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A general synthesis approach for supported bimetallic nanoparticles via surface inorganometallic chemistry

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Abstract: The synthesis of ultrasmall supported bimetallic nanoparticles (between 1 and 3 nanometers in diameter) with well-defined stoichiometry and intimacy between constituent metals remains a substantial challenge. We synthesized ten different supported bimetallic nanoparticles via surface inorganometallic chemistry by decomposing and reducing surface-adsorbed heterometallic double complex salts, which are readily obtained upon sequential adsorption of target cations and anions on a silica substrate. For example, adsorption of $\text{Pd}(\text{NH}_3)_4^{2+}$ followed by adsorption of PtCl_4^{2-} was used to form PdPt nanoparticles. These supported bimetallic nanoparticles show enhanced catalytic performance in acetylene selective hydrogenation, which clearly demonstrate a synergistic effect between constituent metals.

One Sentence Summary: Rational assembly of heterometallic double complex salts provides a versatile platform for the synthesis of well-defined supported bimetallic nanoparticles.

Heterogeneous catalysts that contain bimetallic nanoparticles (NPs) are used in many petrochemical processes, including reforming (1), selective hydrogenation (2, 3) and dehydrogenation (4), and acetoxylation (5). In recent years, bimetallic NPs have been used in biomass conversions (6), electrocatalysis (7-10), and many other catalytic processes (11-13). The difference in catalytic properties of bimetallic NPs compared with their parent metals, originates from their distinct geometric and electronic structures as well as the synergistic effects between the two metals (6, 14-16). In particular, synthetic protocols have been demonstrated crucial to the structural, electronic, and hence catalytic performance of bimetallic NPs. Conventional impregnation method usually results in ill-defined bimetallic NPs with inhomogeneous particle sizes and compositions (17, 18). New strategies for the synthesis of bimetallic NPs include colloidal synthesis (19), surface organometallic chemistry (20), atomic layer deposition (21), coadsorption and coreduction of metal cations (18), and carbothermal shock synthesis (22). Nevertheless, the synthesis of ultrasmall (< 3 nm) supported bimetallic NPs with well-defined stoichiometry and intimacy between constituent metals remains challenging.

We explored the preparation of supported bimetallic NPs by reducing heterometallic double complex salts (DCSs) precursors (e.g. $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]$), which differ from conventional precursors in that the stoichiometry and intimacy of two metals are already established. Although DCSs have received tremendous interest in the study of inorganometallic coordination compounds (23, 24), their poor solubility greatly hinders their applications in many fields (23, 25-27). Limited success has been achieved in the synthesis of supported bimetallic catalysts using DCS precursors. Boellaard et al. (28) described a synthesis of supported Ni-Fe catalysts from double complex salts by mixing two precursors in solution in the presence of a support. Due to the lack of interaction between bulk DCSs and the catalyst support, the deposition of DCSs on the surface of support is less controllable. Rather than depositing DCSs from solution, we show that heterometallic DCSs can be synthesized directly on a substrate by sequential adsorption of complex metal cations and anions (Fig. 1A). The supported DCSs with precisely paired metal cations and anions through electrostatic interactions can be converted to well-defined supported bimetallic NPs upon reduction. This approach eliminates the issue of competitive adsorption of different metal cations in the coadsorption and coreduction methods (18), on the other hand, it also overcomes the solubility issues of DCSs for the bimetallic catalyst synthesis. It can be applied to a large variety of bimetallic NPs, including several bulk

immiscible systems. The bimetallic NPs are extremely small (1 to 3 nm) and have narrow size distributions ($\pm 25\%$), and their bimetallic nature was confirmed by single-NP elemental analysis. These bimetallic catalysts outperform their parent metals in selective hydrogenation of acetylene.

The adsorption of metal cations were carried out on silica (18, 29) [see Supplementary Materials (SM)]. A porous silica support (figure S1) was first dispersed in water, and the pH of the solution was adjusted to 9 to obtain a negatively charged silica surface. After the adsorption of complex metal cations, e.g. $\text{Pd}(\text{NH}_3)_4^{2+}$, silica was then separated from the mother solution, washed with copious water, and dried before the adsorption of metal anions. Our initial attempt for the subsequent anion adsorption using an aqueous solution led to the formation of either large aggregates (figure S2) or monometallic complexes (figure S3). This failure was likely caused by nonnegligible solubility of DCSs in water, that led to dissolution, ripening, or leaching of DCSs. Alternatively, we adopted an aprotic solvent dichloromethane and introduced quaternary ammonium cations to assist dissolution (figures S4 to S6). Complex metal anions in dichloromethane can precisely target the multivalent metal cations preadsorbed on silica to form supported heterometallic DCSs. Further reducing these silica-supported DCSs under a flow of H_2/N_2 (v/v = 1/9) mixture at 400°C afforded the desired silica-supported bimetallic NPs.

