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Oxygen Chemisorption on Titania–Zirconia Mixed Oxide Supported Vanadium Oxide Catalysts

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A series of titania–zirconia mixed oxide supported vanadium oxide catalysts with various V_2O_5 loadings ranging from 2 to 16 wt % have been prepared and characterized by means of oxygen chemisorption, X-ray diffraction, and infrared spectroscopic methods. Oxygen uptakes were measured volumetrically at 195 K with a prereduction of the sample at 773 K and at 640 K with prereduction at the same 640 K temperature. Activity and selectivity of the catalysts for partial oxidation of methanol to formaldehyde were studied at normal atmospheric pressure. XRD and IR results suggest that vanadium oxide exists in a highly dispersed state below 12 wt % V_2O_5 loading and in microcrystalline phase above this loading level. Oxygen uptakes obtained either at 195 K or at 640 K support these observations. Oxygen uptake measured at 640 K with a prereduction of the sample at the same temperature appears to yield reasonably better numerical values of dispersion and oxygen atom site densities. Partial oxidation of methanol to formaldehyde appears to be not very sensitive to the nature of the vanadium oxide phase on TiO_2–ZrO_2 support.

Introduction

Supported vanadium oxide catalysts are well known for catalyzing a great variety of oxidation and ammoxidation reactions including selective catalytic reduction of nitrogen oxides.[1-7] Generally, bulk V_2O_5 cannot be used as catalyst because of its poor thermal stability and mechanical strength. Therefore, vanadia is normally supported on different carriers depending on the nature of reaction to be catalyzed. Titania, in the form of anatase, is considered to be the most successful support for the selective oxidation of *o*-xylene to phthalic anhydride[2,3] as well as for NO reduction with NH_3.[5-7] Similarly, zirconia-supported vanadia is reported to be very active for partial oxidation of methanol to formaldehyde.[8] The beneficial functions of each individual support can be explored fully by using them in combination, which constitute yet another important class of solid supports whose characteristics are not yet studied thoroughly.

High dispersion of the active component on the surface of a support is a necessary condition for an effective supported catalyst.[2a] This dispersion is often controlled, among other factors, by the extent of loading and the nature of the support material. To study the dispersion of vanadium oxide on various supports Nag et al.[9,10] and Reddy et al.[11-13] reported an oxygen chemisorption method, similar to the one reported by Parekh and Weller,[14] for supported molybdena catalysts. In this method, the

supported vanadia catalyst was reduced first at 773 K in a flow of hydrogen and then O_2 was chemisorbed at 195 K to measure the number of oxygen anion vacancies. This technique was frequently referred as low temperature oxygen chemisorption (LTOC). However, Oyama et al.[15] very recently reported that oxygen chemisorption is very sensitive to the temperature used for sample reduction and oxygen adsorption. They further proposed that sample reduction at 640 K and oxygen chemisorption at the same temperature would yield more accurate measurements of the dispersion of vanadia on silica support. In order to understand the significance of both the methods, a systematic study has been initiated by using TiO_2–ZrO_2 mixed oxide as the support material and V_2O_5 as the active component. In this investigation a series of TiO_2–ZrO_2 mixed oxide supported vanadia catalysts with various V_2O_5 loading ranging from 2 to 16 wt % were prepared and were characterized by means of oxygen chemisorption at both 195 K, with a prereduction of the sample at 773 K, and at 640 K, with prereduction of the catalyst at the same 640 K temperature and referred to as high temperature oxygen chemisorption (HTOC). These catalysts were further characterized by means of X-ray diffraction and infrared spectroscopic methods. The catalytic properties of these catalysts were also evaluated for the selective oxidation of methanol to formaldehyde, a structure sensitive reaction.[16]

Experimental Section

Catalyst Preparation. The TiO_2–ZrO_2 mixed oxide (1:1 molar ratio) support was prepared by a coprecipitation method using urea as hydrolyzing agent.[17] The requisite quantities of $TiCl_4$ (Fluka, AR grade), $ZrOCl_2$ (Fluka, AR grade) and urea (Loba-Chemie, GR grade) in aqueous solutions were heated together to 368 K with vigorous stirring. Precipitation was complete after 3 to 4 h of heating, by which time the pH of the

