Structure and Reactivity of Vanadium Oxide Catalysts Supported on Anatase TiO2[†]

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A series of TiO_2 (anatase) supported vanadia catalysts with V_2O_5 loadings ranging from 2 to 12% were characterized by temperature-programmed reduction (TPR), X-ray diffraction, electron spin resonance (ESR), and oxygen chemisorption studies. TPR profiles indicate the presence of a single peak for the reduction and suggest that the reducibility of vanadia depends on its loading on TiO_2. Dispersion of vanadia was determined by the static oxygen chemisorption method at 640 K on the samples prereduced at the same temperature. At low vanadia loadings, i.e., below 6%, vanadium oxide is found to be present in a highly dispersed state. A comparison of dispersion of vanadia determined by low-temperature oxygen chemisorption (samples reduced at 773 K for 6 h and subsequent oxygen chemisorption at 195 K) with that determined at 640 K shows that the latter method provides a better measure of dispersion of vanadia. ESR spectra obtained under ambient conditions for the catalysts reduced at 640 K show the presence of V^{4+} ions in axial symmetry. The results are discussed with the possible surface vanadia species present on TiO_2. The catalytic properties were evaluated for the vapor-phase ammoxidation of 3-picoline to nicotinonitrile and related to the oxygen chemisorption sites.

Introduction

Supported vanadium oxide catalysts have been widely investigated as they represent an important group of catalysts for a number of selective oxidation reactions[1−12] as well as the reduction of NO with NH_3.[12−22] The bulk oxides cannot generally be employed in industrial applications because of their lack of thermal/mechanical strength. In addition, the surface structure of vanadia dispersed on supported oxides is very different from that of bulk phase and consequently exhibits a unique role in catalytic activity and selectivity. In some instances supported vanadia catalysts were used in combination with additives such as oxides of W, Nb, P, and K.[23−26] These additives were found to enhance the catalytic properties and also enhance the life of the vanadia catalysts. Recently, Deo and Wachs[23] reported the influence of various additive oxides on the structure and reactivity of surface vanadia species in V_2O_5/TiO_2 catalysts. Among the supported vanadia systems V_2O_5/TiO_2, in particular, the anatase polymorph of TiO_2 has been extensively employed in environmental catalysis for the selective catalytic reduction of NO_x and also for the oxidation and ammoxidation reactions to synthesize nitriles.[27−31,75,76] According to Vejux and Courtine[32] the higher activity of vanadia supported on anatase polymorph of TiO_2 was ascribed due to their remarkable crystallographic fit between the (010) plane of V_2O_5 and the (010) and (001) plane of anatase TiO_2. On the other hand, the lower activity of rutile supported catalysts was attributed to the misfit of the lattice parameters of the two corresponding bulk phases. Recently Deo et al.[33] characterized V_2O_5 supported on different crystallographic phases of TiO_2 and suggested that the specific titania phase is not a critical parameter in determining the physical or chemical nature of surface vanadia phase. Several spectroscopic and other tech-

niques such as ESCA,[34−38] laser Raman,[39−42] XRD,[32] [51]V NMR,[43−46,67] ESR,[47−53,67] FT-IR,[54−57] TPR,[58−63] EXAFS,[64,65] and oxygen chemisorption[66−71] were extensively employed to find the surface structure and the active phase dispersion in supported vanadia catalysts. On the basis of information derived from the above techniques, it is now generally accepted that, at low vanadia loadings, vanadium oxide remains as a highly dispersed amorphous phase containing isolated vanadium oxide species anchored to the TiO_2 surface by strong interaction. However, at higher vanadia loadings it exists as crystalline V_2O_5 with the so-called monolayer phase.

The study of determining the dispersion of active phase in supported metal oxide systems is an interesting topic of research of recent years for understanding the role of the active phase on catalytic activity/selectivity during the oxidation reactions. To this end, methods such as oxygen chemisorption[66−71] was studied extensively in recent years to find active phase dispersion in supported vanadia systems. Miyamoto et al.[72,73] and Niwa et al.[74] used the reaction of NH_3 with NO to determine the number of V=O groups on the surface of vanadia. Went et al.[42] reported the quantitative dispersion of vanadia supported on anatase titania by using in situ Laser Raman spectroscopy.

