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A fundamental study of platinum tetraammine impregnation of silica
2. The effect of method of preparation, loading, and calcination temperature on (reduced) particle size

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Abstract

Pt/silica catalysts were prepared by adsorption of $Pt(NH_3)_4^{2+}$ from strongly basic impregnation solutions. The pH not only determines the amount of adsorbed Pt but also influences the particle size of the reduced catalyst. The highest dispersions were obtained at lower Pt loading and drying in air at 100 °C followed by reduction in H_2 at 250 °C. With increasing calcination temperature there was a nearly linear decrease in the Pt dispersion. It is suggested that the dispersion is dependent on the distribution of Pt species on silica at the time of reduction. Reduction of Pt^{2+} adsorbed under conditions to give strong electrostatic interaction leads to particles with a dispersion of 1.0. Calcination at temperatures form 150 to 400 °C leads to partial oxidation of PTA to Pt^{4+} species, which reduce to metallic particles with a dispersion of about 0.4. Finally, calcination above 525 °C leads to large metallic Pt particles with a dispersion of about 0.07. By selecting the method of preparation and calcination temperature, very small to large metallic nanoparticles can be prepared.

Keywords: Pt nanoparticles; Pt on silica; Wet impregnation; Catalyst preparation; Calcination; Platinum tetraammine; Pt EXAFS; Pt XANES; QEXAFS

1. Introduction

Supported noble metal catalysts are used in a large number of commercially important processes including hydrogenation, naphtha reforming, oxidation, automotive exhaust catalysts, and fuel cells. In order to maximize the activity, it is necessary to make small particles. Typically, supported catalysts contain particles of about 10–100 Å. It is well known that for some reactions, the particle size affects the rate (per surface atom) and the selectivity. Thus, precise control of the particle size is essential for optimum performance.

Several steps in the preparation including the support composition, metal salt, method of metal addition, pH, metal loading, calcination temperature, etc., affect the ultimate particle size in the reduced catalyst. The importance of these effects are evident in a survey of the literature on the preparation of Pt/SiO_2 catalysts given in Table 1 [1–22]. Incipient wetness or dry impregnation (DI) is often used in the preparation with chloroplatinic acid (H_2PtCl_6 or CPA) [5,6,9,13,16,19,21,22], but may also be used with platinum tetraammine chloride (or nitrate), $Pt(NH_3)_4Cl_2$ or PTA [6,21]. With this method, the desired amount of metal salt is dissolved in sufficient water to just fill the pore volume of the support. Pt on silica catalysts may also be prepared by several nontraditional methods such as a simultaneous sol–gel synthesis of a Pt salt and silica [10,12,18] or by DI with organic solvents [12,20]. The most often used method, however, is to add PTA to silica from a slurry in excess solution [1–5,7,8,11,12,14–17]. This method is commonly called ion exchange, but can more generally be considered wet impregnation (WI). In the WI method of preparation the pH of the neutral or mildly basic impregnating solution slowly becomes more acidic since the point of zero charge (PZC) of silica is about 4. If the impregnating solution is maintained under strongly basic conditions, the silica hydroxyl groups are deprotonated and platinum tetraammine cation is readily deposited on the sup-

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Table 1
Summary of the literature on the method of preparation for Pt/SiO_2 catalysts

Ref.	Pt loading (wt%)	Surface area (m^2/g)	Surface loading ($\mu mol/m^2$)	Method	Precursor	pH final	Calc. (O_2) K	Redc. (H_2) K	Dispersion
1	0.5	nd	–	WI	PTA-Cl_2	7.0 initial	383	673/603	0.31–0.35
1	0.5	nd	–	WI	CPA	2.1 initial	383	673/603	0.20
2,3	6.3	364	0.887	SEA	PTA-OH and Cl_2	8.9	378	673	0.64
4	3.6	200	0.923	SEA	PTA-Cl_2	NH_4OH	773	–	0.30
5	0.8	219	0.187	SEA	CPA to PTA	9–11 at 343 K	393	–	0.75
5	0.4	219	0.094	DI	CPA in acetone	–	393	–	0.53
6	0.05	500	0.005	DI	PTA-NO_3	–	573	473	0.99
6	0.6	500	0.062	DI	PTA-NO_3	–	573	473	0.90
6	3.0	500	0.308	DI	PTA-NO_3	–	573	473	0.60
6	3.1	500	0.318	DI	CPA	–	573	473	0.25
7	0.06	198	0.016	SEA	CPA to PTA	9.74	378	533	1.0
7	0.46	198	0.119	SEA	PTA	9.74	378	533	0.92
7	1.73	198	0.448	SEA	PTA	9.74	378	533	0.58
8	0.01–7	194	0.003–1.85	SEA	PTA-OH	8–10.5	573	673	0.65
9	1.0	260	0.197	DI	CPA	0.2M HCl	723	773	0.41
10	0.83	500–800	0.085–0.053	Sol–gel	PTA-NO_3	4.3	–	–	0.70
11	2.68	200	0.687	SEA	PTA-Cl_2	9.0	Dried desiccator	673	0.56
11	2.68	200	0.687	SEA	PTA-Cl_2	9.0	573	673	0.84
11	2.68	200	0.687	SEA	PTA-Cl_2	9.0	573 Ar	673	0.85
12	1.76	653	0.138	Sol–gel	CPA	1.4	673	673	0.20
	1.62	480	0.173		PTA-NO_3	4.0			0.80
	1.65	632	0.134		$Pt(C_5H_7O_2)_2$	4.8			0.50
12	0.95 (design 2.0%)	714	0.068	WI	PTA-NO_3	8.0	673	673	0.25–0.28
12	0.91	1097	0.043	Ethanol	PTA-NO_3	2.4	673	673	0.10–0.15
	0.91	754	0.062	and acetone	$Pt(AcAc)_2$	1.65			0.10–0.13
12	1.65	632	0.134			5.0	673	673	0.50
	0.8	706	0.058	Sol–gel	$Pt(AcAc)_2$				0.80
	0.65	759	0.044						0.80
	0.40	586	0.035						0.80
13	4.9	200	1.26	DI	$PtCl_4$	–	573	573	0.30
	1.0		0.256						0.50
14	1.0	300	0.171				293	573	0.30
				WI	PTA-Cl_2	12 initial	vacuum	673	0.29
								773	0.28
								773 N_2	0.98
14	2.0	300	0.342	WI	PTA-Cl_2			773	0.78
								1023	0.44
								1073	0.20
15	0.81	220	0.189	SEA	PTA-Cl_2	9.8	673 He	673	0.61
16	2.65	220	0.617				393	673	0.22
	1.44		0.336	DI	CPA				0.41
	0.49		0.114						0.45
16	3.8	220	0.883	SEA	PTA-Cl_2	9.8	Dried	673	0.66
17	1.05	596	0.09	SEA	PTA-OH	–	573	573	0.97
17	0.90	596	0.077						0.34
	0.87	341	0.131	WI	PTA-OH	–	773	573	0.23
	0.93	238	0.20						0.93
	1.02	580	0.09						1.00
	0.89	202	0.226						0.47
18	1.5		0.193	Modified	$Pt(acac)_2$	–			0.39
		399		impregnation	$Pt(acac)_2$		823	373	0.24
				with sol–gel?	CPA				0.10
19	0.5		0.068						1.0
	1.6	377	0.218	DI	CPA	Acidic	393	773	0.50
	2.5		0.34						0.30
	4.6		0.625						0.3

