Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Rare Earth Hydride Supported Ruthenium Catalyst for the Hydrogenation of N-heterocycles: Boosting the Activity *via* a New Hydrogen Transfer Path and Controlling the Stereoselectivity

Yong Wu[a], Hongen Yu[a], Yanru Guo[a], Xiaojing Jiang[a], Yue Qi[a], Bingxue Sun[a], Haiwen Li[b], Jie Zheng[a]*, and Xingguo Li[a]*

[a] College of Chemistry and Molecular Engineering, Peking University, P. R. China, 100871.

[b] Platform of Inter/Transdisciplinary Energy Research (Q-PIT), International Research Center for Hydrogen Energy, International Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University, 744 Motooka Nishi-ku, Fukuoka 819-0395, Japan

*To whom correspondence should be addressed.
Prof. Xingguo Li, xgli@pku.edu.cn, 86-10-62765930 (Tel)
Prof. Jie Zheng, zhengjie@pku.edu.cn, 86-10-62753691 (Tel)

Experimental Details

Materials

Yttrium (Y), lanthanum (La) and Gadolinium (Gd) were purchased from Trillion Metals Co., Ltd. $Ru_3(CO)_{12}$, 2-methylindole (MID), and NEC (NEC) were purchased from Beijing InnoChem Science & Technology Co., Ltd. γ-Al_2O_3 was purchased from Beijing Langely Co., Ltd. H_2 (>99.999 %) was purchased from Beijing Nanfeigongmao Co., Ltd.

Preparation of catalysts

YH_3 (LaH_3, GdH_3) was synthesized by directly hydrogenation of Y (La, Gd) at 623 K under 4 MPa H_2 pressure for 6 h. Then it 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 Ru/YH_3 is as follows. 500 mg ball milled YH_3 (LaH_3, GdH_3) and 52.8 mg $Ru_3(CO)_{12}$ (5 wt% Ru) were mixed simply and then they were heated in a tube furnace in an Argon flow of 50 sccm (standard cubic centimeter per minute) using the following program: 1 $K\cdot min^{-1}$ to 393 K, maintaining at 393 K for 1 h, then 1 $K\cdot min^{-1}$ to 523 K and maintaining at 523 K for 2 h. The obtained sample was hydrogenated once again at 623 K under 4 MPa H_2 pressure for 6 h. The Ru/Al_2O_3, Ru/LaH_3, Ru/GdH_3 were prepared using similar way.

All metal and metal hydrides contained samples are operated and stored in an inert environment for preventing oxidation.

Characterizations of catalysts and measurement of the hydrogen absorption performance

The catalysts were characterized by inductively coupled plasma optical emission spectrometer (ICP-OES, Leeman Prodigy 7), 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, QuantachromeAutosorbiQ automatic gas sorption analyzer), field emission high resolution transmission electron microscope (HRTEM, JEM-2100F) and surface area & pore size analyzer (Quantachrome, Nova 2200e).

The catalytic hydrogenation of NEC was conducted in a SLM microform high-pressure autoclave (150 mL, Beijing Century Senlong experimental apparatus Co., Ltd.). The reaction kinetics curves were obtained using the Sievert's method.[1] In each experiment, NEC (1.0 g) and the catalyst were sealed into the autoclave in an argon-filled glove box, then the autoclave was connected to the high-pressure hydrogen line, evacuated and heated to the designated temperature in vacuum. After reaching the designated temperature, the autoclave was filled with hydrogen to the designated pressure and then disconnected with the high-pressure hydrogen line to initiate hydrogen absorption. The amount of hydrogen absorbed can be calculated by the change of pressure in the system as the void space of the sealed system was previously calibrated. No solvent and stirring bar are used. The liquid products are characterized by nuclear magnetic resonance (NMR, Bruker-400 M, ARX400).

Additional Figures

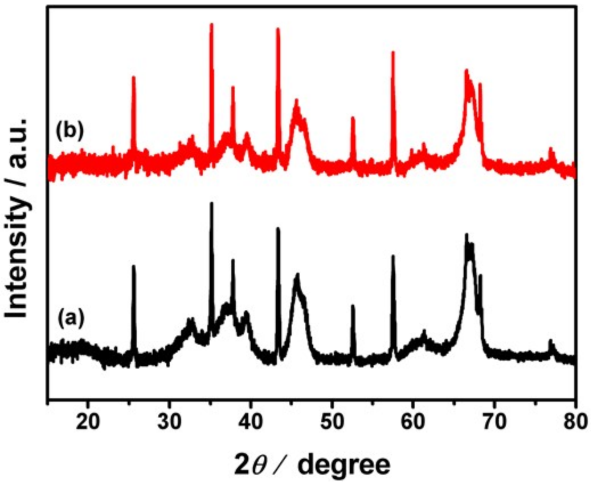

Fig. S1 XRD patterns of (a) Al_2O_3 and (b) Ru/Al_2O_3.

