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In-situ Study of Pt/Cu/Pt(111) Near-Surface Alloy Model Catalyst in CO

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Bimetallic catalyst is one main category of heterogeneous catalyst due to its numerous advantages, tenability, and outstanding performance in many cases [1-3]. By controlling the type and composition of the parent metals, the surface electronic and geometric structures of the bimetallic catalyst can be tuned systematically, hence providing a way to rationally design new catalyst with enhanced catalytic properties.

Based on fundamental surface science study and DFT calculation, Pt/Cu/Pt(111) near-surface alloy (NSA) has been proposed to be a promising catalyst for low-temperature water-gas shift (WGS) reaction. It is because the alloying of Cu in the second layer of Pt(111) causes binding energy of CO to Pt/Cu/Pt(111) is 0.33 eV less than to pure Pt(111)[4], hence reduces the potential of CO poisoning the catalyst. Since catalytic reactions typically occur under ambient pressure of reactants, in-situ studies are required to gain a complete understanding of this NSA catalyst. In particular, geometric and electronic structures of Pt/Cu/Pt(111) surface under ambient pressure of CO are essential to provide a complete understanding about the chemical properties and catalytic activity of this catalyst for reactions involving CO (e.g. WGS, CO oxidation). In this study, high pressure scanning tunneling microscopy (HP-STM) was used to investigate the surface morphology of Pt/Cu/Pt(111) under 1 Torr of CO. Local surface electronic structure was also obtained. In addition, ambient pressure x-ray photoelectron spectroscopy (AP-XPS) was used to obtained in-situ surface chemical information of NSA catalyst under CO exposure.

At first, Pt(111) single-crystal was clean by repeated cycles of argon-ions bombardment and annealing in UHV at 1000 K. Cleanness of sample was checked by STM or XPS. The NSA catalyst was prepared by physical deposition method. Using our e-beam evaporator, 1 ML of Cu was deposited on clean Pt(111) single-crystal, which was being held at 776 K, under UHV environment. The rate of deposition was 1 ML/min. For in-situ STM experiment, CO was introduced to the reactor-like STM chamber in batch mode through a leak valve and STM images were collected. Similarly, the catalyst was put in a reaction-cell and CO was introduced into the cell for in-situ XPS experiments.

Successful formation of an NSA was confirmed by STM images (Figure 1). Figure 1b shows bright rings structure on the Cu/Pt(111) surface (blue shapes) which are speculated to be stress-induced boundaries between atoms stacking in face-center cubic (fcc) and hexagonal close-packed (hcp) sites. However, I did not observe any dislocations in atomic resolved images. Therefore, the bright lines are speculated to be subsurface atoms changing from fcc to hcp stacking. This feature is also shown in Figure 1c. Due to electronic effect, there are different corrugations observed on the image, which indicates the formation of an NSA. The bright protrusions reflect Pt atoms having Cu atoms underneath in the second layer (blue circle in Figure 1c). This is consistent with observation and DFT simulation reported in the literature [4]. The absence of atomic depressions on STM images indicates that there is no Cu atoms incorporated on the surface layer [4].

Figure 2a indicates absorption of CO on the Cu/Pt(111) NSA surface. Bright rings feature of the clean Cu/Pt(111) NSA surface was replaced by bright clusters of approximately 12Å in diameter under CO exposure. These bright clusters appear to have relative height of approximately 1 Å with irregular shapes and distribute rather randomly on the Pt/Cu/Pt(111) surface (Figure 2b). Interestingly, XPS data (Figure 2d) shows formation of atomic carbon on NSA surface under 1 Torr CO. This results implies that Pt/Cu/Pt(111) is capable of dissociating CO at room temperature in contrast to the case of Pt(111) single-crystal. In addition, XPS data also hints that the bright clusters in STM image (Figure 2b) are Pt atoms bulging upon binding and dissociating CO molecules.

In conclusions, incorporation of Cu in the second layer causes significant modification of the surface lattice along with the local electronic structure of the surface as shown in the STM images (Figure 1b,c). These modifications allow Pt/Cu/Pt(111) to be able to dissociate CO even at room temperature.

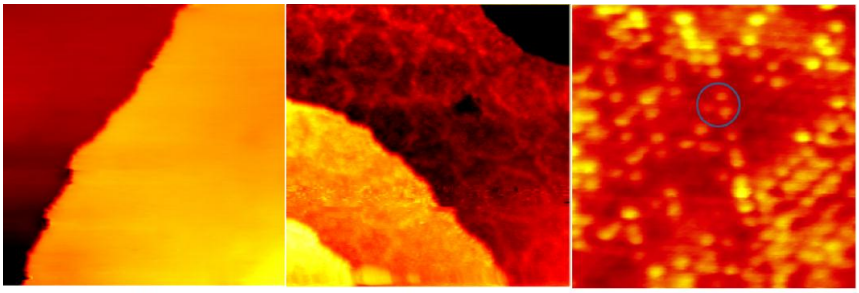

Figure 1: Constant height STM images of (a) clean Pt(111) surface (380Å x 380Å) (b,c) Cu/Pt(111) NSA under UHV and 298K , image sizes are 380Å x 380Å and 51Å x 51Å, respectively. The blue shapes indicate the bright rings structure on the Cu/Pt(111) NSA surface. Blue circle indicates an example of Pt atoms with Cu atoms underneath.

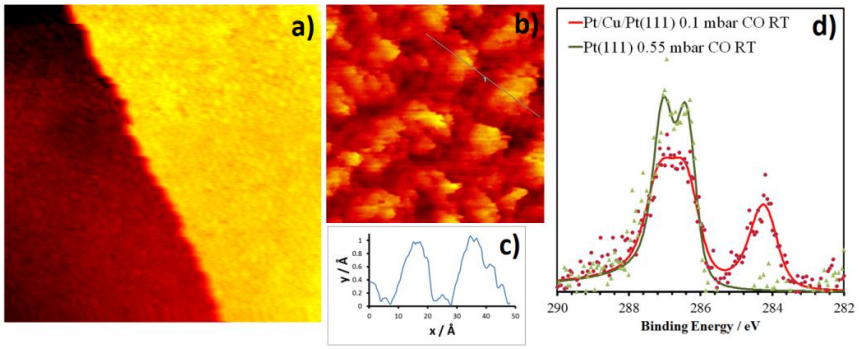

Figure 2: STM images of Pt/Cu/Pt(111) NSA a,b) under 1 Torr of CO at room temperature. c) shows line-scan profile of the indicated line in b). XPS data of C1s (atomic carbon at 284.2 eV and carbon of CO at ~287 eV) is shown in d).

References

[1] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard, Science, 279 (1998) 1913-1915.
[2] N. Toshima, T. Yonezawa, New Journal of Chemistry, 22 (1998) 1179-1201.
[3] J.H. Sinfelt, Bimetallic catalysts : discoveries, concepts, and applications, Wiley, New York, 1983.
[4] J. Knudsen, A.U. Nilekar, R.T. Vang, J. Schnadt, E.L. Kunkes, J.A. Dumesic, M. Mavrikakis, F. Besenbacher, Journal of the American Chemical Society, 129 (2007) 6485-6490.

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