Reducing Carbon Monoxide Contamination in a H_2 Source

This report features the work of Chung-Yuan Mou and his co-workers published in J. Am. Chem. Soc. ***134****, 10251 (2012).*

Hydrogen has been forecast to become an important source of energy in the upcoming years. A major obstruction of hydrogen as an energy source is the difficulty of storage and delivery, apart from safety concerns. The generation of hydrogen on site from a favorable liquid hydrocarbon might be a possible solution to these problems. Because of its small cost, large ratio of hydrogen to carbon and ease of handling, methanol is an ideal liquid fuel to produce hydrogen.

The way to generate hydrogen from methanol is simple and has been widely discussed.[1, 2] The process is divisible basically into four reactions: decomposition of methanol (DM), partial oxidation of methanol (POM), steam reforming of methanol (SRM), and oxidative steam reforming of methanol (OSRM). A major product in the DM reaction is carbon monoxide, CO, that is strongly adsorbed and hence blocks the active sites of Pt on the anode catalyst in the proton-exchange-membrane fuel cell (PEMFC). To overcome this problem, an effective catalytic device is essential for oxidation of CO in a hydrogen environment. Prof. C.-Y. Mou and his co-workers have solved this problem using Au nanoparticles grown on ZnO nanorods as a nanocatalyst system and sought further details of the mechanism of this CO oxidation.[3]

Why was the Au/ZnO system considered for this research topic? Prof. Mou's research team gave an overview and said, "CO oxidation on a supported gold nanocatalyst has been a paradigmatic problem in catalysis during the last two decades". Here they report the first evidence of a strong interaction on the metal

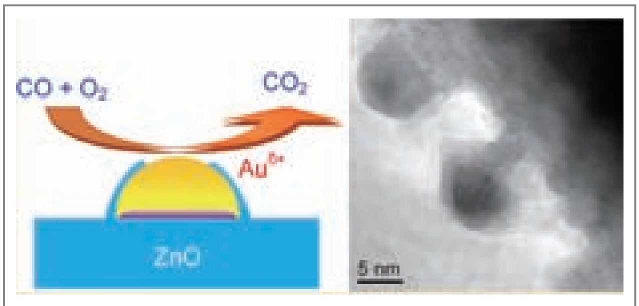

Fig. 1: (left) The animation of the Au/ZnO O-SMSI state for CO oxidation. (right) High-resolution transmission electron microscopic (HRTEM) image of a Au/ZnO nanorod system. (courtesy of Prof. Mou with the figure adapted from the reference)

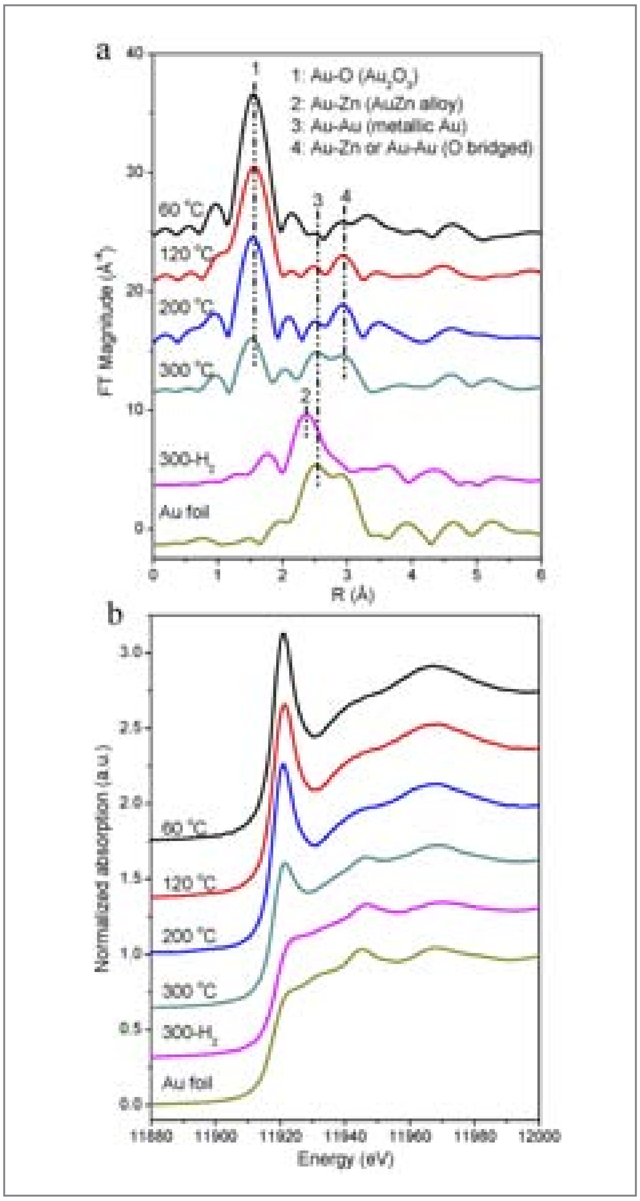

Fig. 2: (a) Fourier transform of k^3-weighted EXAFS spectra (without phase correction) and (b) normalized XANES spectra at the Au L_{III}-edge of a 20Au/ZnO-nanorod catalyst. The catalysts were pretreated under an O_2 atmosphere at 60, 120, 200, and 300 °C followed by pretreatment under a H_2 atmosphere at 300 °C. (courtesy of Prof. Mou with the figure adapted from the reference)