Nicotinamide, a component of the vitamin B group, is an important chemical compound for the metabolism of human beings and animals and is used as a food additive. It is usually synthesized by the ammoxidation of 3-picoline to nicotinonitrile and further hydrolysis of the nitrile formed. Vanadium oxide catalysts either unsupported or supported on anatase TiO_2 are generally used for this ammoxidation process.[27−31,75,76]

In the present investigation we report the characterization of vanadia−titania (anatase) catalysts by TPR, XRD, ESR, and oxygen chemisorption methods. We also report the relation between dispersion of vanadia and catalytic properties of V_2O_5/TiO_2 catalysts during vapor phase ammoxidation of 3-picoline to nicotinonitrile. The purpose of this work is to estimate dispersion of vanadia supported on titania (anatase) as a function

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of V_2O_5 loading and to identify the changes in structure of the vanadia phase with the increase of active phase loading and also to understand the relation between activity/selectivity and oxygen chemisorption sites.

Experimental Section

Catalyst Preparation. Catalyst samples with varying vanadia content from 2 to 12 wt % of V_2O_5 were prepared by impregnation of anatase TiO_2 (Ti−Oxide U.K. Ltd.; surface area 92 m^2 g^{-1}) with an aqueous solution of NH_4VO_3 (Fluka A.G., Switzerland). The samples were dried at 383 K for 16 h and calcined at 773 K for 6 h.

Oxygen Chemisorption. Two methods of oxygen chemisorption were employed to determine the dispersion of V_2O_5 supported on TiO_2. Oxygen chemisorption was measured by a static method using an all Pyrex glass system capable of attaining a vacuum of 10^{-6} Torr. The details of the experimental setup are given elsewhere.[68] In the first method, prior to adsorption measurements the samples were prereduced in a flow of hydrogen (40 mL/min) at 640 K for 2 h. After reduction, the sample was evacuated at the same temperature for 1 h and oxygen adsorption uptakes were determined as the difference between the two successive adsorption isotherms measured at 640 K. The BET surface area of the catalysts was determined by nitrogen physisorption at 77 K. In the second oxygen chemisorption method, i.e., low-temperature oxygen chemisorption (LTOC), about 0.5 g of the catalyst sample was reduced at 773 K for 6 h in a flow of hydrogen (40 mL/min) and pretreated by palladium "de-oxo" and 4A zeolite molecular sieves, and oxygen chemisorption was performed on the reduced sample at 196 K using a dry ice acetone bath. The amount of oxygen chemisorption was determined by the double isotherm method reported Nag et al.[68]

X-ray Diffraction and Electron Spin Resonance. X-ray diffraction studies were carried out on a Philips diffractometer using Cu Kα radiation. ESR measurements were recorded at room temperature on a Bruker ER 200D-SRC X-band spectrometer with 100 kHz modulation. The reduced catalysts for ESR study were prepared in quartz tubes (25 cm long, 4 mm diameter), which formed part of the catalyst reduction apparatus. The reduction was carried out at 640 K for 2 h in a continuous flow (40 mL/min) of low-pressure-purified hydrogen. The setup was subsequently evacuated for 1 h at 10^{-6} Torr. The catalyst thus prepared was transferred to the ESR sample tube and sealed off under vacuum.

Temperature Programmed Reduction. In a typical experiment for the TPR studies, about 100 mg of the sample was dried at 393 K for 2 h in an argon flow and then argon was replaced by 8% hydrogen and argon mixture at room temperature. The heating of the sample was started after stabilizing the system. Hydrogen consumption during TPR was monitored with a gas chromatograph and TCD detector. TPR profiles were recorded with the help of an integrator cum-plotter. To determine the contribution from the empty reactor and pure support, a few blank experiments were also carried out under identical experimental conditions.

