



Supported copper–copper oxide nanoparticles as active, stable and low-cost catalyst in the methanolysis of ammonia–borane for chemical hydrogen storage

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ABSTRACT

The physical mixture of copper (Cu) copper(I) oxide (Cu₂O) and copper(II) oxide (CuO) nanoparticles supported on activated carbon (Cu–Cu₂O–CuO/C) were reproducibly prepared by a simple deposition–reduction technique without using any stabilizer in water at room temperature. The characterization of the resulting material by ICP-OES, P-XRD, XPS, DR-UV/vis, BFTEM and HRTEM techniques reveals that the formation of well-dispersed highly crystalline 3.8 ± 1.7 nm nanoparticles on the surface of activated carbon. These carbon supported Cu–Cu₂O–CuO nanoparticles were employed as heterogeneous catalyst in the methanolysis of ammonia–borane (NH₃BH₃), which has been considered as one of the attractive materials for the efficient storage of hydrogen, under mild conditions. We found that only 3.0 mol % Cu–Cu₂O–CuO/C catalyst is enough to catalyze the methanolysis of ammonia–borane with high activity (TOF = 24 min⁻¹) and conversion (>99%) at room temperature. More importantly, the exceptional stability of supported Cu–Cu₂O–CuO nanoparticles against sintering and leaching make Cu–Cu₂O–CuO/C recyclable catalyst for the methanolysis of ammonia–borane. Cu–Cu₂O–CuO/C catalyst retains >76% of its initial activity with 94% of conversion even at 8th recycle in the methanolysis of ammonia–borane at complete conversion. The study reported here also includes the collection of kinetic data for Cu–Cu₂O–CuO/C catalyzed methanolysis of ammonia–borane depending on catalyst [Cu], substrate [NH₃BH₃] concentrations and temperature to determine the rate expression and the activation parameters (E_a , ΔH^\ddagger , and ΔS^\ddagger) of the catalytic reaction.

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1. Introduction

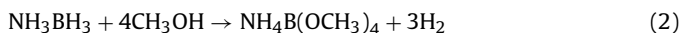
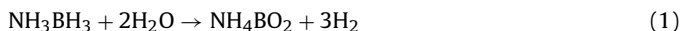
Hydrogen has been considered as a promising and clean energy carrier [1,2] for our future society as it has a high energy density (142 MJ/kg) almost three times higher than that of natural gas (55 MJ/kg) and only water plus small amounts of heat are the byproducts when it is utilized in proton exchange membrane fuel cells (PEMFC) [3,4]. However, controlled storage and release of hydrogen are still technological barriers in the transition from fossil fuels to hydrogen-based fuel cells energy technologies [1–4]. At this concern, a numerous studies have been performed for the development of materials with high volumetric and gravimetric hydrogen storage capacity, as the low density of hydrogen makes

it difficult to store in compressed or liquefied form [5]. In line with this, various porous materials [6–9], boron based chemical hydrides [10–12] and boron–nitrogen compounds [13,14,15–17] have been tested for the chemical hydrogen storage. Among these materials, ammonia–borane (or borane–ammonia complex; AB; NH₃BH₃) has been found to be much better suited for this purpose due to the following advantages: (i) AB has high gravimetric hydrogen storage capacity (19.6 wt%), (ii) it has low molecular weight (30.7 g mol⁻¹), (iii) it is non-flammable and non-explosive under standard conditions [18]. These significant properties make AB unique compared to metal hydrides/B–N compounds or porous materials, where the hydrogen release and uptake can be controlled by temperature and pressure.

Although hydrogen can be released from AB through its' thermal decomposition [19] or dehydrocoupling [20] there is much interest in the transition metal catalyzed hydrolytic dehydrogenation (1) due to favorable kinetics and mild reaction conditions [21].

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However, the hydrolysis of AB in concentrated solutions can cause liberation of ammonia gas that can act as poison to Pt-based fuel cell catalysts [22] and the hydrolysis product of AB is not recyclable due to the strong B–O bonds [14]. These two important issues hinder the practical use of AB-hydrolysis for hydrogen generation system to PEMFCs. In their recent study [23], Ramachandran and co-workers have shown that both problems can be circumvented by using methanol instead of water, as the catalytic methanolysis of ammonia–borane (2) yields hydrogen gas without ammonia evolution, and the methanolysis product, ammonium tetramethoxyborate, is recyclable.



Up to date many heterogeneous catalysts including RuCl_3 , RhCl_3 , PdCl_2 , CoCl_2 [23], $\text{Cu@Cu}_2\text{O}$ [24], $\text{Co-Co}_2\text{B}$, $\text{Ni-Ni}_2\text{B}$, Co-Ni-B [25], PVP-stabilized $\text{Pd}(0)$ [26] $\text{Ru}(0)$ NPs [27], CoPd/C [28], intrazeolite $\text{Rh}(0)$ NPs [29] and montmorillonite confined $\text{Ru}(0)$ NPs [30] have been tested in the methanolysis of ammonia–borane. Unfortunately, most of them used in these schemes suffer from difficult isolation [23–27], low activity [24–28], low stability [23–25,29] or high costs of metals [23,29]. Therefore, the development of highly active, stable and low-cost catalyst that operates under mild conditions remains a challenge in the field.

