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The Sintering of Supported Metal Catalysts

II. Comparison of Sintering Rates of Supported Pt, Ir, and Rh Catalysts in Hydrogen and Oxygen

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Changes in dispersion of alumina supported Pt, Ir, and Rh catalysts due to thermal treatment (250–800°C) in oxygen and hydrogen atmospheres were measured. In oxygen atmospheres the sequence of thermal stability was found to be Rh > Pt > Ir, while in hydrogen atmospheres the sequence was Ir > Rh > Pt. Increases in dispersion due to treatment in oxygen were observed for Pt and Ir catalysts. The observed relative stabilities are compared to qualitative predictions based on sintering mechanisms.

INTRODUCTION

Changes in metal surface area, due to changes in average metal crystallite sizes, occur when supported metal catalysts are exposed to elevated temperatures. Several mechanistic models have been proposed to describe this phenomenon (*1–6*) known as sintering, but discrimination among these models on the basis of experimental data is not possible at the present.

Wynblatt and coworkers (*5, 6*) predicted the thermal stability of some supported Group VIII metal catalysts on the basis of the atomic (or molecular) migration model in oxidizing and reducing atmospheres. In the present study the changes in dispersion in reducing and oxidizing atmospheres as a function of temperature (250 to 800°C) for Al_2O_3-supported Pt, Ir, and Rh catalysts were measured.

EXPERIMENTAL METHODS

Materials. The catalysts that were used in this study are described in Table 1. [The numbering of the catalysts in this series of papers is sequential; i.e., Catalysts 1 and 4 are the same catalysts as Catalysts 1 and 4 in Ref. (*7*).] Catalyst 4A has the same nominal composition as Catalyst 4, but the two catalysts were prepared in separate batches. Although the impregnation technique used in preparing the two batches was the same [procedure has been described previously (*7*)], catalysts with different dispersion resulted (see Table 1).

The metal content of the catalysts prepared by impregnation was calculated from the weight of the support and the amount of metal in the impregnating solutions. The impregnation technique resulted in an uneven distribution of the metal in the support pellets; the metal concentration decreased towards the interior of the pellets. Some fines were formed ($\lesssim 5\%$ by weight

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TABLE 1

Description of Catalysts

Catalyst	Catalyst composition[a]	Method of preparation	Initial dispersion (D_0)	Sample size used for sintering (g)
1	0.5% Pt	Commercial catalyst (Engelhard; Lots 18-381 and 23-288)	0.20	5.0
4	2.0% Pt	Impregnation with H_2PtCl_6 solution[b]	0.28	2.5
4A	2.0% Pt	Impregnation with H_2PtCl_6 solution	0.35	2.5
6	2.0% Ir	Impregnation with $IrCl_3$ solution	0.42	5.0
7	0.5% Rh	Commercial catalyst (Engelhard; Lot 17-941)	0.37	3.0
8	1.0% Rh	Impregnation with $RhCl_3$ solution	0.32	3.0
9	0.5% Ru	Commercial catalyst (Engelhard; Lot 16-988)	(0.07)	6.0
10	1.0% Ru	Impregnation with $RuCl_3$ solution	(0.04)	6.0

[a] All supports were Al_2O_3.

[b] Kaiser KA-201 spherical alumina pellets (−8 to +10 mesh) used as support for all catalysts prepared by impregnation.

of the support used) due to the stirring during the impregnation procedure. The color of these fines indicated that they probably had, on the average, a higher metal content than the impregnated support spheres. Hence, the nominal metal content reported in Table 1 may be somewhat higher than the actual metal content. The metal salts used for the impregnation were obtained from Engelhard Industries.

After impregnation and drying, the catalysts were reduced in flowing hydrogen for 16 hr at 150°C, 2 hr at 250°C, and 1 hr at 500°C. The commercial catalysts were reduced in flowing hydrogen for 2 hr at 250°C and 16 hr at 500°C. After reduction the catalysts were split into smaller portions and stored, exposed to air, at room temperature until use.

The hydrogen used during reduction, sintering, and adsorption was produced, as needed, by a Matheson H_2 generator. The oxygen used during sintering, and the nitrogen, used for flushing and as a carrier gas, were Linde prepurified grade. The nitrogen was passed over a Cu/Cu_2O bed at 350°C for removal of traces of H_2 and O_2 and through a molecular sieve column for H_2O removal.

