Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supplementary Information

A hybrid nanocomposite precursor route to synthesize dispersion-enhanced Ni catalysts for the selective hydrogenation of *o*-chloronitrobenzene

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1. *Mass-transport consideration for catalysts*

For the type of autoclave used, with a stirring speed at 600 rpm, a conservative G–L mass transfer rate of hydrogen is estimated to be 0.1 s^{-1} [1]. Therefore, the hydrogen transfer rate is about 4.7 mol m^{-3} s^{-1} under a hydrogen concentration of 47 mol m^{-3} (P_{H_2} = 2.0 MPa) [2]. In the present system, the highest measured reaction rate is 0.035 mol m^{-3} s^{-1}. As a result, the bulk liquid would be 99% saturated with hydrogen, making the G–L transfer limitation highly unlikely.

The L–S interface mass transfer can be evaluated by the film model. In the absence of interphase concentration gradients in an isothermal system, the ratio ($(Ca)_{\mathrm{A}}$, Carberry number) of the observed reaction rate of species A ($R_{A_{obs}}$) to the maximum mass transfer rate of species A ($R_{A_{max}}$) should be lower than 0.1 for a first-order reaction [3]. $R_{A_{max}}$ value under L–S external mass transfer limitation can be calculated using correlations where several dimensionless numbers are involved (Reynolds, Schmidt and Sherwood) [4,5]. In the present reaction system, the calculated maximum mass transfer rates of hydrogen (A) and *o*-CNB (B) under conditions of transport control and the observed initial reaction rates of hydrogen and *o*-CNB over the catalysts are summarized in Table S1. It can be found that the Carberry number used to assure the absence of L–S mass transfer limitations for both hydrogen and *o*-CNB all are < 0.1.

The importance of internal (intraparticle) diffusion was evaluated by the Weisz-Prater criterion [6]:

$$\Phi_A = \frac{r_{A_{obs}} \rho_p (d_p / 6)^2}{D_{eff,A} \cdot C_A} < 0.15,$$

where the parameter $D_{eff,A}$ is the effective diffusion coefficient of species A in the catalyst, which is estimated using the approximation method of Wilke and Chang [7].As shown in Table S1, the calculated values of Φ with respect to hydrogen and *o*-CNB in three catalyst all are lower than 0.15, indicating that the absence of internal diffusion limitations. As a result, three CNTs-supported Ni catalysts do not present both internal and external mass transport limitations in the hydrogenation of *o*-CNB and thus the intrinsic activity of the catalysts is actually assessed under our reaction conditions.

Table S1. Estimated mass transport parameters of hydrogen (A) and *o*-CNB (B) over different catalysts.

Parameters	Ni/P-CNTs	Ni-L/P-CNTs	IM-Ni/P-CNTs
ρ_p(kg/m^3)	1000	990	1100
d_p (m)	115×10^{-6}	110×10^{-6}	120×10^{-6}
C_A (mol/m^3)	47	47	47
C_B (mol/m^3)	63.5	63.5	63.5
$\mathrm{D}_{\mathrm{eff,A}}$ (m^2/s)	1.13×10^{-9}	1.13×10^{-9}	1.13×10^{-9}
$\mathrm{D}_{\mathrm{eff,B}}$ (m^2/s)	3.05×10^{-9}	3.05×10^{-9}	3.05×10^{-9}
$R_{A_{max}}$(mol/L min)	2.3×10^{-2}	2.5×10^{-2}	1.9×10^{-2}
$R_{B_{max}}$ (mol/L min)	8.4×10^{-2}	9.3×10^{-2}	7.1×10^{-2}
$R_{A_{obs}}$ (mol/L min)	9.3×10^{-6}	2.1×10^{-3}	1.4×10^{-3}
$R_{B_{obs}}$ (mol/L min)	4.4×10^{-6}	8.6×10^{-4}	6.1×10^{-4}
$r_{A_{obs}}$ (mol/kg$_{\mathrm{cat}}$ s)	7.8×10^{-5}	1.7×10^{-2}	1.2×10^{-2}
$r_{B_{obs}}$ (mol/kg$_{\mathrm{cat}}$ s)	3.7×10^{-5}	7.2×10^{-3}	5.1×10^{-3}
$(Ca)_A$	4.1×10^{-4}	8.2×10^{-2}	7.3×10^{-2}
$(Ca)_B$	5.3×10^{-5}	9.3×10^{-3}	8.7×10^{-3}
Φ_A	5.4×10^{-4}	1.1×10^{-1}	9.7×10^{-2}
Φ_B	7.0×10^{-5}	1.2×10^{-2}	1.2×10^{-2}