Table 1 (*Continued*)

Ref.	Pt loading (wt%)	Surface area (m^2/g)	Surface loading ($\mu mol/m^2$)	Method	Precursor	pH final	Calc. (O_2) K	Redc. (H_2) K	Dispersion
19	0.7		0.095						1.20
	1.5	377	0.204	SEA	PTA-Cl_2	9.0	393	773	1.00
	2.5		0.34						0.80
	4.5		0.612						0.90
20	0.5	M-5	–	Organic	Pt$(Acac)_2$	Toluene		673	0.43
		Sol–gel		DH-	Acetyl	Excess	673	H_2/He	0.39
		M-5(DH)		dehydroxylated	acetonate				0.32
		Sol–gel(DH)		support					0.31
20	0.5	M-5	–	Impreg	CPA			673	0.12
		Sol–gel		DH-		Acidic	673	H_2/He	0.12
		M-5(DH)		dehydroxylated		?			0.08
		Sol–gel(DH)		support					0.09
21	1	–	–	DI	PTA[a]	–	773 and up	–	0.39–0.02
22	1	270	0.19	DI	CPA	Acidic ?	Vacuum dried 383	623 to 973	0.84–0.13

DI, dry impregnation; WI, wet impregnation at near neutral pH; SEA, wet impregnation under strongly basic pH.

[a] Text reads $Pt(NO_3)_2(NH_4)_2$, typo assumed.

port. We suggest [23] that it is more correct to describe this interaction as strong electrostatic adsorption (SEA), rather than ion exchange, since the attraction occurs only in strong base sufficient to deprotonate the silanol groups.

Table 1 is a list of the methods of preparation, e.g., DI (with PTA or CPA), WI (where the pH drifts toward neutral pH), and SEA (where the pH remains high) for Pt/silica catalysts reported in the literature. In addition, to the different methods of Pt addition, the metal loading and subsequent calcination and reduction temperatures are also given. A number of trends affecting the dispersion of the reduced catalysts can be identified in Table 1. First, DI with CPA generally gives moderate to poor dispersion, ca. 0.2–0.4 [5,6,9,13,16,19,21,22], with the exception at very low loading. DI of PTA gives higher dispersions than those prepared from CPA, about 0.6–0.9 with higher dispersions at lower Pt loading [6,21]. Preparation of Pt on silica by WI with PTA, i.e., near neutral pH, also gives dispersions, which are moderate to low, generally about 0.3–0.5 [1,14,17]. The highest dispersions are achieved by SEA of PTA; i.e., the pH remains high throughout the metals deposition. For catalysts prepared by SEA and WI, Fig. 1 shows that the Pt dispersion decreases as the metal loading increases. Since the catalysts in Fig. 1 were prepared on silicas with different surface area, the metal loadings were compared on the basis of Pt surface density ($\mu mol/m^2$). While there are only a few examples of catalysts calcined at higher temperatures, at the same Pt surface density, catalysts calcined below 300 °C generally have higher dispersions [2,3,5,7,8,11,16,17,19].

The effect of the method of Pt addition (with PTA) onto silica, metal loading, and calcination temperature between 100 to 675 °C on the dispersion of the reduced catalyst has been determined. In addition, XANES and EXAFS spectroscopies have been used to characterize the Pt species following calcination. Calcination leads to increasing oxidation of Pt^{2+} to Pt^{4+} up to about 500 °C. Above this temperature, there is autoreduction to large metallic particles. Dispersions are higher for catalysts prepared by strong electrostatic adsorption, at low metal loading, and for catalysts that are not calcined.

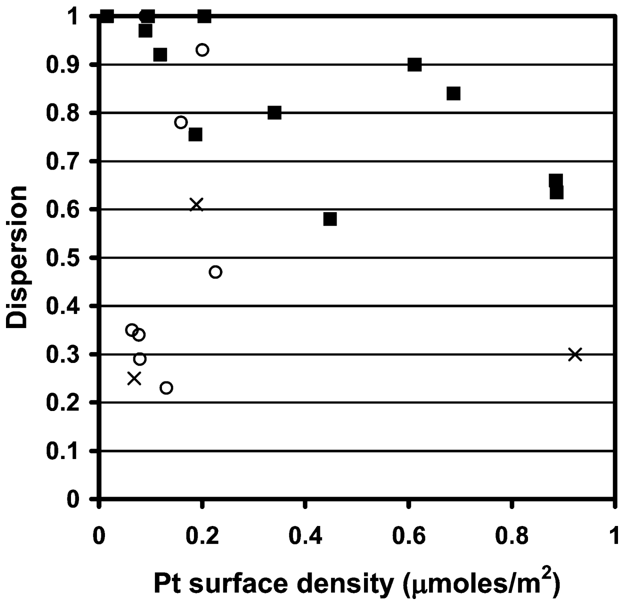

Fig. 1. Pt dispersion versus Pt surface density for Pt/silica catalysts prepared by (open circle) WI; (solid square) SEA calcined at low (373–573 K); and (×) SEA calcined at high (673–773 K) temperature (data taken from the literature).

2. Experimental

Davison 644 silica and platinum tetraammine chloride [$Pt(NH_3)_4Cl_2$, 99.9%] or platinum tetraammine nitrate [$Pt(NH_3)_4(NO_3)_2$] from Aldrich were used. The N_2 BET surface area and pore volume were 290 m^2/g and 1.0 cc/g, respectively, and were not affected by any of the catalyst preparation steps. The PZC of the silica was 6.2, typical of precipitated silica with alkali impurities [23]. The silica was washed with water to remove any residual Na and lowered the PZC to that of alkali-free silica, ca. 4.0 [23]. Since the adsorption of PTA over alkaline and alkaline-free silica has been shown to be identical [24], catalysts were prepared from the as-received, unwashed silica. For the modeling of PTA adsorption, however, a PZC of alkaline-free silica was assumed [24]. The revised physical adsorption (RPA model) for PTA on silica was previously described [23].

