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An examination of catalyst deactivation in *p*-chloronitrobenzene hydrogenation over supported gold

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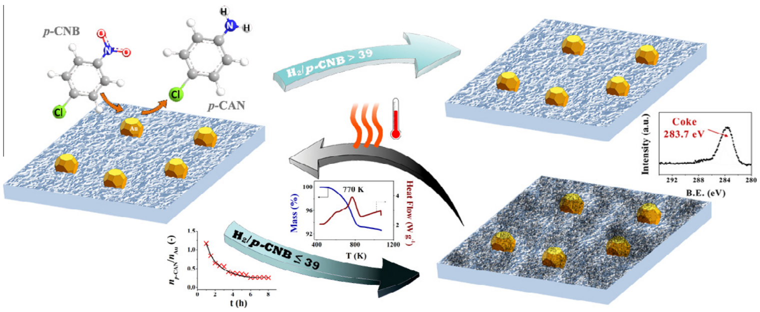
HIGHLIGHTS

- Establish deactivation of Au/Al_2O_3 in *p*-chloronitrobenzene → *p*-chloroaniline.
- Kinetic control explicitly established by parameter and experimental estimation.
- Severe deactivation at H_2/reactant $\leqslant 39$ due to coking (from XPS/TGA–DSC analysis).
- Oxidative/reduction regeneration restores initial activity and selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

The stability of Au/Al_2O_3 in the continuous gas phase (423 K) hydrogenation of *p*-chloronitrobenzene (*p*-CNB) to *p*-chloroaniline (*p*-CAN) has been investigated over an inlet H_2/*p*-CNB = 4–390, *i.e.* from close to stoichiometry to H_2 far in excess. The catalyst (activated unused and spent) has been characterised with respect to specific surface area (SSA)/porosity, temperature programmed reduction (TPR), powder XRD, H_2 chemisorption, STEM, XPS, elemental analysis and TGA–DSC measurements. Activation of Au/Al_2O_3 by TPR in hydrogen generated a narrow Au size distribution (1–8 nm, mean = 3.6 nm) with evidence (from XPS) of (support → metal) charge transfer to generate surface $Au^{\delta-}$. Exclusive *p*-CAN production was achieved under conditions of kinetic control, which were established by parameter estimation and experimental variation of contact time, catalyst particle size and *p*-CNB/catalyst ratio. A temporal decline in activity was observed that was more pronounced at H_2/*p*-CNB $\leqslant 39$. The spent catalyst exhibited equivalent SSA/porosity, Au particle size (from STEM) and electronic character (from XPS) relative to activated unused Au/Al_2O_3. A significant carbon content (6.3% w/w) was determined from elemental analysis and confirmed by XPS and TGA–DSC. This carbon deposit hindered H_2 chemisorption under reaction conditions, leading to suppressed hydrogenation activity. Catalyst regeneration by oxidative/reductive treatment resulted in a restoration of the initial hydrogenation activity, retaining exclusive selectivity to *p*-CAN.

1. Introduction

The chemical sector is experiencing a shift in emphasis from high reactant turnover to catalytic production routes that maximise selectivity to target high value products [1]. Selective

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Nomenclature

D_{eff}	effective diffusivity ($m^2\ s^{-1}$)
d_p	mean catalyst particle diameter (μm)
$D_{p\text{-CNB},H_2}$	molecular diffusivity of *p*-CNB in hydrogen ($m^2\ s^{-1}$)
d_r	reactor diameter (mm)
d_{STEM}	number weighted mean Au diameter (nm)
F	inlet *p*-CNB flow rate ($mmol\ h^{-1}$)
$GHSV$	gas hourly space velocity (h^{-1})
ΔH	enthalpy change of the reaction ($kJ\ mol^{-1}$)
k_{eff}	effective thermal conductivity of the catalyst bed ($W\ m^{-1}\ K^{-1}$)
L	catalyst bed length (cm)
Mw_i	molecular mass of compound "*i*" ($g\ mol^{-1}$)
n	reaction order (–)
n_{Au}	number of moles of Au (mol)
n_i	number of Au particles with diameter "d_i"
$n_{p\text{-CAN}}$	number of moles of *p*-CAN (mol)
P	pressure of the system (atm)
P_0	saturation pressure of N_2 at the temperature of the adsorption measurements (atm)
P_c	critical pressure (atm)
P_{H_2}	hydrogen partial pressure (atm)
r_0	initial reaction rate ($mol_{p\text{-CNB}}\ mol_{Au}\ h^{-1}$)
r_{8h}	reaction rate after 8 h on-stream ($mol_{p\text{-CNB}}\ mol_{Au}\ h^{-1}$)
Re_p	Reynolds number (–)
$S_{p\text{-CAN}}$	selectivity with respect to *p*-CAN (%)
T	temperature of the system (K)
T_c	critical temperature (K)
T_{max}	temperature of maximum H_2 consumption during TPR (K)
ΔT_{max}	maximum temperature differential in the catalyst particle (K)
TOF	turnover frequency (h^{-1})
u	superficial gas velocity ($cm\ s^{-1}$)
ν_{H_2}	kinematic viscosity of hydrogen ($cm^2\ s^{-1}$)
V_c	critical volume ($cm^3\ g^{-1}\ mol^{-1}$)
W	catalyst mass (g)
X_0	initial fractional conversion (–)
$X_{p\text{-CNB}}$	fractional conversion of *p*-CNB (–)
Z_c	critical compressibility factor (–)
Greek symbols	
β_e	Prater number (–)
σ_I	characteristic length of component "*i*" (Å)
$\sigma_{i,j}$	binary pair characteristic length (Å)
$\varepsilon_{Al_2O_3}$	porosity of Al_2O_3 support (–)
$(\varepsilon/k)_{H_2}$	Lenard-Jones potential (K)
$\rho_{Al_2O_3}$	density of Al_2O_3 support ($kg\ m^{-3}$)
τ	contact time (s)
$\tau_{Al_2O_3}$	tortuosity of the Al_2O_3 support (–)
Ω_D	collision integral (–)

