

## Interfacial Effects Improve Catalytic Oxidation

This report features the work of Guangxu Chen, Nanfeng Zheng, and their co-workers published in *Science* **344**, 495 (2014).

The fabrication of multicomponent active sites, particularly metal-metal hydroxide and oxide interfaces, to facilitate the activation of reagents has emerged as an effective method to prepare heterogeneous catalysts with improved activities. For example, Pt/FeO<sub>x</sub> interfaces exhibit excellent catalytic performance in the oxidation of CO.<sup>1,2</sup> The structure and reactivity of such catalysts can be modeled with well defined synthetic nanoparticles.

A research team led by Nanfeng Zheng (Xiamen University, China), Lin Gu (Chinese Academy of Sciences, China) and Jyh-Fu Lee (NSRRC, Taiwan) has developed a novel, collaborative Fe-OH-Pt interface that activates dioxygen to achieve efficient catalytic oxidation of CO near 23 °C.<sup>3</sup> The Fe-OH-Pt interface was fabricated on depositing sub-monolayer iron hydroxide on fine Pt nanocrystals with a colloidal method. The structure of the Fe-OH-Pt interface was characterized with a scanning transmission electron microscope with atomic resolution, X-ray absorption fine structure (XAFS) spectroscopy at BL17C1 of the TLS, and X-ray photoelectron spectroscopy (XPS).

Despite exhibiting a large catalytic activity to oxidize CO, the Pt/Fe(OH)<sub>x</sub> catalyst failed to work steadily, particularly in dry streams. The conversion of CO decreased from 100% to 27% in 70 min when the reaction condition was switched from humid air to dry air. Even in a humid reaction stream, the Pt/Fe(OH)<sub>x</sub> catalyst began to degrade beyond 8 h near 23 °C, as Fig. 1(d) shows. The loss of activity was proposed to result from an instability of the interfacial Fe-OH-Pt sites. As the oxidation of CO is an exothermic reaction, the thermal stability of the Pt/Fe(OH)<sub>x</sub> catalyst was evaluated on subjecting the Pt/Fe(OH)<sub>x</sub> catalyst to thermal treatment at 453 K in dried

air for 2 h, followed by measurements of XPS. After that treatment, ratio A<sub>OH</sub>/A<sub>O</sub> of intensities of lines in the O 1s XPS decreased significantly, indicating that thermally induced decomposition of the overgrown Fe(OH)<sub>x</sub> layer occurred. The limited stability of the Pt/Fe(OH)<sub>x</sub> catalyst is likely due to the easy dehydration of Fe(OH)<sub>x</sub> sub-monolayers into three-dimensional iron oxide-hydroxide or iron oxide, similar to the natural process to form rust. For the Pt/Fe(OH)<sub>x</sub> catalyst, this dehydration decreases the number of active Fe-OH-Pt interfacial sites and thus deactivates the catalyst.

To prevent the loss of these Fe-OH-Pt sites, doping an overgrown Fe(OH)<sub>x</sub> sub-monolayer with Ni<sup>2+</sup> was undertaken. In contrast to Fe<sup>3+</sup>, Ni<sup>2+</sup> forms a stable, layered structure of Ni(OH)<sub>2</sub> with Ni in an environment of nearly perfect octahedral coordination. The overgrown Ni(OH)<sub>2</sub> sub-monolayer can thus spread over the Pt surface more readily than Fe(OH)<sub>x</sub>. Ni/Fe hydroxides have been widely prepared as hydrotalcite-like compounds. The easy formation of hydrotalcite-like Ni/Fe hydroxides was expected to stabilize catalytically active Fe-OH-Pt interfacial sites through the strong interaction between Ni(OH)<sub>x</sub> and Fe(OH)<sub>x</sub>. Moreover, Ni(OH)<sub>2</sub> species are active in the dissociation of adsorbed water molecules and in proton transport. All these unique features of Ni(OH)<sub>2</sub> make Ni<sup>2+</sup> an ideal dopant to stabilize the catalytically active Fe-OH-Pt sites on the surface of Pt nanocrystals.

