JOURNAL OF CATALYSIS 95, 492–500 (1985)

The Influence of Acid–Base Properties of Oxide Supports on Platinum Dispersion during Oxygen Treatments

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Received December 31, 1984; revised May 1, 1985

The role of acid and base properties of oxide supports on the stability of Pt on these supports during oxygen treatment at 550°C was investigated. The acid–base properties were determined by the indicator–titration method. The supports studied were γ-alumina, silica, silica–alumina, magnesia, and silicalite; the Pt was introduced to these supports by impregnation with H_2PtCl_6 or $Pt(C_5H_7O_2)_2$. The introduction of Pt did not significantly affect the acid–base properties. Hydrogen chemisorption and X-ray diffraction were used to determine the changes in Pt dispersion that occurred due to O_2 treatments. It was observed that O_2 treatments at 550°C of Pt on supports with basic sites (γ-Al_2O_3 and MgO) resulted in increases in Pt dispersions, while decreases in Pt dispersion occurred for Pt supported on acidic and neutral supports (silica–alumina, silica, and silicalite).

INTRODUCTION

The superiority of transition aluminas over other refractory oxides as supports for naphtha reforming catalysts was recognized early in the development of reforming catalysts (*1*). Transition aluminas, after addition of small amounts of chlorine or fluorine, have isomerization activity desired for reforming while undesired hydrocracking activity is lower than on other acidic supports. Furthermore, sintered Pt/Al_2O_3 catalysts can be regenerated; i.e., the growth of Pt crystallites which occurs during prolonged use under reforming conditions and during coke burnoff, is at least partially reversible for alumina-supported reforming catalysts.

Regeneration of sintered Pt/Al_2O_3 catalysts, i.e., redispersion of Pt, can be achieved by appropriate oxygen and chlorine treatments (*2–9*). The formation of $Pt—O—Cl—Al_2O_3$ or $Pt—O—Al_2O_3$ surface complexes is responsible for the Pt redispersion (*2, 4*), and the alumina stabilizes the Pt^{4+} formed during oxychlorination at 500 to 550°C (*3*). However, similar oxychlorination treatments of silica-supported Pt do not result in Pt redispersion (*4*). Recent EXAFS results (*10, 11*) have shown that the high dispersions of reduced Rh/Al_2O_3 catalysts are due to interactions between Rh and surface oxygens of the Al_2O_3. Similar metal–support oxygen interactions do not occur for Pt on silica (*10*). Basic O^{2-} sites, which are present on the surface of aluminas but not on silica (*12*), are probably responsible for the interactions of supported metals with alumina surfaces.

The influence of support basicity and acidity on the behavior of supported Pt during O_2 treatments at 550°C is reported in this paper. The supports investigated were alumina, silica, alumina–silica, magnesia, and silicalite. Silicalite is an essentially aluminum-free pentasil zeolite (*13*). Acid–base properties of supports and catalysts were measured by the titration method. The results show that sintering and redispersion phenomena are correlated with support basicity.

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0021-9517/85 $3.00

TABLE 1

Description of Catalysts

Support[a]	Catalyst number	Platinum loading (mass%)	Method of preparation[b]	
			Pt precursor	Solvent
γ-Al_2O_3 (A1)	1	0.5	H_2PtCl_6	Water
	2	0.5	$Pt(C_5H_7O_2)_2$	Chloroform
	3	1.0	H_2PtCl_6	Water
	4	1.0	$Pt(C_5H_7O_2)_2$	Acetone
γ-Al_2O_3 (A2)	5	0.5	H_2PtCl_6	Water
	6	0.5	$Pt(C_5H_7O_2)_2$	Chloroform
SiO_2 (S1)	7	0.5	H_2PtCl_6	Water
	8	0.5	$Pt(C_5H_7O_2)_2$	Chloroform
SiO_2 (S2)	9	0.5	H_2PtCl_6	Water
Silica–alumina	10	0.5	H_2PtCl_6	Water
	11	0.5	$Pt(C_5H_7O_2)_2$	Chloroform
MgO (M1)	12	0.5	H_2PtCl_6	Water
	13	0.5	$Pt(C_5H_7O_2)_2$	Chloroform
MgO (M2)	14	0.5	H_2PtCl_6	Water
	15	0.5	$Pt(C_5H_7O_2)_2$	Acetone
	16	5.0	H_2PtCl_6	Water
Silicalite	17	1.0	$Pt(NH_3)_4Cl_2$	Water

[a] See Table 2 for descriptions of supports.

