Some Physical Properties and Catalytic Activities of Vanadium Oxide (III) Catalyst

By

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Electric conductivities and magnetic susceptibilities of V_2O_3 catalysts containing small amount of MoO_2 or α-Al_2O_3 were measured. The temperature dependencies of these physical properties showed that these catalysts were antiferromagnetic semi-conductor.

In general, addition of small amount of MoO_2 caused increase of effective magnetic moment (μ_{eff}), descent of the Néel temperature (T_N) and decrease of activation energy for electric conduction (E_σ). In the case of addition of Al_2O_3, reverse changes of these properties were observed.

The rates of p-H_2 conversion with these catalysts were also measured. It was asserted that the controlling step for this conversion was the desorption process of H_2, because the temperature at which this conversion became observable correlated closely with the temperature at which adsorbed H_2 began to be desorbed.

Addition of MoO_2 promoted remarkably this conversion rate at low temperature. This promotive action of MoO_2 was explained by reason that the decrease of adsorption heat of H_2 resulted from the decrease of E_σ, that is, the ascent of Fermi level by addition of MoO_2.

In the case of V_2O_3-Al_2O_3 catalyst, reverse action was expected from change of its physical properties, but rather slight improvement of activity for p-H_2 conversion was observed. This result was interpreted by the fact that this catalyst was in the slightly oxidized state favorable for this conversion.

1. Introduction

While the crystal structure and some other physical properties of vana-diumoxide (V_2O_3) have been already reported[1],[2],[3], the effect of the additive compounds to V_2O_3 on its physical properties has not been studied relative to its catalytic activity.

In this report, electric conductivities and magnetic susceptibilities of V_2O_3

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catalysts containing small amount of MoO_2 or Al_2O_3 were measured and a correlation between these physical properties and their catalytic activities for the conversion of p-hydrogen was explained.

2. Experimental

2.1 Apparatus and Procedure

(a)   Magnetic susceptibility—Faraday's method[4] was adopted to measure magnetic susceptibility (χ_g) under the following conditions; magnetic fields, 2000~6000 Oe, temperatures, 0~620°C, pressure 10^{-4} torr.

(b)   Electric conductivity—Electric resistance (D.C.) (R, ohm cm) of catalyst (1.5~2.0 g) placed between two Pt plates (1 cm²) in a Griffith's type cell[5] was measured by Wheatstone bridge at 10^{-3} torr and various temperatures between 80°C and 500°C.

(c)   Adsorption of hydrogen and p-hydrogen conversion—The adsorption of H_2 on some catalysts was followed up by the volume change method under constant pressure.

The rates of p-H_2 conversion were measured by an apparatus for flow method at low pressure.   The diagram of apparatus used are shown in Fig. 1. H_2 was analysed with accuracy of $\pm 2\%$ in p-H_2 content by means of a Pirani gauge which was composed of Pt wire (dia. 0.015 mm, length 18.4 cm).
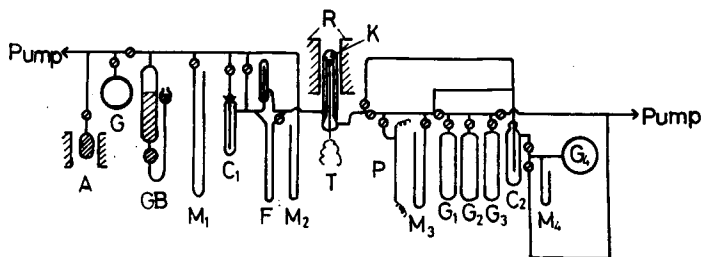

Fig. 1.   Apparatus for p-H_2 conversion
A: Active carbon, R: Reaction tube, K: Catalyst M_1, M_2, M_3, M_4: Manometer, F: Flowmeter, G: H_2-gas holder G_1, G_2, G_3: Sampling tube for reacted gas, G_4: Gas holder C_1, C_2: Capillary for controlling gas flow rate T: Thermocouple, GB: Gas burette

This conversion reaction was 1st order one with respect to H_2 pressure, so a conversion (%) of p-H_2 at constant flow rate (H_2 25 cc/min, 0.5 g cata.) and H_2 pressure (26 mmHg) was adopted as a measure of activity.

