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KINETICS OF HYDROGEN INTERCALATION INTO $VMoO_{5.5}$

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The kinetics of gas phase hydrogen uptake into platinized $VMoO_{5.5}$ to form the bronze $H_{\sim 3.2}VMoO_{5.5}$ is limited by diffusion of atomic hydrogen from Pt crystallites to the mixed oxide (spillover). It is therefore strongly dependent on the precursor platinum salt (H_2PtCl_6, $Pt(NH_3)_4Cl_2$ or $Pt(NH_3)_4(OH)_2$) as well as on the pretreatment conditions between salt deposition and hydrogen exposure, since these parameters determine platinum dispersion. While traditional techniques for metal dispersion measurement, such as CO adsorption or H_2 adsorption/titration are inappropriate for this system, semi-quantitative information on Pt dispersion can be extracted from a simple analysis of the kinetics. These dispersion estimates are in reasonably good agreement with average particle sizes obtained from TEM micrographs.

Many transition metal oxides are known to form hydrogen insertion compounds called “H-bronzes” in the presence of atomic hydrogen. Among these, the mixed bronze $H_xVMoO_{5.5}$ has been the object of several studies [1–4] establishing that up to $x = 3.4$ mole H can be inserted per mole of the parent oxide, using as a hydrogen source H_2 chemisorbed on metal Pt particles.

We have established in a recent paper [5] that the equilibrium stoichiometry of such bronzes for a given pressure as well as their enthalpy of formation are totally independent of the state of the platinum particles. However, this is by no means true of the kinetics of their formation. The aim of this contribution is thus to investigate the effect of the platinum precursor, its pretreatment and final dispersion on the rate of hydrogen intercalation from the gas phase into $VMoO_{5.5}$.

The H-bronze preparation procedure and the chemisorption apparatus have been described elsewhere [5]. Briefly, $VMoO_{5.5}$ was prepared from an acetate solution followed by calcination at 400 ° C. The mixed oxide ($S \simeq 11$ m^2/gr) was then impregnated with a water solution of the platinum precursor in a concentration sufficient to give the required w/w final Pt concentration, and dried at 100 ° C overnight.

The platinum precursor was either H_2PtCl_6 (Aldrich), $Pt(NH_3)_4Cl_2$ (Pfaltz & Bauer) or $Pt(NH_3)_4(OH)_2$ obtained from the chloride form through anion exchange on a Dowex 50X4-400 column.

The product was subjected to pretreatment under air or vacuum for 20 hours at temperatures ranging from 200 to 400 ° C. Vacuum-pretreated samples had to be shortly reexposed to air at RT during transfer from the pretreatment to the reaction cell. Pretreatment conditions for different samples are listed in table 1.

The same hydrogen intercalation procedure was used for all experiments reported here. The samples were evacuated, then contacted with a static hydrogen pressure of ~ 200 Torr, which is sufficient to reach equilibrium values of $x \simeq 3.1$ [5]. The insertion was monitored through the hydrogen pressure decrease in the apparatus. The final pressure was approximately 150 Torr, which is not expected to produce an important change in the bronze stochiometry since the intercalation isotherm is flat in this region.

We tried to obtain independent estimates of Pt particle sizes in different samples. To that effect, Pt-deposited samples were submitted to different pretreatments in a conventional vacuum ramp, and CO adsorption was followed volumetrically at room temperature.

A number of selected samples were also examined by TEM, in bright field mode. This examination was carried out on the sample after pretreatment, but before hydrogen intercalation.

A glimpse of fig. 1, showing the quantity of H intercalated (x = moles H per mole oxide) as a function of time for a series of samples based on Cl-containing Pt salts, is enough to convince oneself that the platinum precursor and pretreatment do have a drastic effect on the intercalation kinetics.

Some kinetic curves consist of two distinct steps of unequal importance separated by a rather long latency period (fig. 1 a,d). In other cases, the existence of two steps is only marked through a break in the kinetic curve with a very short latency period, if any (fig. 1b). In others still, the intercalation is too fast to tell whether it contains several steps.

