JOURNAL OF Materials CHEMISTRY

Spectroscopic and diffractometric study of the V_2O_5/TiO_2 system prepared *via* mechanochemical activation

Lorenzo Dall'Acqua,[a] Marcello Baricco,[a] Francesco Berti,[b] Luca Lietti[c] and Elio Giamello*[a]†

[a]*Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 9, 10125 Torino, Italy*
[b]*ENEL-SRI, Via Volta 1, Cologno Monzese, Italy*
[c]*Dipartimento di Chimica Industriale e Ingegneria Chimica 'G. Natta', Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy*

Materials consisting of a vanadium oxide (VO_x) phase dispersed on a TiO_2 matrix and obtained by mechanochemical activation of the V_2O_5 and TiO_2, are compared with materials obtained by high temperature solid state reaction between the same two oxides. As a consequence of grinding, a non-negligible formation of isolated V^{IV} is evidenced by EPR, whose nature is typically vanadylic (VO^{2+}). Diffuse reflectance UV–VIS spectroscopy indicates that the reduction of the dispersed phase also induces the formation of more reduced vanadium species like V^{III}. Various distinct VO^{2+} species are stabilized on the surface by thermal treatments, and their coordinative environment has been tested by adsorption of NH_3 and H_2O. The phase changes brought about in the TiO_2 matrix by the grinding process as well as the presence of crystalline V_2O_5 have been monitored by XRD.

The transformations induced in solids by milling are the object of increasing attention in chemistry[1] and material science,[2] in particular in the fields of mechanical alloying and nanocrystalline materials.[3–5] Particular attention is paid to understanding the role of various experimental factors during the milling (ball velocity, impact energy, *etc.*) and to model the processes occurring during mechanical activation.[6,7] A mechanochemical reaction in a vibratory mill represents an alternative approach also for the preparation of bulk or supported oxide catalytic systems.[8–11] In the second case this method allows the dispersion of an oxide phase on another one acting as a support, operating in the solid state.[10,11] The supported oxides obtained by this technique are comparable, in terms of stability, with those obtained by classic preparation methods such as impregnation or high temperature solid state reaction. Published work in this field[10,11] shows that oxide systems, prepared by the mechanochemical method, may have interesting catalytic properties. The activities of systems such as Cr/SiO_2 and Mo/SiO_2, utilized for metathesis of propylene and ethylene polymerization respectively, are comparable to or higher than those of the same systems prepared by impregnation of the support and successive reduction (or photoreduction) of the system.

The present paper deals with the V_2O_5/TiO_2 system, widely used both in selective oxidation[12] and in deNO_x catalysis.[13] A recent paper on the same system[14] has shown that considerable increases in catalytic activity and selectivity (selective oxidation of *n*-butane) take place in the case of mechanical treatment of V_2O_5/TiO_2 accompanied by changes of morphology. In the present paper the X-ray diffraction technique is coupled to spectroscopic measurements aimed at monitoring chemical changes in the systems. It will be shown in the following that the mechanochemical route for V_2O_5/TiO_2 preparation has two basic effects, giving rise to: (a) the dispersion of the V_2O_5 phase on the TiO_2 surface; (b) the partial reduction of the supported phase with formation of vanadium ions in various oxidation states, predominantly V^{IV}.

The solids prepared by the mechanochemical method are compared in the present paper with those obtained by high temperature solid state reaction between the same oxides. This latter method was identified, years ago, as a possible alternative to impregnation for V_2O_5/TiO_2 preparation and has therefore been widely investigated.[15] Since the starting materials for these two types of preparations (solid state reaction and milling) are the same (the single oxides) a comparison between the final materials (supported oxides) obtained by the two methods has been tackled in the present work. The process of formation of the supported systems was followed by X-ray diffraction (XRD), electron paramagnetic resonance (EPR), and diffuse reflectance UV–VIS spectroscopy. XRD was employed to analyse the phase composition under various conditions, EPR to monitor the formation of V^{IV} ions and their structural features, and UV–VIS to investigate the redox state of the system. Detailed analyses of milling conditions, impact energy, *etc.*, are beyond the scope of the present paper.