[b] All catalysts, except Catalyst 17, were prepared by impregnation; Catalyst 17 was prepared by exchange.

EXPERIMENTAL METHODS

Catalysts. Catalysts were prepared by impregnation with aqueous solutions of chloroplatinic acid, impregnation with chloroform solutions of platinum acetylacetonate, impregnation with acetone solutions of platinum acetylacetonate, and by exchange with aqueous solution of tetramine Pt(II) chloride. The catalysts used in this study and their preparation methods are presented in Table 1; the physical properties of the supports are given in Table 2.

Impregnation with $Pt(C_5H_7O_2)_2$–$CHCl_3$ solutions consisted of immersion of the support in $CHCl_3$ for 24 h, addition of $Pt(C_5H_7O_2)_2$–$CHCl_3$ solution at room temperature followed by intermitted stirring for 24 h, evacuation of mixture at room temperature until all the liquid had evaporated, and drying of the catalyst in air at 120°C for 6 h. Impregnation with $Pt(C_5H_7O_2)_2$–acetone solutions consisted of wetting the supports with acetone, addition of $Pt(C_5H_7O_2)_2$–acetone solutions followed by intermittent stirring at room temperature for 24 h, slow evaporation of acetone at 35°C until a thick paste formed, and drying at 75°C for 24 h. The impregnation procedure with chloroplatinic acid has been described previously (*6*). Catalysts prepared by impregnation with H_2PtCl_6 were dried in air at 110°C before reduction.

All the dried catalyst prepared by impregnation were reduced in flowing hydrogen at 150°C for 16 h, 250°C for 2 h, and 500°C for 1 h. The reduced catalysts were stored in air until use. It should be pointed out that none of the catalysts prepared by impregnation were calcined at elevated temperatures before reduction. The omission of a calcination step prior to reduction results in catalysts with relatively low Pt dispersions. Relatively low Pt dispersions (≤ 0.5) of the fresh catalysts were desired in the present study since one of the objectives of this work was to determine whether

TABLE 2

Description of Supports

Support	Supplier (source)	Surface area (m^2/g)	Total acidity (meq/g)	Total basicity (meq/g)
γ-Al_2O_3 (A1)	Cabot Corp. (Alon)	100	0.48	0.30
γ-Al_2O_3 (A2)	Kaiser (KA-201)	250	0.76	1.04
Silica (S1)	Degussa (Aerosil-200)	200	0.05	0.0
Silica (S2)	Ventron, Alpha Products	220	n.d.[a]	n.d.[a]
Silica–alumina	Ventron, Alpha Products	125	0.24	0.04
Magnesia (M1)	Decomposition of basic magnesium carbonate	65	0.00	1.16
Magnesia (M2)	Ventron, Alpha Products	90	0.00	3.65
Silicalite	Union Carbide	435[b]	n.d.[a]	n.d.[a]

[a] Not determined.

[b] Single point BET area obtained from supplier.

treatment in oxygen of reduced catalysts can result in increases in Pt dispersions.