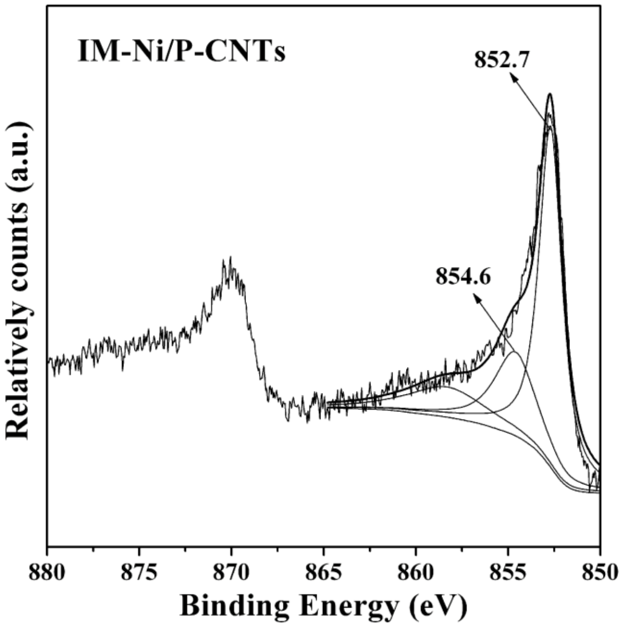

Fig. S1. XPS spectra of Ni 2p region in IM-Ni/P-CNTs.

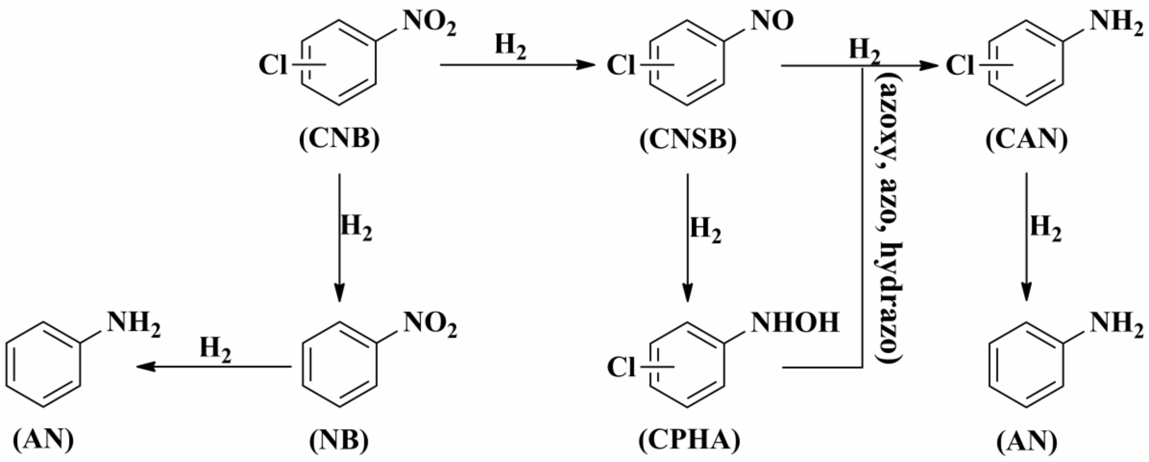

Fig. S2. Possible reaction pathways for the hydrogenation of CNB.

