Supporting Information

Ruthenium supported on MIL-101 as an efficient catalyst for hydrogen generation from hydrolysis of amine boranes

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Experimental

Chemicals and materials

All chemicals were commercial and used without further purification. Chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Sinopharm Chemical Reagent Co., Ltd., 99%), Ruthenium chloride hydrate ($RuCl_3 \cdot nH_2O$, Wuhan Greatwall Chemical Co., Ltd., 99%), methylamine hydrochloride ($CH_3NH_2 \cdot HCl$, Sinopharm Chemical Reagent Co., Ltd, ≥96%), ammonia borane (NH_3-BH_3, AB, Aldrich, 90%), aqueous hydrofluoric acid (HF, Sinopharm Chemical Reagent Co., Ltd., 40%), terephthalic acid ($HO_2CC_6H_4CO_2H$, Sinopharm Chemical Reagent Co., Ltd., 99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd., 96%), Ammonium fluoride (NH_4F, Sinopharm Chemical Reagent Co., Ltd., ≥96%), ethanol (C_2H_5OH, Sinopharm Chemical Reagent Co., Ltd., >99.8%) were used as received. We use

ordinary distilled water as the reaction solvent.

Synthesis of MIL-101

MIL-101 was synthesized using the reported procedure.[S1] Terephthalic acid (332 mg, 2.0 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (800 mg, 2.0 mmol), aqueous HF (0.1 mL, 40 wt%) and de-ionized water (9.6 mL) were placed in a 50 mL Teflon-liner autoclave and heated at 220 °C for 8 h. After natural cooling, the suspension was centrifuged to separate the green powder of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$ ($n \approx 25$), and then further purified by solvothermal treatment in ethanol at 80 ºC for 24 h. The resulting green solid was soaked in NH_4F (1 M) solution at 70 ºC for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered resulting green solid was finally dried overnight at 150 °C under vacuum for further use.

Preparation of methyl ammonia borane(CH_3NH_2-BH_3, MeAB)

MeAB was synthesized by the method reported in the literature.[S2] Sodium borohydride (1.89g, 0.05mol) and methylamine hydrochloride (3.37 g, 0.05mol) were added to a 250 mL two-neck round-bottom flask with a neck connected to a condenser. THF (100 mL) was transferred into the flask, and the contents were vigorously stirring. The reaction was carried out at room temperature under nitrogen atmosphere. After 12 hs, the resultant solution was filtered by suction filtration and the filtrate was concentrated under vacuum at room temperature. After dissolved in 100 mL diethyl ether at 0 °C and stirred for 2 hs, MeAB was obtained by remove the solvent under vacuum.

Synthesis of Ru@MIL-101

Activated MIL-101 (100 mg) was mixed with 10 mL de-ionized water containing

(0.01, 0.03, 0.04, 0.05, 0.07 mmol) $RuCl_3$ and stirring was continued for 12 h at 25℃ to impregnate metal salts, then reduced by sodium borohydride ($NaBH_4$, 75.6 mg) solution with vigorous stirring at 0 °C to yield Ru@MIL-101. The physical mixture of Ru and MIL-101 performed in the similar way. The solution of equal amount $RuCl_3$ reduced by sodium borohydride and then mixed with 50 mg MIL-101.

Hydrolytic dehydrogenation of ammonia borane and methyl ammonia borane

A mixture of 50 mg Ru@MIL-101 and 5 mL de-ionized water were kept in a two-necked round-bottom flask. One neck was connected to a pressure-equalization funnel to introduce 2 mL aqueous solution of NH_3BH_3 (30.8 mg, 1 mmol) or $CH_3NH_2BH_3$(45 mg, 1 mmol), and the other neck was connected to a gas burette to monitor the volume of the gas evolution. The reactions were carried out at 25 ^oC in air. Temperature was varied at 25 ± 0.2 ^oC, 30 ± 0.2 ^oC, 35 ± 0.2 ^oC and 40 ± 0.2 ^oC while the catalyst (50 mg) and AB (or MeAB, 1 mmol) were kept constant to obtain the activation energy (Ea).

