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The Effect of Different Atmospheres on the Sintering of Pt/Al_2O_3 Reforming Catalysts

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The effect of different atmospheres, namely, nitrogen, oxygen and hydrogen on the sintering of diluted samples of Pt/Al_2O_3 reforming catalyst was studied in the temperature range 300–800°C.

It was found that the results of sintering in these atmospheres at temperatures below 400°C are very similar to those previously obtained in the case of unsupported platinum.

The treatment of the catalyst samples at temperatures higher than 400°C in both N_2 and H_2 could lead to an activation; the phenomenon which was observed previously by heating *in vacuo*. However, the treatment in O_2 showed a continuous deactivation over the whole range of studied temperatures. Some interpretations are also given.

1. INTRODUCTION

An extensive work has been done on the sintering of Pt/Al_2O_3 reforming catalysts. However, the majority of the recent investigations dealt with the state of supported platinum in the catalysts, either freshly prepared or sintered under different conditions (*1–8*). It was suggested that supported platinum exists in high dispersion state, although some authors showed that platinum may form some sort of complex compound with alumina base (*5*). The degree of metal dispersion, however, was found to depend on the method of preparation of the catalyst (*9*) and the loss of catalytic efficiency during the heat treatment was accompanied with a marked increase in metallic crystal size (*5, 10*).

Several investigations were also concerned with the study of sintering of Pt/Al_2O_3 in different atmospheres. Therefore, the sintering in air, as well as, in presence of water vapor was studied by Waters and his collaborators (*11*) at temperatures higher than 800°C. The results showed that both activity and surface area decreases with time of sintering achieving certain stationary values. The slow change of γ-alumina to α-alumina, taking place at these temperatures was found to be accompanied with an increase in particle size and with a parallel decrease in surface area.

An interesting study of kinetics of sintering in nitrogen atmosphere was carried out by Hermann and co-workers (*3*), who noted that the chemisorption capacity, taken as a measure of activity, decreases with time of sintering according to second-order equation. Analyzing the data of H:Pt ratio, i.e., the degree of dispersion, the authors came to the conclusion that the transition of platinum atoms from

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atomic or dispersed phase into crystalline or more condensed phase can be considered as a process of second order; the results being in good agreement with those obtained by Maat and Moscou (*12*) for diluted catalysts.

The decrease in degree of metal dispersion with time of sintering was also observed in the works of Gruber (*4*, *13*), during the study of adsorption of H_2, O_2 and CO on Pt/Al_2O_3 catalysts. Metallic particle size was found to increase with time of sintering at 500°C in H_2 atmosphere. In another study of sintering in air, in N_2 and *in vacuo* (*14*), it was found that treatment *in vacuo* at temperatures up to 450°C had no effect on catalytic activity, whereas in air and in N_2 marked decrease of activity could be noted, which was only explained as being due to the decrease in surface area taking place as a result of crystal growth (at $t < 400°C$).

A systematic study carried out by the senior author of the present communication with other collaborators (*15*) on sintering of different diluted Pt/Al_2O_3 catalysts *in vacuo* showed that, in all cases, the activity and the metallic surface area decreased rapidly with time of sintering in the temperature range 300–800°C. However, the stationary values of activity and surface area were found to decrease with temperature up to 400°C, after which both parameters showed a marked increase. Such anomalous increase in activity and surface area, the authors could attribute to the process of dissociation of already formed crystalline phase (or size-enlarged ensembles) (*16*). They suggested that the mobility of surface atoms on the carrier increases and the adsorbed layer changes into "two-dimensional gas." This could lead to the idea that the technical supported catalysts, used under high temperature conditions (e.g., in petrochemical processes) can only function in the form of two-dimensional gas after the dissociation of the subcrystals into small ensembles or even into separated atoms. This point of view was more evidenced by the results of low-temperature chemisorption of H_2 and dissolution in dil HCl (*15*, *16*).

