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Some Physico-chemical Properties of Vanadium Oxide Supported on Silica or γ-Alumina[1]

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The interactions between vanadium(V) oxide and carriers were investigated in the vanadium oxide catalysts supported on silica and γ-alumina by measuring X-ray diffraction patterns, ESR spectra, solubilities into 0.3 N ammoniacal solutions and reduction rates by benzene. A part of vanadium oxide on the carriers was insoluble in an ammoniacal solution, while unsupported vanadium oxide was easily soluble, and the reduction rates of the catalysts were remarkably affected by the carriers and the vanadium oxide contents. ESR spectra revealed that the vanadium oxide was stabilized by interaction with carriers as a square pyramidal one (VO_5) and a tetrahedral one (VO_4) on the surfaces of γ-alumina and silica, respectively. Massive vanadium(V) oxide crystals grew on these interacted layers with the increase of the oxide contents.

Vanadium oxide has been extensively used as a main catalyst in gas phase oxidation of hydrocarbons and extensive studies have been carried out on its catalytic action.

We also studied the vanadium oxide catalysts especially from the view point of structural chemistry.[2] Our works mainly dealt with unsupported vanadium catalysts. In the cases of practical catalysts, however, vanadium oxides are generally supported on carriers such as silica and alumina with high surface area. It is known that these carriers have a profound effect on the activities of catalysts.

It is important to elucidate the action of the main component of the supported catalysts. Nevertheless, very few fundamental research works on this problem have been carried out for vanadium oxide catalysts.[2b,3]

In the present work, some physico-chemical properties of vanadium oxide supported on silica or γ-alumina have been investigated by measuring X-ray diffraction patterns, ESR spectra, solubilities into ammoniacal solutions and reduction rates by benzene vapor in order to clarify the state of vanadium ions in the supported catalysts.

Experimental

Materials. *Silica*: Ethyl silicate purified by distillation three times was hydrolyzed in a water-ethanol mixture at the boiling point. The gel obtained was washed, dried and calcinated at 500°C for 5 hr in dried air stream and was ground to powder of less than 100 mesh.

Alumina: γ-Alumina was obtained by hydrolysis of aluminum isopropoxide, followed by calcination at 650°C for 3 hr, and ground to powder of less than 100 mesh.

Catalysts: Vanadium oxide catalysts supported on silica or γ-alumina were prepared by impregnation of the carrier into an ammoniacal solution of ammonium methavanadate, followed by drying at 110°C and calcination at 500°C for 5 hr in dried air stream. The amount of supported vanadium oxide was analyzed by the usual oxidation-reduction titration method after dissolution of the catalyst into sulfuric acid. Catalysts thus obtained are summarized in Table 1, the vanadium oxide contents being calculated by assuming that vanadium oxide existed as vanadium pentoxide.

TABLE 1. SAMPLES

Samples	V_2O_5 Content (wt%)	Color dry	Color wet	Surface area (m²/g)
SiO_2	0.0	white	white	633
γ-Al_2O_3	0.0			282
V_2O_5	100.0	orange	orange	5.2
Samples supported on SiO_2				
1 S	1.0	white	l. yel. brown	579
2 S	2.0			564
5 S	4.9	cream	yel. brown	530
10 S	9.9	l. yel. brown	d. yel. brown	491
20 S	19.8			339
30 S	29.3			303
50 S	48.4			203
Samples supported on γ-Al_2O_3				
1 A	1.0	white	white	267
2 A	2.0			251
5 A	4.9	cream	cr. gr. yellow	242
10 A	10.0	l. gr. yellow	l. yel. brown	230
15 A	14.9			206
20 A	19.7			192
30 A	29.5	gr. yel. brown	yel. brown	176
50 A	49.2	yel. brown		126

l; light, d; dark, yel; yellowish, cr; creamy, gr; greenish

Procedures. *X-Ray Diffraction*: A Shimadzu X-ray diffractometer GX-3 with copper target was used. The tube voltage and current were 35 kV and 15 mA, respectively. *ESR*: ESR spectra of catalysts evacuated at 400°C for 2 hr and sealed in glass tubes were recorded with a JEOL JES-3BSX spectrometer at room temperature.

