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A pinch of salt to control supported Pt nanoparticle size

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ABSTRACT

A simple way to control supported Pt nanoparticle size is demonstrated in this paper. By varying chloride or nitrate weight loading during the synthesis of catalysts via the method of charge enhanced dry impregnation (CEDI), Pt particles can be grown from about 1–10 nm. Size control was demonstrated over SiO₂, Al₂O₃, Al-doped mesoporous silica, TiO₂, and carbon supports. Sizes were verified by consistent XRD, chemisorption, and STEM measurements. Carbon, silica, and Al-doped silica are most sensitive to chloride-induced precursor sintering, while alumina and titania are least sensitive.

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1. Introduction

In two recent works we have demonstrated a simple way to synthesize supported metal catalysts with high dispersion, called Charge Enhanced Dry Impregnation (CEDI) [1,2]. CEDI combines the simplicity of dry impregnation with the high dispersion rendered by Strong Electrostatic Adsorption (SEA) [3–6]. The normal procedure for dry impregnation (also known as incipient wetness or pore filling impregnation) is followed, except that the impregnating solution is acidified or basified to cause an electrostatic interaction between the support surface and the oppositely charged metal precursor. The amount of acid or base need to overcome the buffering effect of the support surface is surprisingly large [1,7], for example, at DI conditions to obtain the optimal final pH of 11 over alumina, an initial pH of 13.5 must be employed [1, in Supporting information]. CEDI-synthesized Pt particles over alumina, silica, and titania are less than 1.5 nm in diameter (the XRD limit of detection) [2].

In the course of the latter study we noticed a profound effect of the residual balancing ions from the precursor [2]. When cationic Pt tetraammine hydroxide, (NH₃)₄Pt(OH)₂, was used as precursor with CEDI over silica, particles <1.5 nm could easily be synthesized over silica by drying the contacted paste and reducing in flowing hydrogen. However, when Pt tetraammine chloride, (NH₃)₄PtCl₂, was employed at the same conditions and pretreated in the same manner, the particles averaged 8.2 nm in size. Unlike SEA, which

typically employs a large excess of solution such that the balancing ions remain in solution, with CEDI the balancing ions remain in the catalyst. The size could be lowered back to <1.5 nm by eliminating the residual chloride by washing the (NH₃)₄PtCl₂-based sample after impregnation [2, in Supplementary information].

Chloride is often used to redisperse sintered Pt nanoparticles through an oxychloride intermediate [8–10]. In the current study, however, we demonstrate that it as well as nitrate can be used to influence nanoparticle formation from the adsorbed ammine precursors and so sinter the evolved nanoparticles to a controllable extent. This provides a simple way to synthesize a variety of particle sizes at constant metal loading. In this way series of catalysts can be easily prepared to allow the study particle size on reactivity, which is a critical aspect of catalyst design for many reactions [4,11–13].

We examine the effect of chloride and nitrate ions on Pt particles generated from tetraammine precursors over alumina, silica, silica-alumina, titania, and carbon supports. Pt particle size was determined by XRD, STEM and H₂-chemisorption, which gave consistent results, and is correlated with Cl[−]/Pt and NO₃[−]/Pt atomic ratios; the residual ions have the greatest effect over carbon, and least effect over alumina and titania.

2. Material and methods

2.1. Catalyst preparation

Platinum (II) tetraammine hydroxide (Pt(NH₃)₄(OH)₂, PTA-OH) and platinum (II) tetraammine nitrate (Pt(NH₃)₄(NO₃)₂, PTA-NO₃),

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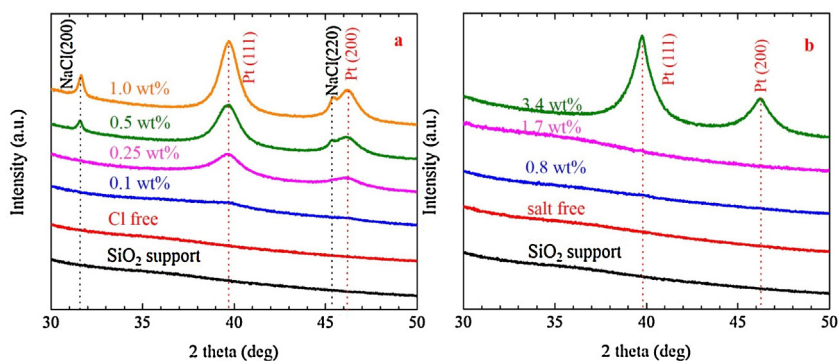


Fig. 1. Salt effect on silica supported Pt particle size growth: Cl^- ions (a) cause a stronger aggregation than NO_3^- ions (b).

purchased from Sigma Aldrich, were used as Pt precursors without any purification. As supports, SiO_2 Aerosil 300, Carbon Timrex, $\gamma\text{-Al}_2\text{O}_3$ SBA-200 and TiO_2 Hombikat were used. The high surface area TiO_2 was first calcined at 400°C for 4 h to avoid structure collapse during reduction process; the other supports were used as received. The properties of the supports, including PZC, BET surface area and pore volume are presented in Table S1.