The preparation of Pt/silicalite (Catalyst 17) was done by exchange of silicalite with an aqueous solution of $Pt(NH_3)_4Cl_2$, containing 13 mg Pt/cm^3 of solution. The mixture was shaken intermittently and allowed to equilibrate for 60 h at room temperature. The solids were filtered from the solution and washed eight times with distilled, deionized water. The catalyst was dried in air at 60°C for 2 h, at 120°C for 5 h, and at 300°C for 3 h, and reduced at 300° in H_2 for 36 h. Previously reported studies (*14, 15*) for Pt supported on silicalite and ZSM-5 indicated that a significant fraction of the Pt after this preparation method is located in the zeolite channels. The Pt content of the Pt/silicalite catalyst was determined by neutron activation analysis. The Pt contents of catalysts prepared by impregnations were calculated from the composition of the impregnation solutions. The chlorine contents of the alumina supports (A1 and A2, Table 2) and Pt/Al_2O_3 prepared by impregnation with H_2PtCl_6 (Catalysts 3 and 5, Table 1) were also determined by neutron activation analysis. The as-received Alon (A1) contained 1.5 wt% Cl; however, thermal treatment of the Alon in dry O_2 at 550°C for 2 h reduced the Cl content to 0.8 wt%. This decrease in Cl content is probably due to decomposition of residual $AlCl_3$ in the Alon. (The Alon was manufactured by flame hydrolysis of aluminum chloride.) The Cl content of Catalyst 3 (1.0 wt% Pt on A1 made by impregnation with H_2PtCl_6) after reduction at 500°C was 1.0 wt%. The Cl content of support A2 was <0.03 wt%; impregnation with H_2PtCl_6 (Catalyst 5) increased the Cl content to 0.5 wt%. The sodium content of A2, as specified by the manufacturer, was 0.2 wt%.

Acid–base properties. The acid–base properties of supports and some reduced Pt–support samples were measured by the nonaqueous indicator method (*16, 17*). The advantages and limitations of the nonaqueous indicator method are discussed in these references. The white solid acid modification of the method (*18*) was used for the Pt-containing samples. Aliquots of samples were tirated with 0.1 *N* solutions of *n*-butylamine in anhydrous benzene for acid site determination. Benzoic acid in anhydrous benzene (0.1 *N*) was used for basic site determinations. The strength distributions of acid and base sites were determined with the indicators listed by Tanabe (*17*), phenolphthalein was used as the indicator for basic sites with $pK_a > 9.3$.

The samples were treated in dry air at

TABLE 3

Strength Distribution of Acidic Sites for Supports and Catalysts

Support or catalyst	n-Butylamine titer as function of pK_a (meq/g of sample)			
	p$K_a < -8.2$	-8.2 to -5.6	-5.6 to -3.0	-3.0 to $+3.3$
γ-Al_2O_3 (A1)	0.21	0.17	0.08	0.02
Catalyst 1	—	—	0.44[a]	0.02
Catalyst 2	0.21	0.17	0.08	0.02
γ-Al_2O_3 (A2)	0.32	0.14	0.26	0.04
Catalyst 5	0.31	0.17	0.29	0.02
Catalyst 6	0.31	0.17	0.24	0.04
SiO_2 (S1)	0.00	0.00	0.00	0.05
Catalyst 7	0.00	0.00	0.00	0.05
Catalyst 8	0.00	0.00	0.00	0.05
Silica–alumina	0.16	0.00	0.08	0.00
MgO (M1 and M2)	0.00	0.00	0.00	0.00

[a] Total acidity with p$K_a < -3.0$.

400°C for 4 h prior to titration measurements. Great care was taken to avoid exposure of the dried samples to moisture since such exposure, either during handling or due to traces of water in the benzene, could significantly affect the acid–base properties of the samples (*16*).

H_2 adsorption and x-ray diffraction measurements. The previously described (*6*) pulse-flow adsorption apparatus and procedures were used to measure H_2 adsorption uptakes. Briefly, the procedure consisted of reducing the sample at 500°C in flowing H_2, degassing at 500°C in flowing, ultrapure N_2, cooling to 22°C in flowing N_2, and measuring the H_2 uptake at 22°C. This H_2 uptake of catalysts not treated in O_2 is referred to as $(H/Pt)_0$. Following this adsorption measurement, the catalyst sample was treated in flowing O_2 at 550°C for the desired time. The O_2 treatment was followed by 500°C reduction, degassing, and H_2 adsorption at 22°C. The H_2 uptake after O_2 treatment, reduction, and degassing is referred to as (H/Pt).

Some of the catalysts were examined by X-ray diffraction (XRD) after various stages of treatment. XRD measurements were done with a Philips diffractometer using the step-scan mode and Cu$K\alpha$ radiation. The range of 36 to 44° of 2θ was scanned at a step size of 0.02° of 2θ and a counting time of 100 s per step. At these conditions, the Pt 111 line at $2\theta = 39.8°$ (the most intense Pt XRD line) was readily detected for Catalysts 16 and 17. Reliable detection of Pt lines for most Pt/Al_2O_3 catalysts was not possible, even at the slow scan rates used, due to the low Pt contents, relatively high Pt dispersions, and interference of γ-Al_2O_3 diffraction lines with Pt lines. At the conditions used for XRD, Pt crystallites ≥ 2.0 nm were readily detected.

