Reply to the Comment on "Sintering and Phase Transformation of V-Loaded Anatase Materials Containing Bulk and Surface V Species"

J. P. Balikdjian, A. Davidson, S. Launay, H. Eckert, and M. Che

Laboratoire de Réactivite de Surface, UMR 7609 CNRS, Université Pierre et Marie Curie, Paris, 75252 Cedex 05, France

We are grateful to Gopinath and Raja for their comment[1] on our paper[2] and to have drawn our attention to the inconsistencies of Figure 4. We sincerely apologize for the inconvenience we may have caused to the readers of our paper.

The main point of contention of Gopinath and Raja finds its origin in the XP spectra of Figure 4 which led them to rebut our conclusion that a bulk to surface migration of vanadium occurs in V-containing anatase samples prepared by a sol−gel method under an Ar flow. Their rebutal is mainly based on XPS arguments and on Figure 4 which contains errors, as discussed below. In contrast, all of the XPS data are correctly quoted in the text and Table 2 of our paper taking Ti2p3/2 at 459.0 eV as reference, following the recommandations of the EUROCAT Oxide group for XPS measurements of V_2O_5/TiO_2 catalysts.[3] We want to stress that our conclusion was derived from a study involving chemical analysis and seven physical techniques (XRD, TEM, N_2 sorption, XPS, Raman, ESR, and ^{51}V NMR).

In their comment, Gopinath and Raja present several arguments which we now would like to discuss:

(1) Gopinath and Raja are entirely correct in saying that the XP spectra of Figure 4 are not consistent with the XPS values quoted in the text. In the corrected version of Figure 4 (see Additions and Corrections, this issue), the XP spectra are now associated with the correct binding energy scales and with the correct labeling of the samples. The two top spectra refer to V-free C450 sample (calcined at 450 °C) and show the O1s and Ti2p peaks, whereas the bottom spectrum refers to V-loaded C900−0.06 sample (calcined at 900 °C, V/Ti atomic ratio of 0.06) and shows the O1s and V2p peaks.

(2) In their comment, it is suggested that "hardly any migration of vanadium to the surface takes place upon calcination". This conclusion is not valid because it is based on the incorrect version of Figure 4. To confirm our conclusion, we show on the additional Figure 1 survey XP spectra (between 700 and 300 eV) of V-free C450 and V-loaded C450−0.06 and C900−0.06 samples. On this figure, the intensity of the V2p signal, weak with C450−0.06, is clearly increased with the C900−0.06 sample. This increase of intensity with the calcination temperature confirms that a bulk to surface migration of the V species takes place upon calcination. This fact is in line with our conclusion that a migration of the V species to the surface occurs. This migration is one of the main results of our study.

(3) The reasoning proposed by Gopinath and Raja to calculate the atomic V/Ti ratio at the surface of the C900−0.06 sample, based on either photoionization cross-section coefficients or a ratio of empirical sensitivity factors derived from measurements performed on pure vanadia and titania references,[4] is correct but applied to a figure containing errors.
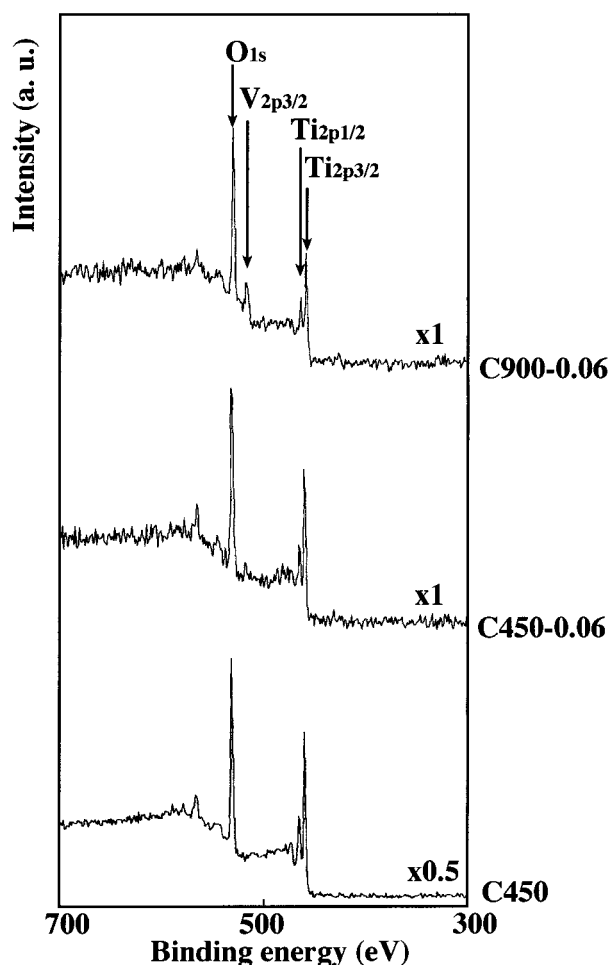
Figure 1. Survey XP spectra (700−300 eV) of V-free C450 and V-loaded C450−0.06 and C900−0.06 samples.

