The controlled synthesis of metal-acid bifunctional catalysts: Selective Pt deposition and nanoparticle synthesis on amorphous aluminosilicates

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Abstract

The rational synthesis of metal-acid bifunctional catalysts based on aluminosilicates will involve control over which domain – alumina or silica – the metal can be deposited on, as well as the control of particle size. These factors determine the ratio and proximity of the metal and acid sites. The control of adsorption selectivity and particle size has been studied by measuring the uptake of anionic and cationic Pt precursors as a function of pH over various types of silica-alumina composites and pure oxide supports, followed by characterization of the nanoparticles resulting from reduction of the precursors.

Results indicate that electrostatic adsorption can be exploited to achieve selective deposition. Ion exchange of cationic precursors also appears to occur over the acid sites. Cationic tetraammine Pt precursors, either electrostatically adsorbed onto silica domains at high pH, or ion exchanged at the acidic alumina-silica adlineation (interface between two oxides) at neutral pH, lead to small (1.7-3.0 nm) nanoparticles. The size of Pt nanoparticles resulting from anionic Pt hexachloride electrostatically deposited onto alumina domains at low pH depends on the size of the alumina domain; a critical domain size is needed to anchor the Pt precursors against sintering.

In the companion paper, the factors controlling metal-acid site intimacy and ratio are demonstrated for the isomerization of n-heptane.

Keywords

Catalyst synthesis, Platinum, aluminosilicates, mixed oxides, Strong Electrostatic Adsorption, Ion Exchange, metal-acid bifunctional catalyst

1 Introduction

Mixed oxides constitute an important class of materials in heterogeneous catalysis due to their vast applications in organic synthesis, petroleum industry and green chemistry [1]. Many of these processes benefit from the new functionalities that these mixed oxides incorporate into the catalytic system. Aluminosilicates, for example, contribute via their acid sites and hence play a major role in petroleum and oil refining applications [2].

Noble metals (e.g., Pt) deposited on aluminosilicates are widely studied as metal-acid bifunctional catalysts where aluminosilicates supply the acid function and noble metal nanoparticles provide a dehydrogenating/hydrogenating function [3-7]. In this domain the focus has recently been mostly directed towards testing new materials with different structures, acid strength and composition [8-15]. However, the synergy by means of balance and proximity between these two types of active sites is often ignored partly due to the lack of control during catalyst synthesis [16-19].

The hydroxyl chemistry of oxide supports plays a key role in the control of the precursor-support interaction. This concept has been utilized to establish the Strong Electrostatic Adsorption (SEA) method of catalyst synthesis [20]. Based on this concept highly dispersed metal nanoparticles could be synthesized on a variety of oxides and carbons [21, 22]. For mixed oxides, surface charge and composition have been shown, as a first approximation, to be simple additive contributions of the properties of individual components [22-24]. This unlocks potential for pH directed selective adsorption on mixed oxides via SEA. With regards to aluminosilicate mixed oxides, silica has a point of zero charge (PZC) of about 4 and so deprotonates in mid to high pH solutions, while alumina has a PZC of about 8.0 and so protonates in the mid to low pH range (Figure 1). Thus, the difference in surface potential between components at different pH can be exploited to selectively adsorb metal ions at different locations. Considering a purely electrostatic nature of adsorption, a cationic metal precursor complex e.g., $\text{Pt}(\text{NH}_3)_4^{2+}$ is more likely to adsorb onto the silica surface at pH greater than the PZC of silica whereas at lower pH an anionic metal precursor e.g., PtCl_6^{2-} will adsorb onto the alumina surface. In addition, any Brønsted sites created at the interface between silica and alumina phases would trigger ion exchange (IE) of cationic metal complexes as shown in Figure 1b.

Figure 1. (a) Theoretical surface potential versus adsorption pH (pH_f) plot for silica (PZC = 4.25) and alumina (PZC = 8.0). Theory (pH shift model) has been elaborated elsewhere [25]. (b) A simplified schematic of differently charged domains of silica-alumina mixed oxide surface at intermediate pH ($\text{pH}=6-8$). Possible adsorption mechanisms of different metal complex ions on this mixed oxide surface have been indicated.

In this study, we have explored the potential to control the location and mechanism of Pt adsorption on mixed oxides through the choice of metal precursor and simple pH adjustment. Sizes of the Pt nanoparticles following reduction of the precursors have been quantified using several techniques e.g., XRD, chemisorption and high resolution electron microscopy. Mixed oxides in the form of physical mixtures, synthesized composites of silica and alumina and commercial amorphous aluminosilicates were studied. Physical mixtures of a nonporous silica and a nonporous alumina with dissimilar sizes were ideal samples to image under the microscope and demonstrate selective metal deposition. Also, mixed oxide composites synthesized on a nonporous silica with 40 nm average particle size added to the ease of characterization via imaging.

2 Materials and Methods

2.1 Materials

Model, nonporous silica (Aerosil® 380, Evonik-Degussa, Average particle size = 7 nm, BET surface area= 380 m²/g) and γ -alumina (Nanodur®, Average particle size = 40 nm, BET surface area=37 m²/g) with contrasting particle sizes were used in the study of physical mixtures.

The silica-alumina mixed oxides (commonly referred to as “Al-Si”) were either synthesized in-house or obtained commercially. The in-house synthesis was based on a method prescribed elsewhere [26, 27]. Briefly, a clear solution containing Al polycations ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{20}]^{7+}$, denoted Al_{13}^{7+}) was prepared. Within 30 min of preparation, silica (~0.1 m² silica/ μ mole of Al in solution) was contacted to this solution and shaken on an orbital shaker for 1 h. During this time part of the Al_{13}^{7+} polycations in solution electrostatically adsorbed onto silica [28]. Following filtration and drying, the Al_{13}^{7+} deposited silica supports were calcined at 550°C for 3 h. One high surface area (Aerosil® 380) and one low surface area (Aerosil® OX50, Evonik-Degussa, 54 m²/g, average particle size = 40 nm) silica were used. Both were pre-calcined at 550°C for 5 h prior to Al_{13}^{7+} deposition which resulted in the reduction of surface area of Aerosil® 380 silica to 240 m²/g. These Al_{13}^{7+} deposited (and calcined) Aerosil® 380 and Aerosil® OX50 silicas will be referred to as Al-HSi 97 and Al-LSi 99 respectively with the numbers representing bulk SiO₂ concentration [wt%] as presented in Table 1.

Table 1. Characteristics of different pure and mixed oxide supports.