Experimental

The precursors of the supported systems investigated in the present work were prepared by simple mixing of V_2O_5 and TiO_2 powders in the appropriate ratio. Three different types of TiO_2 were utilized: anatase (surface area, $A_s = 99\ m^2\ g^{-1}$), rutile ($A_s = 28\ m^2\ g^{-1}$) and Degussa P25, a mixture of anatase and rutile with A_s of $51\ m^2\ g^{-1}$. Samples employing anatase (A) or rutile (R) as a support were loaded with 1 wt.% V_2O_5 (V), while those employing P25 (P) contain 6.5 wt.% V_2O_5. The colours of all the precursors tend to white, the colour of TiO_2, due to the low percentages of V_2O_5 (yellow ochre) in the mixture. To prepare a supported vanadium oxide phase the precursors underwent two distinct types of treatment. In the first one (solid state reaction), a portion of the mixture was calcined in oxygen for 21 hours at 873 K and then evacuated at 10^{-5} Torr (1 Torr = 133.32 Pa) at the same temperature prior to spectroscopic and diffractometric analysis. The second type of treatment consists of milling the precursor mixture for 15 hours in air. Grinding was always performed on 1 g of powdered material in a Retsch MM2 mill utilizing a cylindrical corundum cell of 112 g with an internal volume of about 6.4 cm^3. A 2 g corundum ball with a diameter of 1 cm was used in the mill cell which operated at 80% of its maximum velocity. After grinding the samples were transferred into a silica cell suitable for thermal treatment under vacuum, and

---

† E-mail: giamello@silver.ch.unito.it

Table 1 Labels, preparation procedure, vanadium loadings and phase compositions of the various V_2O_5/TiO_2 samples

sample	preparation	V_2O_5 (wt.%)	TiO_2 phase
VAC	calcined	1	anatase
VRC	calcined	1	rutile
VPC	calcined	6.5	anatase + rutile (P25)
VAM	milled	1	anatase
VRM	milled	1	rutile
VPM	milled	6.5	anatase + rutile (P25)

were submitted to various treatments or gas adsorption as reported in the text. The samples are hereafter labelled with two letters indicating the nature of the two components (VA, VR and VP respectively) and a third letter (C or M) indicating calcined or milled samples respectively. The labels and V_2O_5 contents of all the samples are summarised in Table 1.

EPR spectra were recorded by a Varian E-109 spectrometer equipped with a dual cavity, operating in X-band mode and connected to a personal computer for data handling and elaboration. Several spectra for all types of sample were recorded both at room temperature and at 77 K. A pitch sample ($g = 2.0028$) was used as a standard for g value determination. The experimental spectra were simulated by a version of the SIM14S program (from QCPE) adapted for personal computers. The XRD spectra were recorded by a Philips diffractometer, with a PW 1830 X-ray generator with a Co anticatode ($\lambda_{Co} = 1.7902$ Å) and a wide angle goniometer PW 1050/25. The diffuse reflectance UV–VIS spectra were recorded by a Cary 5 spectrometer.

Results and Discussion

XRD spectra

While the precursor powders are all nearly white, the calcined samples (VAC, VRC, and VPC) exhibit a colour similar to (though less intense than) that of pure V_2O_5 (yellow ochre). Fig. 1 compares the XRD pattern of the VP precursor [V_2O_5 6.5 wt.% mixed with P25, (a)] with those of the calcined [VPC, (b)] and of the ground material [VPM, (c)]. The precursor pattern [Fig. 1(a)] shows the reflections related to anatase and rutile phases typical of P25 TiO_2 and a series of peaks which are related to the crystalline V_2O_5 phase, the amount of which is near the detection limit. The results of calcination and milling treatments clearly differ. In the former case [Fig. 1(b)] the peaks related to anatase and rutile phases are virtually unchanged, while V_2O_5 reflections are still visible, although less intense than in the precursor pattern. This indicates that a fraction of the whole V_2O_5 amount has been dispersed in or on the TiO_2 support. Some evidence, like the yellow colour of the calcined samples and the absence of V^{IV} EPR spectra for this material (*vide infra*), suggests that the surface layer essentially consists of pentavalent vanadium dispersed on the support. Vanadium ions capable of diffusion in the TiO_2 rutile matrix are in fact V^{4+} (isovalent with Ti^{4+}),[16] which are indeed not observed in the calcined materials. It is well known, furthermore, that impregnation of TiO_2 powder surface layers with pentavalent vanadium results in stabilization in the form of surface grafted vanadates.[17] Since the V_2O_5 loading theoretically needed to form a monolayer, in the case of P25 support with 51 m^2 g^{-1} surface area, is about 7.5% by weight,[18] the surface phase in the calcined samples only partially covers the TiO_2 surface.