The purpose of the present article is to continue the previously mentioned study, to throw further light on the effect of different atmospheres on the processes taking place during the heat treatment of diluted Pt/Al_2O_3 catalysts.

The atmospheres chosen for this purpose were H_2 and O_2 which are considered as active atmospheres and N_2 which is thought to be inactive one. Since these gases are widely used in many petrochemical processes, it would be expected, therefore, that the results of the present study can provide additional information in this direction.

2. EXPERIMENTAL METHODS

Catalyst

Three different catalyst samples, corresponding to 0.2, 0.4 and 2% wt platinum were prepared by impregnation of the γ-alumina support with the appropriate quantity of chloroplatinic acid solution in conventional ways. The alumina carrier was previously heated at 850°C to eliminate any changes in its surface characteristics during the sintering study. After filtration, drying for 24 hr at 110°C and calcination at 300°C all samples were reduced in flowing hydrogen for 4 hr at 300°C, as has been described elsewhere (*15*). These conditions resulted in good reproducibility of the adsorption and catalytic activity measurements.

Sintering Technique

The sintering study was carried out in a volumetric apparatus, similar to that used for gas adsorption measurements of conventional design (*18*), with the exception that a quartz sample tube was used for sintering study and the purified gases were introduced from the gas storage flasks into the system with a steady flow rate. The pressure was held manually at 1 atm by adjusting the bulb-buret settings and the level of mercury in the manometer.

With the aim of stabilization of freshly prepared catalyst, evacuation of the samples for 4 hr at 250°C and at pressure of less than 10^{-5} mm was adopted as a standard pretreatment (*19*).

After the gas was allowed to flow in the system with a steady rate, the pretreated sample of 500 mg was heated in this atmosphere for 2 hr at the given temperature in the range 300–800°C. This time of heating, viz. 2 hr, was found, as has been indicated in the previous work (*15*), to be sufficient to attain stationary values of activity and surface area. At the end of each thermal treatment, the catalyst was cooled in the same atmosphere of sintering with a cooling rate of 10°C/min.

Determination of Catalytic Activity

The catalytic activity of freshly prepared catalysts and thermally treated samples was tested in two different model reactions, namely, hydrogenation of cyclohexene (*17*) and decomposition of hydrogen peroxide (*15–17*). Both reactions were found to proceed kinetically as first-order ones. From the results of gasometric measurements, the rate constant in each case was evaluated. It was preferred in this work to use the activity parameter "*A*" instead of the rate constant "*k*," which was determined from the volumes V_{O_2} and V_{H_2} of evolved oxygen and consumed hydrogen in the decomposition of H_2O_2 and hydrogenation of C_6H_{10}, respectively, and from the half-life periods, $t_{1/2}$, according to the following equations (*15*):

$$A_{H_2O_2} = 9 \times 10^{17} \frac{V_{O_2}}{t_{1/2}}$$

and

$$A_{C_6H_{10}} = 4.5 \times 10^{17} \frac{V_{H_2}}{t_{1/2}}.$$

The terms $A_{H_2O_2}$ and $A_{C_6H_{10}}$ denote the number of hydrogen peroxide molecules decomposing per second per gram of catalyst and number of hydrogen molecules consumed in the hydrogenation of C_6H_{10} per second per gram of catalyst, respectively.

Determination of Specific Surface Area of the Carrier, Catalyst Samples and Supported Platinum

The low-temperature adsorption of nitrogen was applied for the determination of specific surface area of the carrier and the catalyst samples, using the BET method (*20*).