2.2 Material

(a) V_2O_3 catalyst—Three kinds of V_2O_3 catalysts were prepared as shown

in Table 1. V_2O_5 was prepared from extra pure grade NH_4VO_3 by the method described previously[6].

<div align="center">Table 1.   Preparation of V_2O_3 catalysts.</div>

Catalyst	Preparation Method
V_2O_3-A	V_2O_5 was reduced by H_2 for 5 hr at 450°C.
V_2O_3-B	V_2O_3-A was exposed in air for 3 months at room temp.
V_2O_3-C	NH_4VO_3 was reduced by H_2 for 1 hr at 500°C.

(b) V_2O_3-MoO_2 catalyst—V_2O_3-MoO_2 catalysts were prepared as follows. V_2O_5 mentioned above and MoO_3 obtained from chemical pure grade $(NH_4)_6$ Mo_7O_{24} by thermal decomposition were mixed in a given ratio, melted together at 350°C and allowed to cool in the furnace, and the solidified samples were ground to powder and reduced by H_2 for 5 hr at 450°C.

(c) V_2O_3-α-Al_2O_3 catalyst—V_2O_3-α-Al_2O_3 catalysts were prepared by the same way as V_2O_3-MoO_2 catalyst from mixtures of V_2O_5 and α-Al_2O_3 which was chemical pure commercial product purified further by washing with nitric acid.

(d)   Hydrogen—H_2 from commercial cylinder was used after usual purification and drying.

H_2 containing equilibrium amount of p-H_2 at -78°C was prepared by contact with an active carbon which was evacuated at 500°C.

3.   Results and Discussion

3.1.   Magnetic Property

The magnetic susceptibilities (χ_g) of V_2O_3 were already studied by G. Foëx[2] in the temperature range $-80\sim400$°C, and it was found that χ_g of V_2O_3 was constant in the range of $110\sim250$°C and obeyed the Curie-Weiss law in the higher temperature range than 250°C, and that the effective magnetic moment (μ_{eff}) was 3.35 Bohr.   But it seems that his V_2O_3 was in a considerably reduced state, because his sample was treated in H_2 at the temperature too high such as $1100\sim$ 1300°C.   This is confirmed also from its large value of μ_{eff} as compared with the spin only value (2.83) of free V^{3+} ion.

The present results of χ_g measurements for three kinds of V_2O_3 catalysts are shown in Fig. 2.   The anomaly observed in χ_g-temperature curves may be caused by the transformation of the antiferromagnetic phase into the paramagnetic one at so-called Néel temperature (T_N).   Above this T_N, χ_g obeyed the Curie-Weiss law

$$\chi_g = \frac{C}{T-\theta_w}, \quad C = N\mu_{eff}^2/3k$$
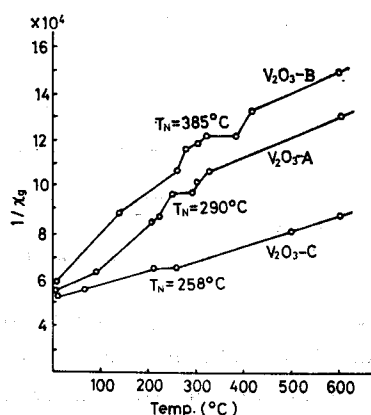
Fig. 2. Correlation between $1/\chi_g$ and temperature for V_2O_3-catalysts.

as Foëx mentioned. Obtained values of T_N, μ_{eff} and Weiss constants (θ_w) are tabulated in Table 2.

Table 2. Some Physical Properties of Catalysts.

