Semiconductive and redox properties of V$_2$O$_5$/TiO$_2$ catalysts

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The dc electrical conductivities of a series of V$_2$O$_5$/TiO$_2$ samples were measured at 250 °C and observed to be sensitive to the V$_2$O$_5$ loadings: 1, 2, 3, 4 and 6 V$_2$O$_5$ wt.% corresponding to 0.9, 1.8, 2.65, 3.5 and 5.3 V atom%. Up to 3% V$_2$O$_5$ loading (half monolayer), the electrical conductivity, slightly but constantly, increased whereas, for ⩾4% vanadium oxide loading, the electrical conductivity increased dramatically by over one order of magnitude. It was concluded that, for low vanadia loadings, well dispersed fractions of a monolayer could be obtained with a better dispersion than that of Eurocat ones, previously studied with the same technique. It appears that the electrical conductivity provides a sensitive method to determine the total amount of V^{5+} ions incorporated in titania during the preparative calcination. *In situ* measurements of the electrical conductivity during oxygen and methanol cycles suggest that methanol reduces both vanadia and titania. Reduction by the introduction of methanol strongly increases the electrical conductivity of the samples, whereas oxygen decreases the conductivity to the original value. The reproducible conductivity levels indicate the reversible redox process occurring during the exposure of the samples to methanol (reduction) and to oxygen (oxidation). No quantitative relationship exists, between the amounts of dissolved V^{5+} ions detected by the variations in electrical conductivity and the methanol oxidation activity, for this series of V$_2$O$_5$/TiO$_2$ samples. TiO$_2$ appears as a reducible, non-inert support in electronic interaction with supported V$_2$O$_5$.

Several reviews outline the importance of supported V$_2$O$_5$ catalysts in various oxidation reactions concerning mostly the mild oxidation of hydrocarbons and the selective catalytic reduction (SCR) of nitrogen oxides by ammonia in flue gases from stationary sources.[1-3] In these oxidation reactions, it is revealed that V$_2$O$_5$ supported on TiO$_2$ is a better catalyst than V$_2$O$_5$ supported on Al$_2$O$_3$ or SiO$_2$. In addition to the role of the support, the V$_2$O$_5$ loading is also crucial in determining the activity and selectivity of the catalyst. An active catalyst possesses a well dispersed V$_2$O$_5$ phase, which is usually more active and selective than bulk V$_2$O$_5$. The behaviour of certain catalysts have been attributed to various factors: (i) the stability of the surface V$_2$O$_5$ phase on TiO$_2$; (ii) the structure of the deposited V$_2$O$_5$ phase; (iii) the strength and the number of V=O bonds; (iv) the acidity of the surface V$_2$O$_5$ and (v) the ease of reduction of the supported V$_2$O$_5$ catalyst. Electrical conductivity measurements appear as a choice method to better characterise V$_2$O$_5$ deposited on TiO$_2$, especially with regard to points (i), (iii) and (v). Very few electrical studies have been devoted to titania–vanadia systems. Some of them concerned either Ti—V—P—O glasses[4] or Ti—V—O gel coatings,[5] whereas only four references were found to be directly related to titania–vanadia catalysts.[6-9] In ref. 6, the authors studied the electrical conductivity of V$_2$O$_5$–TiO$_2$ mixtures heated at 1023 K and concluded that there was dissolution of some V^{4+} ions in the rutile structure. In ref. 7 and 8, the authors followed the variations in the conductivity of V$_2$O$_5$/SiO$_2$–TiO$_2$ catalysts used in (NO + NH$_3$) deNOx reaction. NH$_3$ was found to be a reducing agent with respect to supported V$_2$O$_5$. Similarly, NO alone behaved as a reducing agent, probably because of the formation of NO$_2$. In the presence of oxygen (or air), it was proposed that NO reacted directly from the gas phase with chemisorbed NH$_3$ following an Eley–Rideal mechanism.