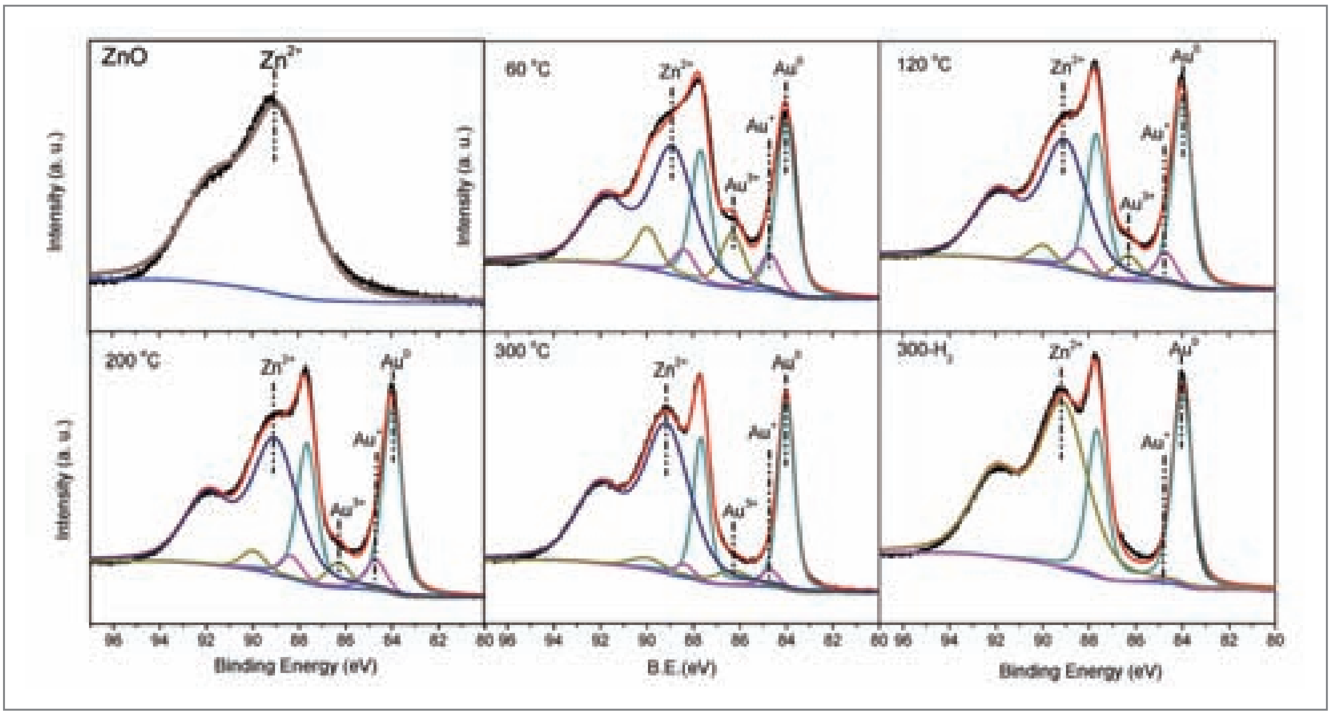

Fig. 3: XPS spectra of Zn 3p and Au 4f of a Au/ZnO-nanorod catalyst. The catalysts were pretreated under an O_2 atmosphere at 60, 120, 200, and 300 °C, followed by pretreatment under a H_2 atmosphere at 300 °C. (courtesy of Prof. Mou with the figure adapted from the reference)

support (SMSI) between gold nano-particles and ZnO nanorods based on the results of structural and spectral characterization. They utilized beamlines **BL17C1** and **BL20A1** at NSRRC in Taiwan for this work.

The SMSI effect is important for a mechanism of CO oxidation. The authors said, "The classical SMSI effect, as discovered by Tauster *et al*. on a TiO_{2}- supported group-VIII metal, was characterized by a major encapsulation of the metal by the support and an electron transfer from the support to the metal after reduction in H_2 at a higher temperature. Since then, much research in catalysis and surface science has been reported that demonstrates extensively that the SMSI in the supported group-VIII metal plays a significant role in affecting the catalytic performance."

For the Au/ZnO system in this work, the authors discovered SMSI states of two kinds, denoted O-SMSI (under oxidative condition at 300 °C) and R-SMSI (under hydrogen treatment at 300 °C). The two cases are reversible on switching between oxygen and hydrogen treatments. The authors concluded, "The O-SMSI state that appeared in our Au/ZnO system was in an opposite sense from that in the classical SMSI observed in the supported group-VIII metals. The R-SMSI state in Au/ZnO occurred under the same reductive pretreatment conditions as the classical SMSI, but it gave a smaller activity on CO oxidation." The authors also said, "We believe that our discovery of the O-SMSI and R-SMSI effects in Au/ZnO nanorods provides a new way to control the interaction between gold and the support as well as its catalytic activity."

The finding of this research might greatly enhance the reaction performance of a fuel cell by decreasing the contamination of hydrogen by CO.

In this research, the synchrotron analysis tools X-ray absorption fine structure (EXAFS & XANES) and X-ray photoelectron spectra (XPS) played important roles in probing the coordination environment as well as the valence state. For further information, please refer to the principal reference[3] and related articles.[1, 2]

References

1. T. Tsoncheva, S. Vankovab, and D. Mehandjiev, Kinet. Catal. Lett. **80**, 383 (2003).
2. G. Mul and A. S. Hirschon, Catal. Today **65**, 69 (2001).
3. X. Liu, M.-H. Liu, Y.-C. Luo, C.-Y. Mou, S.-D. Lin, H. Cheng, J.-M. Chen, J.-F. Lee, and T.-S. Lin, J. Am. Chem. Soc. **134**, 10251 (2012).