Supports	SABulk (m ² /g)	Al ₂ O ₃ [wt%]	Al ₂ O ₃ domain size (nm) ³	PZC ⁴	Desorbed NH ₃ (μ moles/g)
R_Si	54	0	-	4.2	12
R_Al	190	100	4.0	8.1	220
Al-LSi 99	54	1.0 ¹	≤ 1.5	7.0	22
Al-HSi 97	240	2.8 ¹	≤ 1.5	5.6	142
SIRAL 80	320	20.2 ²	≤ 1.5	4.5	290
SIRAL 70	239	30.8 ²	≤ 1.5	4.4	198
SIRAL 40	379	60.7 ²	2.4	5.0	283
SIRAL 20	278	79.6 ²	3.0	6.4	333

¹Calculated from the measured Al concentration before and after deposition using ICP-OES,

²Analytical data provided by the manufacturer, ³Measured using Scherrer equation on (400) and (440) γ -alumina peaks from respective XRD pattern, ⁴Measured using Equilibrium pH at high oxide (EpHL) method [20]

Four commercial Al-Si (SIRAL 20, SIRAL 40, SIRAL 70 and SIRAL 80) provided by Sasol, Germany GmbH were also studied. Each SIRAL sample ID number represents the bulk

concentration [wt%] of silica. These SIRAL samples were originally synthesized using a patented procedure [29] involving hydrolysis of aluminium hexanolate in hexanol (6 wt% Al) solution with deionized water at 90°C followed by mixing the filtered alumina suspension with orthosilicic acid (3 wt% SiO₂) solution. The resulting mixed gels (pseudo-boehmite) were subsequently spray-dried. By varying the amount of orthosilicic acid used, samples containing different silica content were prepared. Before Pt deposition, both sets (commercial and synthesized) of Al-Si samples were washed 3 times with 0.2 M NH₄NO₃ solution (150 ml/2.5 g sample) to ion exchange Na, if present, from the acid sites. This was followed by calcination in air at 550°C for 3 h at 2° C/min ramp rate to obtain the acid form of the catalyst.

Finally, one silica (Aerosil® OX 50) and one γ -alumina (Puralox, SBa 200, BET surface area=190 m²/g, Sasol, Germany GmbH) were used as reference supports. The SBa 200 γ -alumina is commercially synthesized via activation of boehmite phase and will be referred to as “R_Al” in this study. The silica support will be identified as “R_Si”.

2.2 Adsorption experiments

Platinum tetraammine chloride, Pt(NH₃)₄Cl₂ (98%) and chloroplatinic acid, H₂PtCl₆·6H₂O (99.9%) were used as cationic and anionic precursors of Pt, respectively. Both were obtained from Sigma-Aldrich in powder form.

Unless otherwise noted equilibrium adsorption experiments were conducted at 500m²/l surface loadings (SL = total surface area of material in solution). At first, a series of pH (initial pH, pH_i) adjusted aqueous solutions (fixed volume) with known amount of dissolved Pt precursors were prepared and subsequently contacted with the support to reach the desired SL. The resulting slurries were then left on an orbital shaker for 1 h after which their final pHs (pH_f) were recorded. Finally, each slurry solution was filtered using 0.2 μ m syringe filters to collect ~5 ml of the filtrate solution, which was analyzed using Inductively Coupled Plasma (ICP-OES) apparatus. Pt adsorption uptake was calculated from the difference in Pt concentration in solution before and after addition of support.

Langmuir isotherms were developed for anionic PtCl₆²⁻ adsorption on different single and mixed oxides. In this experiment, for each support up to four PtCl₆²⁻ solutions with different platinum concentrations (50-500 ppm i.e. mg/liter and equivalent to 0.00025-0.0025 mol/liter) were prepared. The concentrations were chosen such that the equilibrium (post-adsorption) Pt concentration was $\leq$ 250 ppm. Also in order to maintain constant ionic strength, the experiments were conducted in presence of a background electrolyte (e.g., NaNO₃). Use of the NH₄⁺ exchanged supports to remove Na (procedure described in 2.1) ensured constant and known concentration of background electrolytes. The concentration of 0.0075N was found to be enough to keep the ionic strength constant without being too high to significantly affect the adsorption capacity. The initial pH values were adjusted such that the final pH was that for maximum adsorption of PtCl₆²⁻ on that particular support. Adsorption constants were determined from best fits of the Langmuir isotherm.

2.3 Catalyst preparation and characterization

Following adsorption surveys Pt loaded catalysts were prepared at specific adsorption pHs (pH_f). Reference catalysts were also prepared on R_Si and R_Al supports. After metal adsorption, the filtered solid was dried at room temperature overnight under vacuum and then reduced at 350°C for 1 h in a 10% mixture of H₂/Ar (total flow rate 200 ml/min). Catalysts were also prepared via dry impregnation (DI). In this method, the amount of Pt(NH₃)₄Cl₂ required for specific Pt loading (0.02 M Pt) was dissolved in the amount of de-ionized water (no prior pH adjustment) necessary to fill the pore volume of the support. After synthesis the catalysts were dried and reduced at the condition described above. Reduced samples were subsequently

characterized with different techniques e.g., XRD, Chemisorption, STEM, the specifics of which are described below.

Powder XRD was performed using a Rigaku MiniFlexII bench-top system fitted with a Rigaku D/tex Ultra silicon strip detector [30]. The radiation source was Cu K α radiation (λ = 1.541 Å) at operating condition of 30 kV and 15 mA. All diffractograms were taken at a scan rate of 1°/min and sampling width of 0.02°. Pt particle size was calculated using Scherrer formula (shape factor = 0.94).

Chemisorption was performed using hydrogen pulse titration of oxygen precovered Pt (Micromeritics Autochem II 2920 automated analyzer). First, approximately 0.1 g of catalyst sample was fully reduced in flowing 10% H₂/Ar gas mixture at 350°C for 1 h. This was followed by pure Ar flow at 350°C for 0.5 h (to remove chemisorbed H). Following cooling of the catalyst to 40°C in Ar flow, it was exposed to 10% O₂/He for 0.5 h to ensure saturation with adsorbed atomic oxygen and then purged with pure Ar for 0.5 h to remove residual O₂. Pulses of H₂/Ar were initiated at this point to replace adsorbed oxygen with atomic hydrogen and form H₂O. Hydrogen consumption was quantified via a calibrated, high sensitivity thermal conductivity detector (TCD). H₂ Pulsing was continued until no further H₂ uptake. The overall stoichiometry of Pt to H₂ was assumed to be 0.667:1 [31]. Particle sizes were estimated assuming hemispherical geometry.