Ammoxidation of 3-Picoline. A down flow fixed bed reactor operating at atmospheric pressure and made of Pyrex glass was used to test the catalysts during the ammoxidation of 3-picoline to nicotinonitrile. About 2 g of the catalyst diluted with an equal amount of quartz grains was charged into the reactor and was supported on a glass wool bed. Prior to introducing the reactant 3-picoline with a syringe pump, the
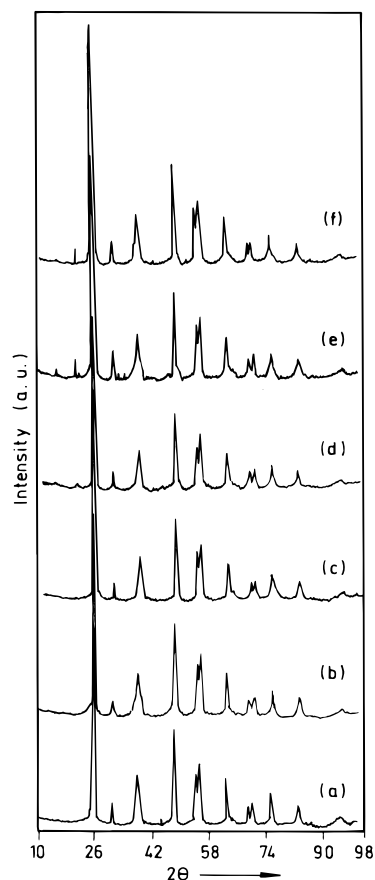

Figure 1. X-ray diffraction patterns of V_2O_5/TiO_2 (anatase) catalysts: (a) 2% V_2O_5/TiO_2; (b) 4%; (c) 6%; (d) 8%; (e) 10%; (f) 12%.

catalyst was reduced at 673 K for 2 h in purified hydrogen flow (40 mL/min). After the prereduction, the reactor was fed with 3-picoline, water, ammonia, and air, keeping the mole ratio of 3-picoline:H_2O:NH_3:air at 1:13:22:44 and the contact time at 0.6 s. The reaction was carried out at various temperatures ranging from 573 to 683 K. The liquid products obtained were mainly nicotinonitrile and were analyzed by the gas chromatograph using OV-17 column. Traces of carbon oxides were also formed during the reaction.

Results and Discussion

Powder X-ray diffraction patterns of various vanadia/anatase catalysts are presented in Figure 1. It can be seen from Figure 1 that all the samples showed XRD peaks due anatase TiO_2 with an intense peak at $2\theta = 25.28$ corresponding to diffraction by planes of (101) of TiO_2 (anatase). However, XRD peaks corresponding to V_2O_5 at $2\theta = 20.26$ can be seen only from a 6 wt % sample in addition to the intense anatase TiO_2 peaks. The intensity of the V_2O_5 peak at $2\theta = 20.26$ increases with vanadia loading in the catalyst. The absence of XRD peaks due to V_2O_5 at lower composition (below 6%) indicates that vanadium oxide is present in a highly dispersed amorphous state on TiO_2. However, at lower loadings of vanadia (<6 wt %) the possibility cannot be ruled out for the presence of vanadia crystallites having size less than 5 nm, which is beyond the detection capacity of the powder X-ray diffraction technique. XRD peaks corresponding to rutile TiO_2 were not observed in all the calcined samples, suggesting that the anatase to rutile phase transition of TiO_2 did not occur at any stage of sample preparation.
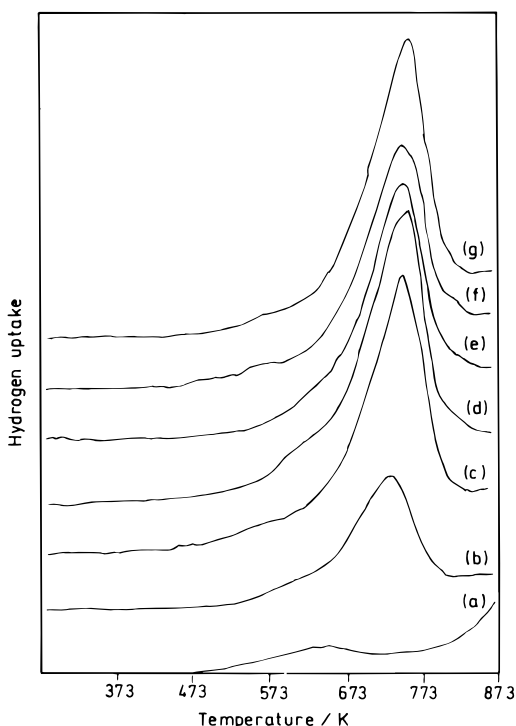
Figure 2. Temperature programmed reduction (TPR) profiles of V_2O_5/TiO_2 (anatase) catalysts: (a) unsupported V_2O_5; (b) 2% V_2O_5/TiO_2; (c) 4%; (d) 6%; (e) 8% (f) 10%; (g) 12%.