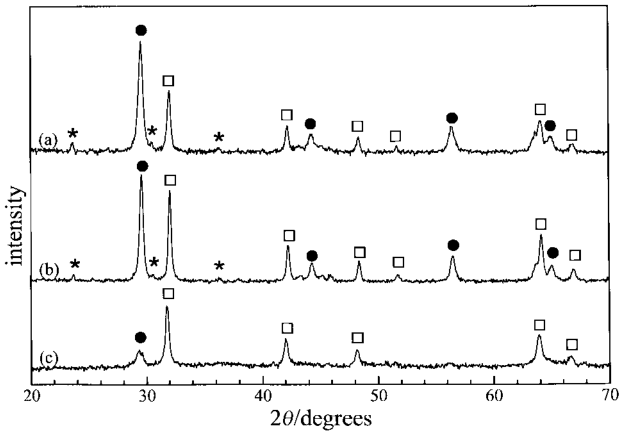

Fig. 1 X-Ray diffraction spectra of: (a) the as prepared 6.5% V_2O_5/TiO_2 (P25) mixture; (b) the same system after thermal treatment for 21 hours at 873 K (VPC) and (c) after 15 hours milling (VPM). The different labels indicate peaks related to TiO_2 anatase (●), TiO_2 rutile (□) and V_2O_5 (*).

The transformations brought about by the milling treatment of the precursor mixture [Fig. 1(c)] are very different and can be summarized as follows. (a) The reflections related to V_2O_5 are absent, indicating that the dispersion of the vanadium oxide phase on TiO_2 induced by the grinding treatment is higher than that observed in the case of high temperature solid state reaction. (b) The reflections related to the TiO_2 phases underwent dramatic alteration, consisting of the strong reduction of the anatase phase peak intensities or, in other words, a net decrease of the anatase to rutile intensity ratio. This phenomenon is reminiscent of the net decrease of the temperature of the anatase–rutile phase transition promoted by vanadia.[19–21] The mechanochemical action has therefore, in the presence of a consistent amount of V_2O_5, a remarkable effect on the anatase–rutile transformation which is not observed upon calcination at 873 K of the same starting material [Fig. 1(b)]. A similar case of structural transformation by ball milling has been reported in the case of alumina.[22]

Due to the low V_2O_5 contents of VA and VR samples, which escape detection, the XRD analysis reported here could not be performed for such samples. However the appearance of weak reflections due to rutile in the XRD diffraction patterns of milled VAM samples, indicates also in this case the ability of the grinding treatment to cause a partial transformation to rutile of the anatase matrix.

EPR spectra

All the precursors and the three samples calcined in oxygen (VAC, VRC, VPC) do not exhibit any EPR signal [Fig. 2(a)]. Surprisingly, as the samples contain the reducible V_2O_5 phase, after outgassing the calcined samples at 873 K no EPR signal due to V^{IV} was observed. The only signal arising upon thermal treatment in vacuum in this case is a narrow line at $g = 2.0034$, probably due to paramagnetic point defects in the TiO_2 matrix (spectrum not reported for sake of simplicity). The systems prepared by direct calcination of the precursor mixture are revealed therefore to be strongly resistant to reduction, differing in this property from the 'classic' impregnated V_2O_5/TiO_2 catalysts.[18] Very different results are obtained by mechanochemical activation in air of the starting precursors. Upon grinding, in fact, all milled samples turn light yellow and, in parallel, an intense signal EPR due to V^{IV} ($3d^1$ electronic configuration) arises. The spectrum of a VAM sample is reported in Fig. 2(b). The profile of this experimental spectrum has been computer simulated [Fig. 2(c)] and the corresponding spin-Hamiltonian parameters are reported in Table 2. Tetravalent vanadium ions exhibit $3d^1$ electronic configuration. Spin resonance takes place, for these ions, at g values lower than the free electron value. The EPR spectrum is complicated by the high number of hyperfine levels, generated by the interaction of the unpaired electron with the $I = 7/2$ ^{51}V

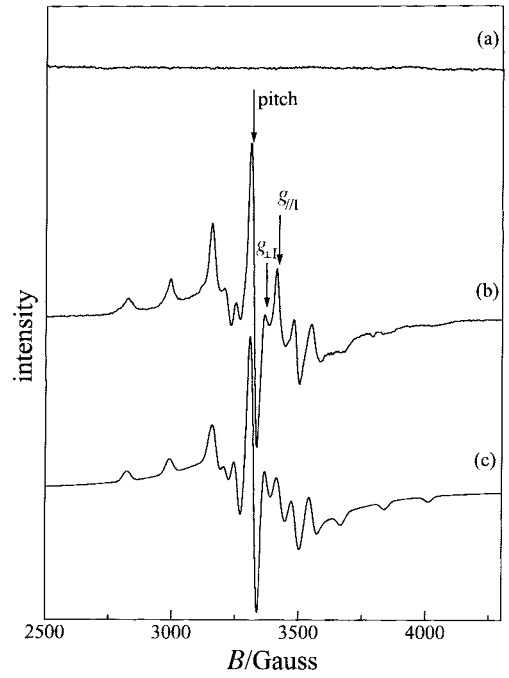

Fig. 2 EPR spectra of: (a) VA precursor evacuated for 1 hour at R.T.; (b) VAM sample milled for 15 hours in air and evacuated for 1 hour at R.T.; (c) computer simulation of spectrum (b)