Sample	Surface area (m²/g)	Electric Conductivity			Magnetic Property			
		R (400°C) (ohm cm)	T_M (°C)	E_σ (e.V)	T_N (°C)	μ_{eff} (B)	θ_w (°K)	$\chi_g (\times 10^6)$
V_2O_3-A	10.7	0.7	256	0.0311	290	2.73	−684	18.0 (8°C)
V_2O_3-B	—	1.5	409	—	385	1.95	−142	16.3 (11°C)
V_2O_3-C	—	1.7	251	0.0274	258	3.04	−433	18.9 (10°C)
V_2O_3-MoO₂								
0.05 mole %	9.85	0.74	232	0.0266	255	2.80	−373	18.7 (10°C)
1 mole%	11.9	0.73	—	—	227	2.98	−594	18.1 (10°C)
5 mole%	11.0	1.2	390	0.0199	404	2.53	−403	15.6 (10°C)
V_2O_3-Al₂O₃								
0.05 mole%	10.1	1.7	367	0.0322	364	2.64	−282	17.5 (11°C)
1 mole%	12.1	1.8	390	0.0357	400	2.63	−488	19.9 (9°C)

μ_{eff} of V_2O_3-A is 2.73 Bohr and slightly smaller than spin only value of free V^{3+} ion, but this small deviation will be attributed to the effect of the contribution of angular momentum of electron to magnetic moment. So it may be assumed that this V_2O_3-A is almost in the nearly stoichiometric composition.

In the case of V_2O_3-B which was prepared by slight oxidation of V_2O_3-A, χ_g is smaller than V_2O_3-A and small value (1.95) of μ_{eff} will be due to the presence of a little amount of V^{5+} or V^{4+} ion.

On the other hand, V_2O_3-C is clearly in a reduced state, because μ_{eff} (3.04) is larger than 2.83 and T_N (258°C) approximately coincides with Foëx's value.

As shown in Fig. 3 and 4, the correlations between χ_g and temperature for V_2O_3-MoO_2 and V_2O_3-Al_2O_3 catalysts were similar with that of V_2O_3, but addition of small amount of MoO_2 (0.05 mole%), μ_{eff} increased and T_N transfered to lower temperature range than V_2O_3-A.
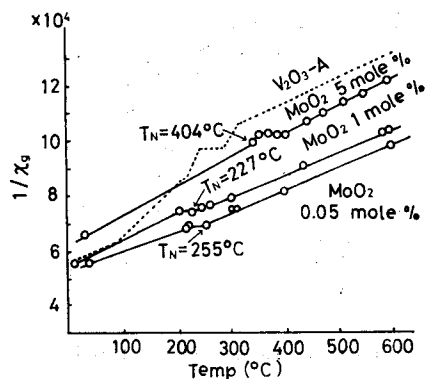

Fig. 3. Correlation between $1/\chi_g$ and temperature for V_2O_3-MoO_2 catalyst. (Dashed line shows the correlation for V_2O_3-A)
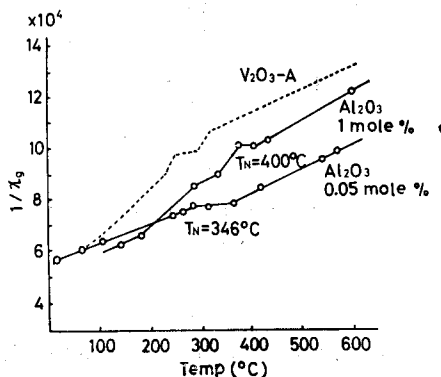
Fig. 4. Correlation between $1/\chi_g$ and temperature for V_2O_3-Al_2O_3 catalyst (Dashed line shows the correlation for V_2O_3-A)

Reverse changes of these properties were observed by addition of Al_2O_3 as summerized in Table 2.

3.2 Electric Conductivity

Corresponding with the change of mangetic properties of V_2O_3 catalysts, their electric resistances (R) varied with temperature and showed maximum values at the temperatures (T_M) which were near to T_N of respective samples as shown in Fig. 5. M. Foëx[1] reported similar results for V_2O_3 reduced under more severe conditions as mentioned above.

In the higher temperature region than T_M, that is, the paramagnetic region, activation energies (E_σ) for electric conduction were calculated by following equation.

$$\sigma = \sigma_0\, e^{-E_\sigma/kT} \quad (\sigma: \text{conductivity})$$

The values of E_σ and T_M of V_2O_3 catalysts are tabulated in Table 2.

