



Preparation and Characterization of Highly Dispersed Vanadium Oxide Catalysts supported on Zirconia*

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Vanadium oxide-based catalysts are well known and extensively employed in industry for the heterogeneous oxidation and ammoxidation of aromatic hydrocarbons [1 - 5]. Generally these catalysts are supported on oxides such as Al_2O_3 , SiO_2 and TiO_2 . Supports are often found to modify the physico-chemical properties of vanadia catalysts. The supported oxides do not form three dimensional crystal phases, but rather a patchy or continuous 'monolayer' covering the support [6, 7]. Recently, ZrO_2 -supported catalysts were found to exhibit better catalytic properties than the catalysts supported on other oxides [8, 9]. In particular, ZrO_2 itself is known to catalyse dehydration, hydrogenation and isomerization reactions [10].

The activity of supported vanadia catalysts depends mainly on the method of preparation, the nature of the support and the dispersion of the active component on the support surface. Considerable efforts have been made to develop methods for determining dispersion of the active component in supported catalysts. These include electron spectroscopy for chemical analysis (ESCA) [11, 12] and low temperature oxygen chemisorption (LTOC) [13 - 22]. The latter method offers the advantage of being simple, inexpensive and rapid in providing quantitative data for determining the dispersion of the active component in supported catalysts and has received increased attention recently as a surface-specific probe for characterization of vanadia [13 - 16], molybdena [17 - 21] and tungsten sulphide [22, 23] catalysts. Attempts have been made to correlate the oxygen chemisorption capacities of the catalysts with their activities for hydrotreating and oxidation reactions. In this communication, we report new complementary results obtained by LTOC and their relation to catalytic activity for partial oxidation of methanol by a series of vanadia catalysts supported on zirconia.

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The zirconia support was prepared by ammoniacal hydrolysis of zirconium oxychloride at pH 9. The resulting hydroxide was calcined in air at 500 °C for 4 h. A series of V_2O_5 catalysts with V_2O_5 loadings of *ca.* 1.83 - 10.38 wt.% supported on ZrO_2 were prepared by impregnating the support material with an aqueous solution containing the requisite amount of NH_4VO_3 . The catalysts were subsequently dried and calcined in air at 500 °C for 6 h. The vanadium content of the catalyst was analysed using atomic absorption spectrometry.

Oxygen chemisorption experiments were performed using a static high vacuum system followed by the method of Parekh and Weller [17]. The details of the experimental procedure are described elsewhere [13]. A flow micro-reactor interfaced with a gas chromatograph and operating under normal atmospheric pressure was used for the vapour-phase oxidation of methanol at 175 °C. The feed gas (air) was passed through two saturators containing methanol. The main reaction product, *i.e.* formaldehyde, was analysed by a column containing 10% Carbowax 20M on Chromosorb. Traces of dimethyl ether were found only at higher vanadia loadings. Pure ZrO_2 was found to be inactive under the experimental conditions.

Results of oxygen chemisorption capacities of various catalysts are plotted as a function of V_2O_5 content in Fig. 1, and other information derived from oxygen chemisorption results is reported in Table 1. Equivalent vanadia areas (EVA) reported in Table 1 of all supported catalysts have been calculated by multiplying oxygen chemisorption capacities of the catalysts with the factor $13.2 \text{ m}^2 \text{ ml}^{-1}$ (which is the ratio of BET surface area of the reduced unsupported V_2O_5 to the volume of oxygen chemisorbed on it) [12]. Figure 1 shows that oxygen chemisorption capacities increase with increasing V_2O_5 content up to 6.53% w/w of V_2O_5 on ZrO_2 and decrease at

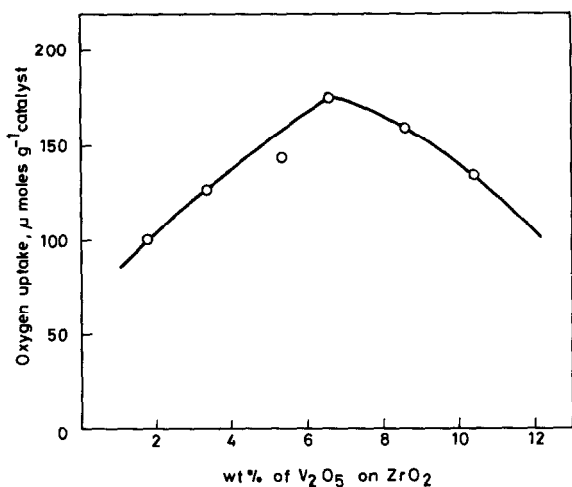


Fig. 1. Oxygen uptake as a function of V_2O_5 loading.

