SUPPORTING INFORMATION

Mesoporous Ni-B Amorphous Alloy Microspheres with Tunable Chamber Structure and Enhanced Hydrogenation Activity

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Summary: 11 Pages; 9 Figures

Experimental procedures for sample preparation, characterization and activity test

1. Sample preparation

In a typical synthesis, 6.0 g of Brij-76 [$C_{18}H_{37}(OCH_2\text{-}CH_2)_{10}OH$], 15 ml of H_2O, 2.0 g $NiCl_2\cdot 6H_2O$ are well mixed by stirring for 120 min at 60°C. Then 2.0 ml of above-mentioned colloid solution is extruded into 20 ml KBH_4 aqueous solution through a syringe with pinhole diameter around 0.50 um. After complete reduction, the solid is washed thoroughly with H_2O and then transferred into 500 ml absolute alcohol (EtOH) to extract surfactant Brij-76 by refluxing at 348 K for 24 h. Finally, the solid product is washed with EtOH for 10 times and kept in EtOH until the time of use. The as-prepared samples are denoted as Ni-B-x-y, where x and y refer to the KBH_4 concentration and reaction temperature (K), respectively. For comparison, the regular Ni-B is also prepared by direct reduction of Ni^{2+} ions with aqueous KBH_4.

2. Characterization

The compositions of Ni-B samples are analyzed by ICP (Varian VISTA-MPX). The amorphous structure is verified by both the XRD (Rigaku D/Max-RB with CuKα) and SAED (JEOL JEM2010). Surface morphologies are observed through TEM (JEOL JEM2010). FTIR spectra are collected on a NEXUS 470 model. N_2 adsorption-desorption isotherms are measured at 77 K using a Quantachrome Nova 4000 analyzer. The pore size distribution and the average pore size are determined by using the BJH model. XPS spectra are collected on a Perkin-Elmer PHI 5000C ESCA system using Al Kα radiation. All the binding energy values are calibrated by using $C_{1S} = 284.6$ eV as a reference.

3. Activity test

In a typical run of experiments, a catalyst containing 0.50 g Ni, 50 ml CNB, and 10 ml EtOH are mixed in a 200 ml autoclave at 353 K and 1.0 MPa H_2 pressure. The reaction system is stirred vigorously (1000 rpm) to eliminate the diffusion effect. The mixture is sampled every 15 min for product analysis on a gas chromatograph (GC, Agilent 1790) under following conditions: FID detector, 2.0 m AC-5 column, injector temperature 513 K, oven temperature programmed from 373 to

513 K at a ramp of 15 K/min, and N_2 carrier gas (30 ml/min). The reproducibility of the results is checked by repeating each result at least three times and is found to be within ±5%.

The cinnamaldehyde and acetonitrile hydrogenation reactions are performed in similar ways with the reaction conditions given in Table 2.

Figures and Schemes

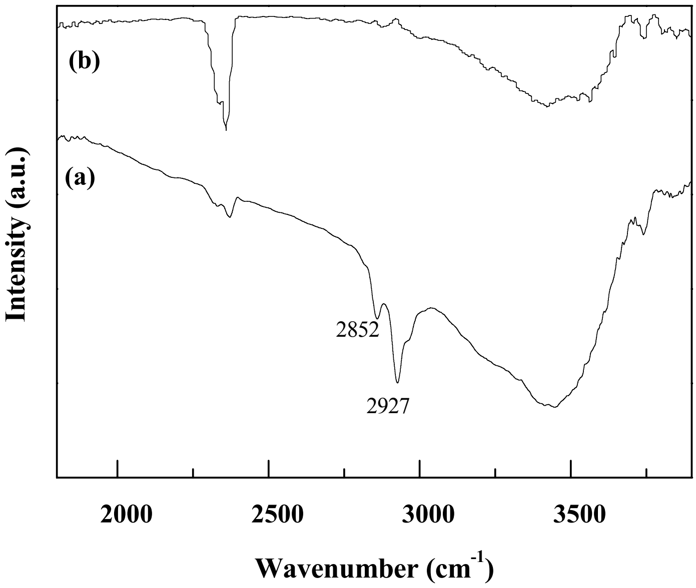


Fig. S1 FTIR spectra of the Ni-B-1-333 sample before (a) and after (b) ethanol extraction.

