Fabrication and characterization of a novel nanoporous Co–Ni–W–B catalyst for rapid hydrogen generation

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Experimental section

Materials

Ammonia borane (NH_3BH_3, 97 %), sodium borohydride ($NaBH_4$, $\geqslant$99 %), cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$, $\geqslant$99 %), nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, $\geqslant$99 %), sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$, $\geqslant$99 %) were purchased from Aldrich chemical Co. All other chemicals were purchased and used without further purification. All experiments were performed using deionized water.

Synthesis of catalysts

Nanoporous Co–Ni–W–B catalysts were prepared by in-situ reduction of metal salts in ethanol solution. Typically, 3 g of $CoSO_4 \cdot 7H_2O$, 0.6 g of $NiSO_4 \cdot 6H_2O$ and 0.6 g of $Na_2WO_4 \cdot 2H_2O$ were first added into 60 mL absolute ethanol. The mixture was stirred for 1 h. Then, a freshly prepared 20 mL $NaBH_4$ solution (10 wt.%) was added by slowly dropping into the above mixture under vigorous stirring. After 1 h, the black catalyst floated on the solution was collected and washed thoroughly with deionized water and absolute ethanol, respectively. Then the sample was dried by leaving in the vacuum at room temperature for 24 h and transferred to glove box immediately (*Caution：The dried nanoporous Co–Ni–W–B catalyst is so highly active that will be ignited if exposed to air directly*). For comparison, the catalyst of Co–Ni–W–B was synthesized in water, while Co-B, Co-Ni-B, Co-W-B was prepared in the ethanol solutions with the consistent conditions.

Characterization of the catalyst

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis (Hitachi S4800) was used to characterize the morphology and the surface composition of the Co–Ni–W–B catalysts. The images were also obtained on a transmission electron microscopy (TEM JEOL JSM-200CX). The crystalline phases were characterized with X-ray diffraction (XRD) on a Philips 1820 X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). The samples were scanned in the range of 2θ=30-

70º at a scanning rate of $0.05ºs^{-1}$ The specific surface areas (SSA) of the catalysts were measured by N_2 adsorptions at -196 ºC using the (Brunauer-Emmett-Teller) BET method (Quantachrome Autosorb iQ2). The samples were degassed at 423 K until the vacuum pressure was below 10^{-4} Pa. Pore size distributions were obtained by using the Barrett-Joyner-Halenda (BJH) model and the desorption branch. An average value was obtained by taking triplet measurements over each sample. The composition of the catalyst was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer Optima 8000).

Hydrogen generation measurement

The hydrogen generated by the catalytic decomposition of AB solution was collected by using the drainage method (The schematic diagram was shown in Fig. S1). In a typical measurement, 0.01 g of catalyst was first placed in a flask bottom and the flask was then sealed with an outlet tube for collecting the generated hydrogen. A solution containing 1 wt.% AB was thermostated in a sealed flask and then 10 mL of the reaction mixture was injected into the reaction flask. The reaction proceeded at a stirring rate of 1000 rpm and the amount of hydrogen generated with time was measured immediately. The reaction temperature was controlled by using a water bath. The amount of hydrogen generated in volume was measured by water displacement method, where the volume of hydrogen is equal to the weight of displaced water, which was determined by a balance. The balance was connected with a computer which was installed with the data collection system. The computer read the balance weight automatically. The hydrogen generation rates and the factors affecting the activity of the catalyst were tested.