The presence of an induction period is not surprising. It has been amply demonstrated that bulk hydrogen intercalation into platinum-coated transition metal oxides from gas phase H_2 happens through hydrogen dissociation on the metal platinum followed by its diffusion onto the oxide. Now the two best instances of induction periods are observed for low-temperature pretreated H_2PtCl_6 (200 ° C in air of vacuum), where the platinum is expected to be initially in the form of $PtCl_4$ or $Pt^{IV}O_xCl_y$ [6], which would be only slowly reduced to metal Pt under the mild reaction conditions used ($T = 60\,°C$, $P = 200$ Torr). Most other pretreatments would produce either directly metallic platinum or the easily reducible PtO; the atomic hydrogen formation sites would then be present

Table 1
Kinetic parameters of hydrogen insertion into Pt/VMoO5.5

Pt precursor	exp	pretreatment	t_0 (s)	$k_1 \times 100$ ($s^{-1/2}$)	range of x vs. $(t - t_0)^{1/2}$ linearity	r_{rel}	d by TEM (Å)	d_{rel} by TEM (Å)	number of particles counted
H_2PtCl_6	15	200 ° C, air	7100	1.9	$0.8 \rightarrow 2.6$ $\rho = 0.9963$ (a)	2.87	(b)	–	–
H_2PtCl_6	12	200 ° C, vac.	10300	2.68	$1.4 \rightarrow 2.8$ $\rho = 0.9985$	1.91	(c)	–	8
H_2PtCl_6	6	300 ° C, air	990	16.85	$1.3 \rightarrow 2.8$ $\rho = 0.9756$	0.76	19.4	0.89	63
H_2PtCl_6	22	400 ° C, air	425	9.77	$< 0.7 \rightarrow 2.85$ $\rho = 0.9941$	1.00	21.9	1.00	171
$Pt(NH_3)_4Cl_2$	4	400 ° C, air	750	3.57	$1 \rightarrow 2.2$ $\rho = 0.9988$	1.65	N.D.	N.D.	–
$Pt(NH_3)_4(OH)_2$	3	350 ° C, air	~ 0	11.4	$< 0.5 \rightarrow 2.7$ $\rho = 0.9966$	0.93	20.2	0.93	155
	25	ditto	~ 550	5.10	$< 1 \rightarrow 2.7$ $\rho = 0.9897$	1.39	N.D.	N.D.	–
$Pt(NH_3)_4(OH)_2$	23 (d)	350 ° C, air	5400	2.30	$1.1 \rightarrow 2.6$ $\rho = 0.9946$	0.79	N.D.	N.D.	–
$Pt(NH_3)_4(OH)_2$	24	350 ° C, vacuum	25	2.19	$1.9 \rightarrow 2.7$ $\rho = 0.9988$ (7 pts only)	2.11	37.9	1.73	154
	26	ditto	~ 0	1.81	$1.85 \rightarrow 2.75$ $\rho = 0.9988$	2.32	N.D.	N.D.	–
$Pt(NH_3)_4(OH)_2$	1	400 ° C, air	1560	10.2	$0.6 \rightarrow 2.5$ $\rho = 0.9958$	0.98	N.D.	N.D.	88
	21	ditto	~ 300	12.3	$0.75 \rightarrow 2.7$ $\rho = 0.9973$	0.89	24.4	1.11	–

(a) ρ is the correlation coefficient of $x_{inserted}$ vs. $(t - t_0)^{1/2}$ in the indicated range.

(b) Too few visible particles. Very heterogeneous dispersion.

(c) A few particles with large diameters (80–120 Å).

(d) Pt loading = 0.15% w for this experiment. Note that the other experimental conditions are the same as for sample #3. Assuming that r_0 is also the same would yield a value for $k = 0.15 \cdot k_{exp\#3} = 0.017$.

