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Promoting Hydrogen Absorption of Liquid Organic Hydrogen Carriers by Solid Metal Hydrides

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Experimental Section

Preparation of catalysts:

YH_3 was synthesized by directly hydrogenation of Y at 350 ˚C under 4 MPa H_2 pressure for 6 h. LaH_3, GdH_3 and YD_3 was synthesized with the similar method. YH_3 was ball-milled to powder in 4 bar H_2 atmosphere with rotating speed of 250 rpm and ball to powder mass ratio 6:1 for 10 h.

Preparation of Ni(500 nm)/Al_2O_3 with 5 wt% Ni loading. 1.0 g γ-Al_2O_3 and 110.8 mg $NiCl_2$ were mixed in 20 mL anhydrous THF by stirring overnight. After distilling the solvent by vacuum, the $NiCl_2$/Al_2O_3 was vacuumed for 2h at 120 ˚C in a closed tube furnace, heated to 450 ˚C. After an hour, it was reduced by 4 MPa H_2 for 2 h. Then it was vacuumed and cooled to 320 ˚C. After that, the furnace was filled with 4 MPa H_2 again and heated at 320 ˚C overnight. Ni/Al_2O_3 in the article represents Ni(500 nm)/Al_2O_3 without extra explanation.

Preparation of Ni(10 nm)/Al_2O_3 with 5 wt% Ni loading. 1.0 g γ-Al_2O_3 and 248 mg $Ni(NO_3)_2$•$6H_2O$ were mixed in 10 mL H_2O by stirring at room temperature overnight. After removing water by freeze drying, the $Ni(NO_3)_2$/Al_2O_3 was heated in a tube furnace in an Ar flow of 50 sccm (standard cubic centimeter per minute) using the following program: 2 ˚C min^{-1} to 120 ˚C, maintaining at 120 °C for 3 h, then 6 ˚C min^{-1} to 500 ˚C and maintaining at 500 ˚C for 4 h. The above procedure is to convert $Ni(NO_3)_2$ to NiO. Then, H_2 flow of 20 sccm is added and the temperature is raised to 550 ˚C at 5 ˚C min^{-1}, maintained at 550 ˚C for 1 h and cooled down to room tempearture to obtain metallic Ni.

Preparation of Ru/Al_2O_3 with 5 wt% Ru loading. 500 mg γ-Al_2O_3 and 52.8 mg $Ru_3(CO)_{12}$ powder were mixed by gentle hand milling for 5 min. The mixture was then heated in a tube furnace in pure Ar flow of 50 sccm according to the following program: 0.8 ˚C min^{-1} from room temperature to 120 ˚C, maintained at 120 ˚C for 1 h, 0.8 ˚C min^{-1} to 250 ˚C, maintained at 250 ˚C for 2 h and cooled to room temperature.

The Ni/Al_2O_3-YH_3 catalyst was obtained by milling 250 mg Ni/Al_2O_3 and 1000 mg YH_3 with a mortar and pestle for about 5 min in an Ar filled glovebox. Other Ni/Al_2O_3-MH or Ru/Al_2O_3-MH catalysts were obtained with the similar method.
All metal and metal hydrides contained samples are operated and stored in an inert environment for preventing oxidation.

Characterizations:

The catalysts were characterized by Powder X-ray diffraction (XRD, PANalytical X'Pert^3 Powder, Cu Kα), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption/mass spectrometry analysis **(**TPD/MS, Quantachrome Autosorb iQ automatic gas sorption analyzer**)**, scanning electron microscope (JSM-IT300) and field emission high resolution transmission electron microscope (HRTEM, JEM-2100F).

