

## Gold Catalysts Supported on Ceria Doped by Al(III) and Sm(III) for Water Gas Shift Reaction

M. Kantcheva<sup>1</sup>, D. Andreeva<sup>2</sup>, I. Ivanov<sup>2</sup>, L. Ilieva<sup>2</sup>, J. W. Sobczak<sup>3</sup>, W. Lisowski<sup>3</sup>

<sup>1</sup>Department of Chemistry, Bilkent University, 06800 Bilkent, Ankara, Turkey

*E-mail:* margi@fen.bilkent.edu.tr

<sup>2</sup>Institute of Catalysis, Bulgarian Academy of Sciences, “Acad. G. Bonchev” str., bl.11, 1113 Sofia, Bulgaria

<sup>3</sup>Institute of Phys. Chem., PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland

Gold catalysts supported on ceria doped by Al(III) and Sm(III) have been characterized by XRD, Raman spectroscopy, XPS and H<sub>2</sub>-TPR. The WGS activity of the materials has been tested and the mechanism of the CO+H<sub>2</sub>O surface reaction has been investigated by in situ FT-IR spectroscopy. The WGS activity of Au/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> is higher than that of the Al<sub>2</sub>O<sub>3</sub>-containing catalyst. The difference in the catalytic behavior is explained by differences in the structural properties of the catalysts. In the gold catalyst doped by Al(III), the oxygen vacancies are found within the bulk of ceria, whereas in the Au/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> sample the vacancies are located most likely around Sm(III). The Au 4f XP spectra of fresh samples reveal higher contribution of dispersed form of Au on the Sm-containing catalyst than on the Al-doped one. The Ce 3d XP spectra disclose also higher concentration of Ce(III) before the catalytic operation in the case of the Sm(III)-modified catalyst as compared with the fresh Al(III)-containing sample. There is no distinct correlation between the reducibility and WGS activity of the studied catalysts.

The amount of formate species, generated during the surface CO+H<sub>2</sub>O reaction and detected by in situ FT-IR, is higher on the Sm(III)- than on the Al(III)-containing catalyst and parallels the catalytic activity. It is concluded that the high activity of Au/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> is related with the high dispersion of Au nanoparticles leading to large number of active Au-support interface sites, which results in high concentration of formate species. According to the FT-IR data, the Au/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples behave differently with regard to the adsorption of water at room temperature: water adsorbs dissociatively on the former catalyst and molecularly adsorbed water has been observed on the Al(III)-doped sample. It can be proposed that the higher concentration of oxygen vacancies on the surface of the Sm(III)-containing catalyst facilitates the dissociation of water. This demonstrates the active role of defective ceria in the latter process. The facile dissociation of water on the Au/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> catalyst accounts also for its better performance in the WGS reaction.