TABLE 1: Results of Temperature Programmed Reduction for Various V_2O_5/TiO_2 (Anatase) Catalysts

catalyst, wt % of V_2O_5 on TiO_2	T_{max} (K)	hydrogen consumed[a] during TPR (mmol)
2	717	4.63
4	735	8.74
6	742	9.64
8	740	8.47
10	739	7.01
12	741	8.90

[a] Calculated by taking the value of hydrogen consumed by the unsupported V_2O_5 (1.1 mmol) as standard.

TPR profiles of various vanadia/titania samples are shown in Figure 2. The dependence of T_{max} on the V_2O_5 content and the amount of hydrogen consumed during TPR are given in Table 1. The results of TPR by various V_2O_5/TiO_2 catalysts show a systematic change in the reduction of vanadia with an increase of vanadia loading. The TPR profiles for all samples have shown only one prominent maximum (T_{max}), and their positions are listed in Table 1. The appearance of single peaks during TPR of the present vanadia−titania catalysts are in good agreement with the literature.[22,61] Baiker et al.[22] have reported that titania supported vanadium oxide catalysts exhibited only one single reduction peak during TPR, if less than four layers of vanadium oxide was deposited. The reduction peak positions (T_{max}) reported in Table 1 show an increase of T_{max} values from 717 to 742 K with an increase of vanadia loading until a loading corresponding to 6% V_2O_5 was reached. Beyond 6% V_2O_5 loading the T_{max} values did not change appreciably with an increase of vanadia loading in the sample. The increase of intensity of TPR profiles with vanadia content indicates that the quantity of hydrogen consumed is also proportional to the vanadia content (Table 1). The amount of hydrogen consumed during TPR indicates that the reducibility of vanadia increases with the vanadia loading on TiO_2. As can be seen from Table 1, at high vanadia loadings (6% and above) the amount of
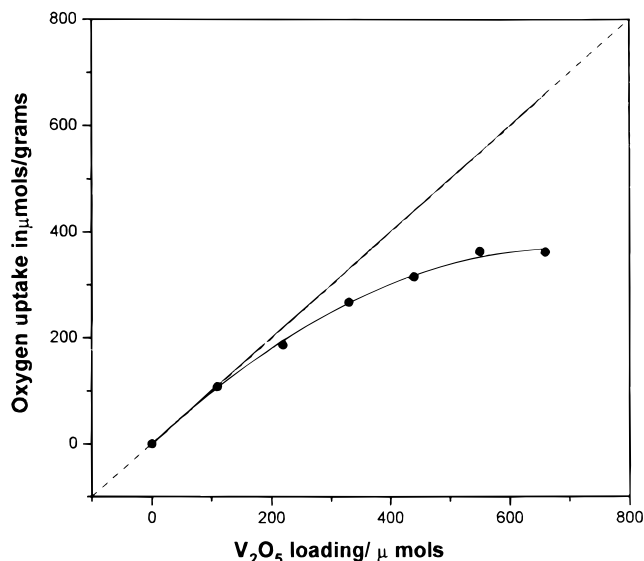

Figure 3. Oxygen uptake plotted as a function of vanadia loading on titania (anatase) ($T_{adsorption} = T_{reduction} = 640$ K).

hydrogen consumption during TPR did not change appreciably, suggesting the presence of the same kind of vanadia species, probably due to the crystalline vanadia phase as evidenced from the XRD results of these samples. TPR results also suggest that at low vanadia loading the interaction of vanadia with titania is stronger compared to higher vanadia contents. The T_{max} values of the present TPR study are very similar to the T_{max} values of recent TPR work of Dias et al.[4] TPR of unsupported V_2O_5 (Figure 2) reveals that it reduces at higher temperature than V_2O_5/TiO_2 catalysts, which is in consistent with the work of Roozeboom et al.[59] They have shown that the supported vanadium oxide catalysts reduce at much lower temperature than bulk vanadia and the reducibility of vanadia is strongly influenced by the kind of support used. Bond et al.,[4,6,9,63] reported that the VO_x monolayer species is reduced in a single step from V^{5+} to V^{3+}, the maximum temp (T_{max}) being about 740 K, which is well below the reduction peak of crystalline V_2O_5.

