

DOCTORAL THESIS

Au/CeO₂ based catalysts for catalytic oxidation of volatile organic compounds and carbon monoxide

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**Au/CeO₂ Based Catalysts for Catalytic Oxidation of Volatile
Organic Compounds and Carbon Monoxide**

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**A thesis submitted in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy**

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ABSTRACT

Catalytic complete oxidation of CO and VOCs is one of the most efficient ways for the abatement of air pollution. It is crucial to prepare catalysts with high activity and long-term stability for practical use. In this work, gold supported on 3-D mesoporous CeO₂, 3-D mesoporous CeO₂-Fe₂O₃, 1-D mesoporous ceria, ceria nanopolyhedra, nanorods and nanocubes as catalysts for CO, butane and benzene complete oxidation have been investigated. The catalysts were characterized in details by various techniques, including ICP-AES, N₂ adsorption-desorption, XRD, XPS, DR UV-Vis, SEM, TEM, EDS, TOF-SIMS, EPR, TPR and TPD, to elucidate the structure-activity relationship.

It was found that the ceria morphology has a profound effect on CO and isobutane oxidation reactions. Ceria nanorods (11.1 nm in diameter) enclosed by (110) and (100) planes showed higher activity than nanocubes (27.5 nm in diameter) bounded by (100) planes, while nanopolyhedra (6.1 nm in diameter) with exposure of (111) planes exhibited the lowest specific reaction rate. The lower activity of nanopolyhedra was ascribed to the fewer number of active surface oxygen species that can be provided on (111) planes. On the contrary, benzene oxidation activity increased with the decrease in ceria particle size and nanopolyhedra showed the highest activity due to its smaller particle size. The deposition of gold significantly enhanced the activity of the surface oxygen and the oxidation activity of ceria. Furthermore, gold dispersion was found to increase with the decrease in ceria particle size. Au/CeO₂-rod exhibited the highest CO oxidation activity due to the synergetic effects arising from the nanosized gold and the well-defined surface of nanorods. Au/CeO₂-polyhedron showed the highest activity in isobutane and benzene oxidation reactions due to its

relatively small ceria particle size and high gold dispersion.

The role of cationic gold in CO and butane oxidation reactions was also investigated. Au/CeO₂ catalysts with different fraction of cationic gold and similar ceria support were prepared. The results suggested that the reducibility of the surface oxygen on ceria can be enhanced by cationic gold species more efficiently than metallic gold and the CO oxidation activity increased with the increasing fraction of cationic gold species. In butane oxidation, the Au⁺ species formed under reaction conditions as surface gold oxide was responsible for the low temperature activity over Au/ceria, while the high temperature activity was enhanced by substitutional Au³⁺ ions.

Since nanosized ceria facilitates the dispersion of gold and the ceria size effect was more profound than morphology effect in benzene oxidation, it is desirable to prepared nano-size ceria supported gold catalysts for VOCs oxidation. In this work, 3-D (CeO₂-48) and 1-D (CeO₂-41) ordered mesoporous ceria materials supported gold catalysts were prepared. CeO₂-48 (3 nm in diameter) and CeO₂-41 (4 nm in diameter) exhibited smaller particle size, larger specific surface area and higher concentration of surface oxygen vacancies than that of alkaline precipitated ceria sample CeO₂-P (7-14 nm in diameter). Superoxide on ceria was found to be the active species for low temperature benzene oxidation. CeO₂-48 with higher Ce³⁺ and oxygen vacancy concentration can stabilize superoxide species at higher temperature than CeO₂-P, thereby achieving higher benzene oxidation activity. Au/CeO₂-48 exhibited excellent benzene oxidation activity with T₅₀ achieved at 151 °C. More importantly, CeO₂-48 with higher amount of structural defects generated after the removal of silica can stabilize gold species better than Au/CeO₂-P. Hence Au/CeO₂-48 showed much higher long-term stability than Au/CeO₂-P.

The physicochemical properties of CeO₂-48 were modified by iron. 3-D mesoporous Fe₂O₃ and Ce-Fe mixed oxide with high surface area (higher than 100 m²g⁻¹) and very small particle size were synthesized through a hard template method. XRD data confirmed the formation of cubic Ce_xFe_{1-x}O₂ and hematite-like solid solution in Ce-Fe mixed oxide. It was found that higher surface oxygen reducibility and higher oxygen mobility were achieved in Ce-Fe mixed oxide than in single CeO₂ or Fe₂O₃, leading to higher CO and isobutane oxidation activity on Ce-Fe mixed oxide. This was due to the weakening of metal-oxygen bonds in the solid solution and the generation of bulk oxygen vacancies by the substitution of Ce⁴⁺ by Fe³⁺. However, the addition of Fe enhanced the evolution from superoxide to other adsorbed oxygen species. Therefore, Ce-Fe mixed oxides showed lower activity than CeO₂-48 in benzene oxidation. For supported gold catalysts, CO and benzene oxidation activity decreased with the increase of Fe content in the support of Au/Ce-Fe, indicating that the interaction between Au-Ce was stronger than that between Au-Fe. On the other hand, Au/CeFe(2:1) achieved 100% isobutane conversion at temperature below 300 °C, while complete oxidation of isobutane was not reached at 500 °C over Au/CeO₂-48. TPR results indicated that the deposition of gold on ceria mainly increased the activity of surface oxygen, while both surface oxygen activity and lattice oxygen mobility was enhanced on Ce-Fe mixed oxides. This suggested that CO and benzene can be oxidized by active surface oxygen species, while both adsorbed oxygen species and lattice oxygen were important for isobutane oxidation.

Key word: CO oxidation, VOCs oxidation, gold, CeO₂, nanopolyhedron, nanorod, nanocube, Ce-Fe mixed oxide

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