Characterization of supported vanadium oxide catalysts by a low-temperature oxygen chemisorption technique

III. The V_2O_5/ZrO_2 system[a]

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Abstract

Low-temperature oxygen chemisorption (LTOC) has been applied to characterize a series of V_2O_5/ZrO_2 catalysts containing up to 10.38% of V_2O_5. The catalysts were also characterized by X-ray diffraction (XRD), and electron spin resonance (ESR). Oxygen chemisorption results suggest the formation of a monolayer of vanadium oxide at a concentration of about 6.53 wt.-% with a high degree of dispersion of vanadia on ZrO_2. X-ray diffraction studies revealed that the phase transition of ZrO_2 (monoclinic to tetragonal) is catalyzed by the presence of vanadia on the support. The ESR results have also shown that the chemical species on the surface and their structure are more affected by the vanadia loading. Oxygen chemisorption capacities of the catalysts were found to correlate with the activities of the catalysts for the partial oxidation of methanol to formaldehyde. A comparison of LTOC results of vanadia supported on zirconia with those of vanadia supported on alumina, silica and titania suggests that the vanadium oxide disperses better on zirconia.

Keywords: catalyst characterization (ESR, LTOC, XRD), dispersion, methanol oxidation, vanadium oxide, vanadium pentoxide–zirconium oxide.

INTRODUCTION

Supported vanadium oxide catalysts find a wide array of applications in partial oxidation and ammoxidation of many important industrial processes [1–3]. The catalysts are usually promoted or supported on high surface area materials to increase their stability, life time and activity. The most commonly used supports are Al_2O_3, TiO_2, and SiO_2. Supports are often found to modify the physicochemical properties of vanadia catalysts. The supported oxides do not form three dimensional crystal phases, but rather a patchy or continuous "monolayer" covering the support [4,5]. Recently, zirconia supported catalysts were found to exhibit better catalytic properties than the catalysts sup-

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ported on other oxides [6–14]. In particular, ZrO_2 itself is known to catalyze dehydration, hydrogenation and isomerization reactions [15].

The efficiency of any supported catalyst depends on the dispersion of the active component on the surface of the support material. This dispersion is often controlled, among other factors, by the extent of active phase loading and the nature of the supported oxide. It is, therefore, highly desirable to investigate the effect of supports on the structure of the supported vanadium oxide catalysts.

Many aspects of vanadia catalysts like methods of preparation, kinetics and mechanism of the reactions, the effect of supports, the influence of promoters and the role of the $V = O$ bond were extensively investigated. Several sophisticated techniques including ESR [16–23], ^{51}V solid state NMR [24–27], electron spectroscopy for chemical analysis (ESCA) [28–32], extended X-ray absorption fine structure (EXAFS) [33–35] and laser Raman spectroscopy [25,30,31,36,37] have been recently employed to characterize these catalysts in order to understand the relation between catalytic activity and structural aspects.

In recent years the low-temperature oxygen chemisorption (LTOC) method has been used quite successfully to obtain quantitative information on the dispersion of the active component in partially reduced metal oxide catalysts [38–56]. This method offers a means of determining the "active" surface area of supported oxide and sulfide phases. In particular, the LTOC method has been used to determine the dispersion of molybdena [38–47], tungsten sulfide [48–50] and vanadia [29,51–55] catalysts employed in hydroprocessing and oxidation reactions, respectively. It has been demonstrated that under certain conditions, oxygen chemisorption capacities of these catalysts can be directly correlated with the hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) activities. We have characterized vanadia catalysts by LTOC and ESR techniques on various supports such as Al_2O_3 [51], SiO_2 [52] and TiO_2 [53]. The LTOC results were correlated with the catalytic activity of methanol oxidation [54]. The present study deals with the LTOC results of vanadium oxide supported on ZrO_2. The catalysts were also characterized by ESR and X-ray diffraction (XRD) for getting information on the structural aspects of the catalysts for relating it to their catalytic activity towards methanol oxidation to formaldehyde. A comparison of these results were made with the oxygen chemisorption results of vanadium oxide catalysts supported on Al_2O_3, SiO_2, and TiO_2.