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solution was approximately 7. The precipitate obtained was then filtered off, washed several times with deionized water to remove chloride ions, dried overnight at 393 K, and finally calcined at 773 K for 4 h. The resulting TiO_2–ZrO_2 mixed oxide support had a N_2 BET surface area of 160 $m^2 g^{-1}$ and was found to be uniform throughout the bulk.[17]

The TiO_2–ZrO_2 (particle size 0.72 mm) supported vanadia catalysts with various V_2O_5 loadings ranging from 2 to 16 wt % were prepared by the standard wet impregnation method using ammonium metavanadate (Fluka, spectroscopic grade) as the vanadium precursor. The impregnated samples were dried at 393 K for 12 h and calcined at 773 K for 4 h in an open air furnace.

Chemisorption Measurements. A conventional standard volumetric high-vacuum (1×10^{-6} Torr) system, with the facility for reducing the samples *in situ* by flowing purified hydrogen (35 cm^3 min^{-1}), was used for low temperature as well as high temperature oxygen chemisorption measurements. For LTOC measurements, the standard procedure employed was the reduction of the catalyst sample for 4 h at 773 K followed by evacuation for 2 h at the same temperature prior to oxygen chemisorption.[9] Amount of O_2 chemisorbed was determined as the difference between the two successive adsorption isotherms at 195 K. Between the first and second oxygen adsorption isotherms the sample was evacuated for 1 h at 195 K. For HTOC measurements the procedure adopted was the reduction of the catalyst sample at 640 K for 4 h followed by evacuation at the same temperature for 2 h and then followed by oxygen uptake by the same double isotherm method. In between the first and second adsorption isotherms the sample was evacuated for 1 h at 640 K, the chemisorption temperature. After the chemisorption experiment the BET surface area of the catalyst was determined by N_2 physisorption at 77 K by taking 0.162 nm^2 as the area of cross-section of the N_2 molecule.

X-ray Diffraction. X-ray powder diffraction patterns have been recorded on a Philips PW 1051 diffractometer by using Ni-filtered Cu Kα radiation.

Infrared Spectra. IR spectra of various samples were recorded on a Perkin-Elmer 283 B spectrometer at ambient conditions. Self-supporting KBr pellets containing the catalyst samples were used to scan the spectra.

Activity Measurements. A differential flow microreactor operating under normal atmospheric pressure and interfaced to a gas chromatograph by a six-way gas sampling valve was used to determine the activities and selectivities of the catalysts. More details are published elsewhere.[12] For each run, about 0.2 g of catalyst was used and the activities and selectivities were measured at 448–498 K in the absence of any diffusional effects. Feed gas consisting of 72, 24, and 4% by volume of nitrogen, oxygen, and methanol vapor, respectively, was fed at a total flow rate of 120–150 mmol h^{-1}. Major products observed were formaldehyde, dimethyl ether with traces of methyl formate, CO, and CO_2 respectively.