Many authors have discussed the uncertainties made on the measurements of concentrations of surface species (see refs 3−6) when using sensitivity coefficients for the V_2O_5/TiO_2 system. Thus, only ratios of surface areas of XPS peaks were given in our paper (Table 2). The S_V/S_{Ti} ratio values quoted were obtained by numerical integration of the V2p and Ti2p XPS peaks after subtraction of a Shirley-type background, using a software provided by the instrument manufacturer. Because of baseline correction, important variations in peaks areas were observed (up to 15% variation), leading to a 0.53 ± 0.10 value in the case of the C900−0.06 sample.

To complement our earlier results, spectra simulations have been performed with a more elaborated software (WINPLOT, LISE laboratory). The additional Figure 2 gives the results of this simulation for V2p and Ti2p peaks of C450−0.06 and C900−0.06. With C450−0.06, the V2p contribution is very weak. With C900−0.06, the V2p signal is much more intense. The V2p3/2 peak, largely asymmetrical, led us to consider the coexistence of V^V and V^{IV} species. A simulation with three distinct components (two resolved V^V 2p3/2 and V^{IV} 2p3/2 contributions + one unresolved (V^V2p1/2, V^{IV}2p1/2) contribution) is presented. The binding energies of V^V 2p3/2 and V^{IV} 2p3/2 peaks (517.3 and 516.2 eV respectively, with an error of ±0.5 eV) are in agreement with the binding energies given in Table 2 of our paper and with current literature.[3]
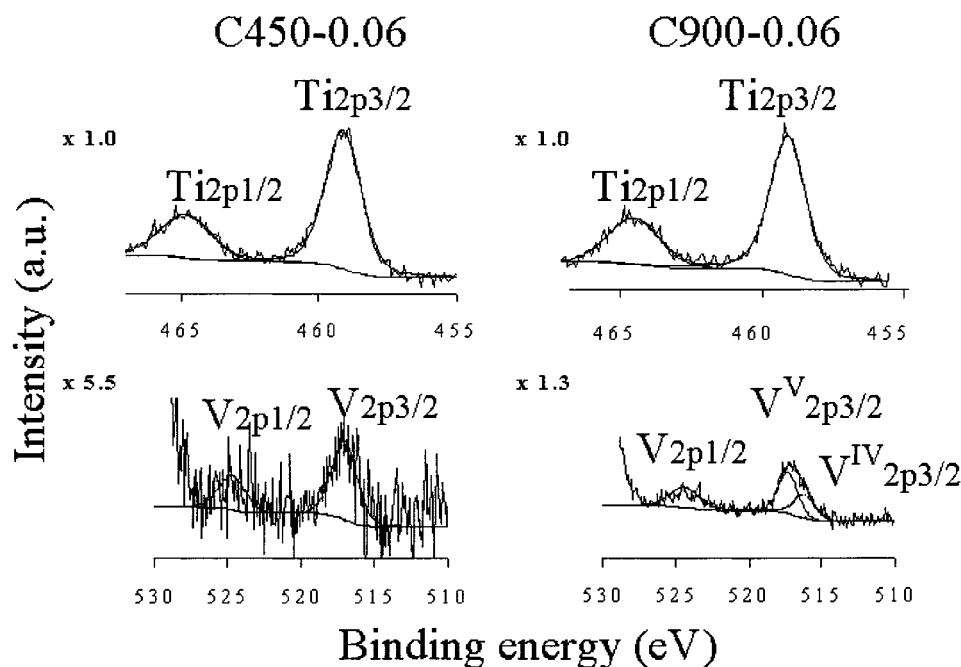
Figure 2. V2p and Ti2p peaks simulations of C450−0.06 and C900−0.06 samples.

Because, in all of the spectra, the V2p1/2 contribution is very small, we have measured only the R_3 and R_4 surface area ratios, corrected by sensitivity factors (V: 2.69 and Ti: 2.39) as defined by Bond et al.,[6] with R_3 = V2p3/2/Ti2p1/2 and R_4 = V2p3/2/Ti2p3/2. Following the method of Bond et al.,[6] R_3 has been scaled to R_4 and the adjusted R_3 and R_4 values were averaged to obtain mean $R_{3,4}$ values. These values for C450−0.06 and C900−0.06 have been found to be equal to 0.11 and 0.41, respectively. Interestingly enough, the value obtained with C900−0.06 is very near to that (0.45) reported by Bond et al.[6] for a V_2O_5/TiO_2 sample obtained by impregnation and corresponding to an atomic V/Ti ratio near 0.06 (6 wt % of vanadia). These observations confirm that, upon calcination, there is a migration of vanadium species from the bulk toward the surface of titania grains and indicate that this migration, already detected at 450 °C, yields to a nearly complete segregation of vanadia onto the titania surface after calcination at 900 °C.