The semiconductive properties of V$_2$O$_5$/TiO$_2$ catalysts were studied for Eurocat catalysts with nominal contents of 1 and 8 wt.% V$_2$O$_5$.[9] It has been found that some V^{5+} ions were able to dissolve in the lattice of TiO$_2$ during the preparation, more precisely during the final calcination, and that the dissolved amount of V^{5+} increased with the nominal content of deposited V$_2$O$_5$. This was subsequently confirmed by chemical analysis. Semiquantitative estimations concerning the amount of dissolved V^{5+} ions could be carried out with the same samples etched in isobutyl alcohol. For these samples, the results of conductivity were in favour of the simultaneous presence of a monolayer of V$_2$O$_5$, of V$_2$O$_5$ particles but also of dissolved V^{5+} ions in the periphery of the support particles.[9] Additionally, it was demonstrated that TiO$_2$ was not an inert support, in contrast to Al$_2$O$_3$ or SiO$_2$, since, under varying partial pressure of oxygen, the formation of anionic vacancies could be observed. Similar results were obtained on V$_2$O$_5$/TiO$_2$ deNOx catalysts prepared by the equilibrium adsorption method.[10]

Here, electrical conductivity was studied to detect possible electronic interactions between carefully designed two-dimensional vanadium oxide species and titania. The molecular structures and reactivities of these surface vanadia species have been extensively investigated over the past few years because of the importance of the applications of such catalytic systems.[11] In addition, methanol oxidation is well known as a sensitive probe reaction to characterise the surface properties of catalysts and the interaction between the deposited surface oxide and the oxide support.[12-15] Therefore, the electrical conductivity of the model V$_2$O$_5$/TiO$_2$ catalysts was followed *in situ* during successive sequences under oxygen and methanol atmospheres, at the same pressures and temperature as those used in catalysis, in order to detect any electronic effect occurring at the surface or at the V$_2$O$_5$/TiO$_2$ interface under working conditions. It can be mentioned that the present catalysts are different from Eurocat ones because of the different nature of the TiO$_2$ supports [Degussa P-25 (50 m^2 g^{-1}) and Thann and Mulhouse (10 m^2 g^{-1}), respectively] and of the preparation procedure.

Experimental

Catalyst preparation and characterization

The V$_2$O$_5$/TiO$_2$ catalysts were prepared by incipient-wetness

impregnation of a solution of vanadium triisopropoxide oxide (Alfa, 95–98% purity) and methanol using TiO$_2$ (P-25, Degussa, 50 m^2 g^{-1}) as the support.[16,17] TiO$_2$ Degussa P-25 consists of non-porous polyhedral particles whose mean size is *ca.* 30 nm. Solutions of known amounts of vanadium tri-isopropoxide oxide and methanol (Fischer-certified ACS, 99.9%) corresponding to the incipient-wetness impregnation volume and the final amount of vanadium required were prepared and mixed with the TiO$_2$ support in a glove-box filled with nitrogen. The impregnated samples were dried at room temperature for 16 h and subsequently heated to 120 °C for 16 h and then at 300 °C for 16 h, all under flowing nitrogen. The final calcination was performed in O$_2$ (Linde, 99.99% pure) and 450 °C for 2 h.

Raman spectra of the catalyst samples were measured to check for the removal of precursor and solvent and compound/crystallite formation. All the samples were found to be well dispersed, unless otherwise mentioned. Half a monolayer and a complete monolayer were estimated to correspond to 3 and 6 wt.% V$_2$O$_5$, respectively.

Electrical conductivity measurements

A sample of V$_2$O$_5$/TiO$_2$ catalyst (95 mg) was placed between two platinum electrodes where it was slightly compressed (*ca.* 10^5 Pa), to ensure good electrical contacts between the grains without modifying the texture or preventing gas–solid interactions on all the surface of the solid. To control the temperature, both electrodes were soldered to thermocouples whose wires were also used, when short-circuited, to determine the electrical conductivity σ of the given powder sample by the formula:

$$\sigma = \frac{1}{R}\frac{t}{S}$$

where R is the electrical resistance measured with an ohmmeter (Kontron, Model DMM 4021) for $1 \leqslant R/\Omega \leqslant 2 \times 10^6$ and with a teraohmmeter (Guildline Instruments Model 9520) for $10^6 \leqslant R/\Omega \leqslant 10^{14}$ and t/S is the geometrical factor including the thickness t (*ca.* 2.5 mm) and the cross-sectional area S of the circular electrodes, whose diameter is equal to 1.00 cm. A general description of this static cell has been given elsewhere.[17]

