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ZIF-8 immobilized nickel nanoparticles: highly effective catalysts for hydrogen generation from hydrolysis of ammonia borane[†]

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Highly dispersed Ni nanoparticles have been successfully immobilized by the zeolitic metal–organic framework ZIF-8 *via* sequential deposition–reduction methods, which show high catalytic activity and long durability for hydrogen generation from hydrolysis of aqueous ammonia borane (NH₃BH₃) at room temperature.

The safe and efficient storage of hydrogen is widely recognized as one of the most challenging technologies in the transformation to a hydrogen-powered society for a long-term solution to current energy problems.¹⁻⁴ With a high hydrogen content, ammonia borane (AB; NH₃BH₃) has become an attractive candidate for chemical hydrogen storage.^{2–4} The hydrogen stored in AB can be released through either pyrolysis² or hydrolysis.^{3,4} Catalytic hydrolysis can generate 3 mol of hydrogen per mol of AB at room temperature, which presents a high hydrogen capacity of up to 9 wt% of the starting materials (AB and H₂O), making itself an effective approach for hydrogen release from AB. So far many catalyst systems have been tested for hydrogen generation from the hydrolysis of AB,^{3,4} among which platinum shows the highest activity.^{3b} For the practical application of this system, it is still essential to develop efficient and economical catalysts and further improve the kinetic properties via controlling the particle size and increasing the surface area of acquired nonnoble metal catalysts, such as Ni nano-catalysts.⁴

On the other hand, due to high porosity, large surface area and chemical tunability, metal–organic frameworks (MOFs) have become highly promising functional hybrid materials,^{5–11} especially in the application of gas sorption and storage,⁶ molecule recognition and separation,⁷ and drug delivery and medical imaging,⁸ as well as for heterogeneous catalysis.⁹ Although MOF based catalyst preparation¹⁰ and pyrolysis¹¹ for hydrogen release from AB have been reported, the application of MOFs in the catalytic hydrolysis reaction system is still a challenging task due to the instability of most of the MOFs in aqueous solution.



Scheme 1 Schematic illustration of preparation of Ni/ZIF-8 from (a) ZIF-8 via (b) Ni(cp)₂/ZIF-8, and (c) catalytic hydrogen generation from hydrolysis of aqueous AB over Ni/ZIF-8.

Taking into account the high chemical (highly stable in AB aqueous solution) and thermal stability (550 °C in N₂) and large surface area, ZIF-8 (Zn(mim)₂, mim = 2-methylimidazolate), a zeolite-type MOF, becomes the most promising candidate as an effective matrix to control the particle size of metal nanoparticles (NPs) and improve their catalytic surface area for hydrolysis of AB.¹² Herein, we report successful preparation and excellent catalytic activity of highly dispersed Ni NPs immobilized by ZIF-8, Ni/ZIF-8, which presents the first successful example of MOF-supported metal catalysts for the hydrogen generation from hydrolysis of AB.

For preparing Ni/ZIF-8 (Scheme 1), a small volatile molecule nickelocene (Ni(cp)₂) was used as the precursor for Ni. The samples of ZIF-8 supported Ni(cp)₂ (Ni(cp)₂/ZIF-8) were synthesized *via* two approaches: chemical vapor deposition (CVD) and chemical liquid deposition (CLD).^{13–15} In the CVD method the samples were prepared by heating the Ni(cp)₂ and ZIF-8 in separated small glass vessels in a Schlenk tube.¹⁴ In the CLD method the samples were prepared by mixing the diethylether solution of Ni(cp)₂ and the methanol suspension of ZIF-8 and removing the solvents *via* volatilization.¹⁵ CVD-Ni/ZIF-8 (1) and CLD-Ni/ZIF-8 (2) with different Ni loadings were obtained by reducing the above intermediate samples, CVD-Ni(cp)₂/ZIF-8 (3) and CLD-Ni(cp)₂/ZIF-8 (4), in a H₂/Ar flow (50 mol% H₂, 50 mL min⁻¹) at 300 °C for 3 hours.

The catalytic activities on hydrolysis of aqueous AB were tested for the prepared samples. Among the samples of 1 with different Ni loadings (1a, 19.0 wt%; 1b, 16.7 wt%; 1c, 8.6 wt%; determined by ICP),¹³ 1a has the highest activity, with which the

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Fig. 1 Hydrogen generation from hydrolysis of aqueous AB (2 mmol in 2 mL water) in the presence of (a) **1a** (10 mg, Ni/AB = 0.016) and (b) **2a** (10 mg, Ni/AB = 0.019) at room temperature.

reaction can be completed ($H_2/AB = 3.0$) in 13 min (Ni/AB = 0.016) (Fig. 1a), giving a turnover frequency (TOF) value of 14.2 mol of H_2 (mol of Ni)⁻¹ min⁻¹. Among the samples of 2 with different Ni loadings (2a, 22.0 wt%; 2b, 14.3 wt%; 2c, 8.4 wt%),¹³ 2a has the highest activity, with which the reaction can be completed in 19 min (Ni/AB = 0.019) (Fig. 1b), giving a TOF value of 8.4 mol of H_2 (mol of Ni)⁻¹·min⁻¹. As a control experiment, 9.0 mg of NiCl₂·6H₂O, corresponding to 2.2 mg of Ni, was reduced using NaBH₄ as reductant to produce Ni NPs without ZIF-8 as support, with which the complete hydrogen release from the same reaction system needed more than 50 min.¹³ Moreover, it is noteworthy that both the turnover frequencies for 1a and 2a are among the highest values for the Ni nano-catalysts ever reported,⁴ which indicates that the framework of ZIF-8 has a high performance for effectively immobilizing the Ni NPs, preventing them from aggregation, and improving the catalytic surface area of the Ni NPs.

