

## Catalysis by Supported Single Metal Atoms

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Single-atom catalysis is emerging as a new frontier in the field of heterogeneous catalysis [1-4]. The drive for research in this field is not only of interest for fundamental understanding but also for practical applications for low cost production of energy and chemicals. Single-atom catalysts (SACs) have recently been successfully synthesized and proved to be effective for many important catalytic reactions with high atom efficiency [2, 4]. The interaction of the deposited metal atoms with the support surface forms new ensembles that provide unique catalytic properties. The challenges for developing SACs include identification of 1) the precise geometric location of the isolated individual metal atoms with respect to the support surface structure and 2) the electronic properties of the supported metal atom. Anchoring of the isolated single metal atoms onto the support surfaces is critical.

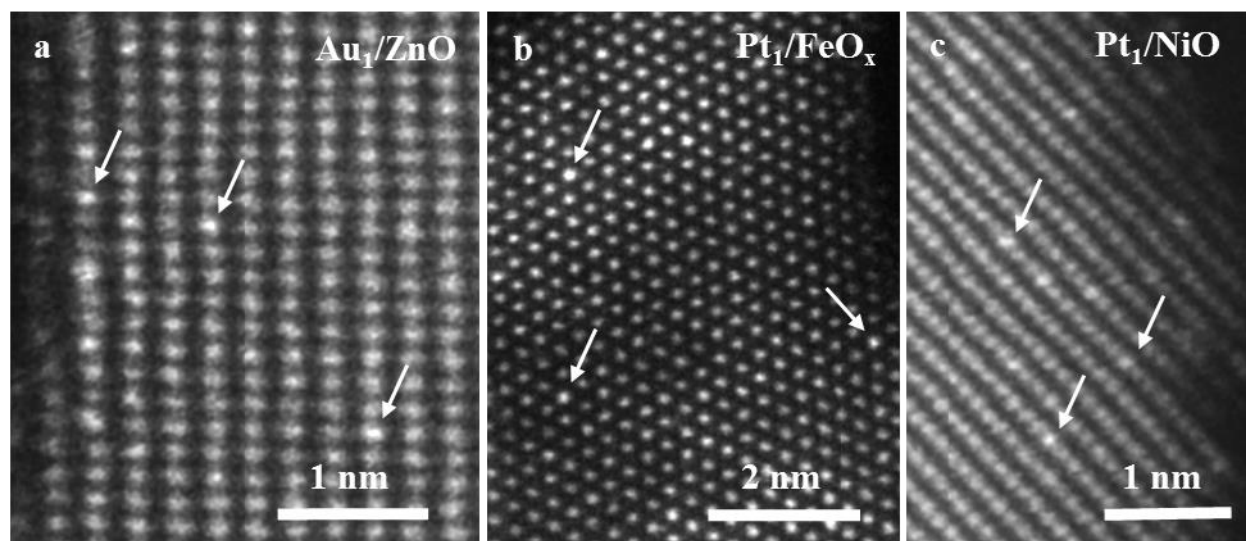
Aberration-corrected STEM (AC-STEM) techniques have proved to be invaluable for unambiguously identifying the nature of the metal dispersion and the structural relationship between the isolated individual metal atoms and the surface atomic structure of the support. Recent characterization of isolated individual metal atoms and their interactions with crystalline support surfaces provided new insights into the stability of SACs. The high-angle annular dark-field (HAADF) imaging mode of AC-STEM is most powerful for locating the supported single noble metal atoms [5]. Figure 1 shows isolated single atoms of Au<sub>1</sub> supported on ZnO nanowires (Fig. 1a), Pt<sub>1</sub> on FeO<sub>x</sub> nanocrystallites (Fig. 1b), and Pt<sub>1</sub> on NiO nanocrystals (Fig. 1c). In these cases, the isolated noble metal atoms are located exactly at the positions of the cation atoms of the crystalline metal oxide surfaces. It is frequently observed that at low levels of noble metal loading the isolated noble metal atoms are preferentially anchored at the surface cation vacancies as clearly demonstrated in Fig. 1.