Results and Discussion

1 Variations in the electrical conductivity of V$_2$O$_5$/TiO$_2$ as a function of surface vanadia coverage

1.1 Definition of a reference state. For (semi)quantitative comparison of the electrical conductivities of the various supported vanadia samples, it is necessary for the solids to have similar textures and identical surface states. This requirement is easily fulfilled, since all the samples have the same support (TiO$_2$ Degussa P-25, mainly anatase). Indeed, the electrical conductivity of a n-type semiconductor power can be written as:

$$\sigma = A[\text{e}^-] \qquad (1)$$

where [e$^-$] is the concentration of quasi-free electrons and A is a textural parameter, which depends on the compression of the powder and on the number and quality of contact points between particles.[17] Because of the nature of the procedure for electrical measurements and of the use of the same TiO$_2$ support, A can be considered to be the same for all the samples under identical conditions.

The common reference state for σ determination has been chosen with the following conditions: 100 Torr oxygen at 250 °C (1 Torr = 133.3 Pa). It has the advantages of (i) eliminating most of the ionically adsorbed species such as H$_3$O$^+$,

OH$^-$, which would produce an additional surface conductivity and (ii) avoiding the formation of surface structure defects, such as anionic vacancies, whose ionization produces additional free electrons, which could mask or perturb the possible electronic interaction between vanadia and titania under neutral conditions.[9] In addition, these conditions are identical to those used in the catalytic oxidation of methanol.[18] The solid was first outgassed for 10 min at room temperature before introduction of 100 Torr O$_2$ and then heated to 250 °C at a heating rate of 5 °C min^{-1}.

1.2 Variations in the steady-state conductivity as a function of surface vanadia coverage. The values of the electrical conductivity σ of V$_2$O$_5$/TiO$_2$ measured at steady state at 250 °C are presented in Fig. 1. 6% V$_2$O$_5$/TiO$_2$ corresponds to a monolayer of surface vanadia species on the TiO$_2$ support.[11] The variations in σ as a function of V$_2$O$_5$ wt.% indicate the presence of three domains: (i) a linear increase of σ *vs.* V$_2$O$_5$ wt.% for $0 \leqslant$ V$_2$O$_5$ (wt.%) $\leqslant 3$. (ii) A slightly steeper increase between 3 and 4 wt.% V$_2$O$_5$ and (iii) a strong increase between 4 and 6 wt.% V$_2$O$_5$, of more than one order of magnitude. Note that trace amounts of crystalline V$_2$O$_5$ particles are present for the 6% V$_2$O$_5$/TiO$_2$ sample.

1.3 Interpretation of $\sigma = f$ (surface vanadia coverage). In a mixture of two conducting oxides, the overall conductivity of the sample becomes governed by the more conducting component at concentrations above a certain percentage, called the percolation threshold.[19] This corresponds to a minimum relative amount, above which the electrical conductivity can be established through preferential paths along the sample constituted exclusively of the more conductive minority phase. It has been estimated to be close to 40% for a mixture of oxides of similar texture (particle size and shape).[20,21] It can also be suggested, in the case of a deposited oxide, that the conductivity data might be explained by a percolation threshold, when the surface coverage of the titania particles reaches a point where there is a connected path from particle to particle that runs through a more conducting V$_2$O$_5$ surface. Such a 'surface percolation threshold' problem has been previously analysed for Sb$_2$O$_4$/SnO$_2$ [22] and for Pt/TiO$_2$.[23,24] For Sb$_2$O$_4$/SnO$_2$, it was expected that the conductivity of SnO$_2$ would decrease sharply when the increasing Sb content corresponded to a monolayer of poorly conductive Sb$_2$O$_4$.
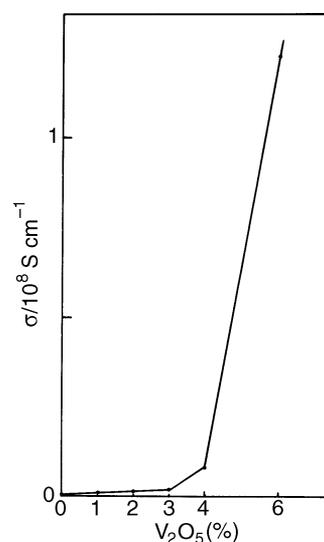
Fig. 1 Variations in the electrical conductivity of the V$_2$O$_5$/TiO$_2$ samples as a function of the percentage of deposited vanadia (T = 250 °C; P_{O_2} = 100 Torr)

