The Sintering of Supported Metal Catalysts

III. The Thermal Stability of Bimetallic Pt–Ir Catalysts Supported on Alumina

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The effects of thermal treatments in oxygen (300 to 600°C) and hydrogen (500 to 800°C) on the metal dispersions of 1% Pt, 1% Ir, and 1% Pt–1% Ir catalysts were studied. Treatment in oxygen at 400 to 600°C resulted in increases in dispersion for the Pt catalyst. Small increases in dispersion for the Ir catalysts were observed after treatment in oxygen at 300°C; at higher temperatures the Ir dispersion decreased significantly. Segregation of the metals occurred in the bimetallic Pt–Ir catalysts during treatment in oxygen. The largest decreases in dispersion due to treatment in hydrogen were observed for the Pt catalyst. Surprisingly, hydrogen treatment of the Ir and Pt–Ir catalysts resulted in essentially the same relative decreases in metal dispersions.

INTRODUCTION

Until recently, platinum supported on alumina was the most commonly used catalyst for the reforming of naphtha. About a decade ago a bimetallic Pt–Re on alumina reforming catalyst came into commercial use (*1*), and in the last decade many bi- and multimetallic supported metal catalysts have been developed for reforming (e.g., *2–7*). One of these new bimetallic reforming catalysts is Pt–Ir/Al₂O₃ (*2*). Deactivation due to coke deposition is much slower for the Pt–Ir catalysts than for the monometallic Pt catalysts (*8, 9*) and hence reforming can be carried out at much lower hydrogen pressures and longer operation between regenerations is possible with the Pt–Ir catalysts.

Sintering (i.e., deactivation due to loss of metal surface area) can occur during reforming operation (i.e., in a reducing atmosphere) and during regeneration (i.e., in an oxidizing atmosphere). Few systematic studies of sintering of bimetallic Pt–Ir catalysts have appeared in the open literature

(*5*). In the present study, the thermal stability of three alumina-supported catalysts (Pt, Ir, and Pt–Ir) in hydrogen and oxygen atmospheres was investigated. The initial dispersions of the three catalysts were approximately equal so that meaningful comparisons of the effects of thermal treatments on dispersion could be made.

EXPERIMENTAL

Materials

Three supported metal catalysts were prepared by impregnation of Alon, a fine γ-Al₂O₃ powder (average alumina particle size ~30 nm) manufactured by Cabot Corp. The three catalysts were 1% Pt/Alon, 1% Ir/Alon, and 1% Pt–1% Ir/Alon. The impregnation technique consisted of wetting the Alon support with 1 ml of distilled deionized water per gram of Alon. This resulted in a smooth paste. An aqeous solution of the metal chloride [Pt(II) and/or Ir(III)] was then added to the paste. The concentration of the metal in the solution was such that 1 ml of solution per gram of catalyst resulted in a catalyst containing 1% by weight of metal for the monometallic catalysts. For preparation of the bimetallic catalyst, the aqueous solution contained

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sufficient Pt and Ir so that the catalyst contained 1% by weight of each metal.

After addition of the metal salt solution the mixture was stirred intermittently for 24 h, followed by drying at ~80°C for 24 h and finally dried at 110°C for another 24 h. The dried catalyst was reduced in flowing hydrogen for 16 h at 150°C, 2 h at 250°C, and 1 h at 500°C. The catalyst samples were purged with nitrogen at 500°C after the reduction, cooled to room temperature in flowing nitrogen, and stored until used. A fourth catalyst, subsequently referred to as the "physical mixture," was prepared by thoroughly mixing equal weights of the reduced 1% Pt and 1% Ir catalysts.

Sintering and Adsorption Procedures

The equipment and procedures used for the sintering and adsorption in this study were similar to those described previously (*10*), i.e., sintering in hydrogen and oxygen was followed by *in situ* hydrogen chemisorption measurements at room temperature using the dynamic pulse technique. A fresh catalyst sample (sample size ~1.7 g) was used for each sintering experiment and the hydrogen adsorption uptake was measured for each sample prior to the thermal treatment (sintering). At least two successive hydrogen adsorption measurements were carried out on each sintered sample. BET surface area measurements were done to determine whether the thermal treatments resulted in changes in support surface area.