Measurement of the hydrogen absorption performance:

Hydrogen absorption of *N*-ethylcarbazole was measured using the Sievert's method for hydrogen storage materials in a SLM microform high-pressure autoclave (150 mL, Beijing Century Senlong experimental apparatus Co., Ltd.). In each experiment, NEC (1.0 g) and the catalyst (25 mg Ni/Al_2O_3 or Ru/Al_2O_3 with or without 100 mg metal hydrides) are sealed into the autoclave in an argon-filled glove box. No solvent is used to maintain the gravimetric hydrogen storage capacity. No effective stirring can be employed as the reactants just cover the bottom of the autoclave. As a result, no stirring bar is used. The reactor is then connected to the high pressure hydrogen line, evacuated and then heated to the designated temperature in vacuum. After reaching the designated temperature, the autoclave is filled with hydrogen to the designated pressure and then disconnected with the high pressure hydrogen line to initiate hydrogen absorption. The void space of the sealed system is previously calibrated so that the amount of hydrogen absorbed can be calculated by the change of pressure in the system. Usually, the reaction is stopped when the pressure remains unchanged over 2 h. The pressure change is around 0.6 MPa when full hydrogenation of NEC is accomplished. The liquid products are characterized by nuclear magnetic resonance (NMR, Bruker-400 M, ARX400) and Fourier transform infrared spectroscopy (FT-IR, Bruker, Tensor 27). In the isotope labelling experiment, the gas in the autoclave after hydrogen absorption was slowly released through a needle valve and guided into a residual gas analyzer (Pfeiffer Omnistar). The solid catalyst is separated by centrifugation, washed by ethanol and then subjected to a temperature programed desorption measurement in Ar flow with a heating rate of 10 °C min^{-1} from room temperature to 800 °C in an automatic gas sorption analyzer (Quantachrome Autosorb iQ) equipped with a mass spectrometer. The hydrogen absorption of other organic substrates was employed by the same method.

Supplementary Figures

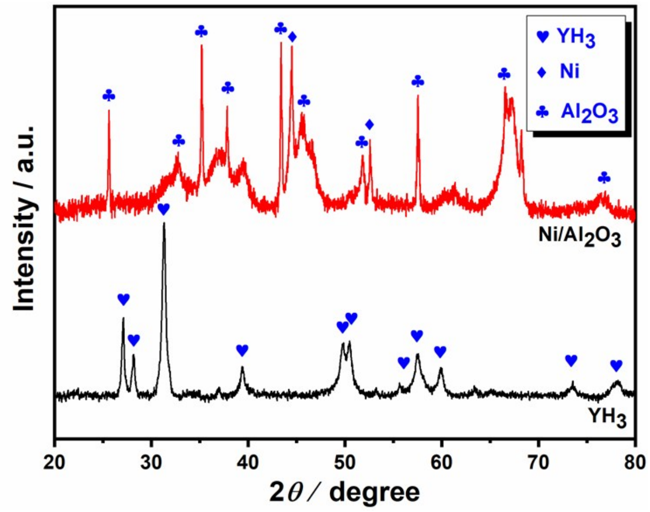

Fig. S1 XRD patterns of Ni/Al_2O_3 and YH_3.

