JOURNAL OF CATALYSIS **116**, 586–589 (1989)

NOTES

On the Surface Structure of Vanadia–Titania Catalysts: Combined Laser–Raman and Fourier Transform–Infrared Investigation

V–Ti oxides represent an important class of commercial catalysts for several reactions including oxidation and ammoxidation of aromatics and methylaromatics (*1*, *2*) and selective catalytic reduction of NO_x by NH_3 (*3*). These systems have also been found to be effective catalysts for the oxidation of methanol to methyl formate (*4*, *5*).

Depending on the V/Ti atomic ratio and the preparation procedure, different phases have been detected, namely pure TiO_2 anatase, pure TiO_2 rutile, V_2O_5, lower vanadium oxides, and solid solutions of V^{4+} in both rutile and anatase forms of TiO_2 (*6*–*10*). Particular interest has been devoted to the so-called TiO_2 anatase monolayer catalysts, where the vanadium oxide is supposed to be dispersed in a monomolecular layer on the support, and different surface models have been proposed. Véjux and Courtine (*11*) suggested that the remarkable crystallographic fit of the (010) face of V_2O_5 with the (001) face of TiO_2 anatase is responsible for the specific reactivity of the vanadia–titania surface. This would imply a nearly octahedral coordination of vanadium. This picture is consistent with the results of recent TEM investigations (*12*, *13*). Wachs *et al.* (*14*), primarily from laser–Raman data, suggested the presence of tetrahedral dioxovanadium centers. This surface model was also proposed by Kozłowski *et al.* (*15*) and Haber *et al.* (*16*) on the basis of EXAFS measurements, while it has been slightly modified by Bond and co-workers (*17*), who proposed tetrahedral oxohydroxy vanadium sites. Other authors using several different techniques including EPR, FT–IR, and DR–UV–Vis spectroscopy provided evidence for the presence of nearly octahedral monooxo VO^{2+} species (*18*–*21*).

In this note new laser–Raman data are reported and compared with FT–IR results. The aim was to verify the surface models already proposed in the literature for V–Ti oxide monolayer catalysts (prepared by impregnation) using a complete set of vibrational data. The question whether these models apply to catalysts prepared by precipitation is also addressed. The precipitation method might be preferred when materials with homogeneous distribution of the constituents are required, as is the case for industrial catalysts experiencing severe erosion problems during operation. Accordingly, two catalyst samples quoted as A and B were considered. Sample A (V_2O_5 nominal content = 7.9% w/w; surface area = 37 m^2/g) was prepared by precipitation at room temperature from $VOCl_3$ and $TiCl_4$ (pH = 8), followed by drying and calcination at 873 K (*5*). The sample was found to consist of a solid solution of V^{4+} in TiO_2 anatase and surface vanadyl species (*5*, *10*). Sample B (V_2O_5 nominal content = 10% w/w; surface area = 48 m^2/g) was prepared by impregnation of TiO_2 Degussa P25 with a solution of NH_4VO_3, drying, and calcination at 723 K. XRD showed that the sample consists of TiO_2 anatase (90%) and rutile, in relative amounts unchanged with respect to those of the pure support, and of small amounts of V_2O_5. Raman spectra were recorded with a Dilor multichannel spectrometer Omars-89 equipped with an array of 512 diodes and microscope Olympus BH-2, using an Ar^+ Spectra Physics laser with the exciting line at 514.6 nm. The laser power at the sample location was changed from 20