Actually, the deposition of Sb_2O_4 gave a strong increase in conductivity because of the n-type doping of SnO_2 by Sb^{5+} ions. For Pt/TiO_2 catalysts with metal loadings as high as 10 wt.%, one could have expected an increase in conductivity, because of a possible improvement in the surface conductivity and in the quality of the intergranular contact points. In fact, the reverse was observed, with a decrease in conductivity[23] or in photoconductivity[24] when the amount of Pt was increased from 0 to 10 wt.%. This was explained by an electron transfer from titania to Pt. These two examples illustrate the fact that, in a supported catalyst, the electrical conductivity is mainly that of the support (in electronic interaction with the supported phase).

In the present case, the above considerations strongly suggest that the overall conductivity measured is essentially that of the support, *i.e.* of titania which is an n-type semiconductor.[17] The variations in conductivity for mixed[25,26] or for supported oxides[22] are generally attributed to a doping effect. This phenomenon results from the dissolution of heterovalent ions in the lattice of the host oxide, which creates free charge carriers (electrons or holes) according to the valence induction law.[27] This dissolution is favoured by calcination, at high temperature, of the support impregnated with the precursor of the deposited oxide. For an n-type semiconductor such as TiO_2, an increase in σ results from the dissolution of a heterocation with a valence higher than 4.

In agreement with the results of ref. 9, it can be proposed that the deposition of vanadia, by impregnation and calcination at 450 °C, is accompanied by a partial dissolution of V^{5+} ions in the surface sublayers of TiO_2. The substitution of a Ti^{4+} ion by a V^{5+} ion induces a free electron of conduction according to the following scheme:
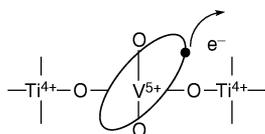
If pentavalent V^{5+} ions are inserted into tetravalent sites, they can only share four valence electrons with four O^{2-} neighbour ions. The fifth electron cannot be shared and is delocalized around the V^{5+} positive centre. Only a small thermal energy is needed to delocalize this electron and promote it into the conduction band. This can be written as:

$$[(V^{5+})e^-] \rightleftharpoons (V^{5+}) + e^- \qquad (2)$$

or

$$D \rightleftharpoons D^+ + e^- \qquad (3)$$
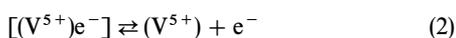
where D represents a donor centre and D^+ its ionized form.

For the V_2O_5/TiO_2 system, it seems that more free electrons are liberated as the amount of deposited V_2O_5 increases, but with different behaviours according to the amount of V_2O_5. For $V_2O_5 \leqslant 3$ wt.%, σ increases linearly with the amount of V_2O_5, but the increase of σ is much less than that of a sample doped in the bulk.[24] By contrast, σ increases strongly for $V_2O_5 > 4$ wt.%. The amounts of dissolved, isolated V^{5+} ions in the first sublayers of titania, cannot be determined quantitatively, since no calibrated V^{5+}-doped titania Degussa P-25 samples are available. Such a determination could be performed in the case of Eurocat catalysts since reference doped solids (etched samples) were available for calibration with dissolved amounts of V^{5+} ions carefully determined by chemical analysis. A rough estimation of the order of magnitude of the amount of dissolved V^{5+} ions could be made if it is assumed that the relative variations $d\sigma/d[V^{5+}(dissolved)]$ due to doping are similar for both families of solids. Such a comparative estimation gives an amount of V^{5+} ions dissolved in titania as *ca.* 10^{-2} atom% for nominal V_2O_5 contents $\leqslant 3$ wt.%. This value is very low and indicative

of a well dispersed V_2O_5 phase at the surface of titania, with only trace amounts of V^{5+} dissolved. This estimation is comparable to that found in ref. 10. From the electrical conductivity results obtained, the present catalysts can be described as follows.

For low amounts of V_2O_5 ($\leqslant 3$ wt.%), the design of a uniform V_2O_5 overlayer on titania has been successfully obtained *i.e.* more than 99.99% deposited vanadia is present at the surface of TiO_2. There are only traces of V^{5+} dissolved.

