



Ni-polymer nanogel hybrid particles: A new strategy for hydrogen production from the hydrolysis of dimethylamine-borane and sodium borohydride



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ABSTRACT

Efficient non-precious metal catalysts are crucial for hydrogen production from borohydride compounds in aqueous media via hydrogen atoms in water. A method for preparing magnetic polymer nanoparticles is developed in this study based on the chemical deposition of nickel onto hydrophilic polymer nanogels. High-resolution transmission electron microscopic and XPS analyses show that Ni exists mainly in the form of NiO in nanogels. Excellent catalytic activities of the nanoparticles are demonstrated for hydrogen generation from the hydrolysis of dimethylamine-borane and sodium borohydride in which the initial TOF (turn-over frequencies) are 376 and 1919 h⁻¹, respectively. Kinetic studies also reveal an Arrhenius activation energy of 50.96 kJ mol⁻¹ for the hydrolysis of dimethylamine-borane and 47.82 kJ mol⁻¹ for the hydrolysis of sodium borohydride, which are lower than those catalyzed by Ru metal. Excellent reusability and the use of water for hydrogen production from dimethylamine-borane provide the additional benefit of using a hybrid catalyst. The principle illustrated in the present study offers a new strategy to explore polymer-transition metal hybrid particles for hydrogen energy technology.

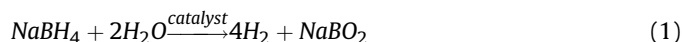
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1. Introduction

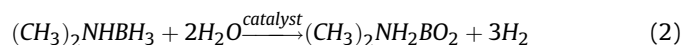
In recent years, hydrogen energy has been seen to be an ideal energy source due to its zero carbon emission and high heat of combustion compared with traditional fossil fuels, and hence, hydrogen has attracted enormous attention [1–3]. A hybrid energy system based on renewable energy sources (solar and wind) coupled with hydrogen technology is technically feasible for stand-alone electricity and heat supply for household applications [4,5]. In the field of mobile device applications, proton exchange membrane hydrogen fuel cells can power unmanned aerial vehicles or submarine vehicles [6,7]. From the application point of view, the safe generation of hydrogen is a prerequisite. Hydride compounds, such as sodium borohydride (NaBH₄) and dimethylamine-borane (abbreviated as DMAB) [(CH₃)₂NHBH₃], are appropriate materials

due to their high efficiency of H₂ production, high stability, and nontoxicity. Their prices are much lower than that of ammonia-borane.

In theory, 1 mol of NaBH₄ can produce 4 mol of H₂ by using hydrogen atoms in water (see Eq. (1)):



while the hydrolysis of DMAB produces 3 mol of H₂ per mole by using 2 mol of water (see Eq. (2)):



Self hydrolysis of DMAB and NaBH₄ is quite slow; however, the reaction can be greatly accelerated with an appropriate catalyst [3]. Previous studies have shown that catalysts, such as Pt, Ru, Rh, Pd, Ni, Co, Fe [1,8–22], or various metal alloys [23–27] can be used for H₂ production from the hydrolysis of NaBH₄. For H₂ production from DMAB, noble metals, such as Pd, Ru, Rh, Ir, Pt and Re, have been investigated for the catalytic dehydrogenation of DMAB

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[28–34]; however, these reactions were mostly conducted in neat organic media, where only 1 mol of H₂ per mole of DMAB could be generated. In addition, the limited reserves and high cost of noble metal catalysts have impeded their wide applications. Therefore, it is very important to develop efficient non-precious metal catalysts that are suitable for H₂ production in aqueous media.

To take the advantage of the hydrogen atoms in water, we report here the hydrolysis of DMAB catalyzed by magnetic nickel particles in aqueous solutions. For optimal performance, the Ni particles are prepared by chemical deposition onto hydrophilic polymer nanogel particles without palladium metal activation. Combining the properties of solids and fluids, nanogels (usually in the tens to hundreds of nanometers in diameter) have swellable, porous structures in water or organic solvent and their chemical functionality and interaction with metals can be tailored [35]. A comparison with H₂ production from NaBH₄ solutions is also made for the hybrid catalyst system.

2. Experimental

2.1. Materials

Potassium persulfate, N-isopropyl acrylamide (NIPAM), 2-acrylamide-2-methyl propanesulfonic acid (AMPS), N-tert-butyl acrylamide (NtBAM), methylene-bis-acrylamide (MBAM), sodium potassium tartrate (C₄H₄O₆KNa), NaOH, NiSO₄·7H₂O, DMAB aqueous solution (10.0 wt% concentration) and NaBH₄ were purchased from Aladdin Reagent Company (Shanghai) in analytical grade. All of these chemical compounds were used as received, without further purification.