The specific surface area of supported platinum was determined by means of chemisorption of pure hydrogen, at liquid nitrogen temperature. The basic principle of this method, as it was first utilized by Boreskov and Kanaukhov (*21*), is to select adsorbate and adsorption parameters in such a way as to minimize adsorption on the support and maximize the adsorption on the metal. At this temperature, adsorption on the support occurred, to an extent, that demanded a correction. This was made by measuring adsorption on the nonmetallized support and by subtracting this value from the total adsorption. This procedure gave the so-called "net adsorption" on the supported metal. The net adsorption is, by itself, a measure of the metal dispersion for a given metal content. The surface area of supported platinum could, therefore, be calculated from the following equation (*15, 16*),

$$S_{Pt} = 2 \times a_{H_2} \times N \times \sigma_{Pt},$$

where a_{H_2} is the number of moles of chemisorbed hydrogen, which represents the net adsorption per gram of Pt, N is Avogadro's number and σ is the cross-sectional area of one platinum atom; being taken as equal to 8 Å^2 (*4*), i.e., the value of the area on the surface, occupied by one adsorbed hydrogen atom.

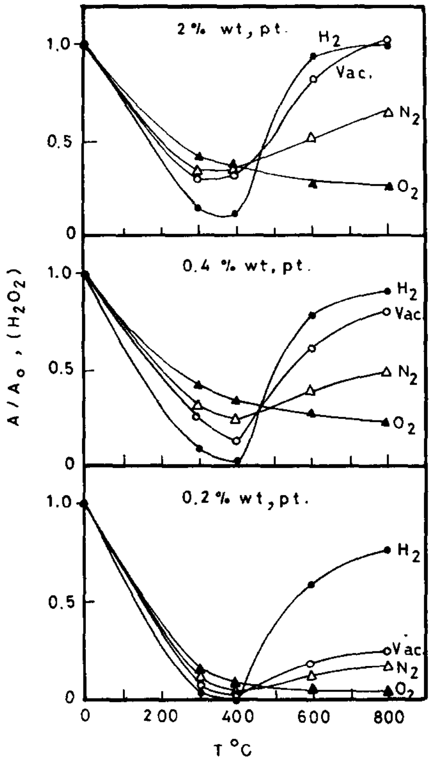

FIG. 1. The catalytic activity, $(A/A_0)_{H_2O_2}$ of Pt/Al_2O_3 catalysts of different % wt Pt, as a function of temperature of sintering in the following atmospheres: (●) H_2 atmosphere; (○) vacuum; (△) N_2 atmosphere; and (▲) oxygen atmosphere.

The degree of dispersion was also estimated from the ratio [H]/[Me], i.e., the ratio of number of atoms of the adsorbed gas per metal atom.

From the first approximation, that all the platinum particles being ideal cubes of uniform size with one face in contact with the support and the remaining five faces exposed, the average size of platinum particles could be determined by the use of the following equation (*22*):

$$a_e = \frac{5}{S_{Pt} \cdot \rho_{Pt}},$$

where a_e is the average particle size, ρ_{Pt} is the density of platinum and S_{Pt} is the surface area of supported platinum.

Determination of Number of Active Atoms on the Catalyst Surface

A preliminary experiment was carried out by placing 3 ml of 2*N* H_2O_2 solution + 100 mg catalyst in the reactor and the catalytic activity (*A*) was determined in the same manner as discussed above. In another experiment, 30 ml of dil HCl were added to the reaction mixture (i.e., the mixture of 3 ml of H_2O_2 and 100 mg catalyst sample), and the degree of deactivation (A_g/A), was, then, determined, where A_g is the activity of the deactivated catalyst. This degree of deactivation was found to be entirely proportional to the number of dissolved active surface atoms[4] (*23*).

After the reaction has been completed, the catalyst was filtered and washed with bidistilled water several times. The filtrate was evaporated and the residue was dissolved in aqua regia and then analyzed, colorimetrically, for platinum. From this, the number of active platinum atoms, N_{Pt}, passing into the solution was determined. It is to be noted, that the catalyst after separation was completely inactive.