2.1. PTA adsorption verses pH

A stock solution of 18,700 mg/L Pt was prepared by adding 31.96 g $Pt(NH_3)_4Cl_2$ to 1.000 L of deionized water. The elemental composition was confirmed by ICP analysis. Concentrated HNO_3, NH_4OH, or NaOH was added to adjust the pH of 50 mL of stock solutions, in 60 mL Nalgene polypropylene bottles. A pH range between 2 and 9 was prepared by the addition of HNO_3 and NH_4OH, while PTA solutions at a pH between 4 and 13.5 were prepared by the addition of HNO_3 and NaOH. The 50 mL of the pH adjusted PTA solutions was added to 14.31 g of the silica, giving a surface loading (surface area of silica per liter of solution) of 83,000 m^2/L. After 1 h, 5 mL of solution were filtered, the Pt concentration was determined by ICP and the Pt loading on silica was calculated by difference. Final pH values were also recorded.

2.2. Catalyst preparation

2.0% Pt on silica by Dry Impregnation (DI): 0.90 g of $Pt(NH_3)_4(NO_3)_2$ in 45 mL H_2O was added to 45 g of silica. The initial pH of the PTA solutions was about 5.0. The catalyst was dried overnight at 100 °C in a forced air, ventilated oven. The Pt elemental analysis determined by ICP was 2.03%.

2.0% Pt on silica by Strong Electrostatic Adsorption (SEA): 45 g of silica was slurried in 400 mL H_2O. The pH was increased to 9.5 by addition of concentrated NH_4OH. 0.90 g of $Pt(NH_3)_4(NO_3)_2$ dissolved in 50 mL H_2O was then added. After 1 h the solid was filtered and washed 2×250 mL H_2O and dried overnight at 100 °C in flowing air. The Pt elemental analysis determined by ICP was 2.06% and indicated that virtually all the PTA in solution had been adsorbed. A similar procedure, except for adjusting the amount of PTA added to the impregnating solution, was followed for preparation of catalysts with other Pt loadings.

The DI and SEA Pt/silica catalysts were calcined in flowing air at temperatures from 100 to 675 °C by heating at 1 °C/min to the final temperature and holding for 3 h. Following calcination, 10 g of catalyst was reduced at atmospheric pressure in flowing H_2 (200 cc/min) by heating from room temperature to 250 °C at 5 °C/min and holding for 2 h. The hydrogen chemisorption capacity was determined on the reduced catalysts by the double isotherm method using a Coulter Omnisorb 100CX instrument. The previously reduced catalyst was rereduced for 1 h and evacuated for 1 h at 250 °C and cooled to room temperature in vacuum. The first isotherm was determined at room temperature. The sample was evacuated at room temperature and the second H_2 isotherm was determined. The hydrogen chemisorption capacity was determined by the difference in the two isotherms extrapolated to zero pressure and assuming a hydrogen atom to surface Pt stoichiometry of 1.0.

2.3. EXAFS and XANES data collection and analysis

X-ray absorption measurements were made on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. A cryogenically cooled double-crystal Si (111) monochromator was used in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.07 s per data point (0.65 eV and 0.05 s for the time series). Measurements were made in transmission mode with the ionization chambers optimized for the maximum current with linear response ($\sim 10^{10}$ photons detected/s) using a mixture of nitrogen and helium in the incident X-ray detector and a mixture of ca. 20% argon in nitrogen in the transmission X-ray detector. A platinum foil spectrum was acquired simultaneously with each measurement for energy calibration.

Catalyst samples were pressed into a cylindrical holder with a thickness chosen to give a total absorbance (μx) of about 3.0, corresponding to approximately 100 mg of catalyst, which resulted in a platinum edge step ($\Delta \mu x$) of ca. 0.5 for 2% Pt on silica. EXAFS and XANES spectra of the calcined catalysts were obtained at room temperature in air. Phase shifts, backscattering amplitudes, and XANES references were obtained from reference compounds: $Pt(NH_3)_4(NO_3)_2$ for Pt^{2+}, $Na_2Pt(OH)_6$ for Pt–O and Pt^{4+}, and Pt foil for Pt^0 and Pt–Pt. The XANES fits of the normalized spectra were made by linear combination of experimental standards. Standard procedures based on WINXAS97 software [25] were used to extract the EXAFS data [26]. The coordination parameters were obtained by a least square fit in k- and r-space of the isolated multiple-shell, k^2-weighted Fourier transform data.

3. Results

3.1. PTA adsorption verses pH

The amount of Pt adsorbed on silica at a surface loading (m^2 of silica per liter of solution) of 83,000 as a function of the final pH of the solution is shown in Fig. 2. The amount of Pt adsorbed on silica is given as surface density

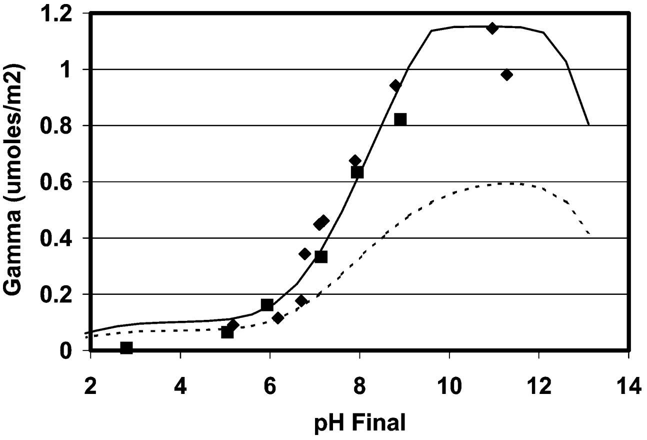

Fig. 2. The uptake of PTA on Davison 644 silica as a function of pH (83,000 m^2/g, 18,700 ppm Pt), basic solutions with NH_4OH (square) or NaOH (diamond). Revised physical adsorption model fit with parameters: PZC $= 4.0$, $\Delta pK = 6.75$, $N_s = 5$ OH/nm^2, number of hydration sheaths (nhs) $= 1.5$ (dotted line) and 2 (solid line).