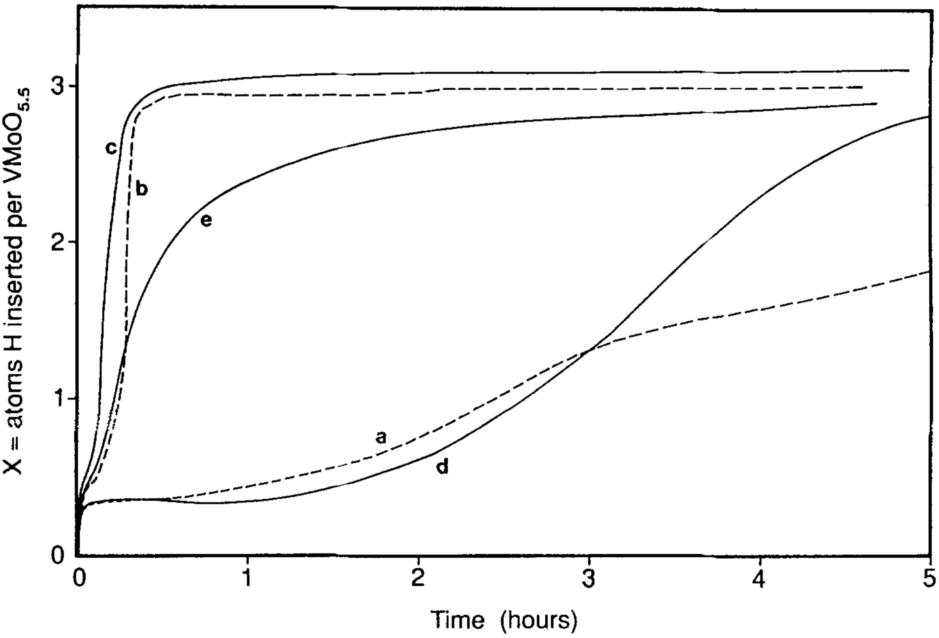

Fig. 1. A few illustrative kinetics of hydrogen uptake by $VMoO_{5.5}$ (i) precursor: H_2PtCl_6, heated in air at 200 °C (a) – experiment #15 heated in air at 300 °C (b) – experiment #6 heated in air at 400 °C (c) – experiment #22 heated under vacuum at 200 °C (d) – experiment #12 (ii) precursor: $Pt(NH_3)_4Cl_2$, heated in air at 400 °C (e) – experiment #4. *N.B*: The same experiment identifications are used as in table 1.

from the beginning of the reaction, and no latency would be observed. Variable induction periods have been reported by Tinet [7] for Pt/MoO_3.

The very fast initial sorption preceding the induction period is something of a quandary, however. It cannot be due solely to adsorption on the platinum surface, since it is present even when platinum is not expected to be initially in the metal form, and since the quantity of H adsorbed in this step ($x \simeq 0.34$) is considerably higher than the total number of platinum atoms (0.013 mole per oxide for 1% loading). Hydrogen physisorption is known to occur in addition to bulk chemisorption, in rather large extent in the case of $VMoO_{5.5}$, but is supposed to be located in cracks formed because of the anisotropic crystallographic cell alteration during bulk H intercalation that the physisorption sites should not exist before the start of the bronze formation. Thus, at the present time, we are unable to provide a satisfactory explanation for the occurrence of fast initial sorption.

The second, and quantitatively more important, absorption step is expected to be diffusion-limited: hydrogen from the saturated surface of the metal Pt crystallites diffuses, through a process called spillover, on the surface and into the bulk of the oxide, where it reacts to form the H-bronze.

Diffusion-limited processes often show a $(\text{time})^{1/2}$ dependency. In fact, if diffusion sites are not all activated at the same time, we have to take into account the activation function of the crystallites $N_{\text{active}}(t) = f(t)$ in the expression of the time dependency. For most of the kinetics that we have observed, $f(t)$ is abrupt enough for this simplified formula to be valid (this case has been called "simultaneous nucleation" by Delmon [9]), i.e. we can find a time t_0 such that the experimental kinetics is reasonably well fitted by:

$$x_{\text{inserted}}(t) = x_1 + k(t - t_0)^{1/2},$$

a "reasonable" fit being one that yields a correlation coefficient > 0.985 between x and $(t - t_0)^{1/2}$ for a range of x values > 1.0. Approximate values of the optimal t_0 and of the corresponding k are given in table 1.