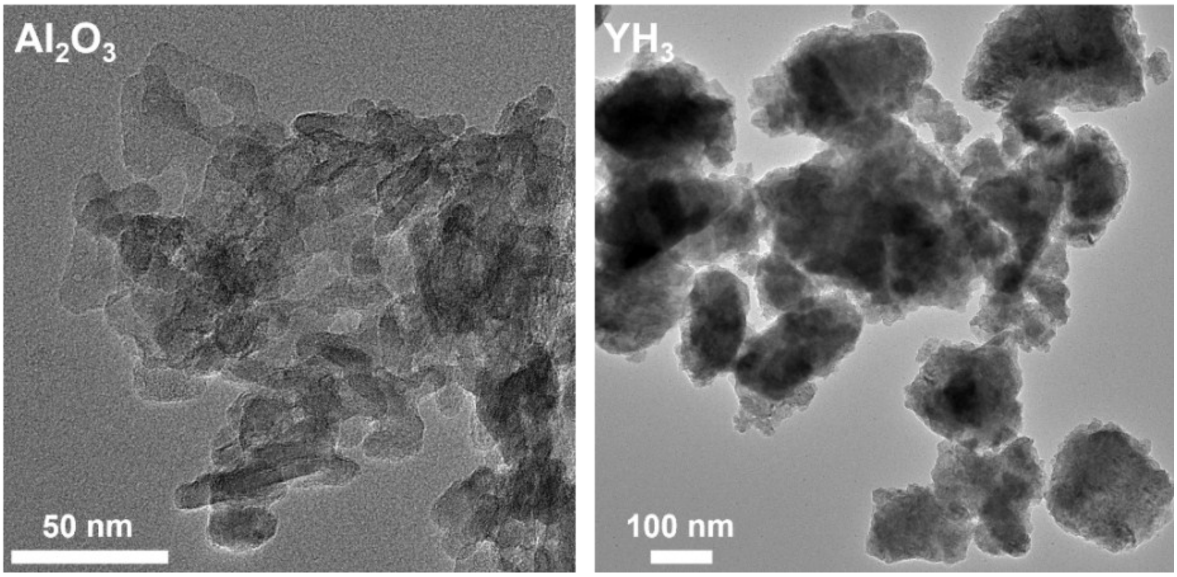

Fig. S2 TEM images of Al_2O_3 and YH_3.