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[1] S. Yoshida, T. Iguchi, S. Ishida, and K. Tarama, Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2a] K. Tarama, S. Teranishi, S. Yoshida, and N. Tamura, "Proceedings 3rd Int. Congress on Catalysis," North-Holland Pub. Co. Amsterdam (1965), p. 282; K. Tarama, S. Teranishi, S. Yoshida, N. Tamura, and S. Ishida, *Kogyo Kagaku Zasshi*, **68**, 1499 (1965); K. Tarama, S. Yoshida, S. Ishida, and H. Kakioka, This Bulletin, **41**, 2840 (1968); K. Tarama, S. Teranishi, and S. Yoshida, *Bull. Inst. Chem. Research, Kyoto Univ.*, **46**, 185 (1968); S. Yoshida, N. Tamura, S. Teranishi, and K. Tarama, *ibid.*, **47**, 246 (1969). b) K. Tarama, S. Teranishi, K. Hattori, and T. Nichibori, *Kogyo Kagaku Zasshi*, **57**, 490 (1954).

[3] L. van Reijen and P. Cossee, *Discussion Faraday Soc.*, **41**, 277 (1966); H. Takahashi, M. Shiotani, H. Kobayashi, and J. Sohma, *J. Catalysis*, **14**, 134 (1969).

Dissolution into an Ammoniacal Solution: The catalyst containing *ca.* 1 g of vanadium oxide was impregnated into 300 m*l* of 0.3 N ammoniacal solution for 24 hr at room temperature. Under this treatment the isolated massive vanadium oxide was easily soluble. Thus, the residue vanadium oxide was regarded to be chemically interacting with the carrier.

Reduction by Benzene Vapour: Reduction rates of vanadium oxide on carriers were determined by measuring the weight loss of the catalysts in a flow of benzene-nitrogen gas by a Shimadzu MTB 50 micro-thermanobalance. Nitrogen gas was saturated with benzene at 2, 5, and 10°C with a flow rate of 30 cc/min and reduction temperatures were in the range 380—450°C.

Results

X-Ray Diffraction. Diagrams of the X-ray diffraction of catalysts are shown in Fig. 1. The catalysts containing more than 20% vanadium oxide on both silica and γ-alumina carriers exhibited diffraction lines due to vanadium(V) oxide (abbreviated as V_2O_5), while those containing less than 10% showed no distinct lines. As a whole, the diffraction lines became intense with the increase of the vanadium oxide content. By precise inspection of the diffraction lines due to V_2O_5 in catalysts, the interplaner spacing of (001) planes (the strongest line) of the catalysts supported on silica (group S) was the same as that of unsupported V_2O_5, while the spacing of the catalysts supported on γ-alumina (group A) was slightly shorter than that of group S. The diffraction lines in the range of high diffraction angle were clearer in group S than in group A.

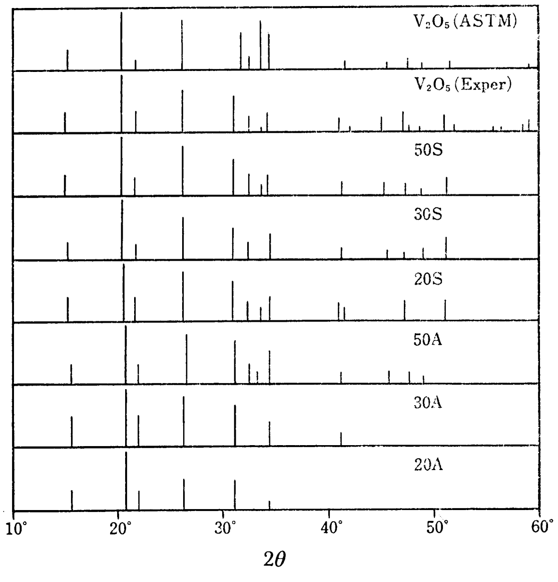

Fig. 1. Diagrams of X-ray diffration of catalysts. Refer to Table 1 for symbols.