RESULTS AND DISCUSSION

Acid–Base Properties

Total acidity and basicity of supports are given in Table 2; strength distributions of acidic and basic sites for supports and some supported Pt catalysts are listed in Tables 3 and 4. The acid–base properties of silicalite were not measured, but these high-silica pentasil zeolites are essentially neutral (*19*).

TABLE 4

Strength Distribution of Basic Sites for Supports and Catalysts

Support or catalyst	Benzoic acid titer as function of pK_a (meq/g of sample)			
	p$K_a > 18.4$	18.4 to 15.0	15.0 to 12.2	12.2 to 9.3
γ-Al_2O_3 (A1)	0.10	0.08	0.00	0.12
γ-Al_2O_3 (A2)	0.42	0.22	0.40	0.00
SiO_2 (S1)	0.00	0.00	0.00	0.00
Silica–alumina	0.00	0.00	0.00	0.04
MgO (M1)	0.00	1.12	0.00	0.04
MgO (M2)	0.00	0.05	3.60	0.00
Catalyst 16	0.00	0.00	3.55	0.00

The two alumina supports (A1 and A2) have similar acid–base properties; i.e., both contain strong acidic (p$K_a < -8.2$) and strong basic (p$K_a > 18.4$) sites, but the Alon (A1) has a higher total concentration of acidic sites (2.9 sites/nm^2) than the Kaiser (A2) alumina (1.8 sites/nm^2). This is probably due to the chlorine content of Alon. However, A2 has a higher concentration of basic sites (2.5 sites/nm^2) than A1 (1.8 sites/nm^2); the Na content of A2 may be responsible for the higher basicity of A2. The silica support S1 (Aerosil-200) had no basicity and only a low concentration of acid sites. This low acidity is probably due to traces of impurities (*20, 21*). The silica–alumina (53% silica) had a low concentration of basic sites and acidity similar to that of the aluminas. The magnesias had no acidity and high concentrations of basic sites with intermediate strengths.

Acidity and basicity of some supported Pt catalysts were measured to determine whether introduction of Pt or the nature of the Pt precursor affected the acid–base properties. Impregnation of the aluminas with Pt, followed by drying and reduction, does not appreciably alter the acidic properties of the aluminas even when H_2PtCl_6 is used in the impregnation (see results for Catalysts 1, 2, 5, and 6, Table 3). Impregnation of A1 with H_2PtCl_6 does not alter the Cl content markedly since A1 already contains significant amounts of chlorine. Hence, the lack of variation of acidity between A1 and Catalyst 1 is not surprising. Impregnation of A 2 with H_2PtCl_6 increases the Cl content form <0.03 to about 0.5 wt%. However, this increase in Cl content only resulted in a slight increase in acidity (cf. A2 and Catalyst 5, Table 3). This again is not surprising since low levels of chlorine do not affect acidity of aluminas significantly (*16*). Similar results were obtained for the silica-supported catalysts (see results for Catalysts 7 and 8, Table 3). The basicity of MgO is not changed significantly even if 5% Pt is introduced by impregnation with H_2PtCl_6 (see results for Catalyst 16, Table 4). These results lead to the conclusion that introduction of Pt to the various supports, using various Pt precursors, does not have a significant effect on the acid–base properties of the support.

Our results with alumina are at variance with those reported by Sharma *et al.* (*22*). These investigators found that coimpregnation of chlorinated γ-Al_2O_3 with 0.35 wt% Pt and 0.04 wt% Ir caused decreases in concentration of weak- and medium-strength acid sites ($-5.6 \leq$ p$K_a \leq +5.0$) of 0.16 to 0.27 sites/nm^2. These decreases in acidity correspond to the elimination of three to five acid sites per metal (Pt + Ir) atom. A decrease in acidity of $\approx$0.1 meq/g of catalyst would have resulted for our 0.5 wt% Pt catalysts if every Pt atom eliminated four acidic sites. The results in Table 3 for Catalysts 1, 2, 4, and 5 show that such a decrease was not observed. Our observations that impregnation of aluminas with Pt does not alter the acidity of the aluminas are in agreement with the results of Kupcha *et al.* (*23*); they found that impregnation of aluminas with Pt does not affect the electron acceptor properties of the supports. The probable cause for the observations by Sharma *et al.* (*22*) was exposure to moisture before or during the titrations. This explanation is substantiated by the results they obtained for their Sample A (a γ-Al_2O_3 obtained by calcination of boehmite). They