(or $\mu mol/m^2$). At pH's below about 6, there is little adsorption. As the pH increases, the amount of Pt adsorbed increases up to a pH of about 10 with a maximum of about 1.1 $\mu mol/m^2$. There was sufficient Pt in solution to give a 1.15 $\mu mol/m^2$ if all the PTA had been adsorbed. The amount of PTA adsorbed is the same from basic solutions adjusted by either NH_4OH or NaOH.

The adsorption was modeled using the parameters determined in the previous study for 200 ppm PTA on silica [23]. The dotted line in Fig. 2 indicates that the shape of the adsorption curve is generally correct, although the model underpredicts the amount of Pt adsorbed at this high surface loading (83,000 compared to 2000 and 30,000 m^2/L in the previous study). Apparently the adsorption capacity is higher for concentrated PTA-impregnating solutions. Better agreement with the data is obtained by assuming that the radius of the PTA hydration sphere decreases from about 2 to 1.5 molecules of water.

Table 2
Pt/SiO_2: the dispersion of the reduced catalysts prepared by SEA and DI of PTA, and calcined at temperatures from 100 to 675 °C

Pt (%)	pH	Base	Calcination temperature (°C)	H/Pt
		Strong electrostatic adsorption of PTA		
0.25	5.0 (initial)	None (WI)	200	0.87
0.63	9.5	NH_4OH	100	0.96
1.05	9.5	NH_4OH	100	1.00
1.05	9.5	NH_4OH	150	1.00
1.05	9.5	NH_4OH	200	0.96
1.05	9.5	NH_4OH	250	0.92
1.05	9.5	NH_4OH	300	0.86
1.05	9.5	NH_4OH	400	0.61
1.05	9.5	NH_4OH	525	0.24
1.05	9.5	NH_4OH	600	0.13
1.05	9.5	NH_4OH	675	0.06
1.23	9.5	NH_4OH	100	0.95
2.06	9.5	NH_4OH	250	0.72
2.06	9.5	NH_4OH	300	0.62
2.06	9.5	NH_4OH	400	0.47
2.06	9.5	NH_4OH	500	0.24
2.06	9.5	NH_4OH	550	0.19
2.06	9.5	NH_4OH	600	0.11
1.63	9.5	KOH (0.46% K)	100	1.26
1.88	9.5	KOH (0.19% K)	100	0.97
		Dry impregnation of PTA		
1.05	5.0	None	100	0.85
1.05	5.0	None	150	0.75
1.05	5.0	None	200	0.58
1.05	5.0	None	250	0.53
1.05	5.0	None	400	0.41
1.05	5.0	None	525	0.30
1.05	5.0	None	600	0.10
1.05	5.0	None	675	0.04
1.50	5.0	None	250	0.29
2.03	5.0	None	100	0.51
2.03	5.0	None	200	0.30
2.03	5.0	None	250	0.29
2.03	5.0	None	400	0.24
2.03	5.0	None	500	0.22
2.03	5.0	None	550	0.19
2.03	5.0	None	600	0.09

3.2. Comparison of SEA and DI preparations

The effect of method of preparation of Pt/silica from PTA on the dispersion of the reduced catalyst, determined by hydrogen chemisorption, is given in Table 2. Dissolution of PTA in water gives a pH of about 5.0. At this initial pH, silica adsorbs only 0.25% Pt of a possible 2.0 wt% (this is the WI method of preparation). Calcination at 200 °C gives a high dispersion, 0.87. By increasing the pH of the adsorption solution with NH_4OH, significantly more PTA can be adsorbed. Various amounts of PTA were added to give the different Pt loading in Table 2. Virtually all PTA in the parent solutions was adsorbed onto the silica surface in the SEA (high pH) preparations. Thus, under these conditions higher loadings should be possible. At loadings up to about 2% Pt, the dispersion is high when the drying temperature is near 100 °C; i.e., the catalyst is not calcined. High dispersion at higher loading may also be possible if catalysts prepared by SEA are not calcined. Catalysts prepared in basic solutions of KOH give similar adsorption capacities and high dispersions as those prepared with NH_4OH; however, some residual KOH is retained on the support.

Catalysts were also prepared by incipient wetness impregnation (DI) at the pH of the PTA solution, ca. 5.0. Generally, the dispersion is lower than similar catalysts prepared by strong electrostatic adsorption. The specific result depends on the Pt loading. For example, at 1% Pt, the dispersion of the DI catalyst dried at 100 °C is 0.85, while the Sel-Ads catalyst is 1.0. At 2% Pt, however, the DI catalyst is 0.51, while the SEA (KOH) catalyst is 0.97. One would expect the dispersion to be very similar at 0.25% Pt since the amount adsorbed at this pH would be the same as that added by DI.

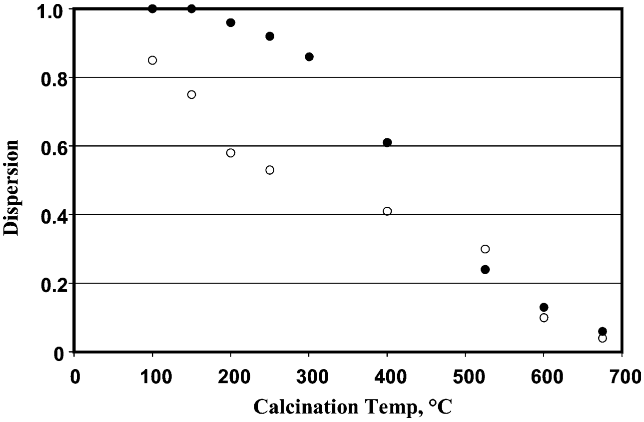

Fig. 3. Dispersion of 1.0% Pt/silica catalysts prepared by SEA (solid circles) and DI (open circles) of PTA and calcined at temperature from 100 to 675 °C.

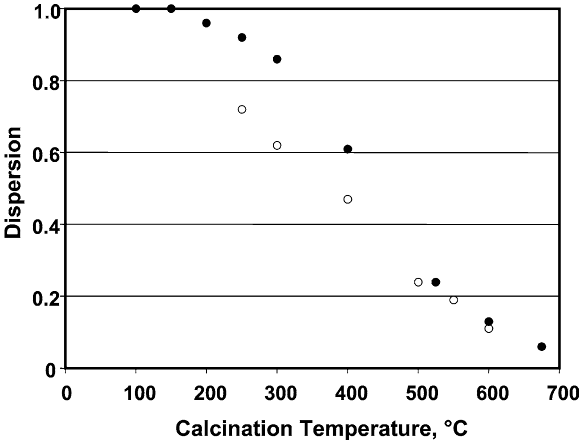

Fig. 4. The effect of calcination temperature and metal loading on dispersion for 1% Pt (solid circles) and 2% Pt (open circles) on silica prepared by SEA.

