Heterogeneous Catalysis

DOI: 10.1002/anie.201202055

Highly Dispersed Surfactant-Free Nickel Nanoparticles and Their Remarkable Catalytic Activity in the Hydrolysis of Ammonia Borane for Hydrogen Generation**

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Hydrogen has been considered as one of the best alternative energy carriers to satisfy the increasing demand for a sustainable and clean energy supply.[1,2] Controlled storage and release of hydrogen are the widely known challenging technologies on the way towards a fuel-cell-based hydrogen economy. Owing to its high hydrogen content, high stability at room temperature, and nontoxicity, the ammonia borane (NH_3BH_3) complex has been identified as one of the most attractive candidates for chemical hydrogen storage.[3–5] Catalytic hydrolysis can generate 3 mol of hydrogen per mol of NH_3BH_3 at room temperature, which presents a high hydrogen capacity up to 9.0 wt% of the starting materials (NH_3BH_3 and H_2O), thus making itself an effective approach for the release of hydrogen stored in NH_3BH_3.[4,5] So far many catalyst systems have been tested for hydrogen generation from hydrolysis of NH_3BH_3,[4,5] among which platinum shows the highest activity.[4b] However, concerning the element abundance and related economic issues, it is clearly a desired goal to prepare low-cost catalysts with high catalytic activity for the terminal practical application of this reaction system in the fuel cell.

Ni catalysts, as versatile non-noble metal catalysts, have attracted much attention owing to their activity in various catalytic reactions as well as in catalyzing hydrogen generation from hydrolysis of NH_3BH_3.[5,6] Various Ni nanoparticles (NPs) have been developed by decomposition of Ni complexes in the presence of surfactants, which are nearly unavoidable for preventing the NPs from aggregation in the solution-phase synthetic methods.[5,6] As the catalytic process takes place on the metal surfaces, the presence of a protective surfactant shell around the metal NPs is unfavorable for catalytic applications. Therefore the preparation of NPs without the existence of any protective surfactant significantly benefits both academic researches and practical applications of NP catalysts. Herein, we report the successful synthesis of non-noble surfactant-free Ni NPs through a dry process and their excellent catalytic activity in hydrolysis of NH_3BH_3 for hydrogen generation with a total turnover frequency (TOF, calculated on the basis of the total amount of Ni) value as high as 30.7 mol of H_2 per mol of Ni per min at room temperature, which is the highest one among all of the Ni nanocatalysts ever reported for this reaction (Table S1 in the Supporting Information).[5] The remarkable improvement of catalytic performance of Ni NPs on this hydrogen generation reaction indicated that the strategy of using a surfactant-free dry process could be an effective approach for the synthesis of highly active metal nanocatalysts for heterogeneous catalytic reactions.

Owing to its accessible porosity, large surface area, high chemical; thermal; and mechanical stability nanoporous carbon, Maxsorb MSC-30, was selected as catalyst support.[7] For the synthesis of Ni NPs through a surfactant-free dry preparation process, the small volatile molecule nickelocene ([$NiCp_2$], Cp = cyclopentadienyl) was used as the precursor of Ni, and a series of MSC-30-supported [$NiCp_2$] ([$NiCp_2$]@MSC-30) samples were synthesized using chemical vapor deposition (CVD) through heating the separated [$NiCp_2$] and MSC-30 in a Schlenk tube in different [$NiCp_2$]/MSC-30 ratios of starting materials.[8,9] The samples of Ni@MSC-30 (**1x**, **x** = **a**–**d**) with different Ni loadings were obtained by reducing the related above intermediate samples, [$NiCp_2$]@MSC-30 (**2x**, the [$NiCp_2$]/MSC-30 weight ratio was 2:1 for **2a**, 1.5:1 for **2b**, 1:1 for **2c**, 0.5:1 for **2d**), in a H_2/Ar flow (50 mol% H_2, 50 mL min^{-1}) at 300 °C for three hours.