High angle annular dark field (HAADF) images were obtained using an aberration-corrected JEOL JEM-ARM200CF (200kV electron) scanning transmission electron microscope (STEM). The instrument has an imaging resolution as low as 0.078 nm and energy resolution 0.35 eV. ImageJ software was used to redraw ~1000 Pt particles on the resulting HAADF images which yielded a representative statistical distribution of particle sizes. Both surface ($d_{s,EM} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$) and volume ($d_{v,EM} = \Sigma n_i d_i^4 / \Sigma n_i d_i^3$) average particle sizes were calculated which were subsequently compared with chemisorption ($d_{s,chemi}$) and XRD ($d_{v,XRD}$) particle sizes respectively. Additionally, elemental maps of Pt, Al and Si were generated using X-Ray Energy Dispersive Spectroscopy (XEDS) acquired through an Oxford Instruments X-Max100TLE SDD detector fitted to the JEM-ARM200CF

NH₃-temperature-programmed desorption (TPD) was conducted on different Pt-free as well as reduced Pt/Al-Si samples in a Micromeritics Autochem II 2920 automated analyzer equipped with a thermal conductivity detector (TCD). The Pt-free supports were used as is or treated at different pHs (pH_f=7.0 and pH_f=11.0) using NH₄OH in 1000 m²/liter slurry solution. After the pH treatment the support was dried and calcined at 550°C for 5 h prior to NH₃-TPD analysis. 0.2 g of sample was first pretreated *in situ* in 50ml/min He flow for 1 h at 500°C. For the reduced Pt/Al-Si samples, this step was replaced by an *in situ* reduction step (350°C, 1 h in 50ml/min flow of 10% H₂/He) followed by temperature increase up to 500°C (1 h) in He flow (50ml/min). This additional treatment did not affect the metal dispersion of the catalysts, as was verified separately using H₂ pulse chemisorption. NH₃ adsorption was initiated at 150°C by flowing 2%NH₃/He at 50ml/min for 0.5 h which was followed by purging with He flow at the same temperature and flow rate for 0.5 h to remove physisorbed NH₃. After that temperature ramping was initiated under He flow at 10°C/min ramp rate for up to 500°C.

²⁷Al NMR spectra were obtained on an Avance 500 spectrometer (Bruker). Samples were fully rehydrated prior to measurement. The conditions for the ²⁷Al NMR spectra were: rotor external diameter 4mm, single pulse detection, Larmor frequency 130.33 MHz, pulse length 5.3 µs, recycle delay 1 s and spinning rate 12 kHz. A 0.1 M solution of aluminum nitrate was used as the 0 ppm reference.

XPS was conducted on the Al-Si to determine component surface fraction using a Kratos AXIS Ultra DLD system equipped with a monochromatic Al K α source operated at 15 keV and 150 W. The pass energy was fixed at 160 eV for the survey scans. A charge neutralizer (CN) was used to compensate for the surface charge.

3 Results

3.1 Selective Pt adsorption over single oxides and their physical mixtures

Anionic PtCl_6^{2-} and cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake surveys on pure components and physical mixtures of silica and alumina in presence of an excess of the platinum precursor are presented in Figure 2. Adsorption studies on silica (denoted as Q_s) and alumina (denoted as Q_a) were conducted at $\text{SL} = 500\text{m}^2/\text{l}$ (open circles and open squares in Figures 2a and b). These can be interpreted in light of the surface potential plot presented in Figure 1. In the acidic pH range, anionic PtCl_6^{2-} adsorption on silica was almost negligible whereas on alumina high uptake was observed (Figure 2a). This was due to the development of high positive surface potential on alumina in the acidic pH range as shown in Figure 1. On silica, surface potential was too insignificant to carry on electrostatic adsorption. On the contrary, at higher pH, according to Figure 2b, away from their respective PZCs, negative surface potentials on silica and alumina enable them to adsorb cationic $\text{Pt}(\text{NH}_3)_4^{2+}$. However, due to significantly higher potential in the basic pH range (see Figure 1), $\text{Pt}(\text{NH}_3)_4^{2+}$ adsorption capacity on silica was nearly 3 times as high as on alumina.

Figure 2. Pt complex adsorption surveys on pure and physical mixtures of silica (S) and alumina (A): (a) Anionic PtCl_6^{2-} on single oxides, (b) cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ on single oxides, (c) Anionic PtCl_6^{2-} on physical mixtures and (d) Cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ on physical mixtures. Initial ppm (mg/L) concentration of Pt present in the solution for each experiment is included in the legend. Dashed lines in (c,d) represent data extrapolated from single oxide uptakes. Two red arrows indicate selected samples (open diamonds) that were analyzed with STEM.

Next, $\text{Pt}(\text{NH}_3)_4^{2+}$ and PtCl_6^{2-} adsorption studies were conducted on physical mixtures of silica and alumina with surface area ratios of 1:1, 1:10 and 10:1. In order to maintain these ratios SLs of $1000\text{m}^2/\text{g}$ ($500+500$), $5500\text{m}^2/\text{g}$ ($500+5000$) and $5500\text{m}^2/\text{g}$ ($5000+500$) were used. Measured uptake data on physical mixtures were also presented in Figures 2c and d. In parallel to this, the component oxide uptakes based on the uptake of the pure components (Figure 2a,b) were extrapolated to the area ratio of the studied physical mixture. These were presented as dashed lines in Figures 2c and d. A reasonably close agreement was observed between the measured uptake on physical mixtures and the extrapolated uptake.

Following uptake survey experiments, two samples from 1:1 physical mixture series were dried, reduced and imaged with high resolution STEM (Figure 3). These two samples (indicated with arrows in Figures 2c and d) were selected for the demonstration of selective Pt adsorption. Contrasting particle sizes of component oxides (inset of Figure 3a) offered easy visual identification of different phases of the physical mixture from the STEM images. In the adsorbed PtCl_6^{2-} series in Figure 2c, the sample synthesized at $\text{pH}_f=3.9$ (uptake corresponding to 3.7 wt% Pt) on 1:1 physical mixture was chosen for STEM imaging. For this sample, according to Figure 3a, Pt^0 particles are mostly present on the alumina domains (large spherical particles) indicating that PtCl_6^{2-} adsorbed selectively onto alumina. On the other hand, from adsorbed $\text{Pt}(\text{NH}_3)_4^{2+}$ series illustrated in Figure 2d, the sample obtained at $\text{pH}_f=8.3$ on the 1:1 physical mixture (open diamond) was imaged. Pt uptake corresponded to 0.7 wt% for this sample. It is evident from the Figure 2d that, at this pH_f , $\text{Pt}(\text{NH}_3)_4^{2+}$ adsorption, albeit low, occurred almost exclusively on silica. This was confirmed from the STEM image in Figure 3b.

Figure 3. STEM images of (a) PtCl_6^{2-} (3.7 wt% Pt, $\text{pH}_f=3.9$) and (b) $\text{Pt}(\text{NH}_3)_4^{2+}$ (0.7 wt% Pt, $\text{pH}_f=8.3$) on 1:1 physical mixtures. Inset of figure (b) shows images of contrasting sizes of model and nonporous alumina (A) and silica (S) particles.

3.2 Characteristics of pure and mixed oxide (Al-Si) supports

XRD profiles of calcined Al-Si supports are shown in Figure 4a. Patterns of pure silica (R_{Si}) and pure γ -alumina (R_{Al}) supports were also included for comparison. Only the Al-rich samples (SIRAL 40 and SIRAL 20) displayed γ -alumina peaks in their respective XRD patterns.

