Catalysis Science & Technology

Electronic Supporting Information

A highly dispersed and stable Ni/mSiO$_2$-AE nanocatalyst for benzoic acid hydrogenation

Huiling Zhang[a‡], Xuejia Gao[a‡], Yuanyuan Ma[a], Xue Han[a,b] , Libo Niu[a]*, and Guoyi Bai[a]*

[a] Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P.R. China.
E-mail address: baiguoyi@hotmail.com(G. Bai), libo_niu@126.com (L. Niu);
Fax: +86-312-5937102;Phone: +86-312-5079359;

[b] Hebei Geological and Mineral Central Laboratory, Baoding 071051, People's Republic of China.
‡ the two authors contribute the same to this work.
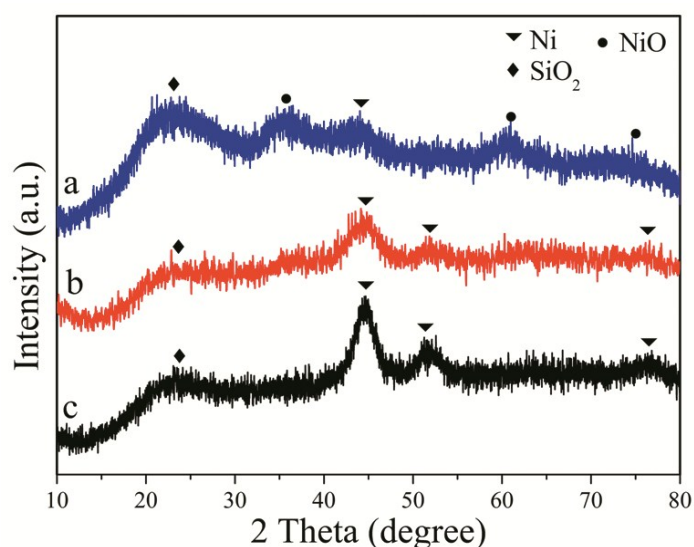
Table of Contents

XRD patterns

Fig. S1 XRD patterns of Ni/mSiO$_2$-AE reduced at different temperatures.(a. 500 °C, b. 600 °C, c. 700 °C)

XRD patterns of the Ni/mSiO$_2$-AE catalyst reduced at different temperatures are shown in Fig. S1. Notably, NiO diffraction peaks at 2θ of 37.3°, 62.9° and 75.4°, together with a broad peak of Ni^0 (at 44.5°), were found in the XRD pattern of the Ni/mSiO$_2$-AE catalyst reduced at 500 °C (Fig. R1a), indicating the partially reduction of the NiO species in Ni/mSiO$_2$-AE at 500 °C (*Appl. Catal., B: Environ.*, 2013, **132–133**, 282–292, *ACS Catal.*, 2014, **4**, 1526-1536.) However, only Ni^0 diffraction peaks at 2θ of 44.5°, 51.8° and 76.4° are found in the XRD patterns of Ni/mSiO$_2$-AE samples reduced at 600 and 700 °C (Fig. R1 b and c) (*J. Catal.*, 2012, **291**, 149–154). In addition, the characteristic diffraction peaks of Ni/mSiO$_2$-AE reduced at 700 °C are sharper than those of Ni/mSiO$_2$-AE reduced at 600 °C, indicating that larger Ni^0 nanoparticles were formed in higher reduction temperature.
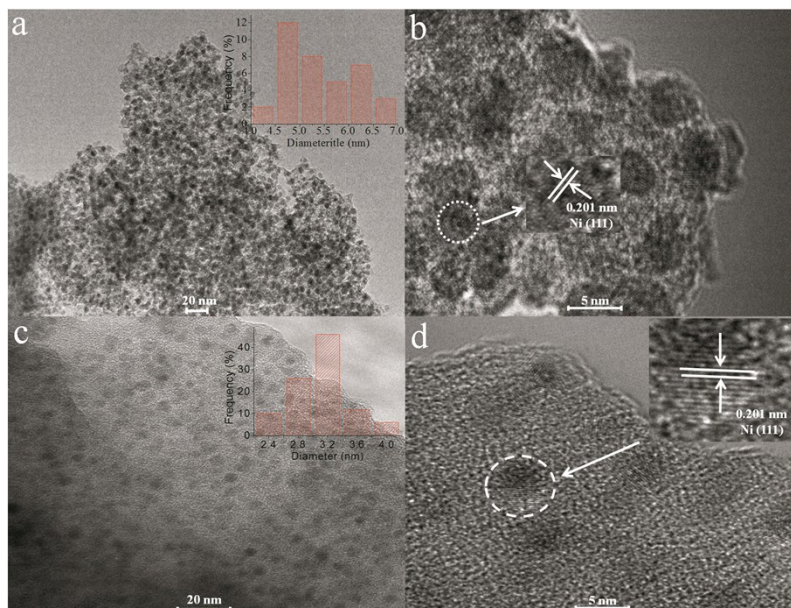
TEM image

