Journal of Catalysis 262 (2009) 235–243

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Pd-promoted selective gas phase hydrogenation of *p*-chloronitrobenzene over alumina supported Au

Fernando Cárdenas-Lizana [a], Santiago Gómez-Quero [a], Antoine Hugon [b], Laurent Delannoy [b], Catherine Louis [b], Mark A. Keane [a,*]

[a] *Chemical Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland*
[b] *Laboratoire de Réactivité de Surface, UMR 7609 CNRS, Université Pierre et Marie Curie-Paris 06, 4 Place Jussieu, 75252 Paris Cedex 05, France*

ARTICLE INFO

Article history:
Received 18 November 2008
Revised 22 December 2008
Accepted 23 December 2008
Available online 22 January 2009

Keywords:
p-Chloronitrobenzene
Selective hydrogenation
p-Chloroaniline
Au/Al_2O_3
$Pd–Au/Al_2O_3$
DRIFTS analysis
TPR
H_2 chemisorption

ABSTRACT

The gas phase hydrogenation of *p*-chloronitrobenzene has been investigated over alumina supported Au (ca. 1%, w/w) prepared by deposition-precipitation with urea (DP) and impregnation in excess solvent (IMP). Both catalysts were 100% selective in terms of $–NO_2$ group reduction, resulting in the sole formation of *p*-chloroaniline. Au–DP exhibited a smaller mean Au size (2.9 nm) compared with Au–IMP (4.5 nm) and delivered a higher (by a factor of 14) specific hydrogenation rate. Bimetallic $Pd–Au/Al_2O_3$ catalysts have also been prepared by DP and IMP with Au/Pd mol/mol = 8, 20 and 88. Catalyst activation by temperature programmed reduction has been monitored and the activated catalysts characterized in terms of H_2 chemisorption, TEM analysis and DRIFTS. DRIFTS measurements using CO as a probe molecule suggest the presence of bimetallic particles and surface Au–Pd interaction. A significant increase (by up to a factor of 3) in activity was observed for $Pd–Au/Al_2O_3$ ($Au/Pd \geqslant 20$) compared with Au/Al_2O_3 where the exclusive conversion of *p*-chloronitrobenzene to *p*-chloroaniline was maintained. At a lower ratio (Au/Pd = 8), nitrobenzene was produced as a result of a Pd catalyzed hydrodechlorination step. Under the same reaction conditions, $Au/Al_2O_3 + Pd/Al_2O_3$ physical mixtures (Au/Pd = 20) delivered higher reaction rates but with the formation of nitrobenzene and aniline, i.e. products of hydrodechlorination and hydrogenation. We attribute the enhanced and exclusive production of *p*-chloroaniline over the supported bimetallics 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.

1. Introduction

Halogenated aromatic amines, with multiple applications in the manufacture of pesticides, herbicides, pigments, pharmaceuticals and cosmetics, are commercially important target products [1]. Existing routes, notably the Bechamp process (Fe promoted reduction in acid media), produce toxic by-products with low overall product yields [2] and there is now a pressing demand for a cleaner technology. We have recently demonstrated that the gas phase hydrogenation of *p*-chloronitrobenzene over Au supported on alumina [3,4] and titania [4] was 100% selective in terms of $–NO_2$ group reduction to *p*-chloroaniline over a prolonged (up to 80 h) time on-stream. 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 [3]. Indeed, two possible reaction pathways are associated with the hydrogenation of *p*-chloronitrobenzene [3,5], as shown in Fig. 1. Path A involves hydrodechlorination to nitrobenzene, which can be further hydrogenated to aniline *via* the nitrosobenzene intermediate. In Path B, the $–NO_2$ group is initially hydrogenated to yield the target product (*p*-chloroaniline), which can undergo subsequent hydrodechlorination to aniline. Both mechanisms have been reported for gas and/or liquid phase catalytic operation over supported metals [3,6–13]. Dechlorination at high conversions is a feature of reactions promoted by supported Ni [7,8], Pd [11,14], Pt [12,13,15], Ru [16], bi-metallic La–NiB [9], Pd–Ru [10], Pd–Pt [10], Pt–M (M = Cr, Mn, Fe, Co, Ni and Cu) [17] and Pt–M (M = Sn, Pb, Ge, Al, Zn) [18] catalysts. Xu et al. [19] have reported that the incorporation of Sn^{4+} in Pd/Al_2O_3 served to limit the degree of *p*-chloronitrobenzene dechlorination in batch liquid reaction and attributed this effect to interaction between Sn^{4+} and the $–NO_2$ group that increased the polarity of the N=O bond and promoted reduction. However, higher conversions of *p*-chloronitrobenzene were accompanied by a decrease in selectivity to *p*-chloroaniline. The main goal of our work is to direct the reaction along Path B,

---

* Corresponding author.
E-mail address: m.a.keane@hw.ac.uk (M.A. Keane).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2008.12.019

