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Gas phase hydrogenation of nitrocyclohexane over supported gold catalysts

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ABSTRACT

We report the first continuous (gas phase) hydrogenation of nitrocyclohexane over oxide (Al_2O_3, TiO_2, CeO_2 and ZrO_2) supported Au catalysts. Thermochemical analysis has established possible thermodynamic constraints and product distribution at equilibrium. The catalysts have been characterised by temperature-programmed reduction (TPR), H_2/O_2 chemisorption/temperature-programmed desorption (TPD), BET surface area/porosity, X-ray diffraction (XRD) and scanning/transmission electron microscopy (STEM/TEM) measurements. The effects of space velocity ($2–6 \times 10^4$ h^{-1}), temperature (353 and 473 K) and H_2 partial pressure (8×10^{-4}–0.93 atm) on catalyst performance have been examined. Selectivity to the target cyclohexanone oxime is sensitive to H_2 pressure, where an increase in temperature favours cyclohexanone with amine/ketone condensation and subsequent reduction to dicyclohexylamine. An increase in turnover frequency was observed with decreasing (surface area weighted) mean Au size (from 7.0 to 4.3 nm) but a lower value was obtained for 3.0 nm Au (on CeO_2) that is linked to suppressed H_2 chemisorption (under reaction conditions) resulting from strong interaction with the partially reduced support. We establish a critical surface interplay between imine, H and –OH that governs selectivity. Au/Al_2O_3 exhibited the highest activity and oxime selectivity (maximum = 95%), Au/CeO_2 promoted near exclusive production of cyclohexanone whereas Au/TiO_2 and Au/ZrO_2 generated a cyclohexylamine/cyclohexanone mixture.

1. Introduction

Cyclohexanone oxime is commercially important as an intermediate in the production of nylon-6, which is widely used in polymer synthesis. Standard cyclohexanone oxime production from cyclohexanone is inefficient due to the low cyclohexanone yields (3–10% [1–3]) obtained in the industrial oxidation of cyclohexane. Moreover, oxime formation from cyclohexanone employs a hydroxylamine salt (usually the sulphate) where the equilibrium must be displaced with addition of ammonia to maintain pH = 7 [4], generating significant quantities of ammonium sulphate waste [5]. A controlled oxidation of cyclohexylamine (obtained from nitrobenzene hydrogenation) can produce the oxime but this necessitates extended reaction times (up to 10 days) to arrive at a 60% yield [6] with the involvement of environmentally toxic chemicals (oleum, halides and nitrogen oxides) and associated waste production [7]. Direct hydrogenation of nitrocyclohexane (NC) to the oxime represents a possible alternative [7,8]. Selectivity in NC hydrogenation is challenging as the oxime can undergo further hydrogenation to an amine (cyclohexylamine) and ketone (cyclohexanone), where the latter requires the participation of water, as shown in Fig. 1. Moreover, condensation involving cyclohexylamine and cyclohexanone can generate cyclohexylcyclohexylidene amine (CCA) with subsequent hydrogenation to dicyclohexylamine (DCA) [8].

A comprehensive search through the literature only unearthed eight reports dealing with NC hydrogenation to oxime [5,7–13]. The earliest work dates from the 1960s where a one step NC hydrogenation was reported by DuPont [9,10] in a liquid phase process operated at 413 K and elevated pressure (35 bar) using a Pd catalyst to give an oxime yield of *ca.* 70%. This work was taken further by Knifton, employing homogenous Cu(I, II) and Ag(I) catalysts with CO as reducing agent to give 89% oxime yield, where efficiency increased in the order: Ag(I) < Cu(II) ≈ Cu(I) [11,13]. There followed a 30 year period of apparent inactivity until Corma et al. [12] reported the use of Au/TiO_2 to promote the reaction in the liquid phase, achieving 91% selectivity at nearly complete NC conversion. The same group subsequently recorded 85% selectivity to the oxime over Na promoted Pt/TiO_2 [8]. A similar level of performance has also been recorded for Pd on carbon nanotubes [5]. In the sequential reaction pathway (Fig. 1), the critical challenge is to circumvent conversion of the reactive imine intermediate *via*

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Nomenclature

a_{ik}	number of atoms of the kth element present in each molecule of species i
A_k	total mole of kth element in the feed (mol)
d_{TEM}	surface area weighted mean Au particle size obtained from TEM analysis (nm)
$\hat{f}_i$	fugacity of species i in the system (atm)
f_i^0	standard-state fugacity of species i (atm)
F	inlet NC molar flow rate (mol h^{-1})
$\bar{G}_i$	partial molar Gibbs free energy of species i (kJ mol^{-1})
G^t	total Gibbs free energy (kJ mol^{-1})
G_i^0	standard Gibbs free energy of species i (kJ mol^{-1})
ΔG^0	standard Gibbs function for the molar reaction (kJ mol^{-1})
$\Delta G_{f_i}^0$	standard Gibbs function for formation of species i (kJ mol^{-1})
n	number of moles of Au in the catalyst bed
n_i	number of moles of species i
N	number of species in the reaction system
P	pressure of the system (atm)
P^0	standard-state pressure, 1 atm
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
S	selectivity (%)
Δt	time-on-stream (h)
T	temperature of the system (K)
TOF	turnover frequency (s^{-1})
x	fractional NC conversion
x_{3h}	fractional conversion after 3 h on-stream
y_i	mole fraction of species i