Sintering and adsorption procedures. The catalyst sample to be sintered was placed into a U-shaped Vycor tube, and the sintering gas (oxygen or hydrogen) was passed through the U-tube at 50 cm^3 (STP)/min. The amounts of catalyst used per charge for the various catalysts are given in Table 1. The U-tube was then placed into a modified Thermolyne Model 86 muffle furnace which had been heated to the desired sintering temperature. After inserting the U-tube, a period 1 to 5 min was required to regain the set temperature. The starting time for the sintering was taken as the time when the furnace had attained the set temperature after the sample insertion. The flow of the gas was maintained throughout the sintering period.

After the catalyst has been sintered for 1 hr, hydrogen adsorption measurements were carried out. The pretreatment for hydrogen adsorption after sintering in oxygen consisted of the following steps:

1. The flowing oxygen was replaced by an inert gas (helium or nitrogen) while the sample was at the sintering temperature. (This step was used to flush the gas-phase oxygen out of the system before the sample was cooled.)
2. The sample was removed from the furnace.
3. The furnace was cooled from the sintering temperature to 500°C. (The cooling required up to 30 min.)
4. The inert gas flow was replaced by hydrogen, 50 cm^3 (STP)/min, while the sample was at room temperature.
5. The sample was placed into the furnace, and the hydrogen flow was continued for 1 hr at 500°C (reduction step).
6. The hydrogen flow was replaced by nitrogen, and the catalyst was kept in flowing nitrogen at 500°C for 2 hr (degassing step).
7. The sample tube was removed from the furnace and immersed into a water bath at room temperature, and hydrogen adsorption uptakes were measured by addition of hydrogen pulses to the nitrogen carrier gas. (Carrier gas flow rate was 45 cm^3 (STP)/min and the size of the injected hydrogen pulses was 18.7 μmol/pulse.)

In earlier experiments the catalyst samples were heated in the inert gas to 500°C before changing to flowing hydrogen for reduction (Steps 4 and 5). Although the two procedures did not result in noticeable differences in hydrogen adsorption uptakes, it is believed that the latter procedure, i.e., introducing the hydrogen at room temperature, is preferable. The exposure of the oxygen-treated samples to hydrogen at room temperature followed by an increase in temperature to 500°C in hydrogen should result in the removal of the majority of oxygen adsorbed on the metal at a relatively low temperature. Heating the oxygen-treated samples to 500°C in the inert gas may result in some changes in the metal dispersion due to the presence of the oxygen on the catalyst (*7*).

After sintering in hydrogen, the sample was removed from the furnace and cooled to room temperature in flowing hydrogen, the furnace was cooled to 500°C, and then Steps 5 to 7 as described for the treatment after sintering in oxygen were performed. Steps 5 and 6 were carried out prior to all hydrogen adsorption measurements. The details of the hydrogen adsorption procedure and the equipment used were the same as described previously (*7*).

The same catalyst sample was sintered consecutively for 1-, 3-, and 12-hr periods at the same conditions (atmosphere and temperature). After each sintering period hydrogen adsorption uptakes were measured. This sequential sintering resulted in cumulative sintering times of 1, 4, and 16 hr. Throughout the sequential sintering procedure the catalyst samples were not removed from the apparatus and were not exposed to air. This sequential sintering procedure was not employed for the 16-hr sintering of Catalyst 4 in oxygen. Fresh catalyst samples were employed for these experiments; the results have been reported previously (*7*).

X-ray diffraction and BET surface area measurements were done to determine changes in support crystalline structure and surface area.

