



Low temperature decomposition of hydrous hydrazine over FeNi/Cu nanoparticles

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ABSTRACT

A simple, surfactant-free liquid-phase reduction of Cu, Ni and Fe salts (e.g. nitrates, chlorides) was used to prepare nanostructured FeNi/Cu catalysts for hydrous hydrazine ($N_2H_4 \cdot H_2O$) decomposition. The synthesis of nanomaterials includes reduction of copper salt using N_2H_4 , followed by rapid reduction of iron and nickel salts by $NaBH_4$. The catalysts were characterized by XRD, BET, TEM, XPS, XANES/EXAFS techniques and their activity and selectivity was studied during hydrous hydrazine decomposition at temperatures ranging from 300 to 345 K. The selectivity to hydrogen increases to $\sim 100\%$ with increasing temperature up to ~ 345 K. The catalytic performance of these materials depends on the structure of NiFe layer formed over a Cu core, which may be controlled by changing of NiFe/Cu mass ratio. Investigation of the catalytic performance for bi- and tri-metallic materials show that main active metal is nickel but a NiFe alloy could be responsible for the increased selectivity. Alloying of nickel with iron coupled with a favorable dispersion on copper nanoparticles remarkably enhances the catalytic conversion and selectivity of hydrogen evolution.

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1. Introduction

Development of hydrogen storage materials remains one of the difficult challenges on the way to a hydrogen energy based technologies. The safe transportation of hydrogen, limitations on volumetric and gravimetric hydrogen storage capacities, handling conditions and recycling of byproducts are major technological barriers preventing the widespread application of hydrogen in energy technologies.

Hydrazine (N_2H_4), a liquid at room temperature, has a hydrogen content of 12.5 wt.%. Studies have shown that hydrazine can be decomposed on supported metals [1], metal nitrides [2,3] or metal carbides [4,5] in two ways: complete decomposition:



and the incomplete decomposition:



The decomposition pathway depends on the catalyst used and reaction conditions (e.g. temperature) [4–9]. SiO_2 -supported Ni, Pd, and Pt catalysts are active even at room temperature [1]. The hydrogen selectivity increases with the reaction temperature in the range of 310–390 K, and then quickly decreases as the reaction temperature is further increased. It is suggested that the two competing reactions (1) and (2) are occurring during hydrazine decomposition over these supported catalysts. At higher temperatures (>670 K), the hydrogen selectivity is $\sim 100\%$ due to the decomposition of NH_3 . The explosive nature of anhydrous hydrazine upon exposure to metal catalyst surfaces, however, limits its application for hydrogen generation.

Hydrous hydrazine, on the other hand, such as hydrazine monohydrate, $N_2H_4 \cdot H_2O$, still contains a large amount of hydrogen, 8.0 wt.%, which is available for hydrogen generation and is much safer, although efforts need to be made to minimize its toxicity. The distinct advantages of using hydrous hydrazine are: generation of only nitrogen as byproduct thus not requiring on-board collection for recycling, and easy recharging using the current infrastructure of liquid fuels. The key to exploit effectively the hydrogen-storage properties of hydrazine is to develop efficient and selective catalysts for H_2 generation from hydrous hydrazine [10–17].

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Among the various unsupported monometallic nano-catalyst, Rh is found to be the most selective (45%) for hydrogen release from hydrous hydrazine decomposition at room temperature [12]. Other metals, such as Co, Ru and Ir, exhibited only 7% selectivity for hydrogen, and Fe, Cu, Ni, Pt and Pd are inactive at room temperature [11]. Bimetallic Ni alloyed with noble metals such as NiRh, NiPt, and NiIr catalysts show enhanced activity and hydrogen selectivity at room temperature. The H₂ selectivity is found to be strongly dependent on the ratio of metals. For example, 100% H₂ selectivity at 298 K is reached when Ni/Rh mass ratio was 0.25 [18].

Graphene-supported NiRh catalyst has been also successfully prepared and tested for hydrous hydrazine decomposition via a facile co-reduction reaction [16]. Graphene plays a key role as a dispersion agent and distinct support for the Rh-Ni nanoparticles. The RhNi-graphene catalyst exhibits 100% H₂ selectivity at room temperature. Thus, noble metal containing nano-catalysts show high catalytic activity and 100% selectivity for hydrous hydrazine decomposition at room temperature.

Recently, emphasis has been placed on the development of suitable reaction conditions for hydrous hydrazine decomposition to hydrogen by using low-cost catalysts [15,17,19]. For example, NiFe bimetallic nanoparticles have been studied as catalysts for this reaction [13–15]. Bimetallic NiFe nanocatalysts are prepared using a surfactant-aided (hexadecyltrimethylammonium bromide) co-reduction process of metal salts in an aqueous solution. These nanoparticles are active at 345 K, and addition of sodium hydroxide is necessary for high H₂ selectivity. A noble metal-free Raney Ni catalyst has also shown high selectivity toward H₂ for hydrous hydrazine decomposition in a basic solution at temperatures of 310–350 K [19]. A supported nickel catalyst has also been proposed for selective decomposition of hydrous hydrazine [17]. In this case Ni-Al hydrotalcite is co-precipitated from a solution of nickel and aluminum salts, which annealed in hydrogen at 670 K results in the formation of nickel nanoparticles on the surface of the support. Although this catalyst exhibits ~100% conversion and ~90% H₂ selectivity, high reduction temperature during preparation hinder its application for the decomposition of hydrous hydrazine.