As Fig. 1(a) illustrates, FeNi(OH)<sub>x</sub> hybrid sub-monolayers were deposited on nanocrystalline Pt seeds, with an evident boundary gap 0.3 nm. STEM-EDS measurements showed clearly that Fe(OH)<sub>x</sub> and Ni(OH)<sub>x</sub> were atomically evenly interconnected with each other on the surface of the obtained Pt/FeNi(OH)<sub>x</sub> nanoparticles (Fig.

1(b)). As an overgrowth of  $\text{FeNi(OH)}_x$  on Pt nanocrystals did not block all Pt sites, Pt sites were present with Ni and Fe on the outermost surface of the  $\text{Pt/FeNi(OH)}_x$  nanoparticles. XANES (Fig. 1(c)) and EXAFS analyses of  $\text{Pt/FeNi(OH)}_x$  enabled a conclusion that the oxidation state of Ni was +2 and in a nearly perfect octahedral coordination as in  $\text{Ni(OH)}_2$  with Ni-O bond distances  $0.205 \pm 0.001$  nm. More importantly, doping with  $\text{Ni}^{2+}$  altered neither the local structure nor oxidation state +3 of Fe in the hydroxide layer, and is expected not to modify the catalytically active Fe-OH-Pt interfacial sites. The O 1s XPS spectrum of  $\text{Pt/FeNi(OH)}_x$  displayed a major signal at 531.3 eV corresponding to -OH groups with  $A_{\text{OH}}/A_0$  ratio 7.5, indicating that the overgrown Fe-Ni layer on Pt was predominantly in the form of hydroxide.

The  $\text{Pt/FeNi(OH)}_x$  hybrid nanoparticles exhibited significantly enhanced stability to oxidize CO. Furthermore, the  $\text{Pt/FeNi(OH)}_x$  catalyst was stable in the reaction stream for more than 28 h with no decreased activity near  $23^\circ\text{C}$  (Fig. 1(d)), while readily achieving 100% conversion of CO to  $\text{CO}_2$ . For comparison, nanoparticles with a  $\text{Ni(OH)}_2$  sub-monolayer grown on Pt nanocrystals, denoted  $\text{Pt/Ni(OH)}_x$ , were prepared and characterized. This  $\text{Pt/Ni(OH)}_x$  catalyst performed worse than  $\text{Pt/Fe(OH)}_x$ . These results confirmed the hypotheses that the Fe-OH-Pt interfaces are catalytically active sites for the oxidation

of CO, and that  $\text{Ni}^{2+}$  doping stabilizes the Fe-OH-Pt interface during catalysis. After thermal treatment (2 h at  $453^\circ\text{K}$ ) under a reactive atmosphere, ratio  $A_{\text{OH}}/A_0$  of the  $\text{Pt/FeNi(OH)}_x$  catalyst remained 7.1.

Although the overgrowth of Fe/Ni-OH sub-monolayers on Pt nanocrystals creates efficient and stable interfaces for CO oxidation, it is not an ideal structure for practical catalysts because most Pt atoms are not located on the surface. To maximize the utilization of Pt and Fe/Ni-OH-Pt interfaces as well, an alloy-assisted strategy was developed. Accordingly, trimetallic  $\text{PtFeNi}$  nanocrystals were first prepared on thermally reducing the metal precursors under a CO atmosphere and then aging in air for several days to yield a highly active catalyst. The mean diameter of the  $\text{PtFeNi}$  nanoparticles was  $4.9 \pm 0.5$  nm. STEM analyses revealed that the  $\text{PtFeNi}$  nanoparticles possess core-shell structures with Pt-enriched cores. Each individual nanoparticle was apparently single-crystalline with fcc structure, but further STEM investigations revealed a lumpy feature on the surface of the air-aged  $\text{PtFeNi}$  nanoparticles. As characterized with elemental mapping, these  $\text{PtFeNi}$  nanoparticles exhibited compositional heterogeneities in the form of small interwoven domains (less than 0.35 nm) on their surfaces. Both XANES and XPS spectra confirmed oxidation states Pt 0, Fe +3 and Ni +2. EXAFS analyses revealed that Fe and Ni in the  $\text{PtFeNi}$