3. RESULTS AND DISCUSSION

1. *The Catalytic Activity as a Function of Temperature of Sintering in Different Atmospheres*

The results of sintering of different diluted samples of Pt/Al_2O_3 reforming catalyst in different atmospheres, namely, vacuum, nitrogen, hydrogen and oxygen are illustrated in Fig. 1. The activity, measured in the decomposition of H_2O_2, is expressed in terms of a relative parameter A/A_0; where *A* is the activity of the catalyst, sintered at given temperature and A_0 is the activity of the freshly prepared catalyst. The sintering results ob-

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[4] It was thought that the deactivation takes place as a result of the dissolution of most active surface atoms. This effect seemed to be due to the combined action of dil HCl and 2*N* H_2O_2.

tained in the reaction of hydrogenation of cyclohexene are given in Table 1; the activity is expressed, also in terms of $(A/A_0)_{C_6H_{10}}$.

The results indicate, clearly, that the activity decreases by heating at temperatures below 400°C in all studied atmospheres. Moreover, nitrogen and oxygen show higher activity values than vacuum and hydrogen in this temperature region. The rate of sintering seems to be impeded by presence of both oxygen and nitrogen. The inhibiting effect of oxygen is, probably, due to the formation of an oxide layer which would, markedly, hinder the recrystallization process (*24–26*).

For nitrogen, however, it appears that the mechanism of sintering is, somewhat, different. It was suggested before that nitrogen might combine with the oxygen, initially, chemisorbed on the surface of fresh catalysts to form NO_2 (g), which is stable up to 2000 K (*27*).

The decreasing order of catalytic activity in this temperature range (below 400°C) can, therefore, be represented in the following atmospheres as:

$$O_2 > N_2 > \text{vac.} > H_2.$$

It is to be noted, that very similar behavior was obtained in the case of sintering of metallic platinum black (*27*), with the same order of decrease in catalytic activity in the above-mentioned atmospheres.

At temperatures higher than 400°C, the catalytic activity increased again in hydrogen and nitrogen as well as *in vacuo*. The increase of activity became more pronounced in presence of H_2, whereas in nitrogen the catalytic activity showed much lower values than in H_2 and *in vacuo*. This activation taking place at $t > 400$°C seems to be very much impeded by presence of oxygen; the activity being continually decreased.

It is clear, also, from these results, that the order of decreasing catalytic activity in this high-temperature region, in contrast to that previously mentioned at lower temperatures, is: $H_2 > \text{vac.} > N_2 > O_2$.

TABLE 1

The Catalytic Activity, $(A/A_0)_{C_6H_{10}}$, of Pt/Al_2O_3 Catalysts (of Different % wt Pt) as a Function of Sintering Temperature in Different Atmospheres

Sintering atmosphere	Sintering temp (°C)	Activity $(A/A_0)_{C_6H_{10}}$ of Pt/Al_2O_3 catalysts containing Pt (%):		
		0.2	0.4	2
Original (freshly prepared catalysts)		1	1	1
N_2	300	0.13	0.35	0.36
	400	0.06	0.30	0.35
	600	0.12	0.40	0.50
	800	0.18	0.48	0.66
H_2	300	0.04	0.10	0.15
	400	0.02	0.03	0.13
	600	0.65	0.80	0.94
	800	0.77	0.91	1.00
O_2	300	0.14	0.41	0.39
	400	0.12	0.38	0.38
	600	0.06	0.30	0.30
	800	0.05	0.26	0.28

2. Surface Area of Pure γ-Alumina Support

The γ-alumina used as support material in this work was calcined at 850°C to eliminate any changes in its surface characteristics during the sintering study. Preliminary experiments showed that the surface area of alumina support was not affected either by different steps involved in the catalyst preparation, e.g., impregnation, calcination and reduction steps or by sintering conditions, i.e., temperature and atmosphere of sintering.

