

Structural-activity relationships of Au based catalysts for the carbonylation of methanol to acetic acid and methyl acetate: Identification of the active sites.

Alexandre Goguet^{a,*}, Y. Saih^a, K. Narasimharao^a, C. Hardacre^{a,*}

^a CenTACat, Queen's University Belfast, Belfast BT9 5AG, U.K.

* Author for correspondence: C. Hardacre@qub.ac.uk; A.Goguet@qub.ac.uk

Introduction

Carboxylic acids and esters such as acetic acid and methyl acetate are important industrial chemicals involved in the manufacture of a variety of intermediary and end-products and many research efforts has been devoted in finding catalysts for the carbonylation of lower alkyl alcohols, such as methanol, and ethers to their corresponding carboxylic acids and esters (See eqn. 1-3).



Although, the homogeneous liquid phase catalytic carbonylation of methanol is well documented [1], several heterogeneous catalytic formulations have also been investigated.[2-6] Recently, gold supported on carbon has been found to be very active and selective for the reaction of carbonylation of methanol to acetic acid or methyl acetate.[7] A 1% Au/C was demonstrated as being as active as and more selective than its iridium counterpart, previously regarded as the most active and selective available catalytic metallic phase. Therein, the high activity of the commercial gold catalyst was only achieved after an induction period of about 60 hours. This induction period has been shown to be reduced using a World Gold Council (WGC) 1% Au/C catalyst which displayed similar activity and selectivity results but only required 5 hours before reaching full activity. In the present work we report on the in-situ XAS structural characterization of the WGC catalyst to identify the nature of the active site and the origin of the induction period observed. XRD, XPS and TEM characterizations of the WGC and the commercial catalyst were also performed to clarify the difference in induction period time between the two catalysts.

Materials and Methods

Catalytic tests were carried out in a fixed-bed tubular stainless steel reactor using 500 mg of 1% Au/C catalyst. The reaction conditions were: 240 °C; 17.2 bara; H₂ flow 25 ml min⁻¹; CO flow 100 ml min⁻¹; Methanol / CH₃I ratio 70/30 liquid flow 12 ml h⁻¹. XAS measurements were performed at the SRS, Daresbury Laboratory on station 9.3. at the gold L_{III} edge using an in-situ cell. XAS data was recorded for the fresh catalyst under air at RT and after exposition of the catalyst to the full reaction mix. Due to the strong X-ray absorption of the CH₃I, it was not possible to take data under high pressure conditions and, therefore, after exposure, the reaction was quenched by replacing the reactant mix by He and by rapidly decreasing the pressure and temperature. *Ex-situ* XRD measurements were performed at room temperature on the fresh and used using a PANalytical X'PERT PRO MPD X-ray diffractometer. Au 4f photoelectron spectra were taken using a Kratos AXIS Ultra DLD XPS spectrometer. TEM analysis was performed on Tecnai F20 Transmission Electron Microscope.

Results and Discussion

The EXAFS data obtained are summarized in table 1. Significant changes in the gold are observed after reaction. The fresh catalyst only exhibits gold-gold distances with the XRD showing metal particles ~12 nm. On exposure to the reaction condition a reduction in Au...Au coordination number is found. Moreover, the analysis of the data clearly indicates the presence of iodine near the gold with a Au...I distance of 2.54 Å. This indicates that when contacted with the CH₃I containing reaction mix at 240 °C and 16 bar, the gold underwent a re-dispersion by formation of gold iodide compounds,. In the case of the commercial catalyst, the fresh catalyst showed much larger particles of ~28 nm. This lower dispersion of the catalyst leads to the large induction period observed on stream. Whilst dissolution of the gold in the commercial catalyst, significant reaction time is required (>24 h) before the gold-gold coordination approaches that of the WGC catalyst on stream. The final state of the catalyst is similar in each case with the active form of the catalyst thought to correspond gold dimers/trimers surrounded by iodine atoms. Further characterizations of the catalysts by XPS and TEM where consistent with these results.

Table 1: Structural parameters from the fitted EXAFS spectra for the two 1%Au/C.

Catalyst	Reaction Time / h	Atom	Distance/Å	CN
Au ^{WGC} /C	As received	Au	2.85	12.0
		Au	4.06	6.0
	After reaction	I	2.54	0.9
		Au	2.85	0.9
Au ^{commercial} /C	As received	Au	2.86	12.0
		Au	4.06	6.0
	After reaction	I	2.55	1.0
		Au	2.87	1.0

Significance

In the present study the active site of gold based catalysts for the carbonylation of methanol has been identified as dimers/trimers of gold with the iodide being critical for the activation of the catalyst and to maintain the catalyst in the active form. In a wider context, this study shows that it may be possible to reactivate gold catalysts after reaction. The practical application of gold based catalytic systems is often limited due to low stability (metal sintering, loss of metal-support interaction). Treatment using methyl iodide may provide an opportunity to reactivate them through metal redispersion.

References

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