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Letter

Photo-oxidation of cyclohexane over alumina-supported vanadium oxide catalyst

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Abstract

Alumina-supported vanadium oxide exhibited specific photocatalytic performance in the oxidation of cyclohexane to produce cyclohexanone. Higher loading of vanadium oxide (above 5 wt.%) on alumina support resulted in reducing activity, suggesting that the active species are stable isolated VO_4 on alumina. © 2001 Elsevier Science B.V. All rights reserved.

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Silica-supported vanadium oxide (VS) is known as a photocatalyst for oxidation of CO [1,2], hydrocarbons [3,4] and alcohols [5], and the photoactive species is accepted to be the isolated vanadates with the specific structure of tetrahedral VO_4 with mono-oxo species. Although the structure of supported vanadium oxide has been studied extensively [6–8] and highly dispersed vanadate realizes the similar structure over many kinds of metal oxide supports like silica, alumina, ziconia, titania, etc., there has been only a few reports on photoactivity of titania-supported vanadium oxide (VT), zirconia-supported vanadium oxide (VZ) and alumina-supported vanadium oxide (VA). In the present work, we have examined the photoactivity of these supported vanadium oxides with photo-oxidation of cyclohexane as a probe reaction. The oxidation of cyclohexane to form cyclohexanone is significantly important reaction since cyclohexanone is an intermediate material to ε-caprolactam which is a raw material for nylon synthesis. The oxidation process of cyclohexane to produce cyclohexanone has been industrialized over cobalt-base catalyst with oxygen above 423 K under high pressure [9]. To make the reaction condition milder, new reaction system has been sought out. Hydrogen peroxide is often used as an oxidizing reagent to achieve the mild reaction condition [10,11]. Nevertheless, realization of oxidation by molecular oxygen is strongly desired. From this point of view, we chose this reaction as a test reaction for photo-oxidation by supported vanadium oxides and eventually, we have found VA an effective photocatalyst. Here, we report the photo-oxidation of cyclohexane over alumina-supported vanadium oxide photocatalyst.

Supported vanadium oxides were prepared by impregnating various supports with aqueous solution of ammonium metavanadate at 353 K for 2 h and evaporation to dryness at 373 K. The supports used in the study were SiO_2 [12] (628 m^2/g), γ-Al_2O_3 (177 m^2/g: JRC-ALO-4), TiO_2 (50 m^2/g: JRC-TIO-4) and ZrO_2

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Table 1
Specific surface area and surface density of the supported vanadium oxides

Sample	Specific surface area ($m^2\ g^{-1}$)	Surface density (V atom/nm^2)
V_2O_5/SiO_2	567	0.29
V_2O_5/Al_2O_3	170	0.97
V_2O_5/ZrO_2	64	2.6
V_2O_5/TiO_2	44	3.7

[13] (64 m^2/g). The sample was kept at 383 K for 12 h, followed by calcination at 773 K for 5 h. Loading amount of V was 2.5 wt.% as V_2O_5. Table 1 shows specific surface area and surface density of vanadium atom about supported vanadium oxide. No crystalline vanadium compounds were detected with XRD analysis. Prior to photo-oxidation, each catalyst sample (0.2 g) was heated at 673 K for 30 min in air and evacuated at 673 K for 30 min, followed by treatment with 9.3×10^3 Pa O_2 for 90 min and evacuation for 30 min at 673 K. After cooling down to room temperature, cyclohexane (0.5 ml: Wako, 99.5%) and acetonitrile (1.5 ml: Wako, 99.5%) were added into a reactor. These substrates were used without further purification. The reaction mixture was stirred by a magnetic stirrer at 298 K for 5 h under oxygen at atmospheric pressure, and irradiated from the side with a 500 W ultrahigh-pressure mercury lamp. During 5 h irradiation, products yield increased linearly with irradiation time. The linearity of the conversion to irradiation time allows to evaluate the catalyst activity. Therefore, we did not prolong the irradiation time more than 5 h. The reactor volume was ca. 150 ml.

