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Dehydrogenation properties of chromium-based ammine borohydrides: $CrCl_3 \cdot nNH_3/3LiBH_4$ ($n = 3$, 4 and 5)

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ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form
3 October 2015
Accepted 3 November 2015
Available online 28 November 2015

Keywords:
Dehydrogenation
Chromium-based ammine borohydrides
Purity

ABSTRACT

Three new chromium-based ammine borohydrides were synthesized by ball milling $CrCl_3 \cdot nNH_3$ ($n = 3$–5) and $LiBH_4$ in a molar ratio of 1:3. Thermogravimetric analysis–mass spectrometry (TG–MS) measurements showed that the chromium-based ammine borohydrides release H_2 in the temperature range of 100–170 °C, concurrent with the evolution of a small amount of NH_3 evolution. The dehydrogenation purity increases with decreasing coordination number of ammonia, with the highest dehydrogenation purity (91.8 mol%) achieved for $CrCl_3 \cdot 3NH_3/3LiBH_4$. Further improvement on the dehydrogenation of $CrCl_3 \cdot 3NH_3/3LiBH_4$ is conducted by the addition of $ZnCl_2$. The 0.5 mol $ZnCl_2$ assisted sample is able to release 7.4 wt.% of hydrogen with a purity of 98.8 mol%.
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Introduction

Storage of hydrogen safely and efficiently is one of the pivotal obstacles to the wide use of hydrogen-fueled vehicles [1]. The conventional hydrogen storage methods, i.e., gaseous hydrogen compression and liquefaction of hydrogen, have the disadvantages such as high pressure involved and energy-consuming process [2,3]. Thus, as an alternative to gas and liquid hydrogen storage, many chemical hydrogen storage systems have been developed by researchers over the past few decades, such as metal hydrides [4,5], complex chemical hydrides [6–11] and B–N-based [12–14] hydrogen storage materials. Among them, ammine metal borohydrides (AMBs), $M(BH_4)_m \cdot nNH_3$ (M = Li [15,16], Mg [17], Ca [18,19], Al [20,21], Y [22], Ti [23], Nb [24], Sc [25], V [25] *etc.*) have attracted great attentions due to their high hydrogen gravimetric densities and low dehydrogenation temperature. It has been demonstrated that the low dehydrogenation temperature is based on the combination reaction between $N\text{-}H^{\delta+}$ and $B\text{-}H^{\delta-}$ [26].

Previous studies have demonstrated that there is a correlation between the electronegativity (χ_p) of the metal center M and the dehydrogenation temperature in AMBs [15–25]. Generally, an increase in the value of χ_p leads to a decrease in the desorption temperature of ammine metal borohydrides. This provides a viable way for developing new ammine metal borohydrides by controlling the χ_p of the cation. Cr has a χ_p of 1.66, indicating that the great potential of chromium-based

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http://dx.doi.org/10.1016/j.ijhydene.2015.11.025
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ammine borohydrides towards favorable dehydrogenation properties. In addition, the coordination number of NH_3 is another crucial factor in tuning the dehydrogenation properties, as it could affect the crystal and electronic structure of AMBs [17,21,23]. For example, the dehydrogenation temperature of $Al(BH_4)_3 \cdot nNH_3$ (n = 5, 4, 3 and 2) lowered with the decrease of the coordination number of NH_3 [21].

Herein, we reported the synthesis of chromium-based ammine borohydrides, $CrCl_3 \cdot nNH_3/3LiBH_4$ (n = 3, 4 and 5), *via* ball-milling $CrCl_3 \cdot nNH_3$ (n = 3, 4 and 5) with $LiBH_4$ in a molar ratio of 1:3, respectively, and their dehydrogenation properties and mechanism were studied in detail.

Experimental

Reagents and synthesis

Anhydrous $LiBH_4$ (95%), $CrCl_3$ (99.99%), $ZnCl_2$ (99.9999%) from Sigma–Aldrich were used as received without further purification, while NH_3 (Alfa Aesar) was purified by soda lime before use. All solid samples were handled in a glovebox equipped with a recirculation and regeneration system, which maintained the oxygen and water concentrations below 1 ppm.