When comparing them with the pristine nanoporous MSC-30, an appreciable decrease in the amount of N_2 adsorption was observed for both the [$NiCp_2$] dispersed MSC-30 and the Ni NPs dispersed into MSC-30. Based on the N_2 adsorption the saturation deposition of [$NiCp_2$] was found to be achieved at the [$NiCp_2$]/MSC-30 ratio of 2:1 (*w*/*w*), and a relative increase in the amount of N_2 adsorption happened after reducing [$NiCp_2$] molecules to Ni NPs by hydrogen (Figure 1), thus indicating that [$NiCp_2$] molecules and Ni NPs were successfully dispersed into the host framework of MSC-30 as in the case of metal NPs loaded to ZIF-8, MIL-101, and other porous materials.[10] The powder X-ray diffraction (PXRD) patterns of the as-prepared samples exhibited that two small broad peaks around 44.3° and 51.6° owing to Ni^0 were detected for all of the prepared samples of **1**,[5a,8] which further proved the Ni loading in MSC-30. The X-ray photoelectron spectroscopy (XPS) investigation of **1a** show that 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, respec-

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[**] We thank JSPS, AIST, and Kobe University for financial support. P.-Z. Li thanks JSPS for a fellowship (DC).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201202055.

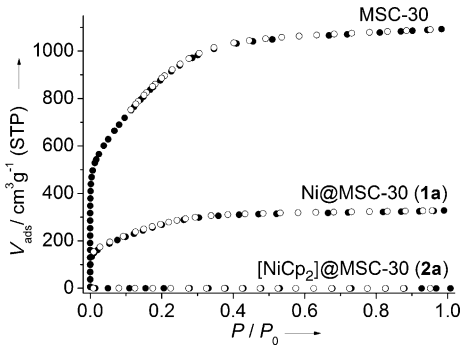

Figure 1. N_2 adsorption isotherms (77 K) of **1a**, **2a**, and pristine nanoporous MSC-30. Curves with filled and empty circles denote the N_2 adsorption and desorption, respectively. STP = standard temperature and pressure.

tively, of metallic Ni^0 of the loaded Ni NPs.[8,11] Even after Ar etching for 240 min, the intensity of the Ni^0 species remains the same, thereby further indicating the highly uniform dispersion of Ni NPs in the host framework of MSC-30.

The catalytic activities on hydrolysis of aqueous NH_3BH_3 were tested for the prepared samples. Among all the samples of **1** with different Ni loadings (**1a**, 18.2 wt%; **1b**, 14.9 wt%; **1c**, 11.7 wt%; **1d**, 7.1 wt%, determined by inductively coupled plasma (ICP) analyses, see Table S2 in the Supporting Information),[8] **1a** has the highest activity, with which the reaction can be completed ($H_2/NH_3BH_3 = 3.0$) within 6.5 min ($Ni/NH_3BH_3 = 0.016$) at room temperature (Figure 2), giving a TOF value as high as 30.7 mol of H_2 per mol of Ni per min,

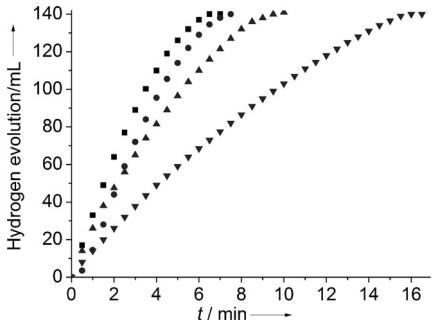

Figure 2. Hydrogen generation by hydrolysis of aqueous NH_3BH_3 (2 mmol in 2 mL water) in the presence of **1a** (■, $Ni/NH_3BH_3 = 0.0155$), **1b** (●, $Ni/NH_3BH_3 = 0.0127$), **1c** (▲, $Ni/NH_3BH_3 = 0.0100$), and **1d** (▼, $Ni/NH_3BH_3 = 0.0060$) at room temperature.

