

Microscopy Insights into Deactivation Mechanism of Au/CeZrO₄ for Low-Temperature Water-Gas Shift Reaction

He, Q.¹, Liu, X.², Carter, J.¹, Althahban, S.³, Nowicka, E.⁴, Freakley, S.¹, Niu, L.⁵, Morgan, D.¹, Li, Y.⁵, Niemantsverdriet, J.⁵, Golunski, S.¹, Kiely, C.³ and Hutchings, G.¹

¹ Cardiff University, United Kingdom, ² The Synfuels China Laboratory for Fundamental Catalysis, China, ³ Lehigh University, United States, ⁴ Technische Universität Berlin, Germany, ⁵ Synfuels China Technology Co., China

The low-temperature water-gas shift (LTS) reaction has seen renewed interests in recent years as a method of removing CO concentration in the reformat stream for fuel cell applications. Au/CeZrO₄ was found to be one of the most active catalysts for this reaction, which undergoes rapid deactivation on-stream (Figure 1). Understanding this deactivation mechanism is needed for improving the catalyst stability. Unlike many other Au catalysts, such as Au/Fe₂O₃, it was reported that Au species on CeZrO₄ was stable and did not agglomerate under LTS condition, which thus cannot be the reason for deactivation. Instead, it was inferred from EXAFS and XPS that Au catalyst deactivates via "de-wetting" the oxide surface due to a hydrolysis process and thus reduces the interaction with the support. However, direct evidence for particle de-wetting was lacking and some contradictory findings on Au/CeO₂ have been reported. [1]

To get better insights into the deactivation mechanism, we use various electron microscopy techniques to study the Au/CeZrO₄ catalysts at different stages of the reaction. Ex-situ electron microscopy found that the fresh catalyst not only has nanoparticles as previously known, but also contains atomically dispersed Au species that are "invisible" in both TEM bright field imaging and Z-contrast HAADF imaging mode, due to the presence of the CeZrO₄ support. These "invisible", atomically dispersed Au species can be detected by X-ray Energy Dispersive Spectrometer(X-EDS). After use, some ultra-small nanoparticles were found that emit a similar level of X-EDS signals, suggesting that they could be formed from the atomically dispersed species during the reaction.

To see whether this agglomeration behaviour is genuine and responsible for deactivation, we carried out "stop-start" electron microscopy and followed the structure evolution of the catalyst. The catalyst sample was dispersed onto an inert SiN membrane and was treated with normal LTS conditions. This allows same sample area to be studied at different stages of the reaction. The representative HAADF images are shown in Figure 1(a). The highlighted area appears to have no Au particles in the fresh state, and a few small 1-2 nm particles emerge after the N₂ heat treatment, which is needed in the LTS process for heating up the catalyst to the reaction temperature (225°C). This suggests us that the atomically dispersed species are already converted into small nanoparticles before the reaction. These smaller particles continue to agglomerate as the reaction carries on. While some larger particles (image insets) remains largely unchanged during the process. These findings have at least two significances: (1) it suggested that the atomically dispersed Au species found in the fresh catalyst may not be participating the LTS reaction, as they were probably converted before the LTS starts; (2) agglomeration of nanoparticles indeed take place in this particular catalyst system, and cannot be ruled out for deactivation mechanism.

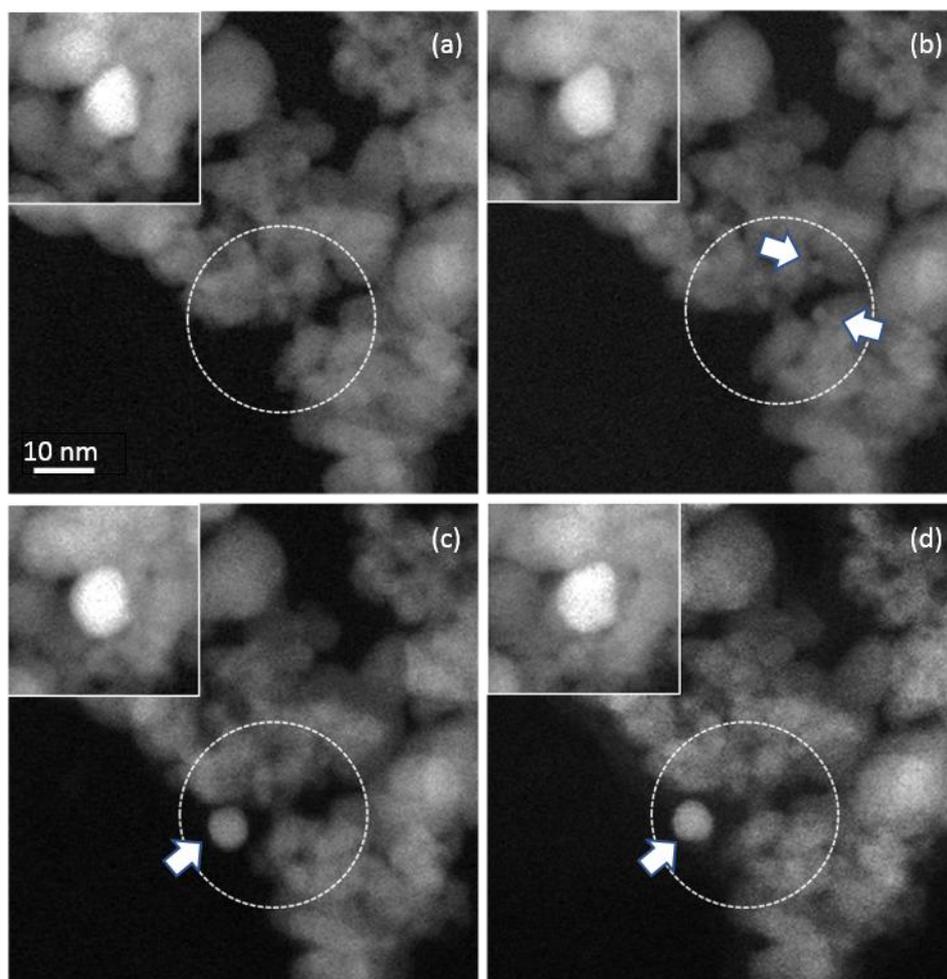


Figure 1. "Stop-Start" STEM-HAADF images of the same region in a 2wt% Au/CeZrO₄ catalyst at different stages of the LTS reaction: a) fresh catalyst; b) after the heat ramp under N₂; c) under the LTS reaction condition for 5 mins and d) after 12 h on-stream. The area was highlighted to show the evolution of Au species. Au nanoparticles were highlighted using white arrows.

References:

[1] Carter, James H., et al. "Activation and Deactivation of Gold/Ceria - Zirconia in the Low-Temperature Water - Gas Shift Reaction." *Angewandte Chemie International Edition*, 2017, **56**(50), 16037-16041.

Acknowledgements

The authors would like to acknowledge the European Research Council grant: After the Goldrush ERC-2011-AdG-291319. X.L. acknowledges financial support from Syngaschem BV, Synfuels China Technology Co., Ltd., and the National Natural Science Foundation of China (NSFC Grant No. 21673273). C.J.K. gratefully acknowledges funding from the National Science Foundation Major Research Instrumentation program (GR# MRI/DMR-1040229). S.A. was supported by a Saudi Arabian student fellowship.