The above references indicate that Ni-based catalysts have high potential for selective decomposition of hydrous hydrazine toward hydrogen and nitrogen at low temperatures. We investigated the possibility of preparing supported NiFe catalysts using a surfactant-free low temperature synthesis process. As support material, copper nanoparticles are selected, as a recent investigation [20] shows that copper may be an efficient “support” for nickel in the water gas shift reaction. In this work we show that copper helps to obtain NiFe nano-size domains during liquid phase reduction process. The NiFe/Cu catalysts show high activity, stability and ~100% hydrogen selectivity at 330–340 K.

2. Experimental

The catalysts were prepared in two stages. In the first stage, copper nanoparticles were produced by solution reduction using copper nitrate hydrate as precursor. 0.4 g of Cu(NO₃)₂·2.5H₂O was dissolved in pure ethyl alcohol (20 ml), then a solution containing 1 M sodium hydroxide (3 ml) and hydrous hydrazine (0.15 ml) is added drop-wise to the copper nitrate solution under vigorous stirring conditions at temperatures of 300 to 350 K for 2 h.

In the second stage, the copper nanoparticles produced were washed several times in deionized water without air exposure and transferred into a three-necked flask. Then, 2 ml of a solution containing iron (FeCl₂·4H₂O) and/or nickel (Ni(NO₃)₂·6H₂O) salts were added to the suspension of copper nanoparticles under vigorous stirring, followed by rapid addition of 2 ml of sodium borohydride (NaBH₄) solution (1 M). The concentrations of iron and nickel salts

were adjusted to produce equimolar quantities of metals after full reduction, as we found early that catalysts with such composition may provide the highest selectivity of hydrazine decomposition toward hydrogen [15]. Synthesis of iron and nickel particles by NaBH₄ reduction was performed under continuous nitrogen flow (rate ~50 ml/min) for about 2 h.

In catalytic experiments, the total volume of metallic suspension was reduced to ~1 ml and hydrous hydrazine (Alfa Aesar, 98%) directly added to the suspension. The catalytic performance of the nanomaterials was evaluated on the basis of the volumetrically measured amount of gases released during the reaction. In these experiments, the gases evolved during the reaction passed through a trap containing 1 M solution of hydrochloric acid to capture the ammonia evolved. Thus, the volume of gas measured equals the sum of nitrogen and hydrogen evolved during hydrous hydrazine decomposition. The compositions of gases were also analyzed by an online gas-chromatograph (Varian 290) using a HAYESEPD column with Ar carrier gas.

The X-ray diffraction (XRD) patterns were obtained in a D8 Advance powder diffractometer (Bruker), using CuK α monochromatized radiation ($\lambda = 0.1541$ nm) at a scan speed of 10 min⁻¹. The scanning angle (2θ) range was varied from 20 to 80, operated at 40 kV and 40 mA.

A Titan 80–300 (FEI, USA) transmission electron microscope with resolution of 0.136 nm in STEM mode and about 0.1 nm information limit in high resolution TEM mode was also used. The TEM is equipped with energy dispersive X-ray spectroscopy (EDS, Oxford Inca) system with a spectral energy resolution of 130 keV.

BET specific surface area determinations were made using N₂ gas adsorption/desorption (~77 K) using an ASAP 2020 apparatus (Micromeritics). Before absorption analysis, the samples are dried at room temperature and then vacuum degassed at 373 K for 6 h.

X-Ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI VersaProbe II spectrometer with an Al K α X-ray source operating at 1486.6 eV and a 90° take-off angle for near surface analysis of O 1s, Cu 2p_{3/2}, Fe 2p_{3/2}, and Ni 2p_{3/2} electronic transitions. Catalyst powders were adhered to brass mounts using a double-sided carbon tape, and loaded into the analysis chamber. Samples were left to outgas overnight in the vacuum system maintained at a pressure less than ~10⁻⁷ Pa. Binding energy values were referenced to the C 1s peak (284.8 eV) that resulted from the adventitious contamination layer. The spectra were analyzed using the Casa XPS software package with relative sensitivity factors obtained from the Kratos library.

XANES measurements of the hydrogen reduced catalysts (at 573 K for 2 h) were made using X-ray absorption spectroscopy at the Advanced Photon Source at Argonne National Laboratory. The measurements were obtained in transmission mode with ionization chambers optimized for the maximum current with linear response (~1010 photons detected/s). A cryogenically cooled double-crystal Si (1 1 1) monochromator with resolution (ΔE) better than 2.5 eV at 8.979 keV (Cu K edge) was used in conjunction with a Rh-coated mirror to minimize the presence of harmonics. The integration time per data point was 1–3 s, and three scans were obtained for each condition. Oxidation states were inferred from XANES data obtained for reference metal oxides and pure metals.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

The synthesis procedure of NiFe/Cu catalysts involves two stages: *copper nanoparticles preparation* by hydrazine reduction of copper nitrate and subsequent *precipitation of nickel and iron*

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