0021-9517/89 $3.00

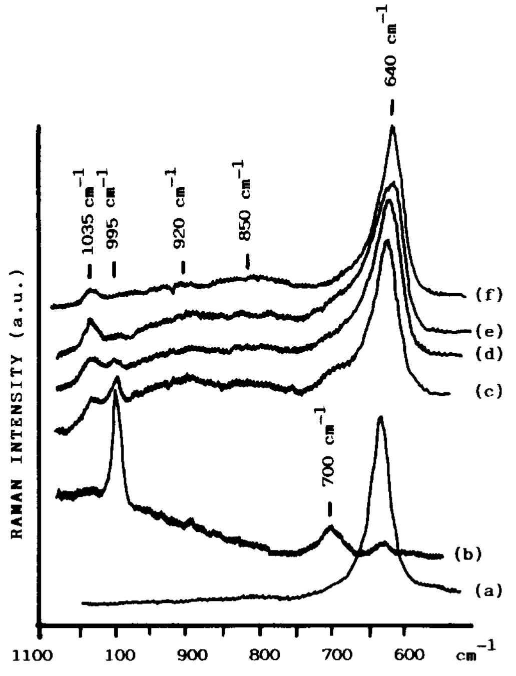

FIG. 1. Laser–Raman microscopy spectra of pure TiO_2 anatase (a), catalyst B (b–e), and catalyst A (f). Spectra b and c refer to two different portions of powder B; spectra c, d, and e are recorded on the same portion by increasing the laser power (c) 20, (d) 70, and (e) 150 mW, respectively.

to 150 mW. IR spectra were collected with a Nicolet MX1 Fourier transform spectrometer.

The laser–Raman microscopy spectra are presented in Fig. 1. Comparison of spectra b and c, which refer to two different portions of sample B, confirms the heterogeneity of the "monolayer" catalyst, in line with XRD results. In fact, spectrum b is essentially that of bulk V_2O_5, with main Raman peaks at 995 and 700 cm^{-1} (*22*), while spectrum c is dominated by the strong major Raman band of TiO_2 anatase at 640 cm^{-1} (*22*). The presence of V_2O_5 in sample B is also confirmed by the IR band at 1015 cm^{-1} (Fig. 2a). The broad Raman absorptions near 920 and 850 cm^{-1} and the sharper ones at 1030 and 995 cm^{-1}, not present in the spectrum of pure TiO_2 and detected in sample B, are associated with V (compare spectra c and a in Fig. 1). By increasing the laser power without any modification of the position of the sample, the band near 995 cm^{-1} decreases in intensity while that at 1030 cm^{-1} increases strongly; the other absorptions are almost unaffected (spectra c, d, and e in Fig. 1). Such a laser beam power effect parallels that observed for molybdena–alumina (*23*) and vanadia–alumina (*24*), which was interpreted as due to dehydration of the supported molybdenyl and vanadyl species.

The IR spectrum of sample B in Fig. 2a (KBr disk exposed to the laboratory atmosphere) is also characterized by a relatively broad band near 990 cm^{-1}. However, if the pressed disk of pure powder of sample B is evacuated at 673 K a band is detected at 1035 cm^{-1} (Fig. 2b); this band is shifted below the cutoff limit of the sample ($\approx$1000 cm^{-1}) by subsequent exposure of the sam-

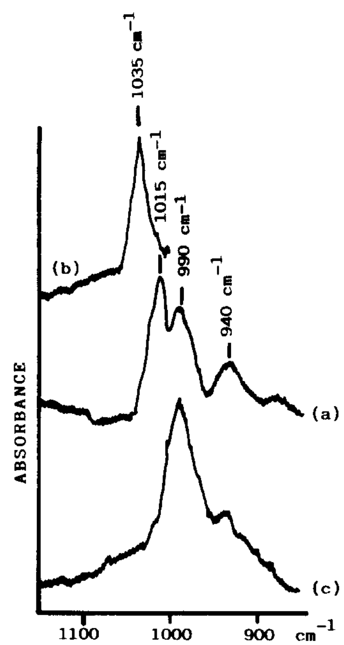

FIG. 2. FT-IR spectra of vanadium oxide species in vanadia–titania catalysts. (a) catalyst B (KBr pressed disk) exposed to air upon subtraction of the spectrum of the TiO_2 support. (b) Catalyst B (pure powder pressed disk) activated *in vacuo* upon subtraction of the pure powder exposed to air (below ~1000 cm^{-1}, the transmittance is nil). (c) Catalyst A (KBr pressed disk) exposed to air upon subtraction of TiO_2 anatase.

ple to a wet atmosphere. As previously shown (*25, 26*), this behavior can be observed by IR monitoring of the first overtone of the band at 1035 cm^{-1}, detected at 2045 cm^{-1}, which is shifted to 1950 cm^{-1} upon water adsorption.

