## Low Temperature Oxygen Chemisorption as a Diagnostic Tool for Evaluating Supported Vanadium Oxide Catalysts for the Selective Oxidation of Methanol to Formaldehyde

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Selective chemisorption of oxygen at -78 °C on the reduced surface of vanadium oxides, supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>, has been found, for the first time, to correlate with the selectivity of these catalysts for the oxidation of methanol to formaldehyde.

Low temperature oxygen chemisorption (L.T.O.C.), conducted under certain conditions, on supported molybdenum oxides and sulphides, and vanadium oxides is often used as a surface characterization tool.<sup>1-5</sup> While L.T.O.C. data in many instances have been found to correlate directly with the hydrogenation and hydrodesulphurization activities of Mobased hydroprocessing catalysts,<sup>2,5</sup> similar studies with supported vanadia catalysts have not yet been reported. A systematic investigation on the applicability of L.T.O.C. in studying the surface structure of supported vanadia has only recently been undertaken.<sup>3,4</sup> However, these studies, and others,<sup>6,7</sup> on this type of catalyst have remained confined exclusively to the catalyst characterization aspect; no effort has so far been made to find out whether or not oxygen uptake data have any bearing on the activity-selectivity of the catalysts, although such studies could provide useful means of evaluating and screening the catalysts as regards their selective properties. In order to fill this gap, we report, for the first time, the correlation between the oxygen uptake capacity of five series of supported vanadia catalysts and their selectivity for the oxidation of methanol to formaldehyde.

The details of the experimental procedure have been given elsewhere.<sup>3</sup> The catalysts containing up to ca. 18% by weight of  $V_2O_5$  were prepared by the standard wet-impregnation technique, and the V contents were determined by atomic absorption spectroscopy. Oxygen chemisorption was performed at -78 °C on the catalysts, pre-reduced in a flow (ca. 40 ml per min) of hydrogen at 500 °C for 6 h, in a specially designed cell attached to a static high-vacuum system. A flow microreactor, interfaced by a 6-way gas sampling valve with a gas chromatograph, was used to study the vapour-phase oxidation of methanol at 175 °C under differential conditions of reactor operation and in the absence of any mass transfer effect. The feed gas consisted of 72, 24, and 4% by volume of nitrogen, oxygen, and methanol vapour respectively. The effluent gas stream containing formaldehyde, CO, CO<sub>2</sub>, dimethyl ether, and unchanged methanol was analysed by the gas chromatograph.

The selectivity for formaldehyde is plotted as a function of oxygen uptake by various catalysts in Figure 1, which clearly demonstrates that the selectivity for formaldehyde yield is directly proportional to the amount of oxygen chemisorbed at -78 °C by the pre-reduced catalysts. As reported elsewhere in connection with the same alumina-3 and silica-supported<sup>4</sup> catalysts, oxygen is chemisorbed at low temperatures selectively on co-ordinatively unsaturated sites, generated upon reduction, having a particular co-ordination environment (or symmetry of V). These sites are located on a highly dispersed vanadia phase which is formed only at low vanadia loadings and remains as a 'patchy monolayer' on the support surface. At higher vanadia loadings, a second phase is formed, in addition to the already existing monolayer phase, and this 'post monolayer' phase, upon reduction, does not chemisorb oxygen at low temperatures.



Figure 1. Selectivity for formaldehyde as a function of low-temperature oxygen uptake (corrected for the uptake of the pure supports) for various catalysts: (a)  $V/Al_2O_3$ ; (b)  $V/ZrO_2$ ; (c)  $V/SiO_2$ ; (d)  $V/CeO_2$ ; and (e)  $V/TiO_2$ . Reaction temperature 175 °C; oxygen : alcohol mole ratio = 6.0. % Selectivity is defined as: 100 (no. of moles of formaldehyde formed/h)/(total no. of moles of alcohol reacted/h).

In the perspective of the above background, the correlation shown here indicates strongly that the catalytic functionality of the dispersed vanadia responsible for the selective oxidation of methanol to formaldehyde is located on the 'patchy monolayer' phase, and that this functionality can be titrated by the newly developed L.T.O.C. technique. It is worth noting that the L.T.O.C. experiments were conducted on prereduced catalysts, while the probe reaction was performed with the catalysts which had not been reduced before reaction. Nevertheless the correlation is still valid and significant because the catalysts were reduced upon first contact with the methanol. Indeed, it is well established that a two-step process consisting of sequential reduction and re-oxidation of the catalyst surface operates under steady states of oxidation reactions.<sup>8</sup> So, although the catalysts were not pre-reduced before the oxidation commenced, we had been essentially dealing with partially reduced catalysts. The results given in Figure 1 also show that  $V/TiO_2$  and  $V/ZrO_2$  are the most and  $V/SiO_2$  the least selective catalysts, while  $V/Al_2O_3$  and V/CeO<sub>2</sub> show intermediate selectivity. The vanadia loading capacity at the maximum of the 'monolayer' coverage was different for different supports, indicating a specific support-catalyst interaction as the origin of high dispersion and of the difference in the selectivity among the different series of catalysts.

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