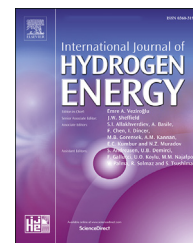




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Ceria supported manganese(0) nanoparticle catalysts for hydrogen generation from the hydrolysis of sodium borohydride

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ABSTRACT

Herein we report for the first time the preparation and catalytic use of the ceria supported manganese(0) nanoparticles in hydrogen generation from the hydrolysis of sodium borohydride. They are in situ formed from the reduction of manganese(II) ions on the surface of ceria nanopowders during the catalytic hydrolysis of sodium borohydride in aqueous solution at room temperature. Manganese(0) nanoparticles are isolated from the reaction solution by centrifugation and characterized by a combination of analytical techniques. Nanoceria supported manganese(0) nanoparticles are highly active and long-lived catalysts providing a turnover frequency of 417 h^{-1} and 45,000 turnovers in hydrogen generation from the hydrolysis of sodium borohydride at $25.0 \pm 0.1 \text{ }^\circ\text{C}$. They also have high durability as they retain 55% of their initial catalytic activity after the fifth cycle of hydrolysis providing a release of 4 equivalent H_2 gas per mol of sodium borohydride. The noticeable activity loss in successive runs of hydrolysis is attributed to the deactivation due to agglomeration. High activity and stability of ceria supported manganese(0) nanoparticles are ascribed to the unique nature of reducible cerium oxide. The formation of cerium(III) defects under catalytic conditions provides strong binding for the manganese(0) nanoparticles to oxide surface which makes the catalytic activity and stability favorable. Our report also includes the results of kinetic study of catalytic hydrolysis of sodium borohydride depending on the temperature, catalyst and substrate concentration.

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Introduction

The use of hydrogen as an environmentally benign energy carrier is expected to play a vital role in transition from fossil fuels to the renewable energy sources on the way towards a sustainable energy future [1–3]. However, the efficient and safe storage of hydrogen has been still a big issue in

applications using hydrogen as energy carrier [4]. Boron based compounds such as sodium borohydride [5], ammonia-borane [6], and dimethylamine-borane [7,8] have been considered as solid hydrogen storage materials. Among them, sodium borohydride (SBH, NaBH_4) appears to be the most promising candidate for safe and efficient hydrogen storage in portable onboard applications due to the following advantageous properties: (i) highly stable in solid state and in solution, (ii)

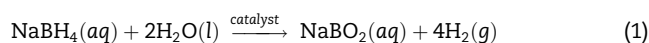
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non-flammable, (iii) nontoxic, (iv) highly soluble in water, (v) safe in practical use, (vi) high hydrogen storage capacity of 10.8% wt, and (vii) its potential as clean fuel for direct liquid-fueled fuel cell (8-electron oxidation) [9–11]. Furthermore, the hydrolysis of its aqueous solution can release 4 mol H₂ per mol of sodium borohydride at low temperature and pressure (Eq. (1)) [12].



