Catal Lett (2008) 124:165–167
DOI 10.1007/s10562-008-9583-5

Reactivation of a Carbon-supported Gold Catalyst for the Hydrochlorination of Acetylene

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Received: 1 April 2008 / Accepted: 15 April 2008 / Published online: 22 July 2008

Abstract Acetylene hydrochlorination using a carbon-supported gold catalyst is studied. Reactivation of the catalyst is demonstrated using a brief treatment of the spent catalyst with boiling aqua regia and the process of reactivation and deactivation is characterised using X-ray photoelectron spectroscopy. Deactivation is considered to be due to loss of Au^{3+} which is restored by the aqua regia treatment.

Keywords Gold catalysis · Catalyst reactivation · Acetylene hydrochlorination

1 Introduction

The hydrochlorination of acetylene is the process in which hydrogen chloride reacts with acetylene to give vinyl chloride. It has been operated as a commercial process for many years using carbon-supported $HgCl_2$ as catalyst [1, 2]. However, its use has largely been superseded by the oxychlorination of ethene, since acetylene is mainly available from coal derived processes and ethene from oil derived processes. Given the preponderance of chemical processes that are now based on oil-derived feedstocks, it is not surprising that acetylene hydrochlorination currently only accounts for a few percent of the total world production of vinyl chloride. However, this trend may be reversed as the demand for the acetylene based process may increase as the focus on deriving hydrocarbons from coal sources increases again.

A major problem with the supported $HgCl_2$ catalyst is rapid deactivation due to the volatility of $HgCl_2$ under reaction conditions [1]. Previously, it has been shown that supported gold catalysts are more active and exhibit a higher stability [3–7]. However, supported gold catalysts were also observed to deactivate and at the reaction temperature (ca. 180 °C) this was due to reduction of the active gold species Au^{3+} to Au^0 [7]. A detailed Mössbauer spectroscopy study [7] showed that treatment of the deactivated catalyst in aqua regia oxidized Au^0 to Au^{3+}, however, at that time we did not investigate this as a method of off-line catalyst reactivation. Since gold is not lost from the catalyst during use, an off-line reactivation may provide a simple method to reuse catalyst charges without the need for recovery of the gold. In this brief paper we report how a supported gold catalyst can be successfully reactivated using a treatment with aqua regia; thereby demonstrating a unique facet of gold catalysis that a catalyst can be totally reactivated by boiling in aqua regia.

2 Experimental

2.1 Catalyst Preparation and Characterisation

The carbon-supported gold catalyst (1 wt% Au/C) was prepared using an incipient wetness impregnation technique and aqua regia as solvent. The carbon (Aldrich, Darco 12–20 mesh) was initially washed with dilute aqueous HCl (1 mol L^{-1}) at 70 °C for 5 h to remove Na, Fe and Cu that are poisons for the hydrochlorination reaction [8]. The carbon was filtered and washed with distilled water (2 L g^{-1}) and dried at 140 °C for 18 h. A solution of $HAuCl_4 \cdot xH_2O$ (Strem, 82 mg, assay 49.7%) in

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aqua regia (3.7 mL) was added dropwise to the acid-washed carbon (Aldrich, Darco 12–20 mesh, 4 g) with stirring. The product was then dried at 140 °C for 18 h and used as a catalyst.

X-ray photoelectron spectroscopy spectra were recorded on a Kratos AXIS-Ultra spectrometer, using a monochromatic AlK_{α} X-ray source (75–150 W) and an analyser pass energy of 160 eV (survey scans) or 20 eV (detailed scans). Binding energies are referenced to the C(1 s) binding energy of carbon taken to be 284.7 eV.

2.2 Catalyst Testing

Catalysts were tested for acetylene hydrochlorination in a fixed bed glass microreactor operating just above atmospheric pressure. Acetylene (5 mL min^{-1}) and hydrogen chloride (5 mL min^{-1}) were fed though a mixing vessel/preheater (70 °C) via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), giving a total GHSV of 870 h^{-1}. The pressure of the reactants, both HCl and C_2H_2 was in the range of 1.1–1.2 bar. This value was chosen both for safety reasons, and to test the catalyst under mild conditions. The products were analysed in two ways. First, the exit gas mixture was passed through a Dreschel bottle containing NaOH at known concentration for a known time to determine the conversion of HCl. Alternatively, the gas stream to be analysed by GC. A reaction temperature of 180 °C was chosen, and blank tests using an empty reactor filled with quartz wool did not display any catalytic activity, even at 250 °C with the reactants under these flow conditions.

3 Results and Discussion

We were prompted to study the effect of aqua regia on catalysts when we observed that gold is particularly difficult to remove from carbon supports using this solvent. In particular, we found that a 24 h treatment of the fresh catalyst with aqua regia with stirring at room temperature leads to relatively little removal of gold, and less than 3% of the total gold present could be removed from a standard 1 wt% Au/C. In addition, even after treating the catalyst with aqua regia under reflux for 4 h, such treatment was able to remove only around 60% of gold, with the remainder is still on the carbon. As indicated in our previous study treatment with aqua regia reoxidised a portion of the gold. For this reason it was decided to use a 1 wt% Au/C catalyst for the hydrochlorination of acetylene, and follow the reaction with time. With the standard reaction conditions selected the conversion of the acetylene was ca. 30% for the fresh catalyst. The conditions were selected so that deactivation could be readily observed as higher conversion might mask deactivation in the fixed bed reactor. After reaction for 4 h the acetylene conversion fell to ca. 22% (Fig. 1). The deactivated catalyst was then cooled in nitrogen and treated with boiling aqua regia for 20 min. This treatment led to less than 1% of gold present being dissolved in the aqua regia, so it is considered that the sample used for the second test has the same total loading as the original catalyst, i.e. 1 wt% gold. The catalyst was recovered and dried and reused as a catalyst. After treatment with aqua regia, the catalytic activity is fully recovered, and both fresh and regenerated catalysts display quite similar activity.