The method of oxygen chemisorption employed was the procedure described by Oyama et al.[66] Figure 3 shows the oxygen uptake at 640 K for various vanadia/titania catalysts plotted as a function of V_2O_5 loading. Pure anatase TiO_2 did not chemisorb oxygen under identical experimental conditions employed for the supported catalysts. The oxygen chemisorption capacities were found to increase with vanadia loading up to 6% (w/w) of V_2O_5 and levels off at higher vanadia loadings. The leveling off of oxygen uptake values at this composition of vanadia was attributed to the formation of a vanadium oxide monolayer on titania. This loading corresponds closely to the theoretical monolayer capacity of vanadium oxide. From the unit cell dimensions of V_2O_5 an average value for a loading corresponding to a monolayer can be calculated as 1.2 mg of V_2O_5/m^2 of the support. Thus Bond et al.[9] reported the weight concentration of V_2O_5 necessary to form a monolayer was 0.09/m^2. Therefore, the monolayer capacity of vanadia in the present anatase TiO_2 is about 8.28% V_2O_5. Thus the saturation level of oxygen chemisorption can be attributed due to formation of the vanadium oxide monolayer on titanium dioxide. The leveling of oxygen uptake (Figure 3) at higher vanadia loadings might be due to the presence of a crystalline vanadia phase, as noticed in the XRD results described earlier, and this phase upon prereduction with hydrogen does not appreciably chemisorb oxygen. At low vanadia loadings the uptake of oxygen

TABLE 2: Results of Oxygen Uptake, Dispersion, Oxygen Atom Site Density, and Surface Area of Various V$_2$O$_5$/TiO$_2$ (Anatase) Catalysts

catalyst compsn, wt % V$_2$O$_5$ on TiO$_2$	surface area, m^2 g^{-1}		oxygen uptake,[a] μmol g^{-1}	oxygen atom site density, 10^{18} m^{-2}	dispersion[c] O/V
	calcined	reduced			
2	63	65	107.4	1.99	0.98
4	55	60	187.0	3.75	0.85
6	46	58	267.7	5.56	0.81
8	48	62	315.3	6.13	0.72
10	45	58	363.1	7.54	0.66
12	42	53	362.3	8.23	0.55

[a] $T_{\text{reduction}} = 640$ K; $T_{\text{adsorption}} = 640$ K. [b] BET surface area determined after oxygen chemisorption. [c] Dispersion = fraction of vanadium atoms at the surface assuming O$_{\text{ads}}$/V$_{\text{surf}}$ = 1.

TABLE 3: Results of Oxygen Uptake, Dispersion, Oxygen Atom Site Density, and Surface Area of Various V$_2$O$_5$/TiO$_2$ (Anatase) Catalysts

catalyst compsn, wt % V$_2$O$_5$ on TiO$_2$	surface area,[b] m^2 g^{-1} reduced	oxygen uptake,[a] μmol g^{-1}	oxygen atom site density	dispersion[c] O/V, 10^{18} m^{-2}
2	65	15.61	0.29	0.14
4	60	33.90	0.68	0.15'
6	58	44.61	0.93	0.14
8	62	53.98	1.05	0.12
10	58	45.06	0.94	0.08
12	53	35.69	0.81	0.05

[a] $T_{\text{reduction}} = 773$ K; $T_{\text{adsorption}} = 195$ K. [b] BET surface area determined after oxygen chemisorption. [c] Dispersion = fraction of vanadium atoms at the surface assuming O$_{\text{ads}}$/V$_{\text{surf}}$ = 1.

approached the dashed line corresponding to a stoichiometry of one oxygen atom per vanadium atom (Figure 3). Using this stoichiometry Oyama et al.[66] defined the dispersion of vanadia as the fraction of total O atoms (determined from oxygen chemisorption uptake) to total V atoms in the sample. A substantial decrease of the dispersion of vanadia is observed with an increase of vanadia content in the catalyst. The information derived from oxygen chemisorption (Table 2) indicates that at low vanadia loadings the dispersion of vanadia approached almost 100%. These findings are in agreement with the oxygen chemisorption results of Went et al.[42] on vanadia supported titania, although they employed a pulse technique for measuring oxygen chemisorption. Went et al.[41] also reported from laser Raman spectroscopy of V$_2$O$_5$/TiO$_2$ catalysts that three types of vanadia species exist on TiO$_2$, namely, monomeric vanadyls, one- and two-dimensional vanadia chains, and crystallites of vanadia. The dispersion values reported in Table 2 are also in good agreement with TPR/TPO studies reported by Went et al.,[42] wherein they found that the ratios of H/V and O/V are almost unity in a series of V$_2$O$_5$/TiO$_2$ (anatase) samples.