All samples were synthesized by the method of Charge Enhanced Dry Impregnation (CEDI) as reported before [1]: PTA-OH or PTA- NO_3 was dissolved into a pore volume's worth of 1 M NH_4OH . With the exception of the mesoporous silica support, the amount of metal used corresponds to the amount able to be adsorbed on the respective surface by electrostatic adsorption, or about $0.8\text{ micromoles/m}^2$ for amorphous silica and titania (5 and 1 wt% respectively), and about $0.5\text{ micromoles/m}^2$ for alumina and carbon (1 and 2 wt% respectively). For the very high surface area Al-dopes mesoporous silica, the metal content was limited to that of the amorphous silica to make 5 wt%. Sodium chloride (NaCl) was added into the solution to achieve Cl^- loadings from 0.1 to 1 wt%. After thorough mixing, the thick slurries were oven dried at 85°C for 2 h to evaporate excess water. The dried powder were then reduced for 1 h in 10% H_2/He at the optimal temperature determined by temperature programmed reduction (TPR), using a ramp rate of 5°C/min .

2.2. Catalyst characterization

TPR was performed on Micromeritics AutoChem II 2920 with a thermal conductivity detector. Samples were first dried in He at 120°C for 1 h to remove moisture. TPR analysis was run in 10% H_2/He and TCD signals were recorded from 40°C to 600°C with a ramp rate of 5°C/min .

Powder XRD analysis was carried out on a Rigaku Miniflex-II with a silica strip detector (D/teX Ultra) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$), operated at 15 kV and 30 mA. Scans were made in the $20^\circ\text{--}80^\circ 2\theta$ range, with a scan rate of $2.0^\circ 2\theta/\text{min}$, Pt diffractions were fit using Gaussian to achieve FWHM values and particle size were calculated by Scherrer equation with a shape factor of 0.94.

Z-contrast STEM imaging for particle size determination in the materials was conducted with a JEOL JEM-2100F HRTEM with CEOS GmbH hexapole STEM probe corrector. Averaged particle sizes (volume averaged-, surface averaged- and number averaged-particle size) were determined by counting approximately 500 particles for each sample.

Chemisorption measurements were also carried out with the Micromeritics Autochem II 2920. Before analysis, all samples were pretreated in situ in flowing H_2 for 2 h at 350°C and then purged with flowing Ar for 30 min before cooling to 40°C in Ar. The catalyst was then contacted with 10% oxygen in helium at 40°C for 30 min

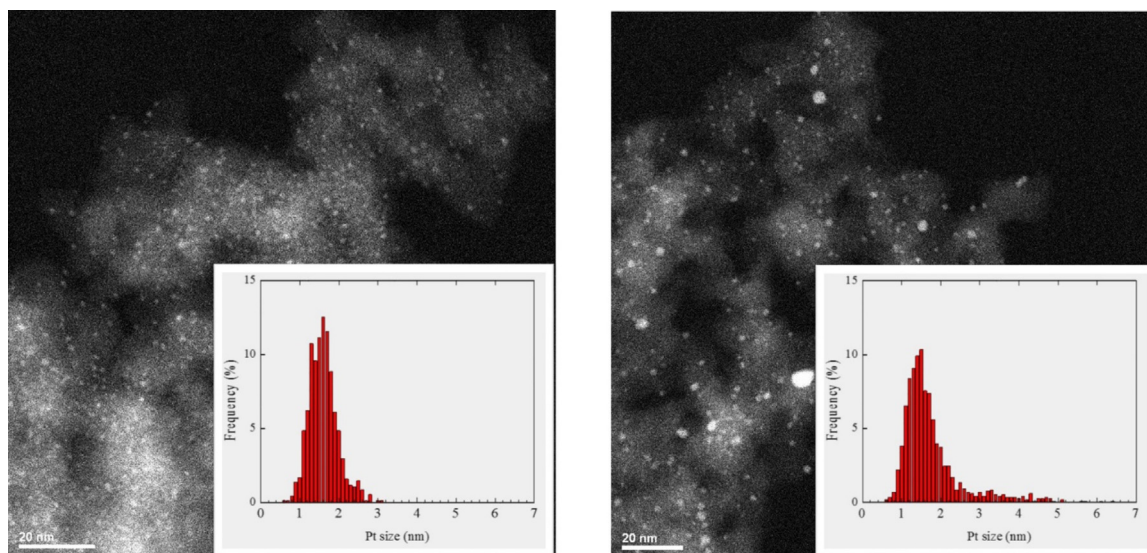


Fig. 2. STEM images and particle size distributions for 5 wt% Pt/silica a) without chloride b) with 0.25 wt% chloride.

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