Stability test

2 mL of solution containing 30.8 mg AB (or 45.0 mg MeAB) was added to 5 mL of water dissolved 50 mg Ru@MIL-101, the evolution of gas was monitored as described above. After the hydrogen generation reaction was completed, new aqueous AB solution (30.8 mg, 2 mL) or MeAB solution was added into the reaction flask. The evolution of gas was monitored using the gas burette. Such cycle tests of the catalyst for the hydrolysis of AB and MeAB were carried out five times in air.

2.7 Characterization

The morphologies and sizes of the samples were observed by using a Tecnai G20 U-

Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu Ka radiation source (λ = 0.154178 nm) with a velocity of 1^{o} min^{-1}. The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after dehydration under vacuum at 150 ºC for 12 h using Quantachrome NOVA 4200e. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP (Thermo Fisher Scientific, USA).

References

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Table S1. Catalytic activity of Ru-based catalysts used for the hydrolytic dehydrogenation of AB

Catalyst	TOF(mol H_2 mol^{-1} metal min^{-1})	Ea (kJ mol^{-1})	Ref.
Ru/C	429.5	34.81	S3
Ru(0)@MWCNT	329	33	S4
PSSA-co-MA stabilized Ru nanoclusters	187.6	54	S5
2.80 wt% Ru@MIL-101	178	--	This study
1.62 wt% Ru@MIL-101	147.6	51.12	This study
Ru/graphene	100	11.7	S6
Ru@Al_2O_3 after acetic acid treatment	83.3	46	S7
Ru/γ-Al_2O_3	77	23	S8
laurate-stabilized ruthenium(0) nanoclusters	75	47	S9
Ru@Co/graphene	40.5	--	S10
Ru@Ni/graphene	39.9	36.6	S11
Ru@Al_2O_3	39.6	48	S7
Ni@Ru	30.6	44	S12
Ru@Ni/C black	29.4	37.9	S13
Ru@Co/C black	29.1	21.2	S13
Ru/γ-Al_2O_3	23.05	67	S14
RuCo (1:1)/γ-Al_2O_3	16.5	47	S15
RuCu/graphene	15.9	30.4	S16
RuCu (1:1)/γ-Al_2O_3	8.2	52	S15

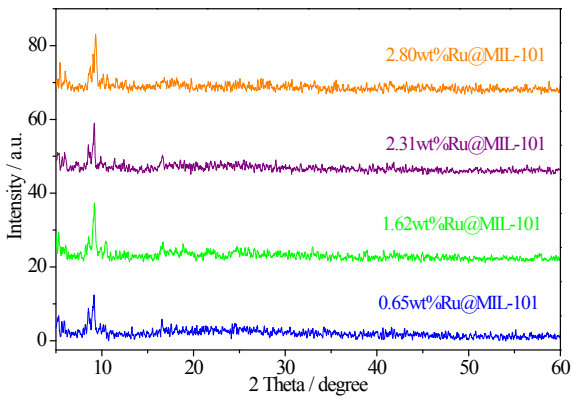

Figure S1 The wide-angle PXRD patterns of samples.

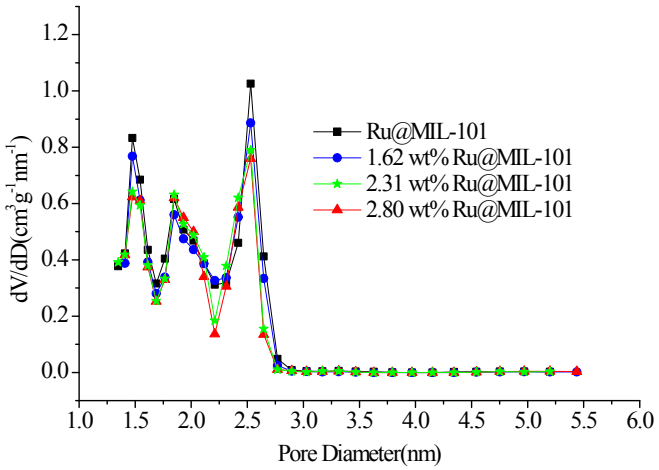

Figure S2 The pore diameter distribution of MIL-101 and Ru@MIL-101.

