Supplementary Information

Carbon-supported Ni as a low-cost, magnetically recoverable and heterogeneous catalyst for hydrodechlorination of chlorobenzene

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1. Mass-transport considerations.

For the type of autoclave used, with a stirring speed at 700 rpm, a conservative G–L mass transfer rate of hydrogen is estimated to be 0.1 s^{-1}.[1] Correspondingly, the hydrogen transfer rate is about 2.5 mol m^{-3} s^{-1} under a hydrogen concentration of 25 mol m^{-3} (P_{H_2} = 1.0 MPa).[2] In the present case, the highest measured reaction rate is about 0.17 mol m^{-3} s^{-1}. As a result, the bulk liquid would be 94% saturated with hydrogen, making the G–L transfer limitation negligible.

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 ($(Ca)_A$, 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 CB (B) under conditions of transport control and the observed initial reaction rates of hydrogen and CB over the catalysts are summarized in Table S1. Obviously, the Carberry number used to assure the absence of L–S mass transfer limitations for both hydrogen and CB all are much smaller than 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 CB in three catalysts 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 CB 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 CB (B) over catalysts.

Parameters	1Ni/C	1.5Ni/C	2Ni/C	2.5Ni/C	3Ni/C	I-Ni/C
ρ_p(kg/m^3)	1318	1453	1628	1705	1813	372.3
d_p (m)	9.5×10^{-6}	9.0×10^{-6}	8.7×10^{-6}	8.0×10^{-6}	8.1×10^{-6}	11×10^{-6}
C_A (mol/m^3)	25	25	25	25	25	25
C_B (mol/m^3)	500	500	500	500	500	500
$D_{eff,A}$ (m^2/s)	4.5×10^{-10}	4.5×10^{-10}	4.5×10^{-10}	4.5×10^{-10}	4.5×10^{-10}	4.5×10^{-10}
$D_{eff,B}$ (m^2/s)	1.61×10^{-10}	1.61×10^{-10}	1.61×10^{-10}	1.61×10^{-10}	1.61×10^{-10}	1.61×10^{-10}
$R_{A_{max}}$ (mol/L min)	1.36	1.38	1.31	1.48	1.36	3.60
$R_{B_{max}}$ (mol/L min)	9.75	9.85	9.41	10.6	9.75	25.7
$R_{A_{obs}}$ (mol/L min)	3.8×10^{-4}	1.4×10^{-3}	4.5×10^{-3}	1.0×10^{-2}	6.5×10^{-3}	2.4×10^{-5}
$R_{B_{obs}}$ (mol/L min)	3.0×10^{-4}	1.0×10^{-3}	3.0×10^{-3}	6.1×10^{-3}	4.8×10^{-3}	2.0×10^{-5}
$r_{A_{obs}}$ (mol/kg$_{cat}$ s)	3.2×10^{-3}	1.2×10^{-2}	3.7×10^{-2}	8.5×10^{-2}	5.4×10^{-2}	2.0×10^{-4}
$r_{B_{obs}}$ (mol/kg$_{cat}$ s)	2.5×10^{-3}	8.4×10^{-3}	2.5×10^{-2}	5.1×10^{-2}	4.0×10^{-2}	1.6×10^{-4}
$(Ca)_A$	2.8×10^{-4}	1.0×10^{-3}	3.4×10^{-3}	6.9×10^{-3}	4.7×10^{-3}	6.6×10^{-6}
$(Ca)_B$	3.0×10^{-5}	1.0×10^{-4}	3.2×10^{-4}	5.8×10^{-4}	4.9×10^{-4}	7.6×10^{-7}
Φ_A	9.4×10^{-4}	3.4×10^{-3}	1.1×10^{-2}	2.3×10^{-2}	1.6×10^{-2}	2.2×10^{-5}
Φ_B	1.0×10^{-4}	3.4×10^{-4}	1.1×10^{-3}	1.9×10^{-3}	1.6×10^{-3}	2.6×10^{-6}

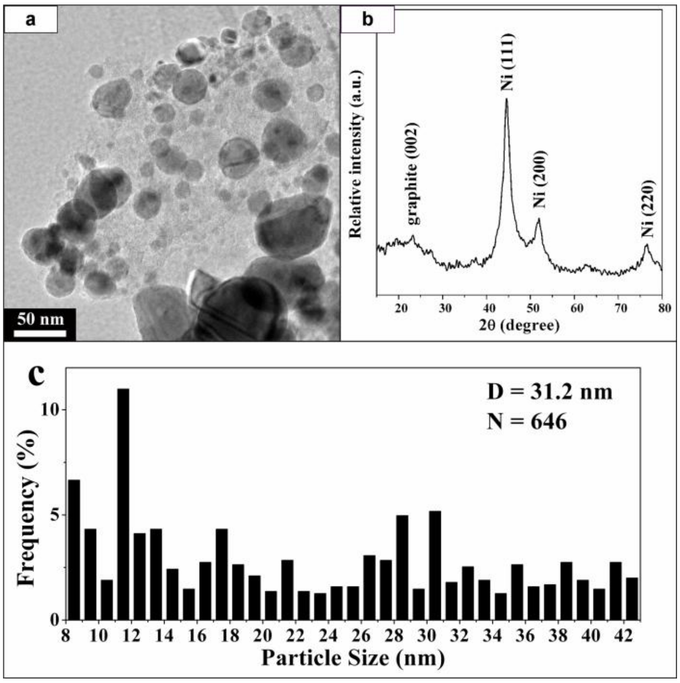

Fig. S1. TEM (a), XRD pattern (b) and histogram of the size distribution (c) of I-Ni/C.

