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Calorimetry

CALORIMETRIC STUDY OF THE KINETICS OF ADSORPTION OF HYDROGEN LOADED TITANIUM OXIDE

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The thermokinetics of the adsorption of hydrogen on a loaded titanium dioxide has been studied by microcalorimetry.

A diffusion process in the open structure of the oxide seems to be the ratóe determining step. Some exceptions at the rule of the *S*-shaped $z-t$ plot were found.

The function "z" is here obtained from the thermokinetics of the process and is constituted by the reciprocal of the time derivative of the fraction of the integral heat of adsorption, i.e., by the reciprocal of the relative heat flow.

A review of empirical isotherms and of theoretical models proposed for the kinetics of adsorption has been recently published [1]. One conclusion of this paper is that the plot of the reciprocal of the rate of adsorption against time is convex at small "t" and concave at large "t" and the region of constant rate sometimes proceeds the convex region.

The present article which deals with the adsorption of hydrogen on a doped titanium dioxide attempts to show that some exceptions to this rule may occur.

Experimental

The material studied was a titania-based catalyst that is proposed for the production of hydrogen by the photocleavage of water [2]. A sample of TiO_2 from Degussa (P–25, surface area 55 m^2/g; 72% anatase, 28% rutile) was loaded

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according to the procedure already described [3] with 1% of RuO_2. Before each set of adsorption-desorption runs the sample was standardized at 673 K for half an hour under a pressure of 6666 Pa of dioxygen and then evacuated at 10^{-4} Pa for 1 hour at 423 K, as this seems to be the best experimental conditions for photocatalysis [3, 11]. This sample will be hereby indicated as P-25/RuO_2. The calorimetric and volumetric isotherms were determined at 300 K employing a Tian–Calvet microcalorimeter connected to a volumetric apparatus described elsewhere [4]. The pressure data were given by a capacitance manometer (Datametrics). All the adsorption and desorption runs were repeated at least twice to check reproducibility.

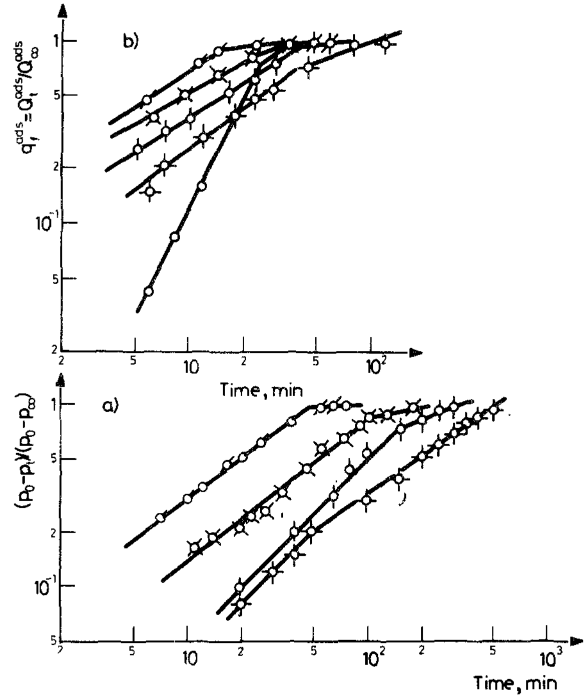

Fig. 1 Adsorption of hydrogen on P-25/RuO_2 at 300 K (first adsorption cycle). Logarithmic plots of dimensionless functions (see text) of equilibrium pressure (a) and heat (b) against time for the following pressures: ○ 640 Pa; ⌀ 1.035 kPa; ⌧ 1.959 kPa; ⏀ 3.946 kPa; ⌖ 10.585 kPa

Results and discussion

In Fig. 1a, b the kinetics for some typical runs of the first adsorption cycle are shown on logarithmic scale, both through equilibrium pressures and adsorption heats. In order to compare runs at different inlet pressure, dimensionless units were chosen for the ordinates, e.g. the fractions of integral heat of adsorption obtained at various time "t", (Q_t/Q_∞), Q_∞ being the value obtained when the calorimeter baseline is reached, and an increasing function of pressure $(p_p - p_t/p_0 - p_\infty)$, which also gives 1 at $t \to \infty$. This function was chosen to better compare pressure and heat kinetics, the difference between initial and final values of pressure being of a few per cent, much less than the variation in heat (see Fig. 1b, 2b).