(4) We now consider "the incomplete phase transformation of anatase to rutile" that we have observed for a sample with V/Ti molar ratio of 0.06 after an "in situ" heat treatment at 900 °C. The calibration of temperature that we have used appears to be correct because the evolution of the XRD data as a function of temperature on a V-free titania reference leads to a temperature of transformation to rutile located within the range of 600−700 °C, in agreement with reports of several other groups (for anatase particles of similar size, see ref 7 and references therein for instance).

(5) In the comment, the authors state that the "formation of Magneli phases with defective rutile structures and that cannot be distinguished experimentally by XRD cannot be ruled out". It appears that no Magneli phases are formed in our samples (prepared under flowing oxygen at temperature lower than 900 °C) because the formation of nonstoichiometric Magneli phases would require a reducing atmosphere and a very high temperature (typically of the order of 1000 °C for titania[8]). Furthermore, there is no evidence of Ti(III) ions by ESR, even at low recording temperature (77 K), and the XP peaks of Ti(IV) ions are symmetrical confirming that no Ti(III) ions are present.

(6) Gopinath and Raja state that "the nature and surface composition of the V/TiO₂ samples prepared in ref 1 is different

from the same material prepared by other groups". The differences are due to the use of a V^{IV} precursor (vanadyl(IV)-acetylacetonate) but also of an inert atmosphere of argon (to avoid reoxidation during the course of the gelification step) to prepare materials by a sol−gel method. The samples thus obtained contain mainly bulk V^{IV} species detected by ESR. These samples are therefore totally different from the ones prepared by other groups and which contain surface V^V species (e.g., EUROCAT TiO₂/V₂O₅ catalysts, EL10V8:[9] impregnation of anatase by vanadyl oxalate; Olivieri et al.:[7] impregnation of titania by ammonium metavanadate). It is therefore not surprising to observe that the behavior of our samples upon calcination is different. Thus, in contrast to what Gopinath and Raja state, our results do not contradict the ones published by other groups, because they concern samples prepared by a different method.

(7) We agree with Gopinath and Raja that "the V influences the structure of anatase to assist to increase in domain size". This is clearly indicated in Table 1 of our paper. Indeed, the specific surface area of the anatase grains obtained by calcination at 450 °C is divided by three when comparing V-free C450 and V-loaded C450−0.06 (atomic V/Ti ratio of 0.06 by chemical analysis, V on the surface seen by XPS). However, we do not agree with the attribution of this increase of domain size to the incorporation of V within the anatase bulk. We rather associate the increase of domain size with the presence of V surface species because no clear difference is observed between the specific surface area of C450 and of C450−0.02 (atomic V/Ti ratio of 0.02, V species are in anatase bulk because XPS fails to detect surface V species).

In conclusion, the comment of Gopinath and Raja,[1] essentially based on XPS arguments, is justified because it was based on the errors contained in Figure 4 of our paper.[2] The errors detected in Figure 4 have been corrected, and additional information about the quantifications made on the XP spectra has been provided. Some independent criticisms made in the comment[1] have been discussed too.

We would like now to insist on the fact that V_2O_5/TiO_2 catalysts are heterogeneous (anatase, rutile, $V_xTi_{(1-x)}O_2$ solid-solutions, vanadia monolayer domains spread on the titania

Comments

J. Phys. Chem. B, Vol. 105, No. 49, 2001 **12431**

surface, vanadia towers extending either directly from bare titania or from vanadia monolayer domains[3-6]). It is therefore difficult to obtain a complete picture of their surface by using one technique only. For this reason, we have characterized our samples by seven independent physical techniques (XRD, TEM, N_2 sorption, XPS, Raman, ESR, and [51]V NMR) associated with chemical analysis results. The main conclusion of our paper is that V species, mainly occluded within the anatase grains after calcination at 450 °C, migrate to the surface upon calcination at 900 °C and that the surface V species assist the transformation of anatase to rutile. On the basis of our earlier results[2] completed by the additional information presented in this comment, the conclusion of our paper is confirmed.

References and Notes

(1) Gopinath, C. S.; Raja, T. *J. Phys. Chem. B* **2001**, *105*, 12427.

(2) Balikdjian, J. P.; Davidson, A.; Launay, S.; Eckert, H.; Che, M. *J. Phys. Chem. B* **2000**, *104*, 8931−8939.

(3) Nogier, J. P.; Delamar, M. (compilers) *Catal. Today* **1994**, *20*, 109−124.

(4) Nogier, J. P.; Jammul, N.; Delamar, M. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *56*, 279−295.

(5) Nogier, J. P.; De Kersabiec, A. M.; Fraissard, J. *Appl. Catal. A* **1999**, *185*, 109−121.

(6) Bond, G. C.; Perez Zurita, J.; Flamerz, S. *Appl. Catal.* **1986**, *27*, 353−362.

(7) Olivieri, G.; Ramis, G.; Busca, G.; Escribano, V. S. *J. Mater. Sci.* **1992**, *3*, 1239−1249.

(8) Bursill, L. A.; Hyde, B. G.; Terasaki, O.; Watanabe, D. *Philos. Mag.* **1969**, *20*, 347−359.

(9) See, EUROCAT Oxide Group *Catal. Today* **1994**, *20*; Chapter 2.