which, notably, is the highest TOF value among all the nickel catalysts ever reported for this reaction.[5] Moreover, when comparing it with the reported poly(vinylpyrrolidone) (PVP)-stabilized Ni NPs,[5d] the surfactant-free Ni@MCS-30 sample shows a catalytic activity that is more than seven times higher. The durability/stability was also tested for **1a** by adding additional equivalents (2 mmol) of NH_3BH_3 into the reacted aqueous solution under ambient atmosphere. There was no significant decrease in catalytic activity even after five runs of the hydrolysis reaction for **1a**.[8] The remarkable improvement compared with the Ni NPs that were prepared in the presence of surfactants indicates that the surfactant-free dry process is an effective approach for the synthesis of highly active metal catalysts.

Then we extended this work to other porous materials. MCM-41, a commonly used mesoporous silica support, also with accessible porosity, large surface area, and high stability,[12] was selected to compare the influence of different porous supports on the catalytic activity of the supported catalysts. The preparation of Ni@MCM-41 (**3x**) via $[NiCp_2]$@MCM-41 (**4x**) was carried out through the same process as that for Ni@MCS-30, and the same phenomena were observed based on N_2 adsorption, PXRD, and XPS measurements.[8] The saturation deposition of $[NiCp_2]$ was found to be achieved at the $[NiCp_2]$/MCM-41 ratio of starting materials of 1.5:1 (*w*/*w*), and the corresponding Ni@MCM-41 (**3a**) was found to have a Ni loading of 19.5 wt%. The complete hydrogen release using **3a** as catalyst in the same reaction system as had been used for **1a** needed about 19.5 min, giving a TOF value of 9.3 mol of H_2 per mol of Ni per min.[8] Compared with **1a**, **3a** gives a lower TOF value, while it is also among the highest values ever reported (Table S1 in the Supporting Information). Taking into account that the same conditions for preparation and catalytic reaction were used, the only explanation should be that the structures of the selected supports, MSC-30 and MCM-41, have high influences on the catalyst preparation and therefore the catalytic results.

The morphologies of MSC-30- and MCM-41-supported Ni NPs were further characterized by transmission electron microscopy (TEM). Both bright-field TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) images showed that the Ni NPs were highly dispersed into the frameworks of MSC-30 in **1a**; these results were in good agreement with the observations of N_2 adsorption, PXRD, and XPS measurements (Figure 3). The mean diameter of the dispersed Ni NPs in **1a** was (6.3 ± 1.7) nm. Although the sizes are a little larger, the catalytic activity is much higher than that of surfactant-protected Ni NPs, such as the reported 3.2 nm Ni NPs;[5e,g] this difference in catalytic activity should be due to the much more effective exposed surface area of the surfactant-free Ni NPs compared to that of surfactant-protected Ni NPs.[5] The TEM and HAADF-STEM images also showed that the Ni NPs were deposited in MCM-41. However, different from Ni@MSC-30, large aggregated nanoparticles were observed in Ni@MCM-41 **3a**, and the mean diameters of the dispersed Ni NPs in **3a** were even higher than 9.5 nm, which is much larger than the diameters in **1a**; this difference in diameters corresponds to the observation that the catalytic activity of **3a** was much lower than that of **1a**. The TEM results provide the direct evidence that the Ni NPs have been highly dispersed into the nanoporous materials, MSC-30 and MCM-41, and the morphologies and catalytic activities of the dispersed Ni NPs highly depend on the structures of selected supports.