RESULTS AND DISCUSSION

Metal Dispersion from Adsorption Uptakes

In order to calculate metal dispersions (the ratio of surface to total metal atoms) from hydrogen adsorption uptakes, one has to know the adsorption stoichiometry,

TABLE 2

Support Surface Areas as a Function of Thermal Treatment

Catalysts	Treatment: Temperature (°C)	Treatment: Time (hr)	Number of determinations	Average specific surface area (m^2/g)
Kaiser KA 201 alumina-supported catalysts (Catalysts 4, 4A, 6, 8, and 10)	Unsintered[a]		4	213 (±19)
	600	16	3	211 (±21)
	700	16	2	180 (± 3)
	800	1	4	157 (± 3)
	800	16	2	135 (± 1)
Engelhard catalysts (Catalysts 1, 7, and 9)	Unsintered[a]		4	103 (± 9)
	700	16	2	104 (±10)
	800	1	1	92
	800	4	1	84
	800	16	2	84 (± 7)

[a] Unsintered catalysts had undergone standard pretreatment and hydrogen adsorption measurements.

i.e., the number of hydrogen atoms adsorbed per surface metal atom. For supported Pt, and to a lesser degree for supported Rh, considerable evidence exists that one hydrogen atom adsorbs per surface metal atom. Very little is known about the adsorption stoichiometry of hydrogen for supported Ir. The dynamic pulse method is not suitable to measure hydrogen adsorption for supported Ru because the adsorption of hydrogen on Ru is an activated process, and several hours of contact with hydrogen are required to attain equilibrium (*8*). Nevertheless, the dynamic method resulted in reproducible hydrogen uptakes (±5%) on supported Ru, but the, magnitude of the uptakes was small, e.g. the uptake on a fresh sample of Catalyst 9 was 1.8 μmol of H_2/g (this is equivalent to $H/Ru = 0.07$). For a similar commercial catalyst Dalla Beta (*9*) obtained $H/Ru = 0.62$ using a static adsorption apparatus. Therefore, the results obtained in the present study for the Ru catalysts are at the best only qualitative.

In the present study we are interested in the relative stability of various supported metal catalysts. The dispersions, D, determined after various treatments were normalized with respect to the dispersion for the fresh catalysts, D_0. This normalized dispersion, D/D_0, is then a measure of change in dispersion due to the thermal treatment. Furthermore, the value of D/D_0 is independent of the hydrogen adsorption stoichiometry as long as this stoichiometry is not a function of the thermal treatment. It is for this reason that the results in the subsequent sections are presented in terms of D/D_0. The average values of D_0 obtained for the various catalysts by assuming that one hydrogen atom adsorbs per surface metal atom are given in Table 1.

Effect of Thermal Treatment on Support Properties

X-ray diffraction studies on unsintered and heavily sintered (800°C in H_2 and O_2) samples showed that no detectable change in the crystalline structure of the support occurred due to the thermal treatments. All the Al_2O_3 supports (unsintered and sintered) displayed diffuse peaks corresponding to γ-Al_2O_3 (or possibly η-Al_2O_3). For the heavily sintered samples, diffraction lines corresponding to the metals were observed. These lines were absent for the unsintered samples.

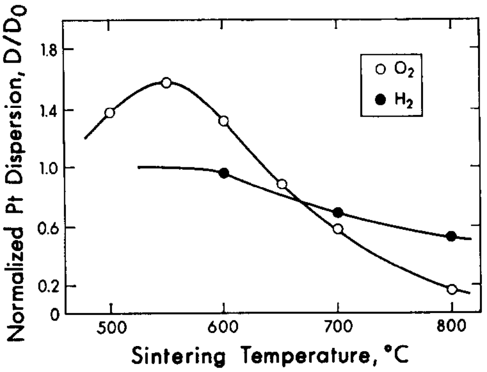

FIG. 1. Effect of treatment in oxygen and hydrogen for 1 hr on the normalized dispersion for Catalyst 1 (0.5% Pt/Al_2O_3).

The thermal treatments did result in changes in support surface area as determined by the BET method. The changes in surface area did not depend on the sintering atmosphere and the supported metal, but only on the temperature and time of treatment. The results are summarized in Table 2. Where more than one determination on the same support material but different metals or different sintering atmospheres was carried out, the standard deviation is given in Table 2. These results show that for the catalysts supported on Kaiser alumina no appreciable changes in support surface area occur during treatment for ≤ 16 hr at temperatures ≤ 600°C. For the Engelhard catalysts the support surface area is approximately constant for treatments at temperatures ≤ 700°C. The high thermal stability of this support is probably due to calcination of these catalysts at an elevated temperature by the manufacturer. Corrections to the measured dispersions due to decreases in support area will be discussed later.