The results of electric resistance measurements for V_2O_3-MoO_2 catalysts are shown in Fig. 6 and Table 2. By addition of small amount of MoO_2 (0.05 mole%), R and E_σ decreased and T_M transfered to low temperature range, but increase of MoO_2 caused reverse changes. In the case of V_2O_3-(1 mole%) MoO_2 catalyst, R was smallest and increased with a rise of temperature in a manner similar to
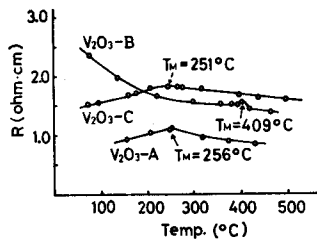
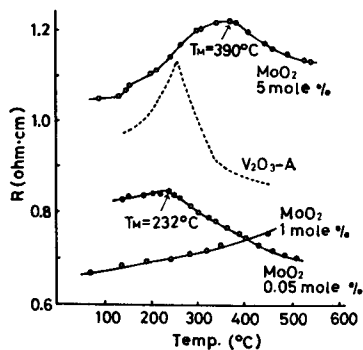Fig. 5. Electric resistance of
V$_2$O$_3$ catalyst

Fig. 6.   Electric resistance of V$_2$O$_3$-
MoO$_2$ catalyst
(Dashed line shows R for V$_2$O$_3$
-A)

metal and T_M was not observed under the temperature range below 450°C.

The temperature-resistance relation for V$_2$O$_3$-Al$_2$O$_3$ catalysts are shown
in Fig. 7.   Addition of small amount of Al$_2$O$_3$ caused the increase of R and E_σ and
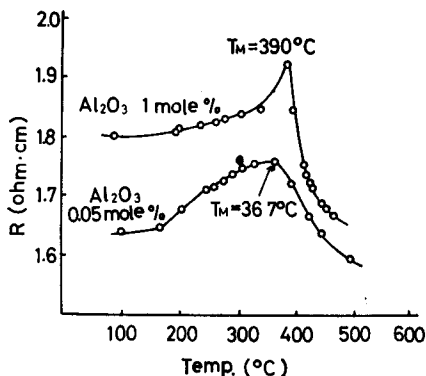the rising of T_M as shown in Table 2.

Fig. 7.   Electric resistance of V$_2$O$_3$-Al$_2$O$_3$ catalyst.

These changes of E_σ reflect the variations of Fermi energies of these catalysts,
that is, addition of MoO$_2$ causes ascent of Fermi level and addition of Al$_2$O$_3$ causes
slight descent.

3.3 Adsorption of H$_2$

The rates of H$_2$ adsorption on V$_2$O$_3$ catalyst obey the following Langmuir's rate
equation for the dissociative adsorption in the initial stage, as reported previously[7].

$$1/V_s = 1/S + 1/kpS \cdot 1/t$$

S : Amount of adsorption sites, mole/g

V_s : Adsorption amount of H_2, mole/g

t : Duration of adsorption, min.

k : Rate constant for adsorption, 1/mmHg. min.

p : Pressure of H_2, mmHg.

In the present cases of V_2O_3-A and V_2O_3-MoO_2 catalysts, similar kinetic relations between $1/V_s$ and $1/t$ were also observed as shown in Fig. 8 and Fig. 9 respectively. The rate constants (k) were calculated from these linear relations and frequency factor (A) and activation energy (E_A) for some catalysts were also calculated and tabulated in Table 3. Addition of small amount of MoO_2 (1 mole%) caused increaes of k, A and E_A.
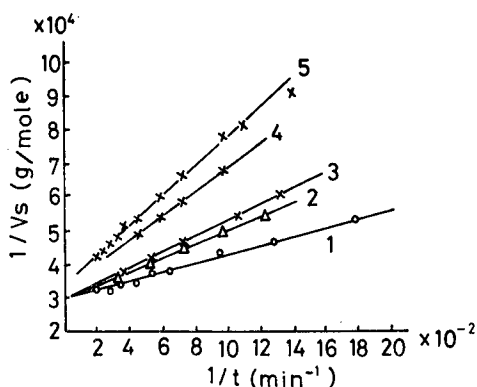