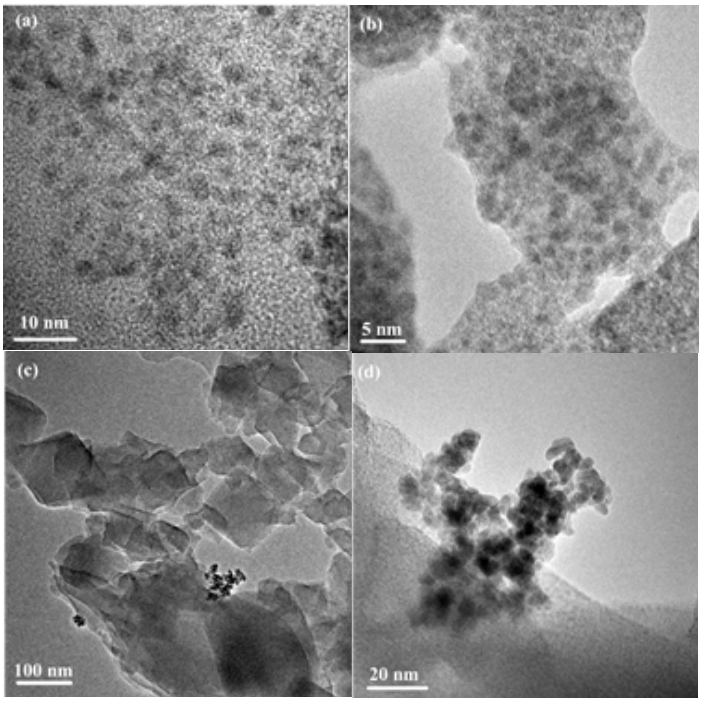

Figure S3. (a-b) TEM images of 2.31 wt% Ru@MIL-101; (c-d) TEM images of a physical mixture of Ru NPs and MIL-101.

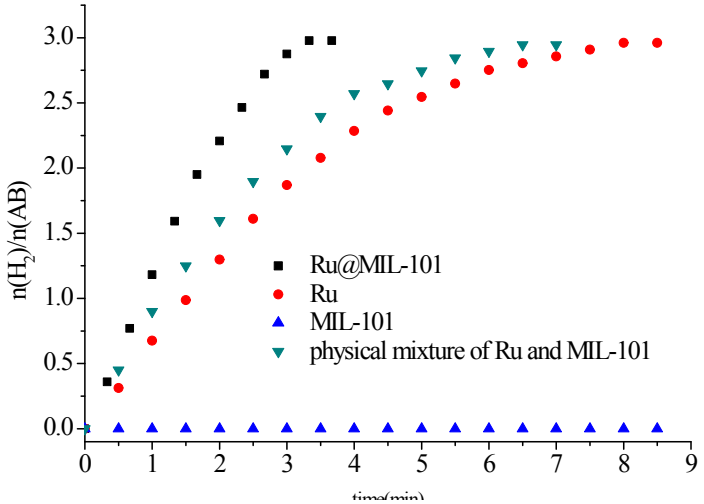

Figure S4. Time plots of catalytic dehydrogenation of AB by Ru, MIL-101, Ru@MIL-101and a physical mixture of Ru NPs and MIL-101. (Ru/AB = 0.008)