A somewhat more precise theoretical treatment may allow us to extract some information from the values of k. Solving the diffusion equation for anything close to a realistic model of $H/Pt/VMoO_{5.5}$ would be very difficult. However, a simplified phenomenological model has been applied to H spillover from small metal particles [10,11]. It is derived by analogy from a problem of heat conduction theory [12]. In this treatment, diffusion is supposed to occur from circular centers (here the Pt particles) of constant concentration c_e and radius r_0 onto a surface characterized by a constant diffusion coefficient D. Then the total number n of H atoms having diffused from *one* Pt particle to the surface at time t is given by:

$$n = 4\pi r_0^2 c_e \left(\left(\frac{T}{\pi} \right)^{1/2} + \frac{T}{4} - \frac{T^{3/2}}{12\pi^{1/2}} + \dots \right) \tag{1}$$

where T is a reduced time: $T = Dt/r_0^2$.

For small values of T, we may keep only the first term in expansion (2), meaning that x_{inserted} is approximately linear with respect to $t^{1/2}$. The slope k would be $4\pi r_0 c_e D^{1/2}$ for one diffusing center; if there are N independent diffusing centers per mole oxide (each with radius r_0), the slope is simply

$$k = 4N\pi^{1/2} r_0 c_e D^{1/2}. \tag{2}$$

The rigorous solution (1) is derived for axial symmetry and is thus only valid for diffusion from a circle into a plane, i.e., surface diffusion. For $VMoO_{5.5}$ bronzes, however, the x vs $t^{1/2}$ linearity extends well beyond the x value that would correspond to full surface coverage, for which an upper bound can be estimated at around $x \simeq 0.05$ (see table 1 for the limits of linearity). However, the surface of some bronze-forming oxides are "self-cleaning" [13], i.e. hydrogen is constantly removed from the surface region by diffusion into the bulk at a high rate, so that surface diffusion could remain rate-limiting in a large range of x values. This supposes (i) a high anisotropy of the diffusion coefficient in different crystal directions, and (ii) a preferential cleavage plane accounting for the larger part of the exposed surface of the oxide, which is indeed compatible with the lamellar habitus of the oxide particles observed by TEM.

Accepting the validity of eq. (2) allows one to estimate the relative radii of the platinum particles for different samples. In (2), D, the effective diffusion coefficient in $VMoO_{5.5}$, is unknown; c_e is the surface H concentration on platinum, which is generally taken as 1 atom per 11.2 $\text{Å}^2 \equiv 1.483 \cdot 10^{-5}$ mole/m^2 at saturation [14]. k is the experimental slope of the x vs $t^{1/2}$ plot. N and r_0, are unknown but not independent since the total platinum loading w (generally 1% in our experiments) must be accounted for by N particles of radius r_0 (supposing at first all particles to be identical). If we assume a hemispherical geometry, this yields:

$$N \cdot \left(2/3\pi r_0^3\right) \cdot \rho_{\mathrm{Pt}} = \frac{w}{1-w} \cdot Mm_{\mathrm{oxide}} \tag{3}$$

where Mm_{oxide} is the molecular weight of the oxide. This second relationship allows us to extract the radius of the diffusing centers:

$$r_0^2 = \frac{Nr_0^3}{Nr_0} = \sqrt{D}\,\frac{w}{1-w} \cdot \frac{5.497 \cdot 10^{-8}}{k} \tag{4}$$

if r_0 is expressed in m, N as a number of Pt particles per mole oxide, c_e in mole/m^2, or:

$$r_0 \propto D^{1/4} k^{-1/2}. \tag{5}$$

Thus we may compute relative particle radii for different experiments:

$$r_{\mathrm{rel}} = \frac{r_i}{r_j} = \left(\frac{k_i}{k_j}\right)^{-1/2} \tag{6}$$

even without an estimate for the diffusion coefficient, provided it remains constant for both experiments. Such relative radii are listed in table 1, arbitrarily attributing the value $r_0 = 1$ to sample #22 (precursor: H_2PtCl_6, pretreated at 200 °C in air). Reasoning on a distribution of particle radii instead of a set of particles with uniform radius, it appears that (4) would give, instead of the usual average $\bar{r}$, the value of $(\bar{r}^3/\bar{r})^{1/2}$. However, it turned out that better correlations are obtained with the average radius than with this more complex statistic, although this may be due to the insufficient size of some of our statistical samples.

