Preparation and Comparison of Supported Gold Nanocatalysts on Anatase, Brookite, Rutile, and P25 Polymorphs of TiO₂ for Catalytic Oxidation of CO

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Scientists working at the Oak Ridge National Laboratory have prepared and characterized gold nanocatalysts supported on anatase, rutile, and brookite, which are polymorphs of titanium dioxide (TiO₂). The objective of this investigation was to probe the effect of different catalyst supports on the gold’s catalytic activities. All catalysts in the study were exposed to an identical sequence of treatment and measurement. The as-synthesized catalysts exhibited high activity rates with concomitant Au reduction upon exposure to the CO-containing reactant stream. The reduction of cationic gold species was verified by x-ray absorption near-edge spectroscopy (XANES), suggesting what the dominant contribution of the reduced gold species to the observed catalytic activity could be. The deactivation of the catalysts was observed following a treatment sequence at temperatures up to 573 K. The brookite-supported gold catalyst sustains the highest catalytic activity after all treatments. Both x-ray diffraction (XRD) and transmission electron microscope (TEM) results indicate that, following the reaction and pretreatment sequences, the gold particles supported by the brookite are smaller than those on the other supports.

In the late 1980s and the early 1990s, Haruta and coworkers (J. Catal. 1989, 115, 301) discovered that gold particles deposited on titanium dioxide exhibited a surprisingly high catalytic activity for low-temperature CO oxidation. This discovery has prompted worldwide research into the applications of gold catalysts in a number of industrially important reactions. The unique catalytic properties of gold nanoparticles have been correlated to many factors and structural parameters. Among them, the type of oxide support used plays a key role in controlling the catalytic activities of gold nanoparticles. The titanium-oxide support used originally by Haruta and coworkers consists of a polymorphic mixture (P25) of anatase and rutile. To more deeply understand the reaction mechanism associated with gold nanoparticles, it is useful to study the support effect induced by allotropic forms. Titanium dioxide is a good candidate because it exists in three different allotropic forms: anatase, brookite, and rutile.

The main objective of our study was to prepare and test Au catalysts supported on three polymorphs of TiO₂, as well as on P25. EXAFS and XANES were employed along with other spectroscopic techniques for probing structural properties associated with the above systems. Our results indicated that when other experimental factors are kept constant, the catalytic activity is not much affected by the variation of the TiO₂ phases. However, the stability of the Au nanoparticles varies with the specific support structure. We demonstrated that the brookite-supported Au catalyst is the most stable catalytic system.

Scanning transmission electron microscopy (STEM) analyses on the most active samples show predominantly 0.5 – 2 nm-sized gold particles on the TiO₂ surface. On rutile and anatase these ultra-small gold nanoparticles are susceptible to aggregation under reaction conditions. Both the XRD and STEM techniques can be used to follow the size variation of gold nanoparticles. In
contrast to the gold catalysts supported on anatase and rutile, the brookite-supported gold catalyst is much more stable. No gold XRD peaks were observed even after extended exposure to catalytic reaction conditions, suggesting that Au nanoparticles are stable on the brookite support under reaction conditions. The Z-contrast microscopy results were obtained on the brookite-supported samples at three different stages: 1) as-synthesized, 2) after reduction at 423 K, and 3) after calcination at 573 K. The micrographs in each of these stages are shown in Figure 1. The Au nanoparticles are visible in the as-synthesized state as very small, apparently thin rafts with sizes of 0.5 to 2 nm (Figure 1a). Little is changed following a mild treatment at 423 K (Figure 1b). The lattice fringes of the needle-like TiO$_2$ crystallite are readily visible in both micrographs. After calcination at 573 K, these small rafts were not observed and Au particles were few or absent in several micrographs obtained by using the highest magnification. The micrograph in Figure 1c shows a single Au particle that is 2 – 3 nm in size and exhibits fringes, suggesting that it is a faceted 3-D particle. At a lower magnification, many particles in the range of 1 – 10 nm are visible, and still lower magnification reveals many particles in the range of 30 – 70 nm.

XANES was used to extract information about the oxidation state of the Au species during the pre-treatment steps used in each of the sequences. Typical XANES spectra are shown for the Au-rutile surface in Figure 2. The pre-edge of the Au L$_{III}$ absorption edges exhibits a sharp peak for the as-synthesized state, indicating that it is highly oxidized, probably mostly in the Au$^{3+}$ state. This peak is slowly diminished by exposure to the reaction mixture of 1% CO/air at room temperature (Figure 2). This result demonstrates that reaction conditions at room temperature bring about the partial reduction of the Au, even though excess oxygen is present. Heating in Ar causes an additional decrease of the peak, indicating that some auto reduction is possible due to heating. Finally, reduction at 423 K causes a complete loss of the peak and leaves a spectrum that, except for slightly less pronounced oscillations, closely matches that of an Au foil. Additional treatments in hydrogen and in oxygen were performed up to 573 K and subsequent spectra were run in the CO/air mixture. These treatments did not further alter the general shape of the spectrum or bring about any growth of the peak at the Au edge. Therefore, no re-oxidation occurs as a result of these treatments or exposure to reaction conditions.

Figure 2. Au XANES spectra of the 14 wt% Au-rutile sample recorded in the as-synthesized state, b) after exposing to the reaction mixture of 1% CO/air for 50 minutes, c) after heating to 473 K in Ar for 30 minutes, and d) after reducing for 30 minutes in 4% H$_2$/He. Spectra were collected using a fluorescence detector.

Figure 1. The HRTEM micrograph of Au on brookite gold catalysts recorded in (a) the as-synthesized state, (b) following mild reduction at 423K, and (c) following calcination at 573 K. Micrographs in (a) and (b) are obtained at $2 \times 10^7$ magnification and (c) is obtained at $5 \times 10^7$ magnification.