Since the self-hydrolysis of sodium borohydride is slow at room temperature, the use of suitable catalysts is required to achieve hydrogen release at appreciable rates from this reaction. So far, many transition metal catalysts have been used in accelerating the hydrolytic dehydrogenation of sodium borohydride [13–18]. Although nanoparticles of noble metals such as platinum [19–21] and ruthenium [22–26], are highly active catalysts in hydrogen generation from the hydrolysis of NaBH₄, significant research has been devoted to find non-noble metal catalysts such as the earth abundant copper [27], nickel [28,29], cobalt [30–33], iron [34] and manganese [35–37] in recent years because of the high cost and limited availability of precious metals. Among the non-noble metals, manganese is the most attractive one because of being very cheap, naturally abundant in the Earth crust, environmentally benign and reactive as well [36]. Despite of many attempts to employ manganese based catalyst in hydrolytic dehydrogenation of sodium borohydride [38–41], the only successful test has recently been reported by Kim and coworkers [36]. In that study the surface of multiwalled carbon nanotubes (MWCNTs) was modified by ionic liquid (IL) to support the manganese(0) nanoparticles [36]. First of all, the expensive combination of multiwalled carbon nanotubes and ionic liquid doesn't match to the targeted goal of developing the earth abundant cheap metal as catalyst in the hydrolysis of sodium borohydride. More importantly, a careful read of the paper [36] indicates that the observed catalytic activity is due to the combination of manganese and nickel present in the system. Nickel has been introduced into the system in the form nickel(II) ion together with the ionic liquid as clearly described in that paper [36]. Of course during the catalytic hydrolysis of sodium borohydride, both manganese(II) and nickel(II) ions can be reduced to form the catalytically active manganese(0) and nickel(0) nanoparticles. Indeed, a control experiment starting with just the MWCNTs/IL (that is, without manganese) demonstrated that about 50% of the catalytic activity was obtained by using MWCNTs/IL, which must be due to the nickel present in the system (Fig. 6 of that paper [36]). It is noteworthy that the catalytic activity of both systems with and without manganese decreases in the course of reaction indicating that the manganese and nickel catalysts are not sufficiently stabilized on the surface of MWCNTs even in the presence of ionic liquid. These and previous results clearly demonstrate that the manganese(0) nanoparticles formed from the sodium borohydride reduction of manganese(II) ion are not stable and need to be effectively stabilized.

In our search for stabilizing agent or supporting materials to make manganese(0) nanoparticles stable at least during catalytic reaction we came up with the ceria, a reducible oxide, which has been recently used as support for the

transition metal nanoparticles [42]. Ceria contains cerium(III) defects which can easily be formed on the surface of cerium oxides due to the high positive standard potential of Ce⁴⁺ → Ce³⁺ (1.76 V in acidic solution) [43]. The presence of cerium(III) defects causes an excess negative charge accumulation on the oxide surface [44,45]. The charge balance on the oxide surface can be established by anchoring metal(0) nanoparticles to oxide surface, which provides strong metal-support interaction, in particular, of the electron rich late transition metal nanoparticles [44,46–49]. Ceria supported metal nanoparticles have been employed as catalysts in many important reactions including the hydrolysis of ammonia borane [50–53].

Herein we report the preparation of ceria supported manganese(0) nanoparticles, hereafter referred to as Mn/CeO₂, and their catalytic use in hydrogen generation from the hydrolysis of sodium borohydride. Mn/CeO₂ could be formed from the in situ reduction of manganese(II) ions impregnated on the surface of ceria nanopowders during the catalytic hydrolysis of sodium borohydride. They could be isolated from the reaction solution by centrifugation as stable nanopowders and characterized by BET, UV–vis, XRD, SEM, SEM-EDX, TEM, STEM and XPS techniques. All the results reveal the formation of uniformly dispersed manganese nanoparticles on the surface of ceria nanopowders. Ceria supported manganese(0) nanoparticles are found to be highly active, recyclable and long lived catalyst with a total turnover number of 45,000 in hydrogen generation from the hydrolysis of NaBH₄ retaining the initial activity even after the fifth use at 25.0 ± 0.1 °C. Our report also includes the results of kinetic study of the catalytic hydrolysis of sodium borohydride depending on the temperature, concentration of substrate and catalyst.

Experimental

Materials

Manganese(II) acetate tetrahydrate (Mn(OAc)₂·4H₂O, 99.99%), sodium borohydride powder (NaBH₄, ≥98%), ceria nanopowders (CeO₂, particle size ~25 nm, BET surface area 48.1 m² g⁻¹), sodium hydroxide (NaOH, ≥98%) and carbon disulfide (CS₂, ≥99%) were purchased from Aldrich. Deionized water was obtained using water purification system (Milli-Q-pure System). All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

Characterization

Solid samples for the analyses by X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), transmission electron microscope (TEM) or Scanning Electron Microscopy (SEM) were harvested from the in situ generated Mn/CeO₂ nanoparticles solution at the end of catalytic hydrolysis of NaBH₄. The XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al K α radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). The C1s peak at 284.5 eV was used as reference for surface

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