TABLE 1

Results of oxygen chemisorption for V_2O_5/ZrO_2 catalysts

Catalyst composition: wt.% of V_2O_5 on ZrO_2	BET surface area ^a ($m^2 g^{-1}$)	Active site density ^b (nm^{-2})	Surface coverage ^c	Equivalent vanadia (EVA) ($m^2 g^{-1}$)	Amount of O_2 chemisorbed ^d (μmol at STP g^{-1})
0.00	84	—	—	—	2
1.83	84	1.41	34.74	29.32	99
3.38	84	1.77	43.48	36.45	123
5.34	79	2.18	63.67	42.40	143
6.53	78	2.69	66.19	51.65	174
8.59	77	2.52	61.97	47.67	161
10.38	73	2.18	53.65	39.23	133

^aBased on unit weight of the catalyst.^bThis is equal to the number of oxygen atoms chemisorbed per unit area of the reduced catalysts.^cDefined as $100 \times$ (equivalent vanadia area/BET surface area of the reduced catalyst).^dValues obtained after deducting from the volume of oxygen chemisorbed by the pure support, *i.e.* $2.00 \mu mol$ (STP) g^{-1} .

higher loadings. This behaviour is attributed to the formation of a monolayer coverage of V_2O_5 on the surface of the ZrO_2 .

Evidence for this observation is provided by X-ray powder diffraction patterns of these samples, wherein the most intense XRD line due to the (001) plane was observed only at higher vanadium content (10.38% w/w). The absence of XRD lines due to V_2O_5 at lower contents indicates that the vanadium oxide is present in a highly dispersed or amorphous state. This observation is also evidenced from the surface coverage results (Table 1) derived from oxygen chemisorption capacities of these catalysts, wherein the surface coverage is found to be highest for the monolayer composition (6.53% w/w V_2O_5). Other information, including surface coverage, active site density and equivalent vanadia area, also shows trends similar to oxygen chemisorption with regard to vanadia loadings (Table 1). The surface coverage results suggest that $\sim 66\%$ of the ZrO_2 surface is covered by the active component. The surface coverage of V_2O_5 on ZrO_2 is higher compared to V_2O_5 supported on $\gamma-Al_2O_3$ [13] and SiO_2 [14]. It is generally believed that oxygen chemisorbs selectively at low temperature ($-78^\circ C$) on coordinatively unsaturated sites (CUS) generated upon reduction, having a particular coordination environment. These sites are located on a highly dispersed vanadia phase, which is formed only at low vanadia loading and remains as a 'patchy monolayer' on the support surface.

The percentage conversion of methanol to formaldehyde is plotted as a function of oxygen uptake by various catalysts in Fig. 2. The results clearly demonstrate that the percentage conversion of methanol to formaldehyde is directly proportional to the amount of oxygen chemisorbed at $-78^\circ C$ by the pre-reduced catalysts. The linear correlation suggests that the catalytic

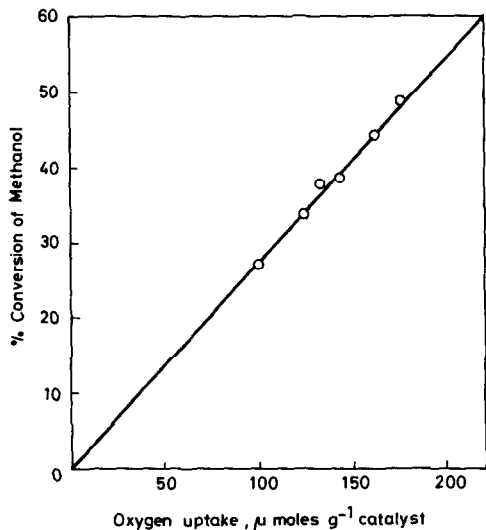


Fig. 2. Percentage conversion of methanol to formaldehyde as a function of oxygen uptake.

functionality of the dispersed vanadia phase on ZrO_2 responsible for the selective oxidation of methanol to formaldehyde is located on the 'patchy monolayer' phase, and this functionality can be titrated by the LTOC method.

