

# PLATINUM-COPPER SINGLE ATOM ALLOYS AS CO-TOLERANT SELECTIVE HYDROGENATION CATALYSTS

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## Abstract

The single atom alloy (SAA) strategy is employed here to design PtCu catalysts, which were prepared both as model single crystal surface and nanoparticle catalysts by physical vapor deposition and galvanic replacement methods, respectively. PtCu SAA catalysts were found to be highly selective for butadiene hydrogenation to butene under mild operating conditions and resistant to CO poisoning.

## Keywords

Single atom alloys, Platinum, Copper, Hydrogenation, CO tolerance

## Introduction

Bimetallic nanoparticles are widely investigated for catalytic applications. SAAs as a limiting case of a bimetallic catalyst offer an attractive prospect to study the activity and selectivity, while if the minority phase is a platinum group metal (PGM), to also decrease the cost of an industrial catalyst dramatically (Kyriakou, G. *et al.*, 2012). Group IB noble metals are known for their high selectivity but low activity for hydrogenation of alkynes and dienes (Segura, Y. *et al.*, 2007). As demonstrated by scanning-tunneling microscopy (STM) and temperature programmed desorption and catalytic experiments (TPD/R), PGMs are capable of dissociating and spilling over hydrogen to the group IB metal area (Kyriakou, G. *et al.*, 2012). Boucher and coworkers have shown that alloying of a trace amount of palladium in copper increases the activity of the latter markedly (Boucher, M. B. *et al.*, 2013). Here we examine PtCu SAAs for the selective hydrogenation of 1,3 butadiene and CO tolerance.

## Results and Discussion

We show that Pt atoms exist as isolated atoms that are well separated from one another on the Cu nanoparticle surface (Figure 1). The PtCu SAAs were formed in low Pt-content nanoparticles (Pt<sub>0.1</sub>Cu<sub>14</sub>/Al<sub>2</sub>O<sub>3</sub>, 0.1 at% Pt and 14 at% Cu on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support), as demonstrated by the lack of Pt-Pt interaction in EXAFS investigation performed at room temperature at the Pt-L<sub>III</sub> edge. The PtCu first shell interaction distance was between the Pt-Pt and Cu-Cu bond lengths which is consistent with alloy formation. As shown in Figure 2, the hydrogenation activity of PtCu SAA catalyst was significantly improved compared to monometallic Cu sample, while high selectivity to butenes was maintained. The reaction rate over the PtCu SAA catalyst at 70 °C was an order of magnitude higher than for monometallic Cu, while both had high selectivity (nearly 90%) to butenes at full conversion.

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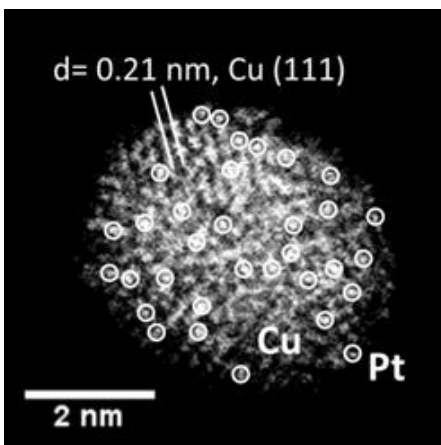


Figure 1. Scanning transmission electron microscopy image of PtCu SAA nanoparticle where the Pt atoms exist as isolated atoms in the Cu lattice.

We also found the PtCu SAA is more CO-tolerant in both UHV and ambient pressure conditions. The CO-TPD shows a CO desorption peak from Pt/Cu(111) SAA at least 50 K below that of Pt(111). Corroborating evidence from CO adsorption performed with concomitant FTIR on PtCu SAA nanoparticle catalysts suggests weaker Pt-CO binding on the PtCu SAA compared to monometallic Pt nanoparticles. In  $H_2/D_2$  exchange tests, HD production characterizes the  $H_2$  dissociation activity of the catalysts. Much higher HD production rate with CO in the gas phase was obtained on PtCu SAA (Figure 3), which demonstrates the CO tolerance of PtCu SAAs in the realistic catalytic conditions.

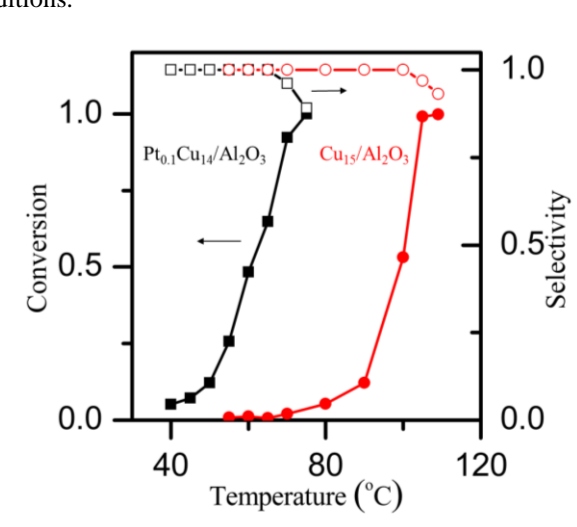


Figure 2. Selective hydrogenation of butadiene as a function of temperature over  $Cu_{15}/Al_2O_3$  and  $Pt_{0.1}Cu_{14}/Al_2O_3$  (SAA), (1, 3-butadiene (1.25%),  $H_2$  (20%) and He (balance).  $WHSV=0.09 h^{-1}$ ).

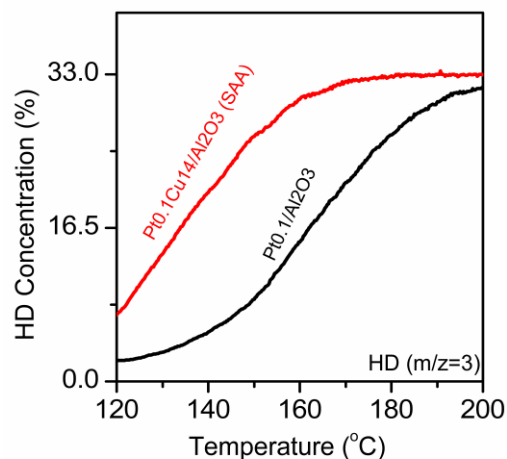


Figure 3.  $H_2$ - $D_2$  exchange as a function of temperature in 33%  $H_2$ , 33%  $D_2$ , 667ppm CO, balance Argon. The total flow rate is 50 ml/min. Each sample was pre-reduced in  $H_2$  at 350 °C ( $Pt_{0.1}Cu_{14}/Al_2O_3$ ) or 400 °C ( $Pt_{0.1}/Al_2O_3$ , 0.1 at% Pt on  $\gamma$ - $Al_2O_3$  support).

## Conclusions

The PtCu SAAs were studied in both model catalyst surfaces and nanoparticles. For the nanoparticle study, the addition of trace amounts of Pt to the Cu nanoparticles significantly improves the hydrogenation activity of the latter without loss of selectivity. Moreover, the highly CO-tolerant feature of PtCu SAA catalysts was demonstrated.

## Acknowledgments

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