Operando Raman-mass spectrometry investigation of hydrogen release by thermolysis of ammonia borane confined in mesoporous materials

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ABSTRACT

Ammonia borane is a promising hydrogen storage material, but its application is hurdled by the slow hydrogen release kinetics from this compound, among other factors. Nanoconfinement of ammonia borane in scaffolding porous materials improves the hydrogen release kinetics and lowers the decomposition temperature, but the mechanisms through which nanoconfinement promotes these effects are still unclear. In this work, hydrogen thermal desorption from ammonia borane which has been incorporated into various mesoporous carriers has been investigated by means of *operando* Raman-Mass Spectrometry methodology. This technique allows the study of molecular transformations of ammonia borane during thermolysis. The sample is in a reactor suitable for spectroscopy. The sample is analyzed with Raman spectroscopy during thermolysis and the released molecules desorbing from the sample are taken by the flowing stream out of the *operando* reactor, an online mass spectrometer analyzes these as they come out. Both measurements are done simultaneously. In order to evaluate the influence of the properties of the host on nanoconfinement, four different scaffolds with different chemical composition and textural properties (pore diameter and volume) have been studied: Cobalt-substituted $AlPO_4$-5 having intercrystalline mesoporosity, a mesoporous gallium oxide and two SBA-15 type materials. Results indicate the presence of crystalline ammonia borane in all impregnated hosts. By thermolysis, all nanoconfined samples begin to evolve hydrogen at a lower temperature than neat ammonia borane, although this effect is much more pronounced on SBA-15 samples. Furthermore, Raman spectra indicate a modification in the mechanism of decomposition in ammonia borane-loaded SBA-15 materials that suggests a chemical interaction between hydride and host.

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1. Introduction

The current energy demand is almost entirely satisfied with fossil fuels, whose reserves are increasingly limited and constitute a constant source of greenhouse gases. It is then necessary to carry out a transition towards alternative fuels that can provide energy without pollution to solve energy shortage [1,2]. Hydrogen is the most abundant element in the universe [3] and hydrogen molecule is the richest one in energy per unit mass; however it is hardly present on Earth in its molecular form. It can act as a clean and efficient carbon-free energy vector between renewable energy sources and final energy users, without generation of pollution as its combustion in a fuel cell produces only water and energy [4,5], with a high efficiency. The term 'hydrogen economy' is commonly used to refer to this approach based on the generation of power by electrochemical oxidation of hydrogen in fuel cell devices.

The advantages of using hydrogen as an energy vector have led to comprehensive investigations about how to solve the problems

of production, storage and transportation of this molecule [6–8]. However, hydrogen storage and delivery remains a very challenging technical and economic issue to be resolved. Compact, light, safe and affordable containment is a critical feature for on-board energy storage. Among other options, solid-state hydrogen storage shows several advantages in terms of storage capacity, safety and costs.

Solid hydrogen storage requires compounds able to reach adequate gravimetric storage capacities (8–20%), fast absorption–desorption kinetics and easy reversibility at moderate temperatures. Considering these requirements, many solid hydrides that can store hydrogen have been tested for reversibility [9–11]. In those materials, hydrogen molecules are dissociating into hydrogen atoms that bind to the bulk material through metallic, covalent, or ionic bonds. Solid-state storage using complex hydrides of light elements like alanates (which contain AlH_4^- anions), borohydrides (which contain BH_4^- anions), amide hydrides (which contain N−H groups) or aminoboranes (which contain the $NH_2BH_3^-$ anion) are currently under study [12,13].

In this context, ammonia borane (NH_3BH_3, AB) is a promising chemical hydride [14–16]. It is a white crystalline inorganic solid with 19.6% mass content of hydrogen whose thermal decomposition releases up to 2 equivalents of hydrogen below 200 °C. Moreover, ammonia borane is stable at ambient conditions. The thermal decomposition of neat NH_3BH_3 is a well-known process [17–20]. NH_3BH_3 delivers H_2 forming a complex polymeric aminoborane $-(NH_2BH_2)_n-$ (PAB) below its melting point (114 °C):

$$n(NH_3BH_3) \rightarrow (NH_2BH_2)_n + nH_2 \quad \Delta H = -21 \text{ kJ} \cdot \text{mol}^{-1} \quad (1)$$
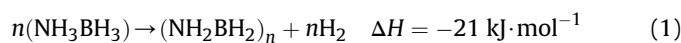
PAB decomposes with further H_2 release above 150 °C, forming polymeric iminoborane $-(NHBH)_n-$ (PIB) and small fractions of ammonia, diborane and borazine (c-$(NHBH)_3$), which are undesirable gaseous by-products:

$$(NH_2BH_2)_n \rightarrow (NHBH)_n + nH_2 \quad \Delta H = -15 \text{ kJ} \cdot \text{mol}^{-1} \quad (2)$$
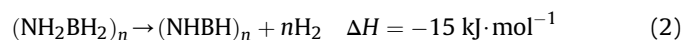
Both reactions are hindered by high activation barriers and correspondingly slow dehydrogenation kinetics at temperatures below 85 °C. Regarding on-board hydrogen storage, NH_3BH_3 thermal decomposition still has to overcome various hurdles such as lowering temperature of decomposition, increasing hydrogen evolution rate or showing reversibility.