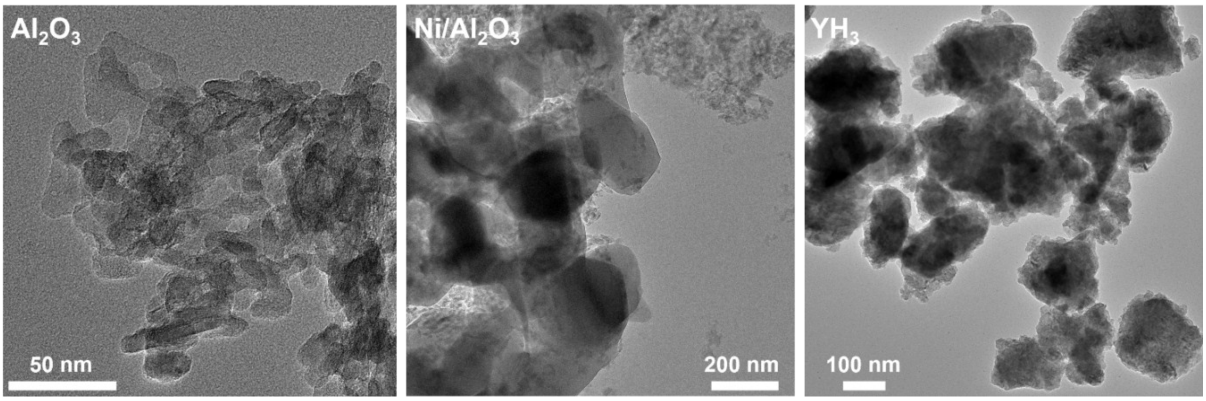

Fig. S2 TEM images of Al_2O_3, Ni/Al_2O_3 and YH_3.

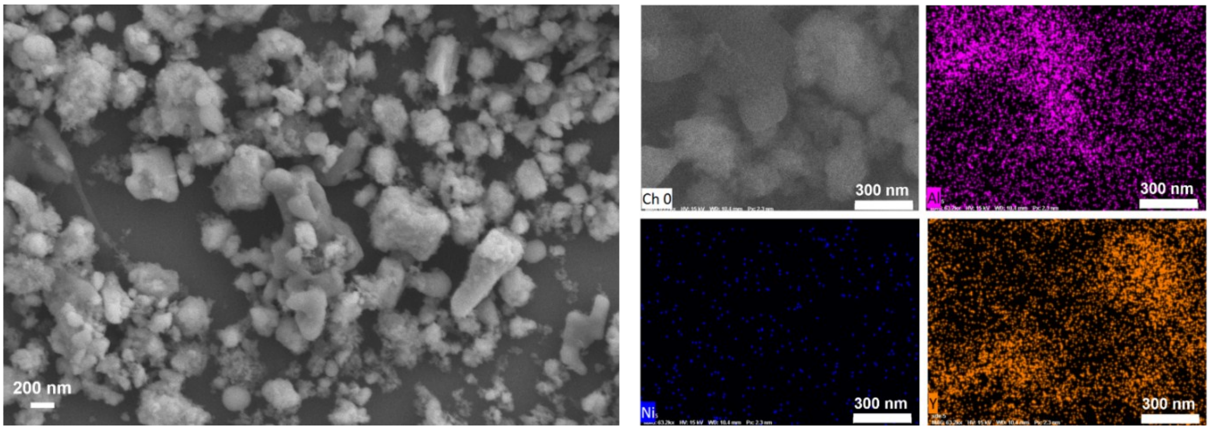

Fig. S3 SEM images and EDX element mappings of Ni/Al_2O_3-YH_3.

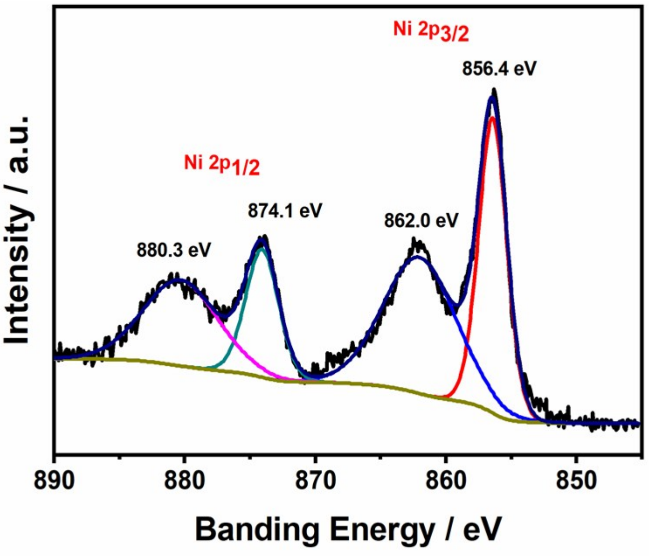

Fig. S4 XPS spectra of Ni/Al_2O_3.

