

## Silica and Titania Supported Ni-Au: Application in Catalytic Hydrodechlorination

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### Introduction

For some time, we have been examining the action of supported Ni [1-3] and Pd [2,4] to promote the hydrodechlorination (HDC) of chloroarenes. This work has been directed at a low energy detoxification/recycle of chloroarene waste streams. Chloroarenes represent a class of commercially important but particularly toxic chemicals that enter the environment as industrial effluent from herbicide/biocide production plants and petrochemical units and have been targeted for some time by the Environmental Protection Agency (EPA) as “priority pollutants”. However, a temporal HDC activity decline is observed as a result of deleterious HCl/metal interactions [1-4]. We have since refocused attention on the Ni system with a view to catalyst formulations that deliver enhanced and stable HDC performance. Some consensus is now emerging from the literature that catalytic HDC is structure sensitive, dependent on metal particle size and electronic structure [2]. One approach to increase HDC activity and stability is the incorporation of a second metal that can influence particle size/dispersion and electronic properties. To this end, we have examined the catalytic action of supported Ni-Au and report here elevated 2,4-dichlorophenol (2,4-DCP) HDC that we link to critical surface characteristics.

### Materials and Methods

Ni-Au/TiO<sub>2</sub> and Ni-Au/SiO<sub>2</sub> (5 wt% Ni and Au/Ni (at.:at.) = 10) were prepared by co-impregnation (IMP) of [Ni(en)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> and [Au(en)<sub>2</sub>]Cl<sub>3</sub>. Ni-Au/TiO<sub>2</sub> was also prepared by co-deposition-precipitation (DP) with urea using HAuCl<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> as precursors. The catalysts were characterized in terms of BET area, TPR, H<sub>2</sub> chemisorption and TEM-EDX.

Before reaction, the IMP and DP catalysts were activated under dry H<sub>2</sub> at 2 °C min<sup>-1</sup> to 330 and 500°C, respectively. HDC performance was assessed over two reaction cycles at  $W_{Ni}/F_{Cl} = 500\text{-}3000 \text{ g}_{Ni} \text{ mol}_{Cl}^{-1} \text{ min}$  and  $W_{Au}/F_{Cl} = 160\text{-}1000 \text{ g}_{Au} \text{ mol}_{Cl}^{-1} \text{ min}$ , where  $W_{Ni}$  ( $W_{Au}$ ) is the mass of Ni (Au) and  $F_{Cl}$  is the inlet Cl molar flow rate. In the first cycle, after catalyst activation, the HDC reaction was conducted for 8 h at 200°C followed by a regeneration in H<sub>2</sub> at 330°C for 12 h and a second HDC cycle was then conducted for 8 h at 200°C.

### Results and Discussion

The IMP Ni/SiO<sub>2</sub> and Ni/TiO<sub>2</sub> samples possessed a similar narrow Ni particle size distribution (1-6 nm). The addition of Au to both Ni/support samples lowered the temperature requirements for Ni<sup>II</sup> reduction and suppressed H<sub>2</sub> chemisorption. The IMP Ni-Au/SiO<sub>2</sub> (10-150 nm) and Ni-Au/TiO<sub>2</sub> (2-95 nm) were characterized by a wider range of particle sizes than

the monometallic Ni catalysts and a variable surface Ni/Au atomic ratio (from <1 to 40). By comparison, Ni-Au/TiO<sub>2</sub> prepared by DP exhibited a narrower particle size (2-60 nm) and a more uniform Ni and Au surface distribution (Ni/Au from <1 to 15).

The titania based catalysts delivered significantly higher specific HDC rates and distinct HDC selectivities when compared with the silica systems (Table 1). While monometallic Au catalysts were inactive, the incorporation of Au, regardless of support or method of preparation, resulted in higher HDC activities. Hydrogen thermal treatment of the bimetallics after reaction resulted in appreciable surface reconstruction, notably a more homogeneous combination of Ni and Au in smaller particles which served to induce enhanced HDC performance in Reaction Cycle 2.

**Table 1.** Specific pseudo first order 2,4-DCP HDC rate constants and the initial selectivity to 2-CP ( $S_{2-CP}$ ), 4-CP ( $S_{4-CP}$ ) and phenol ( $S_{phenol}$ ) over the two reaction cycles.

Catalyst	Reaction Cycle 1				Reaction Cycle 2			
	k*	$S_{2-CP}$ (%)	$S_{4-CP}$ (%)	$S_{phenol}$ (%)	k	$S_{2-CP}$ (%)	$S_{4-CP}$ (%)	$S_{phenol}$ (%)
Ni/TiO <sub>2</sub> -IMP	4.6	17	8	75	3.3	18	13	69
Ni-Au/TiO <sub>2</sub> -IMP	5.2	14	6	80	8.7	10	0	90
Ni-Au/TiO <sub>2</sub> -DP	9.8	6	0	94	11.6	8	0	92
Ni/SiO <sub>2</sub> -IMP	1.3	22	0	78	1.1	23	0	77
Ni-Au/SiO <sub>2</sub> -IMP	3.2	30	0	70	7.7	13	0	87

\*  $10^4 \text{ k}^* (\text{mol}_{Cl} \text{ g}_{Ni}^{-1} \text{ min}^{-1})$

Each bimetallic exhibited higher HDC rate constants than the corresponding monometallic, suggesting a Ni-Au surface synergism that elevates HDC performance. It is tentatively proposed that the Au component serves to activate the C-Cl bond with subsequent attack from reactive hydrogen dissociated at the Ni centres. In contrast to monometallic Ni samples which exhibited irreversible deactivation with repeated use, thermal treatment of the bimetallic catalysts post-reaction served to significantly increase both the HDC rate constant and selectivity to phenol. HDC performance is sensitive to surface Ni/Au composition and is enhanced where either the method of preparation or sample treatment ensures intimate Ni-Au contact and a more homogenous surface Ni/Au composition.

### Significance

Chloroarene HDC is an alternative to disposal/incineration, offering a low energy sustainable approach to reducing the negative environmental impact associated with the activities of a broad industrial sector. The enhanced stable HDC activity recorded for Ni-Au represents a significant improvement over conventional HDC catalysts. Ni-Au bimetallics have not been studied to any great extent - the catalytic synergism that we observe can be exploited in the design of new alternative hydrogenation/hydrogenolysis catalysts to replace monometallic transition metals.

### References

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