production of functionalised anilines (extensively used in the manufacture of pharmaceuticals, agrochemicals and dyes [2]) from the corresponding nitro-compounds is challenging. Conventional methodologies based on the Béchamp process are obsolete due to the generation of large quantities of toxic waste (5–20 times greater than the target amine) in the form of iron hydroxide sludge, neutralisation salts and organic by-products [3]. Catalytic hydrogenation over supported transition metals represents a viable alternative but batch liquid phase reactions require elevated operating pressures (up to 40 atm [4]). A switch to continuous gas phase operation at atmospheric pressure offers clear advantages in terms of energy efficiency for high throughput. We have previously reported the selective gas phase hydrogenation of a range of substituted nitroarenes over oxide supported Au [5–8]. Reaction exclusivity to the target amine was achieved with enhanced rates over smaller Au particles (<5 nm). Targeted $-NO_2$ reduction in the presence of other reactive functionalities (*e.g.* –Cl, $-CH_3$ or –OH) in continuous operation represents a significant advance over non-selective batch and/or continuous processes using Pd [9–12], Pt [13–16], Ru [17] and Ni [18–20] catalysts. Nonetheless, despite the remarkable amine selectivity, reaction over Au catalysts is typically accompanied by a temporal loss of activity [6,21], which must be addressed in the development of a sustainable hydrogenation process.

A search through the literature failed to unearth any published study that has explicitly identified the cause(s) of Au catalyst deactivation in nitroarene hydrogenation in liquid or gas phase operation. Deactivation has been a feature of nitroaromatic (nitrobenzene [22–26] and chloronitrobenzene (CNB) [27,28]) hydrogenation over hydrotalcite [22,23,28], Al_2O_3 [23,27], SiO_2 [25], MgO [23], activated carbon [26] and kieselguhr [24] supported Pd [22,23,27], Ni [26] and Cu [24,25] and attributed to coke deposition [23–26] and/or the deleterious effects of water [22,23] generated as by-product. Vishwanathan et al. [27] reported increased resistance to coke formation during *o*-CNB hydrogenation due to alkali metal doping of Pd/Al_2O_3 but did not provide any clear rationale for this effect. It should be noted that Pietrowski and Wojciechowska did not observe any deactivation in *o*-CNB reduction at high H_2/*o*-CNB molar ratios (~265) over Ru/MgF_2 for up to 5 h on-stream [29]. In this study, we have set out to identify the source of Au catalyst deactivation, taking the selective hydrogenation of *p*-CNB over Au/Al_2O_3 as a model system. To this end, we have evaluated the effect of inlet H_2/nitroarene as a crucial process variable that affects catalyst deactivation [30].

2. Experimental

2.1. Catalyst preparation and activation

The γ-Al_2O_3 support (Puralox, Condea Vista Co.) was used as received. 1.1% w/w Au/Al_2O_3 was prepared by deposition–precipitation (DP) using urea as basification agent. An aqueous mixture of urea (100-fold excess) and $HAuCl_4$ ($4.4 \times 10^{-5}\ mol\ cm^{-3}$) was added to the support (30 g). The suspension was continuously stirred and heated at $2\ K\ min^{-1}$ to 353 K where the pH progressively increased to reach *ca.* 7 after 3 h as a result of thermally induced urea decomposition [31]. The solid was separated by centrifugation, washed with deionised water (with centrifugation between each washing) until chlorine free (confirmed by $AgNO_3$ test) and dried in He ($45\ cm^3\ min^{-1}$) at 373 K ($2\ K\ min^{-1}$) for 5 h. The catalyst was sieved (ATM fine test sieves) to a mean particle diameter (d_p) of 65 μm and stored at 277 K under He in the dark. Prior to use, the catalyst was activated in $60\ cm^3\ min^{-1}$ H_2 at $2\ K\ min^{-1}$ to 603 K, which was maintained for 1 h.

2.2. Catalyst characterisation

The Au content was measured by atomic absorption spectroscopy (Shimadzu AA-6650 spectrometer with an air-acetylene flame) from the diluted extract in aqua regia (25% v/v HNO_3/HCl). Temperature programmed reduction (TPR) and H_2 chemisorption