It is well known that the true thermokinetics may be obtained only after the correction of the thermograms through the heat transfer function of the calorimeter [5], but the rate of hydrogen uptake by titania is very low and the error due to the time constant of the calorimeter (~ 200 sec) may be considered negligible.

On the graphs of Fig. 1 it may be observed that pressure and heat data do not follow the same kinetic trend: in the intermediate region of time heat plots show power numbers that go from 1.70 to 0.63, while for the pressure data the time exponent seems to fluctuate between 1.20 and 0.70.

Instead in Fig. 2 the evolution of equilibrium pressure and heats is shown for some runs in the second and third cycle of hydrogen adsorption. Here the divergence between pressure and heat data is still more pronounced. The physical meaning of this discrepancy will be discussed later.

Figures 1 and 2 clearly depict examples of adsorption in which the rate law is changing not only with the increasing coverage but also with the variation in pressure. For this purpose more detailed information can be obtained from the $z-t$ plot—$z = (\mathrm{d}q_f^{\mathrm{ads}}/\mathrm{d}t)^{-1}$—which is given in Figs 3 and 4 for typical runs of the 1st, 2nd and 3rd cycles of adsorption. From such graphs an exception to the rule of the S-shaped plot proposed in the cited review (1), is primarily noted.

In Figs 3 and 4 (curve I) the initial part of the z-plot has a concave portion $(\mathrm{d}^2z/\mathrm{d}t^2 > 0)$, then there is a linear or constant rate part and finally another concave portion. Instead for the 3rd cycle runs we find the S-shaped plot (see Fig. 4b), and the same is found for the latest runs of the 2nd cycle (curve II, Fig. 4).

The present results obtained at a single temperature do not allow a choice between the kinetic models that might be compatible with these thermokinetic data. In fact, as Aharoni has pointed out [1], the value of the exponent does not indicate unequivocally if a power equation is associated with a diffusion mechanism or with a chemical reaction or with both processes. However, some preliminary considerations may be drawn:

a) As far as the hydrogen adsorption of P–25/$\mathrm{RuO_2}$ is concerned, a diffusion process seems conceivable; rutile and anatase are characterized by an open channel structure [6] in which small molecules can diffuse [7]. Hydrogen diffusion in subsurface layers or in pores has been proposed for $\mathrm{TiO_2}$ [8, 12] and similar mechanisms have been postulated for the SMSI effects that are associated with hydrogen chemisorption on metal-containing catalysts [13, 14]. Irreversible

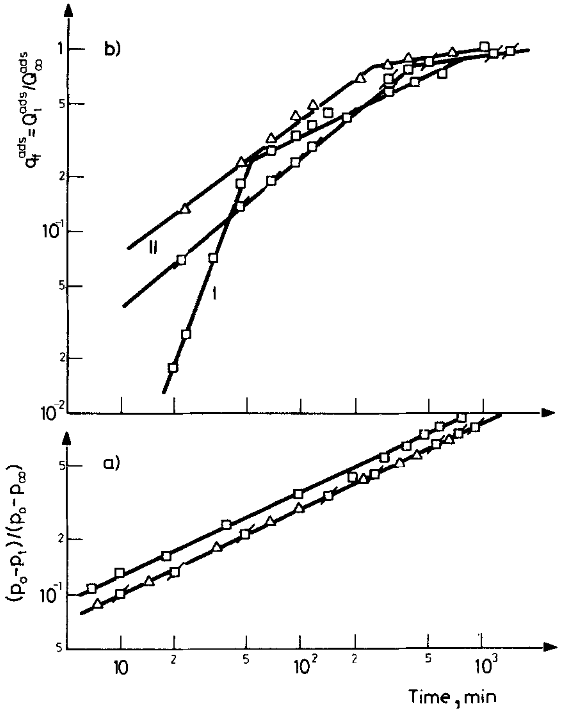

Fig. 2 Adsorption of hydrogen on P-25/RuO$_2$ at 300 K. Logarithmic plots of dimensionless functions (see text) of equilibrium pressure (a) and heat (b) against time for the following pressures: □ 1.173 kPa (second adsorption cycle); □́ 7.900 kPa (second adsorption cycle); △ 5.346 kPa (third adsorption cycle)