EXPERIMENTAL

Zirconia support was prepared by ammonical hydrolysis of zirconium oxychloride (Fluka) at pH 9. The resulting hydroxide was calcined in air at 500°C for 4 h. The V_2O_5/ZrO_2 catalysts were prepared by impregnation of the ZrO_2

support with an aqueous solution containing ammonium metavanadate, followed by drying at $110°C$ and calcining in air at $500°C$ for 4 h. The vanadia loading varied between 1.83–10.38 wt.-% and the vanadium content in the catalysts was determined by atomic absorption spectrometry analysis. X-ray diffraction patterns were obtained on a Phillips PW1051 instrument with nickel filtered Cu $K\alpha$ radiation. ESR measurements were carried out at room temperature on a JEOL FE 3X X-band spectrometer. The sample preparation of the reduced catalysts were reported elsewhere [16].

Oxygen chemisorption experiments were performed with a static high vacuum system (capable of attaining 10^{-6} Torr) connected to a specially designed cell that permitted in situ reduction of the catalysts prior to oxygen chemisorption and subsequent ESR experiments. In a typical experiment, about 0.5 g catalyst was reduced at $500°C$ for 6 h in a flow of hydrogen (40 ml min^{-1}, and pretreated by palladium "deoxo" and a 4A zeolite molecular sieve) and oxygen chemisorption was performed on the reduced sample at $-78°C$. The amount of chemisorbed oxygen was determined by the double isotherm method standardized by Parekh and Weller [38]. The same system was used to determine the BET surface area of the catalysts by nitrogen adsorption at $-196°C$. The details of the experimental procedure are reported elsewhere [51]. A fixed-bed flow microreactor operating at atmospheric pressure and interfaced to a gas chromatograph was used for the vapour phase methanol oxidation reaction at $175°C$. In a typical experiment about 0.25 g catalyst sample was placed in a glass reactor (1.2 cm I.D. and 30 cm long) and plugged between quartz wool at both ends. In order to minimize the adverse thermal effects, the catalyst was diluted to twice its volume with quartz grains of similar particle size. The reactor was continuously fed with methanol vapour generated by passing a nitrogen–oxygen mixture through two saturators kept in series. The feed gas consisted of approximately 72 vol.-% nitrogen and 24 vol.-% oxygen and 4 vol.-% methanol vapour. The main reaction product i.e., formaldehyde, was analyzed by the gas chromatograph, using a column containing 10% carbowax 20M on a chromosorb support. Traces of dimethyl ether were found only at higher vanadia loadings. Pure ZrO_2 was found to be inactive under the experimental conditions.

RESULTS AND DISCUSSION

ZrO_2 exists in three crystallographic polymorphs viz., monoclinic, tetragonal and cubic. The X-ray diffraction patterns of ZrO_2 and some of the V_2O_5/ZrO_2 catalysts are presented in Fig. 1. It can be seen from Fig. 1a that the pure ZrO_2 exists in monoclinic and tetragonal phases as shown by the intense sharp lines at $d_{11\bar{1}} = 3.16$ Å and $d_{111} = 2.834$ Å (due to the monoclinic phase) and $d_{111} = 2.949$ Å (due to the tetragonal phase). The addition of 1.83% V_2O_5 (Fig. 1b) brings a dramatic reversal of the intensities corresponding to the monoclinic and te-

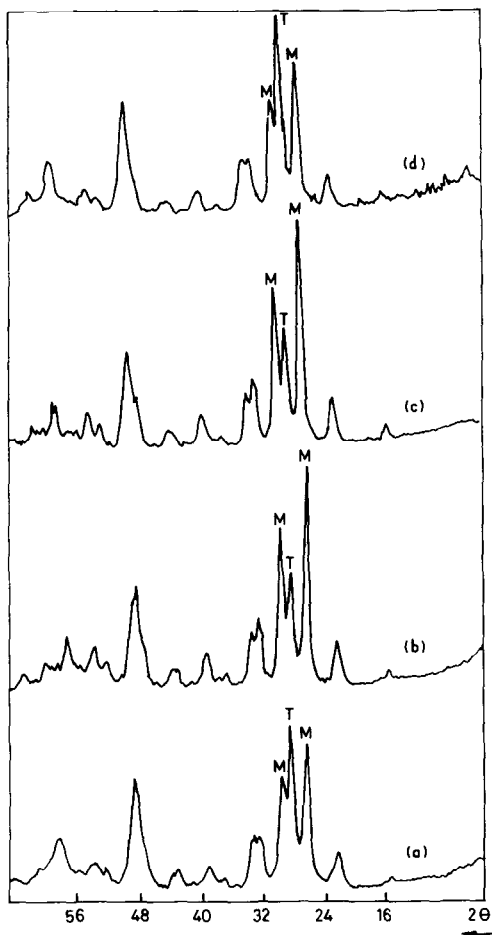Fig. 1. X-ray diffractograms of V_2O_5/ZrO_2 catalysts. M = monoclinic; T = tetragonal. (a) ZrO_2; (b) 1.83% V_2O_5; (c) 8.59% V_2O_5; and (d) 10.38% V_2O_5.

