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

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Vinyl chloride monomer (VCM) is a major commodity chemical with over 30 million tons produced annually; ca. the 90% of the VCM production is used in the manufacture of polyvinyl chloride (PVC). One of the main routes for the production of VCM is the direct hydrochlorination of acetylene, a single step process, traditionally catalysed by carbon-supported mercuric chloride. In 2013, the “Minamata convention on mercury”, prohibited the use of mercury in VCM plants constructed after 2017, while the already existing reactors must be mercury-free by 2022. Following the prediction of Hutchings in 1985, Au supported on carbon has recently been validated as a replacement catalyst for this large scale industrial process. Even though it was predicted and demonstrated in 1985 that gold supported on activated carbon is the most active catalyst for the acetylene hydrochlorination reaction, so far, the absence of operando studies of the acetylene hydrochlorination reaction has hindered the understanding of these systems.

In this study, the nature of the active species in carbon-supported gold catalysts has been investigated using X-ray Absorption spectroscopy (XAS) and Transmission Electron Microscopy (TEM). We show that the active species comprise single-site cationic Au entities. In particular, during the time online studies, distinct changes in the X-ray Absorption Near Edge Structure (XANES) were observed (Figure 1 A), which clearly correlate to the reaction profile. This observation, together with the analysis of the Extended X-ray Absorption Fine Structure (EXAFS) and supported by TEM, lead us to the conclusion that the active site for this reaction is a supported gold cation, including both Au (I) and Au (III), showing analogies with the single-site homogeneous catalysis. The role of reactants was also taken into consideration in the deactivation mechanism of gold on carbon catalyst via an in situ XAS sequential gas flow experiment. Finally, tests performed on high metal loading catalyst allow to observe the deactivation of the catalyst due to the formation of inactive nanoparticles (Figure 1 B).

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.

Figure 1. A) Three-dimensional profile plot of successive Au L₃ edges from XANES spectra acquired in situ as a function of reaction time. B) In situ EXAFS Fourier transform of the same catalyst compared to the reference material (Gold foil)

References

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