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Short communication

Covalently-terminated germanane GeH and $GeCH_3$ for hydrogen generation from catalytic hydrolysis of ammonia borane under visible light irradiation

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ABSTRACT

Covalently-terminated germanane GeH and $GeCH_3$ for hydrogen generation from catalytic hydrolysis of ammonia borane (NH_3BH_3) complex under visible light ($\lambda \geq 420$ nm) has been achieved. Compared with H-terminated germanane GeH, the methyl-terminated germanane $GeCH_3$ exhibits superior catalytic activity and hydrogen selectivity towards hydrolysis of NH_3BH_3, with the turnover frequency (TOF) value of 18.16 mol_{H2}•min^{-1}•mol_{cat}^{-1}, which is nearly 2.4 times higher than that of GeH. In addition, we have demonstrated their good reusability and high stability through cyclic experiments. A proposed mechanism for the H_2 evolution from hydrolysis of NH_3BH_3 over $GeCH_3$ sample is proposed.

1. Introduction

As a power source, fuel cells have attracted considerable attention to meet the ever-increasing demand of portable electronic devices. Among the various types of fuel cells, hydrogen energy, that is H_2, is a globally accepted clean and source-independent energy carrier [1]. The application of hydrogen fuel cells in vehicles or in portable electronic devices certainly requires high gravimetric/volumetric [2] and lightweight H_2 storage capacity [3]. Thus, safe and efficient storage of hydrogen still remains a great challenge in the area of hydrogen energy. To this end, a large number of hydrogen storage approaches and materials have been investigated, such as metal hydrides [4,5], sorbents [6–8], "on-board" reforming of hydrocarbon into hydrogen [9], organic materials [10], and some new-concept materials [11]. Among them, NH_3BH_3 has hydrogen content as high as 19.6 wt%, which is much higher than targeted value for the year 2020 (5.5 wt%) set by the U.S. Department of Energy (DOE) [12]. Because of soluble and stable in aqueous solutions under ordinary storage conditions, NH_3BH_3 has been considered to be a highly potential candidate for "on-board" hydrogen storage applications [13,14]. It can generate hydrogen via an ordinary dissociation and hydrolysis reaction in the presence of a suitable catalyst with H_2 to NH_3BH_3 ratio up to 3.0 at room temperature and its complete hydrolysis reaction is as follows,

$$NH_3BH_3 + 2H_2O \overset{catalyst}{\rightarrow} NH_4BO_2(aq) + 3\,H_2(g) \quad (1)$$

Dehydrogenation of NH_3BH_3 has been widely investigated from both solid-state and solution approaches and a large number of works have been reported [2,13,14]. It is already widely known that NH_3BH_3 aqueous solution is a potential hydrogen source with noble metal catalysts such as Ru, Rh, Pd, Pt and Au [15–17], and so on. However, they are all unsuitable for practical applications due to their limited resources and high price tags. Therefore, the development of low-cost, efficient and safe system is urgent for practical use. In the past few years, to make the NH_3BH_3 a practical H_2 carrier for portable electronics applications, highly efficient catalysts with much reduced usage of noble metals are desired. Germanium (Ge), as a less noble metal, has wide application in the fields of semiconductor [18], electronics [19], solar cell [20], sensing [21], and chemical catalyst [22,23], etc. Recent research has indicated that covalently-terminated germanane materials with various surface ligand termination have systematic optoelectronic properties [24,25] and catalytic properties [26]. By changing the identity of the covalently bound ligand, their electronic structure and properties can be systematically tuned [24]. These covalently-terminated germanane may provide some new insight into the future design and synthesis of practical catalysts for NH_3BH_3 hydrolysis and hydrogen generation. Additionally, to the best of our knowledge, reports on the catalytic hydrolysis of NH_3BH_3 in covalently- terminated germanane have not yet been reported to date.

Herein, we report two covalently-terminated germanane GeH and $GeCH_3$ and study their catalytic hydrolysis of the NH_3BH_3 aqueous solution at room temperature. We demonstrate that compared with H-terminated germanane GeH, the methyl-terminated germanane $GeCH_3$

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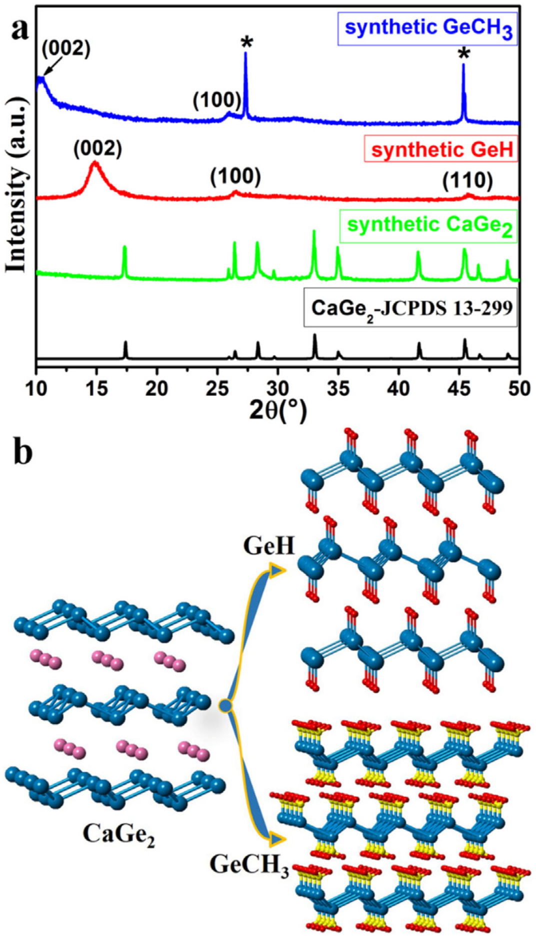

