, N. Tamura and S. Ishida, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1499 (1965).

[7] K. Tarama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 675 (1960); *Ryusan*, **12**, 161 (1959).

The Role of the V=O Bond in Oxidation Reaction. It is generally accepted that the catalysis by V_2O_5 for oxidation reaction is effected by the oxidation-reduction mechanism in which the lattice oxygen of the catalyst is taken away by gas and the catalyst is reoxidized by O_2.

This mechanism seems also to be supported by the finding that the activity of the catalyst in CO-oxidation is closely correlated with its reducibility by CO.

The present authors have presented a hypothesis that the strength of a V=O bond is a controlling factor in the activity of the catalytic oxidation.[1] Recently, Hirota and his collaborators[8] studied the exchange of isotopic oxygen between CO_2 containing ^{18}O and V_2O_5, and showed that this oxygen exchange proceeded through a surface V=O bond of V_2O_5. This finding supports the preceding hypothesis.

Therefore, it can be concluded that the V=O bond on the surface of V_2O_5 performs an important role as the adsorption site and also as the reaction site for the oxidation reaction.

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8) Y. Kera, S. Teratani and K. Hirota, This Bulletin, **40**, 2458 (1967).