The specific surface area determined by nitrogen physisorption for all of the catalysts and oxygen atom site density are reported in Table 2. The specific surface area of the catalysts was found to decrease sharply as a function of vanadia content. This decline of surface area with increasing vanadia loading might be due to blocking of the pores of the support by crystallites of vanadia. It is worth noting here that the leveling off of oxygen uptake (Figure 3) and the dependence of T_{max} during TPR (Table 1) as a function of vanadia in the catalyst exhibits the same trend. The oxygen uptake values and the dispersion of vanadia determined by low-temperature oxygen chemisorption (LTOC) for various V$_2$O$_5$/TiO$_2$ catalysts are reported in Table 3. LTOC experiments were carried out under the experimental conditions reported by Nag et al.[68] for vanadia supported on alumina. Briefly, the procedure involves prereduction of the samples with hydrogen at 773 K for 6 h and measuring oxygen chemisorption at 196 K. The dispersion of vanadia determined by the LTOC (Table 3) method is much lower than the oxygen chemisorption determined at 640 K (Table 2). The lower values of the dispersion of vanadia determined by LTOC might be due the overreduction of the samples by hydrogen at 773 K. It has been reported by Roozeboom et al.[59] from TPR studies of vanadia supported on TiO$_2$ that the V^{5+} species is found to reduce to V^{3+} without significant dispersion of vanadia. The results of TPR described earlier in this study also revealed that the VO$_x$ monolayer species is reduced in a single step from V^{5+} to V^{3+} at 742 K. Thus prereduction of catalysts at 773 K prior to oxygen chemisorption

at 196 K leads to overreduction of the sample and lowers the oxygen uptake.

It is well-established from the recent studies that the reducibility of vanadia supported on oxides such as Al$_2$O$_3$, SiO$_2$, and TiO$_2$ is dependent on the nature of supported oxide and the temperature of reduction. Oyama et al.[66] reported that to achieve complete reduction of vanadia surface without reducing bulk, the reduction must be carried out at 640 K to ensure only surface reduction. They have also shown from XRD that reduction of bulk V$_2$O$_5$ at 773 K leads to V$_2$O$_3$. Recently, Nag and Massoth[35] have reported using gravimetric method in which the reduction of silica supported vanadia with hydrogen at 773 K for 6 h resulted in 70% reduction of V$_2$O$_5$ to V$_2$O$_3$. However, Fierro et al.[77] reduced the V$_2$O$_5$/SiO$_2$ catalysts at 573 K, a temperature low enough to presume any possibility of bulk reduction of V$_2$O$_5$. Our results are thus in agreement with the above works.[35,66] Koranne et al.[62] have also shown from temperature programmed reduction of V$_2$O$_5$/Al$_2$O$_3$ that the average oxidation state of vanadium after reduction to a temperature as high as 1173 K was consistent with the stoichiometry V^{5+} → V^{4+}. Thus the selection of the prereduction temperature is very crucial in determining the dispersion of vanadia in supported catalysts.