Table 2. Samples treated with a 0.3N NH_4OH

Sample	Raw material	V_2O_5 Cont. (wt%)	Colour dry	Colour wet	Surface area (m^2/g)
Samples supported on SiO_2					
10SN	10 S	1.5		cream	595
20SN	20 S	2.2	cream	yellow	554
30SN	30 S	2.6			532
50SN	50 S	2.9		l. yel. brown	472
Samples supported on γ-Al_2O_3					
10AN	10A	2.2	cream	l. gr. yellow	268
15AN	15A	2.9			261
20AN	20A	3.1			254
30AN	30A	3.5	yellow		250
50AN	50A	4.0			240

l; light, yel; yellowish, gr; greenish

Treatment by Ammoniacal Solutions. The residual amount of vanadium oxide in catalysts after treatment with a 0.3 N ammoniacal solution are shown in Table 2 together with the coloration of samples. Generally the amount of the residual vanadium oxide in group A was greater (2—4%) than in group S (1.5—3%). As shown in Table 1, group A had a tinge of green showing existence of a small amount of low-valent vanadium ions and the tone of this color was deepened after treatment with ammoniacal solutions.

Reduction Rates by Benzene Vapour. In the case of the reduction of unsupported V_2O_5 by hydrogen, the change of the weight loss of catalysts caused by reduction consisted of the following three processes as reported by Matsuura.4) (1) The autocatalytically accelerating process in the initial step of the reduction, (2) the steady reduction process and (3) the retarding process.

In process (2), the weight of the catalysts decreased almost linearly with reduction time and reached the value corresponding to the average composition of

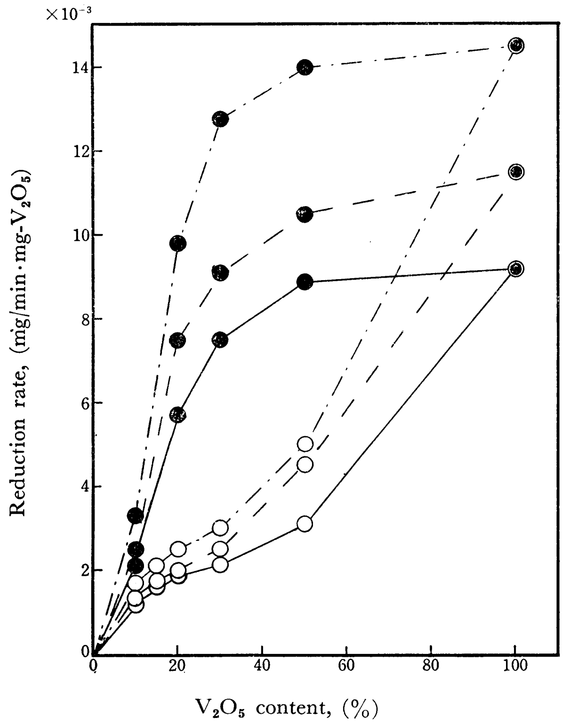

Fig. 2. Reduction rates of catalysts at 420°C.
●; Catalysts supported on silica
○; Catalysts supported on γ-alumina
-·-·-; Benzene concentration in feed 6.1%, — —; 4.6%, ——; 3.2%.

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4) R. Matsuura, *Nippon Kagaku Zasshi*, **82**, 276, (1961).

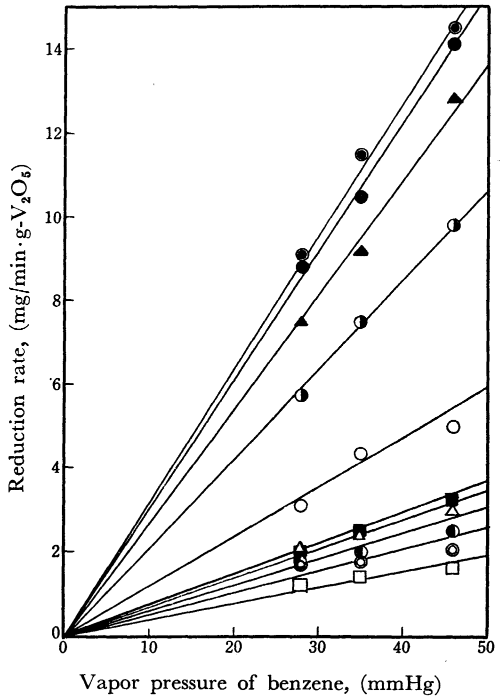

Fig. 3. Reduction rates of catalysts at 420°C.
⊙; V_2O_5, ●; 50S, ▲; 30S, ◑; 20S, ■; 10S, ○; 50A, △; 30A, ◐; 20A, ◎; 15A, □; 10A