Figure 1B shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of ten types of supported bimetallic NPs synthesized by this approach. Large-area transmission electron microscopy (TEM) and HAADF-STEM images and size distributions of these samples are shown in figures S7 to S16. These NPs are mostly smaller than 3 nm in diameter and uniformly dispersed on the silica support. These NPs are smaller than most bimetallic NPs from colloidal synthesis (19), but slightly bigger than these synthesized by coadsorption and coreduction method (18). The polydispersities are similar to the latter. The bimetallic nature of these NPs was confirmed by single-NP energy-dispersive X-ray spectroscopy (EDS) analysis. The composition of several individual NPs was also obtained for each sample, as well as large-area EDS analysis to obtain an average composition of each sample (quantification results are shown in Tables S1 to S10). In all cases, the single-NP analysis confirmed the NPs are bimetallic. Further, the average composition from the single-NP analysis was generally consistent with the average composition provided by large-area EDS analysis, suggesting that the supported DCSs precursors were evenly decomposed into bimetallic NPs.

The bulk phase diagrams of the Cu-Ir, Pd-Ir, and Pt-Ir systems indicate that these metal pair are immiscible below 800°C (30). Interestingly, these systems still form bimetallic NPs with metal ratios near 1. Aberration-corrected HAADF-STEM images of Cu-Ir/SiO₂ and Pd-Ir/SiO₂ show uneven contrast within single NPs (figures S17 and S18), suggesting the occurrence of intraparticle phase segregation at a subnanometer level. This type of nanoscopic phase segregation has been reported in several bimetallic systems, including Cu-Ir (31), Ru-Pd (32), and Pt-Ni (33). The lack of macroscopic phase segregation in M-Ir systems may be partially attributed to the extremely high melting point of Ir metal, which may prevent the nanoscopically phase segregated NPs from coarsening.

In order to validate our proposed surface inorganometallic chemistry for the bimetallic NPs synthesis, we used x-ray photoelectron spectroscopy (XPS) to study the structural evolution of the surface intermediates during the synthesis. The XPS results are shown in Fig. 2 and figures S19 to S27. After the adsorption of complex metal cations (Pd(NH₃)₄²⁺, Pt(NH₃)₄²⁺, and Ru(NH₃)₆²⁺), the XPS signals of metals and nitrogen were observed (Fig. 2, and figures S19 and S23). Weak Cl 2p signals were also observed on these samples (figure S25), indicating that the divalent complex metal cations require an extra Cl⁻ ion to balance the excess positive charge. After the adsorption of complex metal anions (PtCl₄²⁻, IrCl₆²⁻, and AuCl₄⁻), the intensity of Cl 2p signal increased along with the appearance of Pt, Ir, and Au signals, confirming the successful adsorption of complex metal anions.

In addition to the N 1s signal from the NH₃ ligand (400 eV), a new N 1s signal was observed at 402 eV on the nonreduced [Pd(NH₃)₄][PtCl₄]/SiO₂, [Pd(NH₃)₄][IrCl₆]/SiO₂, [Pt(NH₃)₄][IrCl₆]/SiO₂, and [Ru(NH₃)₄][IrCl₆]/SiO₂ samples (Fig. 2 and figure S23) from the N atom in the quaternary ammonium cation, which was used to assist the dissolution. The adsorption of quaternary ammonium cations was required to balance the excess negative charge of the divalent complex anions. No quaternary ammonium cation was needed when a monovalent anion, AuCl₄⁻, was used, and in this case, the N 1s signal at 402 eV was absent for the nonreduced [Pd(NH₃)₄][AuCl₄]/SiO₂ sample (Fig. 2).

Since the adsorption of complex metal anions was carried out in an aprotic solvent, dichloromethane, ion pairs should mostly stay associated and form dipoles. Therefore, the adsorption of complex metal anions may not be solely driven by electrostatic interactions.