A very interesting approach in this sense consists in confining NH_3BH_3 into mesoporous scaffolds [21,22]. This strategy has demonstrated the reduction of activation barriers for hydrogen release upon confinement, speeding up the dehydrogenation reaction, albeit reaction rates are still low for applications. An additional advantage is that the formation of borazine is dramatically reduced [21]. Finally, the exothermicity of the hydrogen desorption reactions is significantly lowered ($\Delta R_H \approx 1 \text{ kJ} \cdot \text{mol H}_2^{-1}$), due to the modification of structural and thermodynamic properties of NH_3BH_3 [21,23].

This work analyzes the role of nanoconfinement of ammonia borane on the thermolysis of the hydride by combining real-time Raman spectroscopy with simultaneous on-line mass spectrometry (MS) of the effluents (*operando* Raman-MS investigation). This technique allows simultaneously evaluating differences in structural/compositional changes of NH_3BH_3 as well as on its hydrogen desorption properties due to its dispersion and destabilization by nanoconfinement. Four different host materials have been tested: two different SBA-15 materials, which were the first type of reported materials for hosting of NH_3BH_3 [21,22], mesoporous Ga_2O_3 material, and mesopores-containing CoAPO-5 microporous materials [24]. These four materials have been selected in order to

analyze the influence of the textural properties of the host on AB nanoconfinement: SBA-15 materials are characterized by high pore volumes and an ordered mesopore structure, while the mesoporous Ga_2O_3 presents lower pore volume with a disordered pore structure, and a CoAPO-5 microporous material, which possesses hierarchical porosity with two kinds of pores conceptually different to the previous ones: (i) the micropores that would extremely confine ammonia borane, and (ii) a scarcely ordered intercrystalline mesoporosity allow to evaluate the possible effect of a much more confined space with presumed diffusion problems. Additionally, experiments with Ga_2O_3 and CoAPO-5 can shed light on the influence of chemical composition of the support (as compared to SBA-15) and its possible catalytic effect, and to the best of authors' knowledge these materials have not been tested before as hosts for nanoconfined AB.

2. Experimental

2.1. Chemicals

Ammonia borane (NH_3BH_3) was supplied by Sigma Aldrich (purity of 97%) and was used without further purification. H_3PO_4 (85% in aqueous solution, Sigma Aldrich), $Al(OH)_3 \cdot xH_2O$ (Sigma Aldrich), $Co(CH_3COO)_2 \cdot 4H_2O$ (98%, Panreac) and *N*-methyl-dicyclohexylamine (97%, Sigma Aldrich) (MCHA) were used for preparing CoAPO-5 material.

For silica synthesis, surfactant Pluronic P123 from Sigma Aldrich, triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($PEO_{20}PPO_{70}PEO_{20}$) and Pluronic PE 10400 ($PEO_{25}PPO_{56}PEO_{25}$) from BASF, were used as structure directing agents. Tetraethoxysilane (≥99%, TEOS) (Merck) and tetramethoxysilane (99%, TMOS) (Aldrich) were used as silica sources. Hydrochloric acid was purchased from Panreac.

For the synthesis of mesoporous Ga_2O_3, gallium (III) nitrate hydrate (99.99%, Strem Chemicals) was used as the inorganic precursor. Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$) (BASF) was used as structure directing agent and ethanol (~99%, Sigma) was used as solvent. For mesoporous materials impregnation, tetrahydrofuran (THF) (≥99.9%, Sigma Aldrich) was utilized.

2.2. Synthesis of supports

Ammonia borane was incorporated into four mesopores-containing materials.

2.2.1. CoAPO-5

Co-substituted microporous material $AlPO_4$-5, CoAPO-5, containing intercrystalline mesoporosity was synthesized by direct incorporation of Co into the $AlPO_4$ framework resulting in an isomorphous substitution of Al ions by Co^{2+}, as described elsewhere [24]. First, cobalt acetate was dissolved in a phosphoric acid aqueous solution under stirring to form a pink solution. Then, a suitable amount of $Al(OH)_3$ was slowly added to the mixture. Finally, the amine MCHA, used as a structure directing agent, was added to the gel and the mixture was stirred for an hour at room temperature. The resulting pink mixture was sealed into a Teflon-lined stainless steel autoclave and statically heated at 180 °C for 18 h. The resulting gel composition was: 0.04 Co:0.96 Al:1.0 P:0.8 MCHA:25 H_2O (molar ratio). The recovered blue solid was filtered, washed with abundant deionized water and dried at room temperature. Before using as host of NH_3BH_3, CoAPO-5 was calcined at 550 °C (heating rate 3 °C·min^{-1}) for 1 h under N_2 flow and subsequently for 5 h under air flow.