tragonal reflections. From Fig. 1b it can be seen that the monoclinic phase is predominant in 1.83% V_2O_5/ZrO_2. A further increase in loading up to 8.59% V_2O_5 causes a steady decrease of the monoclinic phase as seen by the decrease in the intensities of the line at $d_{11\bar{1}} = 3.16$ Å. This observation is in agreement with a decrease of surface area of the catalysts with an increase of vanadia content. However, at 10.38% (Fig. 1d) the tetragonal phase is found to predominate. No XRD lines due to V_2O_5 or a compound formed between V_2O_5 and ZrO_2 are observed, even up to the maximum concentration used in this study. The absence of XRD lines due to V_2O_5 even at the highest concentration of this study indicates that the vanadium oxide is present in a highly dispersed amorphous state on the ZrO_2 surface. As reported by Reijnten [57] the tetrag-

onal to monoclinic phase transformation of zirconia was observed by sintering the catalyst at higher temperatures. Normally, the tetragonal structure appears at temperatures above $1200\,^\circ$C. Below $1000\,^\circ$C the monoclinic structure is quite stable. However a temperature of only $500\,^\circ$C employed in the present investigation is enough to cause the phase transition of ZrO_2. In our earlier studies [58], we observed that the V_2O_5 catalyzes the anatase–rutile phase transition of TiO_2. Similarly also in the present case V_2O_5 seems to cause the lowering of the ZrO_2 phase transformation temperature. However, the mechanism of phase transformation is not clear at this stage. The ESR spectra of unreduced and reduced V_2O_5/ZrO_2 catalysts were obtained at $25\,^\circ$C and are reported in Figs. 2 and 3, respectively. It is noted that unlike the case of the previously reported V_2O_5/Al_2O_3 catalysts [16] well-resolved spectra with hyperfine splitting (hfs) due to ^{51}V ($I=7/2$) of the unreduced samples could be recorded at a temperature as high as room temperature ($25\,^\circ$C). In contrast to these findings, V_2O_5/Al_2O_3 catalysts were found to show ESR with well-resolved hfs at $-164\,^\circ$C [16]. This difference in temperature is due to the par-
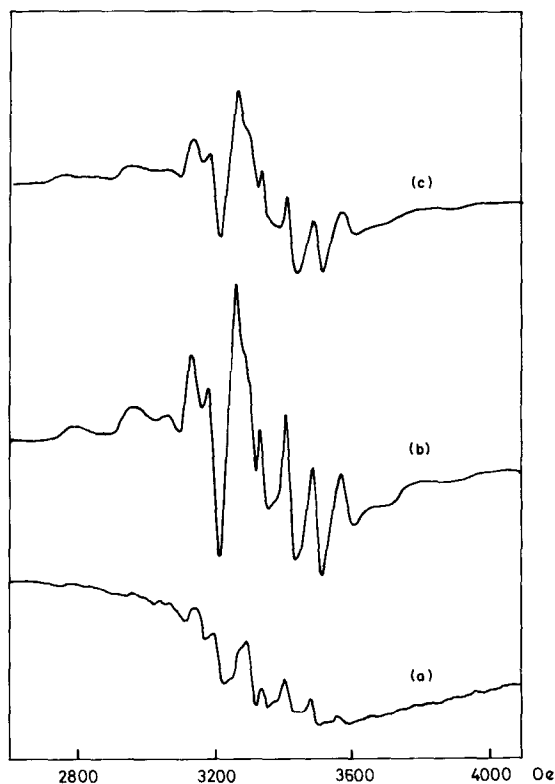