The durability/stability is very important for the practical application of catalysts. We tested the durability of the as-prepared **1a** and **2a** by adding additional equivalents (2 mmol) of AB under ambient atmosphere. There was no significant decrease in catalytic activity even after 5 runs of hydrolysis reactions for both catalysts.¹³ The high activity and long durability/stability of **1a** and **2a** should be due to the fact that the highly dispersed Ni NPs have been effectively immobilized by the frameworks of ZIF-8 (*vide infra*).

 N_2 sorption and powder X-ray diffractions (PXRD) were measured for the samples of 1–4. Appreciable decreases in N_2 sorption as compared with pristine ZIF-8 were observed for all the Ni-loaded samples (Fig. 2a),¹³ indicating that Ni NPs or the related precursor Ni(cp)₂ were dispersed to the frameworks of ZIF-8 in all the samples. The PXRD patterns of all the prepared samples, and also the samples of 1a and 2a after the hydrolysis of AB exhibited that the main diffractions were well consistent with those of pristine ZIF-8, indicating that the framework of ZIF-8 was maintained well in the whole process of catalyst preparation and catalytic hydrolysis of AB. Moreover, in the PXRD patterns, no visible diffraction of Ni was detected for 1 (Fig. 2b), while two small broad peaks around 44.3° and 51.6° due to Ni⁰ were detected for the samples of 2,^{4a,13} indicating



Fig. 2 (a) N_2 adsorption isotherms (77 K) of 1a and 3a. (b) Powder XRD patterns of ZIF-8, 1a before and after catalytic AB hydrolysis, and 3a.

that the framework of ZIF-8 effectively controlled the Ni NPs into small sizes in both 1 and 2.

X-Ray photoelectron spectroscopy (XPS) with Ar etching was applied to **1a** and **2a**. For both samples, well-defined peaks with binding energies of 1022.7 and 1045.9 eV were observed for the $2p_{3/2}$ and $2p_{1/2}$ levels, respectively, of the Zn^{2+} ion in the ZIF-8 framework and well-defined peaks with binding energies of 852.7 and 870.2 eV were detected for the $2p_{3/2}$ and $2p_{1/2}$ levels, respectively, of metallic Ni⁰ of the Ni NPs.^{13,16} Even after Ar etching as long as 240 min, the Ni⁰ species retain their intensity, indicating the highly uniform dispersion of Ni NPs in both **1a** and **2a**.

The morphologies of ZIF-8 immobilized Ni NPs in 1a and 2a were further characterized by transmission electron microscopic (TEM) measurements. Both bright-field TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) images show that the ZIF-8 immobilized Ni NPs were highly dispersed and controlled in small sizes in both 1a and **2a**. The mean diameters were 2.7 ± 0.7 and 4.5 ± 1.0 nm for **1a** and 2a, respectively (Fig. 3 and Fig. S17, ESI[†]).¹³ It should be pointed out that a slight aggregation (Fig. 3b) was also observed for the sample of 2a, corresponding to the observation that the catalytic activity of 2a was lower than that of 1a. The TEM results are in good agreement with PXRD observations, and provide direct evidence that the highly dispersed Ni NPs have been effectively immobilized by ZIF-8 and controlled in small sizes, and therefore exhibit high catalytic activity and durability for hydrolysis of aqueous AB.

As suggested previously, the catalytic process takes place on the metal surfaces where activated complex species might be formed *via* interactions between the NH_3BH_3 molecule and the metal particle surface,^{4a} and therefore finding a method to



Fig. 3 TEM images of (a) 1a and (b) 2a, and HAADF-STEM images of (c) 1a and (d) 2a, revealing that Ni NPs are uniformly dispersed in the frameworks of ZIF-8, especially in 1a.

control particle size and thus increase the surface area of nonnoble metal catalysts will be an effective strategy for developing efficient and economical catalysts used in this catalytic hydrogen generation system.

In summary, highly dispersed Ni NPs with small particle sizes have been successfully immobilized by the frameworks of ZIF-8, which exhibit highly catalytic activity and durability for hydrolysis of ammonia borane (AB). This is the first example of water-stable MOF-supported catalysts for hydrogen generation from hydrolysis of AB. The highly efficient catalysts, especially prepared *via* the CVD-reduction approach, represent a promising step toward the practical applications of water-stable MOFs as effective matrices to immobilize metal NPs in the catalytic hydrolysis reaction system.

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