nucleus, and by the second order effects that tend to produce an asymmetric hyperfine structure with unequal separation of the various lines. The spectrum of the VAM sample in Fig. 2(b) can be understood in terms of the superimposition of a signal due to isolated V^{IV}, characterised by a resolved hyperfine structure (species I), with a wide and unstructured symmetric signal due to V^{IV} magnetically interacting species (species II), *i.e.* to clusters of V^{IV} ions close enough to cause dipolar broadening. In the remaining milled samples (VRM, VPM) the same isolated V^{IV} species (species I) results, independent of the nature of the TiO_2 support. Species II is also present in all ground samples, but is remarkably more abundant for the VPM sample which contains a higher percentage of V_2O_5 (6.5 wt.%).

To measure the amount of V^{IV} formed upon grinding, quantitative tests have been performed, based on double integration of the spectra and comparison of the results with those obtained with standard samples having a known spin concentration. The system employed as standard was $VOSO_4/K_2SO_4$, according to the method proposed by Dyrek and coworkers.[23] The quantitative analysis of the ground solids indicates that the V^{IV} amount increases with increasing milling time. The increase however depends on the type of TiO_2 phase used as a support. Fig. 3(a) reports the V^{IV}/V_{total} ratio as a function of the grinding time for the two samples having the same V_2O_5 loading (1 wt.%). In the case of the VAM sample the V^{IV} intensity reaches a maximum after 9 hours milling, remaining constant in the following 6 hours. The spectral intensity of VRM constantly increases with milling time (total 15 hours), while remaining lower than that recorded for the VAM sample. The maximum amount of V^{IV} formed upon grinding reaches 12% and 18% of the total vanadium amount for the VRM and VAM samples respectively.

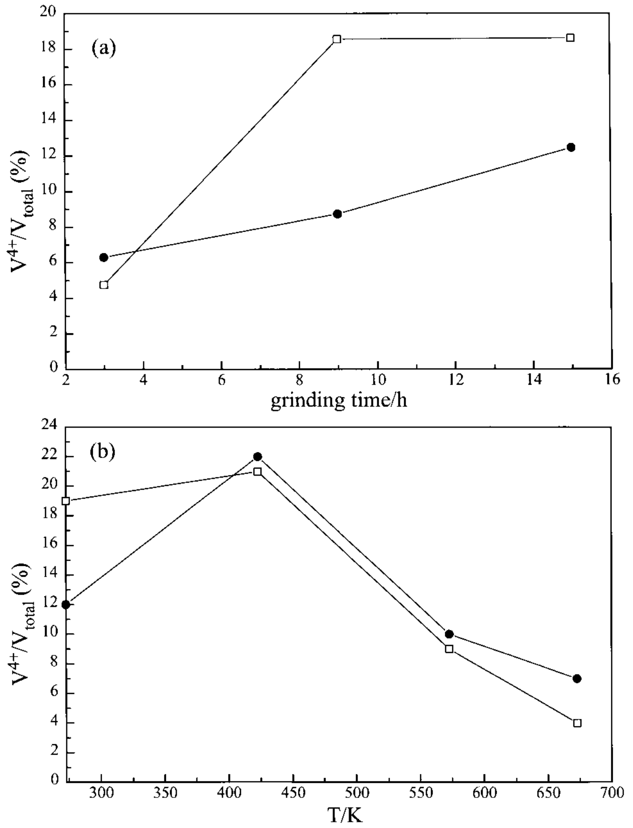

Fig. 3 Influence of grinding time (a) and temperature of evacuation (b) on V^{4+}/V_{total} (%) ratio for VAM (□) and VRM (●) samples

The freshly prepared ground samples were then submitted to annealing treatments in vacuum. The effect of these treatments is described by the spectra in Fig. 4 which are related to the VAM sample. The results for the VRM sample strictly parallel those for VAM and are not reported for the sake of brevity. The EPR spectrum due to the presence of species I and II is not modified by annealing at 423 K [Fig. 4(a)], whereas upon evacuation at 573 K [Fig. 4(b)], a second V^{IV} isolated species (species III in Table 2) arises accompanied, Fig. 3(b), by a decrease of the overall spectral intensity. Upon annealing at 673 K the transformation of the isolated species I into the isolated species III is accomplished [Fig. 4(c)]. The spectral features of species III have been computer simulated [Fig. 4(d)] and the corresponding parameters are reported in Table 2. Species III differs from species I mainly in the value of the ^{51}V hyperfine constants ($A_{\parallel}$ and $A_{\perp}$) which are definitely higher for species III.

