



Supporting Information

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## Supporting information:

### Iron Nanoparticle Catalyzed Hydrolytic Dehydrogenation of Ammonia Borane for Chemical Hydrogen Storage

Jun-Min Yan, Xin-Bo Zhang, Song Han, Hiroshi Shioyama, and Qiang Xu\*

*National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577,*

*Japan; E-mail: [q.xu@aist.go.jp](mailto:q.xu@aist.go.jp)*

**Chemicals:** Ammonia–borane (NH<sub>3</sub>BH<sub>3</sub>, Aldrich, 90%), iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, Wako Pure Chemical Industries, Ltd., > 99%), and sodium borohydride (NaBH<sub>4</sub>, Aldrich, 99%) were used as received.

**Catalytic Study of the Pre-synthesized Fe Nanoparticles:** NaBH<sub>4</sub> (10 mg) was kept in a three-necked round-bottom flask, to which two pressure-equalization funnels were connected for introducing aqueous NH<sub>3</sub>BH<sub>3</sub> solution (0.32 M, 5 mL) and aqueous FeSO<sub>4</sub> solution (0.038 M, 5 mL), respectively. The third neck was connected to a gas burette to monitor the volume of the gas evolution. Firstly, the aqueous solution of FeSO<sub>4</sub> was added to the three-necked round-bottom flask with shaking, and then black Fe metal particles were rapidly generated accompanied by 20 mL of hydrogen release according to the following reactions:

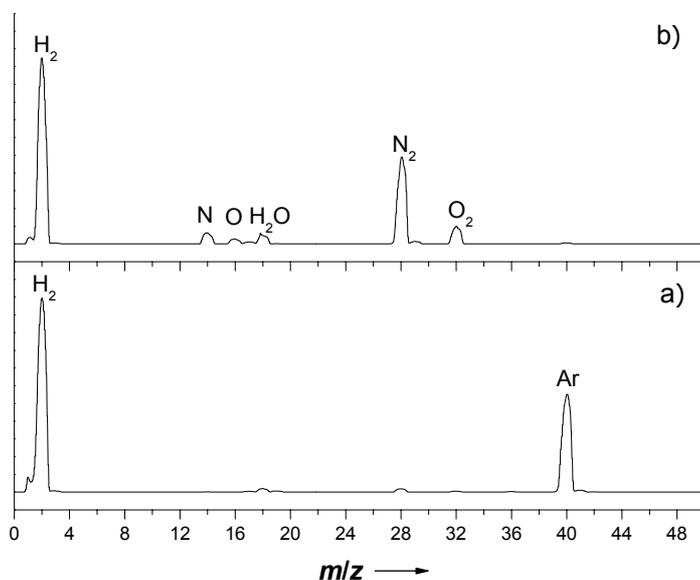




After Fe particles were generated, the solution of  $\text{NH}_3\text{BH}_3$  was then immediately added into the Fe contained solution with violent shaking. The hydrolysis of  $\text{NH}_3\text{BH}_3$  can be briefly expressed as follows:



The reactions were carried out at room temperature in argon and air, respectively.

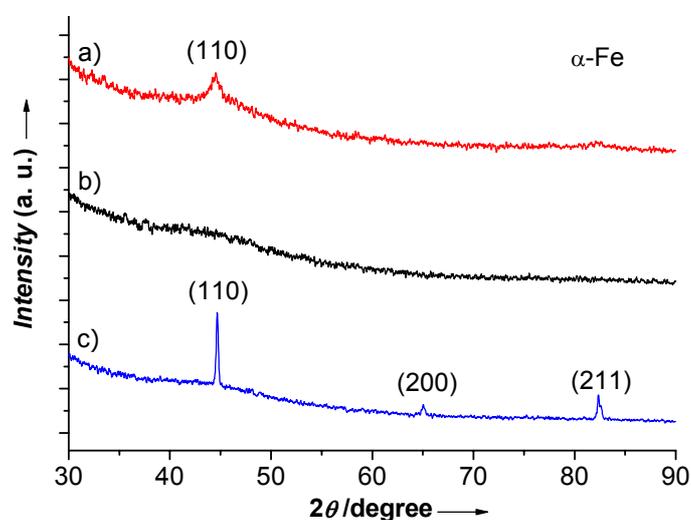


**Figure SI-1** Mass spectra of released gases from aqueous AB solution (0.16 M, 10 mL) catalyzed by in-situ prepared Fe nanoparticles (Fe/AB = 0.12) in a) argon and b) air, respectively.

**Catalytic Study of the in-situ Synthesized Fe Nanoparticles:** A mixture of  $\text{NaBH}_4$  (10 mg) and  $\text{NH}_3\text{BH}_3$  (55 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce aqueous solution of  $\text{FeSO}_4$  (0.019 M, 10 mL). The reaction started when the aqueous  $\text{FeSO}_4$  solution was added to the mixture of  $\text{NaBH}_4$  and  $\text{NH}_3\text{BH}_3$  with violent shaking. Notably, the Fe particles were generated in the presence of the reactant,  $\text{NH}_3\text{BH}_3$ . The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature in argon and air,

respectively. Additionally, the molar ratio of catalyst to reactant ( $\text{Fe}/\text{NH}_3\text{BH}_3$ ) was changed with several values (0.05, 0.08 and 0.12) for catalytic reactions in air. Figure SI-1 shows the mass analysis of the gases generated from the hydrolysis of AB (0.16 M, 10 mL) catalyzed by the in-situ synthesized Fe ( $\text{Fe}/\text{AB} = 0.12$ ) in argon and air, respectively. It is obvious that the released gas was pure  $\text{H}_2$  both in argon and in air. No borazine and the related species were observed in the mass spectra.

