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.

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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 toward 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 regard 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 (Fig. 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., $Pt(NH_3)_4^{2+}$ 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
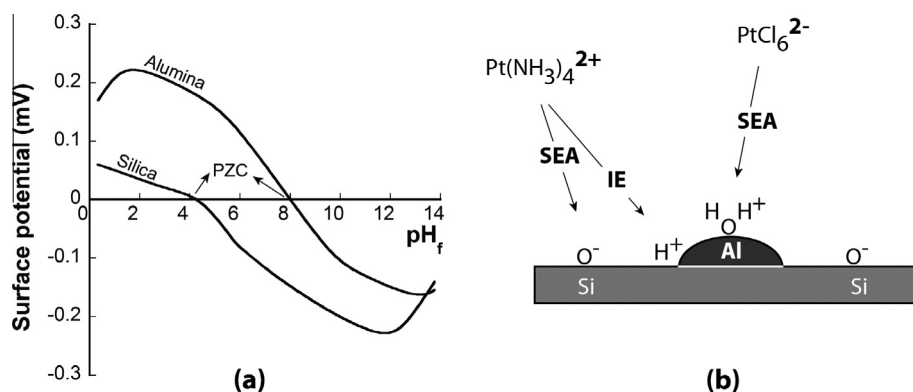
Fig. 1. (a) Theoretical surface potential versus adsorption pH (pH$_f$) plot for silica (PZC = 4.25) and alumina (PZC = 8.0). Theory (pH shift model) has been elaborated elsewhere [25]. (b) A simplified schematic of differently charged domains of silica-alumina mixed oxide surface at intermediate pH (pH = 6–8). Possible adsorption mechanisms of different metal complex ions on this mixed oxide surface have been indicated.

Table 1
Characteristics of different pure and mixed oxide supports.

Supports	SA bulk (m^2/g)	Al$_2$O$_3$ (wt%)	Al$_2$O$_3$ domain size (nm)[c]	PZC[d]	Desorbed NH$_3$ (μmoles/g)
R_Si	54	0	–	4.2	12
R_Al	190	100	4.0	8.1	220
Al-LSi 99	54	1.0[a]	⩽1.5	7.0	22
Al-HSi 97	240	2.8[a]	⩽1.5	5.6	142
SIRAL 80	320	20.2[b]	⩽1.5	4.5	290
SIRAL 70	239	30.8[b]	⩽1.5	4.4	198
SIRAL 40	379	60.7[b]	2.4	5.0	283
SIRAL 20	278	79.6[b]	3.0	6.4	333

[a] Calculated from the measured Al concentration before and after deposition using ICP-OES.
[b] Analytical data provided by the manufacturer.
[c] Measured using Scherrer equation on (400) and (440) γ-alumina peaks from respective XRD pattern.
[d] Measured using equilibrium pH at high oxide (EpHL) method [20].

phases would trigger ion exchange (IE) of cationic metal complexes as shown in Fig. 1b.

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 nonporous silica and nonporous alumina with dissimilar sizes were ideal samples to image under the microscope and demonstrate selective metal deposition. Also, mixed oxide composites synthesized on 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 m^2/g) and γ-alumina (Nanodur®, Average particle size = 40 nm, BET surface area = 37 m^2/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 ([Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{20}$]$^{7+}$, denoted Al$_{13}^{7+}$) was prepared. Within 30 min of preparation, silica (~0.1 m^2 silica/μmole 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 m^2/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 in surface area of Aerosil® 380 silica to 240 m^2/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 SiO$_2$ concentration (wt%) as presented in Table 1.

Four commercial Al-Si samples (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 aluminum 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% SiO$_2$) 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 NH$_4$NO$_3$ 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 m^2/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".