

THE INTRINSIC KINETIC OF REVERSE WATER GAS SHIFT OVER OXIDE SUPPORTED GOLD CATALYSTS: THE ROLE OF INTERFACIAL SITES AND PLASMONIC ENHANCEMENT

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Abstract

Well characterized AuMo_x catalysts were synthesized by controlled surface reactions (CSR) and studied in reverse water gas shift (RWGS) reaction with and without visible light addition. Raman spectroscopy and Energy-dispersive X-ray spectroscopy (EDS) characterizations indicate that the deposition of Mo onto Au nanoparticles occurs preferentially on under-coordinated Au sites, forming Au-Mo interfacial sites. The concentration of Au and Au-Mo interfacial sites on these catalysts was quantified using low temperature (173 K) CO adsorption with Fourier transform infrared spectroscopy (FTIR) and electron microscopy. The turnover rates (CO mole produced per mole of Au or AuMo_x site per min) on the Au and AuMo_x interfacial sites were measured to be 1.0 min⁻¹ and 14 min⁻¹ in the dark conditions and 4.4 min⁻¹ and 63 min⁻¹ under the light conditions at 573 K. The rate per AuMo_x interfacial site is an order of magnitude greater than the rate per Au site under both dark and light conditions. These results indicate that the localized surface plasmon resonance (LSPR) has the same enhancement effect on both Au and AuMo_x catalytic sites.

Keywords

Active site, Bimetallic catalyst, Interfacial sites, Localized surface plasmon resonance (LSPR)

Introduction

Recent studies have suggested the importance of interfacial sites for a variety of reactions including Au/metal-oxide catalysts for CO oxidation, water gas shift reaction and reverse water gas shift reactions. The catalytic active site for these reactions has been proposed to be the interface between a metal-metal oxides. One of the challenges with being able to characterize and quantify these interfacial sites is that conventional synthesis techniques produce a wide range of particle sizes and interfacial sites. Therefore, accurate identification and analysis of the interfacial sites remains as one of the most challenging aspects of the field of heterogeneous catalysis. Being able to identify,

characterize, and quantify interfacial metal-metal oxide catalytic sites would be a significant contribution to the entire field of heterogeneous catalysis. Several recent papers have demonstrated that surface plasmons can enhance chemical reaction rates on Au catalysts due to their ability to absorb visible light through surface plasmon resonance (SPR). It has been suggested that the interface between Au and metal oxide is responsible for the catalytic activity in many plasmon-enhanced reactions such as water splitting, CO oxidation, and RWGS. The objective of the study is to develop a fundamental understanding of the role of interfacial sites between gold and metal oxides by

measuring the intrinsic catalytic activity for RWGS. We prepared well-characterized Au catalysts that have a variety of controlled Au-metal oxide interfacial sites to demonstrate the role of interfacial site in catalyzing RWGS under dark and light conditions.

Materials and Methods

The reference SiO₂ supported Au catalyst was prepared by a deposition-precipitation method. Reference Au/SiO₂ was reduced and transferred to an inert atmosphere glove box without air exposure. AuMo/SiO₂ catalysts which have a variety of controlled Au-metal oxide interfacial sites were prepared by a CSR method described elsewhere in details. Gas phase RWGS reactions were conducted in a fixed-bed down-flow reactor and reactor purchased from Harrick scientific (HVC-MRA-5) to understand the effect that interfacial sites and light.

Results and Discussion

We have recently shown that the addition of small amounts of Mo to an Au/SiO₂ catalyst by the CSR method, increased the RWGS catalytic activity an order of magnitude higher than the reference Au/SiO₂ catalyst under dark condition. Results from reactivity measurements, CO FTIR studies, Raman spectroscopy and x-ray absorption spectroscopy (XAS) indicate that the deposition of Mo onto Au nanoparticles occurs preferentially on under-coordinated Au sites forming well defined Au/MoO_x interfacial sites active for RWGS. Au and AuMo sites were quantified from FTIR spectra of adsorbed CO collected at sub-ambient temperatures. Addition of Mo to the reference Au catalyst produced a decrease in the CO uptake indicating that the original number of Au sites decreased by addition of Mo. The site measurements, in conjunction with the RWGS reaction rates, were then used to estimate the rate contributions from each site. The rate for each catalyst was calculated from the following equation:

$$R_{\text{total}} = S_{\text{Au}} R_{\text{Au}} + S_{\text{AuMo}} R_{\text{AuMo}} \quad (1)$$

Here S_{Au} is the total number of Au sites per gram of catalyst as measured by FTIR-CO measurements. Similarly, S_{AuMo} represents the number of AuMo sites (interfacial sites), as determined from the change in the amount of adsorbed CO relative to Au/SiO₂. R_{Au} and R_{AuMo} are the turnover rates (mole CO produced per mole of Au or AuMo site per minute) relevant to each site. The turnover rates on the Au and AuMo_x interfacial sites were measured to be 1.0 min⁻¹ and 14 min⁻¹ in the dark conditions and 4.4 min⁻¹ and 63 min⁻¹ under the light conditions.

Visible light irradiation of the catalyst caused a decrease in the apparent activation energy from 80.2 ± 3.9 kJ/mol to 55.5 ± 3.1 kJ/mol and 67.5 ± 1.3 kJ/mol to 38.7 ± 1.9 kJ/mol with visible light irradiation over Au/SiO₂ and Au₁Mo_{0.1}/SiO₂, respectively. Visible light irradiation

increased the reaction rate 4.7-4.8 times at 573 K for all Au catalyst containing different amounts of Mo.

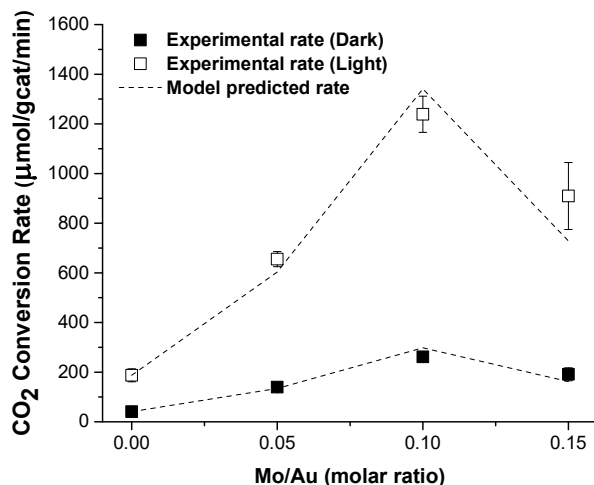


Figure 1. RWGS at 573 K and 8.1 bar of H₂:CO₂ (2:1) for Au/SiO₂ and AuMo_x/SiO₂. Dots and dashed lines indicate experimental and model predicted rates, respectively.

Conclusions

We prepared and tested well-defined Au catalysts containing different amounts of Mo by CSR in RWGS reaction. The concentration of under-coordinated Au and AuMo_x interfacial sites on these catalysts was quantified using FTIR and scanning transmission electron microscopy (STEM). The rate per AuMo_x interfacial site is an order of magnitude greater than the rate per Au site under both dark and light conditions. Visible light addition to the catalyst increased the catalyst activity for RWGS by 4.7-4.8 times by LSPR. The apparent activation energy for the RWGS reaction changed with visible light irradiation over Au/SiO₂ and AuMo_x/SiO₂ catalysts.

Acknowledgments

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