We have tried to obtain an independent estimate of the relative r values obtained from (5) by room temperature CO chemisorption. Unfortunately, this generally successful technique [14] proved impossible to apply for $Pt/VMoO_{5.5}$. Both the first and the second CO adsorption isotherm exhibit, for higher CO pressures ($\sim$ 100–200 Torr), a slow sorption reaching values several times in excess of what would correspond to 100% Pt dispersion: equilibrium could not be reached even after several days of contact with CO.

Another commonly used technique for particle size determination is direct measurement on TEM micrographs and establishment of a size histogram. In the present case, beside the general limitations of the technique such as its insensitivity to particles smaller than ~ 10 Å, it suffers from the relative lack of contrast between Pt particles and the $VMoO_{5.5}$ support. On thin particles, identification of the Pt crystallites was relatively easy, as in the micrograph shown in fig. 2 (precursor: $Pt(NH_3)_4(OH)_2$, pretreated at 350 °C in vacuum). In contrast, the inset shows a micrograph typical of another category where Pt particles are markedly smaller and their blurred contours makes them difficult to distinguish (precursor: $Pt(NH_3)_4(OH)_2$, pretreated at 350 °C in air). In all cases where a sufficient number of platinum particles could be measured to yield meaningful statistics, the average diameters $\bar{d}$ are listed in table 1. It is apparent that the conditions giving the maximum value of k, i.e., the fastest kinetics, also give rise to the highest metal dispersion (smallest average diameter: precursor H_2PtCl_6, pretreated at 300 °C in air, sample #6). Besides, relative diameters obtained from (5) are correlated with the relative average diameters estimated from the size histograms if the same sample is taken as a basis of comparison.

For the sample giving rise to the slowest kinetics (experiment #15: H_2PtCl_6, 200 °C, air), only a few, very large crystallites (diameter 80–120 Å) could be observed, in insufficient number to calculate an average diameter.

Thus, it would seem that the kinetics of hydrogen intercalation indeed yields meaningful estimates of *relative* particle sizes. Absolute sizes could be established by determination of the diffusion coefficient D, or in relation to a reference sample.

A limitation of our treatment of the kinetics is that it does not take into account the uneven repartition of Pt crystallites on the oxide particles. From TEM results, some oxide particles appear almost Pt-free; on the other hand, one can find a few instances of particles that are almost entirely coated by Pt crystallites with a size distribution significantly different from average. Intuitively, this would probably result in the $x = k(t - t_0)^{1/2}$ relation holding only in a limited range of x values, corresponding to the saturation of "well-behaved" oxide particles.

Finally, we must emphasize that this treatment will produce coherent results only when applied to the kinetics of first hydrogen intercalation into the freshly prepared sample. When the oxide is submitted to redox cycles comprising first intercalation, O_2 oxidation, second intercalation, etc. (such as described in ref. [5]), the intercalation kinetics change in a way that can hardly be connected to a modification in the metal dispersion. This complex phenomenon, possibly involving the formation of H_2 dissociating centers on the oxide surface, is currently under investigation.

In summary, the main conclusions of this contribution are twofold. First, it is demonstrated that information on the size of supported metal particles can be extracted from the kinetics of hydrogen spillover when conventional techniques of dispersion measurement (such as H_2 or CO chemisorption) are not available. Second, and on a more practical level, studies purporting to assess the interest of