Herein, we report a facile synthesis of the physical mixture of copper (Cu) copper(I) oxide (Cu_2O) and copper(II) oxide (CuO) nanoparticles (NPs) supported on activated carbon, hereafter referred to as $\text{Cu-Cu}_2\text{O-CuO/C}$, and their excellent catalysis in the AB methanolysis. $\text{Cu-Cu}_2\text{O-CuO/C}$ catalyst was simply and reproducibly prepared through the conventional impregnation followed by simultaneous reduction method [31], and characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance UV-vis (DR-UV/vis), bright field transmission electron microscopy (BFTEM) and high resolution transmission electron microscopy (HRTEM). The sum of their results revealed that the formation of well-dispersed 3.8 ± 1.7 nm $\text{Cu-Cu}_2\text{O-CuO}$ NPs on the surface of activated carbon. The resulting $\text{Cu-Cu}_2\text{O-CuO/C}$ is acting as highly active ($\text{TOF} = 24 \text{ min}^{-1}$) heterogeneous catalyst in the methanolysis of ammonia–borane at 25°C . Moreover, the exceptional durability of supported $\text{Cu-Cu}_2\text{O-CuO}$ NPs against to sintering and leaching make $\text{Cu-Cu}_2\text{O-CuO/C}$ recyclable catalyst for the methanolysis of ammonia–borane. To the best of our knowledge, this is the first supported catalyst that contains only first-row transition metal and shows remarkable activity and stability in the methanolysis of AB.

2. Experimental

2.1. Materials

Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), copper powder (Cu ~99.99%), copper(I) oxide (Cu_2O ~99.99%), copper(II) oxide (CuO ~99.99%), ammonia–borane (NH_3BH_3 ~90%), sodium borohydride (NaBH_4), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$), methanol (CH_3OH) and activated carbon were purchased from Sigma–Aldrich®. Methanol was distilled over Mg and stored in a Schlenk tube under argon atmosphere. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon-coated magnetic stir bars were washed with acetone and copiously rinsed with distilled water before drying in an oven at 150°C .

2.2. Characterization

Cu contents of the samples were determined by ICP-OES (Leeman, Direct Reading Echelle) after each sample was completely dissolved in a mixture of HNO_3/HCl (1/3 ratio). Powder X-ray diffraction (XRD) patterns were recorded with a MAC Science MXP 3TZ diffractometer using $\text{Cu-K}\alpha$ radiation (wavelength 1.54 \AA , 40 kV, 55 mA). BFTEM and HRTEM samples were prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried. The conventional TEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. HRTEM analyses were run on a JEOL JEM-2010F transmission electron microscope operating at 200 kV. The XPS analyses were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic $\text{Al-K}\alpha$ radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W, and pass energy of 23.5 eV). DR-UV/vis analyses were performed on Shimadzu UV-3600 modulated with integrating sphere attachment. ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz. CD_3OD and $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ were used as a lock and an external reference, respectively. At the end of the methanolysis reaction, the resulting solutions were filtered and the filtrates were collected for taking the ^{11}B NMR spectra.

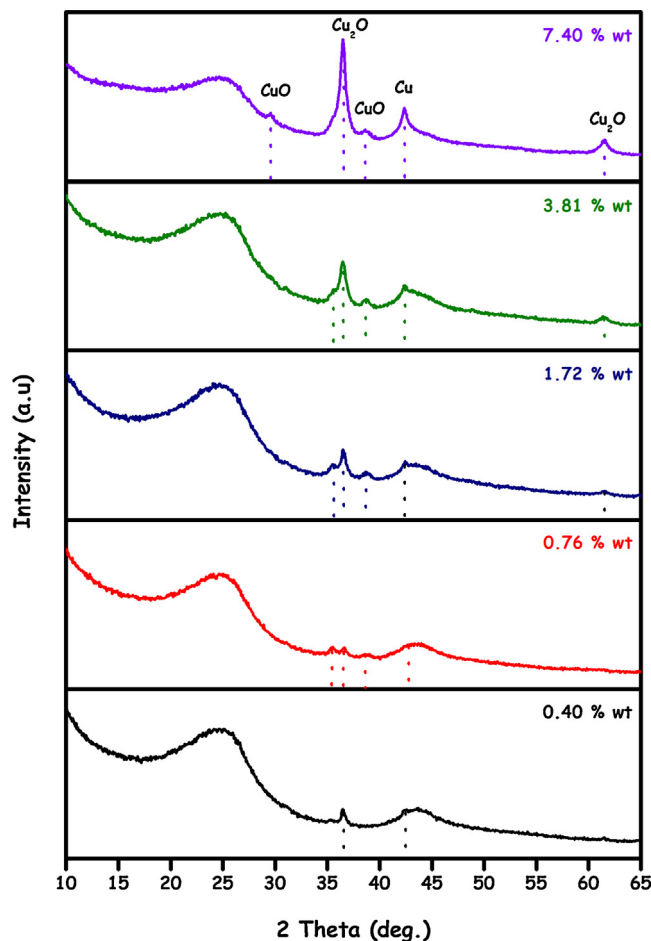


Fig. 1. The powder X-ray diffraction (P-XRD) patterns of $\text{Cu-Cu}_2\text{O-CuO/C}$ samples with various copper loadings (wt% = 0.40, 0.76, 1.72, 3.81, 7.4 as determined by ICP-OES).

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