Fig. S2 TEM images of (a) Ni/mSiO$_2$-AE (700 $^{\circ}$C), (b) HRTEM of Ni/mSiO$_2$-AE (700 $^{\circ}$C), (c) Ni/mSiO$_2$-AE (600 $^{\circ}$C) and (d) HRTEM of Ni/mSiO$_2$-AE (600 $^{\circ}$C).

TEM images of Ni/mSiO$_2$-AE (700 $^{\circ}$C) and Ni/mSiO$_2$-AE (600 $^{\circ}$C) are shown in Fig. S2. As can be seen, the mean size of nickel in Ni/mSiO$_2$-AE (700 $^{\circ}$C) is about 5.5 nm, which is about 1.7 times larger than that of Ni/mSiO$_2$-AE (600 $^{\circ}$C) (3.2 nm), in good agreement with the XRD results.

Table S1

Table. S1 Activities of catalysts reduced at different temperatures

Catalysts	Conversion (%)	Selectivity (%)
Ni/mSiO$_2$-AE(500 ^{o}C)	39.4	96.8
Ni/mSiO$_2$-AE(600 ^{o}C)	98.9	99.1
Ni/mSiO$_2$-AE(700 ^{o}C)	97.9	94.9

Reaction conditions: BA (0.5 g), catalyst (0.1 g), cyclohexane (40 mL),

T=150 ^{o}C, initial P(H$_2$) =5 MPa, reaction time 3 h.

The activities of the Ni/mSiO$_2$-AE catalyst reduced at different temperatures indicated that the Ni/mSiO$_2$-AE catalyst reduced at 600 ^{o}C exhibited similar hydrogenation performance with the catalyst reduced at 700 ^{o}C, both much higher than that of the one reduced at 500 ^{o}C. Considering the energy economy, 600 ^{o}C is selected as an appropriate reduction temperature for Ni/mSiO$_2$-AE.

Table S2

Table S2 TOF values of Ni/mSiO$_2$-AE and reported noble metal catalysts

Catalysts	Conversion (%)	TOF（h^{-1}）
Ir/γ-Al$_2$O$_3$[7]	52	40
Pd/AC[8]	92.0	5.7
Pd/CN[9]	100	0.883
Pd$_x$Ru$_y$[10]	45	----
Rh/C[11]	95.8	----
Ru$_{10}$Pt$_2$[12]	78.5	317
RuPd/CN[13]	100	2066
Ni/mSiO$_2$-AE	98.9[a]	137.4[b]

[a] Reaction conditions: BA (0.5 g), catalyst (0.1 g), cyclohexane (40 mL),
T=150 °C, initial P(H$_2$)=5 MPa, reaction time 3 h;

[b] TOF value were calculated on the basis of the number of moles of benzoic acid converted per mole of active metal per hour,
according to the literature (*Ind. Eng. Chem. Res.*, 2013, **52**, 1224).

---- There was no TOF value in this article.

Superscript 7-13 refer to the serial number of the references in the manuscript.

As can be seen, Ni/mSiO$_2$-AE showed good catalytic activities with a TOF value of 134.7 h^{-1}, much higher than those of Ir/γ-Al$_2$O$_3$[7] (40 h^{-1}), Pd/AC[8] (5.7 h^{-1}), Pd/CN[9] (0.883 h^{-1}), but lower than Ru$_{10}$Pt$_2$[12] (317 h^{-1}) and RuPd/CN[13] (2066 h^{-1}). The above results indicated that the Ni/mSiO$_2$-AE has a comparable activity with most of noble metal catalysts.