For 4 and 6 wt.% V_2O_5, the amounts of dissolved V_2O_5 increase more abruptly as a function of the nominal content. According to ref. 9, this means that, above 3 wt.% V_2O_5, the model of a uniform overlayer does not apply integrally and that some V_2O_5 particles are progressively formed, whereas more V^{5+} ions penetrate the periphery of titania particles. The amounts of V^{5+} dissolved correspond to isolated ions in the sublattice of TiO_2, in substitutional positions with respect to Ti^{4+} sites. They can be present on the whole periphery of titania particles but also at the interface of V_2O_5 particles with the support.[9]

The dissolution of V^{5+} ions seems to be directly connected to the amount of vanadia deposited. The higher concentration of vanadia precursor is the driving force for V^{5+} ion incorporation, by substitution in the lattice of titania during the preparative calcination of the sample. It can be noted that the three domains appearing in Fig. 1 may correspond to those determined by Raman spectroscopy[18,28] but, since V^{5+} ions are not detectable by Raman spectroscopy, it is not possible to establish unequivocally a correlation between the Raman and the conductivity domain. At low loadings (*ca.* 1 wt.% V_2O_5), a single sharp band has been found at *ca.* 1030 cm^{-1}, is due to an isolated four-coordinated surface vanadium oxide species containing one terminal V=O bond and three bridging V—O—Ti bonds.[18,28] Correspondingly, there is a very small V^{5+} dissolution linked to the small slope of the first domain in Fig. 1. At intermediate loadings (2–6 wt.% V_2O_5), a second band is present at *ca.* 930 cm^{-1} which has been assigned to a polymerized four-coordinated surface vanadium species.[15,18] These higher concentrations of deposited V_2O_5 species correspond to a greater quantity of V^{5+} ions dissolved, as indicated by the steeper slope of the second domain in Fig. 1. At high loadings ($\geqslant 6$ wt.% V_2O_5), a third sharp band is present at 994 cm^{-1}, due to crystalline V_2O_5. These highest quantities of deposited vanadia and the presence of vanadia particles, correspond to a much larger number of dissolved V^{5+} ions, illustrated by the steep slope of the third domain (Fig. 1).

Because of the valence induction law,[27] electrical conductivity measurements enable one to detect minute amounts of dissolved V^{5+} ions. Actually, this does not exclude the possible simultaneous presence of dissolved V^{4+} ions but, since these latter ions are isoelectronic with Ti^{4+}, they cannot be detected by this technique. However, since dissolution occurs during the preparative calcination, which is highly oxidative, it can be suggested that most of the dissolved vanadium ions are V^{5+}. Stabilised V^{4+} ions in the rutile structure are observed for higher preparation temperature,[6] above the anatase–rutile transformation threshold.

2 *In situ* electrical conductivity study of V_2O_5/TiO_2 during successive sequences in oxygen and methanol

2.1 Procedure. The catalysts were placed in the reference state determined in Section 1: heating in 100 Torr O_2 at a heating rate of 5 °C min^{-1} up to a final temperature of 230 °C, chosen equal to that used for catalytic tests. After outgassing oxygen, methanol was introduced under a pressure of 45.6 Torr, corresponding to that used in catalysis. After reaching the steady state under methanol, the alcohol was removed and replaced by pure oxygen (100 Torr) to follow the reoxidation

of the catalyst. These sequences were repeated twice to study the reversibility of the redox processes occurring at the surface of the solid. The reaction of methanol oxidation was hence followed *in situ*, but sequentially in separate O_2 and CH_3OH atmospheres for two reasons. First, the electrodes are made of platinum, chosen for its good electrical properties and for its chemical stability and inertness. However, it is not catalytically inactive in the total oxidation reactions and the total number of exposed surface Pt atoms estimated equal to 3.87×10^{15} (6.4 nmol Pt_S) may induce a side catalytic activity in the total oxidation of methanol, which could perturb the *in situ* measurements of the V_2O_5/TiO_2 samples. Secondly, separate sequences give more precise information on the true effect of each reactant upon the electrical properties of the solids.