To investigate the co-ordination state of species I and III, a given pressure (10 Torr) of various gases (CO, NH_3, H_2O) was adsorbed at room temperature on VAM and VRM samples after milling and evacuation at 573 K. In such conditions the sample shows the presence of both species I and III [Fig. 4(b)]. The spectrum profile, reported again for the sake of clarity in Fig. 5(a), is not modified by adsorption of CO, while interaction with NH_3 and H_2O slightly affects species III only, whose parameters tend to approach those of species I [Fig. 5(b)]. Ammonia and water (both diamagnetic basic molecules) are therefore co-ordinated to V^{IV} ions of species III, producing a

Table 2 Spin-Hamiltonian parameters of the various V^{IV} species as derived by computer simulation of the spectra

species	nature	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}
I	isolated	1.940	1.966	1.957	169.8	52.4	91.5
II	interacting	—	—	1.971	—	—	unresolved
III	isolated	1.920	1.982	1.961	193.5	72.5	112.8

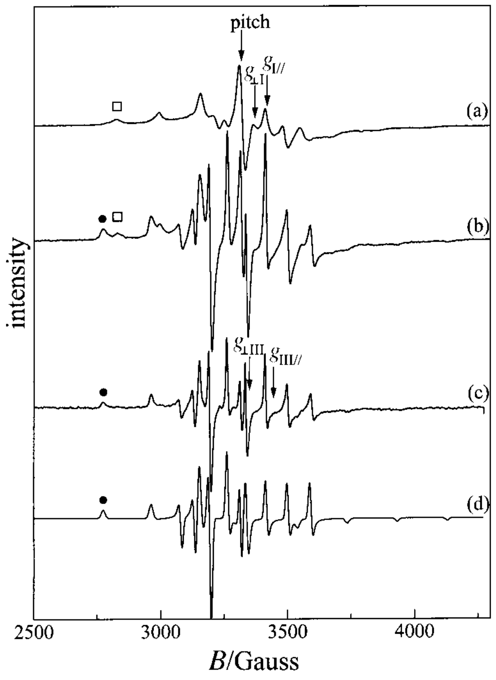

Fig. 4 EPR spectra of a VAM sample after evacuation for 1 hour at various temperatures; (a) $T=423$ K; (b) $T=573$ K; (c) $T=673$ K; (d) computer simulation of spectrum (c). The low field external hyperfine components of the V^{IV} signals are evidenced. The symbols (□) and (●) are for species I and III respectively.

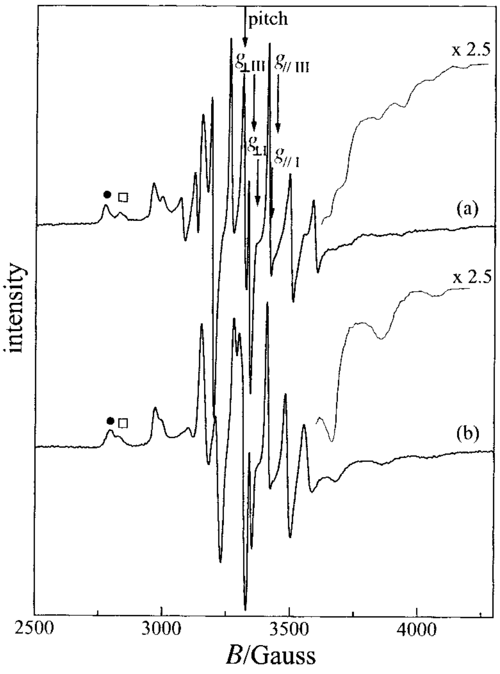

Fig. 5 EPR spectra of a VAM sample (a) after evacuation for 1 hour at 573 K [spectrum also reported in Fig. 4(b)]; (b) after adsorption of 10 Torr NH_3. Labels are as in Fig. 4.

similar effect on the EPR spectrum. The effect of co-ordination is reversible and the starting spectrum is restored by a vacuum treatment at 523 K.

