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Hydrogen production from ammonia borane via hydrogel template synthesized Cu, Ni, Co composites

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ABSTRACT

In situ Co, Cu and Ni nanoparticles were synthesized by chemical reduction of the absorbed Co (II), Cu (II) and Ni (II) ions inside hydrogel networks prepared from 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) and were used as a catalyst system in the generation of hydrogen in hydrolysis of ammonia borane (AB). Several parameters affecting the hydrolysis reaction such as the type of the metal, the amount of catalyst, the initial concentration of AB, and temperature, were investigated. The activation energy values in the hydrolysis reaction of AB solution in the presence p(AMPS)-Co, p(AMPS)-Cu and p(AMPS)-Ni catalyst systems were calculated as E_a = 47.7 kJ mol^{-1}, 48.8 kJ mol^{-1} and 52.8 kJ mol^{-1}, respectively. Thus, the catalytic activity of the metal nanoparticles prepared inside the same hydrogel matrix was found to be Ni < Cu < Co.

1. Introduction

Because of its environmental friendliness, high energy density, clean combustion product (only water), hydrogen is regarded as one of the clean fuels [1–4]. Therefore, much research focuses on hydrogen production from hydrogen storage materials such as Ca_2H, LiH, $NaBH_4$, MgH_2, $LiAlH_4$, KBH_4, $NaAlH_4$ and H_3NBH_3 (ammonia borane) with superior catalyst systems [5–8]. Among these hydrogen storage materials ammonia borane (AB) is an attractive candidate because of its low molecular weight (30.7 g mol^{-1}) and high hydrogen capacity (19.6 wt %) [9–11]. Furthermore, AB has high water solubility (33.6 g AB/100 g water) [12], higher stability in aqueous solution at room temperature [13,14], is nontoxic [15], and has an exothermic hydrolysis reaction ($\Delta H^\circ = -155.97$ kjmol^{-1}) [16].

$$NH_2BH_3(aq) + 2H_2O(l) \xrightarrow{\text{catalyst}} NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \quad (1)$$

AB releases hydrogen gas in the presence of a suitable catalyst at room temperature according to the equation above (Eq. (1)) [17–20]. Recently, numerous transition metal catalyst systems such as: intrazeolite palladium(0) [17]; Co(0) [18], Rh(0) [15,21] and Cu(0) nanoclusters [22]; water soluble polymer stabilized Ni(0) [1], Rh(0) [16], Ru(0) [19,23] and Pd(0) [23] nanoclusters; Cu/Co_3O_4 nanoparticles [2], hollow Ni–SiO_2

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nanospheres [3], Co–B thin film [5], electroplated Co–P catalyst [6], magnetically recyclable Au@Co core-shell nanoparticles [9], Pt_xNi_{1-x} nanoparticles [13], Co nanoparticles [24], Pt- and Ni-based alloy catalysts [25]; monodispersed Ni nanoparticles [26], SiO_2 supported monodispersed Ni nanoparticles [27], Co nanospheres [28] and bimetallic Au–Ni nanoparticles [29]; magnetically recyclable hollow Co–B nanospindles [30] and montmorillonite immobilized Ru nanoparticles [31] have been reported for use in the hydrolysis reaction of AB. Direct utilization of metal nanoparticles as catalyst is somewhat restricted due to aggregation and destabilization [32,33]. To prepare a catalyst with better catalytic activities and to prevent aggregation generally supporting materials such as silicates [3,27–29], clays [31], zeolites [15,17,18,21,22] and most recently hydrogels, have been utilized [7,8,32–35]. Amongst these materials hydrogels attract special attention due to characteristics such as different functional groups in three-dimensional water-swollen, crosslinked hydrophilic polymeric networks providing a unique environment for the preparation and protection of metal nanoparticles. The anionic functional groups $-SO_3^-$ and $-COO^-$ in the hydrogel networks readily form negative charges in aqueous environments to absorb metal ions via electrostatic interactions and then reduce these hydrogel bound metal ions to form metal nanoparticles. Taking advantage of the flexible (swelling and shrinking ability) advantages of hydrogel networks, various metal nanoparticles or nanoclusters can be prepared in situ by reduction of absorbed metal ions with suitable reducing agents such as $NaBH_4$ [7,8,32–35], providing an expanded range of applications from environmental remediation to biomedical applications [36–38].