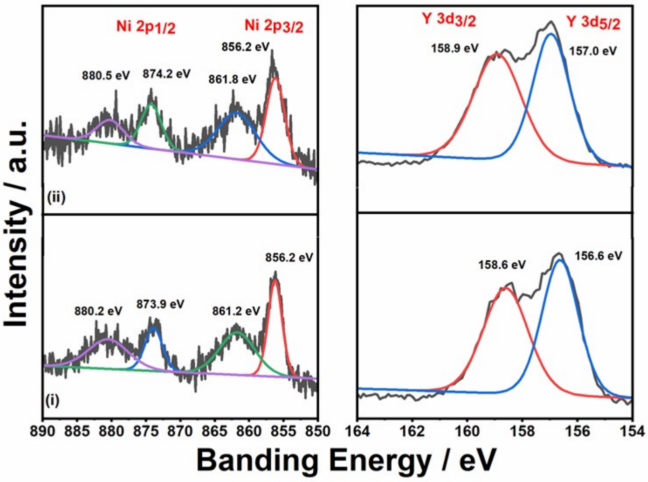

Fig. S5 XPS spectra of Ni/Al_2O_3-YH_3 before (i) and after (ii) catalytic hydrogenation.

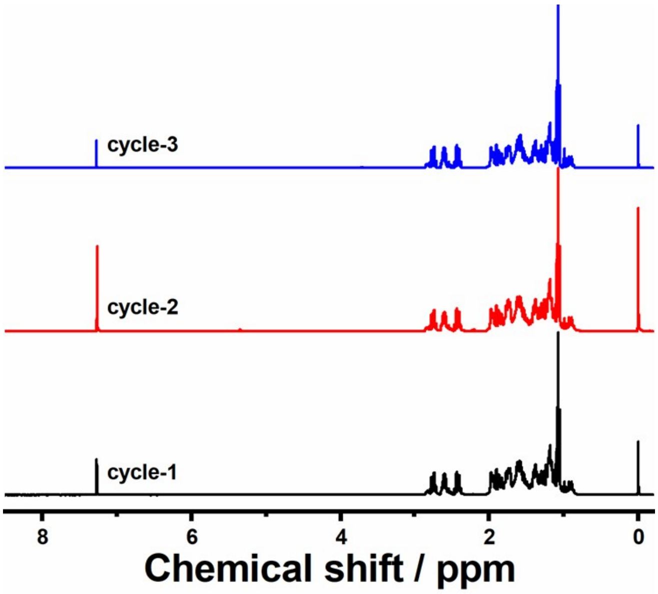

Fig. S6 ^1H NMR spectra of the hydrogenated products (in $CDCl_3$) on Ni/Al_2O_3-YH_3 for three repeated cycles (180 ˚C, 10 MPa H_2, 1.00 g NEC, 125 mg catalyst).

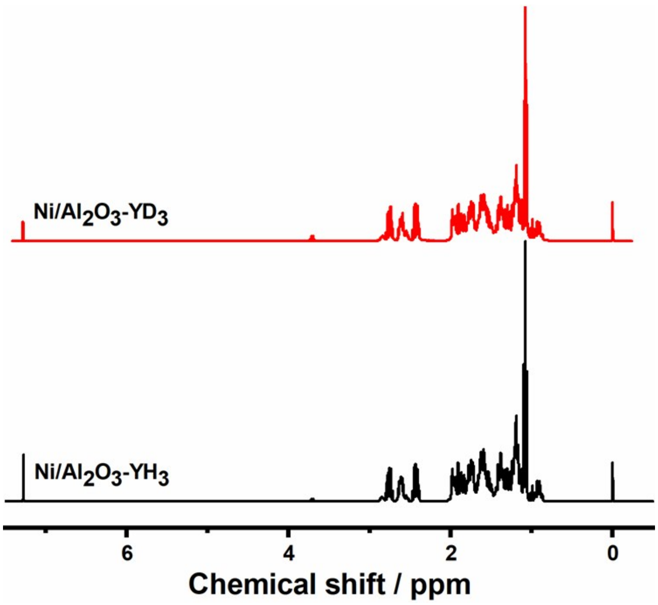

Fig. S7 ^{1}H NMR spectra of the hydrogenated products (in $CDCl_3$) on Ni/Al_2O_3-YH_3 and Ni/Al_2O_3-YD_3 (150 ˚C, 3 MPa H_2, 1.00 g NEC, 125 mg catalyst).