Here it must be noted that SIRAL Al-Sis originally come as uncalcined samples and, in agreement to this, the XRD patterns of these Al-rich Al-Si supports showed clear evidence of the boehmite phase prior to calcination at 550°C (XRD patterns in Figure S-1 in the supplementary information). Upon calcination, boehmite transformed completely to γ -alumina on these supports as shown in Figure 4a. On the other hand, most of the Si-rich Al-Si supports, including SIRAL 80, Al-LSi 99, Al-HSi 97 did not show any evidence of alumina or boehmite phase before or after calcination in their respective XRD patterns. From their respective XRD profiles the γ -alumina peaks at (400) and (440) were used to determine the size of alumina domains. These values are listed in Table 1.

Figure 4. (a) XRD and (b) NH₃-TPD desorption profiles of pure oxides and Al-Si samples. Patterns are ordered with respect to increasing alumina content from top to bottom.

NH₃ desorption profiles of the Al-Si samples (0.2g) compiled in Figure 4b were used to quantify the total number of acid sites (Table 1). The desorption signal of AlSi 99 was very weak compared to the others due to its low surface area (Table 1). All other Al-Si samples exhibited NH₃ desorption peaks at ~250°C which might be largely due to presence of alumina-like domains. Indeed, no NH₃ desorption peaks for R_Si silica (not shown) and a single peak at similar temperature for pure γ -alumina (R_Al) corroborate this possibility (Figure 4b). An additional desorption peak at higher temperature (300-400°C) is more noticeable on silica rich supports e.g., SIRAL 80 and SIRAL 70. Additionally, the acidity of each Al-Si support treated at different pH showed appreciable pH sensitivity particularly in the basic pH range. The results are listed in Table 2 with NH₃-TPD desorption profiles in the supplementary information (Figure S-2).

Table 2. Total acid sites (μ moles/g) from Pt-free and Pt-loaded (0.7 wt%) Al-Si.

Series	pH	Pt precursor	Al-HSi 97	SIRAL 80	SIRAL 70	SIRAL 40	SIRAL 20
-	7-9	Pt-free	185	378	241	341	270
a	7-9	Pt(NH ₃) ₄ ²⁺ (IE)	141	323	-	-	-
-	11-12	Pt-free	220	430	348	359	389

b	11-12	Pt(NH ₃) ₄ ²⁺ (SEA)	199	290	-	420	430
-	4-6	Pt-free	142	290	198	283	333
c	4-6	Pt(NH ₃) ₄ Cl ₂ (DI)	38	344	-	-	-
d	4-6	PtCl ₆ ²⁻ (SEA)	143	360	344	390	385

As it was not possible to confirm the presence of alumina-like domains on the Si-rich Al-Si samples (Al-LSi 99, Al-HSi 97, SIRAL 70 and SIRAL 80) from their respective XRD patterns, elemental mapping (Al and Si) was performed on one of these samples, namely Al-LSi 99 (Figure 5a). We selected this sample due to the regular structure and nonporous nature of Aerosil® OX 50 (fumed silica spheres of about 40nm) that would greatly facilitate its imaging. It was expected that adsorption of the Al₁₃⁷⁺ Keggin precursor on silica would form alumina-like domains of ~1 nm (average size of Al₁₃⁷⁺ Keggin precursor). However, from elemental mapping, alumina domains were found to be in a much more dispersed state on silica. The very small size of these domains explains why they were not be detected by XRD. Furthermore, ²⁷Al NMR study of the Al-HSi 97 sample (an Al-Si sample similar to Al-LSi 99 but prepared using Aerosil® 380 fumed silica with higher surface area and therefore a higher Al content, which makes this sample more convenient for characterization by ²⁷Al MAS NMR) revealed the presence of four (~54ppm) and five (30-35ppm) coordinated aluminum which confirmed interaction between Si and Al [2]. It also revealed the presence of Al atoms in an octahedral environment (~0ppm), which indicates the presence of alumina-like domains. For comparison, the ²⁷Al MAS NMR spectrum of SIRAL 80 is also shown in Figure 5d. It is also composed of 3 NMR signals whose positions are similar to those observed on the spectrum of Al-HSi 97 but with different relative intensities. Although ²⁷Al NMR cannot be used for a quantitative assessment of the Al distribution, one can safely conclude that the difference in the proportions of 4, 5 and 6 coordinated Al in these two samples reflects the difference in the size of the alumina domains for these two samples, the larger domains of SIRAL 80 resulting in a higher proportion of 6-coordinated Al.

Figure 5. (a) STEM micrograph of Al-LSi 99. (b-c) Elemental maps of Si (b) and Al (c) of the bounded area shown in (a). (d) ²⁷Al NMR profiles of synthesized (Al-HSi 97) and commercial (SIRAL 80) Al-Si.

3.3 Pt adsorption surveys on mixed oxides

Anionic and cationic Pt uptake surveys were performed on the Al-Si supports. Pt uptake surveys on Al-Sis synthesized in lab are compiled in Figure 6I and 6II whereas Figure 6III contains uptake surveys on all commercial SIRAL calcined supports. The corresponding parent silica (either Aerosil® OX 50 or Aerosil® 380) on which Al_{13} polycations were deposited was used as the representative silica supports. R_Al was used as representative alumina support.

Figure 6. Anionic PtCl_6^{2-} (A) and cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ (B) adsorption onto (I) Al-LSi 99, (II) Al-HSi 97 and (III) Commercial (SIRAL) supports. Initial Pt concentration = 200ppm (mg/L). SL=1000m²/liter. For comparison, the platinum complex uptakes on 100% silica (R_Al used for part BIII) and on 100% alumina (R_Al) have also been represented Representative error bars are presented in A.I and A.II.

For anionic PtCl_6^{2-} adsorption on mixed oxides (Figure 6A), Pt uptake was in between the PtCl_6^{2-} uptake on alumina and on silica. In this case, since PtCl_6^{2-} adsorbed preferentially onto alumina domains, maximum Pt uptake very much depended on the alumina content on the surface of mixed oxide. This can be further noticed from Figure 6AIII. As alumina content is increased from SIRAL 80 to SIRAL 20, PtCl_6^{2-} uptake approached that on pure alumina surface. In contrast, when comparing cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake on mixed and pure oxides (Figure 6B), a significant difference can be observed. Maximum $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake on mixed oxides with fractional silica and alumina coverage was higher than on single oxides. This is more obvious in SIRAL supports (Figure 6BIII) that possess significantly higher number of acid sites than the synthesized Al-Si materials. These observations hint towards multiple adsorption mechanisms (e.g., ion exchange and strong electrostatic adsorption) on the Al-Si supports which will be discussed later.