TABLE 3. APPARENT ACTIVATION ENERGY OF REDUCTION BY BENZENE VAPOR

Sample	ΔE (kcal/mol)
V_2O_5	37
Samples supported on SiO_2	
10S	43
20S	37
30S	37
50S	26
Samples supported on γ-Al_2O_3	
10A	43
15A	40
20A	40
30A	37
50A	32

vanadium oxide V_2O_4. In process (3), the vanadium oxide on carriers was further reduced from vanadium (IV) oxide to vanadium(III) oxide. The gradient of the linear relation in process (2) was adopted in this paper as the measure of the rate of reduction expressed as weight loss (mg) per unit time (minute) and unit mass of vanadium oxide (mg) contained in the starting samples. Dependence of the reduction rates on the vanadium oxide contents and the vapour pressures of benzene in the feeds are shown in Figs. 2 and 3, respectively. It is clear that the rate of reduction decreased with the decrease of the vanadium oxide content of the catalysts. For the same content of the oxide, the reduction rates were faster for group S than for group A. Figure 3 shows that the reduction rates are proportional to the first order of the vapor pressure of benzene.

The characteristics of the rate of reduction were maintained in the range of reduction temperatures 380—450°C. The apparent activation energies of the reduction ΔE determined from the variation of the rates with reduction temperature are shown in Table 3. The activation energies varied with carriers and vanadium oxide contents.

It was observed that ΔE of group A tended to be larger than that of group S.

The crystalline structures of the reduced samples with the composition V_2O_4 were examined by X-ray diffraction. The sample of unsupported V_2O_5 reduced under the same conditions was composed of two kinds of structures, *i.e.*, the rutile type V_2O_4 and the intermediate "B" named by Sata *et al.*[5,6] In the cases of the supported catalysts, only the latter was observed.

ESR Spectra of Catalysts. The evacuated samples of group A exhibited the characteristic ESR spectra with hfs due to $^{51}V(IV)$ in distorted square pyramidal coordination[3,7] and the resolution of hfs became clear with the decrease of vanadium oxide content. In the cases of group S the spectra changed considerably with the vanadium oxide content. While a broad doublet line was observed for 50S and 30S, spectra with not well-resolved hfs over a very broad absorption line were observed for catalysts containing less than 20% vanadium oxide. Typical examples of the spectra are shown in Fig. 4.

When the catalysts were treated with 0.3 N ammoniacal solution, group A exhibited almost the same spectra as 5A in Fig. 4, but group S exhibited only broad absorption lines.

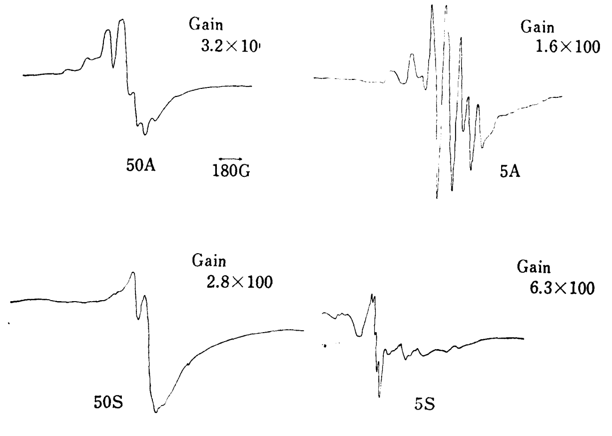

Fig. 4. ESR spectra of catalysts after vacuum treatment at 400°C.

The ESR spectra of group S were affected by moisture and changed to spectra similar to those of group A. As an example, the changes of spectra of 20S by

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5) T. Sata, E. Kodama, and Y. Itoh, *Kogyo Kagaku Zasshi*, **71**, 463 (1968).