Fig. 2. ESR spectra of unreduced V_2O_5/ZrO_2 catalysts at $25\,^\circ$C. (a) 1.83% V_2O_5; (b) 6.53% V_2O_5; and (c) 8.59% V_2O_5.
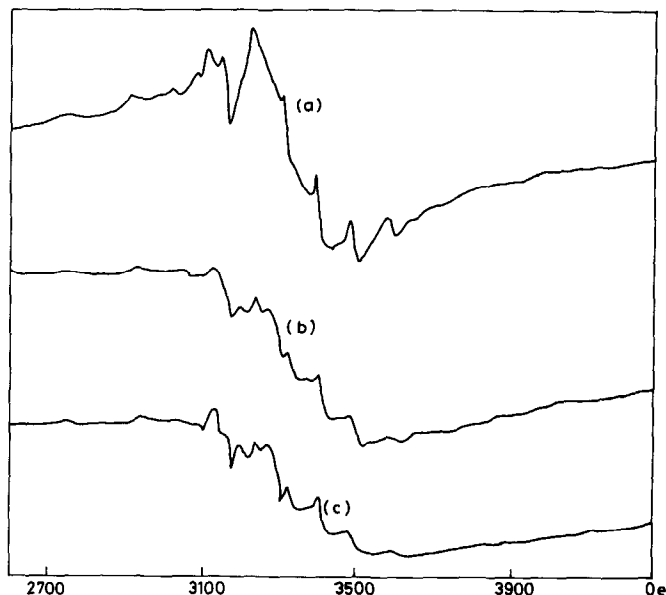
Fig. 3. ESR spectra of reduced V_2O_5/ZrO_2 catalysts at $25\,^\circ$C. (a) 1.83% V_2O_5; (b) 6.53% V_2O_5; and (c) 8.59% V_2O_5.

amagnetic ions with tetrahedral symmetry having very closely spaced ground and excited states. The spectra of these ions could be obtained only at low temperatures and not at $25\,^\circ$C. In this study the spectrum obtained at $25\,^\circ$C is due to the V^{4+} centres present in a distorted tetrahedral symmetry. This distortion might have been caused by the interaction of vanadium with surface oxygen atoms of ZrO_2. As can be seen from Figs. 2 and 3, the spectra of unreduced catalysts are better resolved than the corresponding reduced ones. The intensity of the hyperfine lines increased with V_2O_5 loading up to 6.53% (Fig. 2b) and decreases at higher vanadia contents. The ESR parameters of the catalysts in unreduced and reduced conditions were obtained in the same way as reported in our earlier ESR communication dealing with V_2O_5/Al_2O_3 catalysts [16] and the parameters are listed in Tables 1 and 2. The observed ESR features are due to V^{4+} ions in axially symmetric surroundings. It can be seen from Table 1 consisting of ESR parameters of the unreduced catalysts that the $g_\parallel$ and $g_\perp$ values are nearly constant but the $A_\parallel$ values increase with V_2O_5 loading. This observation indicates that the bond between V_2O_5 and ZrO_2 is heavily perturbed by V_2O_5 loading, assuming that at least some of the oxygen neighbours of V^{4+} belong to ZrO_2.

The spectra of the reduced catalysts are shown in Fig. 3. The ESR parameters are listed in Table 2. During reduction of the catalysts, no change of hfs is observed. However, the intensity of the spectra decreases considerably as van-

TABLE 1

Spin Hamiltonian parameters of V^{4+} in unreduced V_2O_5/ZrO_2 catalysts

Catalyst composition (wt.-% of V_2O_5 on ZrO_2)	$g_{\parallel}$	$g_{\mid}$	$\lvert g \rvert$	$A_{\parallel}, (G)$	$A_{\mid}, (G)$	$\lvert A \rvert, G$
1.83	1.930	2.0050	1.980	188.57	76.43	113.81
3.38	1.935	2.0024	1.980	187.85	77.14	114.04
5.34	1.932	2.0054	1.980	191.43	78.86	116.38
6.53	1.931	2.0039	1.980	191.43	79.29	116.67
8.59	1.935	2.0050	1.981	190.00	82.14	118.09
10.38	1.932	2.0080	1.982	193.57	84.28	120.71