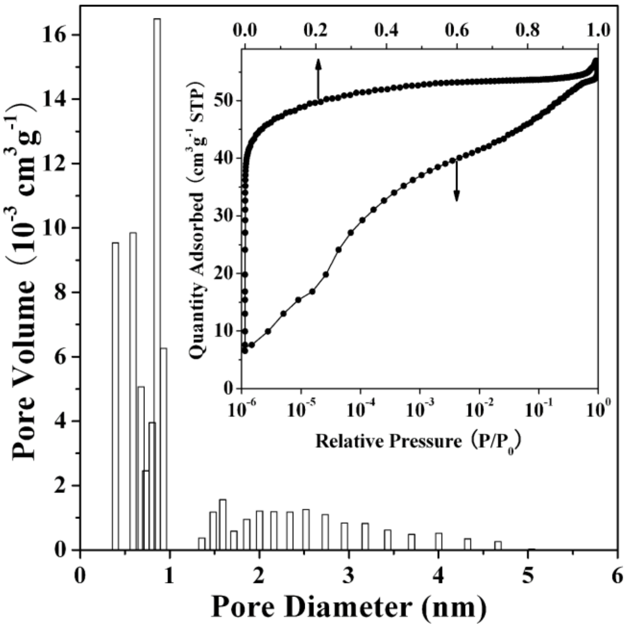

Fig. S2. DFT pore size distribution of I-Ni/C. Inset shows the nitrogen adsorption isotherm.

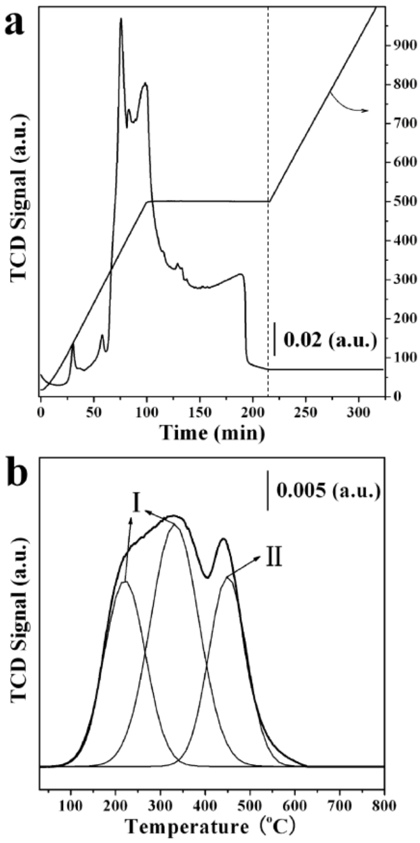

Fig. S3. TPDE profiles (a) of $Ni(NO_3)_2/C$ and H_2-TPD profiles (b) of I-Ni/C.

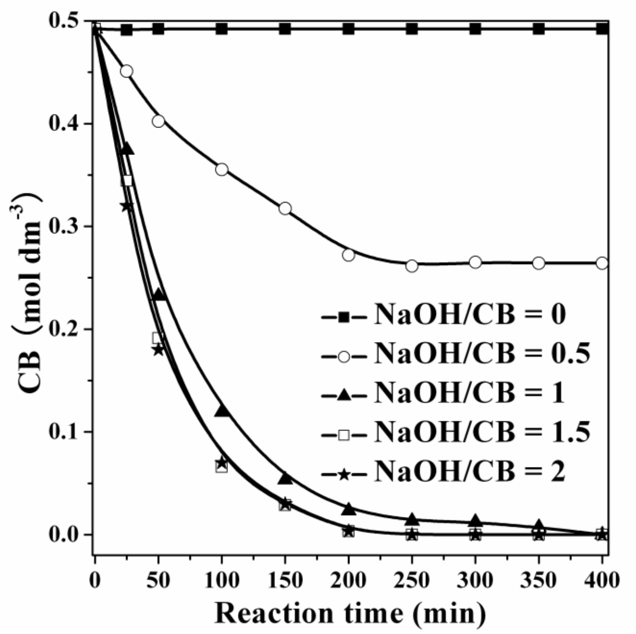

Fig. S4. Effect of NaOH/CB molar ratio on the CB concentration over 2.5Ni/C catalyst.

References

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