ESR technique was used to gain some information about the nature of vanadium species in V$_2$O$_5$/TiO$_2$ supported catalysts. The ESR spectra recorded at 300 K for various V$_2$O$_5$/TiO$_2$ samples reduced in hydrogen are represented in Figure 4. Prior to the ESR measurements, the samples were reduced at 640 K for 2 h in hydrogen under identical conditions employed during the prereduction for oxygen chemisorption measurements. At low vanadia loadings the ESR spectra is well-resolved with hyperfine splitting (hfs) due to ^{51}V ($I = ^7/_2$). The intensity of ESR spectra decreases with an increase of vanadia in the catalyst. As can be seen from Figure 4, the ESR spectra are well-resolved at lower loadings (2% V$_2$O$_5$), and this permitted us to calculate the spin Hamiltonian parameters. The ESR parameters for the sample containing low vanadia content (i.e., 2%) were found to be $g_{11} = 1.9240$, $A_{11} = 180$ G, $g_\perp = 1.9805$, and $A_\perp = 67.86$ G. The analysis of ESR parameters suggests that V^{4+} ions are present in axial symmetry. In contrast, the unreduced samples show poorly resolved spectral features. An examination of the ESR spectra of hydrogen reduced catalysts suggest that the hyperfine structure diffuses at higher vanadia loadings and the spectra resembles that of singlet ESR spectrum of pure V$_2$O$_5$.[47] The broadening of ESR spectra at higher loadings of vanadia might be due to the presence of different surface vanadia species and probably due to crystalline vanadia, as evidenced from XRD results. The present ESR results further support the vanadia dispersion determined by the oxygen
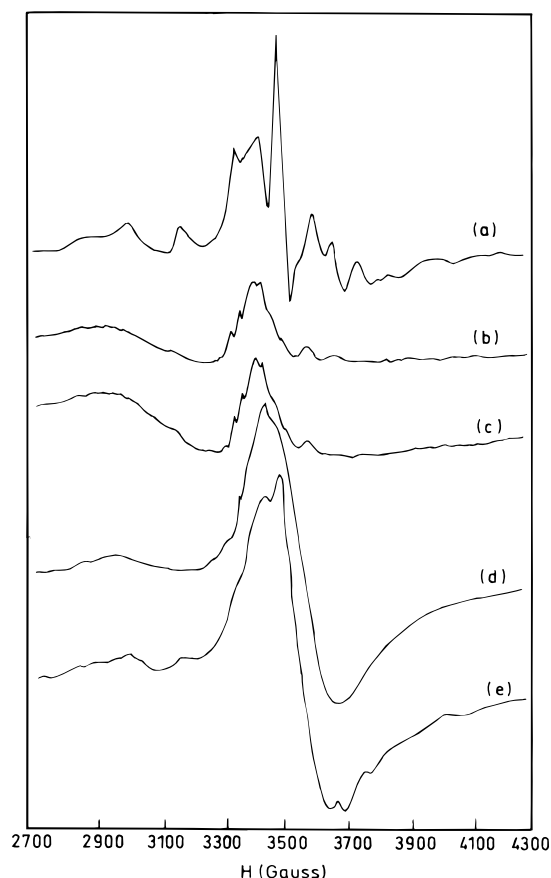
Figure 4. ESR spectra of reduced of V_2O_5/TiO_2 (anatase) catalysts ($T_{reduction} = 640$ K): (a) 2% V_2O_5/TiO_2; (b) 4%; (c) 6%; (d) 8%; (e) 12%.

Figure 5. Ammoxidation of 3-picoline over V_2O_5/TiO_2 (anatase) catalysts (reaction temperature, 633 K).

Figure 6. Relationship between the number of surface V_2O_5 moles and the rate of 3-picoline conversion.

chemisorption method. For example, a dispersion of 98% was obtained for low vanadia loading (2% V_2O_5/TiO_2) catalyst (Table 2). This high dispersion of vanadia is in consistent with the appearance of a well-resolved ESR spectrum due to ^{51}V for this sample. The decrease of intensity of the ESR spectra with an increase of vanadia loading in the catalyst (Figure 4) is attributed to spin−spin coupling. The changes in ESR spectral features with vanadia loading might be due to the presence of different vanadia species on titania.

Figure 5 shows the dependence of activity and selectivity on the vanadia loading during ammoxidation of 3-picoline to nicotinonitrile at 633 K. The conversion of 3-picoline as well as the selectivity to nicotinonitrile was found to be lower at low vanadia loadings and almost independent of vanadia loading beyond 4 wt % of V_2O_5. Pure TiO_2 (anatase) was found to be inactive for the nicotinonitrile formation under the experimental conditions of reaction employed for V_2O_5/TiO_2 catalysts. According to Vejux and Courtine[32] the high activity of V_2O_5 supported on anatase polymorph of TiO_2 was ascribed due to their remarkable crystallographic fit between the (010) plane of V_2O_5 and the (010) and (001) plane of anatase TiO_2.