Results and Discussion

The XRD patterns of V_2O_5/TiO_2–ZrO_2 catalysts are shown in Figure 1. The TiO_2–ZrO_2 mixed oxide support calcined at 773 K is in an amorphous state. No XRD lines due to crystalline V_2O_5 phase can be seen up to about 12 wt % vanadia loading which clearly indicates that vanadium oxide is in a highly dispersed state or the crystallites formed are less than 4 nm. From 12 wt % and above loadings, broad diffraction lines due to crystalline V_2O_5 phase can be noted. This result is in perfect agreement with the theoretical monolayer capacity of TiO_2–ZrO_2 support whose specific surface area is 160 $m^2 g^{-1}$. As formulated by Bond et al.[18] the amount of vanadia needed per square meter of the support for monolayer coverage is about 0.07 wt % V_2O_5. Therefore, the monolayer capacity of TiO_2–ZrO_2 mixed oxide support of 160 $m^2 g^{-1}$ surface area is about 11.2 wt %. The present XRD results are thus in perfect agreement with this estimation.
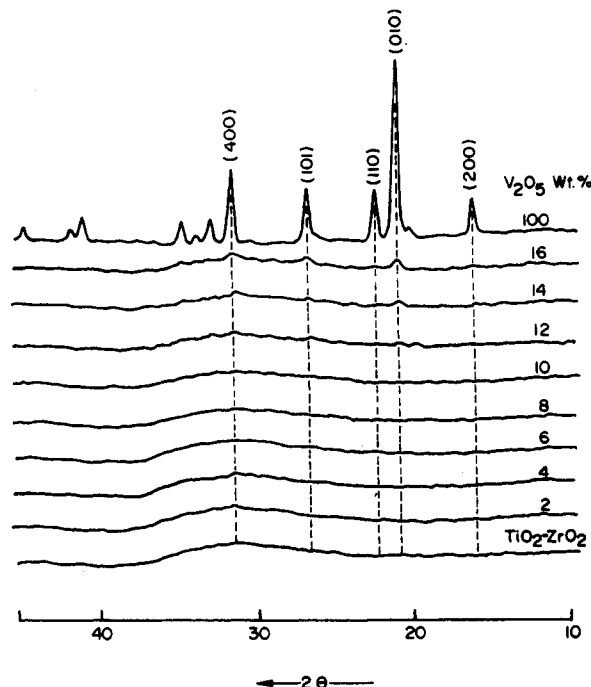

Figure 1. X-ray powder diffraction patterns of V_2O_5/TiO_2–ZrO_2 catalysts.

The IR spectra of V_2O_5/TiO_2–ZrO_2 catalysts of various V_2O_5 loadings obtained at ambient conditions are shown in Figure 2. The spectra of catalysts with V_2O_5 content of 12 wt % and above show two characteristic bands at 1020 and 820 cm^{-1}, respectively. These two bands are characteristic of V_2O_5 corresponding to V=O bond stretching and V—O—V deformation, respectively[9,19]. Thus, vanadia content of up to 12% is stabilized by interaction with the support surface and is present in a form not detectable as bulk V_2O_5. However, different species of vanadium oxide could be traced in the monolayer region. For example, Nakagawa et al.[19c] reported a shift of V=O bond stretching frequency from 1020 (bulk V_2O_5) to 980 cm^{-1} in the IR spectra of vanadium oxide monolayer species supported on titania. According to these authors, the vanadium oxide on the support surface is present as an amorphous V_2O_5 at lower vanadia loadings and amorphous and crystalline V_2O_5 at higher contents. Several studies using IR techniques have also supported these observations.[2a] The IR results of V_2O_5/TiO_2–ZrO_2 catalysts are thus in line with XRD observations. Solid-state ^{51}V NMR spectroscopic study of these catalysts also revealed same information.[20]

Oxygen uptakes at 195 K as well as at 640 K as a function of vanadia loading are shown in Figure 3 and Table I. The TiO_2–ZrO_2 support was also found to chemisorb some small amount of O_2 under the experimental conditions employed in this study. Therefore, the contribution due to pure support alone was subtracted before reporting the results. As can be noted from Figure 3, oxygen uptake increases with increase in vanadia content up to about 12 wt % and then levels off with further loading. This saturation level is the indication of completion of monolayer coverage of vanadium oxide on the support surface.[9–13] An interesting point to mention here is that oxygen uptake trends

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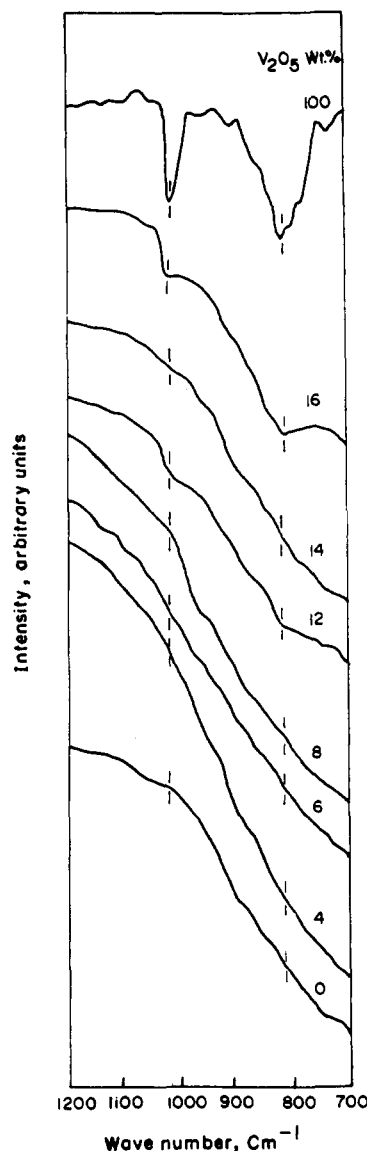
Figure 2. IR spectra of V_2O_5/TiO_2–ZrO_2 catalysts recorded at ambient conditions.

