Adsorption of Cations on TiO$_2$ Particles. A Method to Determine the Surface Density of OH Groups

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The adsorption of some cations (Cu^{2+}, Cd^{2+}, Zn^{2+}) on TiO$_2$ particles is successfully described by a modified Langmuir isotherm, from which the surface density of OH groups on TiO$_2$ is evaluated.

Recently there has been widespread interest in heterogeneous photocatalytic systems that accomplish the photodeposition of metallic ions with a view to prepare well-dispersed metal-loaded semiconductor catalysts[1] or to recover noble or toxic metals from waste water.[2] Much attention has been focused on particulate TiO$_2$ which is used as a photocatalyst owing to its stability with respect to photoanodic and acidic dissolution.[3–7] It is commonly accepted that photodeposition is a process in which metallic ions are adsorbed on the surface of the TiO$_2$ followed by trapping of conduction band electrons. The adsorbtion ability of the metallic ion is an essential factor influencing the deposition rate. In many cases[8,9] it was found that the initial deposition rate varied with the starting concentration of metallic ions according to a Langmuir–Hinshelwood mechanism. This is not in agreement with our experimental results in which the adsorption of three cations (Cu^{2+}, Cd^{2+}, Zn^{2+}) on TiO$_2$ particles cannot be described by the Langmuir adsorption model. Here, we report a modified form of the Langmuir isotherm to elucidate the adsorption of the cations.

The TiO$_2$ powder used in this study was mainly in the anatase form as characterized by an X-ray diffraction spectrum recorded on a D/max-RB diffractometer (Rigaku Co.). TEM measurements (Phillips EM-400) indicate that the mean particle size is *ca.* 150 nm. The specific surface area, measured by the BET method, is *ca.* 10.9 m^2 g^{-1} (Micrometrics ASAP 2400). The adsorption procedure was carried out in a Pyrex glass beaker using a 2.5 g l^{-1} TiO$_2$ suspension, which was prepared by suspending TiO$_2$ powder (0.5 g) in doubly distilled water (200 ml) and sonicating for 20 min. The pH (*ca.* 6.4) of the suspension thus obtained decreased with addition of cations. This is indicative of the replacement of surface protons by adsorbed cations [eqn. (1)], in which one adsorbed

$$\equiv\text{Ti–OH} + \text{M}^{2+} \rightleftharpoons \equiv\text{Ti–OM}^{+} + \text{H}^{+} \qquad (1)$$

cation releases one proton. The adsorbance of cations can thus be determined by measuring the decrease in pH of the TiO$_2$ suspension. Fig. 1 shows the adsorbance of the three cations (Cu^{2+}, Zn^{2+}, Cd^{2+}) as a function of the equilibrium concentration. Of the ions studied, Cu^{2+} shows much stronger adsorption than the other two. This can be attributed to the much lower solubility product of Cu(OH)$_2$ *vs.* Cd(OH)$_2$ of Zn(OH)$_2$. In view of the fact that the data in Fig. 1 do not fit the Langmuir isotherm, it is reasonable to envisage that the process of eqn. (1) does not resemble the adsorption occurring at a solid–gas interface where Langmuir behaviour is observed.

Eqn. (1) is actually a replacement reaction and is a dynamic

$$R_a = k_a c_M N(1 - \theta) \qquad (2)$$

equilibrium. The adsorption rate (R_a) is proportional to the concentration of M^{2+} (c_M) and the number of unoccupied OH sites on TiO$_2$ surface, $N(1 - \theta)$ [eqn. (2)], where N is the total number of OH groups, θ is the surface coverage by M^{2+} and k_a is the rate constant for adsorption. Owing to the involvement of H$^+$ in eqn. (1), the desorption rate (R_d) of M^{2+} depends not only on the number of $\equiv$Ti–OM$^+$ ($N\theta$) but also on the concentration of free H$^+$ (c_H) in the aqueous phase [eqn. (3)]

$$R_d = k_d c_H N\theta \qquad (3)$$

where k_d is the rate constant for desorption. This is in contrast with the situation of Langmuir type adsorption, which can be regarded as a reaction with only the chemisorbed complex as the product. In such cases, the desorption rate of the adsorbates depends solely on the amount of the chemisorbed complex.