Supported Platinum

The normalized dispersions as a function of sintering atmosphere, time, and temperature for the two supported platinum catalysts are shown in Figs. 1 and 2. The changes in dispersion resulting from treatment in oxygen have been discussed previously (*7*). The results are presented for subsequent comparison with other supported metals.

The treatments in hydrogen resulted in monotonic decreases in metal surface area with increasing sintering temperatures. Increasing the sintering times also resulted in decreased values of the dispersion. Sintering

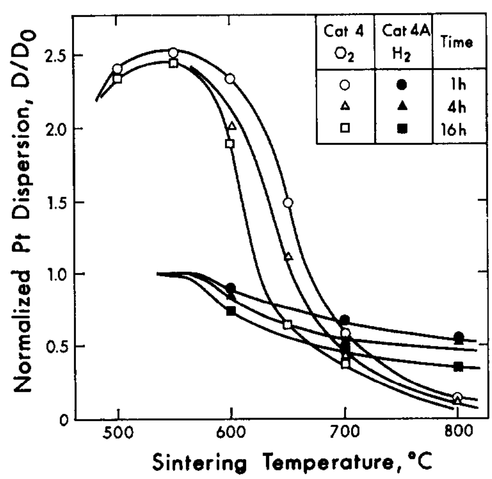

FIG. 2. Effect of treatment in oxygen and hydrogen on the normalized dispersion for Catalysts 4 and 4A (2.0% Pt/Al_2O_3).

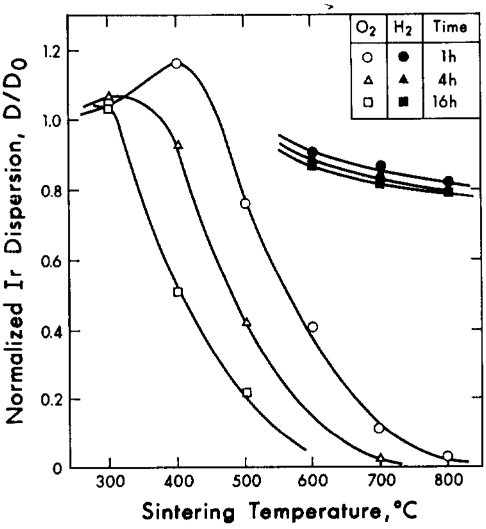

FIG. 3. Effect of treatment in oxygen and hydrogen on the normalized dispersion for Catalyst 6 (2.0% Ir/Al_2O_3).

in hydrogen never resulted in increased Pt dispersions. This is contrary to recent results reported by Hassan *et al.* (*10*). These investigators report a decrease in Pt surface area due to treatment in hydrogen at temperatures below 400°C and an increase at temperatures >400°C. They also report a monotonic decrease in metal surface area with increasing treatment temperature in oxygen atmospheres. We have never observed these types of behavior in the several hundred sintering experiments we have carried out on Pt supported on alumina.

A comparison of the changes in metal surface areas for various metals will be given later in this section.

Supported Iridium

The results presented in Fig. 3 show that supported Ir is considerably more stable in hydrogen than in oxygen atmospheres. Treatment in hydrogen for 16 hr at 800°C resulted in a 20% decrease in dispersion. This is less than the decrease in support surface area (34%) for these treatment conditions. Hence it can be concluded that the loss in Ir dispersion for treatment in hydrogen at temperatures up to 800°C and 16-hr periods is mainly due to collapse of the support pore structure.

Treatment in oxygen at 300°C resulted in small increases in Ir dispersion (~5%) for treatment times of 1 to 16 hr. Treatment at 400°C in oxygen for 1 hr resulted in an 18% increase in dispersion, but increasing the sintering time at 400°C to 4 and 16 hr resulted in 7 and 49% decreases in dispersion. Oxygen treatment at temperatures above 400°C resulted in rapid decreases in Ir dispersion. These results indicate that the sintering mechanism for Ir in oxygen is similar to that of Pt. The higher volatility of Ir oxides compared to Pt oxides (*11*, *12*) causes redispersion at lower temperature range for Ir (300 to 400°C for Ir and 300 to 600 for Pt) and rapid decreases in dispersion at temperatures >400°C. Due to the relatively high vapor pressure of IrO_3 (*11*), it is possible that vapor phase transport contributed significantly to the decreases in measured dispersions after oxygen treatments at 700 and 800°C. Vapor phase transport can decrease the measured dispersion by causing crystallite growth as well as by decreasing the Ir content of the catalysts.

