Pd-Promoted Selective Gas Phase Hydrogenation of *p*-Chloronitrobenzene over Alumina supported Au

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Introduction

Halogenated aromatic amines have multiple applications in the manufacture of pesticides, herbicides, pigments, pharmaceuticals and cosmetics [1]. However, existing routes produce toxic by-products with low overall product yields, and there is now a pressing demand for a cleaner, i.e. more selective, synthesis. We have recently demonstrated that the gas phase hydrogenation of *p*-chloronitrobenzene over Au supported on alumina and titania [2] was 100% selective in terms of $–NO_2$ group reduction to *p*-chloroaniline. However, the level of *p*-chloronitrobenzene conversion was appreciably lower than that delivered by supported Pd, which generated nitrobenzene and aniline (non-selective hydrogenation) as the principal products with a significant temporal loss of activity.

In this work, for the first time, we examine the catalytic action of Pd promoted Au/Al_2O_3 ($Au/Pd \geq 8$) in the selective reduction of *p*-chloronitrobenzene to *p*-chloroaniline. We also assess the feasibility of increasing hydrogenation rate, while maintaining exclusivity in terms of $–NO_2$ reduction, by controlling Au particle size during catalyst preparation and compare two distinct synthesis routes.

Materials and Methods

Monometallic Au (1 wt%) and Pd (0.03 wt%) and bimetallic Pd-Au (1 wt% Au, $Au/Pd \geq 8$) catalysts were prepared on Al_2O_3 support by deposition-precipitation with urea (DP) and impregnation in excess solvent (IMP). The samples were activated in H_2 at 573 K (Au/Al_2O_3) or 773 K (Pd/Al_2O_3 and $Pd\text{-}Au/Al_2O_3$). The catalysts were characterized by TPR, H_2 chemisorption, TEM and DRIFTS combined with CO adsorption. *p*-Chloronitrobenzene hydrogenation (1% v/v *p*-chloronitrobenzene/H_2; $GHSV = 2 \times 10^4$ h^{-1}) was carried out under atmospheric pressure at $T = 393$ K in a continuous fixed bed glass reactor. The initial fractional conversion x_0, which is a measure of initial activity, was extracted from fit convergence of the temporal variation of activity. A pseudo-first order kinetic treatment was used to determine hydrogenation rate constants.

Results and Discussion

The gas phase hydrogenation of *p*-chloronitrobenzene was investigated first over monometallic Au-DP and Au-IMP catalysts. Both Au catalysts were 100 % selective in terms of $-NO_2$ group reduction, resulting in the sole formation of *p*-chloroaniline. Au-DP, which exhibited a smaller mean Au size (2.9 nm) compared with Au-IMP (4.5 nm), delivered a higher specific hydrogenation rate (by a factor of 14) (Figure 1). Bimetallic Pd/Au-DP and Pd/Au-IMP with Au/Pd mol/mol = 20 and 88 exhibited a significant increase (by up to a factor of 3) in activity compared with Au/Al_2O_3, with the exclusive conversion of *p*-chloronitrobenzene to *p*-chloroaniline. At a lower ratio (Au/Pd = 8), nitrobenzene was also produced as a result of a Pd catalysed hydrodechlorination step. Under the same reaction conditions, Au+Pd physical mixtures of monometallic catalysts (Au/Pd = 20) delivered higher reaction rates, but with the formation of nitrobenzene and aniline, ***i.e.*** products of hydrodechlorination and hydrogenation.

DRIFTS measurements using CO as a probe molecule showed that in the case of the Pd-Au samples, the contribution of multi-bonded CO on Pd was reduced compared with Pd catalysts. A geometric effect, due to the formation of bimetallic Pd-Au nanoparticles and surface Au-Pd interaction (which is consistent with TPR and H_2 chemisorption results), and resulting in a decrease in the size and/or the number of Pd ensembles required for multiple bonding can account for this response.

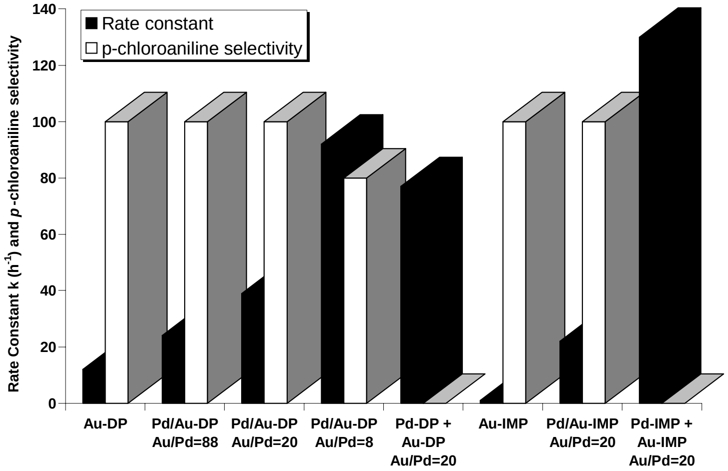

Figure 1. Pseudo-first order initial rate constants (k) and *p*-chloroaniline selectivity (at the same initial fractional conversion, $x_0 \sim 0.12$) for the hydrogenation of *p*-chloronitrobenzene over mono- and bimetallic catalysts and monometallic physical mixtures..

We attribute the enhanced and exclusive production of *p*-chloroaniline over the supported bimetallics with $Au/Pd \geq 20$ to a surface Pd-Au synergism. Our results establish the viability of Pd-promotion in the selective continuous gas phase catalytic hydrogenation of *p*-chloronitrobenzene over supported Au.

References

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