Two samples were chosen for comparison, one with a low V_2O_5 content (1 wt.%) and the other with the highest content (6 wt.%). The titania support was tested under similar conditions to detect, by difference with V_2O_5/TiO_2 samples, possible electronic interactions in the frame of surface oxide–support interactions (SOSI).[15]

2.2 *In situ* variations of σ during various O_2–CH_3OH sequences. The *in situ* electrical conductivity variations for the three solids are presented in Fig. 2. For clarity, the initial times ($t = 0$) corresponding to the first introductions of methanol were slightly shifted for each curve. It can be observed that exposure to methanol strongly increases the electrical conductivity of each sample, whereas oxygen produces the opposite effect. The repetition of the various sequences results in reproducible conductivity levels, which is indicative of reversible redox processes. The different curves and sequences can be interpreted as follows.

2.2.1 *First sequence in* 100 *Torr* O_2 *at* 230 °C. The steady-state conductivity in 100 Torr O_2 gives results similar to those obtained at 250 °C in Section 1: $\sigma(TiO_2) \leqslant \sigma(1\% V_2O_5/TiO_2) \ll \sigma(6\% V_2O_5/TiO_2)$. They confirm the presence of only trace quantities of dissolved V^{5+} in TiO_2 for 1% V_2O_5/TiO_2 and of substantial quantities for 6% V_2O_5/TiO_2, because of the difference of two orders of magnitude in σ, indicative of a strong n-type doping. The n-type semiconductor character for all three solids was confirmed by the increase of σ during outgassing ($d\sigma/dP_{O_2} < 0$) (Fig. 2).
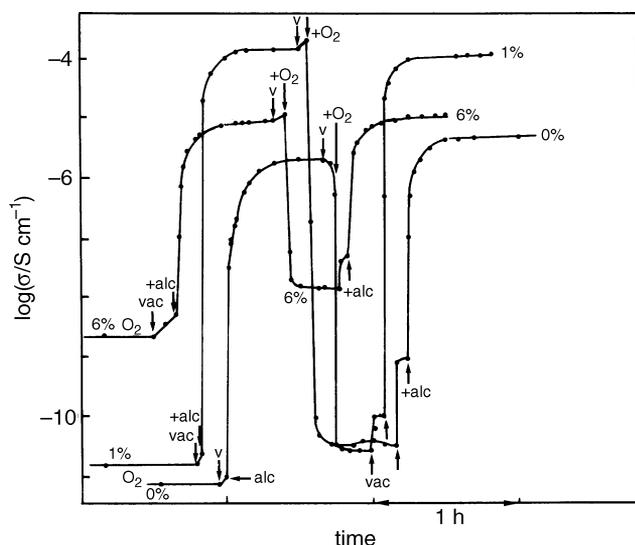
Fig. 2 Semilogarithmic plot of the kinetics of electrical conductivity variations measured at 230 °C during various sequences in 100 Torr O_2 and in 45.6 Torr CH_3OH (+ alc). Each sequence is separated by a brief outgassing, indicated by vac or v.

2.2.2 *First sequence in methanol* (45.6 *Torr*). The introduction of methanol sharply increased σ for all three solids by several orders of magnitude. A steady state was reached within 20–30 min and corresponded to the order: $\sigma(TiO_2) < \sigma(6\% V_2O_5/TiO_2) < \sigma(1\% V_2O_5/TiO_2)$.

The increase in $\sigma(TiO_2)$ under methanol indicates that titania is not an inert support under catalytic conditions, although the turnover frequency (TOF) for V_2O_5/TiO_2 is much more important than that of TiO_2 during methanol oxidation. It has been found that naked titania produced dimethyl ether plus CO_2 instead of methanal on V_2O_5/TiO_2.[29] The strong increase in $\sigma(TiO_2)$ can be ascribed to different sources of electrons. Free electrons can arise from the creation of anionic vacancies, V_O, by reduction of the surface by methanol:

$$3(O_s^{2-})^O + CH_3OH \rightarrow CO_2 + 2H_2O + 3V_O \qquad (4)$$
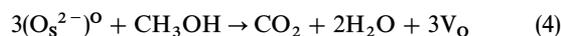
followed by the ionization of the first electron

$$V_O \rightleftarrows V_O^+ + e^- \qquad (5)$$

$(O_s^{2-})^O$ represents a surface anion of the surface. The zero-charge superscript indicates that it is a neutral entity with respect to the solid. V_O represents a filled anionic vacancy and V_O^+ a singly ionized anionic vacancy.