After addition of the metal salt to a support, catalysts are often heated at elevated temperatures in air prior to reduction. The effect of calcination temperature on the Pt dispersion for PTA on silica is also shown in Table 2 and in Fig. 3. For both methods of preparation, the dispersion (after reduction) is highest when the catalyst is dried at 100 °C. At this temperature, both catalysts are white in color. As the heating/calcination temperature increases, the color becomes first light brown and at higher temperature dark brown. As the calcination temperature increases, the dispersion decreases approximately linearly. Above about 500 °C, the dispersion is nearly identical for both methods of preparation.

The effect of metal loading and calcination on dispersion is shown in Fig. 4 for 1 and 2% Pt on silica prepared by SEA of PTA at a pH of 9.5 with NH_4OH. As the metal loading increases, the dispersion is lower at calcination temperatures up to about 500 °C, above which the dispersion is independent of the metal loading.

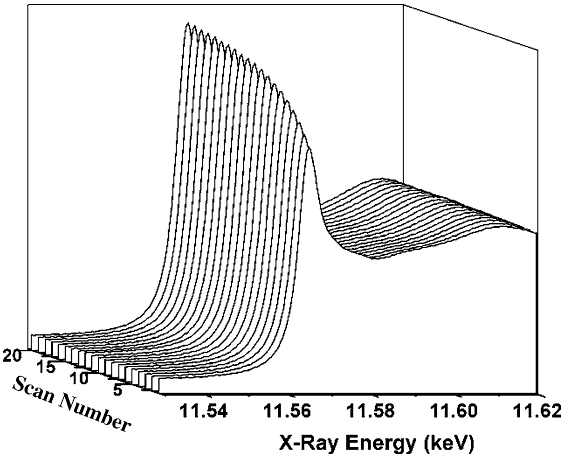

Fig. 5. The XANES spectra (EXAFS region not shown for clarity) from 11.52 to 11.60 eV for 1% Pt on silica prepared by SEA with PTA. The XANES and EXAFS spectra were obtained at room temperature in air every 82 s.

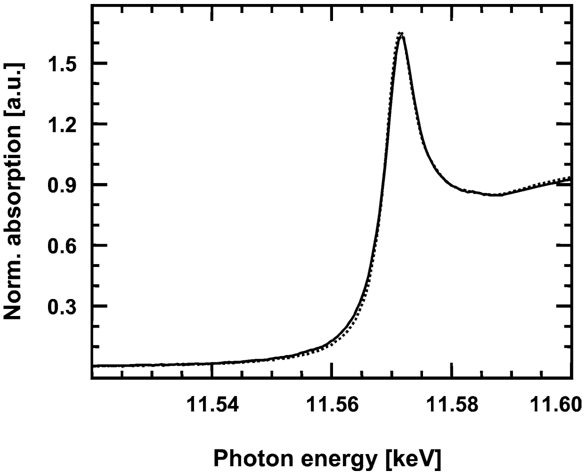

Fig. 6. Normalized XANES spectrum (solid) and fit (11.52–11.60 keV) (dotted) for 1% Pt on silica prepared by SEA of PTA at pH 9.5 with NH_4OH and calcined at 200 °C.

3.3. *XANES and EXAFS spectra for PTA on silica at different calcination temperatures*

As shown in Fig. 5 for samples containing Pt^{2+}, there was a rapid increase in the white line region with subsequent scans. After about 5.5 min, approximately 50% of the Pt had been oxidized to Pt^{4+}, while over 90% had been oxidized after 30 min. In order to determine the true distribution of Pt oxidation states, correction was made for oxidation by the beam. Consecutive scans in this series were obtained every 82 s, and the XANES region from 11.52 to 11.60 keV was fit with a combination of Pt^{2+} and Pt^{4+}. A typical spectrum and fit of a XANES spectrum for the 1% Pt on silica catalyst prepared by SEA and dried at 100 °C is given in Fig. 6. The $\log_{10}$ of the amount of Pt^{2+} verses the time of each scan indicated a first order oxidation of Pt^{2+} by the beam. Extrapolation to zero time indicated that the sample was 100%

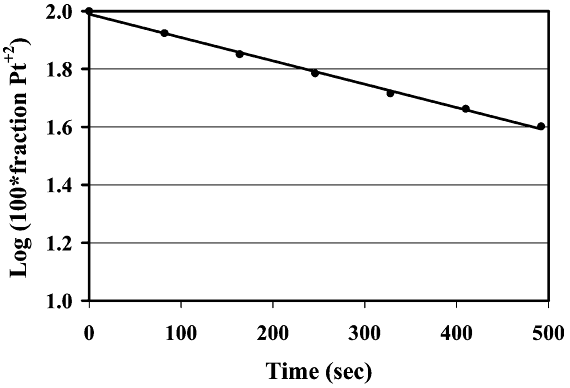

Fig. 7. The first-order kinetic plot for oxidation of Pt^{2+} to Pt^{4+} by the X-ray beam for 1% Pt on silica prepared by SEA. Extrapolation to zero time gives the composition of the oxidation state of adsorbed Pt.

Table 3
XANES fits (from 11.52 to 11.60 eV) of 1% Pt/silica catalysts prepared by SEA and DI of PTA and calcined at temperature from 100 to 675 °C

Calcination temperature (°C)	DI			SEA		
	Pt^{2+}	Pt^{4+}	Pt^0	Pt^{2+}	Pt^{4+}	Pt^0
100	1.0	–	–	1.0	–	–
150	1.0	–	–	1.0	–	–
200	0.54	0.46	–	0.80	0.20	–
250	0.21	0.79	–	0.55	0.45	–
300	–	1.0	–	0.29	0.71	–
400	–	1.0	–	0.28	0.72	–
525	–	1.0	–	–	0.37	0.63
600	–	0.21	0.79	–	0.17	0.83
675	–	0.09	0.91	–	0.10	0.90

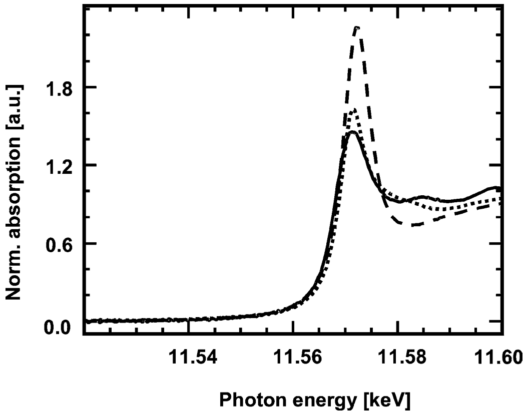

Fig. 8. Normalized XANES spectra for 1% Pt on silica prepared by DI with PTA at a pH 5.0 and calcined at 100 (dotted), 300 (dashed), and 600 °C (solid).