Adsorption isotherms were studied for PtCl_6^{2-} adsorption onto the different Al-Si supports. At low pH and with anionic metal precursors, adsorption is solely electrostatic onto protonated oxide surface. As a result, the adsorption isotherms could be represented with single site Langmuir model. Uptake of PtCl_6^{2-} (τ , $\mu\text{moles/m}^2$) is plotted against equilibrium concentration of Pt in the solution (C_{eq} , ppm) in Figure 7a. For each isotherm, the metal precursor uptake reached a plateau indicating that maximum adsorption on that support has been reached. The plateau also indicates that ionic strength of the solution was reasonably constant and not high enough to cause any retardation in metal uptake. In Figure 7b, the ratios of equilibrium (C_{eq}) to adsorbed (C_{ads}) Pt concentration versus C_{eq} show, for all samples, linear correlation in agreement to the Langmuir model. The Langmuir parameters extracted from these plots are listed in Table S-2 in the supplementary information.

Figure 7. (a) Raw data and (b) linear fitting plots of Langmuir isotherms for PtCl_6^{2-} adsorption on pure alumina (R_Al) and Al-Si supports.

3.4 Characterization of reduced Pt/Al-Si

In order to control Pt location as well as adsorption mechanism, various Pt catalysts were synthesized on the Al-Si supports using different precursors ($\text{Pt}(\text{NH}_3)_4^{2+}$ or PtCl_6^{2-}) and pH of adsorption (pH_f). These catalysts were divided into four series:

- $\text{Pt}(\text{NH}_3)_4^{2+}$ adsorption at intermediate pH_f (6-8),
- $\text{Pt}(\text{NH}_3)_4^{2+}$ adsorption at high pH_f (11-12),
- $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ deposition via dry impregnation (due to strong buffering ability of the support, pH_f in this case will approach the PZC),
- PtCl_6^{2-} adsorption at low pH (4.0-4.5).

A nominal 0.7 wt% Pt loading was prepared in each series with each Al-Si support.

For series (a) samples, as it was difficult to adjust the final pH (pH_f) to a precise value (e.g., 7.0), a narrow range of intermediate pH_f (6-8) was deemed acceptable. Electrostatic adsorption of $\text{Pt}(\text{NH}_3)_4^{2+}$ on pure silica and alumina was almost negligible ($\leq 0.2 \mu\text{moles/m}^2$) in this pH range (Figure 6B) as expected from their respective PZCs. This, coupled with significant $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake on the Al-Si supports in this pH range indicates that a non-electrostatic (presumably, ion exchange (IE)) adsorption would be the dominant adsorption mechanism here. On the contrary, series (b) and (d) represent electrostatically adsorbed samples using cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ and anionic PtCl_6^{2-} precursors respectively. To ensure a dominant role of electrostatic adsorption, pH_f was adjusted to a significantly higher (series b) or lower (series d) value than the PZCs of each component. An overlap with the non-electrostatic mechanism cannot be completely ruled out for the predominantly electrostatically adsorbed series (b) samples.

Following reduction, all the catalysts were characterized using XRD, chemisorption and STEM for the determination of the average Pt particle size (Table 3). Although originally intended for 0.7 wt%, the actual metal loadings converted from Pt uptake varied moderately and have been listed in Table 3. Here it should be noted that XRD and chemisorption reveal volume ($d_{v,\text{XRD}}$) and surface ($d_{s,\text{chemi}}$) averaged particle sizes respectively [32]. These values were compared with the respective volume and surface averaged particle size obtained from STEM images. XRD profiles of representative catalyst samples are presented in Figure 8. Profiles of Pt/Al-rich Al-Si (SIRAL 20, SIRAL 40) were only included in the supplementary information (Figure S-4) due to overlapping Pt and γ -alumina peaks which made Pt particle sizing from XRD problematic. From Figures 8a and b and Table 2 it can be summarized that small, well-dispersed Pt on Al-Si catalysts could be prepared via IE (Series a) and SEA (Series b) of $\text{Pt}(\text{NH}_3)_4^{2+}$ even for Al-rich Al-Si materials (SIRAL 40 and SIRAL 20) with no considerable difference in particle size between them. A representative STEM image of series (b) catalyst, shown in Figure 9a, confirms high dispersion of Pt particles for this series.

Table 3. Characteristics of 0.7% Pt/Al-Si samples.

Series	wt% Pt	Support	Precursor	Mechanism	pH_f	Particle size [nm]			
						$d_{s,\text{chemi}}$	$d_{s,\text{EM}}$	$d_{v,\text{EM}}$	$d_{v,\text{XRD}}$
b	0.69	R_Si	$\text{Pt}(\text{NH}_3)_4^{2+}$	SEA	11.2	2.0	-	-	<1.5
d	0.72	R_Al	PtCl_6^{2-}	SEA	4.1	2.4	-	-	ND
a	0.70	Al-LSi 99	$\text{Pt}(\text{NH}_3)_4^{2+}$	IE	8.0	2.2	2.1	2.1	<1.5
b	0.75	Al-LSi 99	$\text{Pt}(\text{NH}_3)_4^{2+}$	SEA	11.9	2.1	1.7	1.8	<1.5
c	0.70	Al-LSi 99	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	DI	-	>10	-	-	10.5
d	0.73	Al-LSi 99	PtCl_6^{2-}	SEA	4.4	>10	Irr	Irr	3.0
a	0.75	Al-HSi 97	$\text{Pt}(\text{NH}_3)_4^{2+}$	IE	7.7	1.7	-	-	<1.5
b	0.76	Al-HSi 97	$\text{Pt}(\text{NH}_3)_4^{2+}$	SEA	11.7	1.7	-	-	<1.5
c	0.70	Al-HSi 97	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	DI	-	1.8	-	-	1.7
d	0.72	Al-HSi 97	PtCl_6^{2-}	SEA	4.4	>10	-	-	3.6
a	0.66	SIRAL 80	$\text{Pt}(\text{NH}_3)_4^{2+}$	IE	6.3	1.7	-	-	<1.5
b	0.66	SIRAL 80	$\text{Pt}(\text{NH}_3)_4^{2+}$	SEA	11.6	1.8	-	-	<1.5

c	0.70	SIRAL 80	Pt(NH ₃) ₄ Cl ₂	DI	-	2.7	-	-	2.9
d	0.72	SIRAL 80	PtCl ₆ ²⁻	SEA	4.2	>10	Irr	Irr	2.9
d	0.60	SIRAL 70	PtCl ₆ ²⁻	SEA	4.2	>10	-	-	4.7
b	0.65	SIRAL 40	Pt(NH ₃) ₄ ²⁺	SEA	11.5	2.5	-	-	ND
d	0.60	SIRAL 40	PtCl ₆ ²⁻	SEA	4.2	2.9	-	-	ND
b	0.71	SIRAL 20	Pt(NH ₃) ₄ ²⁺	SEA	11.3	3.0	-	-	ND
d	0.72	SIRAL 20	PtCl ₆ ²⁻	SEA	4.4	2.8	2.9	4.1	ND

Irr=Large particles, ND=Not determined (Presence of γ -alumina peaks on XRD prevents accurate determination of particle size).

