



The role of hydrogen partial pressure in the gas phase hydrogenation of *p*-chloronitrobenzene over alumina supported Au and Pd: A consideration of reaction thermodynamics and kinetics

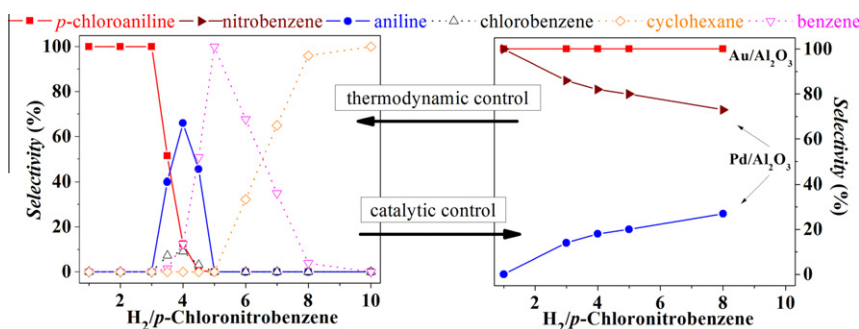
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HIGHLIGHTS

- First reported thermodynamic/kinetic analysis of *p*-chloronitrobenzene hydrogenation.
- Selective -NO_2 reduction over Au/ Al_2O_3 from excess H_2 to stoichiometric conditions.
- Pd/ Al_2O_3 activates -NO_2 and -Cl , promoting hydrogenation/hydrodechlorination.
- Coupling of Au/ Al_2O_3 and Pd/ Al_2O_3 surface characteristics with performance.
- Kinetic model that accounts for rate dependence on H_2 partial pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

The gas phase hydrogenation of *p*-chloronitrobenzene (*p*-CNB) over alumina supported Au and Pd has been subjected to thermodynamic and kinetic analyses where the H_2 partial pressure was varied from excess ($\text{H}_2/p\text{-CNB}$ up to 2300) to lean (stoichiometric) conditions. The catalysts have been characterised by temperature-programmed reduction (TPR), H_2 chemisorption/temperature-programmed desorption (TPD), BET surface area/porosity, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) measurements. Both catalysts exhibited nano-scale metal particles (mean diameter = 4.5 nm (Au) and 2.4 nm (Pd)) with the formation (from XPS analysis) of electron-rich $\text{Pd}^{\delta-}$ but no significant electron transfer between Au and Al_2O_3 . Under thermodynamic control, cyclohexane is the only product where $\text{H}_2/p\text{-CNB} \geq 10$ with product (*p*-chloroaniline, aniline, chlorobenzene, benzene and cyclohexane) dependence on $\text{H}_2/p\text{-CNB}$ in the range 1–8; at a given $\text{H}_2/p\text{-CNB}$, reaction temperature (373–473 K) has a negligible effect. Under conditions of catalytic control, Au/ Al_2O_3 generated *p*-chloroaniline as the sole product while Pd/ Al_2O_3 promoted hydrodechlorination to nitrobenzene and hydrogenation to aniline. A kinetic model is presented that accounts for the rate dependence on H_2 partial pressure, where the maximum turnover frequency delivered by Au/ Al_2O_3 (with a lower H_2 adsorption coefficient) was an order magnitude lower than that recorded for Pd/ Al_2O_3 . Adsorption of *p*-CNB on $\text{Pd}^{\delta-}$ via the aromatic ring is proposed that serves to activate both -NO_2 and -Cl for attack whereas Au/ Al_2O_3 selectively activates -NO_2 , leading to exclusive production of *p*-chloroaniline.

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1. Introduction

Catalysis plays a critical role in the chemical industry and, given pressing eco-efficient and financial demands, it is estimated that

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