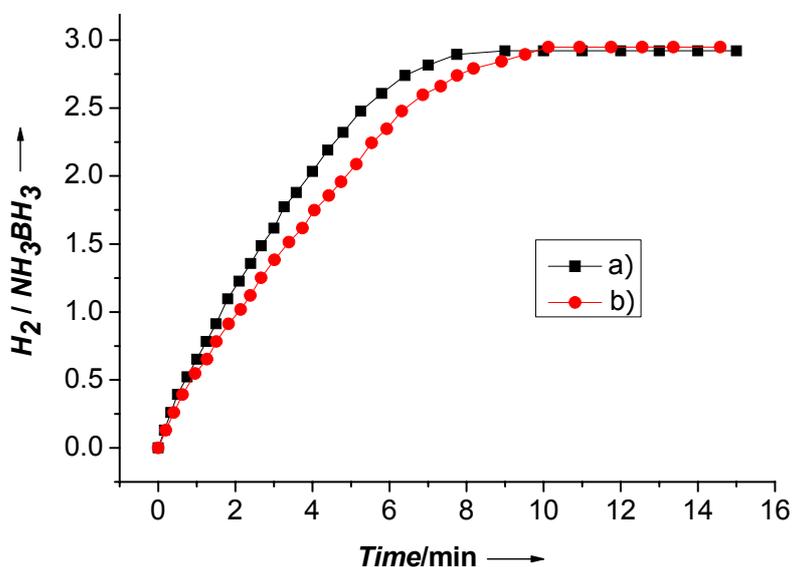
**Heat Treatment of the in-situ Synthesized Fe:** After the in-situ synthesized Fe was separated from the solution and dried in argon atmosphere, it was transferred into a furnace where a continuous argon gas flow was introduced at the rate of 30 mL/min. Then the furnace temperature was elevated to 873 K and maintained for 3 h. The as-obtained Fe sample after heat treatment was used for the XRD analysis.



**Figure SI-2.** X-ray diffraction patterns of a) the pre-synthesized and b) the in-situ synthesized Fe nanoparticles after dried at room temperature in argon atmosphere, and c) the in-situ synthesized Fe sample after heat treatment at 873 K for 3 h in argon atmosphere.

**Recycle / Stability Test of the in-situ Synthesized Fe Nanoparticles in Air:** After the hydrogen generation reaction was completed, the above in-situ synthesized Fe

nanoparticles ( $\text{Fe}/\text{NH}_3\text{BH}_3 = 0.12$ ) were magnetically attracted to the bottom of the reaction flask by a strong magnet (we took about 40 seconds to wait for the Fe particles to settle), and the upper solution was removed. Then the new  $\text{NH}_3\text{BH}_3$  aqueous solution (0.16 M, 10 mL) was added into the reaction flask. The evolution of gas was monitored using the gas burette. Such recycle experiments for the in-situ synthesized Fe catalyst were repeated for 20 times in air. As shown in Figure SI-3, even after 20 times of the recycle test, the activity of the as-prepared iron catalyst has no obvious decrease.



**Figure SI-3** The  $\text{H}_2/\text{NH}_3\text{BH}_3$  molar ratio of hydrogen generated from aqueous solution (0.16 M, 10 mL) vs. reaction time catalyzed by in-situ synthesized Fe at a) recycle number 1 and b) recycle number 20 ( $\text{Fe}/\text{AB} = 0.12$ ) at room temperature in air.

**Catalyst Characterization:** Powder X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with  $\text{Cu K}\alpha$  for the pre-synthesized and in-situ synthesized Fe nanoparticles after removed from the reaction solution and dried in argon atmosphere. A glass substrate holding the powder sample was covered by an adhesive tape on the surface to prevent the sample from exposure to air during

the measurements. Transmission electron microscope (TEM, Hitachi H-9000NA) and select area electron diffraction (SAED) were applied for the detailed microstructure information. The TEM and SAED samples were prepared by depositing one or two droplets of the nanoparticle suspension onto the amorphous carbon coated copper grids, which were dried in argon atmosphere. Mass analysis was performed using a Balzers Prisma QMS 200 mass spectrometer to analyze the generated gas. The surface areas were measured by N<sub>2</sub> adsorption at liquid N<sub>2</sub> temperature with a micromeritics ASAP 2010 BET analyzer. The obtained BET surface areas are 15 and 13 m<sup>2</sup>/g for pre-synthesized and in-situ synthesized Fe nanoparticles, respectively.

**Safety Precaution:** The handling of the present system in air may be dangerous because the heat generated from the oxidation of Fe metal particles may ignite the flammable H<sub>2</sub> released from the NH<sub>3</sub>BH<sub>3</sub> solution. Avoid exposing dry Fe metal particles to air when the H<sub>2</sub> gas was released from the NH<sub>3</sub>BH<sub>3</sub> solution.