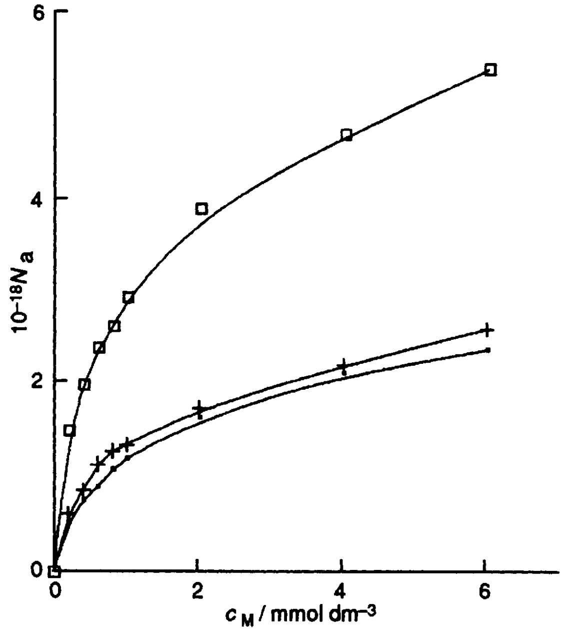

Fig. 1 Number of cations adsorbed onto the TiO$_2$ powder surface (N_a) as a function of the equilibrium concentration (c_M) in the suspension; Cu^{2+} (□), Zn^{2+} (■), Cd^{2+} (+)

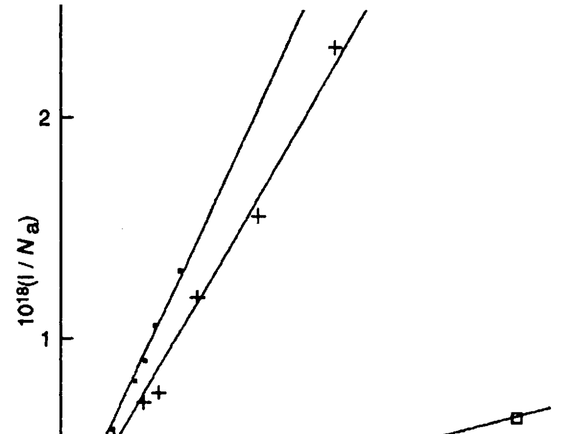

Fig. 2 Plots of $1/N_a$ *vs.* c_H/c_M for Cu^{2+} (□), Zn^{2+} (■) and Cd^{2+} (+). Data were obtained from Fig. 1.

At equilibrium, the rates of adsorption and desorption are equal, and θ can be evaluated from eqn. (4) where $K = k_a/k_d$ is

$$\theta = Kc_M/(Kc_M + c_H) \quad (4)$$

the adsorption equilibrium constant. One can see that eqn. (4) is a modified form of the Langmuir isotherm as a consequence of the effect of H^+ on the adsorption–desorption equilibrium. The number of adsorbed cations (N_a) can then be obtained [eqn. (5)].

$$N_a = N\theta = NKc_M/(Kc_M + c_H) \quad (5)$$

A plot of $1/N_a$ *vs.* c_H/c_M should be a straight line with a slope of $1/NK$ and an intercept of $1/N$. This is confirmed by the results shown in Fig. 2, in which all of the plots show good linearity. The significant difference in slopes for Cu^{2+} ($10^3\ K = 14.1$) and Zn^{2+}, Cd^{2+} ($10^3\ K = 2.2, 2.4$) reflects the difference in adsorption ability of Cu^{2+} relative to Zn^{2+}, Cd^{2+}.

For each of the cations the intercepts in Fig. 2 are almost identical as predicted from eqn. (5) despite the wide variation in adsorption behaviour. On the basis of the total number of the OH groups (N) on 0.5 g TiO_2 and the specific surface area of the TiO_2 powder, the surface density of OH groups (σ) on TiO_2 can be estimated. Values of 1.5, 1.4 and 1.2 per nm^{-2} were obtained in the Cu^{2+}, Cd^{2+} and Zn^{2+} experiments and can be compared with the value (1.3 per nm^{-2}) obtained by acid-base titration.[10] The close agreement of these σ values provides additional support for the adsorption model represented by eqns. (4) and (5).

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