Figure 3. Oxygen uptake as a function of V_2O_5 loading on TiO_2–ZrO_2 support: ●, O_2 uptake at 195 K; ○, O_2 uptake at 640 K.

observed are same irrespective of their different pre-reduction and adsorption temperatures. However, the numerical values are different. Thus, oxygen uptake appears to be sensitive to the temperatures of reduction and estimation as well as the V_2O_5 content.[15] In the case of HTOC measurements, at very low loadings the slope of the uptake versus V_2O_5 loading plot approaches unity, indicating a limiting stoichiometry of $O_2/V_2O_5 = 1$. Using this stoichiometry, Oyama et al.[15] defined the dispersion as the ratio of molecular oxygen uptake divided by V_2O_5 content. These dispersions derived from both LTOC and HTOC uptakes are listed in Table I. The ratio of atomic oxygen uptake to the BET surface area of the sample gives oxygen atom site density.[9,15] The numerical values of oxygen atom site densities are also listed in Table I.

The N_2 BET surface areas of various samples were determined after H_2 reduction and subsequent O_2 uptake measurements. These samples were, of course, evacuated for longer times in order to remove any preadsorbed O_2 in the pores of the catalyst particles. As can be noted from Table I, the BET surface area of various catalysts decreases with increase in V_2O_5 loading. The decrease in BET surface areas with increase in vanadia loading also indicates a monolayer formation following arguments presented by Weller[14b] for Mo/Al_2O_3 catalysts. This loss
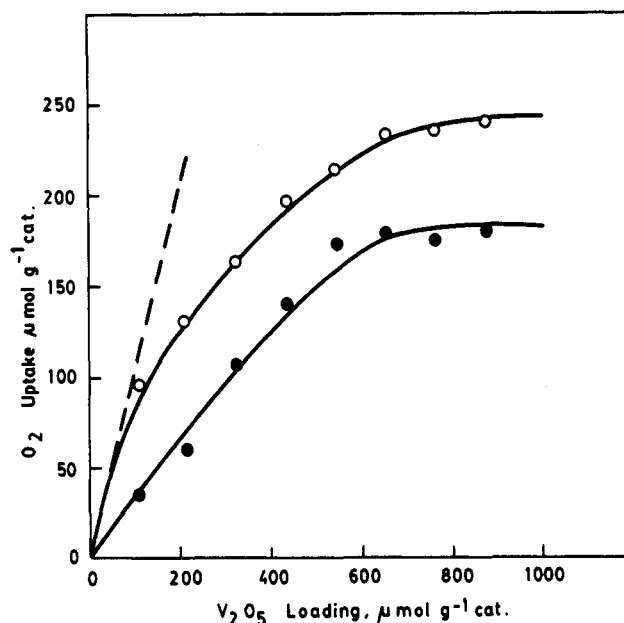
in surface area appears to be due to support pore blocking by the dispersed vanadium oxide phase during the preparation step. The loss in surface area is more pronounced in the case of LTOC measured samples. These samples were reduced at 773 K before O_2 uptake measurements. Therefore, the additional loss may presumably be due to the sintering of support material during high temperature reduction in H_2 atmosphere. Oxygen atom site density as a function of V_2O_5 content increases again up to 12 wt % loading and then approaches a limiting value. The apparent dispersion decreases with increase in V_2O_5 loading. The decrease is very rapid in the lower loadings and approaches a limiting value at higher loadings. This is a general phenomena in any supported catalyst system.[14,21] The numerical values of oxygen atom site density and apparent dispersion obtained from HTOC measurements are higher than the corresponding LTOC measurements. In any case, the oxygen atom site density obtained from O_2 uptake measurements is less than the average number density of V=O groups on the low-index planes of V_2O_5 (5.0×10^{18} m^{-2}).[15] These results, of course, suggest that the oxygen chemisorption techniques (both) described here samples the surface but not the bulk.

