

Active Sites for the Oxidation of Carbon Monoxide on V₂O₅ Catalysts

Kenji Mori, Akira Miyamoto,* Toshiaki Ui, and Yuichi Murakami

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

Surface defects such as steps, kinks, or vacancies are active sites for the oxidation of CO on V₂O₅ catalysts; the activity of surface V=O species located in the smooth (010) face is much lower than that of the surface defects.

Surface V=O species located in the (010) face of V₂O₅ have been considered to be active sites for various reactions including the oxidation of hydrocarbons and the reaction of NO with NH₃ in the presence of O₂.¹⁻³ Although much research has been done on the oxidation of CO on vanadium oxide catalysts, the active site for this reaction has been a subject of controversy.^{2,4} This is partly because the ¹⁸O-tracer technique does not necessarily give decisive evidence, since the oxygen of CO₂ can readily exchange with the lattice oxygen of V₂O₅.^{2,5} In this study, the structure sensitivity of this reaction and the relationship between the reaction rate and the amount of V=O species have been examined in order to solve this problem.

A V₂O₅-FRESH catalyst was prepared by the thermal decomposition of ammonium metavanadate at 773 K in flowing O₂. A V₂O₅-FUSED catalyst was prepared by fusing the V₂O₅-FRESH catalyst at 1073 K for 18 h in air, followed by gradual cooling to room temperature. A V₂O₅-REDOX catalyst was prepared from the V₂O₅-FUSED catalyst by reduction-oxidation treatment, *i.e.* reduction in flowing H₂ at 673 K for 1 h followed by reoxidation in flowing O₂ (20%) at 673 K for 1 h (this redox cycle was repeated 5 times). The number of surface V=O species on the catalyst was determined using the rectangular pulse technique described previously.⁶ XPS spectra of the catalysts were measured on a Shimadzu ESCA 750 electron spectrometer. Kinetic studies were carried out using the flow technique with *T* = 613–743 K, [CO] = 4.5%, and [O₂] = 0–75.2%. I.r. spectra of the catalysts under steady state conditions at various concentrations of O₂ were measured on JASCO EDR-31 emissionless *i.r.* diffuse reflectance spectrometer using KBr as a diluent.⁷

Table 1. Rate and specific rate for the oxidation of CO on vanadium oxide catalysts.^a

Catalyst	BET ^b surface area/m ² g ⁻¹	Density of surface V=O ^c /μmol m ⁻²	Rate/μmol g ⁻¹ s ⁻¹	Specific rate/μmol m ⁻² s ⁻¹
V ₂ O ₅ -FRESH	5.4	4.1	9.65	1.79
V ₂ O ₅ -FUSED	0.8	5.0	0.06	0.08
V ₂ O ₅ -REDOX	0.8	5.0	0.11	0.14

^a Reaction condition: temperature, 673 K; concentration of CO, 4.5 mol%; concentration of O₂, 75.2 mol%. ^b BET = Brunauer-Emmett-Teller. ^c This is defined as the number of surface V=O species divided by the BET surface area.

Table 1 shows the rate and specific rate for the oxidation of CO when an excess of oxygen was present, where the rate of the reaction was zeroth order with respect to [O₂], and where the catalyst was confirmed to be in its highest oxidation state, *i.e.* V⁵⁺. Here, the specific rate is defined as the rate of CO oxidation per unit surface area of the catalyst. The specific rate for the V₂O₅-FUSED catalyst was *ca.* 20 times smaller than that for the V₂O₅-FRESH catalyst (Table 1), indicating that the specific activity of the V₂O₅-FRESH catalyst significantly decreased on fusion. The specific rate, however, for the V₂O₅-REDOX catalyst was *ca.* twice as large as that for the V₂O₅-FUSED catalyst. A similar relationship was also found to hold for the reaction at temperatures between 673 and 743 K.

Figure 1(a) shows the rate of oxidation of CO and the amount of V=O species in the catalyst at steady state at

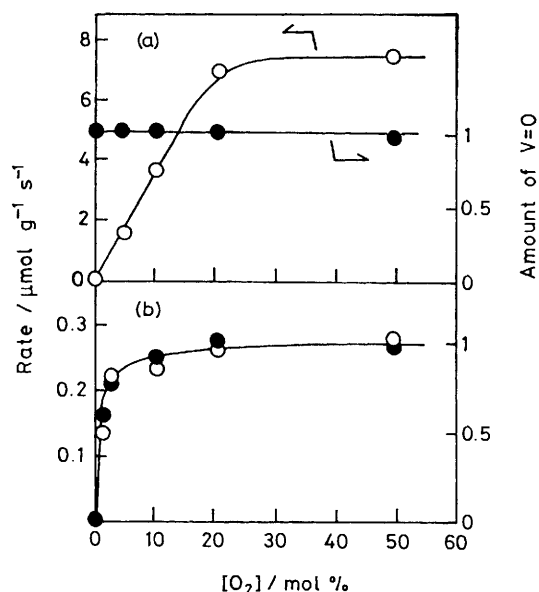


Figure 1. Reaction rate and amount of V=O in the catalyst in the steady state CO oxidation at various concentrations of O_2 . (a) The V_2O_5 -FRESH catalyst. $T = 658 \text{ K}$; $[CO] = 4.5 \text{ mol } \%$. (b) The V_2O_5 -FUSED catalyst. $T = 743 \text{ K}$; $[CO] = 4.5 \text{ mol } \%$. The amount of V=O species in the catalyst was evaluated using the Kubelka-Munk equation from the absorption peak at 1020 cm^{-1} assignable to the V=O stretching vibration. \circ = reaction rate, \bullet = amount of V=O.