Fig. 1 shows the result of photo-oxidation of cyclohexane with gaseous oxygen over various supported vanadium oxides. Cyclohexanol and cyclohexanone were obtained as main products under irradiation of the light, and the formation of trace amount of cyclohexandiol and cyclohexandione was confirmed. Any products were not observed in the dark at all, indicating that all the catalyst samples showed photoactivity. VA exhibited the highest activity in the four samples and the activities of VS, VT and VZ were quite lower than that of VA. To confirm the activity of alumina or V_2O_5 itself, we carried out the photoreaction with these metal oxide samples. No products were formed under photo-irradiation of alumina nor V_2O_5. We conclude that the active species is vanadium species supported on alumina. The 55 μmol vanadium atom exists in each 200 mg of 2.5 wt.% supported vanadium oxide and the apparent turn over number (TON) of the photo-oxidation of cyclohexane on VA was calculated for the 5 h reaction. The TON is 1.9 and this indicates that VA acts as a photocatalyst.

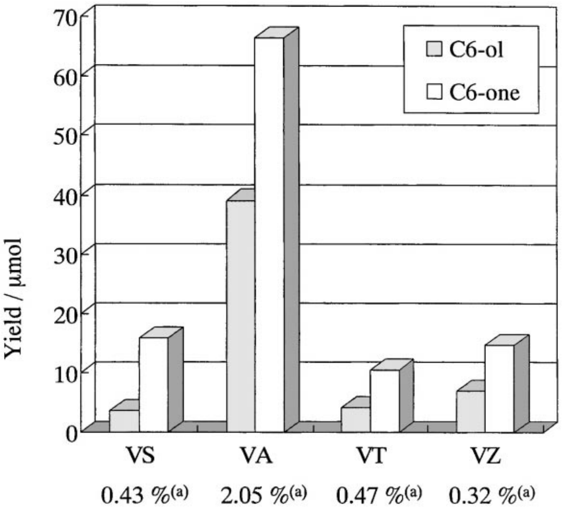

Fig. 1. The result of photo-oxidation of cyclohexane with gaseous oxygen over various supported vanadium oxides.[(a)] Conversion based on cyclohexane at 5 h irradiation.

The four samples showed similar tendency of the selectivities to cyclohexanol and cyclohexanone. The produced amount of cyclohexanone was higher than that of cyclohexanol over each sample and the ratio of cyclohexanol to cyclohexanone was ca. 0.6. The selectivity suggests that oxidation of cyclohexane proceeds in the same way over the four catalyst samples. Since we used an integrated reactor, we guess that consecutive oxidation of cyclohexanol to cyclohexanone is not a main path and ketone forms in parallel to alcohol.

Fig. 2 shows an effect of loading amount of vanadium oxide on alumina upon products yield for 5 h reaction. The total yield of cyclohexanol and cyclohexanone exhibited the highest between 2.5 and 5.0 wt.%. And, the loading amount for the best yield of cyclohexanol and cyclohexanone was 2.5 wt.%, respectively. The total yield was almost proportional to the loading amount up to 2.5 wt.% and decreased over 5.0 wt.%. It is known that vanadium oxide can be highly dispersed on alumina at low loading and stabilized as isolated VO_4 species [6–8,14–16]. Gao and Wachs [6]

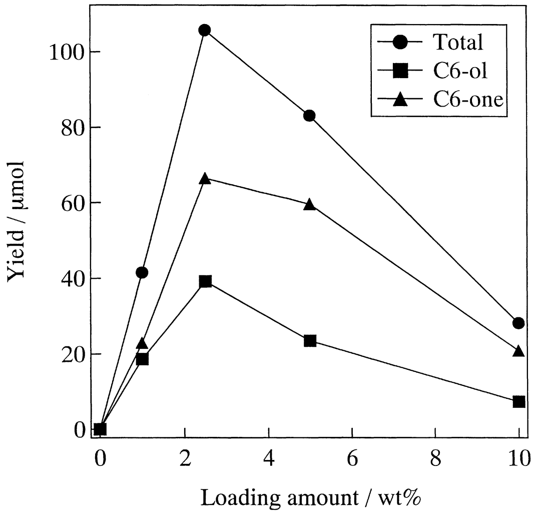

Fig. 2. The effect of loading amount of vanadium oxide on alumina upon products yield.