RESULTS

The dynamic pulse method was used to measure hydrogen chemisorption on fresh and sintered catalyst samples. (The use of hydrogen chemisorption uptakes measured by the dynamic method for determination of metal dispersions is discussed in the following section.) A fresh catalyst sample was used for each of the sintering experiments and hydrogen adsorption measurements were carried out on each sample prior to the thermal treatment. The average hydrogen uptake for the fresh catalysts, expressed as the hydrogen-to-metal ratio (H/M = atoms of hydrogen adsorbed per metal atom), are given in Table 1. The variation in the H/M ratios for different samples of catalyst from the same batch was the highest for the Pt/Alon catalyst (C.V. = 8.25%). For the other three catalysts the coefficient of variation was about 5%. These variations are mainly due to inhomogeneities among samples from the same batch and are not due to uncertainties in the hydrogen adsorption measurements. The average coefficient of variance for repeat hydrogen adsorption measurements on the same catalyst sample was <2% for all four catalysts.

TABLE 1

Hydrogen Adsorption Results for Fresh Catalyst Samples

Catalyst	Catalyst composition[a]	Average hydrogen-to-metal atomic ratio	Number of fresh samples	Standard deviation	
				H/M ratio	(%)
1	1% Pt	0.406	18	0.034	8.3
2	1% Ir	0.443	16	0.024	5.4
3	1% Pt and 1% Ir[b]	0.429	16	0.020	4.7
4	50–50 mixture of catalysts 1 and 2	0.437	13	0.022	5.1

[a] All supported on Alon (a γ-Al₂O₃).
[b] Prepared by coimpregnation.

After the hydrogen uptake had been measured on the fresh sample, the catalyst was treated in flowing hydrogen or oxygen at elevated temperatures. Thermal treatment times of 1 and 16 h were used. The temperature range for treatment in oxygen was 300 to 600°C and sintering in hydrogen was done at 650 and 800°C.

The measured relative changes in metal dispersion as a result of thermal treatment in oxygen are shown in Figs. 1 and 2. The results are expressed in terms of "normalized dispersions," D/D_0, where D is equal to the H/M ratio of the thermally treated sample and D_0 is the H/M ratio for the fresh catalyst sample. The measured value of D_0 for each sample was used to calculate D/D_0; i.e., D_0 is not equal to the average value of H/M listed in Table 1. The results for thermal treatment in flowing hydrogen are presented in Fig. 3. The dashed lines in Figs. 1, 2, and 3 correspond to the arithmetic average of the D/D_0 values for the 1% Pt and 1% Ir catalysts.

Total surface area measurements were carried out on fresh and sintered samples to determine whether the thermal treatments caused changes in the support surface areas. The total surface area of all the fresh catalyst samples (after the drying and reduction procedure described previously)
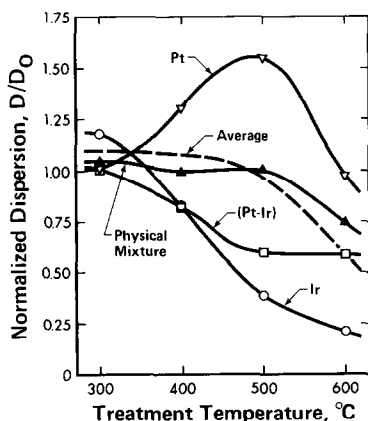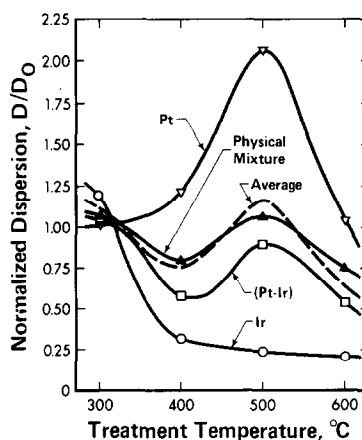

FIG. 2. Effect of treatment in oxygen for 1 h at various temperatures on the normalized metal dispersion for catalysts 1 to 4.

was 96 m²/g. The most severe thermal treatments (16 h at 800°C in hydrogen) reduced the total surface area to 93 m²/g.

DISCUSSION

Hydrogen Chemisorption for Determination of Metal Dispersion

Hydrogen chemisorption uptakes were used to determine metal dispersions for

FIG. 1. Effect of treatment in oxygen for 1 h at various temperatures on the normalized metal dispersion for catalysts 1 to 4 (see Table 1).
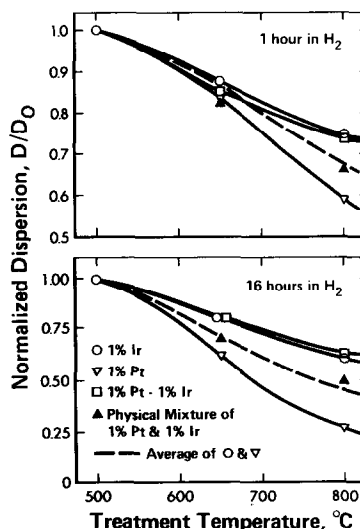