The stability of the nanoporous Co–Ni–W–B catalyst was determined by investigating the changes in the hydrogen generation rate. The generation of hydrogen stopped upon the depletion of the AB in the solution. The catalyst was collected, rinsed with deionized water thoroughly and recycled for further usage. Then the same amount of AB was added into recycled catalyst dispersed solution and this was carried out for the ten additional cycles.
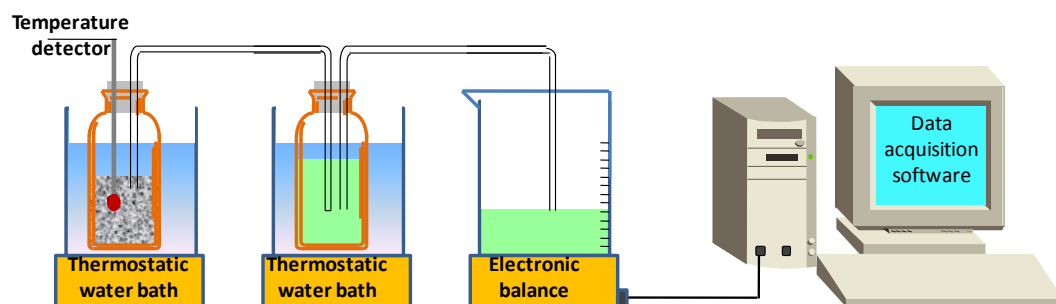
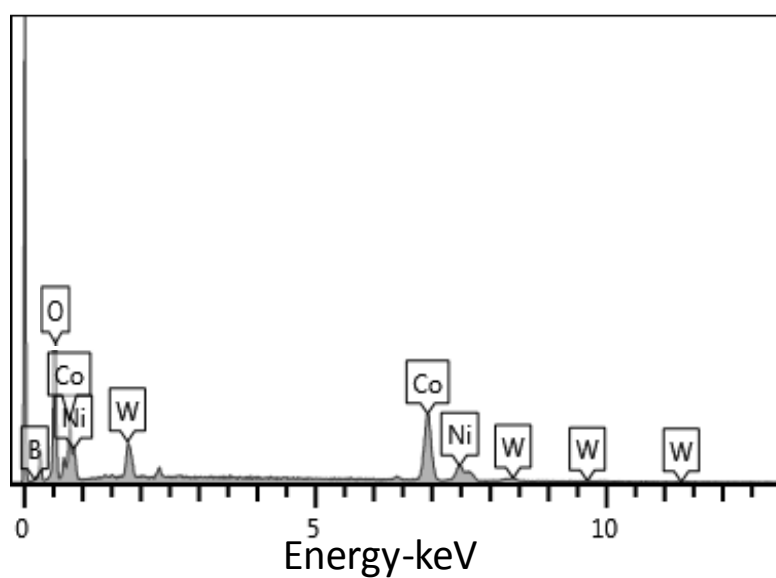Fig.S1. Schematic diagram of the hydrogen generation system.

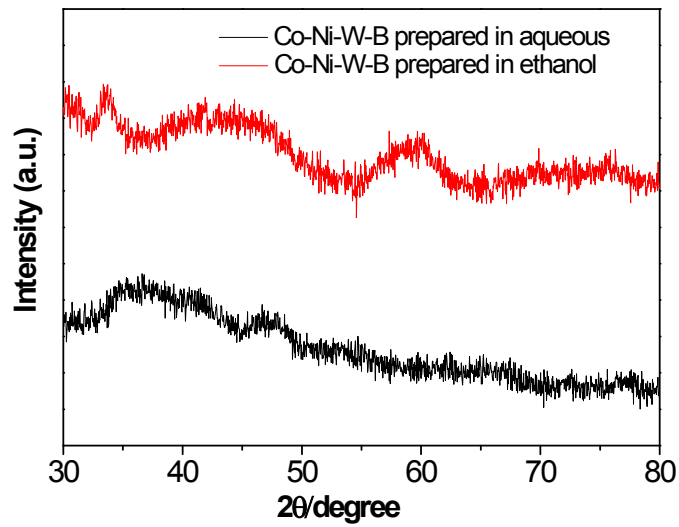Fig.S2. EDX spectrum of Co–Ni–W–B prepared in ethanol.

Fig. S3. XRD patterns of Co–Ni–W–B power prepared in aqueous solution and in ethanol, respectively.
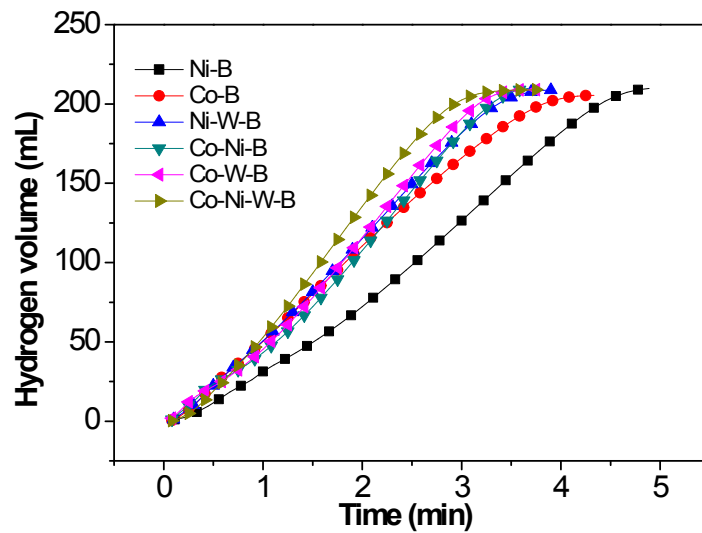