Thus vanadium oxide is found to disperse better on ZrO_2 than on Al_2O_3 [13] and SiO_2 [14], and shows higher selectivity towards partial oxidation of methanol.

References

- 1 D. J. Hucknall, *Selective Oxidation of Hydrocarbons*, Academic Press, London, 1974.
- 2 G. C. Bond, A. J. Sarkany and G. D. Parfitt, *J. Catal.*, **57** (1979) 476.
- 3 A. Andersson and S. T. Lundin, *J. Catal.*, **58** (1979) 383.
- 4 F. Roozeboom, P. D. Cordingley and P. J. Gellings, *J. Catal.*, **68** (1981) 464.
- 5 A. J. Van Hengstum, J. G. Van Omman, H. Bosch and P. J. Gellings, *Proc. 8th Int. Congr. Catal.*, Berlin, 1984, IV-297.
- 6 N. K. Nag, *J. Catal.*, **92** (1985) 432.
- 7 G. Bergeret, P. Gallezot, K. V. R. Chary, B. Rama Rao and V. S. Subrahmanyam, *Appl. Catal.*, **40** (1988) 191.
- 8 B. M. Reddy, K. V. R. Chary, B. Rama Rao, C. S. Sunandana, V. S. Subrahmanyam and N. K. Nag, *Polyhedron*, **5** (1986) 191.
- 9 T. Ono, H. Miyata and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. 1*, **83** (1987) 1761.
- 10 Y. Nakano, T. Iizuka, H. Hattori and K. Tanabe, *J. Catal.*, **59** (1979) 1.
- 11 N. K. Nag, *J. Phys. Chem.*, **91** (1987) 2324.
- 12 F. E. Massoth, G. Muralidhar and J. Shabtai, *J. Catal.*, **85** (1984) 53.
- 13 N. K. Nag, K. V. R. Chary, B. M. Reddy, B. Rama Rao and V. S. Subrahmanyam, *Appl. Catal.*, **9** (1984) 225.
- 14 N. K. Nag, K. V. R. Chary, B. Rama Rao and V. S. Subrahmanyam, *Appl. Catal.*, **31** (1987) 73.
- 15 K. V. R. Chary, *J. Chem. Soc., Chem. Commun.*, (1989) 104.

- 16 N. K. Nag, K. V. R. Chary and V. S. Subrahmanyam, *J. Chem. Soc., Chem. Commun.*, (1986) 1147.
- 17 B. S. Parekh and S. W. Weller, *J. Catal.*, 47 (1977) 100.
- 18 W. Zmierczak, G. Muralidhar and F. E. Massoth, *J. Catal.*, 77 (1982) 432.
- 19 B. M. Reddy, K. V. R. Chary, V. S. Subrahmanyam and N. K. Nag, *J. Chem. Soc., Faraday Trans. 1*, 81 (1985) 1655.
- 20 K. V. R. Chary, *J. Chem. Soc., Chem. Commun.*, (1989) 1057.
- 21 K. V. R. Chary, V. Vijayakumar and S. K. Masthan, *J. Chem. Soc., Chem. Commun.*, (1989) 1339.
- 22 K. S. P. Rao, K. V. R. Chary, B. Rama Rao, V. S. Subrahmanyam and N. K. Nag, *Appl. Catal.*, 41 (1988) 165.
- 23 K. S. P. Rao, S. K. Masthan, G. Muralidhar, K. V. R. Chary and V. S. Subrahmanyam, *J. Chem. Soc., Chem. Commun.*, (1988) 375.