

Reactivation of a Supported Gold Catalyst for Acetylene Hydrochlorination

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A novel high activity, carbon supported, gold catalyst for acetylene hydrochlorination which can be successfully reactivated by HCl treatment is reported.

Acetylene hydrochlorination is an important industrial process for the manufacture of vinyl chloride monomer (VCM) and currently *ca.* 6% of the world production is based on this process. For many years the catalyst utilised for this reaction consisted of HgCl_2 supported on activated carbon.¹ Whilst this catalyst has both high activity and selectivity, it rapidly deactivates under typical reaction conditions and this activity decay has been ascribed to loss of volatile active components (HgCl_2 , Hg) during reaction.^{2,3} Industrial catalysts therefore have to be replaced periodically, which can be a major cause of lost production capacity. Recently we proposed⁴ a correlation between catalytic activity for this reaction and the standard electrode potential of the metal, and on this basis predicted that Au-based catalysts should be superior to the current HgCl_2 catalysts. Here we present results which confirm that Au is a most effective catalyst for acetylene hydrochlorination. The major problem of steady decline in activity on use has received scant attention to date. We have successfully addressed this problem and report a facile HCl reactivation procedure which is highly effective for Au-based catalysts.

Catalysts were prepared by adsorption of metal chlorides from aqueous solution (70 °C, 5 h) onto Sorbonorit-3 activated

carbon. In a typical experiment, catalyst (2 g) was dried *in situ* in a pyrex fixed bed reactor (N_2 , 80 °C, 0.5 h) and then treated with C_2H_2 -HCl (1 : 1.1 molar ratio) at a total gas hourly space velocity (GHSV) of *ca.* 1100 h^{-1} . Unreacted HCl was

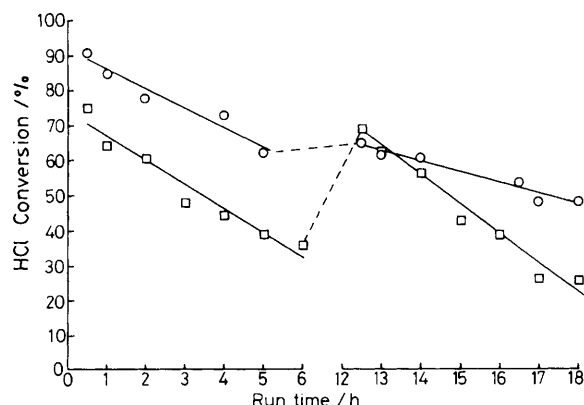


Figure 1. Effect of HCl treatment on deactivated catalysts. --- denotes HCl treatment (GHSV 580 h^{-1} , 180 °C, 6 h); \square HAuCl_4 -C (2% Au); \circ HgCl_2 -C (9% Hg).

Table 1. Catalytic performance of acetylene hydrochlorination catalysts.

Catalyst	Metal /% by mass	GHSV /h ⁻¹	Initial activity ^a	HCl conversion/% at reaction time (min)				
				30	60	120	240	300
HgCl ₂ -C	1.9	1180	3.5 × 10 ²	44.4	39.3	32.8	21.5	16.0
HgCl ₂ -C	9	1210	1.5 × 10 ²	91.0	85.0	77.5	72.5	61.9
HAuCl ₄ -C	2	1190	5.4 × 10 ²	75.2	64.5	60.3	44.6	39.0

^a Extrapolated to zero reaction time, mol HCl converted/mol metal/h.

removed from the reactor effluent by scrubbing with aqueous NaOH and analysed by back titration to determine HCl conversion. The gases were subsequently analysed by gas chromatography to determine product selectivity.

Comparison of catalyst activity (Table 1) indicates clearly that on either a molar or mass basis, Au-based catalysts are more active for acetylene hydrochlorination, confirming our previous correlation.⁴ Selectivity for VCM was >99% for all catalysts examined. All catalysts steadily deactivated with increased reaction time, but no deterioration in catalyst selectivity was observed. Following reaction, the 9% HgCl₂-C and 2% HAuCl₄-C catalysts were treated with HCl (GHSV *ca.* 580 h⁻¹, 180 °C, 6 h) and the treated catalysts were subsequently re-reacted with C₂H₂-HCl as before. Typical results are shown in Figure 1 and these clearly show that HCl treatment successfully restores almost full activity to the 2% HAuCl₄-C catalyst, whilst being totally ineffective for the 9% HgCl₂-C catalyst. Gold based catalysts were successfully operated for a number of deactivation/reactivation cycles with no major deterioration in catalyst performance being observed. In addition, catalyst selectivity was not affected by the reactivation procedure.

The results may have significance with respect to the reaction mechanism. Correlation of catalytic activity with the standard electrode potential is indicative of a redox cycle

involving the metal. In the case of the HgCl₂-C catalyst the formation of Hg would lead to deactivation due to loss of the volatile metal and indeed metallic Hg is observed in traps downstream from the reactor, and analysis of the catalyst following reaction confirmed that *ca.* 25% of the Hg had been lost on use. Volatilisation of gold metal is much less likely (as was confirmed by analysis of catalysts before and after use) and in this case deactivation is thought to be caused by lack of gold re-oxidation to the active oxidation level during reaction. HCl treatment in the absence of acetylene facilitates this re-oxidation process, but other treatments may also be effective and further studies are continuing in our laboratories.

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