TABLE 5

Influence of O_2 Treatment at 550°C on H_2 Adsorption Uptakes (H_2 Uptakes Measured after Reduction at 500°C)

Support	Catalyst	Platinum precursor	O_2 treatment time (h)	Hydrogen uptakes (H atom/Pt atom)		$\frac{(H/Pt)}{(H/Pt)_0}$
				$(H/Pt)_0$	(H/Pt)	
γ-Al_2O_3 (A1)	1	H_2PtCl_6	1	0.29	0.62	2.1
			16		0.64	2.2
	2	$Pt(C_5H_7O_2)_2$	1	0.54	1.08	2.0
			3		1.11	2.1
	3	H_2PtCl_6	1	0.33	0.68	2.1
			16		0.69	2.1
	4	$Pt(C_5H_7O_2)_2$	1	0.27	0.71	2.7
			16		0.61	2.3
γ-Al_2O_3 (A2)	5	H_2PtCl_6	1	0.24	0.51	2.1
			16		0.52	2.2
	6	$Pt(C_5H_7O_2)_2$	1	0.46	1.02	2.2
			3		1.06	2.3
SiO_2 (S1)	7	H_2PtCl_6	1	0.40	0.31	0.78
			3		0.26	0.68
	8	$Pt(C_5H_7O_2)_2$	1	0.40	0.35	0.88
			3		0.28	0.70
SiO_2 (S2)	9	H_2PtCl_6	1	0.20	0.08	0.4
			3		0.04	0.2
Silica–alumina	10	H_2PtCl_6	1	0.31	0.18	0.58
			3		0.14	0.45
	11	$Pt(C_5H_7O_2)_2$	1	0.09	0.04	0.4
MgO (M1)	12	H_2PtCl_6	1	0.04	0.11	2.7
	13	$Pt(C_5H_7O_2)_2$	1	0.00	0.00	—
MgO (M2)	14	H_2PtCl_6	1	0.00	0.00	—
	15	$Pt(C_5H_7O_2)_2$	1	0.00	0.00	—
	16	H_2PtCl_6	1	0.06	0.16	2.7
			3		0.19	3.2
Silicalite	17	$Pt(NH_3)_4Cl_2$	1	0.47	0.14	0.30

did not observe any strong acidity for this sample; we have always found significant concentration of strong-acid sites on γ-Al_2O_3 obtained by this method, but exposure to moisture significantly affects the acidity of these samples.

Influence of 550°C Oxygen Treatment

In previous studies (*6, 24, 25*) we observed that oxygen treatment of reduced Pt/γ-Al_2O_3 catalysts at 400 to 550°C resulted in increases in hydrogen adsorption uptakes. The results in Table 5 show the effect of oxygen treatment at 550°C on subsequent hydrogen adsorption for Pt on various supports. The results for Pt on alumina are similar to those reported previously for catalysts prepared by impregnation with H_2PtCl_6 (*6, 24, 25*); i.e., treatment in O_2 at 550°C results in about a twofold increase in H_2 adsorption [$(H/Pt)/(H/Pt)_0 = 2.0$ to 2.7]. This increase was observed for Pt/γAl_2O_3 prepared by impregnation with either H_2PtCl_6 or $Pt(C_5H_7O_2)_2$, but catalysts prepared by impregnation with $Pt(C_5H_7O_2)_2$ (Catalysts 2, 4, and 6) had a higher absolute H_2 uptake than catalysts prepared by impregnation with H_2PtCl_6 (Catalysts 1, 3, and 5).