Figure 8. XRD patterns of 0.7% Pt/Al-Si catalysts on (I) Al-LSi 99, (II) Al-HSi 97 and (III) SIRAL 80 supports from a) Pt(NH₃)₄²⁺ deposition at intermediate pH (series a), b) Pt(NH₃)₄²⁺ at high pH (series b), c) Pt(NH₃)₄Cl₂ deposition via DI (series c), and d) PtCl₆²⁻ at low pH (series d).

Pt particle size of series c catalysts prepared via DI method varied with support (Table 3 and Figure 8). A catalyst prepared on weakly acidic Al-LSi 99 support had the largest overall Pt particle size (>10nm) as verified from XRD and chemisorption (Table 3). However, on more acidic supports e.g., Al-HSi 97 and SIRAL 80, Pt particles were more dispersed. This hints at the possible role of ion exchange on Pt dispersion in this catalyst series. XRD and chemisorption on series a, b and c catalysts showed excellent agreement in terms of Pt particle size (Table 3).

Figure 9. STEM images of 0.7% Pt on (a) Al-LSi 99 using $\text{Pt}(\text{NH}_3)_4^{2+}$ at $\text{pH}_f=11.9$ (series b), (b) Al-LSi 99 using PtCl_6^{2-} at $\text{pH}_f=4.4$ (series d), (c) SICAL 80 using PtCl_6^{2-} at $\text{pH}_f=4.2$ (series d) and (d) SICAL 20 using PtCl_6^{2-} precursor $\text{pH}_f=4.2$ (series d). Inset of figure b, c and d show high magnification images (scale bar=5 nm).

Pt particle size of series (d) catalysts (SEA of PtCl_6^{2-} at $\text{pH}\sim 4$) showed a large discrepancy between XRD (3-4 nm) and chemisorption (>10 nm) sizes particularly for the Si-rich Al-Si supports (Table 3). STEM images of some of these catalysts confirmed very poor dispersion of Pt particles (Figures 9b and c). Moreover, higher magnification images (inset of Figures 9b and c) revealed that the irregularly shaped particles are comprised of aggregates of small Pt nanoparticles of ~ 3 nm. This explains the discrepancy between chemisorption and XRD particle size with the latter reflecting the size of the primary particles. However, in case of Al-rich Al-Si materials (SICAL 20, SICAL 40) Pt dispersion and particle size improved noticeably (Table 3 and Figure 9d). PtCl_6^{2-} on pure γ -alumina (R_Al) yielded slightly lower Pt particle size in comparison with the Al-rich Al-Si samples (Table 3).

The total number of acid sites of selected Pt/Al-Si catalysts (desorption profiles in Figure S-3 of the supplementary information) prepared at specific pH_f s (Series a-d) were compared with their parent Al-Si (no Pt) supports treated at similar pH_f s (Table 2). Such comparison reveals several trends. All the $\text{Pt}(\text{NH}_3)_4^{2+}$ deposited Pt/Al-Si catalysts synthesized via IE (Series a) or SEA (Series b) on the Si-rich Al-Si (Al-HSi 97 and SICAL 80) supports experienced significant

loss of acidity. Contrarily, on the Al-rich SIRALs (SIRAL 40 and SIRAL 20) the acidity increased with $\text{Pt}(\text{NH}_3)_4^{2+}$ deposition via SEA (Series b). Next, the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ deposited DI samples (Series c) revealed contrasting acidity trends. On Al-HSi 97, acidity decreased appreciably upon Pt deposition whereas on SIRAL 80, it increased. Finally, on the anionic PtCl_6^{2-} adsorbed samples (Series d) at low pH all but Al-HSi 97 gained appreciable acidity. These results will be interpreted in lights of various factors (e.g., method of preparation, Cl^- effect) later in the discussion.

4. Discussion

4.1 Quantification of SEA versus IE on mixed oxides

In Figure 2, both cationic and anionic platinum complex adsorption surveys on physical mixtures showed reasonable agreement with the dashed lines extrapolated from the component oxides. This indicates that platinum uptake occurred almost exclusively by electrostatic adsorption. This was further verified from the STEM images in Figure 3. Thus, employing the right pH and metal precursor combination, one can achieve selective adsorption of platinum. Selective uptake prevailed even in presence of a large excess of the non-attractive component.

Schreier et al. observed that cationic Pt and Cu adsorption surveys on zeolites cannot be explained with a single adsorption mechanism [33]. They suggested that in addition to ion exchange at the Al exchange sites of zeolites, cationic Pt could also electrostatically adsorb onto silanol groups. Such a dual adsorption mechanism can be used to explain high overall $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake on the SIRAL series (see Figure 6 III (B)) for which a significant amount of acid sites can be expected based on NH_3 -TPD results.

In order to isolate and quantify the role of each of these two mechanisms (SEA and IE) it is essential to know the component (alumina or silica) surface coverage on these Al-Si supports. Surface coverage of each Al-Si was determined using three different techniques: XPS, PZC and PtCl_6^{2-} uptake. Each of these techniques has its own limitations:

- XPS is not strictly surface sensitive (sampling depth = 2-10 nm) [34]. Hence, for the synthesized Al-Si materials where Al is deposited on silica in very small, thin domains it is possible that XPS records a higher silica surface fraction than actual.
- The PZC method translates strictly surface sensitive PZC values of Al-Si supports to surface coverage using the 2-surface model [23]. For example, deposition of Al_{13}^{7+} Keggin precursor on OX 50 silica shifted the PZC from 4.0 (silica) to 7.0 (Al-Si), which translates to about 45% alumina coverage according to the PZC method. However, this method does not account for the presence of (stronger) Brønsted acid sites at the interface between the silica and alumina and their effect on PZC. The presence of strong(er) Brønsted acid sites is expected to create a permanent (or at least extending over a broad pH range) negative surface charge. Therefore, measured PZCs of Al-Si supports with reasonably high acid site densities may translate to a significant overestimation of the coverage by the low PZC component (e.g., silica in this case).
- A third way to estimate component surface coverage is to use the anionic PtCl_6^{2-} uptake data. It is reasonable to assume that anionic metal uptake on Al-Si materials at low pH would be exclusively electrostatic and exclusively onto alumina. Hence alumina surface coverage can be estimated by extrapolating anionic metal uptake on single oxides to fit with the anionic uptake on Al-Si supports (Figure 6 I, II, III, A).

The results of these three surface coverage estimates are given in Table 4.