Additionally, dipole-dipole and dipole-induced dipole interactions between the anionic complex and the surface may also play important roles. The surface chemistry described here works well for silica surface but may not be simply extended to other types of support. For instance, alumina has higher point of zero charge compared to silica (18). Thus, complex metal anions are normally adopted for the synthesis of alumina-supported noble metal catalysts. Extending our synthesis strategy to alumina support may require substantial efforts on solvent engineering of metal precursors. Furthermore, one should be aware that chloride binds strongly to the alumina surface and may change the surface properties.

The metallophilic interaction between the adsorbed complex metal cations and anions was confirmed by ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy, indicating the formation of supported DCSs. DCSs usually exhibit distinct colors originating from their metal-metal interactions; many DCSs are named after their colors, e.g. Magnus' green salt $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, and Vauquelin's pink salt $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$ (23). Because of the relatively low loadings, the supported complex species obtained by our sequential adsorption approach do not exhibit noticeable colors. Nevertheless, the supported $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]/\text{SiO}_2$ synthesized by sequential adsorption shows identical UV-Vis absorption bands (315, 390, and 535 nm) with bulk DCS $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]$, which exhibits a pink color (34, 35). In contrast, the UV-Vis spectra of the impregnated $\text{Pd}(\text{NH}_3)_4\text{Cl}_2/\text{SiO}_2$ and $\text{K}_2\text{PtCl}_4/\text{SiO}_2$ were different from the spectra of $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]/\text{SiO}_2$.

The amorphous nature of supported DCSs was confirmed by electron microscopy studies. No NPs were observed on the supported DCSs initially (Fig. 3A). However, within 2 min of electron beam exposure, many NPs in the 1 to 2 nm size range were observed, indicating the *in situ* decomposition of DCSs associated with the electron beam damage. Extended x-ray absorption fine structure (EXAFS) measurements of Ir L_{III}-edge were performed in order to study the structural evolution of coordination sphere of Ir atoms. As shown in Fig. 3B, the EXAFS spectra of nonreduced $[\text{Ru}(\text{NH}_3)_6][\text{IrCl}_6]/\text{SiO}_2$ and $[\text{Pd}(\text{NH}_3)_4][\text{IrCl}_6]/\text{SiO}_2$ were similar to that of the $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ reference. The major peak between 1.5 to 2.5 Å we associated with the Ir-Cl bond in IrCl_6^{2-} . After the reduction of $[\text{Ru}(\text{NH}_3)_6][\text{IrCl}_6]/\text{SiO}_2$ at 400°C under a hydrogen atmosphere, a new peak appeared between 2.5 to 3 Å, corresponding to Ir-M (M= Ru or Ir) bonds. XPS analysis of the reduced DCSs/ SiO_2 samples confirmed the reduction of metal

atoms into metallic states (figures S20 and S22). Further, the disappearance of N 1s and Cl 2p signals indicated the successful removal of ligands (figures S24, S26, and S27).

The catalytic performance of the supported bimetallic NPs was evaluated for acetylene hydrogenation under noncompetitive conditions (figures S28 to S30). The bimetallic catalysts (Pd-Ir/SiO₂, Pd-Pt/SiO₂, Pd-Au/SiO₂, Pt-Ir/SiO₂, and Ru-Pt/SiO₂) generally showed higher catalytic activity and lower alkane selectivity compared to their parent metals. Ru-Ir/SiO₂ was an exception, in that it showed the same negligible activity as its parent metals. Among the group VIII metals, Ru and Ir often showed the strongest binding strengths for many types of adsorbates (36), which might explain the low activity of Ru/SiO₂, Ir/SiO₂, and Ru-Ir/SiO₂ in acetylene hydrogenation. The enhanced activity and suppressed ethane selectivity of bimetallic Pd-M/SiO₂ and Pt-M/SiO₂ compared to their parent metals, could be partly attributed to the relatively weaker binding strengths of acetylene and ethylene on these bimetallic NPs (2, 3).