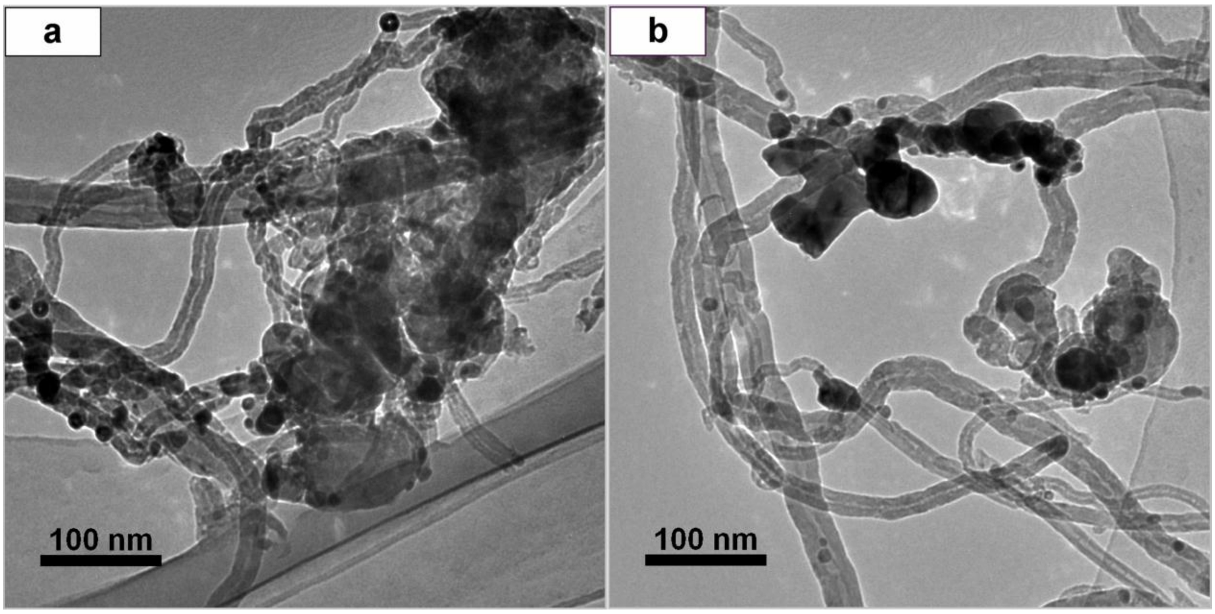

Fig. S3. TEM images of IM-Ni/P-CNTs (a,b)

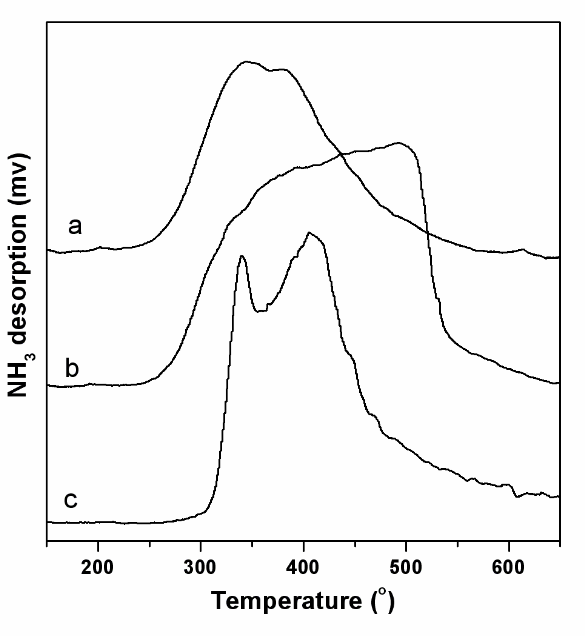

Fig. S4 NH_3-TPD profiles of Ni/P-CNTs (a), Ni-L/P-CNTs (b) and IM-Ni/P-CNTs (c)

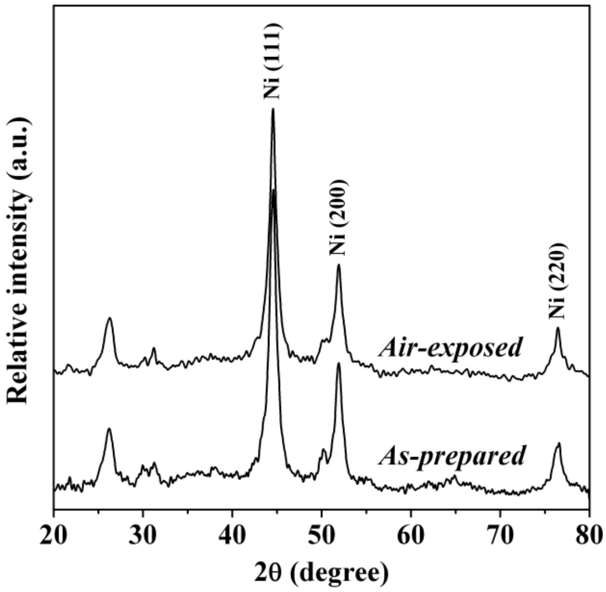

Fig. S5. XRD patterns of as-prepared and air-exposed Ni-L/P-CNTs.

References

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