The alumina support had the following properties:

BET surface area (m^2/g)	113.5
Pore size range (Å)	35–200
Impurities (ppm)	
Alkali (Na_2O)	35
Alkaline earths	143
Silicon	18
Iron	73

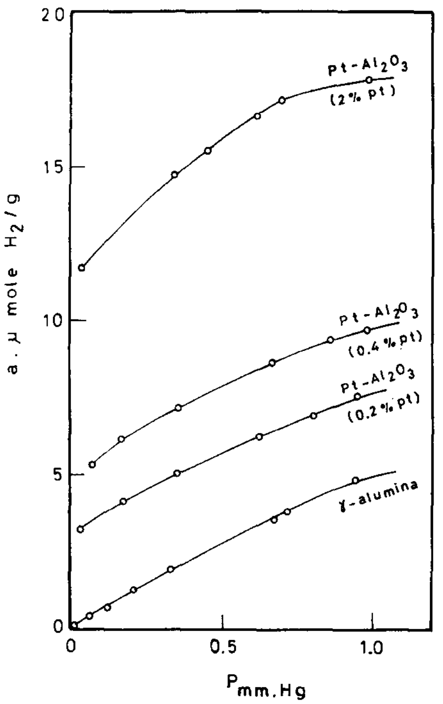

FIG. 2. Chemisorption isotherms for γ-alumina support and freshly prepared supported Pt/Al_2O_3 catalysts.

3. Metal Dispersion and Specific Surface Area of Supported Platinum as a Function of Temperature of Sintering in Different Atmospheres

The difference between the total adsorption on the catalyst and the adsorption on the corresponding support under identical conditions was taken as the net adsorption of hydrogen on the metal. Figure 2 illustrates the chemisorption isotherms (micromoles hydrogen adsorbed per gram of sample versus pressure in mm Hg) for γ-alumina support and freshly prepared supported catalysts of different metal content.

From these isotherms, the following parameters were calculated:

a. The metallic surface area, taking an average value of 8 Å², for the place usually occupied by a Pt atom.

b. The H:Pt ratio, which is considered as the physically most significant measure of the degree of metal dispersion.

c. The average particle size of supported Pt.

The calculation of these terms required a number of assumptions, as has been discussed before by many authors (*1*, *2*, *4*, *22*). The chemisorption data of freshly prepared catalysts are summarized in Table 2.

The specific surface area of platinum, supported on the surface of the catalysts, sintered in different atmospheres is illustrated in Fig. 3 as a function of sintering temperature.

It is clear from Fig. 3 that the metallic surface area decreases in all cases, in the temperature range below 400°C in an exactly similar manner as the catalytic activity. At temperatures higher than 400°C, the surface area shows an increase, similar to that obtained in activity and with the same, previously mentioned, order, i.e., $H_2 >$ vac. $> N_2 > O_2$. The surface area of supported platinum increases, markedly, with the rise of temperature in both hydrogen and nitrogen but in oxygen, the surface decreases, continuously, with temperature.

Moreover, data of Table 3 show that a lowering in H:Pt ratio and consequently an increase in average particle size is observed at temperatures below 400°C, especially in H_2 atmosphere. After 400°C, the degree of dispersion increases again and

TABLE 2

Chemisorption Data of Fresh Pt/Al_2O_3 Catalysts

1 Catalyst samples (% wt Pt)	2 Net ads. (moles H_2/g Pt)	3 H:Pt ratio	4 Surface area (m²/g Pt)	5 Av particle size, a_e (Å)
0.2	13.3	0.59	145	16
0.4	4.9	0.51	123	19
2.0	2.8	0.30	72	32

the particle size decreases, which provides evidence for the dissociation to separate atoms or ensembles of smaller size. In oxygen, the data indicate that the continuous decrease in activity and surface area is accompanied with a substantial decrease in the degree of dispersion and with a continuous increase in the particle size, i.e., without dissociation.

4. The Number of Active Surface Atoms of Platinum as a Function of Temperature of Sintering

The variation of number of active surface atoms of platinum, N_{Pt}, determined from the dissolution in the mixture of $2N$ H_2O_2–HCl, as has been discussed before in this communication, with temperature of sintering in different atmospheres is indicated in Table 4. The obtained data are very close to those of activity and metallic surface area. In N_2 and H_2, the number of surface atoms decreases with temperature up to 400°C, after which a marked increase can be clearly observed.

