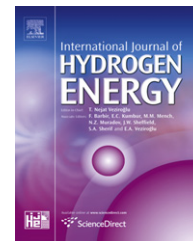


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Improved hydrogen desorption properties of ammonia borane by Ni-modified metal-organic frameworks

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ABSTRACT

Ammonia borane (AB) has attracted intensive study because of its low molecular weight and abnormally high gravimetric hydrogen capacity. However, the slow kinetics, irreversibility, and formation of volatile materials (borazine and ammonia) of AB limit its practical application. In this paper, new strategies by doping AB in metal-organic framework MIL-101 (denoted as AB/MIL-101) or in Ni modified MIL-101 (denoted as AB/Ni@MIL-101) are developed for hydrogen storage. In AB/MIL-101 samples, dehydrogenation did not present any induction period and undesirable by-product borazine, and decomposition thermodynamics and kinetics are improved. For AB/Ni@MIL-101, the peak temperature of AB dehydrogenation was shifted to 75 °C, which is the first report of such a big decrease (40 °C) in the decomposition temperature of AB. Furthermore, borazine and ammonia emissions that are harmful for proton exchange membrane fuel cells, were not detected. The interaction between AB and MIL-101 is discussed based on both theoretical calculations and experiments. Results show that Cr–N and B–O bonds have generated in AB/MIL-101 nanocomposites, and the decomposition mechanism of AB has changed.

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1. Introduction

Hydrogen has been suggested as a future carrier of renewable energy because its combustion product is water, a zero pollutant. Though hydrogen production has made remarkable progress [1,2], safe, efficient, compact and inexpensive hydrogen storage systems remain to be developed [3,4]. It has been demonstrated that the greatest potential method to store

hydrogen is by using solid media, such as hydrides [5,6] and sorbent materials [7–9]. Ammonia borane (NH₃BH₃, denoted as AB) has recently attracted great interest as a promising candidate material for hydrogen storage due to its high gravimetric hydrogen capacity (19.6 wt.%) and low molecular weight (30.7 g mol⁻¹) [10]. However, the practical application of AB is handicapped by its slow thermal kinetics below 100 °C, the emission of poisonous byproducts (borazine, ammonia and

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diborane), severe material foaming during the dehydrogenation and irreversibility. Proton exchange membrane fuel cells (PEMFC) normally work at 80 °C and in the absence of species poisonous to their catalysts. In the PEMFC, only ppm level ammonia will cause poisoning of the catalysts. The elimination of poisonous byproducts and decrease of decomposition temperature, therefore, play a very important role for AB used in PEMFC. To overcome these barriers, a number of approaches have been developed, including activation by transition metal catalysts [11–15], ionic liquids [16] and acid catalysts [17]. Despite considerable effort, these have not met the requirement of PEMFC. New approaches that are more practicable remain to be developed.

Recent reports show that materials structured at the nanoscale can decrease their H₂ desorption enthalpy and enhance the kinetics relative to the bulk materials [18,19]. Carbon cryogel and mesoporous silica infiltrated with AB have been demonstrated to significantly improve the kinetics and decrease the temperature for hydrogen release [20,21]. However, the hydrogen release temperature is still higher than 85 °C and there is no concern on the prevention of ammonia formation. Therefore, a breakthrough in this research area calls upon the synthesis of new nanostructured materials that can provide a stronger nanoscale effect. Metal-organic frameworks (MOFs) are promising candidates as new scaffolds due to their ordered crystalline lattice, adjustable pore sizes and acceptable thermal stabilities, as well as especially excellent catalytic performances [22]. It has been shown that metal clusters and hydrides could be confined in MOFs [23,24]. Recent study also shows that AB filled in MOFs enhances kinetics and eliminates ammonia [25]. In this system, molar ratio of AB to MOF was 1:1. Because of high molecular weight of MOF, AB mass content is relatively low. In addition, the interaction between AB and MOFs is still unclear. It is important to investigate the interaction between AB and MOFs so that to design new AB/MOFs materials.