One of the characteristics of SACs is that the dispersion of the active metal is 100% and thus the activity of the SACs should increase linearly with the amount of metal loading and the specific activity of the SAC should be the same regardless of the loading amount of the noble metal. It is, however, extremely challenging to synthesize SACs with high levels of metal loading. By developing a modified adsorption-deposition method we recently succeeded synthesizing high metal loading SACs as shown in Fig. 2b. With such SACs of different levels of metal loading their catalytic properties can be evaluated. As shown in Fig. 2a, the specific activity for CO oxidation on Pt<sub>1</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts at different temperatures does not depend on the loading levels of the Pt metal. The challenges in fully understanding the nature of SACs include 1) the electron transfer processes between the metal atoms and the supports and 2) the vertical location of the individual metal atoms with respect to the surface atoms of the supports. Imaging of supported metal atoms, accurate identification of their atomic positions with respect to the support surface, determination of the electronic charge on the metal atoms, and identification of the metal anchoring mechanisms, especially at elevated temperatures and under gas environment, are all critical to enhancing the performance of SACs and to developing practical SACs for broad applications [6].

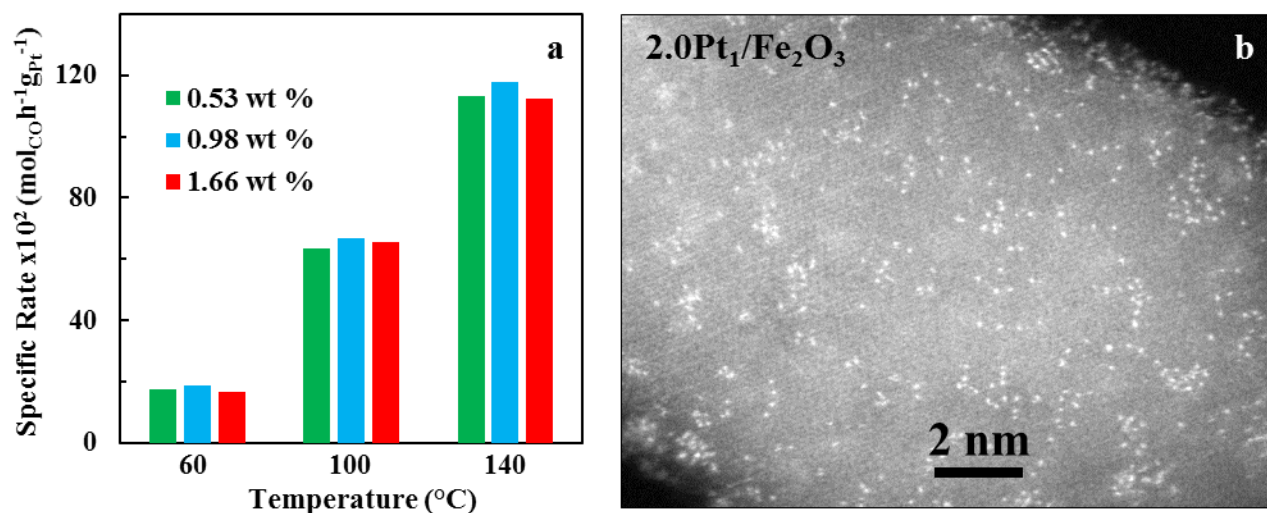
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**Figure 1.** STEM-HAADF images of (a)  $\text{Au}_1/\text{ZnO}$  nanowires, (b)  $\text{Pt}_1/\text{FeO}_x$  nanocrystallites and (c)  $\text{Pt}_1/\text{NiO}$  nanocrystals clearly show that the isolated Au and Pt single atoms (indicated by the white arrows) occupy the cation positions of the metal oxide support materials.



**Figure 2.** Specific rates of CO oxidation reaction on  $\text{Pt}_1/\text{Fe}_2\text{O}_3$  single-atom catalysts at different reaction temperatures (a) and STEM-HAADF image of a highly loaded  $\text{Pt}_1/\text{Fe}_2\text{O}_3$  single-atom catalyst (nominal loading of 2.0 wt % Pt) reveals distribution and dispersion of single Pt atoms on  $\text{Fe}_2\text{O}_3$  nanocrystallites (b). Surface defects such as steps, cation and anion vacancies, hydroxyl groups, etc. may play an important role in anchoring the Pt atoms.