TABLE 2

Spin Hamiltonian parameters of V^{4+} in reduced V_2O_5/ZrO_2 catalysts

Catalyst composition (wt.-% of V_2O_5 on ZrO_2)	$g_{\parallel}$	$g_{\mid}$	$\lvert g \rvert$	$A_{\parallel}, (G)$	$A_{\mid}, (G)$	$\lvert A \rvert, G$
1.83	1.935	1.997	1.976	195.71	80.71	119.04
3.38	1.933	2.001	1.978	195.71	80.71	119.04
5.34	1.931	2.007	1.982	198.57	85.00	122.85
6.53	1.932	2.006	1.981	194.28	85.71	121.90
8.59	1.960	2.002	1.988	174.28	70.00	104.76
10.38	1.931	1.996	1.974	191.42	62.85	105.70

adia loading increases in the catalysts. A comparison of Figs. 2 and 3 shows that the hyperfine structures of the ESR spectra tends to broaden in the reduced state. It is interesting to note from Table 2 that $A_{\mid}$ values of the catalysts increase with increasing vanadia loading, reaching a maximum at 6.53% and decrease at higher V_2O_5 loadings. The well-resolved ESR spectra of the unreduced catalyst and a maximum value of $A_{\mid}$ of the reduced catalyst at 6.53% V_2O_5 suggests that vanadium oxide is well dispersed on ZrO_2 at this composition. This observation is supported by the oxygen chemisorption results of the LTOC method.

The oxygen chemisorption capacity results of various catalysts are presented in Table 3. Pure ZrO_2 was also reduced under identical conditions and oxygen was adsorbed on it. The amount of oxygen chemisorbed on pure ZrO_2 is found to be negligible. It can be seen from Table 3 that oxygen uptake values increase with V_2O_5 loading up to 6.53% and decrease thereafter at higher loadings of V_2O_5. This observation is attributed to the formation of a "monolayer" of vanadia on the surface of ZrO_2, and this is further supported by our ESR results described earlier in this study, wherein, a well-resolved spectrum is obtained at this composition. The decrease in oxygen uptake capacity beyond

TABLE 3

Results of oxygen chemisorption for V_2O_5/ZrO_2 catalysts

Catalyst composition (wt.-% of V_2O_5 on ZrO_2)	BET surface area[α] ($m^2 g^{-1}$)	Active site density[β] (nm^{-2})	Surface coverage[γ]	Equivalent vanadia area (EVA) ($m^2 g^{-1}$)	Amount of O_2[δ] chemisorbed (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

[α]Based on unit weight of the catalyst.

[β]This is equal to the number of oxygen atoms chemisorbed per unit area of the reduced catalysts.

[γ]Defined as $100\times$ (equivalent vanadia area/BET surface area of the reduced catalyst).

[δ]Values obtained after deducting from the volume of oxygen chemisorbed by the pure support, i.e., $2 \mu mol$ (STP) g^{-1}.

monolayer composition (6.53% V_2O_5), is due to the formation of a different surface vanadia species and this phase, upon reduction, does not appreciably chemisorb oxygen. During reduction, coordinatively unsaturated sites (CUS) of vanadia are generated and are capable of chemisorption of oxygen at $-78\,^{\circ}C$ in the monolayer region. Interestingly, these findings are in agreement with the LTOC results of vanadium oxide supported on γ-Al_2O_3 [51], SiO_2 [52] and TiO_2 [53]. The other information derived from the oxygen chemisorption capacities such as equivalent vanadia areas (EVA), surface coverage and the active site density for various V_2O_5/ZrO_2 catalysts are presented in Table 3. The equivalent vanadia areas (EVA) of all the supported catalysts have been calculated by multiplying oxygen chemisorption capacities of the catalysts with the factor 13.2 m^2 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) [51]. The surface coverage values for all the supported catalysts reported in Table 3 are the percentage of the ratio of equivalent vanadia area to the BET surface area of the reduced catalysts. The results of surface coverage, active site density and equivalent vanadia area for all the supported catalysts have also shown similar trends as the LTOC with regard to vanadia loading on ZrO_2. A comparison of the active site density results of the present work with vanadia supported on Al_2O_3 [51], SiO_2 [52] and TiO_2 [53] also suggests that vanadium oxide is dispersed better on ZrO_2. The surface coverage results of vanadia supported on various oxides such as γ-Al_2O_3, SiO_2, TiO_2 (anatase) and ZrO_2 are represented in Fig. 4. The surface coverage values calculated from oxygen chemisorption capacities of various catalysts decreases in the order of V_2O_5/ZrO_2, V_2O_5/TiO_2 (anatase), V_2O_5/Al_2O_3, and V_2O_5/SiO_2. The results of Fig. 4 suggest that vanadium oxide disperses better on zirconia than the other support oxides and about 66% of the ZrO_2 surface is covered by the active oxygen chemisorption sites. The results also indicate that the interaction between active phase and support is higher in ZrO_2 and lower in SiO_2. Similar conclusions were drawn by the recent work of Niwa et al. [14].

