Active Sites of Gold-Ceria Nanorods for Low-Temperature CO Oxidation Reaction: Operando X-Ray Diffraction and Absorption Studies

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Introduction and Objectives

Since 1990's, gold nanostructures that interact strongly with oxide supports were reported to be extremely active for many redox reactions, such as CO oxidation [1]. Such unique catalytic properties were found to be strongly dependent on the local crystal and electronic structures of active Au centers, i. e. particle size and size-distribution, oxidation states, coordination number with surrounding ions, etc. X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) have been widely used as the structural detectors for the heterogeneous catalysts [2]. Therefore, operando XRD & XAFS (XANES and EXAFS) techniques are especially helpful on the studies of reaction mechanisms, i. e. reaction pathways, and active sites. Here, we will focus on studies of active sites of gold-ceria nanorods for the low-temperature CO oxidation reaction with the aids of operando XRD and XAS measurements.

Results and Discussion

The 1 at.% Au-CeO_2 nanorods were prepared by the deposition-precipitation method reported previously [3]. In-situ XRD patterns were collected during CO oxidation reaction (1%CO/4%O_2/He) under a "steady-state" mode between -65 and 70 °C (15 °C/step). The fresh Au-CeO_2 catalysts were pre-oxidized (20%O_2/He, 300 °C) or pre-reduced (5%H_2/He, 200 °C) before the catalytic tests. The pre-reduced Au-CeO_2 sample showed higher CO conversion below room-temperature than the pre-oxidized one (Figure 1), although their apparent activation energies between -35 and -5 °C were very close (13–15 kJ/mol). To our surprise, the lattice constants of the CeO_2 support for both pre-oxidized and pre-reduced conditions were unchanged (around 5.40 Å, see Figure 1) during the whole reactions, indicating that the creation of oxygen vacancies or Ce^{3+} ion may not be required to activate the gold catalysts. The operando XAFS measurements (Au L-III edge) were carried out under the same reaction conditions, but kept at room-temperature. The EXAFS fittings (not shown) determined that the ionic gold (Au-O, CN = 2.1±0.9) was the main phase in the pre-oxidized sample, while metallic gold (average particle size: 1.3 nm) was dominant in the pre-reduced one. XANES data, together with the linear combination results inserted in Figure 2, display that the Au in pre-oxidized catalyst was gradually reduced even under the room-temperature reaction. This is also consisted with

the XRD results in Figure 1a, i. e. the activity was enhanced (400–600 min) after the cool-down and heat-up cycle. The Au oxidation states were kept in metallic form for the pre-reduced sample during the reaction. In summary, metallic gold is more active than the ionic gold in Au-CeO_2 nanorods for the low-temperature oxygen-rich CO oxidation reaction.

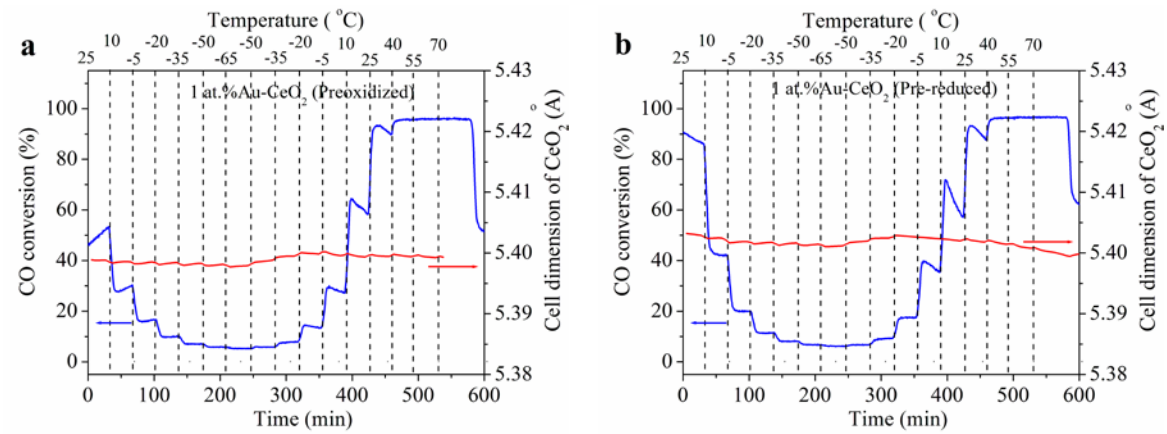

Figure 1. CO conversion (blue line) and cell dimension of CeO_2 (red line) as a function of reaction time for the Au-CeO_2 nanorods: (a) Pre-oxidized; (b) Pre-reduced.

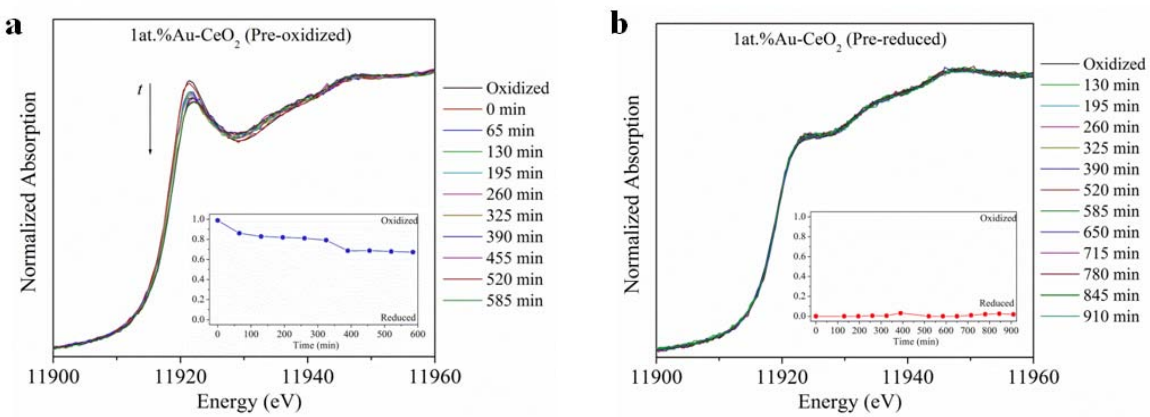

Figure 2. In-situ XANES (Au L-III edge) spectra for the Au-CeO_2 nanorods under CO oxidation conditions at room temperature: (a) Pre-oxidized; (b) Pre-reduced.

Conclusions

The operando XRD and XAFS results on gold-ceria nanorods confirmed that metallic (pre-reduced) Au is more active than ionic Au (pre-oxidized) for the low-temperature CO oxidation reaction, while the reduction of the CeO_2 support is not necessary to activate the catalysts. The active sites could be well-dispersed gold atoms/clusters (< 1~2 nm) stabilized by the oxide matrix.

References

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