Fig. S4. (a) Effect of catalysts type on the HG rate of AB (Batch system, 30 ºC, 1.0 wt. % AB, 0.01 g catalyst)
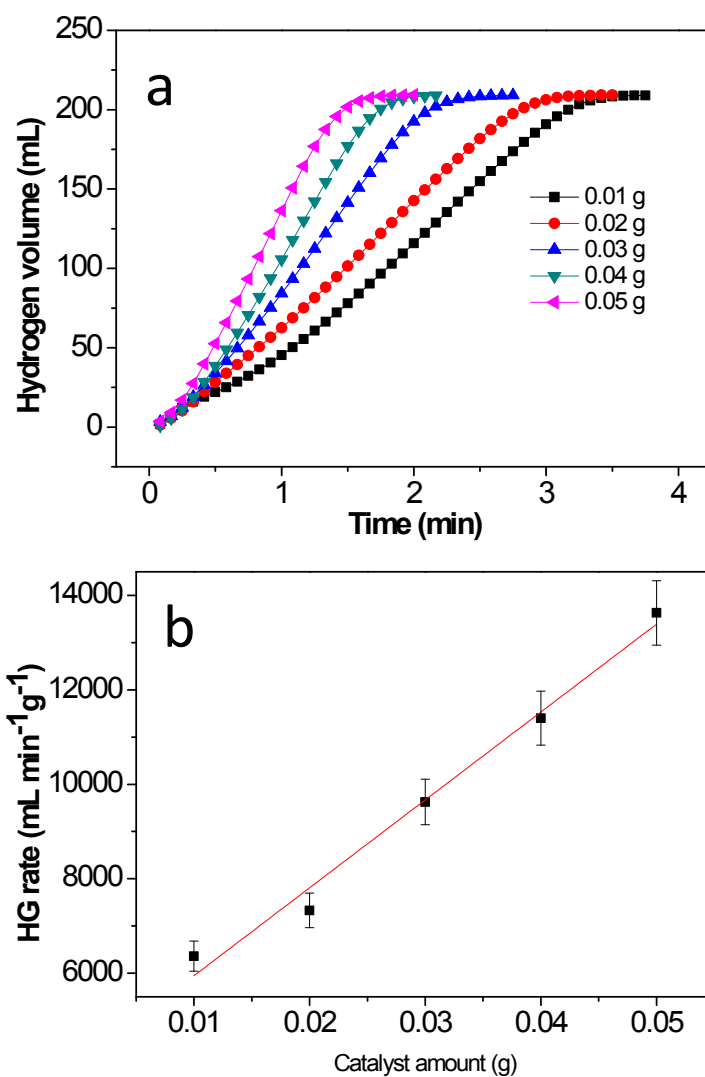
Fig. S5. (a) Effect of varied AB concentration on the hydrogen gnereation rate of AB;
(b) plot of the HG rate vs. AB concentration. (Batch system, 30 ℃, 0.01 g catalyst)
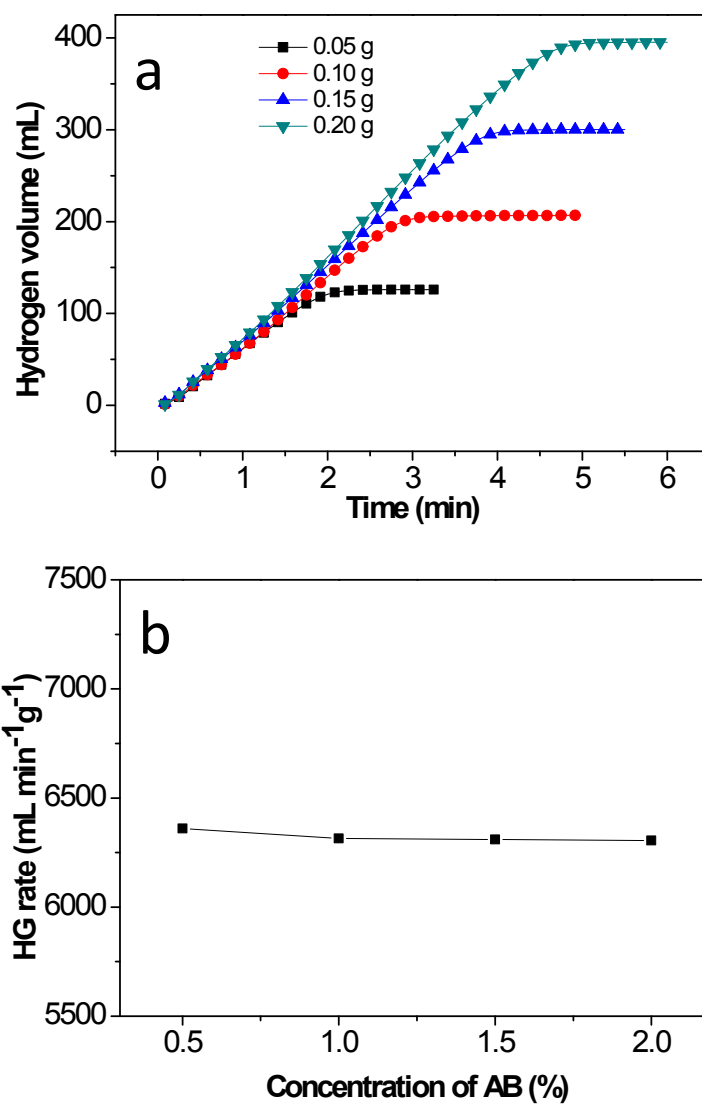
Fig. S6. (a) Effect of varied the amount of catalyst on the HG rate of AB; (b) the HG rate as a function