Oxygen treatment at 550°C of silica, silica–alumina, and silicalite-supported Pt did not result in increases in H_2 adsorption. Oxygen treatment at 550°C for these catalysts, regardless of Pt precursor, always resulted in decreases in H_2 adsorption. Similar O_2 treatment of Pt/MgO catalysts prepared by impregnation with H_2PtCl_6 caused increases in H_2 adsorption; however, the absolute values of the H/Pt ratios were low (≤ 0.3). Pt/MgO catalysts prepared by im-

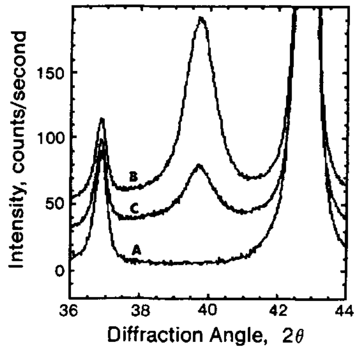

FIG. 1. XRD patterns of MgO and 5% Pt/MgO (Catalyst 16): A = MgO; B = 5% Pt/MgO reduced at 500°C; C= sample used for B and then treated in O_2 at 550°C for 1 h and reduced at 500°C. (Patterns B and C are offset for clarity.)

pregnation with $Pt(C_5H_7O_2)_2$ did not adsorb H_2 (see Catalysts 13 and 15, Table 5). More detailed results of the anomalous H_2 adsorption on Pt/MgO have been presented elsewhere (*26*), and further investigations of the Pt/MgO system are in progress.

XRD was used to determine whether O_2 treatment at 550°C causes changes in Pt crystallite sizes, since H_2 adsorption uptakes may not reflect Pt dispersion. Figure 1 shows XRD patterns for reduced samples of Catalyst 16 (5% Pt/MgO). The high Pt loading was used to obtain relatively large diffraction intensities for Pt lines. XRD patterns for the 0.5% Pt/MgO catalysts had weak Pt diffraction lines indicating that the Pt was well dispersed in these catalysts. The freshly reduced 5% Pt/MgO catalyst displayed an intense Pt 111 line (see Fig. 1, Pattern C at $2\theta = 39.8°$). Oxygen treatment followed by reduction caused a three- to fourfold decrease in the integrated intensity of the Pt 111 line (cf. Patterns B and C, Fig. 1). This means that over 70% of the Pt in the O_2-treated, reduced sample is present in crystallites smaller than 2.0 nm. If >70% of the Pt is present in Pt crystallites <2.0 nm in size, then the Pt dispersion is >0.35. However, the H/Pt ratio after 1-h O_2 treatment at 550°C was only 0.16 (see Catalyst 16, Table 5). These results again show that H/Pt ratios for Pt/MgO do not correspond to Pt dispersions.

Results of XRD studies on the 1% Pt/silicalite catalysts in Fig. 2 clearly show that O_2 treatment at 550°C causes growth of Pt crystallites and increases the fraction of XRD-detected Pt. The integrated intensity of the Pt 111 line increased about twofold as a result of 1-h O_2 treatment at 500°C (cf. Patterns B and C, Fig. 2). This indicates that approximately half of the Pt in the freshly reduced sample is present in Pt crystallites <2.0 nm in size. The Pt crystallite sizes of the XRD-detected Pt, based on the integral width of the 111 Pt line, are ≈9 nm for the freshly reduced catalyst (Pattern B, Fig. 2) and ≈12 nm for the O_2-treated catalyst (Pattern C, Fig. 2). The decrease in H_2 adsorption as a result of O_2 treatment (see Table 5) is in agreement with the XRD-determined increases in Pt crystallite size. XRD studies of Pt on γ-Al_2O_3 are complicated by the broad 222 line of γ-Al_2O_3 at $2\theta = 39.5°$ which masks the Pt 111 line. This is illustrated in Fig. 3 for the 1% Pt/γ-Al_2O_3 catalyst. Patterns B and C in Fig. 1 have higher intensities in the 38 to 42 °2θ region than the support (Pattern A), but Pattern B, before O_2 treatment, and Pattern C, after O_2 treatment, appear to be similar. However, point-by-point subtraction of Pattern C from Pattern B, resulting in Pattern D,

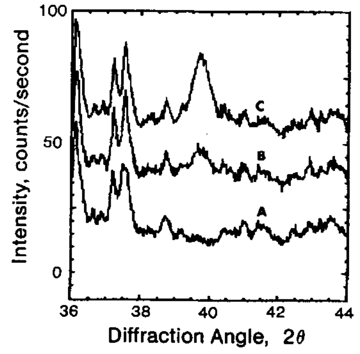

FIG. 2. XRD patterns of silicalite and 1% Pt/silicalite (Catalyst 17): A = silicalite; B = Catalyst 17 reduced at 500°C; C = sample used for B and then treated in O_2 at 550°C for 1 h and reduced at 500°C. (Patterns B and C are offset for clarity.)