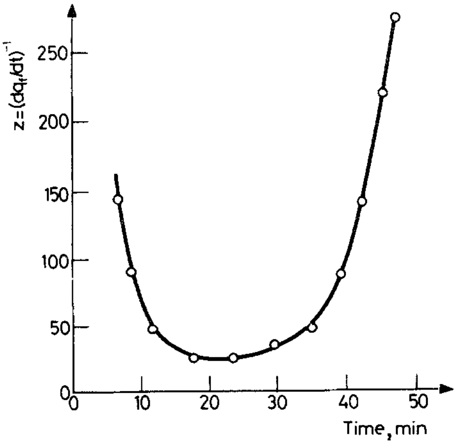

Fig. 3 Adsorption of hydrogen on P-25/RuO$_2$ at 300 K. Data replotted as "z" against "t". ○ 1st adsorption cycle, p_e = 640 Pa

adsorption of H_2 has been even detected on silica gel at − 196° [15]: this adsorption presumably occurs in small micropores and increases linearly with time. For an ammonia synthesis catalyst irreversible hydrogen was considered to be dissolved in the subsurface layer [10]. When hydrogen is adsorbed on nickel oxide, it may diffuse as H_2^+ into the lattice or away from the initial adsorption site [16, 17]. Hydrogen sorption at low pressure by γ-Al_2O_3 was found to be time dependent at 27° and some surface diffusion of an entity other than hydrogen atom or ion was suggested in order to explain the chemisorption kinetics [18]. According to Fubini et al. [9], a diffusion process can account for the very low heat of adsorption of H_2 on ZnO in spite of the irreversibility of the process.

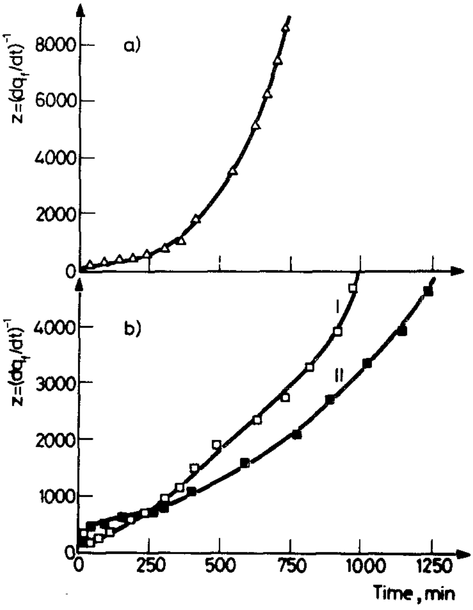

Fig. 4 Adsorption of hydrogen on P–25/RuO_2 at 300 K. Data replotted as "z" against "t". □ p_e = 1.173 kPa (2nd adsorption cycle); ▪ p_e = 7.900 kPa (2nd adsorption cycle); △ p_e = 5.346 kPa (3rd adsorption cycle)

In the present work a process with slow kinetics was found as the surface coverage increases, while the equilibrium pressure was reached faster than the thermal equilibrium. This fact and the low energy of interaction (≃ 10 kJ/mol) [25] suggest a molecular process. Similar energies have been detected for hydrogen adsorption on a platinum foil at high coverage and have been interpreted in terms of molecular state of adsorbed hydrogen [21]. Furthermore some rough calculations with the data of Figs 1, 2, 5 in the intermediate pressure region, assuming a transient diffusion into an infinite cylinder [20], indicated a diffusion coefficient of about 10^{-4} cm^2 sec^{-1}, one order less than those obtained by Bates et al. [19] for atomic diffusion parallel to the *c* axis in rutile. Therefore the hypothesis of molecular diffusion in a heterogeneous medium seems more acceptable for our results.

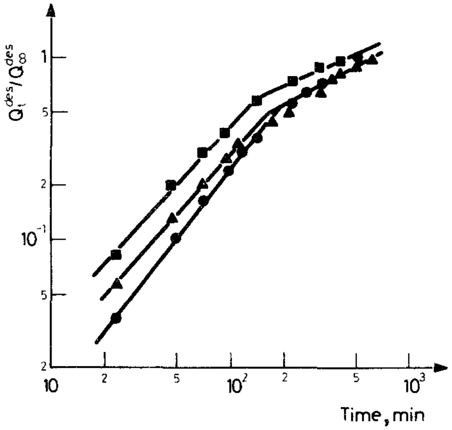

Fig. 5 Desorption of hydrogen from *P*–25/RuO_2 at 300 K. Logarithmic plot of dimensionless function of desorption heats against time. ● 1st adsorption-desorption cycle; ■ 2nd adsorption-desorption cycle; ▲ 3rd adsorption-desorption cycle

