In situ study of the deactivation of single-site gold catalyst during acetylene hydrochlorination using synchrotron radiation

Grazia Malta,[a] Simon J. Freakley,[a] Simon A. Kondrat,[b] Christopher J. Kiely[c] and Graham J. Hutchings[a]

[a] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK*
[b] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK*
[c] *Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania, PA 18015, USA*
**Corresponding author: maltag@cardiff.ac.uk*

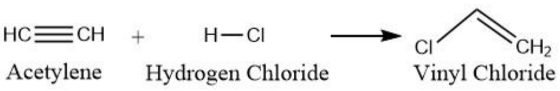
Abstract: The recent validation of gold catalysts for the acetylene hydrochlorination reaction to produce vinyl chloride monomer (VCM) is leading to the first large scale application of a Au catalyst.[1] In this study, we have performed an in situ and operando study of the deactivation of gold on carbon catalyst for the acetylene hydrochlorination reaction using X-ray Absorption Spectroscopy (XAS) analysis and in situ X-ray Powder Diffraction (XRD) in order to understand the possible deactivation patterns for gold on carbon catalyst for the acetylene hydrochlorination reaction. Transmission electron microscopy (TEM) and have been also performed.

Keywords: Gold catalyst, Deactivation, Acetylene Hydrochlorination.

1. Introduction

Vinyl chloride monomer (VCM) is a major commodity chemical and it is the key material to produce Polyvinyl chloride (PVC). VCM production started already in early 1900s with the direct hydrochlorination of acetylene (Scheme 1) traditionally catalyzed by carbon-supported mercuric chloride.

After the Minamata Convention on Mercury 2013, the use of mercury for the VCM production is prohibited.[2] Following the prediction of Hutchings in 1985,[3] Au supported on carbon has recently been validated as a replacement catalyst for this large scale industrial process.[1] To definitively identify the nature of the Au species under reaction conditions for this industrially relevant reaction, we recently performed for the first time an operando x-ray absorption fine structure (XAFS) experiment to characterize a series of gold on activated carbon catalysts under operating conditions.[4]



Scheme 1. Hydrochlorination of acetylene to vinyl chloride monomer.

This study will provide new details of the nature of the active catalyst, studying its deactivation in situ.

2. Experimental (or Theoretical)

We prepared a 1 weight % (wt.%) and a 2wt.% gold on activated carbon catalysts by wet impregnation of the $HAuCl_4$ precursor dissolved in aqua regia (named respectively 1% Au/C-AR and 2% Au/C-AR). These materials have been characterized by in-situ X-ray Powder Diffraction (XRD) to monitor the thermal stability. While, to obtain information about the gold oxidation state and the bonding environment around the gold atoms, we performed in situ X-ray absorption fine structure (XAFS) experiments at the Au L_3 absorption edge, (B18 beamline of Diamond Light Source, Harwell, UK). Ex-situ HAADF-STEM characterizations have also been performed to furtherer enforce our interpretations.

3. Results and discussion

An in situ XRD study of the 1% Au/C catalyst was performed to check the thermal stability of this material (Figure 1). The catalyst has been heated up to 350 °C under inert gas. The dispersed Au(III)/Au(I) species showed high thermal stability from ambient temperature up to 250 ºC. On reaching 300 °C, reflections

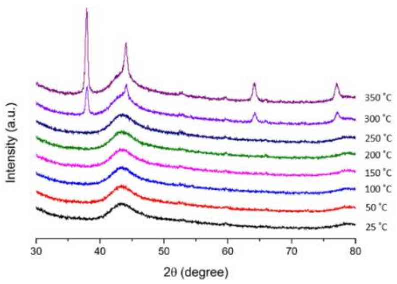


Figure 1. In situ X-ray powder diffraction patterns of the 1% Au/C-AR.

corresponding to (111), (200), (220) and (310) Au lattice planes were clearly visible, suggesting the presence of discrete Au nanoparticles, showing the thermal decomposition of Au(III) and Au(I) species into the thermodynamically favored metal nanoparticles.

To clarify the influence of the single reactants, we performed a sequential flow experiment. After reaching the steady state conditions we exposed the catalyst to only HCl diluted in argon [HCl/Ar].

The XAFS spectra recorded showed no contribution from Au(0), in contrast with a recent reported behavior,[5] and, upon reintroduction of the reaction mixture, the catalyst did not show any sign of deactivation.

Once we reached the steady state condition, the catalyst was exposed to dilute acetylene [C_2H_2/Ar]. In the near EXAFS the loss of oscillation that can be attributed to the displacing of chlorine by the acetylene, strongly suggesting the formation of Au-C_2H_2 species.

Finally, the reaction mixture was re-introduced resulting in a decrease in VCM productivity. Acetylene, and the possible formation of gold acetylide species, can be so considered as a vector for deactivation.

Because we showed already the high thermal stability of 1%Au/C-AR catalyst under reaction condition, we decide to perform an in situ XAFS characterization of a 2% Au/C-AR catalyst. During the time-on-line, a decrease in white-line has been observed due the increase of the contribution of the Au(0). The EXAFS show for the first time the appearance of a Au-Au signal (Figure 2a). Because XAFS is a global averaging technique, we performed TEM analysis to further interpret this result. TEM images show the material is still comprise of atomically dispersed gold atom but also gold nanoparticles that were not detected in the fresh material (Figure 2b).

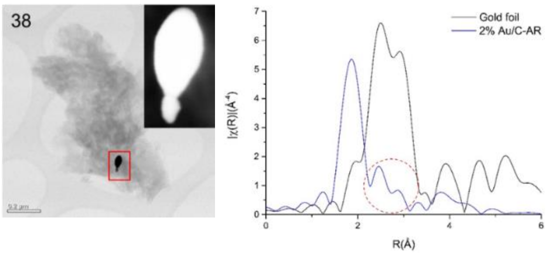


Figure 2. a) Representative TEM image of the used 2%Au/C-AR catalyst. b) In situ EXAFS Fourier transform of the same catalyst compared to the refence material (Gold foil)

4. Conclusions

In this study, the role of reactants was taken into consideration in the deactivation mechanism of gold on carbon catalyst *via* an in situ XAFS sequential gas flow experiment. A very interesting result was obtaining while flowing only C_2H_2/Ar. In this case an unusual Au species was observed in XANES spectrum, and the EXAFS Fourier transform indicates the acetylene displacement of chlorine ligands. This gold-acetylene species is also shown to be a vector for the catalyst deactivation.

Test performed on high metal loading catalyst (2%Au/C-AR) allow to observe the in-situ deactivation of the catalyst due to the formation of inactive nanoparticles. The formation of Au(0) under reaction conditions could be directly correlated with a decrease in VCM productivity.

Finally, we reaffirm that in situ XAFS is important for studying the properties of this single site Au catalyst under various gas compositions and during deactivation.

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