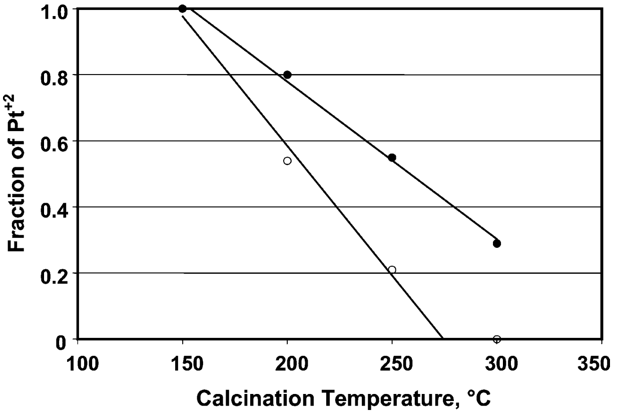

Fig. 9. The fraction of Pt^{2+} on silica after calcination of PTA from 100 to 300 °C, SEA (solid circle) and DI (open circle).

Pt^{2+} (Fig. 7). Catalysts containing only Pt^{4+} or metallic Pt did not change in the beam during data collection.

The XANES fits of 1% Pt on silica prepared by DI and SEA and calcined at temperatures from 100 to 675 °C are given in Table 3. For both methods of preparation, at 100 °C Pt is present as Pt^{2+}. As the drying/calcination temperature increases, the white line increases due to partial oxidation of PTA to Pt^{4+} (Fig. 8). The fraction of Pt^{4+} is larger for the catalyst prepared by DI, which is fully oxidized at 300 °C (Fig. 9). Even at 400 °C, not all the PTA adsorbed onto silica has been oxidized. These results are consistent with previous results, which show that PTA is not fully decomposed in air at 300 °C [27]. Above 500 °C (in air), there is a decrease in the white line intensity due to autoreduction to metallic Pt (Fig. 8). The fraction of metallic Pt increases with increasing calcination temperature. Generally, the fraction of metallic Pt at high calcination temperature is very similar for both methods of preparation.

The EXAFS fits of the isolated shells of the calcined catalysts are given in Table 4. A typical k^2-weighted spectrum and r-space fit are shown in Fig. 10. At 100 °C, for both methods of preparation the EXAFS indicates that there are 4 Pt–O (or Pt–N) scatters at a distance of 2.05 Å, indicating no change in the PTA upon contact with silica. EXAFS cannot distinguish between a N or O backscattering atom. As the calcination temperature increases, there is a continual increase in the Pt–O coordination number (Fig. 11). These changes parallel the increase in white line intensity confirming the oxidation of PTA by calcination. On the catalyst prepared by DI, Pt^{4+} oxide with 6 Pt–O bonds is formed at 300 °C and remains the dominant species up to a calcination temperature of 525 °C. Calcination at temperatures higher than 525 °C leads to formation of metallic Pt with a near-neighbor bond length of 2.77 Å (see also Fig. 11). Since a fraction of the metallic particles are oxidized, it is not possible to directly estimate the particle size from the Pt–Pt coordination number. However, if one estimates the fraction of metallic Pt from the XANES, a reasonable estimate can be made from the EXAFS. For example, the fraction of metallic Pt in the DI catalyst calcined at 600 °C is 0.79. Therefore, the actual Pt–Pt coordination number is about 10.6 (8.4/0.79), indicating large metallic Pt particles; fully coordinated bulk platinum has a nearest neighbor coordination number of 12. Formation of metallic Pt by air calcination always leads to large particles. Furthermore, the EXAFS coordination numbers and hydrogen chemisorption results indicate that the dispersion is similar for both methods of preparation at all metal loadings.

Table 4
EXAFS fits (k^2: $\Delta k = 3.0$ to 9.8 Å^{-1}, $\Delta r1.2 = 2.8$ Å for Pt–O; k^2: $\Delta k = 3.0$ to 13.8 Å^{-1}, $\Delta r1.5 = 3.1$ Å for Pt–Pt) of 1% Pt/silica catalysts prepared by SEA and DI of PTA and calcined at temperature from 100 to 675 °C

Calcination temperature (°C)	Scatter	CN	R (Å)	DWF ($\times 10^3$)	E_0 (eV)
Strong electrostatic adsorption of PTA at a pH 9.5 with NH_4OH					
100	Pt–O	4	2.05	−0.1	0.2
150	Pt–O	4.3	2.05	0.1	0.7
200	Pt–O	4.5	2.05	0.1	0.7
250	Pt–O	4.8	2.03	1.7	0.0
300	Pt–O	5.4	2.03	1.3	−0.8
400	Pt–O	5.2	2.04	1.2	−0.5
525	Pt–O	2.5	2.03	0.5	−1.0
	Pt–Pt	6.5	2.77	1.5	−1.5
600	Pt–O	1.5	2.05	0.7	2.0
	Pt–Pt	8.3	2.77	0.5	−1.1
675	Pt–O	0.7	2.04	0.7	1.0
	Pt–Pt	9.7	2.77	0.5	−0.5
Dry impregnation with PTA at a pH 5.0					
100	Pt–O	4	2.05	0.2	0.1
150	Pt–O	4	2.05	0.1	0.1
200	Pt–O	4.7	2.04	1.1	0.1
250	Pt–O	5.6	2.03	0.9	−0.6
300	Pt–O	6.0	2.04	1.2	−0.3
400	Pt–O	6.0	2.04	1.1	0.0
525	Pt–O	6.0	2.04	1.1	0.3
600	Pt–O	1.5	2.02	0.5	−0.9
	Pt–Pt	8.4	2.77	0.2	−1.7
675	Pt–O	0.8	2.03	1.0	2.0
	Pt–Pt	10.0	2.77	0.4	−1.4