Along these lines it can be assumed that on increasing the laser power, sample B is heated, which causes water desorption as during activation *in vacuo*. Note that sample B presents a strong absorption in the UV–visible spectrum at the wavelength of the laser exciting line (514 nm). Accordingly the band at 1030 cm^{-1} is assigned to the $\nu_{V=O}$ stretching mode of a water-free surface vanadyl bond, while that at 995 cm^{-1} would be due to the corresponding hydrated species. The strict correspondence of the $\nu_{V=O}$ Raman and FT–IR frequencies indicates that these bands cannot be associated with dioxo species. In this case, two bands, typically separated by about 10–30 cm^{-1}, are expected in both IR and Raman spectra with opposite relative intensity (*27*). Accordingly, the band at 1030 cm^{-1} can be assigned to the $\nu_{V=O}$ vibration of surface monooxo species with a coordinate unsaturation and the band at 995 cm^{-1} to the same species which is saturated when the surface is wet. The $\nu_{V=O}$ band of the saturated species accidentally coincides with the most intense Raman band of bulk V_2O_5; however, the most intense IR band of bulk V_2O_5 is detected at 1020 cm^{-1}. Therefore the combined use of Raman and IR spectroscopies and the analysis of both wet and dry samples are required to discriminate between bulk vanadia and surface vanadyl absorptions. On the other hand, the broad Raman absorptions centered at 920 and 850 cm^{-1} and the IR band at 940 cm^{-1} (Fig. 2) may be associated with $\nu_{V=O}$ from V_xO_y "clusters" (*28*), for which previous evidence has been reported by ESR and FT–IR in the overtone region (*21*). Based on the frequencies these clusters may correspond to tetrahedral dioxo species proposed by other authors (*14–16*).

Sample A showed together with the bands assigned to V_xO_y clusters only the Raman band at 1030 cm^{-1} already at low laser power (Fig. 1f). This may be explained by considering that sample A is a V–Ti oxide solid solution characterized by the incorporation of V^{4+} into the bulk (*5, 10*). This results in a much stronger absorption at about 500 nm associated with *d–d* electron transitions of the $3d^1$/V(IV) centers and eventually causes a stronger temperature rise in the sample upon exposure to the laser power. In any case the IR absorption detected at 990 cm^{-1} for KBr disks exposed to air and the $2\nu_{V=O}$ overtone at 2045 cm^{-1} for the pure powder pressed disks activated *in vacuo* (almost opaque below 1100 cm^{-1}) indicate that surface vanadyls similar to those reported for monolayer vanadium catalysts are present also in sample A, although the coverage is not complete (*5*).

In conclusion the above IR and Raman data indicate that (i) the surface structure of the "monolayer"-type V–Ti oxide catalysts comprises monooxo vanadyl species, which can be either coordinatively saturated on the wet surface or coordinatively unsaturated on the dry surface, and by V_xO_y "clusters"; and (ii) the same model applies to the surface of precipitated V–Ti oxide catalysts.

ACKNOWLEDGMENT

This work was supported by the Ministero della Pubblica Istruzione (Rome).

REFERENCES

1. Cullis, C. F., and Hucknall, D. J., *in* Spec. Per. Rep. "Catalysis" (G. C. Bond and G. Webb, Eds.), Vol. 5, p. 273. Royal Society of Chemistry, London, 1982.
2. Gellings, P. J., *in* Spec. Per. Rep. "Catalysis" (G. C. Bond and G. Webb, Eds.), Vol. 7, p. 105. Royal Society of Chemistry, London, 1985.
3. Bosch, H., and Janssen, F., *Catal. Today* **2,** 369 (1988).
4. Forzatti, P., Tronconi, E., Busca, G., and Tittarelli, P., *Catal. Today* **1,** 209 (1987).
5. Tronconi, E., Elmi, A. S., Ferlazzo, N., Forzatti, P., Busca, G., and Tittarelli, P., *Ind. Eng. Chem. Res.* **26,** 1269 (1987); Busca, G., Elmi A. S., and Forzatti P., *J. Phys. Chem.* **91,** 5263 (1987).
6. Gąsior, I., Gąsior, M., Grzybowska, B.,

Kozlowski, R., and Słoczynski, J., *Bull. Acad. Pol. Sci.* **27** (11), 829 (1979).