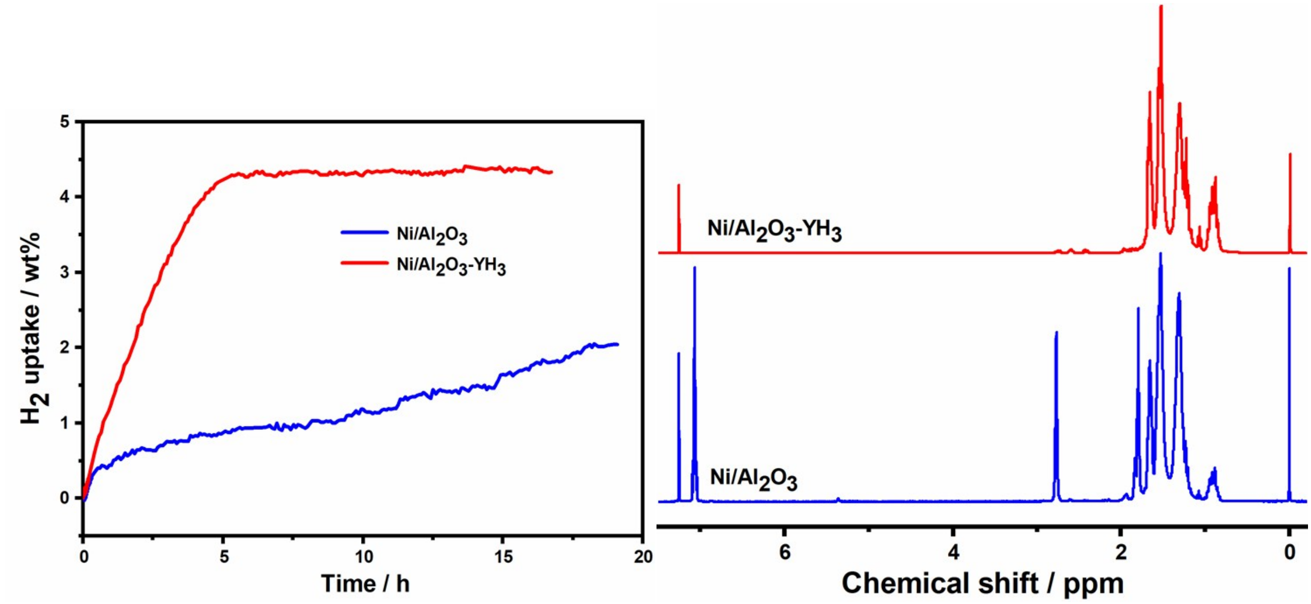

Fig. S8 Hydrogen absorption kinetics (left) and ^{1}H NMR spectra of the hydrogenated products (in $CDCl_3$) (right) on Ni/Al_2O_3 and Ni/Al_2O_3-YH_3 catalysts for hydrogenation of tetrahydronaphthalene (150 ˚C, 10 MPa H_2, 1.00 g tetrahydronaphthalene).

