Adsorption of Vanadium–Oxo Species on Pure and Peroxide-treated TiO_2 (Anatase)

Margarita M. Kantcheva and Konstantin I. Hadjiivanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

The capacity of TiO_2 (anatase) for adsorption of vanadium–oxo species from acidic solutions increases after pre-treatment with hydrogen peroxide.

Ion-exchanged and grafted vanadia–titania catalysts are widely studied due to their possible use in some processes of partial oxidation.[1-3] However, the very low vanadia coating which is usually reached is the reason for the presence of relatively high amounts of coordinatively unsaturated (CUS) Ti^{4+} ions on the catalyst surfaces.[1] These cations are active in full combustion,[4] as a result of which the catalysts possess a low selectivity. Here we propose a method of synthesis of ion-exchanged vanadia–titania catalysts without CUS titanium ions on their surfaces.

Anatase was prepared by hydrolysis of titanium tetrachloride as described earlier.[5] A modified adsorbent was obtained after treating anatase with a 5% H_2O_2 (without stabiliser) solution followed by drying in air at 25 °C.[6] Portions of these samples were suspended in 0.06 mol dm^{-3} solutions of V^{5+} prepared by dissolving ammonium vanadate in dilute nitric acid (final pH 0.5). After 2 h the precipitates were filtered off, washed with water, dried and calcined in air at 400 °C for 1 h. Some characteristics of the samples investigated, as well as the symbols used further on, are presented in Table 1.

A five-valent state of vanadium was established for both VT samples by diffuse reflectance (DR) UV–VIS spectroscopy and X-ray photoelectron spectroscopy (XPS). To determine the localization of the deposited species, the IR spectra of probe-molecules were studied. Fig. 1(*a*) presents the IR spectra of T1, VT1 and VT2 in the ν_{OH} region after vacuum treatment at 400 °C (the T2 sample will not be considered since the adsorbed peroxide decomposes during the activation[6]). It is evident that the surface hydroxy groups characteristic of anatase (bands at 3740 and 3700 cm^{-1}) do not exist on either VT sample. Bands at 3675–3660 cm^{-1}, assigned to VO–H stretchings,[1] are detected for them. These spectra clearly show that the Ti–OH groups have reacted with vanadium-containing species during the syntheses of VT samples.

Fig. 1(*b*) presents the IR spectra of absorbed CO. With the T1 sample, α and β carbonyls are detected,[5] the corresponding bands being at 2206 and 2187 cm^{-1}. The spectrum of CO adsorbed on VT1 reveals that only β-Ti^{4+}–CO carbonyls are

Table 1 Some characteristics of the TiO_2 and V–Ti–O samples

Sample[c]	Symbol	$S/m^2\,g^{-1}$	V:Ti ratio[a]	V^{5+}/nm^{-2} [b]
TiO_2	T1	165	—	—
T1 treated with H_2O_2	T2	167	—	—
V^{5+} on T1	VT1	136	4.3 : 100	1.6
V^{5+} on T2	VT2	142	7.2 : 100	2.2

[a] According to XPS. [b] According to atomic absorption data. [c] All samples had the anatase structure (XRD).

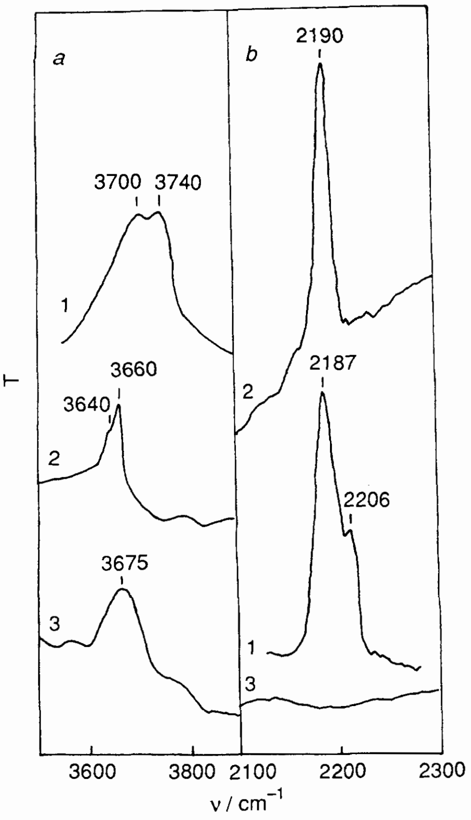

Fig. 1 (*a*) IR spectra of the surface OH groups and (*b*) IR spectra of adsorbed CO, 45 Torr; 1, T1; 2, VT1 and 3, VT2

formed (a band at 2190 cm^{-1}) whereas the α-sites are blocked. This picture is analogous to that reported by Busca *et al.*[1] for grafted vanadia–titania catalysts. The contact of VT2 with CO does not lead to formation of any carbonyls, *i.e.* in this case all CUS titanium cations are blocked.

The results obtained indicate the following sites of distribution of vanadium–oxo species when exchanged on anatase: (*i*) the sites where surface OH groups are localized and (*ii*) in vicinity of the α-Lewis acid sites. When anatase is pre-treated with H_2O_2, the β-Lewis acid sites are also blocked. This difference is explained by the possibility of formation of Ti–O–O–V bridges favouring the adsorption of vanadium–oxo species. These conclusions are in good agreement with the observed concentrations of vanadium–oxo species.

Finally, it should be noted that catalysts synthesized as the VT2 sample may be selective in partial oxidation processes due to the absence of CUS Ti^{4+} ions on their surfaces.

Received, 25th March 1991; Com. 1/01404H

References

1 G. Busca, L. Marchetti, G. Centi and F. Trifirò, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1003.
2 G. C. Bond, J. P. Zurita, S. Flamerz, P. J. Gellings, H. Bosch, J. G. van Ommen and B. J. Kip, *Appl. Catal.*, 1986, **22**, 361.
3 F. Roozeboom, M. C. Mittelmeijer-Hazeleger, J. A. Monlijn, J. Medema, V. H. J. de.Beer and P. J. Gellings, *J. Phys. Chem.*, 1980, **84**, 2783.
4 I. E. Wachs, R. I. Saleh, S. S. Chan and C. C. Chersich, *Appl. Catal.*, 1985, **15**, 339.
5 K. I. Hadjiivanov, D. G. Klissurski and A. A. Davydov, *J. Catal.*, 1989, **116**, 498.
6 D. Klissurski, K. Hadjiivanov, M. Kantcheva and L. Gyurova, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 385.