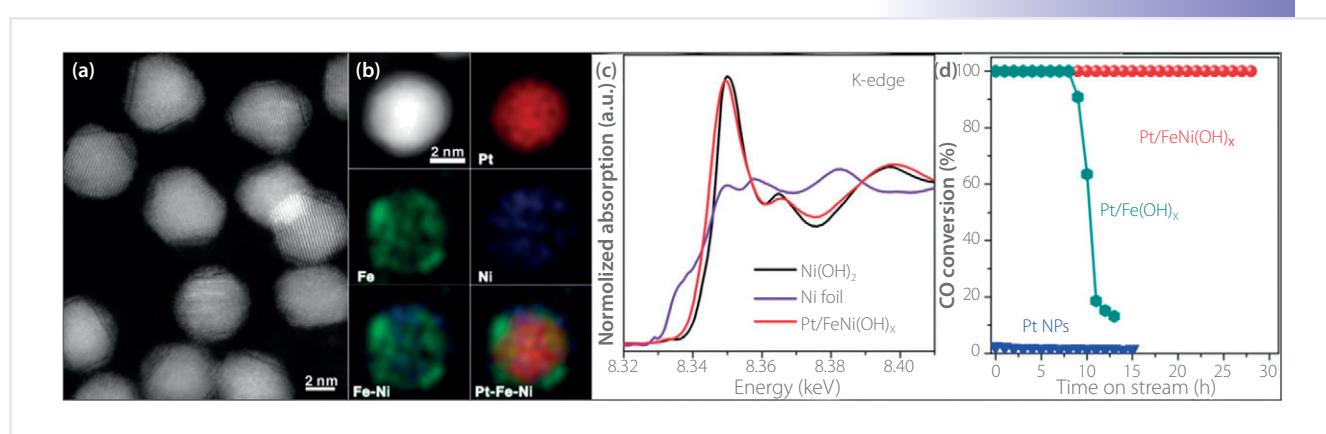


Fig. 1: (a) Representative large-angle annular dark-field STEM image of a  $\text{Pt/FeNi(OH)}_x$  nanocomposite. (b) STEM-EDS elemental mapping of a single  $\text{Pt/FeNi(OH)}_x$  nanoparticle. (c) XANES at the Ni K-edge of  $\text{Pt/FeNi(OH)}_x$  nanocomposite. (d) Reaction performance of various catalysts as a function of time on stream. Reaction conditions were 1% CO, 16%  $\text{O}_2$ ,  $\text{N}_2$  balance, temperature  $303\text{ K}$ , space velocity  $400\text{ L g}^{-1}\text{Pt h}^{-1}$ , humidity  $50 \pm 5\%$ , pressure = 0.1 MPa. (Reproduced from Ref. 3)

catalyst are both six-coordinate with respect to oxygen. The core level XPS spectrum of O 1s displayed a signal at 531.5 eV corresponding to –OH groups. These XAFS and XPS results demonstrated that PtFeNi nanoparticles possess the same interfacial sites discussed above for the Pt/FeNi(OH)<sub>x</sub> catalyst.

More importantly, the developed alloy-assisted strategy allowed the preparation of practical catalysts with maximally utilized Pt. As determined by titration with CO, the PtFeNi catalyst showed a Pt dispersion 63.9%, indicating that Pt atoms were highly dispersed on the surface of the catalyst. The catalytic performance of the PtFeNi catalyst in CO oxidation was enhanced 1.4–1.8 times that of the overgrown Pt/FeNi(OH)<sub>x</sub> catalyst having the same proportion of Pt. The PtFeNi catalyst exhibited great stability, both in a reaction stream and during pro-

longed storage: no decay of catalytic activity was experienced after more than one month in the reaction stream of CO with humid air. Even after storage near 23 °C in ambient air for one year, no deterioration of catalytic performance of the PtFeNi catalyst was found. The excellent catalytic performance of the PtFeNi catalyst makes it a promising candidate for practical applications to remove CO from humid air or a H<sub>2</sub>-rich stream. (Reported by Jyh-Fu Lee)

## References

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