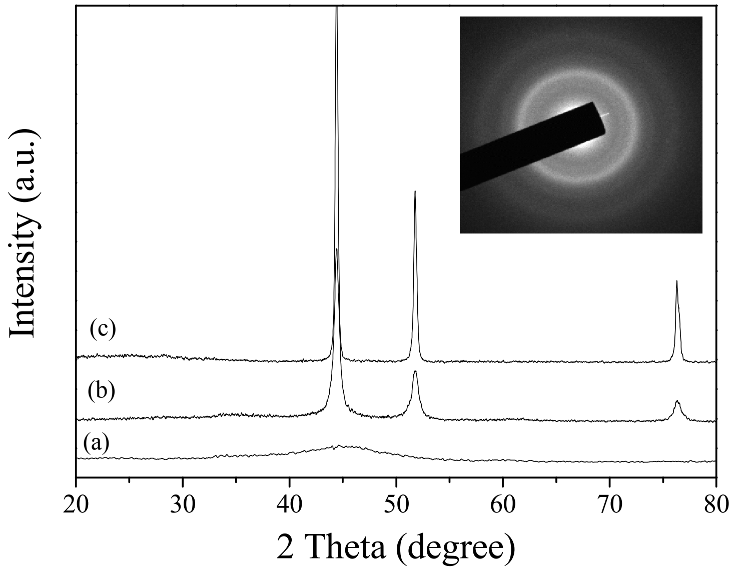
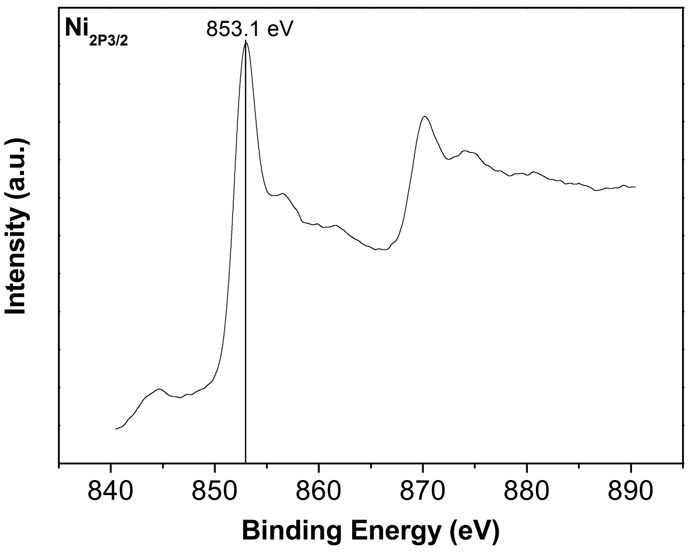


Fig. S2 XRD patterns of the Ni-B-1-333 samples. (a) as-received, (b) after being treated at 573 K in argon atmosphere for 2 h, and (c) after being treated at 873 K in argon atmosphere for 2 h. The inset is the SAED image indicative of typical amorphous structure.



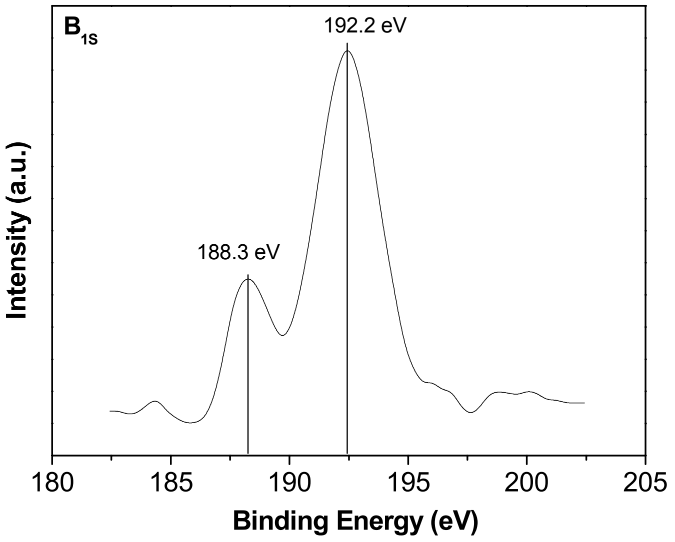


Fig. S3 XPS spectra of the Ni-B-1-333 sample solution.