The oxygen atom site densities calculated from LTOC measurements on V_2O_5/Al_2O_3[9] and V_2O_5/SiO_2[10,12] catalysts were found to be less than the average number density of V=O groups. Oyama et al.[15] also noted similar observation from O_2 uptake measurements under LTOC conditions on an V_2O_5/SiO_2 catalyst containing 9.8 wt % V_2O_5. However, in the case of unsupported V_2O_5, the oxygen atom site densities calculated from O_2 uptakes obtained either at LTOC or HTOC conditions were found to be comparable.[9,15] It was therefore felt that the observation of the same number from both different approaches may be just coincidental.[15] Oyama et al.[15] further argued that overreduction (773 K) and underestimation (195 K) are the strong reasons to get the same O_2 uptakes, since both are opposing effects. However, in the case of supported systems LTOC results yielded low oxygen atom site densities and of course varied depending on the nature of support material used.[9,10,12] No concrete explanation is

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Table I. Oxygen Uptake, BET Surface Area, Oxygen Atom Site Density, and Dispersion on Various V_2O_5/TiO_2-ZrO_2 Catalysts

sample code	V_2O_5 content, wt %	LTOC[a]				HTOC[b]			
		O_2 uptake, μmol g^{-1}	SA,[c] m^2 g^{-1}	site density,[d] 10^{18} m^{-2}	disp[e] (O/V)	O_2 uptake, μmol g^{-1}	SA,[c] m^2 g^{-1}	site density,[d] 10^{18} m^{-2}	disp[e] (O/V)
VTZ-1	2	35.2	154	0.27	0.32	96.1	164	0.71	0.87
VTZ-2	4	60.0	138	0.52	0.27	129.4	147	1.06	0.59
VTZ-3	6	111.5	123	1.09	0.34	161.4	139	1.40	0.49
VTZ-4	8	140.2	116	1.46	0.32	196.4	126	1.88	0.45
VTZ-5	10	173.0	107	1.95	0.31	223.1	140	1.92	0.41
VTZ-6	12	178.5	108	2.00	0.27	232.7	126	2.22	0.35
VTZ-7	14	173.5	103	2.03	0.22	233.8	126	2.28	0.31
VTZ-8	16	178.4	103	2.09	0.20	241.3	120	2.42	0.27

[a] Sample reduction at 773 K and O_2 uptake at 195 K. [b] Sample reduction at 640 K and O_2 uptake at 640 K. [c] Surface area after O_2 uptake and subsequent evacuation (1×10^{-6} Torr). [d] Oxygen atom site density. [e] Dispersion = fraction of V atoms at the surface.

apparent at present; however, the observed results give an impression that all the coordinatively unsaturated V sites (CUS) generated upon reduction of the catalyst sample are not capable of chemisorbing oxygen at 195 K. As envisaged earlier,[10] oxygen chemisorption on V centers may or may not be subject to activation energy depending on the symmetry of the V centers having the CUS. Literature[22] shows that V centers with tetrahedral symmetry, V_{Td}, chemisorb oxygen without activation energy, while those with octahedral or square pyramidal symmetry had to overcome a considerable amount of activation energy of chemisorption. Therefore, the extent of reduction of supported oxide thus forming the different vanadium oxide species is assumed to be the major contributor for total O_2 uptake at 195 K. Reduction of bulk V_2O_5 at 773 K resulted in about 90% of conversion to V_2O_3, whereas the V_2O_5/Al_2O_3 samples showed an average degree of reduction closely corresponding to VO_2 and V_2O_5/SiO_2 catalysts to V_2O_3 of 70%.[23] Therefore, all these factors are assumed to reflect in O_2 uptake measurements when conducted especially under LTOC conditions. However, based on Raman and XRD measurements Oyama et al.[15] conclude that sample reduction at 640 K and O_2 uptake at the same temperature would give more meaningful information with respect to the number of V=O groups. From the present study however, it appears that both measurements convey the same message. The numerical values, of course, depend on the method of oxygen uptake adopted in addition to the nature of support material and the extent of loading.