FIG. 3. Effect of treatment in hydrogen for 1 and 16 h at various temperatures on the normalized metal dispersion for catalysts 1 to 4.

fresh and thermally treated catalyst samples. Prior to each adsorption measurement the catalyst samples were reduced *in situ* in flowing hydrogen for 1 h at 500°C and degassed in flowing nitrogen for 2 h at 500°C. Dautzenberg and co-workers (*11, 12*) recently reported that treatment of Pt/Al_2O_3 catalysts in hydrogen at temperatures $\simeq 500°C$ results in subsequent hydrogen chemisorption uptakes that are not proportional to the Pt dispersion. They measured, for example (*12*), an H/Pt ratio of 0.90 for a 0.8 Pt/Al_2O_3 catalyst after reduction at 400°C and an H/Pt ratio of 0.49 after the same catalyst was treated in H_2 at 500°C for 16 h. X-Ray diffraction and electron microscopy results did not indicate a loss of Pt dispersion due to the treatment in H_2 at 500°C. They attributed the decrease in the H/Pt ratio to the formation of a Pt–alumina complex which does not adsorb hydrogen. They state (*12*) that it is incorrect to characterize Pt/Al_2O_3 catalysts which have been treated at high temperatures in H_2 or O_2 by H/Pt ratios. All the results reported in the present study are based on H/Pt ratios measured on samples that had been exposed to H_2 and/or O_2 at temperatures $\geq 500°C$. Hence, we have to show that the H/metal ratios reported in this paper are a measure of the metal dispersion.

Reduction of Pt/Al_2O_3 catalyst in hydrogen at 500°C before hydrogen uptake measurements has been employed commonly in the past (e.g., *13–16*). These different investigations measured H/Pt ratios of 0.8 to 0.99 after reduction in hydrogen at 500°C for periods of up to 16 h. Wilson and Hall (*14*) investigated the effect of thermal treatments in hydrogen for temperatures of up to 700°C on Pt dispersions for Pt/Al_2O_3 catalysts. Comparisons of measured H/Pt ratios and electron microscopy results led to the conclusion that one hydrogen atom adsorbs per Pt surface atom on these catalysts sintered in hydrogen. In our laboratory we have also measured hydrogen chemisorption uptakes on catalyst after

treatment in hydrogen at elevated temperatures (e.g., *17*). Our results are in agreement with those of Wilson and Hall (*14*), and we have never observed decreases in H/Pt ratios of the magnitude reported by Dautzenberg and co-workers (*11, 12*) for treatment of Pt/Al_2O_3 catalysts in hydrogen at temperatures of $\leq 600°C$ (also see result shown in Fig. 3).

Furthermore, repeat hydrogen chemisorption measurements were done for all the sintered catalyst samples. Prior to each adsorption measurement the catalyst sample was treated in flowing hydrogen at 500°C for 1 h. The results of the repeat adsorption measurements are summarized in Table 2 (D_1 and D_2 refer to the measured hydrogen atom-to-metal ratio for the first and second adsorption, respectively). For the fresh and oxygen sintered samples, D_2 was, on the average, less than D_1 by less than 2%. For the Pt/Al_2O_3 catalyst treated in hydrogen at 650 and 800°C, D_2 was, on the average, slightly higher than D_1. The results in Figs. 1 and 2 show that treatment of Pt/Al_2O_3 catalysts in oxygen at 300°C does not alter the subsequently measured H/Pt ratio. (All catalysts were reduced in hydrogen at 500°C prior to the thermal treatments and again exposed to H_2 at 500°C after the thermal treatments.)

On the basis of the above observations we conclude that measured H/Pt ratios for Pt/Al_2O_3 catalysts reduced at 500°C and degassed at 500°C provide a quantitative indication of the platinum dispersion. The anomalous results reported by Dautzenberg and co-workers (*11, 12*) may be due to the low temperatures at which the hydrogen uptakes were measured, $-78°C$ (*11*) and $0°C$ (*12*), and/or the relatively low evacuation temperature (400°C). Evacuation at 400°C may be sufficient to remove adsorbed hydrogen from catalysts that have not been treated in hydrogen at elevated temperatures, but according to Menon and Froment (*18*) desorption of hydrogen becomes more difficult after Pt/Al_2O_3 catalysts have been exposed to high temperatures. Menon and