Fig. 1. (a) XRD patterns of the as-prepared $CaGe_2$, GeH, $GeCH_3$ samples and standard $CaGe_2$ taken from JCPDS file (no. 13-299). The starred peaks correspond to diffraction reflections of an internal Ge standard. (b) Schematic illustration of crystal structure transition of $CaGe_2$ to GeH and $GeCH_3$ (calcium = pink, germanium = blue, hydrogen = red, carbon = yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

present more superior catalytic activity and stability, with the TOF value of 18.16 $mol_{H2}{\cdot}min^{-1}{\cdot}mol_{cat}^{-1}$ under visible light irradiation ($\lambda \geq 420$ nm). And a proposed mechanism for the H_2 evolution from hydrolysis of NH_3BH_3 over $GeCH_3$ sample is proposed. In a manner of speaking, a hydrogen generation system for portable fuel cells may be established on the basis of the catalytic hydrolysis of NH_3BH_3.

2. Materials and methods

The whole experimental part was depicted in Supplementary information.

3. Results and discussion

Fig. 1a shows the powder X-ray diffraction (XRD) patterns of the as-prepared $CaGe_2$ precursor, GeH and $GeCH_3$ samples. Zintl phase $CaGe_2$ crystals as a precursor were synthesized by using an induced-melting method (for reaction equipment diagram see Fig. S1). Compared with the standard $CaGe_2$ card (JCPDS Card No. 13-299), $CaGe_2$ is pure without the appearance of any other impurities. To synthesize GeH and $GeCH_3$, $CaGe_2$ reacted with concentrated HCl and CH_3I following an clear ion-exchange process by the topotactic deintercalation [27,28], which can be described as the following chemical equations (2) and (3),

$$CaGe_2 + HCl \rightarrow GeH + CaCl_2 \tag{2}$$

$$CaGe_2 + CH_3I \rightarrow GeCH_3 + CaI_2 \tag{3}$$

In general, to synthesize GeH, the as-prepared $CaGe_2$ crystals as precursors were mixed with concentrated HCl for 48 hours at room temperature. $GeCH_3$ was fabricated by a tentative solvothermal process by using the as-prepared $CaGe_2$ crystals as precursors similarly. As shown in Fig. 1a, the XRD peaks of GeH and $GeCH_3$ samples are in good agreement with the result that reported previously [27,28]. It can be seen from the crystal structural transformation diagram from $CaGe_2$ to GeH and $GeCH_3$ (illustrated as shown in Fig. 1b) that the crystal structure of $CaGe_2$ unit cell (two layers per unit cell) consists of hexagonal, puckered sp^3 layers of Ge^- atoms that are separated by Ca^{2+} ions. Then GeH was obtained by the substitute of Ca by H in $CaGe_2$. Analogously, compared to the original hexagonal $CaGe_2$, the Ca^{2+} in $CaGe_2$ was replaced by the CH_3 group resulting formation of $GeCH_3$ which both belonged to 2H unit cell. To sum up, through the analogical reaction, Ge^- anions bond to the H atom and CH_3 group, Cl^- and I^- anions react with Ca^{2+} cations to form a soluble CaI_2 and CaI_2 species, which is easily eliminated by washing.

The morphologis of as-prepared GeH and $GeCH_3$ samples were characterized by scanning electron microscopy (SEM). As shown in Fig. S2 (a) and (b), the morphologies of as-prepared GeH and $GeCH_3$ samples show a stacked structure consisted of numerous GeH and $GeCH_3$ thin layers with thickness of 20 ~ 100 nm. From the high-resolution transmission electron microscopy (HRTEM) images (see Fig. 2(a) and (b)) of GeH and $GeCH_3$ samples, indicate that GeH and $GeCH_3$ sheets are composed of fine crystallites. The bottom-right and bottom-left corner insets separately are the patterns from selected area electron diffraction (SAED) analyses of GeH and $GeCH_3$ samples. It is observed that both show the well resolved lattice spacing of 0.196 nm and 0.335 nm, which match well with the (110) plane spacing of hexagonal GeH [26] and the (100) plane of hexagonal $GeCH_3$ phase [28].

The UV-Vis-NIR diffused reflectance spectrum (DRS) of GeH and $GeCH_3$ samples shown in Fig. S3 (a) and (b), indicate that the as-prepared GeH and $GeCH_3$ samples have a strong light absorption in the whole visible light region. With direct band gap [27,28], the values of the band gap are 1.58 eV and 1.69 eV for GeH and $GeCH_3$ samples,

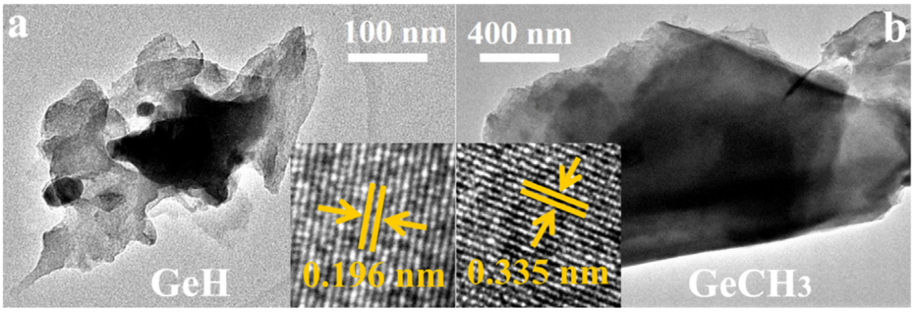

Fig. 2. The HRTEM images of (a) GeH and (b) $GeCH_3$ samples. The insets are SAED pattern and the lattice image of the GeH and $GeCH_3$ sheet, respectively.