Fig. 8. H_2-adsorption rate for V_2O_3.
1. at 342°C and 400.5 mmHg
2. at 342°C and 300.8 mmHg
3. at 342°C and 199.1 mmHg
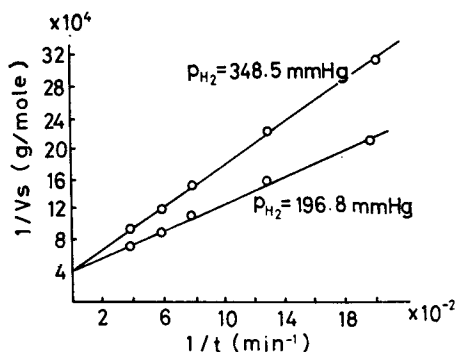4. at 319°C and 195.5 mmHg
5. at 300°C and 200.7 mmHg

Fig. 9. H_2-adsorption rate for V_2O_3–1 mole
% MoO_2 at 186°C

Table 3. Kinetic data for H_2-adsorption.

Catalyst	Surface area (m²/g)	E_A (Kcal/mole)	A (1/mmHg.min)	k (200°C) (1/mmHg.min)	Temperature range °C
V_2O_3-A	10.7	8.36	1.695	1.85×10^{-4}	200~300
		16.1	1.27×10^2	8.81×10^{-5}(300°C)	300~350
V_2O_3-MoO_2 1 mole%	11.9	15.3	2.72×10^3	2.29×10^{-4}	168~170
3 mole%	11.9	14.2	1.564×10^2	4.32×10^{-5}	262~322
5 mole%	11.0	8.9	1.812	1.38×10^{-4}	236~263

To determine the temperature (T_d) at which adsorbed H_2 began to be desorbed from the catalyst surface, the following experiments were performed. After attaining to adsorption equilibrium at 250°C, the catalyst-H_2 system was cooled rapidly to room temperature and then desorbed amount of H_2 with temperature rising of a rate of 1°C/min was measured. An example of experimental result for V_2O_3-A is shown in Fig. 10, and T_d determed for several catalysts are tabulated in Table 4. T_d of V_2O_3-MoO_2 was remarkably lower than that of V_2O_3-A or V_3O_3-Al_2O_3.
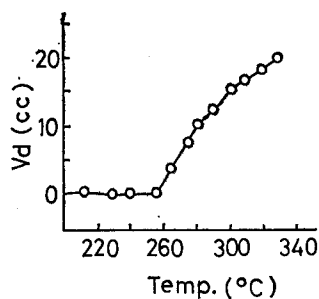

Fig. 10.   Desorption of H_2 from V_2O_3
surface
V_d: Desorbed amount of H_2; V_2O_3:
4.02 g; P_{H_2}: 27.8 mmHg

Table 4. T_d and T_H for several catalysts.

Catalyst	T_d	T_H
V_2O_3-A	270	257
V_2O_3-MoO_2 (1 mole%)	190	195
V_2O_3-MoO_2 (3 mole%)	180	190
V_2O_3-Al_2O_3 (1 mole%)	270	250

3.4   Conversion of p-H_2

The conversion rates of p-H_2 to o-H_2 were measured on several catalysts under the temperature range from 180° to 400°C. The results obtained at H_2 pressure (26 mmHg) on V_2O_3 catalyst are shown in Table 5 and Fig. 11. V_2O_3-B catalyst was initially very active, but its activity was unstable and fell low after the repetition of reaction. On the other hand, V_2O_3-A catalyst was active with reproducibility at higher temperature than 275°C.

The observed results for V_2O_3-MoO_2 and -Al_2O_3 catalysts are shown in Fig. 12. Addition of MoO_2 promoted the activity of V_2O_3 especially in the low temperature region. As shown in Table 4, the temperature (T_H) at which the conversion of
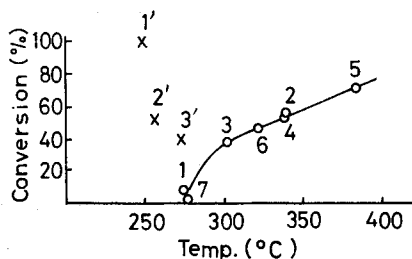
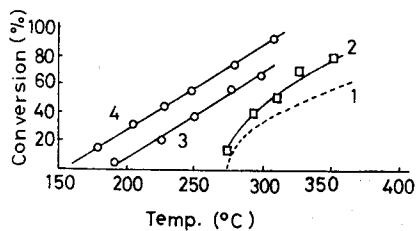Fig. 11. p-H_2 conversion with V_2O_3
(Numbers show Ex. No. in Table 5)