As suggested previously, the catalytic process takes place on the metal surfaces where activated complex species might be formed through interactions between the NH_3BH_3 molecule and the metal particle surface,[5a] and therefore finding a method to increase the effective surface area of non-noble

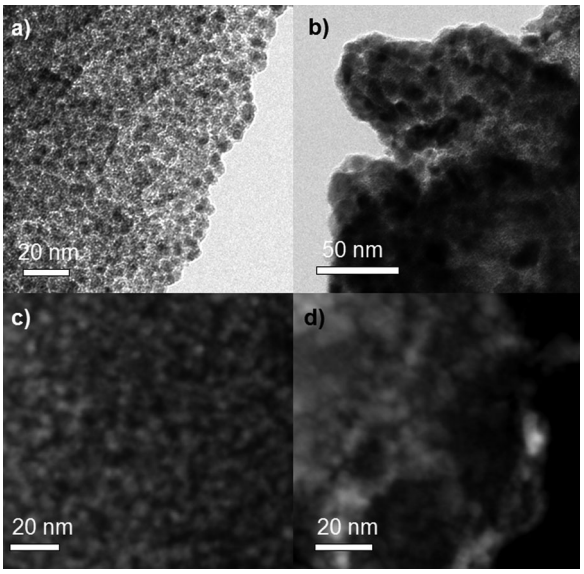

Figure 3. TEM images of a) **1a** and b) **3a**, and HAADF-STEM images of c) **1a** and d) **3a** reveal that Ni NPs are dispersed into the supports, MSC-30 and MCM-41, respectively.

metal nanocatalysts will be a powerful strategy for developing efficient and economical catalysts in this catalytic hydrogen generation system. This work demonstrated that, based on careful selection of catalyst supports, the strategy of using a surfactant-free dry process could be an effective approach for the synthesis of highly active metal nanocatalysts.

In summary, highly dispersed surfactant-free Ni NPs have been successfully deposited into porous carbon, Maxsorb MSC-30, through a dry process, which gives NPs that exhibit remarkably high catalytic activity for hydrogen generation from hydrolysis of ammonia borane. Detailed investigations showed that the structures of the selected supports have high influences on the morphologies and catalytic results of deposited surfactant-free metal NPs. This remarkable improvement of the catalytic performance of the non-noble metal catalysts demonstrates a promising step towards the application of ammonia borane as a feasible chemical hydrogen storage material in a fuel-cell-based hydrogen economy.

Experimental Section

Preparation of Ni@MSC-30:[8,9] For **1a**, the samples of [$NiCp_2$] (120 mg) and MSC-30 (60 mg) were placed separately in a Schlenk tube. After evacuating for 30 min at room temperature, the reaction tube was closed under static vacuum and heated to 110 °C for 24 h, and then the [$NiCp_2$]@MSC-30 (**2a**) was obtained. Ni@MSC-30 (**1a**, 18.2 wt % Ni loading based on ICP result) was obtained by reducing **2a** in a H_2/Ar flow (50 mol % H_2, 50 mL min^{-1}) at 300 °C for three hours. For **1b**, **1c**, and **1d** the weight ratios of starting materials ([$NiCp_2$]/MSC-30) were 90 mg/60 mg, 60 mg/60 mg, and 30 mg/60 mg, respectively, and the Ni loadings based on ICP results were 14.9, 11.7, and 7.1 wt %, respectively.

Preparation of Ni@MCM-41:[8,9] The samples of Ni@MCM-41 were prepared in a similar procedure as those of Ni@MSC-30. For **3a**, **3b**, and **3c** the weight ratios of starting materials ([$NiCp_2$]/MCM-41) were 90 mg/60 mg, 60 mg/60 mg, and 30 mg/60 mg, respectively, and the Ni loadings based on ICP results were 19.5, 14.0, and 7.2 wt %, respectively.

Hydrolytic dehydrogenation of NH_3BH_3:[4a,d,8] The catalytic reactions were carried out by mixing the aqueous suspension of Ni@MSC-30 or Ni@MCM-41 (10 mg) and aqueous NH_3BH_3 (63.5 mg in 2 mL water) in a round bottom flask at room temperature, and a gas burette was used for monitoring the gas evolution.

Received: March 15, 2012
Published online: May 24, 2012

Keywords: heterogeneous catalysis · hydrogen · nanoparticles · nickel · supported catalysts

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[7] Maxsorb MSC-30, also known as AX21, is a high-surface-area super-activated nanoporous carbon in powder shape, now commercialized by Kansai Coke and Chemical Co. Ltd.

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