The catalysts were examined using X-ray photoelectron spectroscopy to detect the presence and role of different gold species. The fresh catalysts show the presence of the Au^{3+} component with a binding energy at 90 eV, but this component is not present after reaction. The signal assigned to Au^{3+} is recovered after treatment with aqua regia, and again after the second reaction the signal is missing from the spectrum (Fig. 2). It is worth noting that the effect observed is due to the reaction conditions that the catalyst is exposed to and not to the thermal treatment alone; in fact X-ray photoelectron spectroscopy data for a thermally treated catalyst in the absence of reactants for 4 h at 180 °C did not show any changes in the gold X-ray photoelectron spectrum. These results are important because they directly correlate gold oxidation state with catalytic activity confirming the previous study [7], and it is possible to state that the reduction of gold is involved in the catalyst deactivation process, or in another way, that the presence of Au^{3+} leads to a catalyst with enhanced performance. While we demonstrate that the supported gold catalyst for acetylene hydrochlorination can be achieved using an off-line reactivation with this aggressive

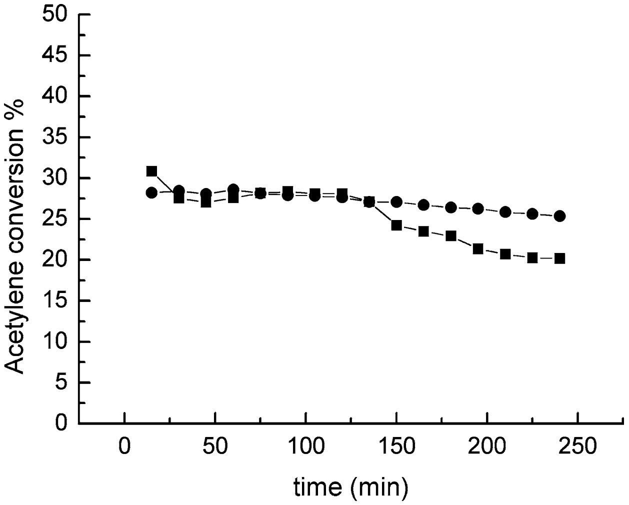

Fig. 1 Activity trend for the hydrochlorination reaction, over Au/C, (■) fresh catalyst and (●) regenerated catalyst using a short treatment with aqua regia

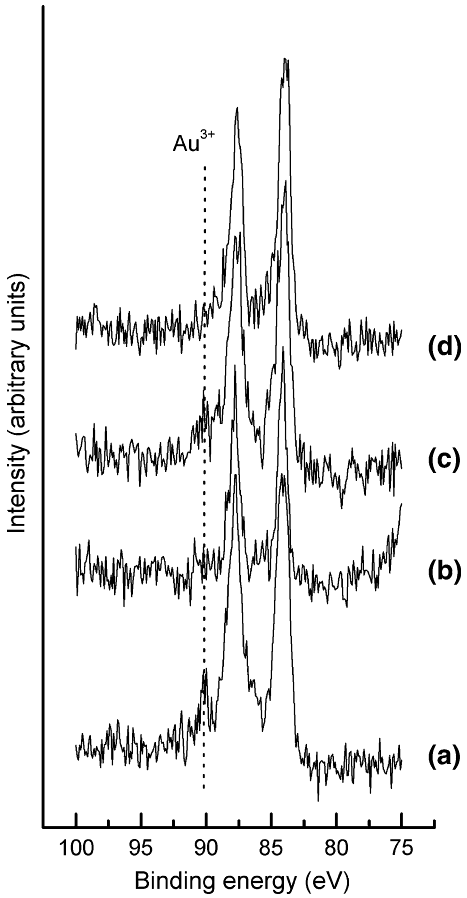

Fig. 2 Au 4f XPS spectra of Au/C catalysts, (**a**) before reaction it is possible to detect the presence of Au^{3+} while (**b**) after reaction Au^{3+} is reduced; (**c**) after regeneration it is possible to detect again the presence of Au^{3+} and (**d**) after regeneration and after the second reaction Au^{3+} is reduced

treatment, for an industrial application it is more likely that an on-line reactivation method will be preferred since this does not require removal of the catalyst from the reactor. Such on line methods include treatment with Cl_2, HCl and NO [9] although these methods require considerably longer reactivation times.

In conclusion we have shown that the carbon-supported catalyst for the hydrochlorination of acetylene can be fully reactivated by an off-line treatment with boiling aqua regia. This behaviour is, perhaps, unique for heterogeneous catalysts.

Acknowledgments We acknowledge the support of the Engineering and Physical Sciences Research Council (EPSRC) of the UK and Johnson Matthey plc (project ATHENA) and the European Union (project AURICAT; Contract HPRN-CT-2002-00174). In addition we thank the World Gold Council who have provided sponsorship for the studentship of MC under the GROW scheme.

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