Preparation of $CrCl_3 \cdot 5NH_3$

$$CrCl_3(s) + 5NH_3(l) \xrightarrow{NH_3(l)} CrCl_3 \cdot 5NH_3(s) \quad (1)$$

$CrCl_3 \cdot 5NH_3$ was first prepared by reacting $CrCl_3$ with NH_3 in liquid ammonia according to Eq. (1). Approximately 0.5 g of $CrCl_3$ was transferred to the reaction vessel under an argon atmosphere. After the argon was evacuated, purified dry NH_3 gas was purged into the flask with $CrCl_3$ and was kept under 4 atm NH_3 atmosphere overnight under ice-water bath until $CrCl_3$ was saturated. After excessive ammonia was evacuated, the molar ratio of NH_3 to $CrCl_3$ was determined gravimetrically to be 5.0, confirming the formation of $CrCl_3 \cdot 5NH_3$.

Preparation of ammine chromium borohydrides

These ammine chromium borohydrides were prepared by ball-milling the mixtures of $CrCl_3 \cdot nNH_3$ (n = 3, 4 and 5) and $LiBH_4$ in a molar ratio of 1:3 using Planetary QM-3SP2 with a ball-to-powder ratio of 30:1. For the $ZnCl_2$ added samples, $CrCl_3 \cdot 3NH_3$:$LiBH_4$:$ZnCl_2$ with a mole ratio of 1:3:n (n = 0.25 and 0.5) was ball milled as above conditions. To avoid the temperature of the powder in the vessel increasing, the milling process was carried out by alternating 12 min of milling and 6 min of rest. The ball milling rate is 200 rpm.

Instrument and analysis

Temperature-programmed-desorption (TPD) were performed to measure the dehydrogenation behavior on a semi-automatic Sievert's apparatus. A sample with a mass of approximately 0.1 g was heated from room temperature to 250 °C at a heating rate of 5 °C min^{-1} under argon atmosphere (1 bar).

The contents of H_2 and NH_3 in the emission gas were determined using gravimetric and volumetric results. Firstly, the mass percent (W_p) and mole per gram (M_p) of gas released from the samples were calculated from the weights of the samples and volumetric results, then the mole proportion of H_2 (C_{H_2}) and NH_3 (C_{NH_3}) can be calculated from the following two equations,

$$C_{H_2} + C_{NH_3} = 1 \quad (2)$$

$$(C_{H_2} \times 2.02 + C_{NH_3} \times 17.03) \times M_p = W_p \quad (3)$$

Simultaneous thermal gravimetric analysis and mass spectrometry (TGA-MS, QMS 403) were conducted to investigate the hydrogen release property of the as-prepared samples. Typically, 5–10 mg quantities of the sample were heated from room temperature to 250 °C under 1 atm argon atmosphere with a heating rate of 5 °C min^{-1}.

Synchrotron X-ray powder diffraction data were collected on the Powder Diffraction Beamline, Australian Synchrotron by a Mythen-II detector with a wavelength of 0.7286 Å and 1.0329 Å. For phase identification and structure determination, the samples were loaded into a pre-dried 0.7 mm boron-silica glass capillary inside an argon-filled glove-box. The capillary was sealed with vacuum grease for X-ray diffraction measurements.

Fourier transform infrared (FT-IR) (Magna-IR 550 II, Nicolet) analyses were conducted to confirm the chemical bonds in the sample. Products were pressed with KBr and then loaded into a sealed chamber with a CaF_2 window for the measurement. Anhydrous KBr was used as a pellet material.

Results and discussion

Synthesis and characterization of ammine chromium chlorides

The thermal decomposition behavior of $CrCl_3 \cdot 5NH_3$ is shown in Fig. 1. It distinctly shows a three-stage decomposition with

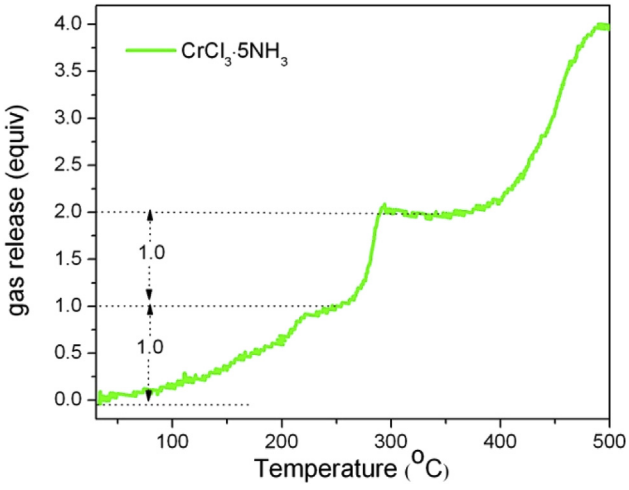

Fig. 1 – TPD result for $CrCl_3 \cdot 5NH_3$ with a heating rate of 5 °C min^{-1}.

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