reported that polymerized VO_4 species appeared at 7.0 wt.% loading (2.2 atoms/nm^2) and increased with an increase in V_2O_5 loading. A drop of activity of the sample with higher loadings than 5.0 wt.% would be attributed to the polymerization of VO_4 species. In the present reaction, we conclude that highly dispersed VO_4 species over alumina is the active species. Actually, in cases of VZ and VT, their surface vanadium atom density (2.6 and 3.7 atoms/nm^2) is high so that the polymerized VO_4 and VO_5 would be the main species and VZ and VT exhibited poorer activity than VA.

On the other hand, although VS shows much lower vanadium density than VA, the activity is very poor. Surface structure depends on the density as well as on the state of the sample. In cases of VA, VZ [6] and presumably VT, the surface species do not change by hydration. However, surface vanadates over silica change their structure easily by hydration [6,14–17], i.e. isolated $VO_4 \rightarrow$ polymerized VO_5/VO_6. The oxidation of cyclohexane fatally produces water molecules at the vicinity of vanadium atoms. The adsorption of H_2O changes surface vanadates to polymerized one. Therefore, catalytic reaction is terminated by the formation of polyvanadates.

As a conclusion, the active species for photooxidation of cyclohexane is stable isolated VO_4 species. In order to improve the activity, the preparation of the catalyst sample of high vanadium content with stable isolated VO_4 is necessary.

References

[1] S. Yoshida, Y. Matsumura, S. Noda, T. Funabiki, J. Chem. Soc., Faraday Trans. 1 (77) (1981) 2237.
[2] M. Anpo, I. Tanahashi, Y. Kubokawa, J. Phys. Chem. 84 (1980) 3440.
[3] S. Yoshida, Y. Magatani, S. Noda, T. Funabiki, J. Chem. Soc., Chem. Commum. (1982) 601.
[4] S. Kalliaguin, B.N. Shelomov, V.B. Kazansky, J. Catal. 55 (1978) 384.
[5] T. Tanaka, Y. Nishimura, S. Kawasaki, M. Ooe, T. Funabiki, S. Yoshida, J. Catal. 118 (1989) 327.
[6] X. Gao, I.E. Wachs, J. Phys. Chem. B 104 (2000) 1261.
[7] A. Khodakov, B. Olthof, A.T. Bell, E. Iglesia, J. Catal 181 (1999) 205.
[8] B. Olthof, A. Khodakov, A.T. Bell, E. Iglesia, J. Phys. Chem. B 104 (2000) 1516.
[9] D.D. Davis, D.R. Kemp, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 1, Wiley, New York, 1991, p. 466.
[10] W.A. Carvalho, M. Wallau, U. Schuchardt, J. Mol. Catal. 144 (1999) 91.
[11] E. Armengol, A. Corma, V. Fornés, H. García, J. Primo, Appl. Catal. A: General. 181 (1999) 305.
[12] S. Yoshida, T. Matsuzaki, K. Mori, K. Tarama, Bull. Chem. Soc. Jpn. 47 (1974) 1564.
[13] Y. Kohno, T. Tanaka, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 94 (1998) 1875.
[14] S. Yoshida, T. Tanaka, Y. Nishimura, H. Mizutani, T. Funabiki, Proc. 9th Int. Congr. Catal. 3 (1988) 1473.
[15] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 1 (84) (1988) 2987.
[16] S. Yoshida, T. Tanaka, T. Harada, T. Hiraiwa, H. Kanai, T. Funabiki, Catal. Lett. 12 (1992) 277.
[17] X. Gao, S.R. Bare, B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. B 102 (1998) 10842.