

Deactivation mechanisms in gold based low temperature water gas shift catalysts

Christopher Hardacre,^{1,*} R. Burch,¹ Y. Chen,¹ A. Goguet,¹ F. Meunier,¹ P. Hu,¹ R.W. Joyner,¹ N. Maguire,¹ B.S. Mun,² S.O. Shekhtman,¹ D. Thompsett,³ D. Tibiletti¹

¹CentACat and School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, UK; ²ALS, Berkeley Lab, 1 Cyclotron Rd, Berkeley, CA 94720 USA; ³Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK

*c.hardacre@qub.ac.uk

Introduction

Although recent results on gold supported CeO₂ based supports^{1,2,3,4} have displayed promising results for the WGS reaction, there is a difficulty in preparing highly active gold catalysts which do not deactivate.⁵ For these systems the deactivation has been associated with the formation of carbonates⁶ or formates,⁷ the sintering of Au⁴ and the loss of oxide surface area.⁸ However, there has been no consensus, to date. We have demonstrated that the active site of gold in a range of Au/CeZrO₄ catalysts is likely to be associated with the interface between gold clusters and the oxide support.⁴ The present paper reports on the use of *in situ* EXAFS, DRIFTS, high pressure XPS coupled with DFT calculations to elucidate the mechanism by which these highly active Au/CeZrO₄ catalysts for low temperature WGS deactivate.

Materials and Methods

The activity of a 2wt% Au/CeZrO₄ catalyst for the WGS reaction was tested between 100 and 450 °C (2.0% CO, 2.5% CO₂, 7.5% H₂O, 8.1% H₂ in N₂ – GSV: 40 L g⁻¹ h⁻¹) in an apparatus, detailed elsewhere.⁹ *In situ* EXAFS was performed in a glass reaction cell using similar conditions as for the catalytic tests. High pressure XPS was performed on station 9.3.2 at the ALS under 400 mTorr total pressure with a ratio of CO:CO₂:H₂O:H₂ of 1:1:1:1. TAP characterization was carried out using a TAP-I using a CO multipulse experiment. The *in-situ* DRIFTS experiments were carried out as described previously.¹⁰

Results and Discussion

Excellent low temperature WGS activity was found for the 2% Au/CeZrO₄ catalysts with the equilibrium conversion reached at ~200 °C. However, on increasing the WGS reaction temperature above 250 °C, significant deactivation was observed with the temperature for 50% conversion rising from 140 °C to 220 °C. A similar decrease in activity was also observed if the temperature was maintained at 200 °C with the catalyst showing a gradual deactivation over a period of 30 h. The rate of deactivation was determined by the water content and under high humidity (>10% water) rapid loss of activity was found. Using a CO multipulse characterization of the catalyst, TAP was employed to study the number of active sites and the rate constants for CO removal. Over the 2% Au/CeZrO₄ catalyst the results mimicked the WGS activity results with a large drop from apparent rate constant between 250 and 300 °C from 2000 s⁻¹ to 1000 s⁻¹.

EXAFS of the fresh catalyst showed that the local structure around the gold is dominated by the presence of oxygen co-ordination at ~ 2 Å which is consistent with bond distances found in a gold oxide. Additional features at 3-4 Å were also found and were fitted to cerium

co-ordination in the second shell. Under the WGS reaction conditions, the *in-situ* EXAFS showed that the gold transforms into Au⁰ state forming metallic clusters of ~ 50 atoms. Importantly, despite the change in activity of the catalyst on thermal cycling no agglomeration of the metal particles was observed and the 1st shell co-ordination remained at ~ 6. From the XANES data, on exposure to air at 150 °C following WGS at 100 °C, significant reoxidation occurred with 15% of the gold found to be reoxidisable. Exposure to higher temperatures under WGS conditions (350 °C) followed by exposure to air at 150 °C showed that less gold can be reoxidised (<5%). High pressure XPS on the 2% Au/CeZrO₄ catalyst under reaction conditions at 150 °C and 300 °C also showed the presence of Au⁰ in good agreement with the XANES. However, at higher temperature a 50% decrease in intensity of the gold 4f XPS peaks was observed. *In-situ* DRIFTS studies also indicated that the Au⁰ is where the CO adsorbs. Under WGS conditions a single band at 2096 cm⁻¹ was found which has previously been assigned to a CO-Au⁰ species.¹¹ This feature is found to reduce in intensity with increasing reaction time.

Both thermal and hydrothermal deactivation mechanisms are thought to be the result of the Au particle dewetting and the loss of metal-support interaction. This is in excellent agreement with DFT results which indicate that the presence of surface hydroxyl groups destabilise gold clusters and that, even in the absence of hydroxyls, the gold cluster-support interaction is less favourable than gold-gold interactions.

Significance

Low temperature WGS catalysis is important for the production of clean hydrogen; however, these systems need to have long lifetimes and need to be robust in terms of changes in temperature and gas composition. This study has identified where improvements in the catalyst design need to be achieved if such systems are to be used commercially. Furthermore, this is the first comprehensive experimental and theoretical investigation of the structure/function relationship for gold catalysts.

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