various concentrations of O_2 . As shown, the rate increased linearly with increasing $[O_2]$ up to 20 mol%. Above this concentration, it was almost constant. The steady state amount of V=O species in the V_2O_5 -FRESH catalyst as measured by i.r. spectroscopy, on the other hand, did not change with $[O_2]$; in other words, the V_2O_5 catalyst was held in the highest oxidation state, V^{5+} , irrespective of $[O_2]$. Figure 1(b) shows the relationship for the V_2O_5 -FUSED catalyst. As may be seen, the amount of V=O species and the reaction rate changed similarly with $[O_2]$. The reaction on the V_2O_5 -FUSED catalyst took place even after stoppage of the gaseous O_2 supply, indicating participation of the bulk V=O species in the oxidation of CO. However, reaction on the V_2O_5 -FRESH catalyst stopped almost immediately after the stoppage of gaseous O_2 supply. These data indicate that the V=O species located in the smooth (010) face are active sites for the reaction on the V_2O_5 -FUSED catalyst, but not on the V_2O_5 -FRESH catalyst.

The specific activity of the V_2O_5 -FRESH catalyst is much higher than that of the V_2O_5 -FUSED catalyst (Table 1). This strengthens the conclusion that the V=O species located in

the smooth (010) face are not active sites for the oxidation on the V_2O_5 -FRESH catalyst. If they were, then the specific activity of the catalyst should be almost the same as that on the V_2O_5 -FUSED catalyst, because the density of surface V=O species on the V_2O_5 -FRESH catalyst is almost the same as that on the V_2O_5 -FUSED catalyst (Table 1). Fusion of a solid would generally lead to a smooth surface with a decreased number of surface defects while severe redox treatment of a solid with few surface defects would tend to increase their number. No impurity peaks were observed in the XPS spectrum of the V_2O_5 -FRESH, V_2O_5 -FUSED, or V_2O_5 -REDOX catalysts except for the C_{1s} peak at 284.6 eV . A significant decrease in the specific rate for the V_2O_5 -FRESH on fusing and a marked increase in the specific rate for the V_2O_5 -FUSED on the redox treatment therefore leads us to the conclusion that the active sites for the oxidation of CO are oxygen species located at surface defects for the V_2O_5 -FRESH and V_2O_5 -REDOX catalysts, but they are the surface V=O species located in the smooth (010) face for the V_2O_5 -FUSED catalyst; the activity of the former is significantly higher than that of the latter.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan. The authors thank Mr T. Iwana (Products R & D Center, Daikyo Oil Co. Ltd.) for the measurement of XPS spectra.

Received, 3rd November 1981; Com. 1289

References

- 1 K. Tarama, S. Teranishi, S. Yoshida, and N. Tamura, Proc. 3rd Int. Congr. Catal., North-Holland Publishing Co., 1965, p. 282.
- 2 K. Hirota, Y. Kera, and S. Teratani, *J. Phys. Chem.*, 1968, **72**, 3133.
- 3 D. J. Cole, C. F. Cullis, and D. J. Hucknall, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2185; G. C. Bond, A. J. Sárkány, and G. D. Parfitt, *J. Catal.*, 1979, **57**, 176; M. Akimoto, M. Usami, and E. Echigiya, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2195; M. Inomata, A. Miyamoto, and Y. Murakami, *J. Chem. Soc., Chem. Commun.*, 1980, 233; *J. Catal.*, 1980, **62**, 140.
- 4 M. Ya. Kon', V. A. Shvets, and V. G. Kazanskii, *Kinet. Katal.*, 1972, **13**, 735; M. R. Goldwasser and D. L. Trimm, *Ind. Eng. Chem., Prod. Res. Dev.*, 1979, **18**, 27; F. Roozeboom, A. J. van Dillen, J. W. Geus, and P. J. Gellings, *ibid.*, 1981, **20**, 304.
- 5 Y. Kera, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2841; H. Kakioka, V. Ducarme, and S. J. Teichner, *J. Chim. Phys. Phys. Chim. Biol.*, 1971, **68**, 1715, 1722, 1726.
- 6 A. Miyamoto, Y. Yamazaki, M. Inomata, and Y. Murakami, *J. Phys. Chem.*, 1981, **85**, 2366; M. Inomata, A. Miyamoto, and Y. Murakami, *ibid.*, p. 2372.
- 7 M. Niwa, T. Hattori, M. Takahashi, K. Shirai, M. Watanabe, and Y. Murakami, *Anal. Chem.*, 1979, **51**, 46.