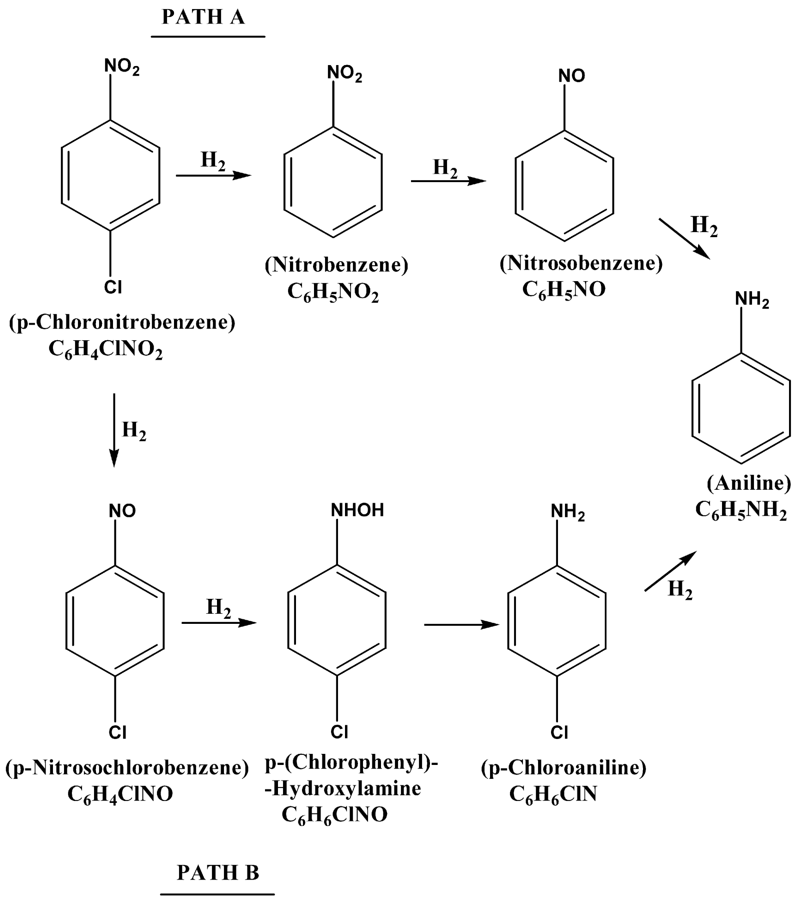

Fig. 1. Reaction pathways associated with the hydrogen mediated conversion of *p*-chloronitrobenzene.

elevating the level of *p*-chloroaniline production without the formation of aniline in continuous flow operation.

Catalytic hydrogenation over supported Au has been proposed to depend on the preparation method [20], metal particle size/morphology [21] and support surface chemistry [22]. The optimum supported Au particle size is still a matter of some debate but it is commonly accepted that, in order to achieve high activity, the presence of particles smaller than ca. 5 nm is crucial. An increase in Au dispersion, with a consequent decrease in Au particle size, increases the proportion of surface low coordination sites on which H_2 can dissociate [23,24]. Nevertheless, there is some evidence of a lower limit in terms of Au particle size (ca. 2 nm), below which activity decreases due to quantum effects [25,26]. The ultimate degree of dispersion is dependent on catalyst synthesis and Okumura et al. [27] obtained, in the case of (ca. 1%, w/w) Au/Al_2O_3 prepared by deposition-precipitation (DP) and impregnation (IMP), an order of magnitude difference in the mean Au diameter (DP = 3 nm, IMP = 37 nm). Grisel et al. [28] also recorded an appreciably smaller Au particle size (3–5 nm) by DP synthesis when compared with IMP. Catalytic activity may also be enhanced through the use of promoters, which can serve to modify the electronic properties of the active site [29]. In the case of Au catalysis, the number of studies that have considered the use of promoters in hydrogenation reactions is very limited but we can flag the work of Gluhoi et al. [30,31] who demonstrated enhanced activity in NO reduction over Al_2O_3-supported combinations of Au with CeO_x and LiO_2, ascribing the promotional effect of the metal oxides to the formation of small and thermally stable Au particles. Moreover, Nutt et al. [32] reported enhanced activity in the hydrogen mediated dechlorination of C_2HCl_3 over Au–Pd/Al_2O_3 when compared with Pd/Al_2O_3 which they attributed to Au/Pd interactions, an effect that extended to unsupported Au/Pd nanoparticles [33].

With a view to elevating the catalytic activity of Au, we have considered the possible role of Pd, with high activity in gas phase $-NO_2$ group reduction [3,5,34–36], as a promoter. In this paper, we examine, for the first time, the catalytic action of Pd promoted Au/Al_2O_3 ($Au/Pd \geqslant 8$) 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 IMP and DP as two distinct synthesis routes.

2. Experimental

2.1. Catalyst preparation and activation

The monometallic Au and bimetallic Pd–Au catalysts were prepared by deposition-precipitation (DP) with urea [37] and impregnation (IMP) in excess solvent using Al_2O_3 (AluC Degussa, 110 $m^2\,g^{-1}$) as support. In the case of the DP synthesis, a suspension of the support (3 g) in distilled water (100 cm^3) was placed in an ultrasound bath in order to disperse the support particles. The suspension was then placed in a reactor, 190 cm^3 of distilled water was added and the mixture was heated to 353 K at which point 6 cm^3 of a solution of $HAuCl_4$ (10 $g\,dm^{-3}$), corresponding to the desired Au loading (1%, w/w), was added with a ca. 100-fold excess of urea. The pH of the suspension (initially ca. 2.5) progressively increased to reach ca. 7 after 16 h. The solids obtained were separated by centrifugation, washed three times with deionized water (with centrifugation between each washing) and dried