Fig. 12. p-H_2 conversion with V_2O_3, V_2O_3-
MoO_2 and V_2O_3-Al_2O_3
1. V_2O_3-A, 2. V_2O_3-Al_2O_3 (1 mole %)
3. V_2O_3-MoO_2 (1 mole %)
4. V_2O_3-MoO_2 (3 mole %)

Table 5. Conversion of p-H_2 with V_2O_3 catalyst.

Catalyst	Ex. No.	Temp. (°C)	Conversion (%)
V_2O_3-B	1′	248	100
	2′	256	51
	3′	272	40
V_2O_3-A	1	275	8
	2	339	53
(V_2O_3-B was reduced	3	301	38
by H_2 at 400°C for	4	338	52
12 hr.)	5	384	70
	6	323	46
	7	278	1

p-H_2 becomes observable correlates closely with T_d mentioned in previous section.

These results reveal that a desorption process of adsorbed H_2 is a controlling step of conversion rate with these catalysts.

3.5 Correlation between physical properties and catalytic activities.

The electric and magnetic properties of V_2O_3 catalysts investigated in this report show that they are antiferromagnetic semiconductors as reported already[2),3)].

The effects of additive substances such as MoO_2 and α-Al_2O_3 on these physical properties are slightly complicated, but in general, addition of small amount of MoO_2 causes the increase of μ_{eff} in the paramagnetic phase, the decrease of E_σ and the descents of T_N and T_M and in the case of addition of Al_2O_3, reverse changes of these properties are observed.

The changes of E_σ shown in Table 2 reflect the variations of Fermi energies,

that is, Fermi level ascends by addition of MoO_2 and slightly descends by addition of Al_2O_3.

On the other hand, MoO_2 promotes desorption of adsorbed H_2 at low temperature. This fact is closely related with the ascent of Fermi level which results in decrease of adsorption heat of H_2, electron donating gas. Because rate of p-H_2 conversion with these catalysts are controlled by desorption rate of H_2 as mentioned in previous section, one of the main factors of the promotive action of MoO_2 is probably ascribed to this decrease of adsorption heat of H_2.

In spite of the reverse change of physical properties caused by addition of Al_2O_3, the activity of V_2O_3-Al_2O_3 catalyst for p-H_2 conversion is rather a little higher than that of V_2O_3-A catalyst. This fact may be explained as follows. The magnetic moment μ_{eff} of this V_2O_3-Al_2O_3 catalyst is smaller than that of V_2O_3-A, so this catalyst is in the slightly oxidized state which is favorable for p-H_2 conversion in the light of a fact that V_2O_3-B oxidized slightly is more active than V_2O_3-A. This promotive factor is balanced by the suppresive factor which correlates with the decrease of desorption rate of H_2 caused by descent of Fermi level. So the activity of V_2O_3-Al_2O_3 catalyst for p-H_2 conversion is slightly large as mentioned above.

References

1) M. Foëx, Compt. rend. **229**, 880 (1949).
2) G. Foëx and J. Wucher, ibid., **229**, 882 (1949).
3) S. Teranishi and K. Tarama, J. Chem. Phys., **27**, 1217 (1957).
4) cf. P.W. Selwood "Magneto Chemistry" 2nd Ed. p. 11, Interscience Pub. Co. (1956).
5) R.H. Griffith, P.R. Chapmann and P.R. Lindars, Discus. Faraday Soc., **8**, 258 (1950).
6) K. Tarama and S. Teranishi, J. Chem. Soc. Japan Ind. Chem. Sect., (Kogyo Kagaku Zasshi), **56**, 303 (1953).
7) K. Tarama and S. Teranishi, ibid., **55**, 316 (1952).