The nature of the surface state of vanadia supported on silica and alumina has been investigated by various workers [16–33,51,52]. These studies reveal that the state of the supported vanadia phase and the distribution of the vanadium oxide species strongly depend on the nature of the support and the extent of vanadia loading. At low vanadia loadings V_2O_5 is highly dispersed on the support [51]. However, at higher loadings, formation of bulky three-dimensional V_2O_5 crystallites are reported [51]. Our present ESR results provide further information about the nature of the monolayer phase of vanadia and the oxygen chemisorption sites. Several important points can be noted from Figs. 2 and 3. First, unlike the case of the V_2O_5/Al_2O_3 system [16] the hyperfine splitting (hfs) pattern due to ^{51}V ($I=7/2$) is observable only at high temperatures, i.e., $25\,^{\circ}C$ for both the unreduced and reduced samples indicating that the vanadium oxide remains stabilized on the zirconia surface as V^{4+}
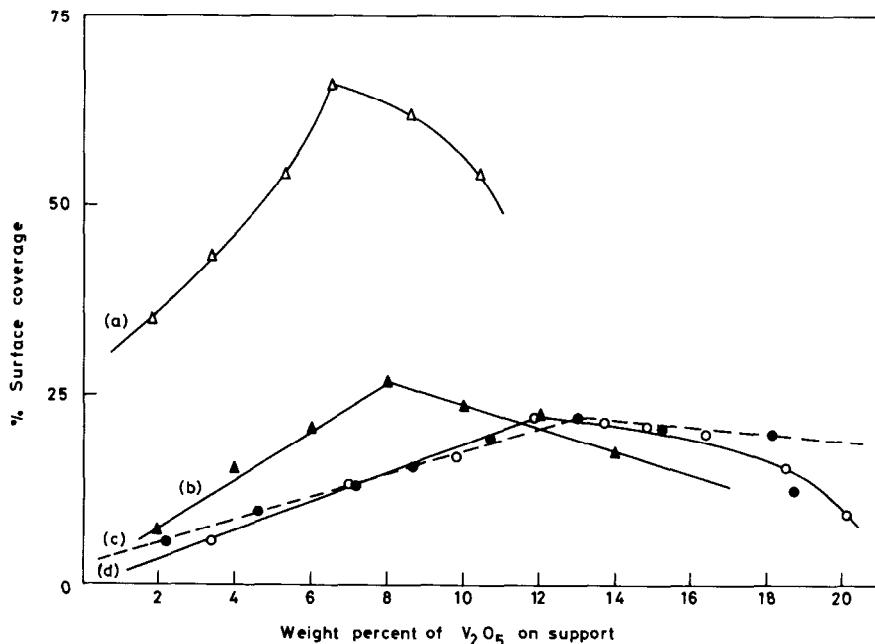
Fig. 4. Percent surface coverage of vanadia supported on various oxides as a function of vanadia loading. (a) $\triangle = V_2O_5/ZrO_2$; (b) $\blacktriangle = V_2O_5/TiO_2$ (anatase); (c) $\bullet = V_2O_5/SiO_2$; and (d) $\bigcirc = V_2O_5/\gamma\text{-}Al_2O_3$.