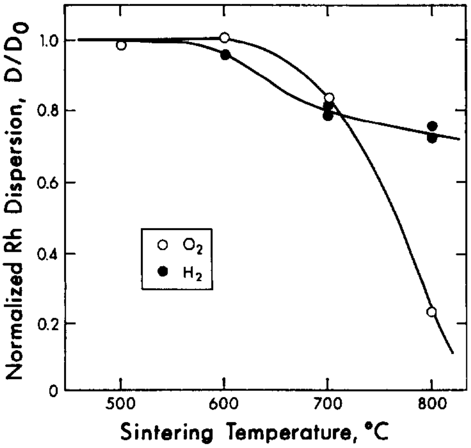

FIG. 4. Effect of treatment in oxygen and hydrogen for 1 hr on the normalized dispersion for Catalyst 8 (1.0% Rh/Al_2O_3).

Supported Rhodium

The normalized dispersion of the two Rh catalysts as a function of treatment temperature, time, and atmosphere are presented in Figs. 4 and 5. Treatment in oxygen did not result in any appreciable increases in dispersion. Sintering experiments in oxygen at 300 and 400°C resulted in a $D/D_0 \approx 1.0$. To determine whether treatment of sintered catalysts in oxygen at <600°C results in increases in dispersion, a sintered sample of Catalyst 7 (750°C in oxygen for 8 h, $D/D_0 = 0.62$) was treated in oxygen at 500°C for 16 hr. After the 500°C treatment D/D_0 was found to be 0.59. A sintered sample of Catalyst 8 (800°C in oxygen for 1 hr; $D/D_0 = 0.24$) was subsequently treated in oxygen at

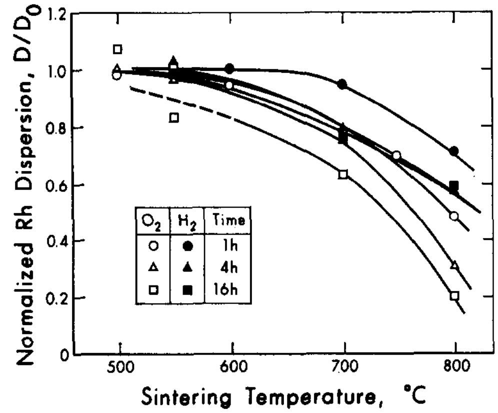

FIG. 5. Effect of treatment in oxygen and hydrogen on the normalized dispersion for Catalyst 7 (0.5% Rh/Al_2O_3).

500°C for 16 hr. D/D_0 after this treatment was 0.29. These results show that treatment in oxygen at 500°C does not result in significant redispersion of Rh supported on alumina.

Nevertheless, the presence of oxygen appears to have a retarding effect on the rate of metal surface area loss at temperatures $\lesssim$600°C. This is very noticeable when comparing the changes in dispersion for hydrogen and oxygen treatment of Catalyst 8 (Fig. 4). At temperatures $\lesssim$700°C the dispersion after treatment in oxygen is higher than the dispersion for similar treatment in hydrogen. This effect is less noticeable for Catalyst 7, but in this case the decrease of dispersion in oxygen at temperatures >700°C for oxygen treatment is higher than that for treatment in hydrogen, while at <700°C the decrease in dispersion is about the same for both atmospheres (with the exception of the 1-hr treatment in hydrogen). Comparing the 1-hr sintering (Figs. 4 and 5) shows that Catalyst 8 is less stable than Catalyst 7 during treatment in oxygen even if the larger loss of support surface area for Catalyst 8 is taken into account.