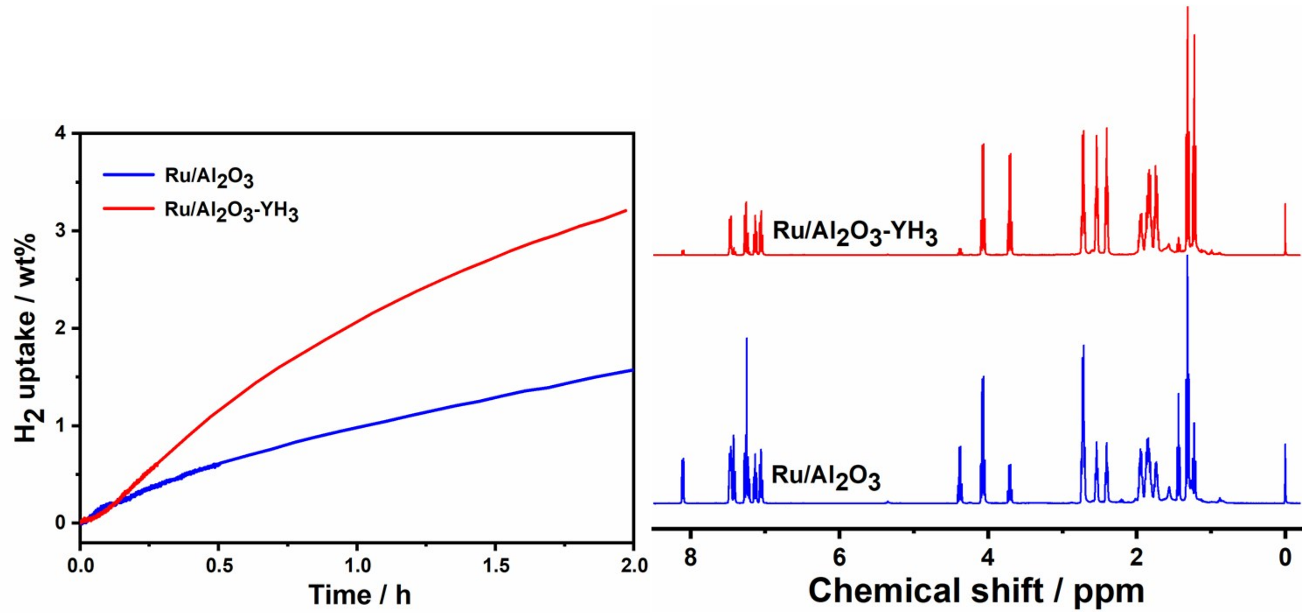

Fig. S9 Hydrogen absorption kinetics (left) and ^{1}H NMR spectra of the hydrogenated products (in $CDCl_3$) (right) on Ru/Al_2O_3 and Ru/Al_2O_3-YH_3 catalysts (150 ˚C, 1.3 MPa H_2, 1.00 g NEC).