7. Bond, G. C., Sárkány, A. J., and Parfitt, G. D., *J. Catal.* **57**, 476 (1979).
8. Andersson, A., and Andersson, S. L. T., *in* "Solid State Chemistry in Catalysis," ACS Symposium Series 279 (R. K. Grasselli and J. F. Bradzil, Eds.), p. 121. American Chemical Society, Washington, DC, 1985.
9. Slinkard, W. F., and DeGroot, P. B., *J. Catal.* **68**, 423 (1981).
10. Busca, G., Tittarelli, P., Tronconi, E., and Forzatti, P., *J. Solid State Chem.* **67**, 91 (1987).
11. Véjux, A., and Courtine, P., *J. Solid State Chem.* **23**, 93 (1978).
12. Véjux, A., and Courtine, P., *J. Solid State Chem.* **63**, 179 (1986).
13. Kang, Z. C., and Bao, Q.X., *Appl. Catal.* **26**, 251 (1986).
14. Wachs, I. E., Saleh, R. Y., Chan, S. S., and Cherich, C. C., *Appl. Catal.* **15**, 339 (1985).
15. Kozłowski, R., Pettifer, R. F., and Thomas, J. M., *J. Phys. Chem.* **87**, 5176 (1983).
16. Haber, J., Kozłowska, A., Kozłowski, R., *J. Catal.* **102**, 52 (1986).
17. Bond G. C., Perez Zurita, J., Flamerz, S., Gellings, P. J., Bosch, H., van Ommen, J. G., and Kip, B. J., *Appl. Catal.* **22**, 361 (1986).
18. Mériaudeau, P., and Védrine, J. C., *Nouv. J. Chim.* **2**, 133 (1978).
19. Inomata, M., Mori, M., Miyamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **87**, 754 (1983).
20. Rusiecka, M., Grzybowska, B., and Gąsior, M., *Appl. Catal.* **10**, 101 (1984).
21. Busca, G., Centi, G., Marchetti, L., and Trifirò, F., *Langmuir* **2**, 568 (1986).
22. Beattie, I. R., and Gilson, T. R., *J. Chem. Soc. A*, 2322 (1969); Beattie, I. R., and Gilson, T. R., *Proc. R. Soc. London Ser. A* **307**, 407 (1968).
23. Payen, E., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Raman Spectrosc.* **17**, 233 (1986).
24. Le Coustumer, L. R., Taouk, B., Le Meur, M., Payen, E., Guelton, M., and Grimblot, J., *J. Phys. Chem.* **92**, 1230 (1988).
25. Busca, G., and Lavalley, J. C., *Spectrochim. Acta Part A* **42**, 443 (1986).
26. Busca, G., *Langmuir* **2**, 577 (1986).
27. Ahlborn, E., Diemann, E., and Muller, A., *Z. Anorg. Allg. Chem.* **394**, 1 (1972); Satyanarayana, D. N., *Bull. Chem. Soc. Japan* **37**, 1736 (1964).
28. Griffith, W. P., and Wickins, T. D., *J. Chem. Soc. A*, 1066 (1969); Dupuis, T., and Lorenzelli, V., *J. Therm. Anal.* **1**, 15 (1969).

CINZIA CRISTIANI
PIO FORZATTI[1]

Dipartimento di Chimica Industriale ed Ingegneria Chimica "G. Natta"
Politecnico di Milano
Piazza Leonardo da Vinci 32
20133 Milan, Italy

GUIDO BUSCA

Istituto di Chimica
Facoltà di Ingegneria
Università di Genova
Fiera del Mare, Padiglione D
16129, Genoa, Italy

Received June 9, 1987; revised November 15, 1988

---

[1] To whom correspondence should be addressed.