of the Co–Ni–W–B catalyst amount. (Batch system, 30 ºC, 1.0 wt. % AB, 0.01 g catalyst)
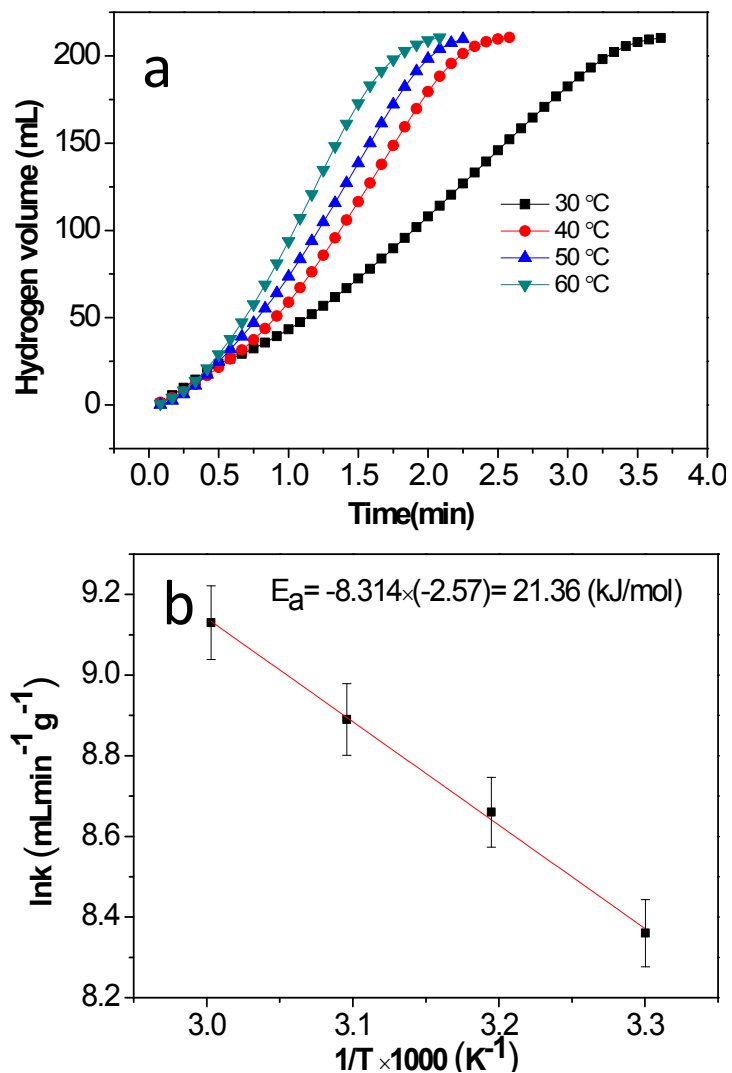
Fig. S7. (a) HG kinetics curves and (b) the Arrhenius plot obtained using the 1.0 wt.% AB solution and employing the nanoporous Co–Ni–W–B catalyst at different solution temperatures.
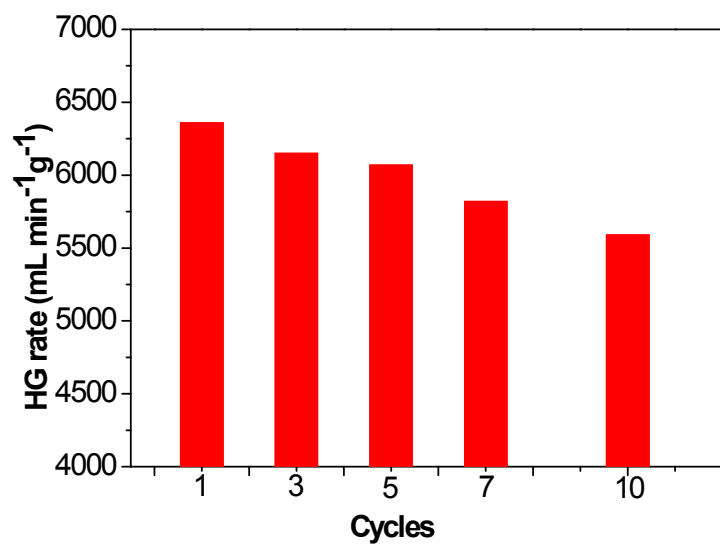
Fig. S8. Multi-cycles operations of nanoporous Co–Ni–W–B catalysts employing a 1.0 wt.% AB solution at 30 ºC .