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# Carbon spheres from lactose as green catalyst for fast hydrogen production via methanolysis

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ABSTRACT

Micrometer sized carbon spheres (CSs) are prepared in a single step using lactose precursor via hydrothermal method. These CSs are chemically modified with 3-chloro-2-hydroxypropyl ammonium chloride (CHPACl) and triethylenetetramine (TETA) to generate amine groups on the particle surface. Modified CSs with TETA was protonated with HCl as CSs-TETA-HCl that the zeta potential is increased to +40.3 ± 0.70 from −51.4 ± 4.66 mV. The catalytic performance of CSs are tested as catalysts in the methanolysis of $NaBH_4$, and the best catalytic performance as 2586 mL $min^{-1}$ $g^{-1}$ hydrogen generation rate (HGR) was obtained by CSs-TETA-HCl catalyst at 298 K as metal free catalyst. Furthermore, various parameters such as the amount of $NaBH_4$, the reaction temperature, and the reusability of CSs-TETA-HCl particles are investigated. More importantly, relatively low activation energy, 23.82 kJ $mol^{-1}$ for CSs-TETA-HCl catalyzed $NaBH_4$ methanolysis reaction is obtained in comparison to metal nanoparticle and metal free catalysts reported for the same purpose in the literature.



## Introduction

The green, renewable and clean energy source, hydrogen ($H_2$) that is one of the most promising candidate to replace fossil lead fuels due to its high energy density, 142 MJ/kg that is almost three times higher than petroleum, 47 MJ/kg [1] lead researchers to seek new routes to generate this gas. In recent years, many $H_2$ generation reactions including photocatalysis, biomass conversion, electrolysis of water, and so on have been extensively investigated. However, its controllable generation and storage are still the greatest challenge for their economical applications. Therefore, the onboard production of $H_2$ from different carries such sodium borohydride ($NaBH_4$), ammonium borane ($NH_3BH_3$), and aluminum boranes and various other metal hydrides are considered with suitable catalyst as promising source. Because of the ease and innate natural properties such as high hydrogen storage capacity (10.8 wt%), no transportation obstacle, controllable hydrogen releasing ability, stability, and non-flammable feature makes $NaBH_4$ is a choice of $H_2$ carrier for many research [2,3]. The methanolysis reaction of $NaBH_4$ abide the following equation:

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \quad (1)$$

In the literature, various types of metal catalysts such as $MnO_x/Al_2O_3$ [4], $CoCl_2$ [5], Co-Cu-B [6], $Co/Al_2O_3$ [7], Co-$TiO_2$ [8], Fe-B nanoparticles [9], $NiP/SiO_2$ [10], and Ru- $Al_2O_3$ [2] have been reported as catalyst in the methanolysis reaction of

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$NaBH_4$. However, these materials are highly costly, not very stable, toxic in some cases, and inapt catalytic durability and not environmentally benign. Therefore, there is a great deal of research in designing better and alternative catalyst systems. Some of the most recently employed metal free catalyst for this purpose are polymeric ionic liquids [11–13], silica particles [14], halloysite clay nanotubes [15], natural microgranular cellulose [16], poly(ethyleneimine) microgel [17], and quaternized polymeric microgels [18], Recently, many carbon based materials such as graphene, carbon nano tubes (CNT) and carbon particles have been employed for different purposes including as support for the preparation variety of catalytic metal nanoparticle. Amongst the carbon-based materials, carbon spheres are very interesting because of their morphology and pore structure as well as the size can be controlled. These parameters can be controlled based on; (1) carbon sources such as sucrose, glucose, lactose, starch, pectin, chitosan, alginic acid, tannins, graphene oxide, phenolic resin, resorcinol, polymers and so on [19], (2) carbonization techniques such as hydrothermal, piroliz, microwave, and acid treatments [20], and (3) process type such as reaction time and temperature, precursor concentration and so on [21]. Carbon spheres (CSs) are micron sized spherical carbon particles [22] that have a great potential in various types of applications such as $CO_2$ capture, adsorption, separation and purification of dyes, and other contaminants, and encapsulation of biomacromolecules, especially energy storage and conversion materials as catalyst supports, fuel cells, supercapacitors, and lithium batteries [22,23]. The main reason for their versatile usage and applications are related to their unique properties such as their readily preparational methods from cheap and renewable precursors (sucrose, lactose etc), good corrosion resistance, moderate conductivity and high surface area and so on [20,24,25].

