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Hydrogen Generation

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

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Iron, the most ubiquitous of the transition metals and the fourth most plentiful element in the Earth's crust, has been studied intensively because of its very potent magnetic and catalytic properties.[1] However, its reactivity with respect to water and oxygen, especially on a nanoscale, generally limits its applications to a non-oxidizing environment where water and oxygen are not present.[2] Recent studies involving coating Fe nanoparticles with an outer shell have succeeded in minimizing their oxidation and agglomeration.[3] However, the presence of protective shell around the Fe particles is unfavorable for catalytic applications, where surface Fe active sites are needed.[4] It is therefore understandable that, to date, there has been no report on the catalytic application of Fe nanoparticles without any protective shell other than the solvent components in aqueous solution in air.[5] Fe nanoparticles that exert their powerful catalytic ability in aqueous solution or even in air will therefore significantly benefit both academic research and practical applications of iron-based materials.

The search for effective hydrogen-storage materials is one of the most difficult challenges as we move towards a hydrogen-powered society as a long-term solution to current energy problems.[6] Ammonia borane (AB; NH_3BH_3) has a hydrogen content of 19.6 wt%, which exceeds that of gasoline and therefore makes it an attractive candidate for chemical hydrogen-storage applications.[7–9] The development of efficient and economical catalysts to further improve the kinetic properties under moderate conditions is therefore important for the practical application of this system.[8,9] Herein we report the excellent catalytic activity of Fe nanoparticles with no protective shell for the hydrolytic dehydrogenation of aqueous AB under argon and even in air at room temperature.

The Fe nanoparticles were pre-synthesized by reduction of $FeSO_4$ with $NaBH_4$ and then AB was immediately added to the solution to be catalytically hydrolyzed (AB/$FeSO_4$/$NaBH_4$ 1.0:0.12:0.16).[10] The gas generated was identified by mass spectrometry and its amount was measured volumetrically.[10] Although black Fe nanoparticles were obtained rapidly, the evolution of 134 mL of hydrogen took more than 160 min (Figure 1 a). The molar ratio of hydrolytically generated H_2 to initial AB is close to 3.0, thereby indicating that dehydrogenation is complete.[10] However, the catalytic reaction rate is still quite low, although it is much better than that of γ-Al_2O_3-supported highly crystalline Fe nanoparticles, which do not catalyze this reaction.[8d]

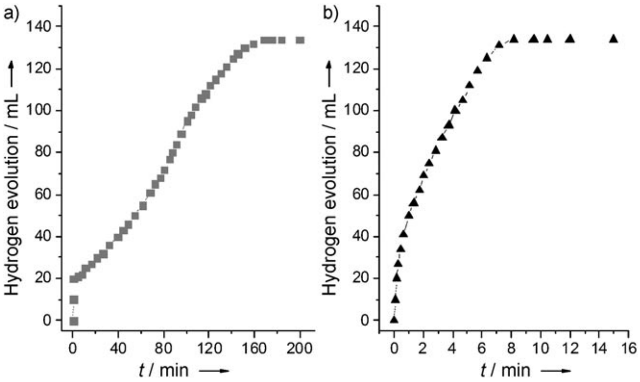

Figure 1. Hydrogen generation by hydrolysis of aqueous AB (0.16 M, 10 mL) in the presence of a) the pre-synthesized and b) in situ synthesized Fe catalysts (Fe/AB = 0.12) at room temperature under argon.

Unexpectedly, we found a simple method for the in situ synthesis of Fe nanoparticles that exhibit high catalytic activity in this reaction. $FeSO_4$ was reduced with $NaBH_4$ in the presence of AB by vigorous shaking (AB/$FeSO_4$/$NaBH_4$ 1.0:0.12:0.16).[10] The H_2 generation performance of this in situ prepared Fe catalyst is shown in Figure 1 b. To our surprise, with this highly active Fe catalyst the hydrolysis of AB is completed within only 8 min. This catalytic activity is about 20-times higher than that of the pre-synthesized Fe nanoparticles.

We analyzed the X-ray diffraction patterns of the two Fe samples after drying at room temperature under argon to determine the differences responsible for these two distinct catalytic activities. Interestingly, we found that the pre-synthesized Fe particles are composed of α-Fe crystallites[10] whereas the in situ prepared Fe exists as an amorphous phase.[10] This amorphous sample also crystallizes into α-Fe after heating at 873 K for 3 h under argon,[10] thereby indicating that the main component of the amorphous phase is zero-valent Fe.

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TEM and selective area electron diffraction (SAED) images of the pre-synthesized and in situ synthesized Fe samples were also recorded to investigate the microstructure of the two samples further (Figure 2). As can be seen from Figure 2a, the pre-synthesized Fe sample is composed of particles approximately 3 nm or less in size which are aggregated into larger particles with a size of less than 100 nm. These larger particles are also agglomerated. The related SAED pattern (Figure 2a, inset) demonstrates that this sample is polycrystalline, which is in good agreement with the X-ray diffraction result. Figure 2b shows that the in situ prepared Fe sample contains aggregates with an average diameter of 60 nm and that each aggregate is also an assembly of many smaller Fe nanoparticles. The SAED pattern (Figure 2b, inset) demonstrates the diffuse diffraction rings of an amorphous phase, which is again consistent with the X-ray diffraction result.