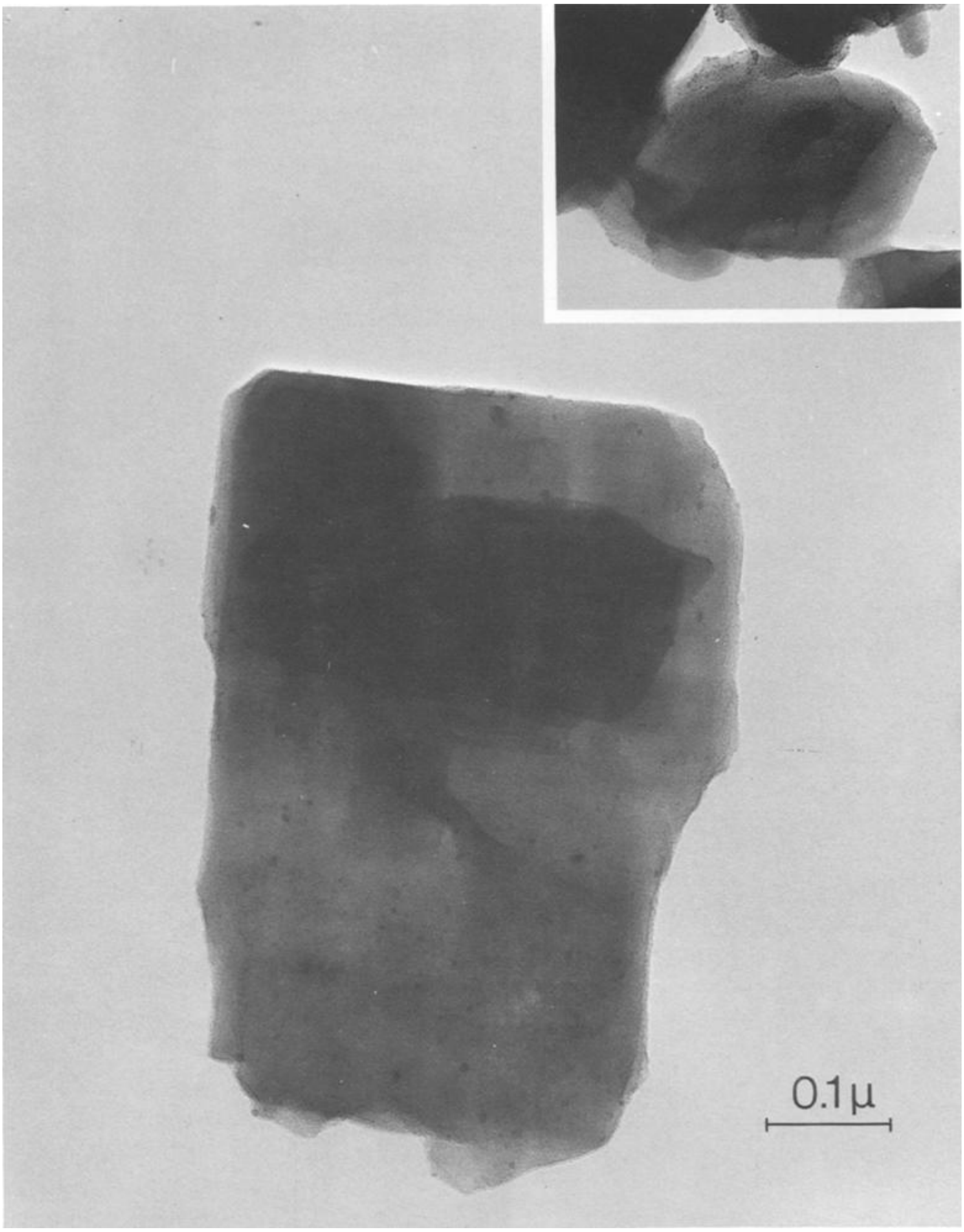

Fig. 2. Electron micrograph of two samples of Pt-coated $VMoO_{5.5}$. The large, isolated particle is $VMoO_{5.5}$ impregnated with $Pt(NH_3)_4(OH)_2$, pretreated at 350 ° C in vacuum. The inset shows $VMoO_{5.5}$ impregnated with $Pt(NH_3)_4(OH)_2$, pretreated at 350 ° C in air.

H-bronzes as hydrogen storage media should not overlook the influence of the supported metal precursor and pretreatment, since the wrong choice for these parameters will result in very slow kinetics of intercalation which might be mistakenly considered as an intrinsic property of the bronze.

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