The EPR spectrum of the VPM sample (6.5 wt.% V_2O_5) after milling and evacuation for 1 hour at 423 K is analogous to those of the VAM and VRM samples in the same conditions except for a larger amount of the interacting species (species II). However, upon increasing the evacuation temperature to 573 K and 673 K, the EPR spectrum of VPM remains unchanged and the appearance of species III is not observed.

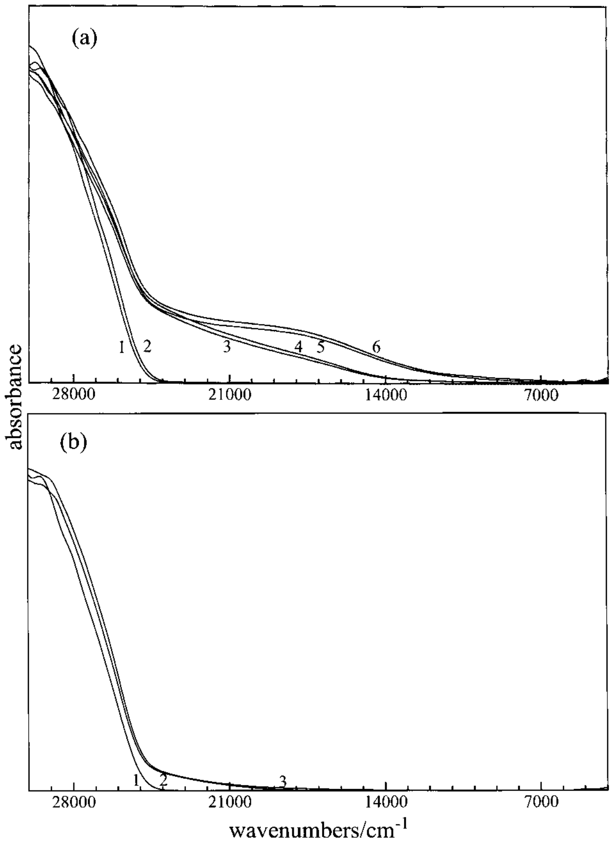

Fig. 6 (a) Diffuse reflectance UV–VIS spectra of: 1, TiO_2 rutile matrix; 2, VR precursor; 3, VRM milled sample; 4, VRM after evacuation for 1 hour at 423 K; 5, VRM after evacuation for 1 hour at 673 K; 6, after adsorption of 10 Torr of NH_3 on sample 5. (b) Diffuse reflectance UV–VIS spectra of: 1, TiO_2 rutile matrix; 2, VRC sample (calcined for 21 hours at 873 K in air); 3, after evacuation at 873 K of sample 2.

UV–VIS spectra

The diffuse reflectance UV–VIS spectra of both the ground VRM sample [Fig. 6(a)] and the calcined VRC sample [Fig. 6(b)] were recorded after all the steps to which the samples were submitted. In Fig. 6(a) spectrum 1 of the rutile TiO_2 matrix is reported, for comparison, which shows the well known band at 32 000 cm^{-1} due to the charge transfer transition $O^{2-} \rightarrow Ti^{4+}$. The edge is only weakly modified by mixing TiO_2 with 1 wt.% V_2O_5 [Fig. 6(a), spectrum 2]. The grinding treatment brings about, in contrast, the formation of a marked and wide absorption in the visible region [Fig. 6(a), spectrum 3], which is basically due to the reduction of the supported phase with formation of V^{IV} (absorption around 16 000 cm^{-1}) and of an even more reduced vanadium oxide phase (lower absorption frequencies).[24] The annealing treatments at 423 K and 673 K further increase the intensity of these absorptions that extend towards the infrared boundary [Fig. 6(a), spectra 4, 5]. The co-ordination of NH_3 does not substantially change the diffuse reflectance spectral profile of the sample annealed at 673 K [Fig. 6(a), spectrum 6].

The UV–VIS spectra obtained for calcined samples are quite different from those observed for the ground material. Spectra 2 and 3 in Fig. 6(b) are due to a VRC sample calcined at 873 K in air (2), followed by evacuation at the same temperature (3). Spectrum 1 in Fig. 6(b) reports the TiO_2 rutile spectrum for comparison. Note that the high temperature solid state interaction between V_2O_5 and TiO_2 does not give rise to the formation of V^{IV} or reduced vanadium oxide phases, in agreement with the previously reported EPR data. The slight modification of spectra 2 and 3 in Fig. 6(b) with respect to that of the pure matrix is due to the dispersion of the V_2O_5 phase on the surface (also revealed by the previously reported

XRD patterns) which is the main result of the V_2O_5/TiO_2 interaction in the solid state.

