

BES019. Nanostructured, Metal-Modified Oxide Catalysts for Steam Reforming of Methanol and the Water-Gas Shift Reactions

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effectively catalyze the low-temperature water-gas shift and methanol steam reforming reactions. Abstract

The project follows a comprehensive and complementary approach to elucidate the metal-oxide interaction at the atomic scale for the reactions of interest to fuel processing for hydrogen generation. Accordingly, different activities in the synthesis, characterization, and testing of the catalysts are underway at Tufts and at Columbia. Various oxides, namely; ceria, iron oxide, zirconia, and zinc oxide, are prepared, typically by hydrothermal techniques, as single crystals with nm-dimensions which have moderately-high surface areas and can thus be used as practical metal supports. Such nanocrystals serve as platforms to study how different surfaces can disperse the deposited metals, e.g. Au or Pt, and to identify potential shape effects for the reactions under investigation. The results can be compared to extended single crystal surfaces investigated under vacuum in a systematic way, bridging the pressure and materials gap between surface science and catalysis.

During the past year, several parallel efforts have continued at both schools, and these will be detailed in the annual report. Briefly, we have completed a detailed structural study of Cu-doped ceria for the WGS reaction. We have also completed a comparative study of Pt-metals and Au in ceria nanoshapes for the methanol decomposition reaction, and found that Au on ceria follows the methylformate pathway without any CO production up to 250 °C, while the Pt metals on ceria easily decompose methoxy to CO and H₂. The latter are thus not suitable candidates for methanol steam reforming because their selectivity to H₂ would be limited by the WGS reaction equilibrium. The Flynn group at Columbia has continued the STM/STS study of the structural effects of Au adatoms on Fe₃O₄(111) surfaces and the adsorption of CO and H₂O. As already reported,¹ the CO adsorbs linearly atop the Au adatoms, the latter bound tightly over the uncapped surface oxygens of the Fe-terminated surface. Present data from the H₂O adsorption at 260K indicate that water molecules preferentially adsorb on the Fe atoms neighboring the Au adatoms. To complement this study, nanoshapes of Fe₃O₄ were made and Au was deposited on them by various techniques to examine the Au/Fe₃O₄ interaction and reactivity as a function of the magnetite shape. This work is in progress.

We have also conducted an extensive study of Au on CeO₂ nanoshapes as catalysts for the SRM reaction,^{2,3} and more recently prepared Au/ZnO nanoshapes, and compared this catalyst to Au/ceria.⁴ On both oxides, sub-nm gold clusters and atoms are present

Objectives

The overall goal of this project is to elucidate the role of metal ions anchored on oxide supports, and the role of oxide structures in stabilizing the metal ions in their active state for catalyzing reactions of interest to fuel reforming for hydrogen generation. The concentration and types of oxygen defects are strong functions of the size, shape, and composition of the oxide nanoparticles. Novel chemical synthesis techniques are employed to control the size and shape of oxide nanoparticles used to evaluate the structure sensitivity of the reactions of interest; and to design catalysts with optimal metal distribution on the oxide supports.

Technical Barriers

Novel catalysts for the efficient conversion of fuels to hydrogen that possess the required high stability for practical fuel cell application are needed. These catalysts should also be highly active and contain minimum amounts of costly platinum metals to allow rapid development of hydrogen generation and purification schemes for use with low-temperature fuel cells. The current DOE project investigates trace amounts of sub-nm clusters and ions of gold or platinum in nanostructured oxides (ceria, iron oxide, zinc oxide) as potential new catalysts meeting these requirements. Our findings to date point to the importance of the particle size, shape, and oxygen defect density of the host oxide for proper distribution of the active metal sites to

on the active catalyst, while gold nanoparticles are inactive. An important mechanistic finding is that the SRM reaction proceeds through the methyl formate route on fully dispersed gold on ceria or zinc oxide. Interestingly, the WGS pathway is not involved in the SRM reaction on Au/CeO₂ or Au/ZnO. Methanol dehydrogenation, methyl formate hydrolysis and formic acid decomposition are the steps producing CO₂ and H₂. While both reactions are catalyzed by Au/ceria at the same low temperatures, we have found that methanol is the preferred adsorbate on gold. Since the water-gas shift reaction is not part of the SRM pathway below 250°C, the selectivity to H₂ exceeds the equilibrium value based on the former reaction. The practical implications of these findings are obvious.