Greek symbols

λ_k	Lagrange multiplier
$\bar{\mu}_i$	chemical potential of species i (kJ mol^{-1})
$\hat{\phi}_i$	fugacity coefficient of species i

steps C and D. The high activation energy barrier for dissociative H_2 adsorption on supported Au can be significant in this reaction system and has been used to good effect in selective hydrogenation [14], notably in the conversion of nitroarenes [15], aldehydes [16,17], ketones [18] and 1,3-butadiene [16,19]. Shimizu and co-workers [7] have compared the performance of oxide (Al_2O_3, SiO_2, MgO and TiO_2) supported Au in NC hydrogenation where Au/Al_2O_3 exhibited the highest oxime yield (86%). The limited applications of Au catalysts in NC hydrogenation have been conducted in batch liquid phase at high pressures (up to 15 bar) where all the products presented in Fig. 1 were obtained with additional unidentified by-products [7] and ε-caprolactam [20].

In this study, we provide the first report of NC hydrogenation in continuous gas phase (at 1 atm) operation. We can flag a recent "white paper" [21], which identified a switch from batch to continuous processing as #1 priority for sustainable manufacture in the fine chemical sector. We first examine possible thermodynamic constraints and then focus on the use of Au/Al_2O_3 to probe the effect of critical process parameters, *i.e.* space velocity, temperature and H_2 partial pressure. In addition, we have studied the role of the support (Au on Al_2O_3, TiO_2, CeO_2 and ZrO_2) and identify the surface interactions that determine catalyst performance.

2. Thermodynamic analysis

Chemical thermodynamics provide a useful guide to the maximum conversion (and selectivity response) that is possible under given reaction conditions and is an essential initial consideration in the design of a catalytic process [22]. Each organic intermediate and product presented in Fig. 1 in addition to H_2, H_2O and NH_3 were considered in the thermodynamic calculations. Setting the inlet NC at 1 mol, product distribution at equilibrium was determined with varying reaction temperature (353–473 K) at a total pressure of 1 atm, where the H_2/NC molar ratio was kept constant at 2500 (a representative value that was typically employed in catalyst testing). The equilibrium calculations were carried out using CHEMCAD (Version 6) where the Gibbs reactor facility was applied to obtain product composition [23]. Two general approaches can be taken in thermodynamic equilibrium calculations, *i.e.* non-stoichiometric and stoichiometric. In the non-stoichiometric method employed in this study, the equilibrium composition of the system is found by direct minimisation of the Gibbs free energy for a given set of species without any specification of the possible reactions that might take place in the system. In the stoichiometric approach, the system is described by a group of stoichiometrically independent reactions, which are typically chosen arbitrarily from a set of possible reactions. Analysis of the system response taking arbitrarily chosen chemical reactions can lead to erroneous conclusions. The equation of state for fugacity employed the Soave–Redlich–Kwong approach [22]. The total Gibbs function is given by

$$G^t = \sum_{i=1}^{N} n_i \bar{G}_i = \sum_{i=1}^{N} n_i \bar{\mu}_i = \sum n_i G_i^0 + RT \sum n_i \ln \frac{\hat{f}_i}{f_i^0} \qquad (1)$$

For gas phase reaction equilibrium, $\hat{f}_i = \hat{\phi}_i y_i P$, $f_i^0 = P^0$ and $\Delta G^0 = \Delta G_{f_i}^0$ and the minimum Gibbs free energy of each gaseous species and total for the system can be expressed by

$$\Delta G_{f_i}^0 + RT \ln \frac{\hat{\phi}_i y_i P}{P^0} + \sum_k \lambda_k a_{ik} = 0 \qquad (2)$$

$$\sum_{i-1}^{N} n_i \left(\Delta G_{f_i}^0 + RT \ln \frac{\hat{\phi}_i y_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) = 0 \qquad (3)$$

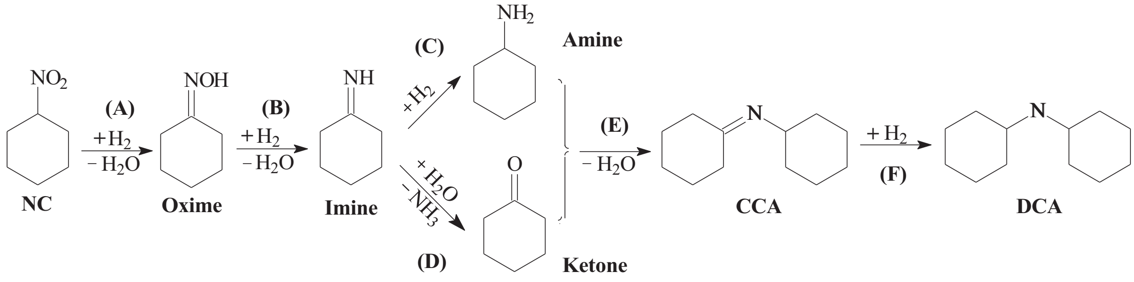

Fig. 1. Reaction pathway associated with the hydrogenation of nitrocyclohexane (NC).