The situation is reversed for treatment in hydrogen; i.e., Catalyst 8 appears to have a greater thermal stability than Catalyst 7. For Catalyst 8 the dispersion decreased significantly when the sintering temperature was increased from 600 to 700°C. Increasing the sintering temperature to 800°C resulted in a relatively small decrease in dispersion. This was an unexpected observation, but repeat experiments with fresh catalyst samples resulted in excellent reproducibility (see Fig. 4). Examining the changes in support surface areas due to thermal treatment (Table 2) leads to the conclusion that the loss in Rh dispersion for Catalyst 8 is mainly due to loss in support area which would result in making some of the Rh inaccessible to hydrogen during adsorption. For Catalyst 7 the loss in support surface area is insufficient to account for the total loss in dispersion (e.g., sintering at 800°C for 16 hr resulted in a 41% decrease in dispersion, while the support surface area decreased only 18%).

Differences in the initial crystallite size distributions, support–metal interactions, and metal loading could all be responsible for the different behavior of the two Rh catalysts. It is impossible on the basis of the data obtained in this work to determine which, if any, of these factors are the causes of the observed behavior.

Supported Ruthenium

As mentioned previously, the hydrogen adsorption results for supported Ru were only qualitative, but some general conclusions based on these results are nevertheless possible. All oxygen treatments (250 to 500°C) resulted in large decreases in hydrogen adsorption uptakes. Treatment of Catalyst 9 in oxygen for 1 hr at 400 and 500°C resulted in decreases in measured hydrogen uptakes of 44 and 58%, respectively. The same treatments for Catalyst 10 resulted in 69 and 83% decreases in hydrogen uptakes, while treatment at 250°C for 16 hr in oxygen resulted in a 70% decrease. Hence, supported Ru

TABLE 3

Effect of Changes in Support Surface Area on Dispersion

Catalyst	700°C and 16 hr		800°C and 1 hr		800°C and 16 hr	
	(D/D_0)	$(D/D_0)(S_0/S)$[a]	(D/D_0)	$(D/D_0)(S_0/S)$	(D/D_0)	$(D/D_0)(S_0/S)$
Treatment in hydrogen						
1	—	—	0.54	0.60	—	—
4A	0.47	0.56	0.53	0.72	0.37	0.58
6	0.82	0.97	0.82	1.11	0.80	1.26
7	0.78	0.78	0.74	0.83	0.59	0.72
8	—	—	0.73	0.99	—	—
9	—	—	0.95	1.06	—	—
10	—	—	2.29	3.11	—	—
Treatment in oxygen						
1	—	—	0.16	0.18	—	—
4	0.40	0.47	0.14	0.19	—	—
6	(<0.02)	(<0.02)	0.046	0.06	(~0.00)	(~0.00)
7	0.63	0.63	0.49	0.55	0.21	0.26
8	—	—	0.24	0.33	—	—

[a] S_0 and S are the specific surface areas of the support for unsintered and sintered samples listed in Table 2

sinters more rapidly in oxygen than any of the other supported metals investigated. Some of the observed decreases in hydrogen adsorption may have been due to the loss of Ru due to sublimation of Ru oxides.

The results for the sintering in hydrogen are not as easily interpreted since treatment at 600 to 800°C for 1 hr resulted in increases in hydrogen uptakes for Catalyst 10 and in decreases for Catalyst 9. It is not certain whether the increases in H/Ru for Catalyst 10 were due to increases in dispersion or increases in the rate of hydrogen adsorption caused by the treatment. Based on all the results obtained, we conclude that in hydrogen supported Ru is more stable than supported Pt and Rh and equally or slightly less stable than supported Ir.

Comparison of Stability of Supported Metals

It is difficult to compare the stability of different catalysts since various factors can influence the stability. These factors include the initial dispersion, the crystallite size distribution, the metal loading, and the nature of the support. In order to compare the stability of catalysts in oxygen and hydrogen as a function of temperature, all these factors should be kept constant. Unfortunately, it is in general not possible to obtain constant initial conditions for the catalysts.

An approximate method for obtaining the relative stabilities of various catalysts is to compare relative change in dispersion, i.e., compare normalized dispersions. Correction for the change in support surface area should also be made. The results of these corrections are shown in Table 3. In making these corrections it was assumed that the loss in support surface area is proportional to the loss in accessible metal. This procedure probably overestimates the fraction of metal which becomes inaccessible to hydrogen because nitrogen was used in the BET surface area measurements and some of the internal pore structure after sintering may be accessible to hydrogen but not to nitrogen. It is believed that this is the reason that some of the normalized dispersions corrected for loss in surface area exceed unity for the Ir catalyst.