The second possible source of quasi-free electrons in titania can originate from the consumption of negatively charged adsorbed species, such as oxygen ionosorbates [O_2^- (ads), O^-(ads) or O^{2-}(ads).]. If O^-(ads) seems to be the most probable ionosorbed species to be consumed at 230 °C, the corresponding reaction would be:

$$CH_3OH + 3 O^-(ads) \rightarrow CO_2 + 2 H_2O + 3e^- \qquad (6)$$

It is difficult to choose definitively between eqn. (4) and (6). However, at the end of the sequence under methanol at 230 °C, titania remains white, which means that its surface reduction is limited and that the consumption of O^- species seems more probable.

By contrast, V_2O_5/TiO_2 samples are much more conducting than the TiO_2 support alone. This is confirmed by the fact that, at the end of the CH_3OH period, 1% V_2O_5/TiO_2 is greyish in colour, whereas 6% V_2O_5/TiO_2 is dark grey, thus indicating that the supported vanadia has been partly reduced. Since the conductivity measured is that of the support (see Section 1.3), the higher conductivity of V_2O_5/TiO_2 must be due to some electron transfer from reduced surface vanadia species to the titania support.

This electron transfer is spontaneous and can be easily explained. When vanadia is reduced, the electron concentration increases and the Fermi level of the oxide goes up. Since vanadia is more reducible than titania (see ref. 30, ch. 3.5), its Fermi level increases more significantly than that of titania, thus creating a spontaneous electron transfer to titania.

$$e^-(V_2O_5) \rightleftarrows e^-(TiO_2) \qquad (7)$$
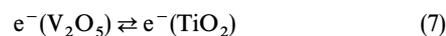
The alignment of the Fermi levels of both phases corresponds to that described for vanadia[31] and bismuth molybdates,[32] both deposited on titania. The higher conductivity level for the smaller content (1%) under methanol (Fig. 2) is indicative of a stronger electron donor effect. This can be related to the higher dispersion degree of deposited vanadia, which is in agreement with the model of an overlayer of V_2O_5 without bulk particles[18,28] without appreciable dissolution of V^{5+} in TiO_2, as deduced from Section 1.3.

The influence of the presence of vanadia at the surface of titania can be seen during the prompt outgassing of methanol: $\sigma(V_2O_5/TiO_2)$ increases, whereas $\sigma(TiO_2)$ decreases (Fig. 2). The pumping of the gas phase increases the transfer from reduced vanadia to titania. This could be due to the removal of some electrophilic oxygenated compounds from the surface.

Alternatively, the decrease in $\sigma(TiO_2)$ could be due to the removal of OH groups, whose presence favours surface conduction, probably with the participation of some protons.

2.2.3 *Second period under oxygen.* The introduction of oxygen drastically decreases σ for all three samples, indicating a strong reoxidation of the surface. However, the final σ level, measured at steady state, is significantly higher than that obtained at the end of the pretreatment (sequence 1). This indicates that a certain degree of reduction persists in O_2 after the first period in methanol and this cannot be eliminated by 100 Torr oxygen at 230 °C. This effect seems more pronounced for the 6% V_2O_5/TiO_2 sample.

For the TiO_2 support alone, the decrease in σ can be attributed to various electron-consuming reactions involving oxygen such as (i) the filling of anionic vacancies:

$$\tfrac{1}{2}O_2(g) + V_O^+ + e^- \rightarrow (O_s^{2-})^0 \qquad (8)$$
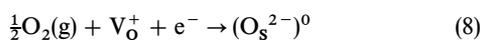
and/or (ii) the reconstitution of the initial pool of ionosorbed oxygen species

$$O_2 + e^- \rightarrow O_2^- \qquad (9)$$

$$O_2 + 2e^- \rightarrow 2O^- \qquad (10)$$

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \qquad (11)$$

For V_2O_5/TiO_2, the decrease in σ can be ascribed to two simultaneous phenomena: (i) the reoxidation of the support as described above [eqn. (8)–(11)] and (ii) the reoxidation of reduced vanadia which requires the restitution of some free electrons from titania.

$$e^-_{(TiO_2)} \rightleftarrows e^-_{(V_2O_5)} \qquad (12)$$

or:

$$2x\, e^-_{(TiO_2)} + \frac{x}{2}O_2 + V_2O_{5-x} \rightarrow V_2O_5 \qquad (13)$$
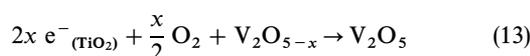
2.2.4 *Second sequence under methanol.* The kinetic curves $\sigma = f(t)$ under methanol for both V_2O_5/TiO_2 samples are quite reproducible (Fig. 2). This indicates that the reduction of vanadia and the correlative electron transfer to titania correspond to a reversible redox process at the surface of the biphasic solids.