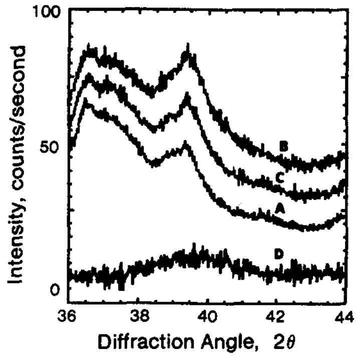

FIG. 3. XRD patterns of γ-Al_2O_3 (A1) and 1% Pt/γ-Al_2O_3 (Catalyst 4): A = γ-Al_2O_3 (A1); B = Catalyst 4 reduced at 500°C; C = sample used for B and then treated in O_2 at 550°C for 16 h and reduced at 500°C; D = Pattern C subtracted from Pattern B. (Patterns B and C are offset for clarity.)

shows that the intensity of the Pt 111 line has decreased slightly as a result of O_2 treatment. This is in qualitative agreement with the increased H/Pt as a result of O_2 treatment.

Acid–Base Properties and Pt Dispersion after O_2 Treatment

Comparison of support acid–base properties (Tables 3 and 4) with the influence of O_2 treatment at 550°C on subsequent H_2 adsorption uptakes (Table 5) shows that increases in H_2 uptakes only occur for supports with basic sites of medium and/or high strengths, i.e., aluminas and magnesias. Oxygen treatment at 550°C of Pt on acidic supports, such as silica–alumina which has very low weak basicity, and essentially neutral supports, such as silica and silicalite, always caused decreases in H_2 uptakes. XRD results, e.g., Figs. 1 to 3, show that increases in H_2 uptakes are accompanied by decreases in average Pt crystallite sizes. Hence, oxygen treatment at 550°C can cause redispersion of Pt on supports with basic sites, while similar treatments of Pt on supports that do not have appreciable basicity results in sintering, i.e., a decrease in Pt dispersion.

The current observations are in agreement with a previously proposed mechanism for sintering and redispersion (*6*). This mechanism proposes that Pt oxide species are formed on the Pt crystallites and these Pt oxides migrate across the support. Sintering occurs if the interactions of these mobile species with the support are weak, and increase in dispersion occurs if the migrating species are trapped by strong interactions with the support. The PtO_x formed on the Pt crystallites may decompose to Pt^0 and oxygen on the support. On nonbasic supports the mobile Pt species do not interact strongly with specific sites on the support and sintering results. On basic supports the migrating Pt species interact strongly with the basic sites and increases in dispersion result. Basic O^{2-} sites stabilize Pt^{n+} (*3*) as well as Rh^0 (*10, 11*). These results support our conclusion that basic sites are responsible for redispersion during O_2 treatment.

SUMMARY AND CONCLUSIONS

The behavior of supported Pt during oxygen treatment at elevated temperatures is strongly affected by the acid–base properties of the support. On supports without basic sites only sintering was observed, while on supports with medium and/or strong basic sites increases in dispersion occurred as a result of O_2 treatment. XRD and chemisorption results were in qualitative agreement; however, the H/Pt ratios measured for Pt/γ-Al_2O_3 prepared by impregnation with H_2PtCl_6 and for Pt/MgO probably do not correspond to Pt dispersions. The H/Pt ratios for these catalysts were consistently lower than the Pt dispersions indicated by XRD intensities and linewidths. More detailed investigations dealing with the quantitative disagreement between H_2 chemisorption and XRD results are planned.

ACKNOWLEDGMENT

We acknowledge the support of this research by the National Sciences and Engineering Research Council of Canada.

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