Table 4. Estimation of alumina surface coverage of Al-Si supports using different techniques

Support	alumina surface coverage [area%]		
	via XPS	via PZC	via PtCl_6^{2-} uptake
R_Al	-	-	100
Al-LSi 99	5	45	42
Al-HSi 97	10	16	50
SIRAL 80	28	3	11
SIRAL 70	25	3	30
SIRAL 40	57	10	62
SIRAL 20	83	35	78

As expected from the above mentioned limitations, discrepancies exist between the alumina surface coverage obtained by these three techniques. Interestingly, surface coverage values estimated by XPS were close to bulk fractions (listed in Table 1), as expected from the high penetration depth of XPS in light materials. The alumina surface fraction estimated based on PZC measurements are comparatively very low for the SIRAL series likely due to the presence of Brønsted sites as mentioned above. In principle, the most accurate value should be that based on PtCl_6^{2-} uptake data. Although this method may not be as direct as the other techniques it is preferred for its applicability to all supports, without any serious compromise on accuracy. Selective metal adsorption is thus a novel yet simple technique to analyze surface composition of metal oxide Al-Si samples. Also using the bulk alumina compositions of synthesized Al-LSi 99 and Al-HSi 97 supports (Table 1), the fractional areas covered by 1 nm alumina (approximated) domains were calculated to be 67% and 50% respectively (detail calculation in the supplementary information). These numbers also indicate that alumina domains are indeed present as clusters as opposed to solid solution.

Using the surface coverage values, several important parameters can be estimated. Firstly, the contribution of non-electrostatic adsorption as a function of pH can be estimated. Using the surface area normalized $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake on single oxides and alumina surface coverage (calculated based on PtCl_6^{2-} uptake), electrostatic uptake on Al-Si supports could be calculated. This contribution was deducted from the total $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake measured on Al-Si supports (Figure 6B) to quantify non-electrostatic (assumed IE) uptake. Plotted in Figure 10, this non-electrostatic $\text{Pt}(\text{NH}_3)_4^{2+}$ uptake showed significant pH sensitivity although it has been previously postulated that ion exchange would be pH insensitive [33]. However, that postulation was based on the study on zeolites, i.e. materials containing strong Brønsted acid sites. In comparison, the acid sites of the Al-Si supports (amorphous silica-aluminas) are considerably weaker and hence may act differently.

Figure 10. Non-electrostatic (presumably, IE) cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ uptakes (open circles) on (a) SIRAL 80, (b) SIRAL 70, (c) SIRAL 40 and (d) SIRAL 20 supports. Other data points represent acid sites by NH_3 -TPD measured at different pH for each Al-Si support (metal free). Error bars from multiple TPD measurements are presented for (a) and (c). For “Corrected (1:1)” and “Corrected (1:2)” 1 $\text{Pt}(\text{NH}_3)_4^{2+}$ per 1 and 2 acid sites respectively were considered.

Secondly, the non-electrostatic uptake can be correlated with the number of non-alumina acid sites. Al-Si samples treated at different pH showed significant changes in the number and strength of the acid sites with pH (Table 2). These acid sites include the contribution of the alumina-like domains, the value of which can be quantified knowing the surface coverage of alumina and surface area normalized acid site density of a representative alumina sample (detail procedure included in the supplementary information). This amount is then subtracted from the total number of acid sites in order to obtain a corrected number of acid sites (that would correspond to the adlineation acid sites) for each Al-Si support (metal-free) treated at different pHs. The results have been plotted in Figure 10 to compare with non-electrostatic uptake. In this figure the numbers of adlineation acid sites have been presented in equivalent $\text{Pt}(\text{NH}_3)_4^{2+}$ uptakes by considering 1 $\text{Pt}(\text{NH}_3)_4^{2+}$ per acid site (labeled as “Corrected (1:1)”) and 1 $\text{Pt}(\text{NH}_3)_4^{2+}$ per 2 acid sites (labeled as “Corrected (1:2)”). Despite the simple assumptions in Figure 10, reasonable agreement between non-electrostatic uptake and acid sites at the ad-lineation is observed for the Si-rich Al-Si samples (SIRAL 80 and SIRAL 70). On the other hand, there is no clear correlation for the Al-rich and particularly the SIRAL 20 sample. However, as this sample contains a high fraction of alumina (80 wt% alumina surface coverage by alumina of 78%, see Table 3), one can expect that the evaluation of the number of adlineation sites on SIRAL 20 would be very approximate.

4.2 Pt dispersion on Al-Si

On the Al-Si supports, a combination of high pH-cationic precursor resulted in small platinum nanoparticles (Table 3). On the contrary, for anionic PtCl_6^{2-} adsorption at low pH particularly for the Si-rich Al-Si supports, Pt particles were aggregated, resulting in strong discrepancies between XRD and chemisorption sizes. The electrostatic nature of oxide components dictates that, at low pH, metal ion adsorption should occur exclusively on alumina (as demonstrated in section 3.1). In agreement with this, elemental (Pt, Si and Al) mappings of the reduced samples prepared by PtCl_6^{2-} adsorption on Si-rich Al-Si supports (Figure 11), revealed overlapping Pt and Al domains. This strongly hints at initially selective Pt adsorption on alumina domains via electrostatic adsorption. The electrostatic nature of PtCl_6^{2-} uptake surveys on the Al-Si samples displayed in Figure 6 also supports this assertion. Moreover, the coarser nature of alumina domains at the Pt overlapped locations, compared to the metal free Al-LSi 99 support in Figure 5c, suggests possible migration of alumina domains during reduction treatment in presence of Pt.

Figure 11. Al, Pt and Si elemental mapping of 0.7% Pt (PtCl_6^{2-}) over Al-LSi 99. As a guide to the eye, the contour of the platinum particle has been drawn from the Pt elemental mapping card and reported on the Al elemental mapping card (dashed green line).

Weak adsorption can potentially prevent PtCl_6^{2-} from remaining anchored on small alumina domains during reduction. To test this, Langmuir isotherms were developed for the adsorption of PtCl_6^{2-} on all Al-Si supports (Figure 7). The adsorption constant, K_{ads} values generated from the isotherms (Table S-2) have been plotted in Figure 12 with respect to the alumina domain sizes listed in Table 1. Pt dispersions measured by chemisorption are also plotted versus alumina domain size. Since most of the Al-Sis contained boehmite prior to calcination (that were converted to γ -alumina upon calcination), adsorption isotherms were also developed for representative γ -alumina support, R_Al, which was commercially synthesized from boehmite.

Figure 12. Dispersion (chemisorption) of 0.7% Pt (prepared using $PtCl_6^{2-}$) over γ -alumina (R_Al) and Al-Si supports with respect to the size of alumina domains obtained from XRD. For the Si-rich Al-Si supports, the size of the alumina domains has been arbitrarily set to 1 nm as it could not be evaluated using XRD). Adsorption constants (K_{ads}) have been added on the secondary Y-axis.