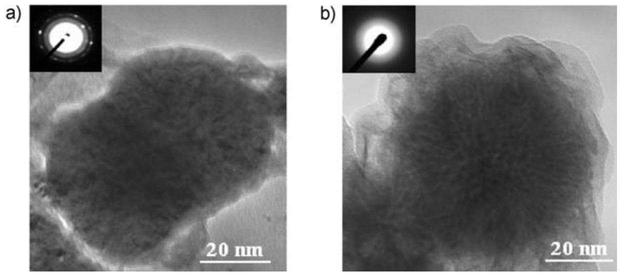

Figure 2. TEM micrographs and the corresponding SAED patterns (insets) of a) the pre-synthesized and b) the in situ synthesized Fe nanoparticles.

Besides the differences in crystallinity of these two samples, the difference in their states of dispersal in aqueous solution should be considered. Thus, the pre-synthesized Fe nanoparticles are agglomerated in the absence of a surfactant or dispersing agent, whereas the in situ prepared Fe nanoparticles form a perfect suspension in aqueous solution and no wholesale agglomeration of the insoluble metal is observed. This lack of agglomeration indicates that AB can serve as both a reactant and an efficient dispersing agent for the synthesis of Fe nanoparticles in aqueous solution.

To determine whether the phase (amorphous or well-dispersed) of the Fe nanoparticles has a significant effect on their catalytic activity, both types of Fe nanoparticles were forced to completely aggregate at the bottom of the two reactors by using a strong magnet; their catalytic activities were then tested. The results show that the catalytic activities of both types of Fe nanoparticles are degraded when they aggregate. However, the reaction time of the amorphous sample (45 min) is still much shorter than that of the crystalline one (630 min), thereby indicating that the influence of the dispersion state on the catalytic activity is not dominant. Thus, we conclude that the amorphous character is essential to the high activity of Fe nanoparticles for catalytic H_2 generation from AB aqueous solution, and that the presence of AB is helpful for the preparation of amorphous Fe nanoparticles. This could be due to the fact that the amorphous catalyst has a much greater structural distortion and therefore a much higher concentration of active sites for the catalytic reactions than its crystalline counterpart.[11]

The in situ synthesized amorphous Fe also has a high catalytic activity in air. Figure 3 shows a plot of the amount of H_2 released from an AB (0.16 M, 10 mL) solution with various Fe/AB molar ratios. The hydrolysis of AB is complete in approximately 35, 15, and 8.5 min at Fe/AB molar ratios of 0.05, 0.08, and 0.12, respectively. Any further increase in the Fe/AB ratio has almost no effect on the reaction rate. The excellent catalytic activity of the in situ prepared Fe in air is much better than that of the pre-prepared Fe, where less than half of the total H_2 is released in 300 min (Fe/AB = 0.12).

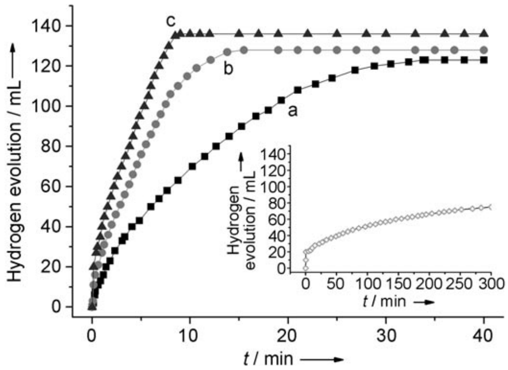

Figure 3. Hydrogen evolution by hydrolysis of AB (0.16 M, 10 mL) in the presence of in situ synthesized Fe with Fe/AB molar ratios of a) 0.05, b) 0.08, and c) 0.12 and pre-prepared Fe (inset, Fe/AB = 0.12; longer reaction time) in air.

Platinum-based materials, such as Pt/C, PtO_2, Pt black, and K_2PtCl_4, have been reported to exhibit the highest activities for the hydrolysis of AB, with completion times ranging from 2 to 15 min.[8c] Our in situ synthesized amorphous Fe catalyst therefore has a catalytic activity similar to that of platinum-based materials in aqueous solution even in air. Moreover, the as-prepared Fe catalyst can readily be recycled by magnetic decantation and reused up to 20 times with no obvious loss of activity in air.[10] This efficient and economical catalyst and the mild reaction conditions it can be used under represent a promising step toward the development of AB as a viable on-board hydrogen-storage medium.

In summary, we have developed a simple but efficient method for preparing amorphous Fe nanoparticles with high catalytic activity for the generation of H_2 from ammonia borane, even in air, which can be readily recycled. This is the first example where Fe nanoparticles with no protective shell have been used in water and in air. This amorphous catalyst is likely to be useful for fuel cells, metal/air batteries, and electrochemical sensors, and could also provide excellent opportunities for studying the molecular mechanisms of heterogeneous catalysis.

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