In this study CSs was synthesized and chemically modified, and used as catalyst for the first time in the methanolysis reaction of $NaBH_4$. There is a considerable interest for the functionalization or surface modification of CSs for environmental applications and sustainable energy resources [22]. Zhu et al. was reported that CSs as a template for cobalt catalyst preparation its' use as catalyst in the hydrolysis of $NaBH_4$ [26]. However, there is no research for the direct use of CSs as catalyst in the methanolysis reaction $H_2$ generation. Therefore, herein, CSs were chemically modified with different amine sources such as 3-CHPACl and TETA as CSs-CHPACl and CSs-DETA, and then, CSs-TETA were protonated with HCl and tested in methanolysis of $NaBH_4$ determine the effects of the modifying agents on the catalytic performances of modified CSs. Various parameters such as the $NaBH_4$ concentration, the reusability of CSs-TETA-HCl were investigated. Furthermore, the reaction kinetics such as activation energy, enthalpy, and entropy were also evaluated.

## Materials and methods

### Materials

Lactose monohydrate (MW 360.32, Merck, 99%) was used in the synthesis of carbon sphere (CS). 3-chloro-2-hydroxypropyl ammonium chloride solution (CHPACl, 65%, Fluka), triethylenetetramine (TETA, technical grade, 60%, Aldrich), epichlorohydrin (ECH, >99%, Sigma Aldrich) were used for modification reaction of CSs. Hydrochloric acid (HCl, 36–38%, Sigma Aldrich) was used for synthesis and protonation of CSs. Sodium borohydride ($NaBH_4$, 98%, Merck) was used as $H_2$ sources. Methanol (99.9%, Sigma-Aldrich) was used as reaction medium. Dimethylformamide (DMF, 99%, Merck) and ethanol (99%, Birkim) were used as solvent in the reaction and washing processes. All aqueous solutions were preparing using distilled water (DI) with 18.2 MΩ cm (Millipore-Direct Q3UV).

### Synthesis of carbon spheres

Carbon spheres (CSs) were prepared according to a method described in the literature with a slight modification [27]. In a typical procedure, 5.4 g lactose was dispersed in 12 mL DI water in a 40 mL glass vial. After mixing for 5 min, 12 mL concentrated HCl was added to the lactose solution, and the color of mixture was turned transparent from milky white. The prepared mixture was incubated in an autoclave for 3 h at 100 °C. After this 3 h incubation period, the color of the mixture turned completely black that indicates the successful synthesis of CS. The as prepared CS were neutralized with 100 mL 5 M NaOH following by centrifugation at 35544*g* for 10 min. The solid precipitate was washed and centrifuged six times with DI water for the complete cleaning and for the removal of NaCl. The washed particles were dispersed in minimum amount of DI water and heated at 100 °C for 6 h to obtain powdery CSs, and then the dried particles were stored in plastic bag for further use.

### Modification and protonation of carbon spheres

CSs were chemically reacted with CHPACl and TETA in their corresponding solutions. Separately, 0.25 g CSs and 4 mL of CHPACl solution were dispersed in 20 mL 0.2 M NaOH and mixed for 1 h. After 1 h, these two solutions were combined and mixed at 250 rpm for 12 h. For the modification of CS with TETA, 1 g CS was treated with 0.2 M 40 mL of NaOH solution for 30 min, then washed with water one time by centrifugation at 35544*g* for 10 min. Then the wet CSs were placed into 50 mL reaction flask containing 20 mL DMF, and immediately 2 mL ECH was added to this suspension. The reaction was carried out at 90 °C at 800 rpm mixing rate. After 1 h, 2 mL of TETA was added and the reaction and the mixing continued for 1 h more. The TETA modified carbon spheres was washed by water: ethanol mixture two times by centrifugation at 35544*g* for 10 min. For the protonation process, 0.25 g modified CSs with TETA (CSs-TETA) were dispersed in 40 mL 1 M HCl solution and mixed at 250 rpm for 2 h. The modified and protonated, CSs-TETA-HCl was washed with DI water for four times, and ethanol for one time by centrifugation at 35544*g* for 10 min each. Then prepared CS based particles were dried with a heat gun and kept in a closed container for further use.

### Characterization of carbon based materials

The size and morphology of CSs were visualized by optic microscope (Olympus BX53) and Scanning electron microscopy

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