in both oxidized and reduced conditions. Second, the hfs pattern and the axially symmetrical ESR parameters (given in Tables 1 and 2) are characteristic of V^{4+} species in tetrahedral symmetry [21,22]. However, because the paramagnetic ions (d^1 species in the present case) are in tetrahedral symmetry and have very closely spaced ground and excited energy states, the spectra of these ions can be only obtained at very low temperatures and not at 25°C, as observed here, unless the energy gap between the ground and the excited states is increased by the influence of some distorting ligand fields. Since in the present study the ESR spectra are obtained at 25°C, it is concluded that the V^{4+} centers are in distorted tetrahedral symmetry. This distortion may have stemmed from the interaction of vanadium with the surface oxygen atoms of ZrO_2. In contrast V_2O_5/Al_2O_3 catalysts showed ESR with well-resolved hfs characteristics of vanadium centers in square pyramidal surroundings and the ESR signals could be obtained only at temperatures as low as −164°C [16]. Third, the ESR spectra of the unreduced V_2O_5/ZrO_2 catalysts are more resolved (Fig. 2) than the reduced V_2O_5/ZrO_2 catalysts (Fig. 3) and show a slightly higher intensity as compared with those of the reduced ones. The intensity of the ESR spectra for the unreduced catalysts [Fig. 2] is found to increase as a function of V_2O_5 loading until the monolayer composition (6.53% V_2O_5) is reached and then the hfs tends to diffuse in the post monolayer region.

The percentage conversion of methanol during partial oxidation at 175 °C is plotted as a function of oxygen uptake by various catalysts in Fig. 5, which clearly demonstrates that the percentage conversion of methanol is directly proportional to the amount of oxygen chemisorbed at −78 °C by the prereduced catalysts. The main reaction product i.e., formaldehyde was found at the lower vanadia loadings. Traces of dimethyl ether was found at higher vanadia loadings. In the case of V_2O_5/γ-Al_2O_3 and V_2O_5/SiO_2 [54] catalysts dimethyl ether (due to the dehydration of methanol) and formaldehyde (due to partial oxidation) were obtained under the similar experiment conditions. However, V_2O_5/TiO_2 (anatase) catalysts have shown selective oxidation of methanol to formaldehyde [53]. As reported in our earlier studies [51,52] in connection with V_2O_5/Al_2O_3 and V_2O_5/SiO_2 catalysts, oxygen chemisorbed at low temperatures selectively on coordinatively unsaturated sites (CUS) generated upon reduction and having a particular coordination environment. 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 [51,52]. 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 significantly at low temperatures. In the perspective of the above background, the linear correlation in Fig. 5 between the oxygen chemisorption capacity of the catalysts and the percentage conversion of methanol strongly indicates that the catalytic functionality of the dispersed vanadia phase is responsible for the selective oxidation of methanol to
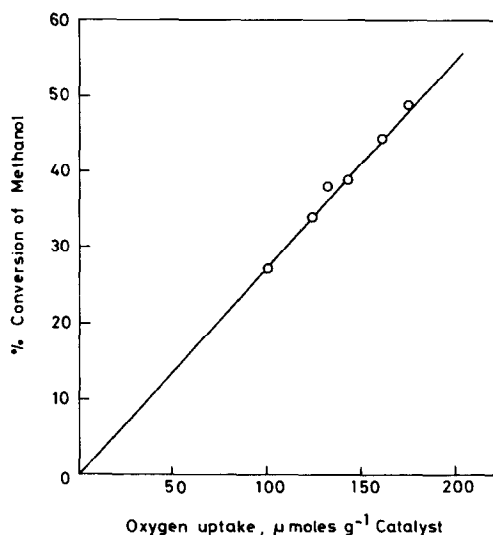

Fig. 5. Conversion of methanol as a function of low-temperature oxygen uptake (corrected for the uptake of pure ZrO_2) for various V_2O_5/ZrO_2 catalysts.

formaldehyde and is located on the "patchy monolayer" phase and that this functionality can be titrated by the LTOC method. It is generally agreed that the mechanism of partial oxidation of methanol involves the dissociative adsorption of methanol to form a surface bound methoxyl group and the subsequent cleavage of a C–H bond of the methyl group [59,60]. It is firmly established that the latter step is the rate determining step.

In conclusion, the present results of LTOC in conjunction with other techniques like ESR and XRD indicate that it can be applied as an useful method for the characterisation of supported vanadia catalysts. The LTOC results are found to provide information about the dispersion and active surface area of the supported vanadia phase. The results also provide valuable information about the effect of supports on the dispersion and these supports considerably modify the dispersion of vanadium oxide. Thus vanadium oxide is found to disperse better on ZrO_2 than on Al_2O_3, SiO_2 and TiO_2 and shows a higher selectivity towards partial oxidation of methanol to formaldehyde.

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