

## Selective Exposure of the V=O Species on the Surface of Vanadium Oxide Supported on Titania and Alumina

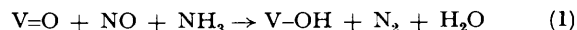
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**Summary** By measuring the quantity of surface V=O species on  $V_2O_5$ -TiO<sub>2</sub> and  $V_2O_5$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing various amounts of  $V_2O_5$ , we have found that, for  $V_2O_5$ -TiO<sub>2</sub> catalysts, the (010) face of  $V_2O_5$  is selectively exposed to the surface but, for  $V_2O_5$ -Al<sub>2</sub>O<sub>3</sub> and unsupported catalysts, various crystal faces of  $V_2O_5$  are exposed in addition to the (010) face.

THE effect of TiO<sub>2</sub> supports on promoting partial oxidations of hydrocarbons on vanadium oxide is currently a topic of investigation.<sup>1-3</sup> Although the role of the surface V=O species as an active site has been studied, quantitative measurements of the number of surface V=O species on supported  $V_2O_5$  catalysts have not been carried out. Recently, use of the rectangular pulse technique<sup>4</sup> has been proposed to determine the quantity of surface V=O species on unsupported  $V_2O_5$  catalysts. This method is based on the introduction of a mixture of NO and NH<sub>3</sub> which

comprises the rectangular pulse (the pulse width is usually 60 s) and the detection of the concentration profile of N<sub>2</sub> produced in equation (1). Here, this method was applied



to investigate the surface structure of  $V_2O_5$  on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> carriers.

TiO<sub>2</sub> composed of anatase with a small amount of rutile was prepared by calcination of TiO<sub>2</sub> (Nippon Aerosil) in O<sub>2</sub> at 773 K. Al<sub>2</sub>O<sub>3</sub> was obtained commercially (Sumitomo  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). The BET surface areas of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were 40.0 and 190.5 m<sup>2</sup> g<sup>-1</sup>, respectively. Vanadium oxide supported on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> carriers was prepared by impregnating the carriers with an oxalic acid solution of ammonium metavanadate followed by calcination at 773 K in a stream of O<sub>2</sub>. The quantity of surface V=O species on the catalysts was measured using the rectangular pulse technique described previously.<sup>4</sup> Since the V=O species is

located on the (010) face of the  $V_2O_5$  crystal and the surface density of the V=O species in the (010) face is known to be  $4.872 \text{ nm}^{-2}$ ,<sup>5</sup> the area of the (010) face of  $V_2O_5$  can be calculated from the number of surface V=O species.

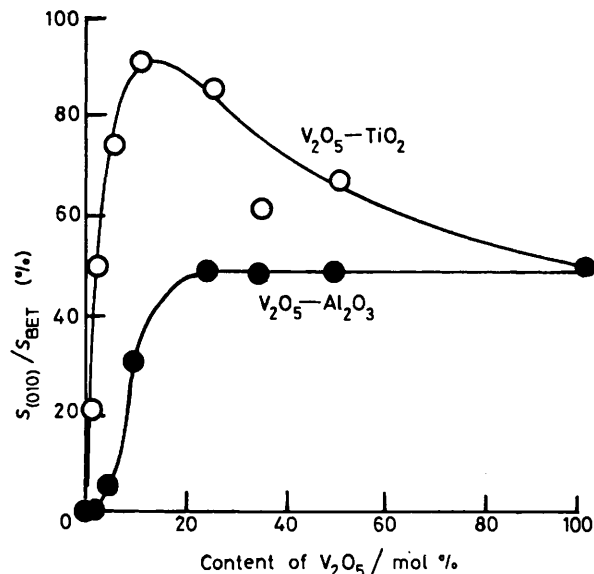


FIGURE. Ratio of the area of the (010) face of  $V_2O_5$  [ $S_{(010)}$ ] to the BET surface area [ $S_{\text{BET}}$ ] for  $V_2O_5$ -TiO<sub>2</sub> (○) and  $V_2O_5$ -Al<sub>2</sub>O<sub>3</sub> (●) catalysts with various contents of  $V_2O_5$ . 0 mol % of  $V_2O_5$ : carriers only; 100 mol % of  $V_2O_5$ : unsupported  $V_2O_5$ .

The Figure shows the area of the (010) face of  $V_2O_5$  as a percentage of the total surface area as measured by the BET method. For  $V_2O_5$ -TiO<sub>2</sub> catalysts, as the content of  $V_2O_5$  increases, the fraction occupied by the (010) face increases linearly, indicating that the surface of TiO<sub>2</sub> is gradually covered by  $V_2O_5$ . When the  $V_2O_5$  content was 10 mol%, the (010) face reached its maximum fraction of the total surface area (90%) and the specific area of the (010) face of  $V_2O_5$  ( $26.4 \text{ m}^2 \text{ g}^{-1}$ ) was ca. 10 times that of unsupported  $V_2O_5$  ( $2.7 \text{ m}^2 \text{ g}^{-1}$ ). When the  $V_2O_5$  content was further increased, the fraction of the surface occupied by the (010) face decreased to reach the value of unsupported  $V_2O_5$  (50% at 100 mol%  $V_2O_5$  content) where various crystal faces of  $V_2O_5$  are thought to be exposed in addition to the (010) face. In other words, when the  $V_2O_5$  content is 10 mol%,  $V_2O_5$  covers the surface of TiO<sub>2</sub> to expose selectively the (010) face to the surface. However, as shown in the Figure, the fraction of the surface occupied by the (010) face of  $V_2O_5$ -Al<sub>2</sub>O<sub>3</sub> catalysts did not exceed 50%, the value of unsupported  $V_2O_5$  catalyst, at any  $V_2O_5$  content. These data clearly indicate that on  $V_2O_5$ -TiO<sub>2</sub> catalysts, the V=O species is selectively exposed to the surface by the interaction of the (010) face of  $V_2O_5$  with the surface of the TiO<sub>2</sub> support,<sup>6</sup> whereas such an effect cannot be expected for  $V_2O_5$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

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<sup>1</sup> D. J. Cole, C. F. Cullis, and D. J. Hucknall, *J.C.S. Faraday I*, 1976, **72**, 2185.

<sup>2</sup> G. C. Bond, A. J. Sárkány, and G. D. Parfitt, *J. Catalysis*, 1979, **57**, 176.

<sup>3</sup> M. Akimoto, M. Usami, and E. Echigoya, *Bull. Chem. Soc. Japan*, 1978, **51**, 2195.

<sup>4</sup> A. Miyamoto, Y. Yamazaki, M. Inomata, and Y. Murakami, *Chem. Letters*, 1978, 1355.

<sup>5</sup> A. Byström, K. A. Wilhelmi, and O. Bronzen, *Acta Chem. Scand.*, 1950, **4**, 1119.

<sup>6</sup> A. Vejux and P. Courtine, *J. Solid State Chem.*, 1978, **23**, 93.