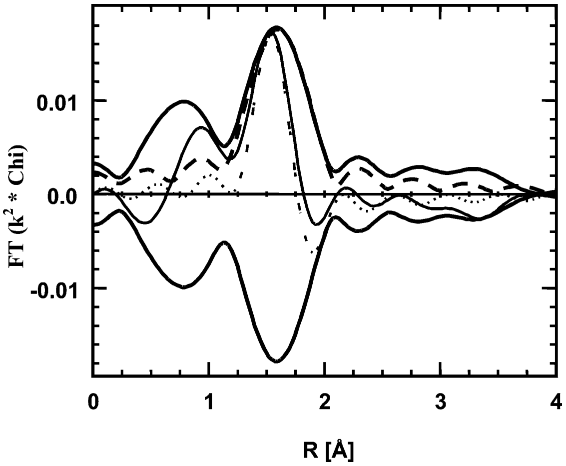

Fig. 10. k^2-weighted Fourier transform of EXAFS raw data (real part FT, solid; imaginary part FT, thin solid) plus fit of the isolated shell (k^2, $\Delta k = 3.04$–9.75 Å^{-1}, $\Delta r = 1.25$–2.08 Å) (real part FT, dashed; imaginary part FT, dotted) for 1% Pt on silica prepared by SEA of PTA at a pH 9.5 and calcined at 200 °C.

4. Discussion

In the previous study [23], a monolayer of PTA adsorbed onto silica was determined to have a steric maximum of 0.87 μmol/m^2, assuming that the cation retains a hydration sphere equivalent to about two water molecules. This value was consistent with experiments performed at surface loadings of 1000 and 5000 m^2/L, much lower than that currently employed. At 83,000 m^2/L (Fig. 2), to achieve quantitative agreement between theory and experiment it is necessary to reduce the radius of the hydrated Pt cation. Physically this implies that a higher packing density of PTA can be achieved at higher (solution) concentrations. A more complete study of the effect of PTA concentration on the maximum amount adsorbed is in progress. While modifications to the RPA model need to be quantified at high loading, the electrostatic interpretation of adsorption, i.e., the Coulombic attraction between the PTA cation and the negatively charged, deprotonated silanol surface, gives, at least, a good qualitative interpretation of the impregnation phenomenon and can be used to explain a number of trends in Pt dispersion in Table 1 and the present data.

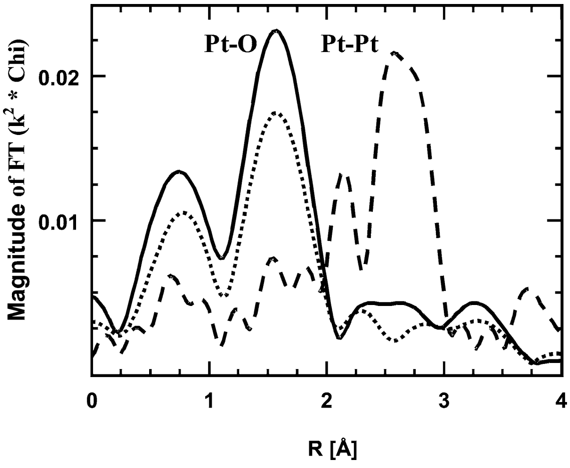

Fig. 11. Magnitude of the k^2-weighted Fourier transform for 1% Pt on silica prepared by DI with PTA at a pH 5.0 and calcined at 100 (dotted, $\Delta k = 3.04$–9.75 Å^{-1}), 300 (solid, $\Delta k = 3.04$–9.75 Å^{-1}), and 600 °C (dashed, $\Delta k = 2.74$–13.82 Å^{-1}).

4.1. *A correlation of strong electrostatic adsorption with Pt dispersion*

The assumption of the electrostatic model is that there is a strong Coulombic attraction when the PTA cation is contacted with a negatively charged silica surface. This occurs only when the hydroxide concentration of impregnating solution is large compared to the number of hydroxyls on the silica surface, i.e., at a pH above about 9. On the other hand, for impregnation of PTA at a pH where the number of silanol groups is much larger than the number of hydroxide ions initially in solution, the pH approaches the PZC of the silica and there is little negative charge on the silica surface [28]. The previous (Table 1) and current results will now be examined in light of this model.

First, DI preparations with CPA, with the exception of very low loadings, give low dispersion compared to PTA preparations. At the pH of an impregnation solution consisting of CPA, ca. 3, few silanol groups would be expected to be protonated. Thus, only a small amount of $PtCl_6{}^{2-}$ would strongly adsorbed on silica. Nonadsorbed anionic Pt complexes will agglomerate during drying. DI of CPA on planar silica supports results in large Pt crystallites, which have been imaged by electron microscopy [29].

For Pt silica prepared by DI with PTA, the dispersions are also relatively poor, except at low surface loading; see, for example, Refs. [6,21], Table 2 and Fig. 2. At DI conditions for typical high surface area oxides, i.e., generally near neutral pH, the oxide buffering effect will decrease the pH toward the PZC [28]. In other words, for impregnating solutions with an initial pH between about 4 to 7, the number of surface silanol groups greatly exceeds the number of hydroxide ions solution. The number of hydroxide ions depend both on the pH and on the amount of solution per square meter surface area of silica. Under typical DI and WI (at neutral pH) conditions, only a small number of silanol groups are negatively charged; therefore, only a small amount of PTA is strongly adsorbed. As the loading increases, much of the Pt salt is physically deposited onto the support and leads to moderate to poor dispersions.

Even for Pt/silica catalysts prepared by DI with initially basic PTA solutions, there is an insufficient amount of base to provide adequate negative charge on the support. Thus, much of the PTA is physically adsorbed. From Table 1 [1,14,17] and Fig. 1, catalysts prepared from (initially) mildly basic solutions (WI preparation) had low Pt dispersion.

The condition for strong electrostatic adsorption between silica and PTA depends on addition of sufficient base to deprotonate enough silanol groups to adsorb all of the Pt cations. Preparations of catalysts prepared by SEA of PTA [2–5,7,8,11,12,15–17,19] are given in Table 2 and Figs. 2 and 3 in the current work.

While the dispersions of the catalysts prepared by SEA are generally greater than 0.6 and are often near 1.0, it is also true that increasing calcination temperature generally leads to lower dispersion of the reduced catalyst. The previously reported literature together with the current results is shown in Fig. 12. The results from this study have been plotted separately as a function of calcination temperature. Several clear trends emerge from Figs. 1–4 and 12. First, the highest dispersions are obtained when the catalysts are not calcined, but reduced directly after drying at 100 °C. This was also previously reported [19,30]. With all other preparation conditions equivalent, Figs. 2 and 3 clearly demonstrate that higher temperature calcination leads to a monotonic decrease in dispersion. This is true for both DI and SEA preparations. Furthermore, the loss of dispersion that occurs with elevated calcination temperatures increases with increasing metal loading for both types of preparations (Table 2 and Fig. 3).