The initial increase in the rate of adsorption (see curve (I), Fig. 4a) might be due to an activated entry into the channels: only when the surface pressure has reached a critical value can the diffusion take place. The hypothesis of a diffusion process, which is independent of the external pressure, may also explain the trend of the curves (I, II) in Fig. 2b: in the intermediate region there is a higher rate at a smaller equilibrium pressure. The fact that an exact parabolic law is not always found in the intermediate region of the plots of Figs 1b or 2b might be explained assuming a more complex diffusion equation (e.g. with the linear term) or the interference of some chemisorption kinetics. diffusion into the bulk might be favoured by bulk Ti^{3+} produced during the pretreatment [22]. Some more complex mechanisms, e.g. some chemisorption kinetics. Diffusion into the bulk might be favoured by bulk activation on the Ru or RuO_x sites might occur, while adsorption of H_2 at metal-TiO_x interface sites cannot be excluded [23, 24].

Another independent proof that supports the hypothesis of a diffusion process comes from the thermokinetics of the desorption runs (Fig. 5). The exponents in this case, ranging from 1.25 to 0.9 are close to those in the last adsorption runs of the corresponding cycle.

The final portion of the $z-t$ plot follows in all cases a concave trend as foreseen by a Langmuir-type equation (1); some deviation in the slope of the kinetic isotherms might be due to experimental errors that in this region may be easily connected to instrumentation limits.

The thermokinetic data of this work, the discrepancies between the absolute variation for pressure and heat data, and the trend of the volumetric and calorimetric isotherms reported elsewhere [25], are consistent with the hypothesis that the pressure values correspond to a pseudo equilibrium situation in the gas phase. The physical meaning of this hypothesis already proposed for the H_2—ZnO system [19] is that the bulk pressure changes that tend to equilibrate the internal diffusion become so small and slow as to be practically undetectable by a manometer. In this sense the heat data are more representative of the H_2—TiO_2 interaction, as they come from a more sensitive instrument and are directly related to the adsorption on the internal surface.

Further measurements at different adsorption temperatures and with other adsorbents are necessary, however, to confirm the hypothesis of a marked influence of a diffusion process on the kinetic mechanism of hydrogen uptake on titanium dioxide.

Conclusions

The $z-t$ plot method recently proposed [1] in the study of the kinetics of adsorption may be applied to calorimetric data in the case of a slow process like hydrogen adsorption on a loaded titanium dioxide.

For this system the thermokinetics is changing not only with the increasing coverage but also with the equilibrium pressure: some exceptions to the rule of the S-shaped t-plot were noted. The fact that the adsorption rate of hydrogen on P–25/RuO_2 is independent of external pressure in the intermediate range is interpreted by a hypothesis of molecular diffusion into a heterogeneous medium: this is consistent also with the small value of the adsorption heat. As an exact parabolic law is not always found, some chemisorption kinetics (e.g. adsorption at RuO_x or at metal-TiO_x interface sites) cannot, however, be excluded. On the other hand the discrepancy between heat and pressure kinetics suggests that studies of H_2—TiO_2 systems based on bulk pressure changes lead to incorrect conclusions as manometric data are probably related to pseudo-equilibrium situations.

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Zusammenfassung — Mittels Mikrokalorimetrie wurden die thermokinetischen Eigenschaften der Wasserstoffadsorption an auf Träger befindlichen Titandioxid untersucht. Dabei wurde festgestellt, daß der Diffusionsprozeß in der offenen Struktur des Oxides anscheinend der geschwindigkeitsbestimmende ist. Einige Ausnahmen der Regel für die *S*-förmige $z-t$ Kurve wurden gefunden. Die Funktion „z" wird hier aus den thermokinetischen Eigenschaften des Prozesses erhalten und wird durch das Reziproke der ersten Ableitung der Integralfunktion der Adsorptionswärme, d. h. durch das Reziproke des relativen Wärmeflusses bestimmt.

Резюме — Методом микрокалориметрии изучена термокинетика адсорбции водорода наполненной двуокисью титана. Представляется, что стадией определяющей скорость реакции, является диффузионный процесс в открытой структуре окиси. Найдены некоторые исключения из правила *S*-образной графической зависимости z. В данном случае функция z была получена из термокинетики процесса и может быть представлена обратной временной производной фракции интегральной теплоты адсорбции, т. е. обратной величиной относительного теплового потока.