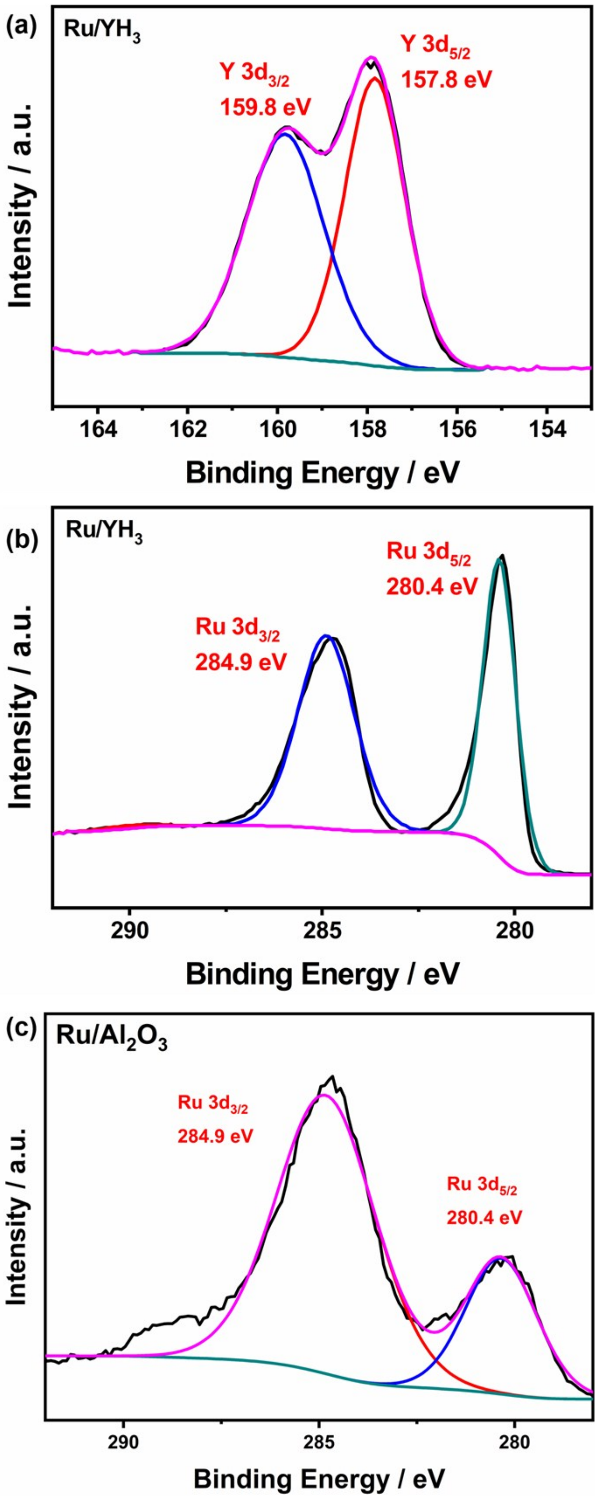

Fig. S3 XPS spectra of a-b) Ru/YH_3 and c) Ru/Al_2O_3.

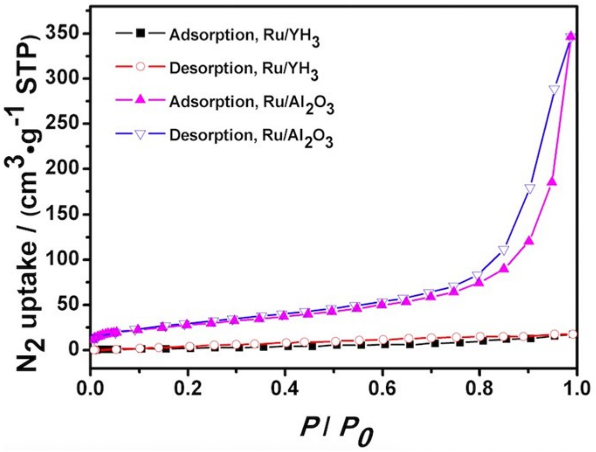

Fig. S4 Nitrogen adsorption/desorption isotherms of Ru/YH_3 and Ru/Al_2O_3 (77 K).

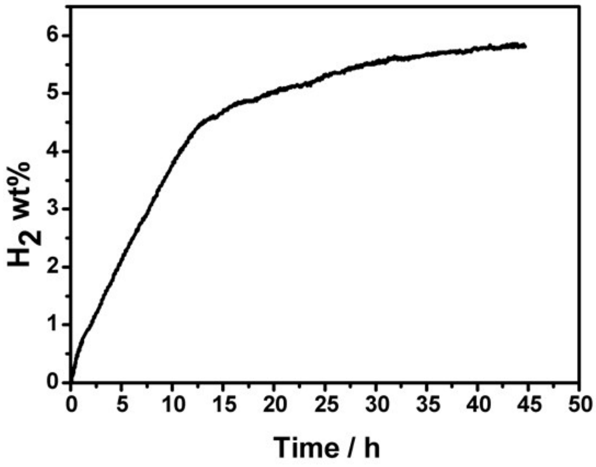

Fig. S5 Hydrogen absorption kinetics of *N*-ethylcarbazole using Ru/YH_3 as catalyst (363 K, 7 MPa H_2, 1.00 g NEC, 50 mg catalyst).

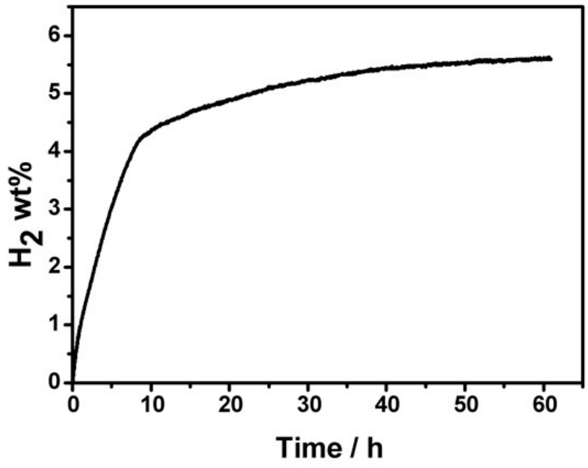

Fig. S6 Hydrogen absorption kinetics of *N*-ethylcarbazole using Ru/YH_3 as catalyst (403 K, 3 MPa H_2, 1.00 g NEC, 50 mg catalyst).