All the Si-rich Al-Si samples on which size and/or bulk content of alumina were too small to be identified from their respective XRD patterns (Figure 4a) showed low $PtCl_6^{2-}$ adsorption constants as well as low Pt dispersion. On the other hand, Al-Si samples with alumina domains discernible from their respective XRD patterns (e.g., SICAL 20, SICAL 40) showed reasonably high adsorption constants and Pt dispersion. Average sizes of alumina domains on these two Al-rich Al-Si supports were calculated using Scherrer equation on 2 distinct γ -alumina peaks indexed as (400) and (440) and were found to be 2.4 nm and 3.0 nm for SICAL 40 and SICAL 20 respectively. For the pure alumina support (R_Al), size of alumina domains were found to be moderately larger (4.0 nm). Overall, these results suggest that a critical size of alumina domain is necessary for strong $PtCl_6^{2-}$ adsorption and therefore better dispersion after high temperature reduction.

Catalyst synthesized via dry impregnation (DI) of $Pt(NH_3)_4Cl_2$ on Al-HSi 97 and SICAL 80 also carry strong evidence of the IE. Due to high buffering by oxide supports, the DI method normally results in a pH close to the PZC where there usually exists little or no metal-support interaction [25]. The resulting metal particle size from DI method is usually relatively large. However, the fact that Pt particle size was actually relatively small on the Al-HSi 97 and SICAL 80 supports (Table 3 and Figure 8c) suggests that IE, which can occur close to the PZC of the mixed oxide, (as already shown for the series a samples), contributed to the metal-support interaction. Also Brønsted protons of aluminosilicates are known to anchor and stabilize metal particles [37, 38]. As a result, Pt particle size becomes smaller which results in a closer proximity between metal and acid sites. In that respect, these series c catalysts are fairly identical to series a and b except for the number of acid sites (Table 2). On the contrary, the DI method yielded larger Pt particle size on Al-LSi 99 support (Table 3 and Figure 8c). It is likely due to a too limited number of ion exchange sites on this weakly acidic support. It is important to mention here that the PZCs of these Al-Si samples are slightly higher than the PZC of silica and significantly lower

than that of alumina. This means that at the PZC of the Al-Si samples, the surface fraction of alumina would be positively charged and would not favor electrostatic $\text{Pt}(\text{NH}_3)_4^{2+}$ adsorption. On the other hand, the silica fraction will be positively charged at the Al-Si PZC. However, at this pH the potential would be too low (Figure 1) to favor electrostatic adsorption.

4.3 Acidity of Pt/Al-Si catalysts

Various factors could affect the acidity of Pt/Al-Si catalysts. From the listed data in Table 2 it is evident that the synthesis pH is one of them. At high pH, even without Pt deposition the acidity of all the tested samples increased appreciably. Similar findings were reported by Handjani et al. [36]. They suggested that the change of pH and subsequent thermal treatment caused redistribution of Al which prompted such acidity change. Hence, the respective pH treated Al-Sis are used as references. With regard to these, the loss in acidity of cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ deposited series a and b (via SEA/IE) catalysts on Si-rich Al-Si supports becomes apparent in Table 2. This could have been triggered by the ion-exchanged cationic Pt complexes on the Brønsted acid sites. The same trend was not obvious in series c (dominating adsorption mechanism is IE) or Al-rich Al-Si supported series b catalysts. This suggests possible contributions from additional factor(s) e.g., residual Cl^- ions.

However, both in series a and b, excess volume of impregnating Pt solution was used which was eventually filtered following Pt adsorption. With limited adsorption potential for Cl^- on predominantly negatively charged Al-Si surface at high pH it could be envisaged that the post-adsorption filtration removed majority of the residual Cl^- . Hence the overall decrease in acidity of the Si-rich Al-Si supports upon Pt deposition (Table 2) was primarily due to the IE mechanism. However, as Cl^- retention ability enhances with Al content in Al-Si, the removal of Cl^- from the more Al-rich Al-Si supports (SIRAL 40 and SIRAL 20) via filtration was probably not as effective. Thus the increase in the acidity of the resulting series b catalysts might be due to the presence of residual Cl^- (Table 2). On the other hand, since no excess solution (hence no filtration) was used in the DI method, the resulting series c catalysts retained at least a significant portion of residual Cl^- . As a result, once again the acidity increased particularly on the SIRAL 80 supported series c catalyst (Table 2). Moreover, the enhanced presence of Cl^- caused by the use chlorided PtCl_6^{2-} precursor could explain the acidity increase on the series d catalysts. One exception to this trend was the Al-HSi 97 supported catalysts for which acidity sharply decreased in the series c sample (From 142 to 38 $\mu\text{moles/g}$) and remained largely unchanged for series d (From 142 to 143 $\mu\text{moles/g}$). The chloride retention ability of this support with lowest Al content (3%) was probably considerably less than the SIRAL supports with higher Al content (20% or above).

Conclusion

In this study the potential to control Pt deposition on silica-alumina supports was explored by exploiting the difference in charging behavior of the two component oxides (silica and alumina) in solution and of the acid sites generated at the interface between them. For the simplest case, using physical mixtures of the two component oxides, selective Pt deposition was clearly demonstrated through appropriate choice of precursor and adsorption pH. However, for mixed oxides intimate mixing between the two phases (particularly, small alumina domains) led to a more complicated behavior. Using cationic Pt precursors, $\text{Pt}(\text{NH}_3)_4^{2+}$, at moderate to high pH two adsorption mechanisms (strong electrostatic adsorption and ion-exchange at the acid sites present on the interface between the two oxides) were identified by comparing adsorption uptakes on mixed oxides with those on mixtures of pure components. From the surface composition of

mixed oxides, contributions from these two adsorption mechanisms were separated and quantified. Trends of the ion exchange uptake with respect to pH agreed reasonably with total number of acid sites quantified using NH₃-TPD experiments. All the 0.7 wt% Pt catalysts synthesized using cationic Pt precursor yielded small (≤ 3.0 nm) Pt particle size. However, for the samples prepared by adsorption of the anionic Pt precursor (H₂PtCl₆), it was observed that small Pt particles aggregated significantly on silica rich Al-Si mixed oxides due to a too small size of the alumina domains in these mixed oxides. There appears to be a critical alumina domain size of about 2.4 nm to anchor strongly anionic precursors on alumina.

In a companion paper [39] the catalysts synthesized here are analyzed in a metal-acid bifunctional reaction. Overall, the method demonstrated here can be applied to many other composite oxides of academic and industrial significance for selective deposition.

Acknowledgements

The authors would like to thank Dr. Alan Nicholls at University of Illinois at Chicago for the XEDS mapping and Dr. Yannick Millot at Laboratoire de Réactivité de Surface (LRS) for ²⁷Al NMR. JRR gratefully acknowledges partial support from NSF OIA-1539105.

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