Here, we select chromium(III) terephthalate (MIL-101) as a host material for detailed investigation because it has a huge cell volume that is necessary to confine more AB. MIL-101 is thermally stable up to 275 °C, and also stable when treated with various organic solvents at room temperature or under solvothermal conditions [26]. This enables MIL-101 to be used without decomposition during materials preparation and H₂ desorption from AB at suitable conditions. The presence of numerous unsaturated Cr^{III} sites in MIL-101 provides an intrinsic chelating property with an electron-rich functional group, making it as a catalyst. Our previous study showed that MOFs can be modified by catalysts to improve their hydrogen storage property [27], and the first-principle calculations play an important role in the study of hydrogen storage materials [28,29]. Therefore, here we propose a new method to improve hydrogen storage of ammonia borane by doping it with metal-organic frameworks modified by Ni catalyst for the first time. The peak temperature of AB dehydrogenation was shifted to 75 °C (114 °C for neat AB). This is the first report of such a big decrease (40 °C) in the decomposition temperature. Furthermore, poisoning species like NH₃ and borazine have been inhibited. In AB/MIL-101 nanocomposites, improved thermal decomposition thermodynamics and kinetics of AB have been observed. The interaction between AB and MOFs is investigated by the experiments and first-principle calculation in the present work.

2. Experimental

2.1. Sample preparation

MIL-101 was synthesized according to reported procedures [26]. MIL-101 was heated to 200 °C for 3 h under Ar to remove the coordinated water, then stored in a Unilab91200 glove box (MBraun Co., Germany) filled with purified argon. 3% Ni@MIL-101 was prepared by adding 3 ml of 0.18 mol L⁻¹ NiCl₂ solution to 1 g activated MIL-101, and dried at 60 °C under vacuum overnight and further dried at 180 °C under Ar for 2 h, finally reduced by 3 MPa H₂ at 200 °C for 3 h, then stored in a glove box for further use. Absolute density of activated MIL-101 and Ni@MIL-101 are 1.522 g cm⁻³ and 1.756 g cm⁻³, respectively, which were measured by an AccuPyc 1330 Pycnometer. This also demonstrated that the Ni content in Ni@MIL-101 is 3%.

All further sample handling was conducted under a dry and inert atmosphere using either Schlenk equipment or an Ar filled glove box with a circulation purifier. NH₃BH₃ (97% Sigma–Aldrich) was dissolved in THF (99.9% Acros) for use (0.5 mol L⁻¹). 50%AB/Ni@MIL-101, 50%AB/MIL-101, 20%AB/MIL-101 and 7% AB/MIL-101 (where the weight percent is used in all the text unless stated elsewhere) were prepared by dosing 200 mg framework with 13.0, 13.0, 3.2 and 1.0 ml 0.5 mol L⁻¹ AB solution, respectively. Because of the porous nature of the frameworks, the internal channels of MIL-101 were filled rapidly by a capillary effect. The mixture was dried at 0 °C under vacuum with stirring (200 r/min) for 6 h, further dried at room temperature for more than 30 h.

2.2. Sample characterization

X-ray powder diffraction (XRD) was collected on a conventional PANalytical X-ray Diffractometer at 40 kV, 40 mA, with a scan speed of 5° min⁻¹ and a step size of 0.02° in 2θ, using Cu Kα radiation. Infrared spectroscopy was performed with a Nicolet 380 FTIR spectrometer at room temperature in the range of 400–4000 cm⁻¹, with samples in KBr pellets. The gaseous compositions from AB decomposition were detected by a coupled TG/MS technique. Thermo-gravimetric analysis (TG) was carried out on a Cahn Thermax 500 and Mass spectra (MS) were performed on a multi-component online gas analyzer GAM 200. All thermal analyses were measured from room temperature to 260 °C at a heating rate of 1 °C min⁻¹ under Ar gas flow. The XPS measurements were conducted using VG ESCALAB MK2. All spectra were acquired at a working pressure of 1.5 × 10⁻⁵ Pa with Al Kα excitation at 12.5 kV. DSC measurement was carried out with a DSC Q1000 analyzer under N₂ atmosphere. The PCT curves were measured by a Sieverts-type apparatus (Advanced Materials Crop. USA). UV–Vis spectra were measured with a Cintra 20 (Australian) spectrometer in reflection mode. N₂ adsorption–desorption measurement was performed on Quantachrome Autosorb-1 at 77 K.

2.3. Calculation method

All electron spin-polarized density functional theory (DFT) code DMol3 [36] was employed in the present calculation. The generalized gradient approximation (GGA) with the

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