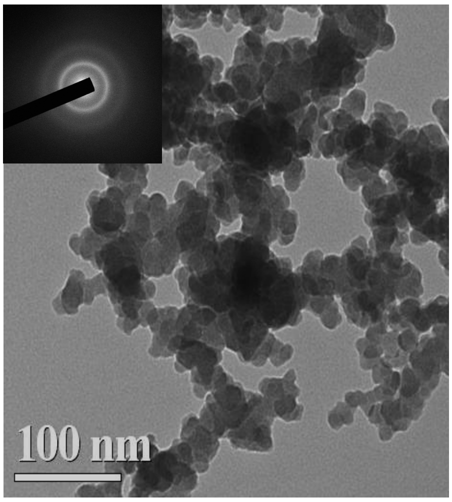


Fig. S4 TEM morphology of the regular Ni-B obtained by direct reduction of $NiCl_2$ with KBH_4 in aqueous solution. The attached SAED image is indicative of the Ni-B amorphous alloys.

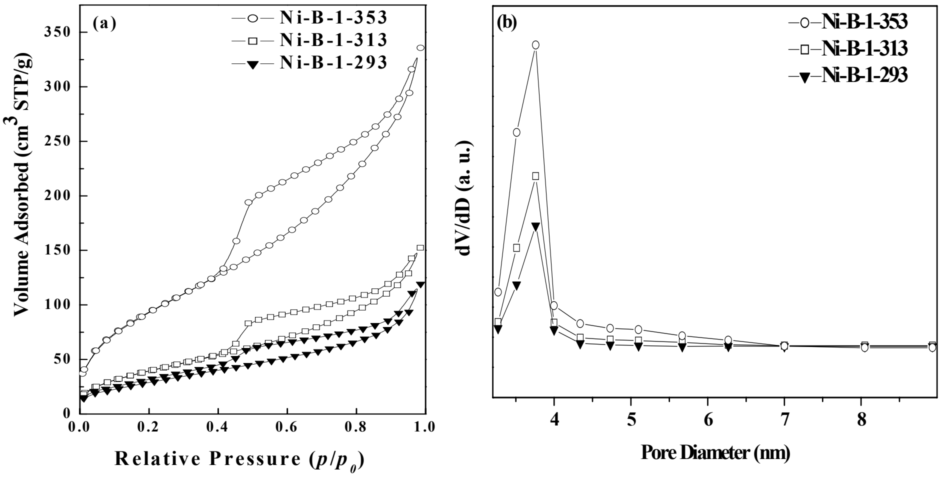


Fig. S5 N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of Ni-B-1-353, Ni-B-1-313, and Ni-B-1-293 samples.

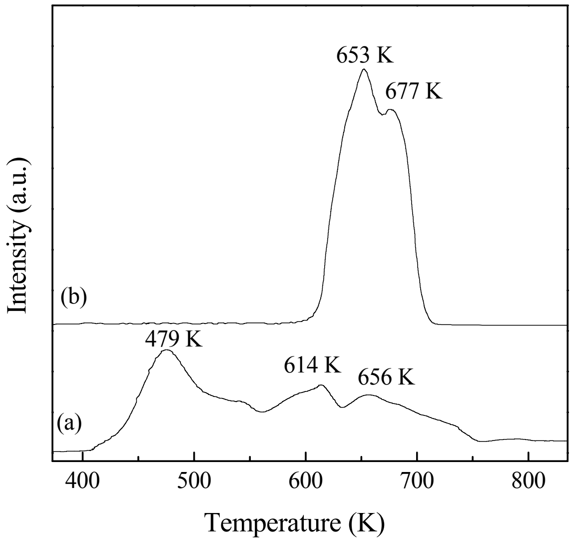


Fig. S6 H_2-TPD curves obtained on (a) the regular Ni-B and (b) the Ni-B-1-333 catalysts.