Previously, our group reported the synthesis of p(AMPS) hydrogel networks and its use in the preparation of Ni, Co, Fe, and Cu nanoparticles and utilization of these particles in the reduction of 2- and 4-nitrophenols [32,33]. The in situ prepared Ni and Co nanoparticles in p(AMPS) hydrogel networks used as catalyst in the hydrolysis of $NaBH_4$ [7,8] were also reported. In addition to Co and Ni metal nanoparticles, we report the preparation of Cu nanoparticles in p(AMPS) networks and their utilization as catalyst in the hydrolysis of AB in aqueous media. Additionally, after using the p(AMPS)-M (M: Co, Ni, Cu) catalyst system in the generation of hydrogen, the metal catalyst can be readily removed from the hydrogel template and it can then be reloaded with desired metal catalysts. The reaction kinetics were investigated under different reaction conditions and various parameters, such as AB concentration, temperature, catalyst amount and type, affecting the hydrolysis processes of AB were evaluated. The reaction was carried out at five different temperatures to calculate the activation parameters. The activity and repetitive usage of the catalyst–hydrogel system was also investigated.

2. Experimental

2.1. Materials

In hydrogel synthesis, 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) as monomer, N,N′-methylenebisacrylamide (MBA) as crosslinker, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (MPA) as UV initiator were used and purchased from Sigma–Aldrich and Acros Chemical Companies. $NiCl_2.6H_2O$ (Riedel de Haen), $CoCl_2{\cdot}6H_2O$ (Aldrich) and $CuCl_2{\cdot}2H_2O$ (Aldrich) as metal ion sources and $NaBH_4$ (Aldrich) as reducing agent were used for in situ metal particle preparation. NH_3BH_3 (Aldrich) was used as hydrogen source. All the reagents were of analytical grade or highest purity available, used without further purification.

The 18.2 MΩ cm (Millipore Direct-Q3 UV) distilled water was used for preparation, washing of hydrogels, and for preparation of the reagents. The metal nanoparticle content of p(AMPS) hydrogels was determined via Thermogravimetric Analysis (SII TG/DTA 6300) and Inductively Coupled Plasma-Atomic Spectrometry (Varian Liberty II AX Sequential ICP-AES) measurements. TG measurements were performed between 50 and 1200 °C with10 °C/min heating rate under 100 ml/min nitrogen flow.

2.2. Hydrogel synthesis and in situ metal particles preparation

P(AMPS) hydrogels were synthesized according to the procedure in the literature [7,8]. Synthesis of metal nanoparticles inside the hydrogel network was carried out by using 100 mg dry hydrogel according to the procedure in the literature [7,8,32–35].

2.3. Catalytic hydrolysis and kinetic studies of AB

The catalytic activity of in situ metal nanoparticles inside p(AMPS) hydrogels in the hydrolysis of AB was determined by measuring the hydrogen generation rate. All the experiments were carried out by using 50 mM 50 ml AB (0.077 g) solution and 100 mg dried hydrogel, containing different metal nanoparticles, in a 100 ml reaction flask. The reactions were performed at 1000 rpm mixing rate at 30 °C in 1 atm if not stated. The generated amount of hydrogen gas at specified time intervals was passed through 100 ml of concentrated H_2SO_4 to remove water vapor from the gas washing bottle and the amount of hydrogen gas was determined from the inverted volumetric cylinder, based on the principle of substitution (filled water was replaced by produced H_2 gas). All the experiments were conducted three times and the constructed graphs are presented with standard deviation.

In order to determine the effect of the types of catalysts, 100 mg of hydrogel containing 12.4 mg Co, 11.0 mg Cu or 11.8 mg Ni nanoparticles (determined by ICP-AES measurements) was crushed and used by placing into a reaction flask containing aqueous solution of 50 mM 50 ml AB at 30 °C for the hydrolysis reaction.

In order to determine the effect of the amount of catalyst on the hydrolysis reaction of AB at 30 °C and 1000 rpm mixing rate, five different amounts (50–500 mg) of Co nanoparticle-containing hydrogels were placed into 50 mM 50 ml AB solution. The weights of the hydrogels containing Co nanoparticles were 50 mg, 100 mg, 150 mg, 300 mg and 500 mg.

For the kinetic studies, 100 mg crushed hydrogel-Co composites were used in hydrolysis of 50 mM 50 ml AB