Report Highlights

During the past year we have focused on the investigation of potential shape effects of ceria and zinc oxide on the water-gas shift (WGS) and steam reforming of methanol (SRM) at low temperatures. We have found that a small amount (<1wt.%) of gold fully dispersed on ceria single crystals prepared as nanorods (10±2.8 by 50-200 nm) of {110} and {100} crystal surfaces) shows excellent catalytic activity in both the SRM and the WGS reactions at temperatures < 250°C. The ceria nanorods bind and stabilize gold as atoms and clusters (< 1nm, TEM invisible). On the other hand, gold nanoparticles (~ 3nm) deposited on the {100} surfaces of ceria nanocubes (30±11 nm) are inactive for either reaction up to 250°C. On ZnO nanoshapes, we find that gold can be dispersed fully on short nanorods and nanopolyhedra comprised of the polar (0001) surfaces. These are highly SRM- active and selective to H₂. Figure 1 compares CH₃OH-TPSR results over these two types of catalysts, and a commercial Cu-ZnO catalyst,

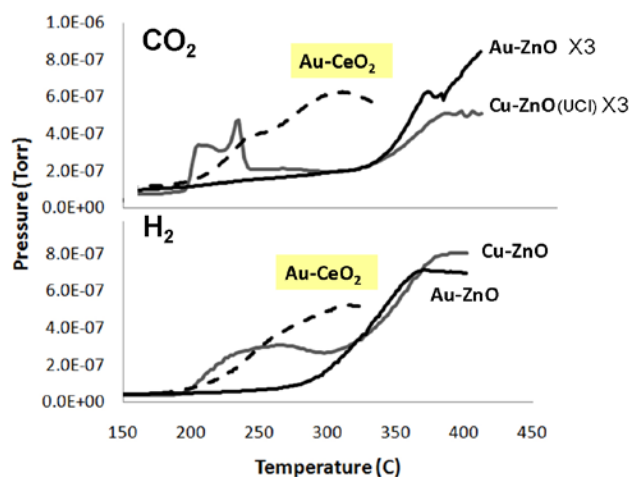


FIGURE 1. Methanol-TPSR

UCI (G-66B). The maximum hydrogen yield was obtained on the Au-CeO₂ nanorods.

Methylformate (not shown) is produced from the coupling of methanol on the gold catalysts. With surface water, this is hydrolyzed to formic acid, which decomposes to produce CO₂ and H₂. Fig.2 shows SRM-TPSR on the Au/CeO₂ nanorods. There is a wide temperature window over which only these two products are measured by mass spectrometry. The production of CO begins above 250 °C. Thus, Au/CeO₂ is an excellent prospect for the low-temperature SRM reaction, coupled with PEM fuel cell operation. The water-gas shift reaction is not part of the pathway.^{2,3} This is interesting because this same catalyst is very active for WGS even at 150 °C.⁵ We have further investigated the catalyst selectivity in steady-state isothermal tests and found that the WGS reaction is suppressed by methanol; i.e. methanol, not CO, is the preferred adsorbate on gold. The results from 1% Au/ZnO nanopolyhedra were similar. Since the water-gas shift reaction is not part of the SRM pathway below 250 °C, the selectivity to H₂ exceeds the equilibrium value based on the former reaction. The practical implications of these findings are obvious.

Overall, we have found that the shape effect of the oxide nanocrystals is indirect, i.e. the catalytic activity depends on the number of fully dispersed gold species on ceria or zinc oxide. The shape effect simply means that the (110) surfaces of ceria and the (0001) surfaces of zinc oxide achieve better dispersion of gold than other surfaces. Indeed, in kinetic measurements, we found the same activation energy for Au on any ceria shape. The rates, properly scaled with the amount of dispersed gold are the same, i.e. the TOFs are the same. In conclusion, the Au/Ceria catalyst shows good activity and stability for both the WGS and SRM reactions. Because of its

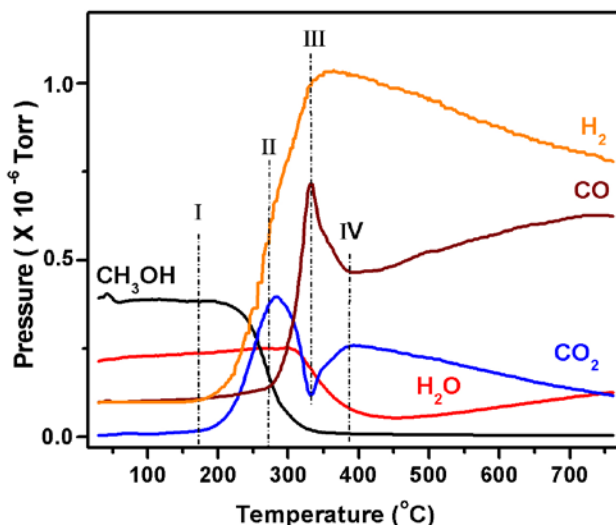


FIGURE 2. (CH₃OH + H₂O)-TPSR

high CO₂ selectivity in SRM below 250°C, this catalyst merits further evaluation for practical applications to future fuel processing and fuel cell systems.