6) The intermediate B corresponds to VO_x reported by M. Kato, M. Taniguchi, and T. Kubo (*Kogyo Kagaku Zasshi*, **69**, 2102 (1966)) and its composition is believed to be VO_2.

7) K. Tarama, S. Teranishi, S. Yoshida, and H. Yoshida, This Bulletin, **34**, 1195 (1961).

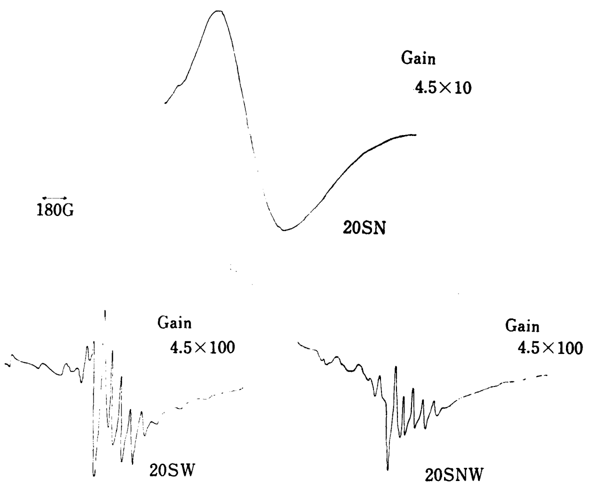

Fig.5 . ESR spectra of 20S after dampening and treatment with a 0.3 N ammoniacal solution.
20SW; Dampened in air after vacuum treatment at 400°C.
20SN; Evacuated at 400°C after treatment with a 0.3 N ammoniacal solution.
20SNW; Dampened sample of 20SN.

treatment with an ammoniacal solution and dampening are shown in Fig. 5.

Discussion

The results obtained indicate that in the supported vanadium oxide catalysts, vanadium oxide is not only dispersed on the carriers with high surface area, but also interacted chemically with the carriers.

Characteristic Behavior of Vanadium Oxide on Carriers. The main features of the results could be summarized as follows. 1) A tinge of green colour and considerable intensity of ESR spectrum of the supported vanadium oxide suggested that tetravalent vanadium ions (V^{4+}) existed in a larger amount in the supported catalysts than in unsupported V_2O_5 (the amount of V^{4+} in V_2O_5 has been estimated to be about 0.6 atom %.[8]).

2) On the carriers, vanadium oxide insoluble in 0.3 N ammoniacal solution existed and the amount was greater in group A than in group S.

3) Both rutile type V_2O_4 and the intermediate "B" were produced in the course of the reduction of unsupported V_2O_5, but rutile type V_2O_4 was not produced in the case of the supported catalysts.

4) The supported samples were more stable against reduction by benzene vapour than unsupported V_2O_5. The tendency was remarkable especially for the samples supported on γ-alumina.

The reduction rates of vanadium oxide catalysts by benzene followed the "parabolic law" which indicates the rate determining step is the diffusion process of oxygen ions within crystals at rather low temtemperature (327°C).[2b,9] In the present research, however, the rate of reduction was proportional to time, that is, of zeroth order with respect to the amount of unreduced vanadium oxide and was proportional to the vapour pressure of benzene. This seems to indicate that the diffusion process of oxygen ions within the crystal is fast enough for the reduction process and the rate determining step of reduction is the uptake of oxygen from vanadium oxide surface by gaseous benzene or adsorbed benzene with low coverage.

If this is the case, the rate would be controlled mainly by the bond strength of oxygen-vanadium ions on the surface. The results obtained reveal that the carriers, especially γ-alumina, affect the bond strength of oxygen-vanadium ions on the surface of vanadium oxide.

Structure of Vanadium Oxide Supported on γ-alumina. Experiments of the reduction and dissolution in 0.3 N ammoniacal solutions of group A showed that considerable interaction between vanadium oxide and γ-alumina took place during the course of preparation, while X-ray diffraction indicated that the vanadium oxide on the γ-alumina was essentially V_2O_5 with a small modification and no special new compounds were formed. The question whether new compounds were formed or not should depend on further investigations since X-ray diffractometry was not useful for samples containing less than 10% V_2O_5. However, such compounds do not seem to be formed because the ESR spectra of 20A and 5A were essentially the same.