The highest σ value is obtained for 1 wt.% V_2O_5/TiO_2 which primarily contains vanadium oxide monomers at the surface of titania. It can be suggested that the reduction of V_2O_5 monomers occurs at the bridging V—O support bonds which are very numerous in this highly dispersed sample
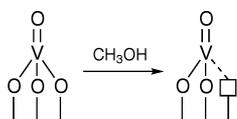
The oxygen vacancy thus generated would lose at least one electron by transference to the support, thus increasing the conductivity of the whole sample (Fig. 2).

It can be mentioned that these conductivity results agree qualitatively with those of Morrison, who found an increase in conductivity and in the Fermi level for V_2O_5/TiO_2 catalysts when exposed to 1 Torr xylene and for Fe–Mo–O/TiO_2 catalysts when exposed to 12 Torr methanol at 250 °C.[31]

3 Comparison of conductivity measurements with methanol oxidation activity

The variation in the electrical conductivity, σ, of the series of monolayer V_2O_5/TiO_2 catalysts indicates a strong dependence of σ on V_2O_5 loading (coverage). Up to 3% V_2O_5, the conductivity constantly increases with the increase in vanadium oxide coverage. However, for $\geqslant$4% V_2O_5 the conductivity increases steeply, by over one order of magnitude, up to

6% V_2O_5 where a small amount of bulk V_2O_5 is present on the TiO_2 surface. Catalytically, however, the V_2O_5/TiO_2 samples behave differently during the methanol oxidation reaction.

The methanol oxidation reaction is known to probe the redox activity of the surface metal oxide species.[29] Methanol oxidation over monolayer V_2O_5/TiO_2 catalysts indicate that the TOF, which is a measure of the efficiency of each surface vanadium oxide site, is independent of the vanadium oxide loading, and the activity [moles of methanol converted (g catalyst time)$^{-1}$] increases linearly with vanadium oxide loading until monolayer coverages are reached. Thus, comparison of the electrical conductivity with the redox activity of the surface vanadium oxide phase suggests that no direct and quantitative relationship exists, since σ depends strongly on the vanadium oxide loading, whereas the methanol oxidation activity varies linearly with vanadium oxide loading up to monolayer coverages. Electrical conductivity measurements indicate qualitatively that both V_2O_5 and TiO_2 undergo redox cycles under methanol and oxygen and remain permanently in electronic interaction.

Conclusions

Measurement of electrical conductivity appears to be a sensitive method to determine the amounts of dissolved V^{5+} ions in the periphery of particles of titania or at the V_2O_5/TiO_2 interface. Below 4% V_2O_5, V_2O_5 could be successfully deposited (*ca.* 99.99%) as a surface overlayer on titania. Only traces of V^{5+} were dissolved in titania, the amounts being proportional to the nominal percentages of V_2O_5. For V_2O_5 $\geqslant$ 4%, the amount of dissolved V^{5+} increased drastically. This would correspond to the beginning of the existence of V_2O_5 particles in addition to the V_2O_5 overlayer, with a corresponding increase in V^{5+} ions dissolved, probably at the V_2O_5/TiO_2 interface, as suggested in ref. 9.

Under successive sequences in oxygen and methanol, the surface of V_2O_5/TiO_2 followed reversible redox processes. Methanol reduced both vanadia and titania. The reduction of the support involves either lattice anions, thus forming anionic vacancies, or ionosorbed oxygen species, and accounts for its own catalytic activity. The high increase in σ in methanol for 1% V_2O_5/TiO_2 supports the idea of a highly dispersed vanadia phase. The higher reduction of vanadia causes electron transfer to titania, explaining the higher conductivity of vanadia-containing samples.

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