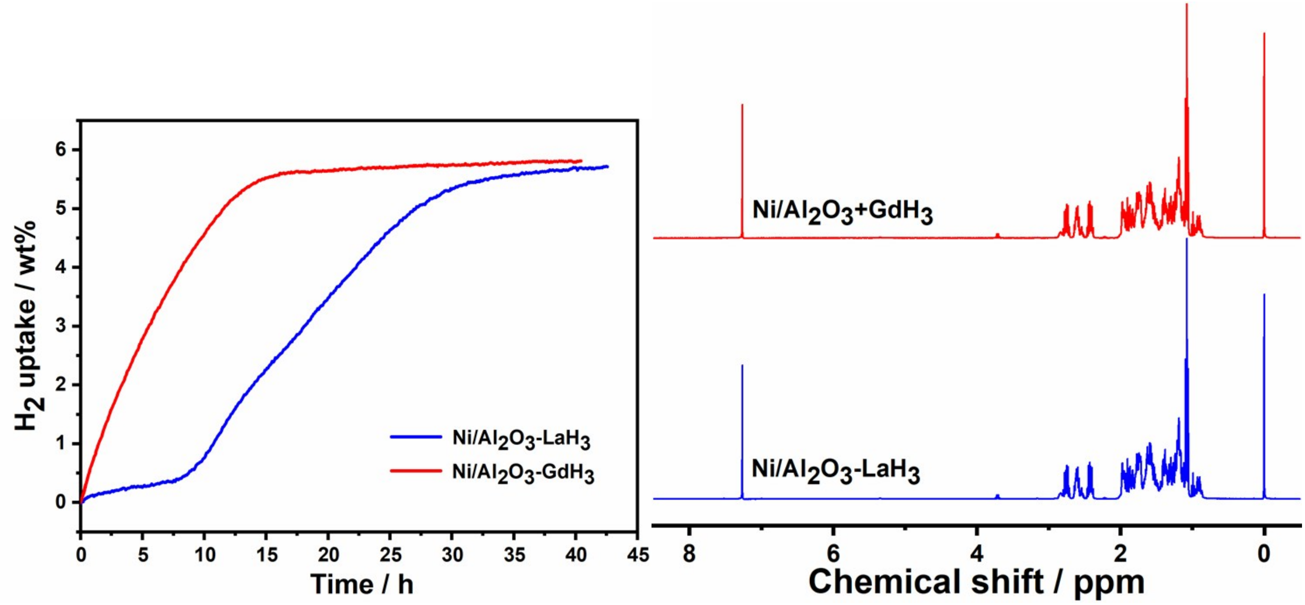

Fig. S10 Hydrogen absorption kinetics (left) and ^{1}H NMR spectra of the hydrogenated products (in $CDCl_3$) (right) on Ni/Al_2O_3-MH catalysts (150 ˚C, 3 MPa H_2, 1.00 g NEC).

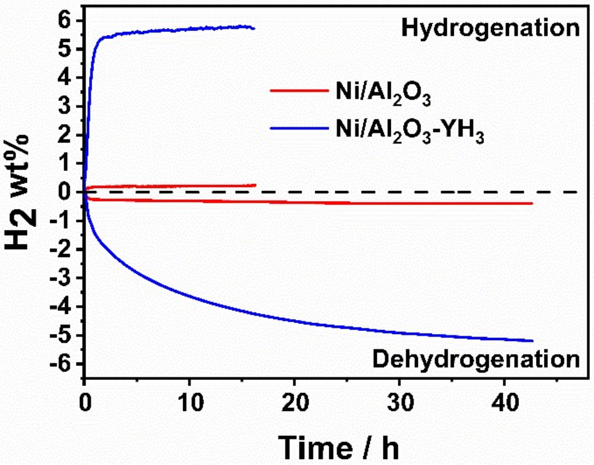

Fig. S11 Hydrogen absorption and desorption kinetics of NEC on Ni/Al_2O_3 and Ni/Al_2O_3-YH_3 catalysts (1.00 g NEC, 25 mg Ni/Al_2O_3, 100 mg YH_3; 180 ˚C, 10 MPa H_2 for absorption and 200 ˚C, 0.1 MPa H_2 for desorption).

Supplementary Table.

Table S1. Catalytic hydrogen absorption performance of NEC using Ni based catalysts.

Catalysts	Ni loading	Condition	Catalyst/NEC mass ratio	Ni/NEC mass ratio	Time / h	Yield / %	Rates / wt% H_2 h^{-1} (mg metal)$^{-1}$	References
Ni/Al_2O_3	20 wt%	200 ˚C, 6 MPa H_2	0.15	0.03	6.4	91.2	0.48	[18]
Ni/SiO_2-Al_2O_3	65 wt%	130 ˚C, 7 MPa H_2	0.20	0.13	7.0	50	0.21	[14]
Raney-Ni	100 wt%	180 ˚C, 5 MPa H_2	0.10	0.10	1.3	86.2	0.66	[17]
Ni/Al_2O_3-YH_3	1 wt%	150 ˚C, 3 MPa H_2	0.125	1.25 x 10^{-3}	5.6	100	14.3	This work
Ni/Al_2O_3-YH_3	1 wt%	180 ˚C, 10 MPa H_2	0.125	1.25 x 10^{-3}	1.5	100	53.3	This work
Ni/Al_2O_3-YH_3	1 wt%	165 ˚C, 10 MPa H_2	0.125	1.25 x 10^{-3}	4.0	100	20.0	This work
Ni/Al_2O_3-YH_3	1 wt%	135 ˚C, 10 MPa H_2	0.125	1.25 x 10^{-3}	8.0	100	10.0	This work