Nature of the reduced V species

The experiments reported previously indicate that two distinct effects are caused by mechanochemical treatments of V_2O_5/TiO_2 mixtures: the first one is the vanadium oxide dispersion on the matrix, as indicated by XRD results (Fig. 1) and the second is the partial reduction of V^{V} to V^{IV}, and probably also to V^{III}, as indicated by EPR (Fig. 2) and UV–VIS spectra (Fig. 6). The reduction to V^{IV} is indicated by the constant growth of the corresponding EPR signal as a function of the grinding time [Fig. 3(a)]. The formation of V^{III} is inferred to occur mainly during the thermal treatments performed after milling as indicated by the decrease of the V^{IV} EPR peak intensity [Fig. 3(b)] and by the increase of the low frequency absorption in the UV–VIS spectrum [Fig. 6(a)]. These effects, however, could also be related to the formation of EPR silent V^{IV} 'clusters' in poorly organised vanadia-like domains formed under these experimental conditions. As to the mechanism of reduction under mechanical treatment, though no direct evidence is available, we suppose that it is similar to that acting in cases of thermally annealed systems, *i.e.* the depletion of oxygen by the reducible vanadium pentoxide phase. The dispersion of V_2O_5 is also obtained (though to a lesser extent than for milled samples) by calcination of the solid at 873 K, as indicated by Fig. 1(b), where weak V_2O_5 peaks are still visible. However as indicated by the EPR spectra of the calcined samples under various conditions, calcined systems seem very resistant to reduction and V^{IV} formation is not observed after any of the treatments. On the other hand, the milling treatment, even when carried out in oxidative atmosphere (air), is able to promote the interaction of the two phases and to give rise to the reduction of V^{V} to V^{IV} and even more reduced states.

The V^{IV} species, obtained by milling of VAM, VRM and VPM samples (namely species I and II), are respectively due to isolated and interacting V^{IV} centres. Comparing the parameters in Table 2 with those reported in the literature,[25,26] it turns out that the isolated species I has parameters which are intermediate between those of surface VO^{2+} vanadylic ions and those of V^{4+} interstitial bulk ions. The energy connected to the mechanical treatment probably causes diffusion of a fraction of vanadium ions in the first layers of the support, thus giving rise to species I. This latter species is co-ordinatively saturated, as demonstrated by the fact that its spectral features remain unchanged upon interaction with NH_3 and H_2O molecules (Fig. 5).

As far as signal II is concerned, this is typical of interacting V^{IV} species: the structure of isolated V^{IV} is smeared out in this case by the dipolar magnetic interaction between neighbouring species.

Analysis of the EPR literature indicates that species III is typical of VO^{2+} vanadylic surface ions with axial symmetry. Species III parameters in fact are very similar to those recorded for impregnated V/TiO_2 systems[12,17] which mainly contain surface anchored vanadylic groups. The spectral modifications induced by adsorption of basic molecules indicate (Fig. 5) that species III is indeed coordinatively unsatured and thus surface exposed. The spectral modification upon adsorption is completely reversible at 523 K in vacuum. At this temperature the co-ordinating molecule is desorbed and the EPR spectrum recovers its previous features.

The intensity decrease of the EPR spectra of VAM and VRM samples upon treatment in vacuum at increasing temperature can be explained in terms of further reduction of the supported vanadium oxide phase with formation of reduced centres such as V^{III}, which are invisible in the EPR. This hypothesis is in clear agreement with the UV–VIS results which indicate that the intensity decrease of the EPR spectra at high temperature [Fig. 3(b)] and the onset of new absorptions in the region around 10 000–15 000 cm^{-1} [Fig. 6(a)], assigned to reduced V phases, are strictly parallel phenomena.

Conclusions

The mechanochemical method has been found to be rather suitable for the preparation of V_2O_5/TiO_2 supported oxide systems. The dispersion of the vanadium phase is more efficiently attained by the milling treatment than by thermal treatment at high temperature of comparable or higher duration. Surprisingly the ground systems more closely resemble the analogous systems prepared by wet impregnation in that in these two cases surface vanadium ions are quite easily reduced to lower oxidation states by thermal annealing[18,26] and are able to co-ordinate basic molecules from the gas phase. The same does not apply for calcined samples which appear very resistant to reduction. This finding is in nice agreement with Boldyrev's statement[2] indicating that the products of mechanochemical reactions may be different from those of thermochemical reactions for the same reactants. The mechanochemical treatment has some influence on the phase composition of the support. This has been observed in terms of decrease of the abundance of the anatase phase with respect to rutile upon milling a mixed TiO_2 (P25) in the presence of V_2O_5. These kinds of phenomena indicate the occurrence of a marked effect of the mechanical treatment on the structure of, at least, the first layers of the solid crystallites. Similar effects, which are of course not present in systems prepared by impregnation from solution, suggest that the solids prepared by grinding could be potentially interesting for their catalytic properties. The analysis of the catalytic properties of the prepared materials was beyond the scope of the present investigation. However we limit ourselves to the recollection of two facts. In the case of *n*-butane oxidation to maleic anhydride[14] both activity and selectivity were found to increase upon mechanical activation of the V_2O_5/TiO_2 catalyst. Furthermore the VAM system described in the present work has been preliminarily tested in the selective catalytic reduction (SCR) of nitric oxide by NH_3 at 420 K. The system was found to be quite efficient in ammonia oxidation and poorly active in $deNO_x$-SCR reactions, indicating promising qualities in the field of oxidation rather than in that of $deNO_x$ catalysis.