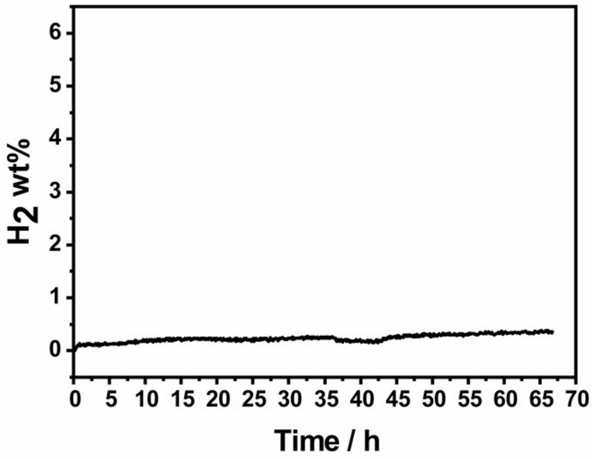

Fig. S7 Hydrogen absorption kinetics of *N*-ethylcarbazole using YH_3 as catalyst (423 K, 3 MPa H_2, 1.00 g NEC, 50 mg catalyst).

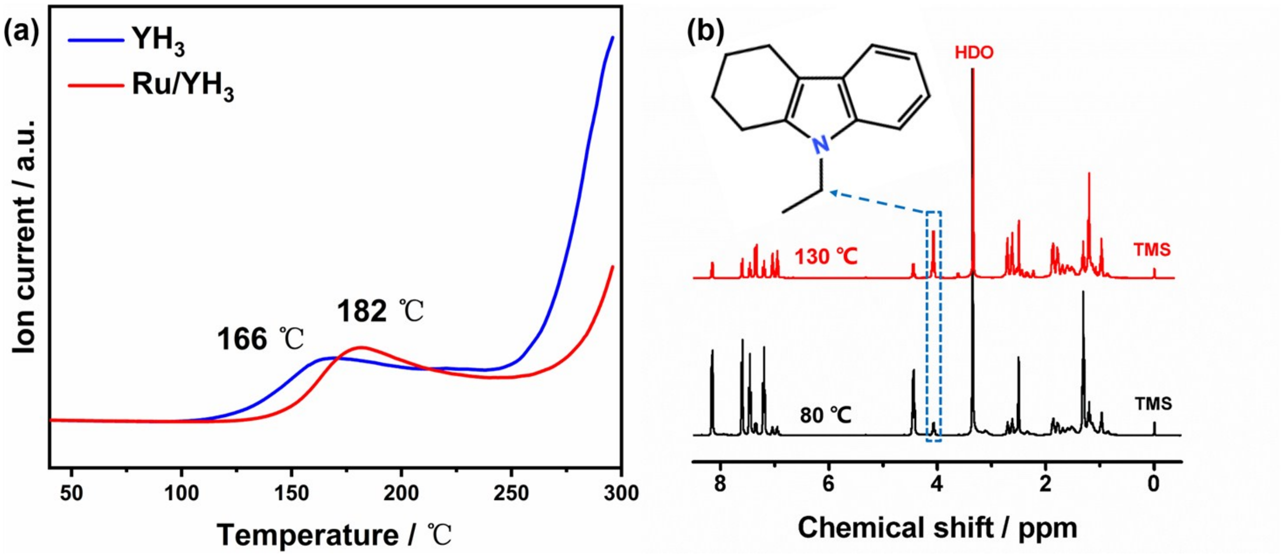

Fig. S8 (a) TPD/MS curves (H_2 signals) of YH_3 and Ru/YH_3 (Argon flow); (b) ^{1}H NMR spectra of products of hydrogenation of *N*-ethylcarbazole using Ru/YH_3 as catalyst and hydrogen source at 353 K and 403 K for 48 h in vacuum (d^6-DMSO).

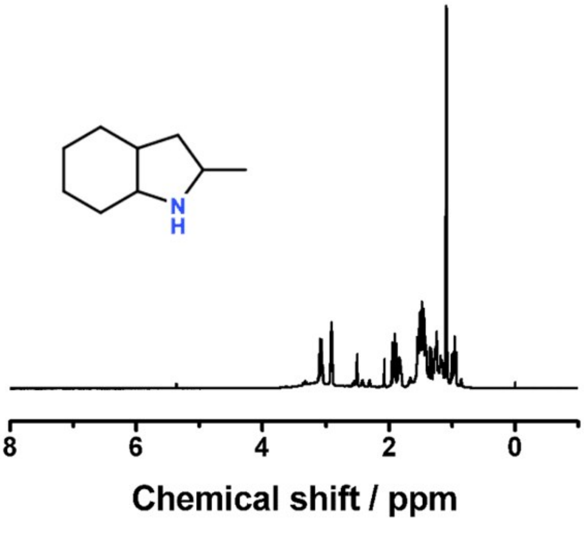

Fig. S9 ^{1}H NMR spectra of hydrogenation product of 2-methylindole using Ru/YH_3 as catalyst (403 K, 7MPa H_2, 1.00 g substrates, 50 mg catalyst, d^6-DMSO).

Notes and references

1 R. Checchetto, G. Trettel and A. Miotello, *Meas. Sci. Technol.*, 2004, **15**, 127-130.