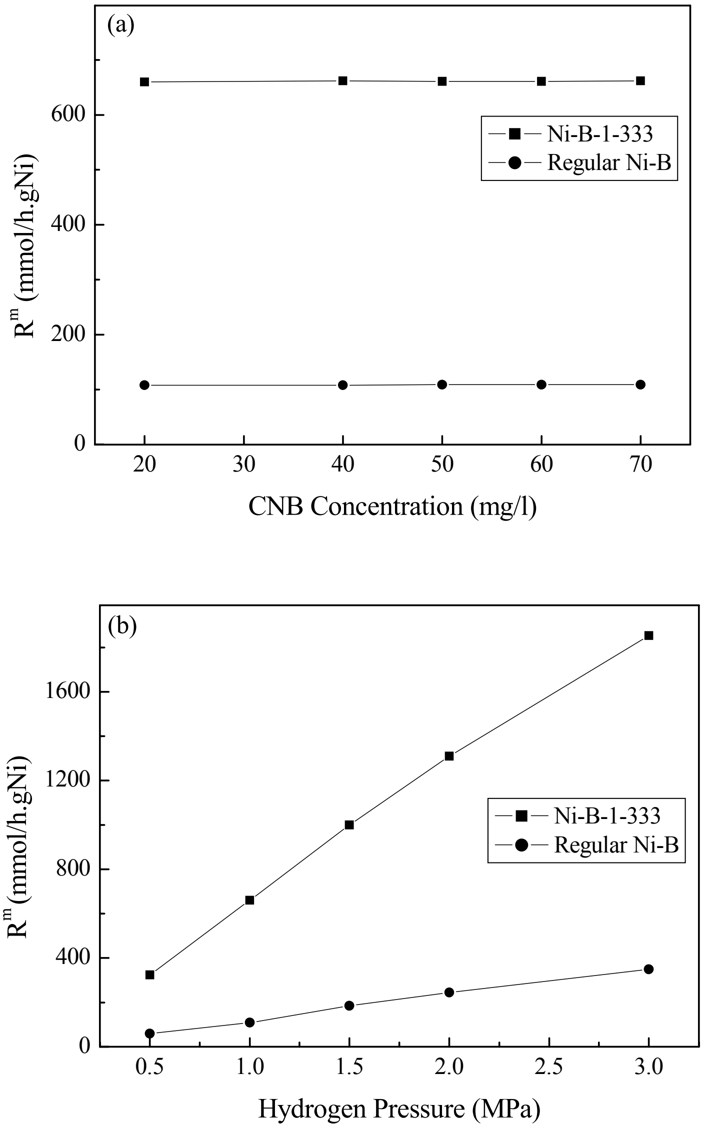
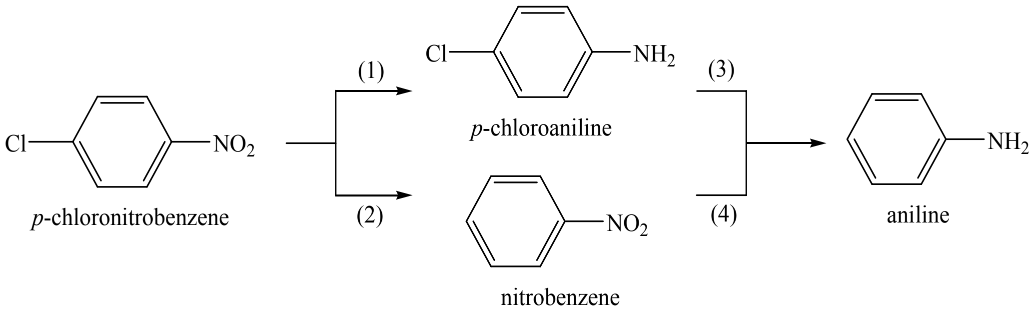


Fig. S7 Effects of (a) the CNB concentration and (b) the hydrogen pressure on the CNB hydrogenation rate over the Ni-B-1-333 and regular Ni-B amorphous alloy catalysts. Other reaction conditions are given in Table 1.



Scheme S1 Reaction route of p-chloronitrobenzene (CNB) hydrogenation.