It is to be noted, that the heat treatment in O_2 at 600 and 700°C could not lead to a detectable change in number of active atoms on the surface of the studied catalyst samples containing 0.4 and 2% wt Pt, although a continuous decrease in this parameter could be obtained with rise of temperature in the case of a more diluted sample, i.e., 0.2% wt Pt.

4. CONCLUSION

Taking into consideration the conditions of catalyst preparation and heat treatment applied in the present study, it appears possible, from the foregoing discussion, to divide the studied temperatures into two regions:

a. Low-temperature region, below 400°C, which may be considered as a sintering or deactivation region.

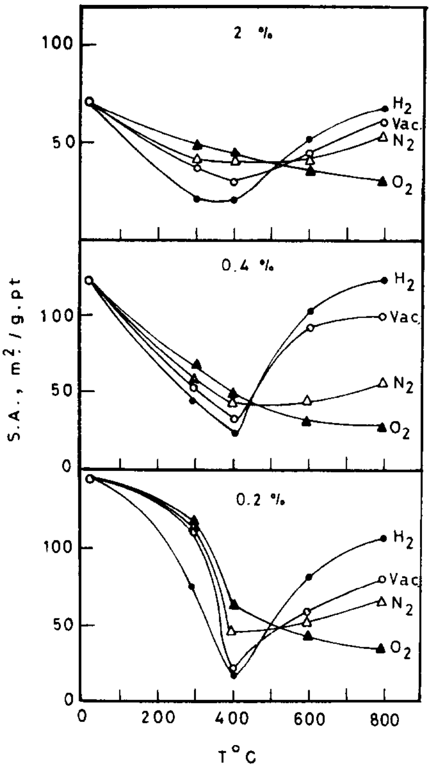

FIG. 3. Specific surface area of supported platinum (calculated from H_2 chemisorption), as a function of temperature of sintering in the following atmospheres: (●) H_2 atmosphere; (○) vacuum; (△) N_2 atmosphere; and (▲) oxygen atmosphere.

b. High-temperature region, higher than 400°C, during which another process comes into operation beside the sintering process. This new process, namely, the dissociation of already formed platinum crystallites may lead to a sharp increase in both activity and surface area parameters.

On the basis of these two temperature regions, the obtained results may be formulated as follows:

1. During heat treatments below Tamman's temperature, $T_{Tam.}$, where the mobility of surface atoms is relatively small ($T_{Tam.}$ for Pt = 409°C), deactivation was observed in all studied atmospheres as a result of recrystallization. Hydrogen, however, showed a larger deactivating effect, since reduction is involved, making re-

TABLE 3

The Degree of Dispersion, [H]/[Pt], and Average Particle Size a_e (Å), as a Function of Sintering Temperature in Different Atmospheres

Sintering atmosphere	Sintering temp (°C)	Pt/Al_2O_3 catalyst samples, containing Pt (%):					
		0.2		0.4		2	
		H/Pt	a_e	H/Pt	a_e	H/Pt	a_e
N_2	300	0.456	20	0.236	42	0.175	55
	400	0.183	48	0.178	52	0.170	58
	600	0.212	42	0.186	49	0.178	57
	800	0.264	35	0.228	42	0.225	44
H_2	300	0.305	31	0.186	54	0.190	115
	400	0.081	100	0.103	103	0.106	121
	600	0.325	28	0.423	24	0.430	44
	800	0.420	22	0.505	20	0.507	35
O_2	300	0.476	19	0.281	33	0.211	50
	400	0.272	35	0.207	47	0.186	53
	600	0.171	55	0.145	67	0.144	70
	800	0.134	73	0.112	75	0.122	87

