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


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(Received October 9, 1989; revised November 21, 1989)

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 Al₂O₃, SiO₂ and TiO₂. 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, ZrO₂-supported catalysts were found to exhibit better catalytic properties than the catalysts supported on other oxides [8, 9]. In particular, ZrO₂ 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 vanadía [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 vanadía catalysts supported on zirconia.

*IICT Communication No. 2415.
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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 V₂O₅ catalysts with V₂O₅ loadings of ca. 1.83 - 10.38 wt.% supported on ZrO₂ were prepared by impregnating the support material with an aqueous solution containing the requisite amount of NH₄VO₃. 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 ZrO₂ was found to be inactive under the experimental conditions.

Results of oxygen chemisorption capacities of various catalysts are plotted as a function of V₂O₅ 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 m² ml⁻¹ (which is the ratio of BET surface area of the reduced unsupported V₂O₅ to the volume of oxygen chemisorbed on it) [12]. Figure 1 shows that oxygen chemisorption capacities increase with increasing V₂O₅ content up to 6.53% w/w of V₂O₅ on ZrO₂ and decrease at
TABLE 1
Results of oxygen chemisorption for V₂O₅/ZrO₂ catalysts

<table>
<thead>
<tr>
<th>Catalyst composition: wt.% of V₂O₅ on ZrO₂</th>
<th>BET surface areaa (m² g⁻¹)</th>
<th>Active site densityb (nm⁻²)</th>
<th>Surface coveragec</th>
<th>Equivalent vanadia (FVA) (µmol at STP g⁻¹)</th>
<th>Amount of O₂ chemisorbedd (µmol at STP g⁻¹)</th>
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</thead>
<tbody>
<tr>
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<td>2.18</td>
<td>53.65</td>
<td>39.23</td>
<td>133</td>
</tr>
</tbody>
</table>

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 100X (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 µmol (STP) g⁻¹.

higher loadings. This behaviour is attributed to the formation of a monolayer coverage of V₂O₅ on the surface of the ZrO₂.

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 V₂O₅ 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 V₂O₅). 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 ~66% of the ZrO₂ surface is covered by the active component. The surface coverage of V₂O₅ on ZrO₂ is higher compared to V₂O₅ supported on γ-Al₂O₃ [13] and SiO₂ [14]. It is generally believed that oxygen chemisorbs selectively at low temperature (−78 °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 °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$_2$O$_3$ [13] and SiO$_2$ [14], and shows higher selectivity towards partial oxidation of methanol.

References