4.2. The control of Pt particle size

The loss in dispersion due to increasing calcination temperature has been considered to be due to the loss of ammonia ligands leading to disruption of the strong metal complex-support interaction. Alternatively, sintering of the volatile (neutral) metal species during calcination was thought to lead to larger particles [31–33]. In this study, independent of the method of preparation, calcination of PTA at temperatures as low as 150 °C affects the reduced particle size. By controlling the calcination temperature and method of Pt addition, one can obtain supported Pt catalysts of different particle size from very small to very large.

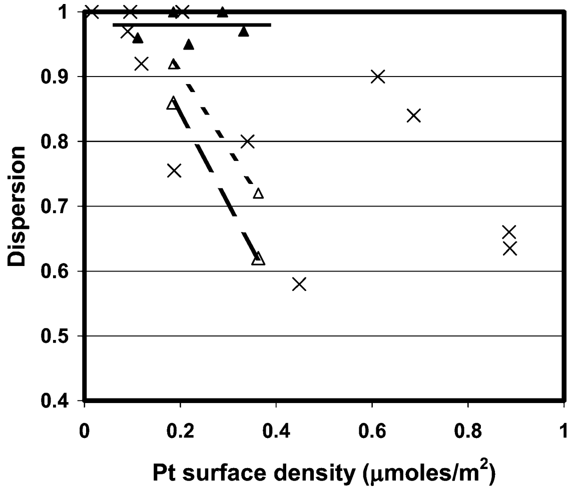

Fig. 12. Effect of Pt surface density (μmol/m^2) and calcination on the dispersion of reduced Pt/silica catalysts prepared by SEA: (×) literature calcined between 100 and 300 °C; this study, solid triangle and solid line-dried at 100 °C; (small open triangle and dotted line) calcined at 250 °C; and (large open triangle and dashed line) calcined at 300 °C.

From the linear dependence of the dispersion in Fig. 3 and the fraction of Pt species from the XANES fits, one can estimate the dispersion of the Pt particles resulting from reduction of Pt^{2+}, Pt^{4+}, and Pt^0 present after calcination. Assuming strongly adsorbed PTA gives a dispersion of 1.0, one can estimate the dispersion of PTA present during DI preparation. For 1% Pt on silica prepared by DI and dried at 100 °C, 0.25% Pt is strongly adsorbed; i.e., the amount strongly adsorbed at a pH of 5.5. Therefore, with a total dispersion of 0.85, the remaining PTA leads to Pt particles with a dispersion of about 0.80 $[0.85 = (0.25 \times 1.0) + 0.75(X)]$. Although silica prepared by DI does not have the sufficient (negative) surface charge to strongly adsorb the majority of the Pt, PTA interacts sufficiently well to give moderately high dispersions, ca. 0.8.

Similarly, one can calculate the dispersion for platinum particles resulting from the reduction of the Pt^{4+} species produced during calcination. For example, at 250 °C the 1% Pt/silica catalyst prepared by SEA has a dispersion of 0.61 with 28% Pt^{2+}. The reduction of these Pt^{4+} species, therefore, results in metal particles with a dispersion of about 0.4. A similar value is obtained for Pt^{4+} species on the DI catalyst, indicating that Pt^{4+} oxides interact with the support in an equivalent way for both methods of preparation, and these species reduce to give metallic particles with lower dispersion than Pt^{2+}. The loss in dispersion due to calcination at temperature less than about 400 °C is directly proportional to the amount of Pt^{4+} independent of the temperature. This implies that the loss in dispersion is not due to sintering of the supported Pt species, but due to the change in the oxidation state of those species and the strength of the interaction of these species with the silica surface.

A similar analysis can be made for the dispersion of metallic Pt formed by calcination. Assuming that reduction of Pt^{4+} species leads to Pt particles with a dispersion of 0.4, the dispersion of the metallic Pt can be estimated to be about 0.07. A similar value is obtained for both methods of preparation. Since formation of metallic Pt (in air) occurs above about 525 °C, calcination at these temperatures would be expected to always lead to low dispersion.

In addition to controlling the uptake of Pt and the dispersion of the reduced particles, the Coulombic attraction between PTA and the deprotonated support also lowers the rate of oxidation to Pt^{4+} during calcination (Fig. 9). If the dispersion is the sum of the different Pt species as discussed above, differences in dispersion, therefore, imply differences in the amount of each Pt species. For example, in Fig. 4 both 1 and 2% Pt catalysts contain strongly adsorbed Pt. However, after calcination at 300 °C these have different dispersions. This would suggest that the fraction of Pt^{4+} is higher in the latter catalyst. Thus, the rate of oxidation even for strongly adsorbed PTA is loading dependent, and the lower loaded catalysts appear to be more resistant to oxidation. This may in part explain why some studies find that strongly adsorbed PTA on silica gives high dispersion even after calcination at 300 °C, while we find a loss in dispersion at the same temperature. Additional work is required to confirm this possibility.

5. Conclusion

These results demonstrate that Pt/silica catalysts prepared by strong electrostatic adsorption of platinum tetraammine cation from a strongly basic impregnation solutions not only determine the amount of adsorbed Pt but also influence the particle size and size distribution of the reduced catalyst. The highest dispersions were obtained by the SEA method of preparation and drying at 100 °C. With increasing calcination temperature there was a linear decrease in the Pt dispersion. The loss in dispersion for catalysts prepared by the SEA was lower than those prepared by the DI method. The data suggest that the dispersion is dependent on the distribution of Pt species on silica at the time of reduction. Reduction of strongly adsorbed Pt^{2+} leads to particles with a dispersion of 1.0. Reduction of nonelectrostatically deposited PTA present on catalysts prepared by DI gives dispersions of about 0.8. Calcination at temperatures from 150 to 400 °C leads to partial oxidation of PTA to Pt^{4+} species. It is proposed that reduction of the latter gives metallic particles with a dispersion of about 0.4. Finally, calcination above 525 °C leads to large metallic Pt particles with a dispersion of about 0.07. By combination of the method of preparation and calcination temperature, very small to large metallic nanoparticles can be prepared.

Acknowledgments

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