The ESR spectra of group A indicated the existence of square pyramidal vanadium oxide (VO_5) which resembled the (VO_5) unit in V_2O_5 crystal.[10] The well-resolved hfs observed for catalysts of low concentration of vanadium showed that unpaired electrons of vanadium(IV) ion were isolated from each other. Thus (VO_5) might be stabilized in an isolated state on the γ-alumina by chemical interaction. For the catalysts of high concentration of vanadium, the ESR spectra were distorted due to interaction of electrons by the possible formation of a small $(VO_5)_n$ network. The massive V_2O_5 crystal observed by X-ray diffraction would be formed by accumulation of vanadium oxide over $(VO_5)_n$ networks.

Structure of Vanadium Oxide Supported on Silica. Although silica has a larger surface area than γ-alumina, X-ray diffraction indicated that the crystal of V_2O_5 developed on silica better than on γ-alumina and the interspacing of the lattice planes was the same as that of pure V_2O_5. The rate of reduction of 50S was almost the same as that of unsupported V_2O_5.

These results show that on silica the same crystal phase exists as pure V_2O_5, when the vanadium oxide content is high. However, the fact that 50S and 30S did not produce rutile type V_2O_5 during the course of reduction by benzene indicated that the crystal phase was slightly perturbed by silica.

In the case of the catalysts of low concentration of vanadium oxide, the ESR spectra were composed of not well-resolved hfs and differ from those of group A.

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[8] S. Yoshida, *Shokubai*, **10**, 90 (1968).

[9] K. Tarama and S. Teranishi, *Kogyo Kagaku Zasshi*, **56**, 302 (1953).

[10] A. Bystrom, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, **4**, 1119 (1950).

However, the characteristics of square pyramidally coordinated V(IV) ions was observed when samples were dampened as shown in Fig. 5. It is known that tetrahedrally coordinated V(IV) ions could not be detected by ESR at room temperature.[3] From these facts, the spectra could be assigned to distorted square pyramidally coordinated V(IV) ions $(VO_5)'_n$. The spectrum of 20SN which was obtained by treatment of 20S with a 0.3 N ammoniacal solution was broad singlet and changed to a spectrum characteristic of square pyramidal (VO_5) by dampening (Fig. 5).

From these effects of dampening, the broad absorption line of 20SN does not seem to be produced by dipole-dipole interaction of unpaired electrons, but might be assigned to tetrahedrally coordinated V(IV) ions (VO_4) with short spin-lattice relaxation time.

Thus vanadium oxide would be stabilized on silica surface as (VO_4) at first, followed by the formation of $(VO_5)'_n$ and V_2O_5 with the increase of the vanadium oxide content.

Thus, the structure of vanadium oxide on silica or γ-alumina could be represented schematically as in Fig. 6.

In conclusion, it was found that these carriers interacted chemically with vanadium oxide and affected its structure and that $(VO_5)_n$ which contained square pyramidal VO_5 interacted with γ-Al_2O_3 was more stable against reduction by benzene than $(VO_5)'_n$ which comprised distorted $(VO_5)_n$ and tetrahedral VO_4 on SiO_2.

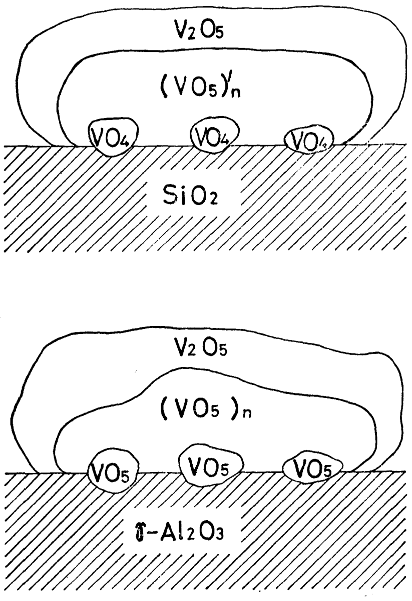

Fig. 6. Schematic representations of vanadium oxides on carriers.