A Method for the Quantitative Determination of the Basic, Acidic, and Total Surface Hydroxy Content of TiO_2

J. A. Rob van Veen,* Fred T. G. Veltmaat, and Gert Jonkers

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

The number and type of hydroxy groups on a TiO_2 surface can be determined using a combination of wet chemical techniques, F^- exchange, OH^- and $Fe(acac)_3$ (Hacac = pentane-2,4-dione) adsorption, and i.r. spectroscopy.

The determination of the number and type of hydroxy groups on oxidic surfaces has been the subject of many studies.[1] However, a reliable quantitative method has not yet been developed; spectroscopic methods and the various chemical methods in isolation often leading to contradictory results. For TiO_2, the situation is exemplified by two recent publications, one[2] of which uses a theoretical value for the number of total OH/nm^2 (derived from an i.r. study of γ-Al_2O_3) and the other[3] relies on titration with NaOH; the hydroxy-group contents derived *via* these methods differ by a factor of 4 (see also the discussion in ref. 4). We have developed a procedure which would appear to yield the actual amount of surface hydroxy groups on a TiO_2 surface and their character (acidic or basic). It will be illustrated below, using a TiO_2 sample from Degussa (P 25; 50 $m^2\ g^{-1}$, 90% anatase) as the example.

The i.r. spectrum (OH stretch region) of TiO_2 is shown in Figure 1. The spectrum roughly consists of two bands, the one at higher frequencies corresponding to the more basic hydroxy groups and the one at lower frequencies to the more acidic ones.[5] It is not possible to derive the relative number of acidic and basic OH groups present on the surface at room temperature from i.r. measurements, since, apart from the

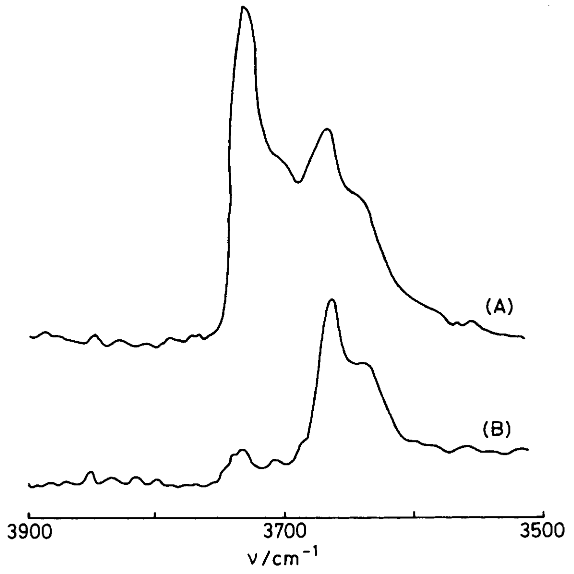

Figure 1. Fourier-transform i.r. spectra of TiO_2 (P 25) in the OH stretch region: (A), untreated sample, after evacuation at 250 °C; (B), sample exchanged with F^- (exchange 95% complete according to the isotherm results, Figure 2), after evacuation at 250 °C.

fact that the relative extinction coefficients are not known, (i) at that temperature adsorbed water interferes with the measurement, and (ii) raising the temperature to remove it (200 °C at least is necessary) affects the low-frequency band far more than the high-frequency one, the intensity ratio thus varying with the temperature. However, it turns out that the required number can be determined using a combination of i.r. spectroscopy with chemical methods, in which the former is not used as an independent method, but only to check on the precise chemistry of the latter.

According to Boehm,[6] the basic hydroxy groups on TiO_2 can be determined by exchanging them with fluoride ions at constant pH. Using a somewhat higher pH than Boehm we get the results reported in Figure 2(A). Since i.r. spectroscopy (Figure 1) shows that the F^- exchange is in fact with basic hydroxy groups only, the data of Figure 2(A) fix their number at 0.14 mmol g^{-1}.

Adsorption of NaOH has been used by Boehm to determine the number of acidic OH groups, but his results have been criticized (discussion in ref. 4) on the grounds that progressive charging of the TiO_2 surface will affect the dissociation constants of the remaining OH groups, thus precluding a reliable determination of their number. To some extent at least, the effects of surface charging can be suppressed by adding an inert salt (*e.g.* $NaNO_3$). The adsorption isotherms of NaOH on TiO_2 in the presence and absence of $NaNO_3$ are shown in Figure 2(B). A large difference is observed, showing that surface charging is indeed affecting the outcome of the NaOH titration. The curve obtained in the presence of 3 M $NaNO_3$ would appear to consist of two parts, which we interpret as follows: at low concentrations of NaOH, only the acidic OH groups will react with OH^- ions; at higher concentrations, however, the more basic ones will also start to be involved. If this interpretation is correct, we derive for the total amount of OH groups the value of 0.47 mmol g^{-1}, this being the limiting value of OH^- which had reacted at high $C'(OH^-)$, see Figure 2(B). The division into acidic and basic OH groups can be effected as proposed by Boehm,[4] *viz.* by fitting the data points corresponding to the higher values of $C'(OH^-)$ to the Langmuir equation, and subtracting from each value of OH^- reacted the estimated contribution due to the acidic OH groups. The best fit is obtained when we take the amount of acidic OH groups to be 0.33 mmol g^{-1}, which leaves for the amount of basic groups 0.14 mmol g^{-1}, the latter value being in good agreement with the one derived above. The numbers reported are estimated to be accurate to ±0.01 mmol g^{-1}.