Future Directions

All the activities highlighted above are continuing in the near future. A new task in the project, already underway, is the synthesis, characterization and evaluation of surface alloys on nanoscale oxides for the reactions of methanol under study. Of particular interest is the PdAu system, which is being evaluated on ZnO. We will continue to focus a major part of our effort on detailed examinations of the shape effect of the oxide host and propose general catalyst design guidelines as appropriate. The desired outcome is a good mechanistic understanding of the chemistries under investigation, and the evolution of the key catalyst structures. References and Publications (since 2006) acknowledging the DOE Grant

1. K.T. Rim, D. Eom, L. Liu, E. Stolyarova, J.M. Raitano, S.-W. Chan, M. Flytzani-Stephanopoulos, and G.W. Flynn, *Catalytic gold nanoparticles on an iron oxide surface: a scanning tunneling microscopy and spectroscopy study*, J. Phys. Chem. C 113 (2009) 10198.
2. N.Yi, R. Si, H. Saltsburg, and M. Flytzani-Stephanopoulos, *Steam reforming of methanol over ceria and gold-ceria nanoshapes*, Appl. Catal. B 95 (1-2) (2010) 87-92.
3. N.Yi, R. Si, H. Saltsburg, and M. Flytzani-Stephanopoulos, *Nanostructured Au-CeO₂ catalysts for low-temperature steam reforming of methanol and the water-gas shift reactions*, Energy & Environ. Science, in press (2010).
4. N.Yi, M. Boucher, F. Gittleson, M. Flytzani-Stephanopoulos, *Dispersed gold species on CeO₂ and ZnO nanoshapes for low-temperature steam reforming of methanol*, invited paper, J. Phys. Chem. C, in preparation.
5. R. Si, M. Flytzani-Stephanopoulos, *Shape and crystal-plane effects of nanoscale ceria on the activity of Au-CeO₂ catalysts for the water-gas shift reaction*, Angew. Chem. Int. Ed. 47 (2008) 2884-2887.
6. W. Deng, D. Carpenter, N. Yi, and M. Flytzani-Stephanopoulos, *Comparison of the activity of Au/CeO₂ and Au/Fe₂O₃ catalysts for the CO oxidation and the water-gas shift reactions*, Topics in Catalysis 44 (2007) 199-208.
7. L.F. Allard, A. Borisevich, W. Deng, R. Si, M. Flytzani-Stephanopoulos, S.H. Overbury, *Evolution of gold structure during thermal treatment of Au/FeOx catalysts revealed by aberration-corrected electron microscopy*, J. Electr. Micr., 58 (2009) 199-212.
8. W. Deng, A. Frenkel, R. Si, and M. Flytzani-Stephanopoulos, *Reaction-relevant gold structures in the low temperature water-gas shift reaction on Au-CeO₂*, J. Phys. Chem. C 112 (2008) 12834-12840.
9. W. Deng and M. Flytzani-Stephanopoulos, Angew. Chem. Int. Ed. 45 (2006) 2285-2289.
10. F. Zhang, J.M. Raitano, Chih-Hao Chen, J.C. Hanson, W. Caliebe, S. Khalid, and S.-W. Chan, *Phase stability in ceria-zirconia binary oxide nanoparticles: The effect of the Ce³⁺ concentration and the redox environment*, J. Appl. Phys. 99 (2006) 0843131-38.
11. D. Pierre, W. Deng and M. Flytzani-Stephanopoulos, Topics in Catalysis 46, 363-373 (2007)
12. F.C. Meunier, D. Reid, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, W. Deng and M. Flytzani-Stephanopoulos, J. Catal. 247 (2007) 269-79.
13. Po-Yi Wu, J. Pike, F. Zhang, and S.-W. Chan, *Low temperature synthesis of ZnO nanoparticles*, Int'l J. Appl. Cer.Techn. 3 (2006) 272-278.
14. M. Manzoli, F. Boccuzzi, A. Chiorino, F. Vindigni, W. Deng, M. Flytzani-Stephanopoulos, *Spectroscopic features and reactivity of CO adsorbed on different Au/CeO₂ catalysts*, J. Catal. 245, 308-315 (2007).
15. F. Zhang, P.J. Chupra, S. Lun, A. Lui, J.C. Hanson, W. Caliebe, P.L. Lee, and S.-W. Chan, Chem. Materials 19 (2007) 3118-3126.
16. M. Flytzani-Stephanopoulos and R. Si, *Copper-Ceria catalysts for the water-gas shift reaction*; review article, E-book chapter, Bentham Publishers, in press (2010).