TABLE 2

Summary of Repeat Hydrogen Adsorption Measurements on the Same Sample

Catalyst	Sintering atmosphere	$[(H/M)_1 - (H/M)_2]^a$	Number of samples	Percentage standard deviation
1	Unsintered	+0.003	12	1.9
	Oxygen	+0.006	12	4.4
	Hydrogen[b]	−0.005	6	3.7
2	Unsintered	+0.009	9	1.5
	Oxygen	+0.005	8	3.0
	Hydrogen[b]	+0.003	7	0.6
3	Unsintered	+0.006	4	1.1
	Oxygen	+0.007	11	2.9
	Hydrogen[b]	+0.005	4	1.5

Note. Reduction at 500°C in hydrogen carried out prior to each repeat measurement.

[a] Average difference between the hydrogen-to-metal ratios for the first and second hydrogen adsorptions.

[b] For samples sintered in hydrogen at 650 and 800°C.

Froment also found that the changes in hydrogen desorption behavior are not due to metal-support interactions. Further work is required to determine the changes that occur in Pt surface structure when Pt is exposed to hydrogen at high temperatures.

Various adsorption stoichiometries have been reported for hydrogen adsorption on supported Ir and Pt–Ir catalysts (*19–23*). Total hydrogen adsorption uptakes, measured by gravimetric (*20*) and volumetric (*21–23*) methods, corresponding to hydrogen-to-metal (H/M) ratios much larger than unity have been reported. But the amount of strongly ("irreversibly") adsorbed hydrogen, obtained by room temperature evacuation and readsorption, results in H/M ratios that are ≤1 (*20–22*). Sinfelt and Via (*21*) used the H/M ratios, based on the strongly adsorbed hydrogen, as a measure of the metal dispersion for Pt–Ir catalysts.

The dynamic pulse method used in the present work for measuring hydrogen adsorption uptakes only measures strongly adsorbed hydrogen. Therefore, we believe that the measured H/M ratios are approximately equal to the metal dispersion. Even if the measured H/M ratios are not equal to the metal dispersion, the normalized dispersion, D/D_0, plotted in Figs. 1 to 3, still

gives the correct quantitative changes in dispersion as long as the hydrogen adsorption stoichiometry is independent of metal dispersion.

Sintering in Oxygen

Several investigators (*9, 17, 20–26*) have reported the effects of calcination in air or oxygen on the dispersion of Ir and Pt–Ir catalysts. Most investigators (*9, 17, 21, 23–25*) have found that even short exposure to air or oxygen at temperatures above 450°C results in large losses in metal surface area (i.e., increases in crystallite size), but Tournayan *et al.* (*20*) report that calcination of unreduced 0.3% Ir/Al_2O_3 and 0.3% Pt–0.3% Ir/Al_2O_3 catalysts in air at 520°C for 4 h results in catalysts with a narrow crystallite size distribution having an average crystallite size of less than 1.5 nm. Kozlov *et al.* (*26*) report that the addition of 0.05% Ir to a 0.5% Pt/Al_2O_3 catalyst decreases the loss in metal surface area due to calcination in air at 700 and 800°C.

Our results for the sintering in oxygen of reduced Pt, Ir, and Pt–Ir catalysts are shown in Figs. 1 and 2. The general behavior of the Pt and Ir catalysts is similar to those reported previously (*17*). The slight differences are believed to be due to the

different alumina supports used in the previous study. The results clearly show that treatment of Ir/Al$_2$O$_3$ catalysts in oxygen at temperatures above 400°C results in significant decreases in metal dispersion. Modest increases in Ir dispersions (~20%) were obtained after treatment in oxygen at 300°C. This increase in dispersion seems to be independent of treatment time for times of 1 to 16 h. The measured dispersions for the physical mixture were, within experimental error, equal to the arithmetic averages for the Pt and Ir catalysts for 1- and 16-h treatments (cf. the dashed lines, which represent the arithmetic averages, with the results for the physical mixture in Figs. 1 and 2).

No significant increases in dispersion above the initial dispersion were observed for the Pt–Ir catalyst for any of the oxygen treatments used in this study. Treatment of the Pt–Ir catalyst in oxygen for 1 h at temperatures of 400 to 600°C resulted in dispersions that were quite different from those obtained for the Pt and Ir catalysts. The dispersions for the physical mixture also did not correspond to those obtained for the Pt–Ir catalyst. This indicates that in the fresh Pt–Ir catalyst interactions existed between the Pt and Ir; i.e., bimetallic Pt–Ir crystallites were present in the fresh catalyst. On the other hand, the dispersions of the Pt–Ir catalyst after treatment in oxygen for 16 h mimic those obtained for the physical mixture. The somewhat lower values of D/D_0 obtained for the Pt–Ir catalyst are probably due to the higher metal loading of this catalyst. The Pt–Ir catalyst contained 2.0 wt% metal (1% Pt and 1% Ir) while the physical mixture contained 1.0 wt% metal (i.e., a mixture of 1% Pt/Al$_2$O$_3$ and 1% Ir/Al$_2$O$_3$).