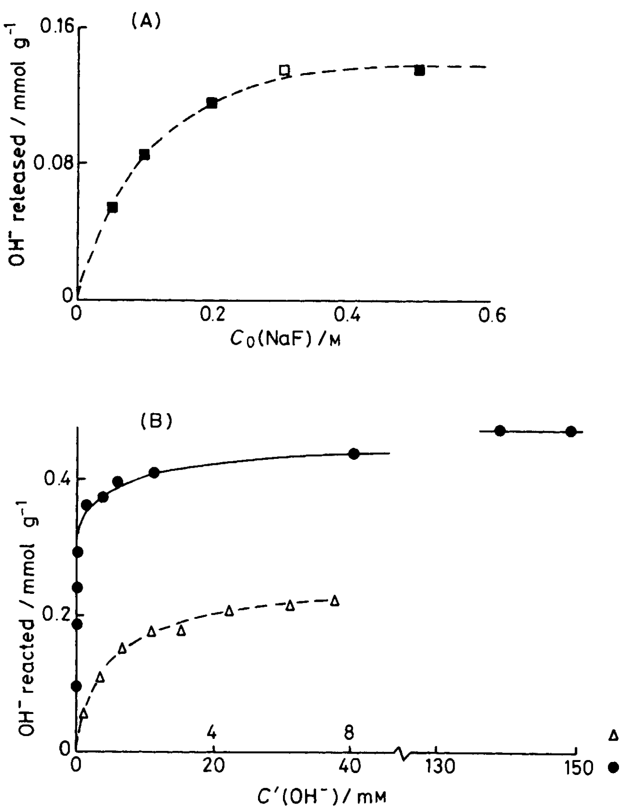

Figure 2. (A) OH^- released *vs.* initial NaF concentration, TiO_2 (P 25), pH 7.8. The i.r. spectrum of the sample corresponding to □ is shown in Figure 1(B). (B) NaOH adsorption isotherms on TiO_2, ●, in the presence, and △, in the absence of 3 M $NaNO_3$.

Of course, we need an independent check on the total number of OH groups, and we found it, by accident, in the reaction of $Fe(acac)_3$ (Hacac = pentane-2,4-dione) with a TiO_2 surface [reaction (1)], where S denotes surface (solvent: toluene). No physisorption takes place, and Ti^{4+} surface sites are not involved either (there is no adsorption on a surface dehydroxylated at 600 °C, if the adsorption experiment is carried out with exclusion of moisture). I.r. spectroscopy shows that $Fe(acac)_3$ reacts with all hydroxy groups. The total amount of Fe adsorbed, γ, can be deduced from the reduction in optical density of the $Fe(acac)_3$–toluene solution ($\lambda_{max.}$ 354 nm), while a value for x can be derived from differential thermal analysis–mass spectrometric experiments on $Fe(acac)_x$–TiO_2 yielding for our sample $\gamma = 0.204$ mmol g^{-1} and $x = 0.75$, respectively. From these values a total OH content of 0.46 mmol g^{-1} is calculated, in very satisfactory agreement with the NaOH–3M $NaNO_3$ titration result.

$$(3-x)\text{S–OH} + \text{Fe(acac)}_3 \rightarrow (\text{S–O})_{3-x}\text{Fe(acac)}_x + (3-x)\text{acacH} \quad (1)$$

For another TiO_2 sample, from Shugai (48 m^2 g^{-1}; 90% anatase), the same combination of F^- exchange, NaOH and $Fe(acac)_3$ adsorption, and i.r. spectroscopy also leads to mutually consistent results, the numbers being: acidic OH, 0.22 mmol g^{-1}; basic OH, 0.090 mmol g^{-1} (ratio acidic/basic = 2.4 as in the P 25 case). We conclude, therefore, that this combination of methods leads to a quantitative determination of the actual surface hydroxy content of TiO_2 and their division into acidic and basic types.

Received, 17th July 1985; Com. 1043

References

1 H.-P. Boehm and H. Knözinger, in 'Catalysis, Science and Technology,' eds. J. R. Anderson and M. Boudart, Vol. 4, Springer–Verlag, Berlin, 1983, p. 39.

2 R. Sprycha, *J. Colloid Interface Sci.*, 1984, **102**, 173.

3 Y. Oosawa and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1984, 1629.

4 H. P. Boehm, *Discuss. Faraday Soc.*, 1971, **52**, 264, and following discussion.

5 H. Knözinger and P. Ratnasamy, *Catal. Rev.-Sci. Eng.*, 1978, **17**, 31.

6 H. Hermann, U. Kaluza, and H. P. Boehm, *Z. Anorg. Allg. Chem.*, 1970, **372**, 308.