Oxidation of methanol to formaldehyde was studied between 448 and 498 K on all samples. Activity and selectivity results obtained at 498 K are shown in Figure 4 as a function of V_2O_5 loading on TiO_2-ZrO_2 support. All samples revealed similar behavior regardless of their dispersion. Total conversion was found to increase marginally with increase in V_2O_5 loading up to again 12 wt % V_2O_5 loading after which a limiting value was observed. However, no appreciable change in the selectivity to formaldehyde product was noted. Titania-zirconia support and pure V_2O_5 also showed a considerably smaller activity with reasonably good selectivity to formaldehyde. The other major products observed on titania-zirconia and V_2O_5 were dimethyl ether and CO/CO_2, respectively. The dispersed vanadium oxide phase appears to be more active than the crystalline phase. The activity trend on various samples is thus in line with other information obtained from XRD, IR, and O_2 uptake measurements. No appreciable variation in the selectivities indicates that this reaction may not be that much
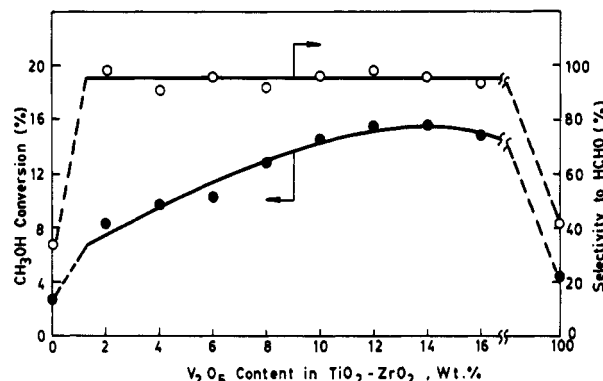

Figure 4. Partial oxidation of methanol to formaldehyde as a function of V_2O_5 on TiO_2-ZrO_2.

sensitive to the vanadium oxide environment. A similar result was also noted by Oyama et al.[24-25] on V_2O_5/SiO_2 catalyst for methanol and ethane oxidation. A comparison of the activity and selectivity results with the results of V_2O_5/SiO_2 catalysts published earlier[12] shows that the V_2O_5/TiO_2-ZrO_2 catalysts are more active and selective than the corresponding SiO_2 supported catalysts.

The present study thus reveals that vanadium oxide in the lower loading regions, i.e., below monolayer capacity, exists in a highly dispersed state, probably monomeric species at very low loadings and dimeric species at slightly higher loadings.[26] However, at very high loadings, i.e., above monolayer capacity, it exists in the form of a microcrstalline V_2O_5 phase. A similar behavior of the vanadium oxide phase on various other supports such as Al_2O_3, SiO_2, TiO_2, and SnO_2 was also observed earlier.[2,26-28]

Conclusions

The following conclusions can be drawn from this study:

(1) The TiO_2-ZrO_2 mixed oxide appears to be a promising support material for the dispersion of vanadium oxide.

(2) Highly dispersed vanadium oxide monolayer catalysts with vanadia loadings nearly equivalent to theoretical monolayer capacity of the support material can be obtained when TiO_2-ZrO_2 mixed oxide is used as the support material.

(3) The V_2O_5/TiO_2-ZrO_2 catalyst also appears to be very active for partial oxidation of methanol to formaldehyde.

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This reaction, however, appears to be not very sensitive to the nature of the vanadium oxide phase.

(4) Oxygen uptake measurements either at 195 or at 640 K give valuable information like oxygen atom site density and dispersion.

(5) As pointed out by Oyama et al.[15] the oxygen uptakes measured at 640 K with a prereduction of the sample at the same temperature probably avoids bulk and over-reduction of vanadium oxide and most importantly sintering of the support material.