References

1 J. J. Gilman, *Science*, 1996, **274**, 65.
2 V. V. Boldyrev, *J. Chim. Phys.*, 1986, **83**, 821.
3 *Proceedings of the International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials,* ed A. R. Yavary, *Mater. Sci. Forum*, 1995, **179–181**.
4 *Proceedings of the International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials,* ed. D. Fiorani and M. Magini, *Mater. Sci. Forum*, 1997, **235–238** (Part I).
5 S. Begin-Colin, F. Wolf and G. Le Caer, *J. Phys. III*, 1997, **7**, 473.
6 S. Begin-Colin, G. Le Caer, A. Mocellin, C. Jurenka and M. Zandona, *J. Solid State Chem.*, 1996, **127**, 98.
7 G. Mulas, S. Loiselle, L. Schiffini and G. Cocco, *J. Solid State Chem.*, 1997, **129**, 263.
8 V. A. Zazhigalov, J. Haber, J. Stoch, L. V. Bogutskaya and I. V. Bacherikova, *Appl. Catal., A*, 1996, **135**, 155.
9 J. Haber, V. A. Zazhigalov, J. Stoch, L. V. Bogutskaya and I. V. Batcherikova, *Catal. Today*, 1997, **33**, 39.
10 A. A. Bobyshev, V. B. Kazanskii, I. R. Kibardina, V. A. Radtsig and B. N. Shelimov, *Kinet Katal.*, 1990, **30**, 1427.
11 A. A. Bobyshev, V. B. Kazanskii, I. R. Kibardina and B. N. Shelimov, *Kinet. Katal.*, 1992, **33**, 363.
12 A. Bielansky and J. Haber, *Oxygen in Catalysis*, Marcel Dekker, New York, 1991.

13 M. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
14 V. A. Zazhigalov, J. Haber, J. Stoch, L. V. Bogutskaya and I. V. Bacherikova, *Stud. Surf. Sci. Catal.*, 1996, **101**, 1039.
15 G. Centi, E. Giamello, D. Pinelli and F. Trifirò, *J. Catal.*, 1991, **130**, 220.
16 R. Gallay. J. J. Van der Klink and J. Moser, *Phys. Rev. B*, 1986, **34**, 3060.
17 G. T. Went, L. I. Len and A. T. Bell, *J. Catal.*, 1992, **134**, 479.
18 L. I. Allemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello and F. Bregani, *J. Catal.*, 1995, **155**, 117.
19 G. C. Bond, A. J. Sàrkàny and G. D. Parfitt, *J. Catal.*, 1979, **57**, 476.
20 M. Galàn-Fereres, R. Mariscal, L. J. Alemany, J. L. G. Fierro and J. A. Anderson, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3711.
21 A. M. Banares, L. J. Alemany, J. Luis, M. C. Carmen, M. A. Larrubia, F. Delgado, M. L. Granados, A. Martinez-Arias, J. M. Blasco and J. L. G. Fierro, *J. Solid State Chem.*, 1996, **124**, 69.
22 P. A. Zielinski, R. Schulz, S. Kaliaguine and A. Van Neste, *J. Mater. Res.*, 1993, **8**, 2985.
23 K. Dyrek, A. Rokosz and A. Madej, *Appl. Magn. Reson.*, 1994, **6**, 309.
24 J. E. Spessard, *Spectrochim. Acta, Part A*, 1972, **28**, 1925.
25 A. Davidson and M. Che, *J. Phys. Chem.*, 1992, **96**, 9909.
26 M. C. Paganini, L. Dall'Acqua, E. Giamello, L. Lietti, P. Forzatti and G. Busca, *J. Catal.*, 1997, **166**, 195.

Paper 7/08631H; *Received* 1*st December*, 1997