Andersson[28] also studied the acid−base properties of V−Ti−O catalysts in the ammoxidation of 3-picoline. It was found that a high activity in the ammoxidation of 3-picoline corresponds to a relatively small amount of acidic sites. A catalyst selective in the formation of nicotinonitrile requires a high concentration of both acidic and basic sites. The conditions in the ammoxidation of 3-picoline are both reductive and oxidative; i.e., the hydrocarbons consume oxygen from the catalyst, which is then reoxidized. It can be expected that, under the steady
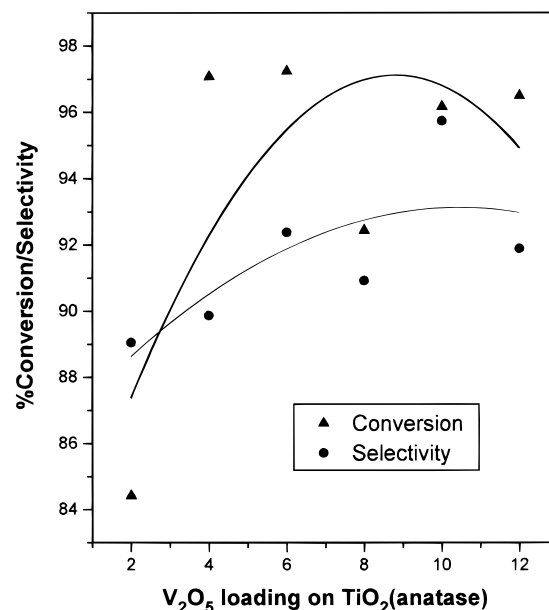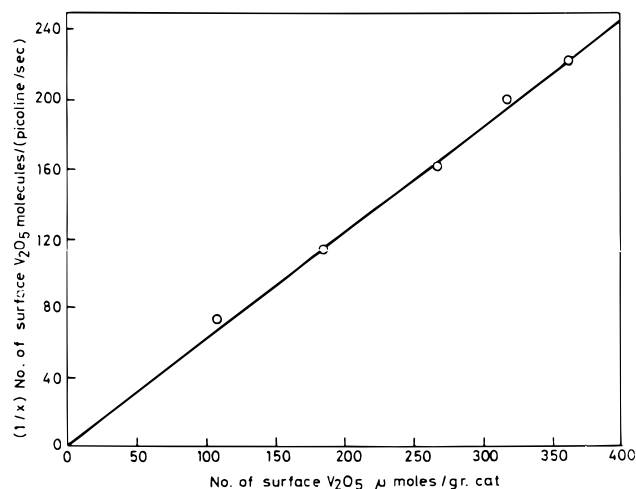
state conditions, the catalyst will contain a certain amount of lower oxides formed by reduction of the originally charged catalyst.

The enhanced activity of V_2O_5 on TiO_2 (anatase) in oxidation and ammoxidation reactions has been explained by two different hypotheses.[31] The first takes into consideration the presence of a crystallographic fit between the growth planes of anatase of TiO_2 and (010) planes of V_2O_5, the one containing the V═O bonds.[32] This remarkable fit leads to the preferential exposure of the vanadyl centers, thus the active sites.[11,48] The second hypothesis deals instead with the presence of a strong chemical interaction between the surface of anatase and vanadium oxide. The interaction derives from the reaction of surface hydroxyl groups of TiO_2 with vanadium, giving rise to the formation of a monolayer, where the V═O bond is characterized by a different bond strength and higher activity.

To find the relation between the ammoxidation activity of 3-picoline and the dispersion of vanadia, a plot of $1/X$ versus the number of surface V_2O_5 moles is shown in Figure 6, where X is equal to rate of picoline molecules converted per second per surface V_2O_5. A linear relationship passing through the origin was obtained, which clearly demonstrates that 3-picoline

conversion is directly related to oxygen chemisorption measured at 640 K. As reported elsewhere in connection with vanadium oxide catalysts supported on alumina[68] and on silica,[69] oxygen is chemisorbed at low temperatures selectively 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 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, and this postmonolayer phase does not appreciably chemisorb oxygen (see Figure 3). In the perspective of the above background, the correlation shown here indicates that the catalytic functionality of the dispersed vanadia phase supported on titania is responsible for the ammoxidation of 3-picoline to nicotinonitrile is located on a patchy monolayer phase and this functionality can be titrated by the oxygen chemisorption method described in this work.

Conclusions

The results of temperature-programmed reduction and oxygen chemisorption suggest that vanadium oxide is highly dispersed on titania support. Oxygen chemisorption measured at 640 K after the samples were prereduced at the same temperature provides a better method for determining the vanadia dispersion on titania than the samples reduced at 773 K. TPR results provide important information about the reducibility of vanadia supported on titania. ESR, XRD results further support the findings of oxygen chemisorption. The catalytic activity during 3-picoline ammoxidation is directly related to dispersion of vanadia.

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