We further studied Pd-Pt bimetallic NPs with different compositions in acetylene hydrogenation under competitive conditions (Figs. 4A and 4B, figures S31 to S33). The compositions of supported Pd-Pt bimetallic NPs were adjusted by coadsorption of complex metal cations followed by adsorption of complex metal anions. For instance, equal molar Pd(NH₃)₄²⁺ and Pt(NH₃)₄²⁺ cations were coadsorbed on SiO₂, followed by adsorption of PdCl₄²⁻ or PtCl₄²⁻ anions and subsequent reduction, yielding (Pd_{0.5}Pt_{0.5})-Pd/SiO₂ or (Pd_{0.5}Pt_{0.5})-Pt/SiO₂, respectively (figure S34). Compared to the monometallic Pd/SiO₂ and Pt/SiO₂, the three bimetallic catalysts prepared by sequential adsorption method, (Pd_{0.5}Pt_{0.5})-Pd/SiO₂, (Pd_{0.5}Pt_{0.5})-Pt/SiO₂, and Pd-Pt/SiO₂, all showed enhanced catalytic activity and suppressed alkane selectivity in acetylene hydrogenation in the presence of high concentration propylene. Moreover, three bimetallic catalysts were prepared by coadsorption and coreduction of Pd(NH₃)₄²⁺ and Pt(NH₃)₄²⁺ cations (figure S35) (18), Pd_{0.25}Pt_{0.75}/SiO₂, Pd_{0.5}Pt_{0.5}/SiO₂, and Pd_{0.75}Pt_{0.25}/SiO₂, which showed lower activity than a physical mixture of Pd/SiO₂ and Pt/SiO₂, and their alkane selectivity is greater than those prepared by sequential adsorption method.

IR spectroscopy with CO as a probe molecule was used to study the surface properties of these monometallic and bimetallic catalysts (Fig. 4C). We found that the bridge CO peak was very sensitive to the type of metals (1920 cm⁻¹ and 1790 cm⁻¹ for Pd and Pt surfaces, respectively). Interestingly, the IR spectra of Pd_{0.5}Pt_{0.5}/SiO₂ catalyst prepared by coadsorption

method exhibits a Pt-like feature, whereas the Pd-Pt/SiO₂ catalyst prepared by sequential adsorption method exhibits a Pd-like feature. This suggests that the surfaces of the bimetallic NPs prepared by coadsorption and sequential adsorption methods are Pt-rich and Pd-rich, respectively. The superior intrinsic activity of Pd and the electronic modification by Pt underneath might be the origin of the improved catalytic performance of the Pd-Pt/SiO₂ catalyst prepared by sequential adsorption method.

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Author contributions: K.D. conceived the concept, designed the experiments, synthesized and characterized the nanoparticles, performed catalytic tests, and wrote the paper; D.A.C. performed HAADF-STEM and single-NP EDS characterization; L.Z. carried out IR, TGA, XRD, and nitrogen sorption measurements; Z.C. assisted with data analysis and manuscript preparation; A.D.R. carried out EXAFS measurements; I.N.I. carried out UV-Vis measurements; D.C. performed XPS characterization. **Competing interests:** K.D. has filed provisional patent application no. 62/721,690 regarding the synthesis of supported bimetallic nanoparticles via double complex salts. **Data and materials availability:** All data is available in the main text or the supplementary materials.

Supplementary Materials:

Materials and Methods

Figures S1-S35

Tables S1-S11

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Fig. 1. Schematic illustration and electron microscopy analysis of the supported bimetallic NPs. (A) A schematic illustration of the “Surface Inorganometallic Chemistry” for the synthesis of supported bimetallic NPs. (B) HAADF-STEM images of ten types of supported bimetallic NPs synthesized by this approach. All scale bars are 10 nm.

Fig. 2. XPS and UV-Vis spectra of supported DCSs and reference compounds. The structure of $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]/\text{SiO}_2$ is illustrated on the right. The absorption bands associated with the metallophilic interaction between Pd and Pt metal centers are marked by dashed lines.

Fig. 3. Structural evolution of supported DCSs upon reduction. (A) HAADF-STEM images of nonreduced $[\text{Ru}(\text{NH}_3)_6][\text{IrCl}_6]/\text{SiO}_2$ synthesized by sequential adsorption. (B) Fourier transforms of EXAFS spectra of various Ir-containing samples at the Ir L_{III} -edge: $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ reference; nonreduced $[\text{Ru}(\text{NH}_3)_6][\text{IrCl}_6]/\text{SiO}_2$ and $[\text{Pd}(\text{NH}_3)_4][\text{IrCl}_6]/\text{SiO}_2$, and reduced Ru-Ir/ SiO_2 synthesized by sequential adsorption.

Fig. 4. Catalysis and IR studies of the supported bimetallic NPs. (A and B) Catalytic performance of supported monometallic and bimetallic NPs in acetylene hydrogenation. (C) IR spectra of CO molecule adsorbed on various catalysts. Pd-Pt/ SiO_2 and $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{SiO}_2$ are synthesized by sequential adsorption (this work) and coadsorption (*Ref. 18*) methods, respectively. All catalysts were reduced at 400°C . Experimental details are given in the Supplementary Materials.