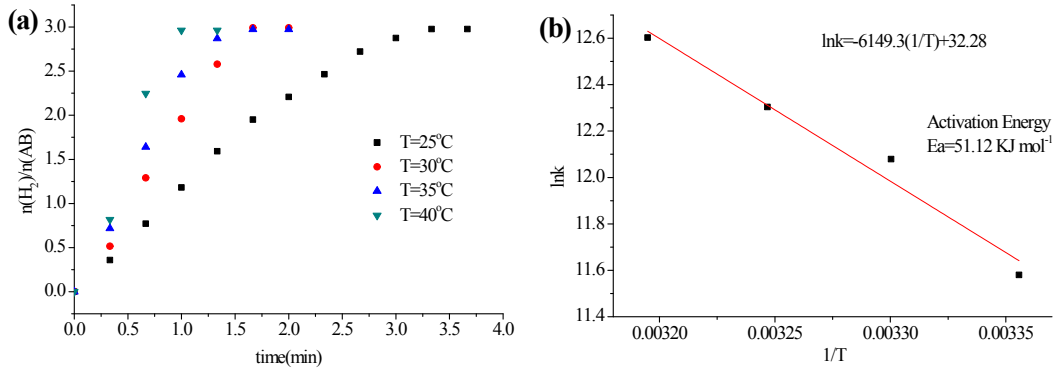

Figure S5. (a) Time course plots for hydrogen generation by the decomposition of AB by 1.62 wt% Ru@MIL-101 at different temperatures. (b) Plot of ln k versus 1/T during the AB decomposition over 1.62 wt% Ru@MIL-101 at different temperatures .

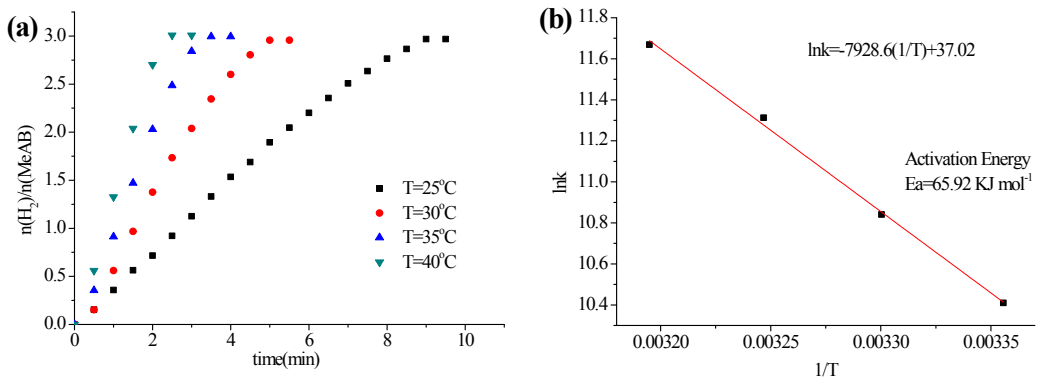

Figure S6. (a) Time course plots for hydrogen generation by the decomposition of MeAB by 1.62 wt% Ru@MIL-101 at different temperatures. (b) Plot of ln k versus 1/T during the MeAB decomposition over 1.62 wt% Ru@MIL-101 at different temperatures .

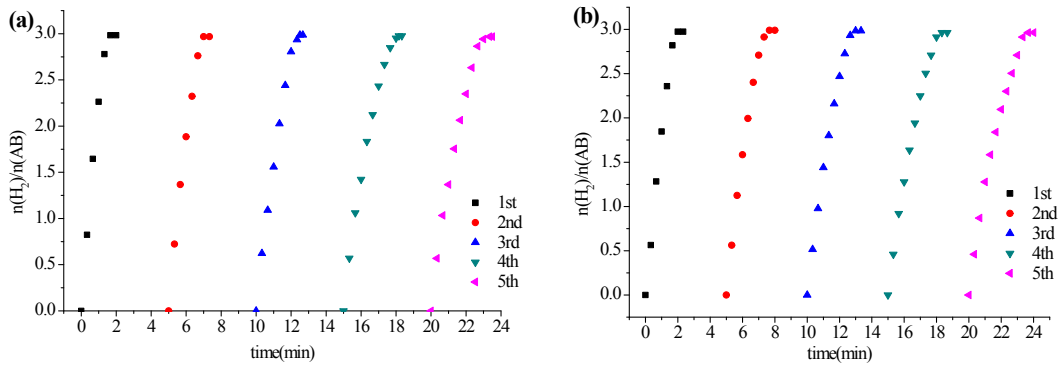

Figure S7. Durability test of (a) 2.31 wt% Ru@MIL-101 and (b) 2.80 wt% Ru@MIL-101 for decomposition of AB.