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The Kinetics of Pt-Black Catalyst Sintering in Different Atmospheres

The effect of different atmospheres on the sintering of Pt-black was studied first by Baird *et al.* (*1*, *2*), in the temperature range of 400–900 K. It was shown that the presence of hydrogen resulted in sintering at temperatures lower by about 400 K than in atmospheres without hydrogen. Hydrogen causes certain surface relaxation and lattice strain decrease even at room temperature (*3*). It was supposed that the so-called δ-hydrogen has a special importance in the sintering process. This has a T_{des} of 570 K and is situated probably in interstitial positions as suggested by Tsuchiya *et al.* (*4*).

Metallurgists distinguish three different phase of sintering (*5*): (i) Initial or neck growth stage is accompanied by the loss of several percents of the surface area but there is no grain growth. (ii) The coalescence stage begins when grain growth first occurs. (iii) During the final stage the pore phase is pinched off and shrinks to zero. The kinetic equation for grain growth is

$$D^m - D_0^m = Kt \exp(-E/kT) \qquad (1)$$

Where D and D_0 are the most probable initial and momentary grain diameters, t is time, E the activation energy for the process. The exponent m is 3 for coalescence control (*6*) and 2 for grain boundary diffusion (*7*). Values lower than 2 were obtained in some experiments at low temperature but it increased with increasing temperature and approached too close to the melting point (*8*). On the other hand the time (t) dependence of the exposed metal surface area (S) for supported catalysts is (*9*)

$$dS/dt = KS^n \qquad (2)$$

where K is an Arrhenius-type constant. Exponent n varies between 2 and 8 depending on the nature of the rate-controlling process, if it is the sintering of the metal particles and not surface migration then n is 2 or 3. The integral of this equation is equivalent to Eq. (1) ($m = n - 1$) if we consider that the reciprocal surface area is proportional to the grain diameter in this stage of sintering (*10*). Lebedev *et al.* (*11*) reported $n = 2$ and a phenomenological activation energy 77 kJ/mol for Pt-black sintering under vacuum.

The aim of the present work was to attempt at a quantitative description of Pt-black sintering promoted by hydrogen. By doing so we hope to obtain a deeper insight into the formation of the sintered Pt which represents a Pt–H system (depending on the conditions of sintering) and which may contain also other impurities (*12*).

EXPERIMENTAL

Pt-black was produced by reduction of p.a. $H_2PtCl_6 \cdot 6H_2O$ by formaldehyde in the presence of concentrated KOH at 20–25°C (*13*). Its mean diameter and strain was 15 nm and 4.49×10^{-3}, respectively.

Changes of the particle size were followed during *in situ* thermal treatment by a DRON-2 diffractometer using Ni-filtered Cu$K\alpha$ radiation. The heating rate of temperature-programmed measurements was 2 K/min in all of the cases. In the case of isothermal measurements the given temperature was reached by a heating rate of about 100 K/min.

During the measurements seven peaks of the Pt diffractogram (111), (200), (220), (311), (222), (331), (420), were permanently scanned. Because of the comparatively fast sintering during thermal treatment the scanning rate had to be set as high as possible.

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TABLE 1

The Results of Isothermal Heat Treatments

Time (min)	Pt in H_2 at 420 K		Pt in He at 570 K		Prereduced Pt in He at 670 K	
	D (nm)	$e \times 10^3$	D (nm)	$e \times 10^3$	D (nm)	$e \times 10^3$
0	18.8	3.63	14.5	4.49	18.5	2.49
5	24.0	1.28	14.5	1.90	32.1	1.40
10	27.5	1.29	16.3	2.20	37.5	1.00
15	29.0	1.28	19.5	2.25	43.7	0.95
20	36.2	1.49	20.4	2.40	49.4	0.85
25	41.3	1.58	22.0	2.45	56.7	0.85
30	45.7	1.63	22.7	2.45	66.2	0.90
35	49.5	1.66			76.0	0.90
40	52.8	1.67			86.6	0.95
45	55.4	1.66			90.7	0.95
50	55.6	1.62				

This is why simplified methods had to be used in the evaluation of the results. Jones' method (*14*) was used for the correction of $K\alpha$-doublet and Ruland's method (*15*) for correcting instrumental broadening.

Assuming spherical crystallites (which are close to those observed by electron microscopy (*2*, *12*)) and homogenous lattice strain distribution in all crystallographic directions the best least-square fit to the experimental results was obtained presuming the size and distortion profiles both to be Cauchy type. Consequently the L mean diameter of the crystallites and the e strain were determined according to

$$\Delta 2\theta \cos\theta = (\lambda/L) + 4e \sin\theta \qquad (3)$$

Here $\Delta 2\theta$ is the corrected half-maximum intensity breadth, θ the Bragg angle, λ the X-ray wavelength, $e = \Delta d/d$, d the interplanar spacing (*16*). It is known that these simplifications strongly influence the absolute accuracy of the evaluation but for our purpose the relative accuracy of the measured values (i.e., the real value is proportional to the measured one) is sufficient.