The reason for the change in behavior of the Pt–Ir catalyst with treatment time in oxygen is believed to be caused by segregation of the Pt and Ir. Short treatment times (≤ 1 h) in oxygen at ≥ 400°C results in growth of metal crystallites accompanied by segregation of the bimetallic crystallites

into Pt-rich and Ir-rich crystallites. The sintering behavior during this stage is different than that for individual Pt and Ir catalysts due to the Pt–Ir interactions. For more extended periods of treatment in oxygen segregation into essentially monometallic particles has occurred and the behavior is approximately that of a physical mixture. This segregation of bimetallic Pt–Ir crystallites has been observed by Sinfelt and Via (21) and is caused by the transport of IrO$_3$ species (21). The high D/D_0 value obtained after treatment in oxygen for 16 h at 500°C is caused by the redispersion of Pt. The similarity in behavior observed for the Pt–Ir catalyst and the physical mixtures for treatment in oxygen for 16 h suggests that the Ir does not markedly influence the redispersion of Pt once segregation has occurred.

Sintering in Hydrogen

Very little information on the effects of thermal treatment in hydrogen on the metal dispersion of supported Ir and Pt–Ir catalysts is available in the literature. We have previously reported that Ir/Al$_2$O$_3$ catalysts are considerably more resistant to sintering in hydrogen than Pt/Al$_2$O$_3$ catalysts (17). Foger and Anderson (25) reported that treatment of a 0.9% Ir/SiO$_2$ catalyst in hydrogen for 3 h at 700°C resulted in an 18-fold decrease in Ir dispersion. We have never observed such large decreases in Ir dispersion due to treatment in hydrogen, even at 800°C for 16 h, for alumina-supported Ir catalysts. Ramaswamy et al. (27) found that the relative rates of sintering of Pt/Al$_2$O$_3$ and Pt–Ir/Al$_2$O$_3$ (Pt-to-Ir ratio $\simeq 10 : 1$) catalysts were similar. Our results, shown in Fig. 3, for a catalyst having a 1 : 1 Pt–Ir ratio show different behavior.

We found that the normalized dispersions of the Pt–Ir catalyst as a function of treatment temperature in hydrogen are essentially equal to the normalized dispersions obtained for the monometallic Ir catalyst (see Fig. 3). This similarity was observed for both 1- and 16-h treatments.

This observation is puzzling since it was expected that Pt–Ir catalysts in a reducing atmosphere would behave more like Pt because in hydrogen the surface of Pt–Ir crystallites should be enriched in Pt (9). We cannot offer an explanation for this observed behavior, but it is certainly caused by Pt–Ir interactions and the Pt and Ir do not segregate into monometallic crystallites during treatment in hydrogen. It is unlikely that the results are due to anomolies in the hydrogen adsorption since hydrogen adsorption uptakes on the physical mixture of Pt and Ir catalysts agreed very well with the arithmetic averages obtained from the individual Pt and Ir catalysts [compare the measured uptakes on the physical mixture (Δ) with the averages given by the dashed lines in Fig. 3].

Additional experiments, using techniques other than hydrogen chemisorption (possibly electron miscroscopy, X-ray diffraction, and kinetic studies), will have to be done in order to obtain information about the changes caused by treatment of Pt–Ir catalysts in hydrogen at elevated temperatures.

CONCLUSIONS

The coimpregnation of alumina with Pt and Ir chlorides, followed by reduction in hydrogen results in a catalyst containing bimetallic crystallites. Treatment of this bimetallic catalyst in oxygen at temperature above ~400°C results in segregation of the metals into monometallic crystallites. [This occurrence is well documented by the work of Sinfelt and Via (21).] Treatment in hydrogen, even at 800°C, does not result in this segregation. Changes in dispersion of bimetallic Pt–Ir catalysts during thermal treatment in hydrogen are essentially equal to those obtained for monometallic Ir catalysts. Room temperature hydrogen chemisorption uptakes on Pt, Ir, and Pt–Ir catalysts reduced in hydrogen at 500°C and degassed at 500°C are a reliable measure of the metal dispersion.

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