Based on the results presented in Figs. 1 to 5 and Table 3, the order of decreasing stability is

$$\mathrm{Rh} > \mathrm{Pt} > \mathrm{Ir} > (\mathrm{Ru}) \qquad (1)$$

in oxygen, and

$$\mathrm{Ir} \gtrsim (\mathrm{Ru}) > \mathrm{Rh} > \mathrm{Pt} \qquad (2)$$

in hydrogen.

The sequence of stability in oxygen, given by Eq. (1), is in agreement with the predictions of Wynnblatt and coworkers (*5, 6*). The predictions of relative stability of metals in oxygen were based on the heats of formation of metal oxides; increases in the exothermicity of the metal oxide formation cause decreases in the stability. Hence, it can be concluded that the sintering for all these supported metals occurs by the transport of metal oxide species. The possible steps involved in the transport of metal oxides have been discussed previously (*7*). The observed relative stability sequence in hydrogen, given by Eq. (2), is in agreement with the predictions given by Anderson (*13*). The predictions are based on the premise that stability increases with increasing heats of sublimation of the metal. Wynblatt and coworkers (*6, 7*), using the same basis for their predictions, state that the stabilities of Rh and Pt are approximately equal. On the basis of reported heats of sublimation, the thermal stability of Rh should be slightly less or approximately equal to that of Pt. Reported heats of sublimation of Rh range from 548 to 577 kJ/mol (131 to 138 kcal/mol) with a mean value of 556 kJ/mol (*14, 15*), and the values for Pt range from 561 to 569 kJ/mol with a mean value of 565 kJ/mol (*14, 16*).

In the present work the stabilities of the Rh catalysts were significantly higher than those of the Pt catalysts. It may be argued that the stability sequence based on relative changes in dispersion yields wrong results due to different initial conditions. This is not the case since catalysts with high initial dispersions generally have larger decreases in relative dispersions than similar catalysts (same support and metal loading) with lower initial dispersions. The initial dispersions of both Rh catalysts were in general higher than those of the Pt catalysts. The deviations from the predictions are believed to be caused by metal–support and/or metal–hydrogen interactions. The predictions do not include these interactions which, in our opinion, play an important role in the sintering of supported metal catalysts. Systematic experiments to determine the influence of the support on the sintering of supported metal catalysts should be carried out.

The results for sintering in oxygen cannot, in our opinion, be explained in terms of the crystallite migration model developed by Ruckenstein and Pulvermacher (*1, 2*). The high thermal stability of supported Ir in hydrogen also appears to be contrary to the crystallite migration model. The agreement between the thermal stability sequences observed and those predicted by the molecular (or atomic) transport mechanism leads to the conclusion that sintering of supported metal occurs mainly by molecular transport.

CONCLUSIONS

The sequence of stabilities of Al_2O_3-supported metal catalysts during treatment at elevated temperatures was found to be Rh > Pt > Ir > (Ru) in oxygen and Ir $\gtrsim$ (Ru) > Rh > Pt in hydrogen. The stabilities in oxygen are in agreement with predictions based on the heats of formation of metal oxides. Hence, sintering in oxygen probably occurs by the transport of metal oxide molecules. The observed increases in dispersion during treatment in oxygen for Pt and Ir are believed to be the result of metal oxide–support interactions. The observed stability sequence in hydrogen atmospheres is in approximate agreement with the prediction of increasing stability with increasing heats of sublimation. Unfortunately, the predicted sequence is the same for both atomic and crystallite migration mechanisms, and hence, cannot be used to differentiate between mechanisms.

The predictions based on oxide vapor pressure (in oxygen atmospheres) and on heats of sublimation (in hydrogen atmospheres) neglect the metal–support or metal oxide–support interactions. If these interactions are significant under sintering conditions, different sequences of stability may result. Experiments to determine the influence of supports on the thermal stability of supported metal catalysts are required.

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