TABLE 4

The Number of Active Surface Atoms of Platinum Dissolved in dil HCl as a Function of Temperature of Sintering in Different Atmospheres

Sintering atmosphere	Sintering temp (°C)	No. of active surface atoms of Pt, $N_{\mathrm{Pt}}(\times 10^{15})$, in Pt/$Al_2O_3$ catalyst samples containing Pt (% wt):		
		0.2	0.4	2
Freshly prepared samples		8.0	13.5	67.0
N_2	300	1.8	3.1	11.0
	400	1.3	2.5	8.0
	600	3.0	5.5	30.0
	800	5.0	9.0	45.0
H_2	300	0.5	1.2	6.0
	400	0.3	0.9	4.0
	600	4.5	7.8	40.0
	800	6.1	10.6	55.0
O_2	300	2.5	8.2	31.0
	400	1.8	6.3	21.0
	600	1.7	6.0	17.0
	800	1.5	6.0	17.0

crystallization much easier. Such deactivating effect becomes much less *in vacuo*. In oxygen and nitrogen atmospheres, the rate of sintering seemed to be markedly inhibited, as indicated from the high values of activity and surface area. The impedence of the rate of sintering in these two atmospheres proceeds, however, along widely different ways. In oxygen, the formation of chemisorbed oxide layer retarded to a great extent the recrystallization process (*24–26*). Nitrogen, on the other hand, may combine with oxygen, which was initially chemisorbed on the surface during the catalyst preparation, forming the chemisorbed product NO_2 (*27*).

The results of this part indicate clearly that the behavior of sintering of diluted Pt/Al_2O_3 catalysts is very similar to that of unsupported platinum (*27*), showing the same order of decrease in activity at given temperatures according to the following atmospheres, i.e., $O_2 > N_2 >$ vac $> H_2$.

2. A higher temperatures (i.e., $> T_{\mathrm{Tam.}}$ of Pt), where the mobility of the surface platinum atoms becomes appreciable, the

obtained results seem to reflect the net effect of both sintering (or association to more or less ideal subcrystals; this being the normal tendency that takes place at high temperatures) and activation (or dissociation of already formed subcrystals, which takes place as a result of increasing two-dimensional migration of surface atoms). Completely different pictures can thus be obtained according to the atmosphere of thermal treatment:

i. During the heat treatment in H_2 atmosphere, the mobility of surface atoms increases markedly, since hydrogen assists, most probably, in the removal of chemisorbed oxygen on the surface, leading thereby to its cleaning. In this case, the dissociation tendency exceeds, to a great extent, the normal crystallization tendency with the net result of the development of an activation effect as being indicated from activity and surface area data, as well as from the results of metal dispersion, i.e., from the increase in H:Pt ratio, a_e and N_{Pt} with rise of temperature.

ii. Heating *in vacuo*, can also accelerate the removal of several gases adsorbed on the surface, resulting in an increase in the mobility of surface atoms. A net activation effect is also obtained in this case, but the effect seems to be a little less than in H_2.

iii. The mobility of surface atoms in the presence of nitrogen atmosphere seems to be restricted, to some extent, due to adsorption or to the fact that even nitrogen might combine with oxygen, chemisorbed on the surface of fresh catalyst and form chemisorbed $NO_2(g)$, which is stable up to 2000 K (*27*). The rate of activation (i.e., dissociation) appears therefore, to be somewhat inhibited as compared to H_2 and vacuum atmospheres. This is shown by the lower values of activity and surface area obtained in N_2 atmosphere. It is also noticed that the obtained results approach those of vacuum treatment as the metal content decreases.

iv. The restriction of the mobility of surface atoms becomes much more pronounced in the presence of oxygen, the chemisorption of which becomes more appreciable with the increase of temperature. This effect would, mostly, lead to the establishment of an equilibrium between recrystallization and dissociation processes, giving nearly constant values over a wide range of temperature. In some cases net deactivation can even be observed.

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