2.2. Preparation of polymer nanogel-supported Ni particles

In a typical synthesis, NIPAM (1.13 g), AMPS (0.104 g), NtBAM (0.254 g), MBAM (0.046 g) and potassium persulfate (0.053 g) were dissolved in water (50 mL) in a three-necked flask with a N₂ gas inlet and a reflux condenser. N₂ gas was bubbled through the mixture with stirring for 20 min to remove oxygen. The mixture was stirred in a water bath at 70 °C. After 5 h, the precipitation polymerization reaction was completed, and copolymer nanogel particles of P(NIPAM-co-AMPS-co-NtBAM) were obtained for the subsequent experiments.

Fifteen milliliters of the above copolymer aqueous dispersions and 1.39 g of NiSO₄·7H₂O in 35 mL of water were mixed in a beaker. After stirring for 15 h, the mixture was filtered by a 100-nm pore-sized polyethersulfone membrane filter and then washed three times with distilled water. Next, the Ni²⁺ impregnated copolymer nanogel was dispersed in water (40 mL) and then mixed with NaBH₄ (0.10 g in 10 mL H₂O) for 15 h for reduction, resulting in Ni-modified gel particle seeds.

Electroless Ni plating was performed after the Ni-modified gel particle seeds were added to a Ni-complex electroless plating bath with sodium potassium tartrate (6.5 g), NaOH (3 g), NiSO₄·7H₂O (2.39 g) and NaBH₄ (0.3 g). The mixture was mechanically stirred for 2 h at 90 °C. After the reaction, the nanospheres were filtered and dried under vacuum, yielding a black catalyst.

2.3. Catalytic activities of the nanogel-supported Ni particles for H₂ production from NaBH₄

The catalysis reactions were performed in a procedure similar to that of our previous report [36]. Briefly, the nanogel supported catalyst was mixed with 0.095 g of NaBH₄ in a flask that was tightly sealed and positioned in a thermostat bath. Water (50 mL) was charged into the flask by using a syringe. The volume of the H₂

generated was recorded by using an upside-down graded cylinder charged with water, in which the gas can replace the water at different times. The slope of the H₂ volume versus time in the initial linear section can be used to determine the H₂ production rate (k).

2.4. Catalytic activities of the polymer nanogel-supported Ni particles for the hydrolysis of DMAB

The catalysts were mixed with 16 mL of water in a three-necked flask that was tightly sealed and placed in a thermostat bath. Four milliliters of a DMAB aqueous solution was charged into the flask through a syringe to fully reduce the Ni metal. After the reaction, the catalyst was dispersed in 18 mL of water in a 50 °C water bath after centrifuging the solution. Next, 2.0 mL of a DMAB aqueous solution was added. The H₂ gas produced thereafter was recorded by using a procedure similar to the above-described measurement of H₂ production from NaBH₄.

The H₂ generation rate was also measured at different solution temperatures (from 308.15 to 328.15 K for NaBH₄ and from 313.15 to 333.15 K for DMAB) to determine the activation parameters involved in the catalytic hydrolysis reaction. The measurement was also undertaken with different amounts of the catalyst (0.002, 0.004, 0.008, and 0.012 g for NaBH₄ and 0.020, 0.025, 0.030, and 0.040 g for DMAB) and different concentrations of DMAB (81, 162, 324, and 486 mM). For the recyclability test, the catalyst was collected by centrifuging from the reaction solutions, washed thoroughly in water, and then used for the next round.

2.5. Characterization of the nanogel-supported Ni particles

The catalyst was investigated using a JEM-2100 electron microscope at an acceleration voltage of 200 kV. The hydrodynamic diameters were measured using a Nanophox dynamic light scattering analyzer (Sympatec GmbH, Germany). The Ni contents were analyzed using a Prodigy XP ICP atomic emission spectrometer (Leeman Labs, USA). K-ALPHA X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Company) analysis was performed to identify the oxidation state of nickel on the surface of the catalyst.

3. Results and discussion

3.1. Characterization of the polymer nanogel-supported Ni particles

Nanogel-supported Ni particles were prepared by a novel electroless plating process in which the activation of the polymer nanogel particles was achieved by impregnation in a Ni salt solution that replaced traditional noble metal seeding, followed by chemical reduction. The polymer nanogel particles were prepared by precipitation polymerization of N-isopropyl acrylamide, 2-acrylamide-2-methyl propanesulfonic acid, and N-tert-butyl acrylamide. The Ni-deposited nanogel particles were analyzed using transmission electron microscopy (TEM). Fig. 1(a) shows that nickel is highly dispersed in the polymer nanogel particles (black areas in the image). The average size of the copolymer nanogels before electroless plating is 210 nm, while that after plating is approximately 225 nm. Introduction of nickel does not dramatically expand or shrink the size of the nanogel particles, which is suggestive of the highly porous nature of the nanogels in water. Nickel metal is continuously spread throughout the nanogel particles because of the sufficient number of pores that are present in the hydrophilic particles. Dynamic light scattering characterization of the Ni-embedded nanogel particles in water shows that their hydrodynamic diameters are approximately 411.9 nm, which are larger than those shown in the TEM image because the nanogels swell in water during the light scattering analysis. This result also

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