The synchronous values of $\Delta 2\theta \cos\theta$ for the seven peaks were taken from the plots of $\Delta 2\theta \cos\theta$ vs time.

RESULTS AND DISCUSSION

The results of isothermal sintering are collected in Table 1. The d grain diameter vs time results in linear plots with $m = 2$ in Eq. (1) for sintering in hydrogen and $m = 3$ in helium. In order to investigate the role of adsorbed oxygen a sample was kept in hydrogen for an hour then in helium for 3 days, both at room temperature. Under these circumstances all surface oxygen is presumably removed from platinum (*17*). The sintering kinetics of this sample could be described by Eq. (1), using $m = 1$.

Temperature-programmed measurements (TPM) were carried out in order to determine the phenomenological activation energy of the sintering. The results are shown in Table 2. On their basis activation energies of 128, 40, and 54 kJ could be calculated for sintering in helium ($m = 3$), in hydrogen ($m = 2$), and in helium with prereduced surface ($m = 1$), respectively. The activation energy in helium with prereduced surface (54 kJ/mol) is only slightly higher than that in hydrogen (40 kJ/mol). On this basis it seems that the effect of hydrogen on the sintering is no more than removing oxygen from the surface. This was

TABLE 2

The Results of Temperature-Programmed Measurements[a]

T (K)	Pt in H_2		Pt in He		Prereduced Pt in He	
	D (nm)	$e \times 10^3$	D (nm)	$e \times 10^3$	D (nm)	$e \times 10^3$
373	14.8	2.47				
398	14.1	2.02				
423	14.0	1.65				
448	14.2	1.32				
473	15.4	1.09			18.5	2.49
498	16.7	1.25	15.2	4.36	18.8	2.17
523	18.4	0.92	17.1	4.29	19.0	2.04
548	20.2	0.50	18.0	3.97	19.0	1.86
573	22.2	0.07	19.4	3.41	19.1	1.71
598	25.9	0.12	22.2	3.01	19.1	1.54
623	30.0	0.22	24.6	2.19	19.3	1.41
648	35.2	0.36	29.1	1.16	19.2	1.21
673	41.4	0.22	40.3	0.56	19.4	1.06
698			62.6	0.59	19.4	0.87
723			82.9	0.54	19.8	0.74
748			96.4	0.53	19.8	0.56
773			87.6	0.38	20.0	0.42
798			90.2	0.37	21.1	0.30
823			91.2	0.36	22.7	0.23
848					24.5	0.10
873					26.8	0.05

[a] Heating rate: 2°C/min.

one of the possibilities suggested in (*1*). The value of Lebedev *et al.* (77 kJ/mol for sintering under vacuum) is higher than our result, so we think that some chemisorbed hydrogen remained on the surface of our platinum even over 700 K when the sintering began. This strongly bound chemisorbed hydrogen (*17, 18*) may have decreased the activation energy. It desorbs only above 800 K.

CONCLUSIONS

As electron micrographs indicate (*1, 2, 12*) unsintered Pt has a fine dendritic structure in which the individual crystallites are connected to each other. This dendritic structure must have rather high surface free energy and also high lattice distortion (*3*), supplying thus the basic driving force of sintering. The energy barrier of the surface migration of Pt atoms determines its starting temperature. This energy barrier is strongly influenced by presence of alien adsorbed species. Hydrogen occupying the low energy places of the surface and coordinating to the Pt atoms migrating through high energy places decreases the unevenness of surface energy for the migrating Pt atoms and makes possible the formation of a quasi-liquid Pt–hydrogen surface layer which transports the Pt atoms from the higher surface curvature to the lower. This is a typical grain boundary process. Indeed, its exponent in Eq. (2) is $m = 2$. If there is no hydrogen on the surface the activation energy is nearly doubled and the m exponent decreased to 1 as if the temperature had been strongly decreased from close to the melting point (*8*), although sintering occurs at a higher temperature than that in hydrogen. Chemisorbed oxygen has an opposite effect than hydrogen because the Pt–O double bound is much stronger than the Pt–H and the Pt–O surface layer has much stronger structure; consequently the mobility of the platinum atoms is much smaller. Indeed the initial stage of sintering increased to about 5 min from almost nothing (see Table 1). Coalescence as a rate-controlling step is indicated by the exponent $m = 3$ and the activation energy being more than triple than in hydrogen.

Carbonaceous and Si impurities of the sample (*12, 20*) may have an additional influence: their accumulation on the surface can hinder the sintering (*2, 3*). This accumulation may also be strongly influenced by the adsorbed gases (*12, 21–23*).

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