



# Alumina based doped templated carbons: A comparative study with zeolite and silica gel templates



Sohan Bir Singh, Mahuya De\*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

## ARTICLE INFO

### Article history:

Received 19 January 2017

Received in revised form

17 August 2017

Accepted 27 August 2017

Available online 30 August 2017

### Keywords:

Alumina

Templated carbon

Platinum

Hydrogen storage

## ABSTRACT

Alumina based templates were used for preparation of nitrogen and platinum doped templated carbons and compared with silica gel and zeolite templated carbons. For alumina based templated carbons, 5–6 times higher surface area was obtained compared to corresponding templates while that for zeolite and silica gel templates, it was only 1–2 times higher. The surface area of surfactant modified alumina templated carbon was comparable with that of microporous zeolite templated carbon but pore size and volume was comparable to that of mesoporous silica templated carbon. Higher dispersion of the Pt metal was observed within the matrix of mesoporous templates with highest for surfactant modified alumina templated carbon. The morphology of surfactant modified alumina templated carbon was similar to that of silica gel templated carbon and co-doping with platinum resulted in nodule like structure. At 25 bar and  $-196\text{ }^{\circ}\text{C}$  the hydrogen uptake was in the range of 4–3.4 wt% and decreased linearly with decrease in surface area. Both surface area and pore volume dropped for all Pt co-doped samples. However uptake capacity varied; for co-doped silica gel and zeolite templated carbons it was reduced, while that of co-doped alumina based templated carbons it increased. The highest hydrogen uptake of 4.1 wt% for surfactant modified alumina templated co-doped carbon was attributed to synergistic effect of significant surface area, highest pore volume and highly dispersed platinum. The study concludes that alumina based templates are equally good or better for synthesis of the templated carbons.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

The porous carbon materials have been used as adsorbents, catalysts, supports, electrode materials, gas storage materials etc. because of high surface area, high pore volume, chemical inertness, good mechanical stability and easier availability [1–3]. Many studies are reported on different type of porous carbon materials including activated carbon, carbon fiber, carbon nanotube, for hydrogen storage application [4–15].

The preparation of porous carbon materials via templating method is another promising technology [16]. The structures of the templated carbon depend on type of template, carbon precursor, and synthesis conditions [6]. The templated carbons are synthesized by impregnation of various carbon precursors (such as sucrose, furfural alcohol, acetonitrile, propylene, butylene, etc) on inorganic templates [17–19]. Zeolite and silica are most reported inorganic templates for preparation of microporous and mesoporous

templated carbons respectively. High surface area, well-ordered pore structure and narrow/uniform pore size distribution have been reported for templated carbons [6,17]. Quite varied hydrogen uptake values have been documented. Guan et al. [20] reported 3.1 wt% hydrogen uptake at  $-196\text{ }^{\circ}\text{C}$  and 20 bar for microporous templated carbon synthesized from zeolite Y template. For silica based mesoporous templated carbons, Attia et al. [6] reported hydrogen uptake capacity of 2.41 wt% at  $-196\text{ }^{\circ}\text{C}$  and 73 bar.

The hydrogen storage capacity of carbon material primarily depends on surface area and pore structure [21]. Further studies have established that hydrogen storage capacity is enhanced by adding non-metals (such as N, B, S, P) and metals (such as Pt, Pd, Ni, Ru) to various carbon materials including CNTs, activated carbons, MOF and templated carbons [22–27]. Presence of non-metals in carbon matrix reported to activate hydrogen [28]. Alam et al. [13] reported 3.9 wt% hydrogen uptake at  $-196\text{ }^{\circ}\text{C}$  and 20 bar for nitrogen doped microporous templated carbon synthesized from zeolite  $\beta$ . Under similar condition Yongde et al. [10] reported 3.4 wt% hydrogen uptake for silica based mesoporous templated carbons. Metals are reported to act as catalytic site and promote

\* Corresponding author.

E-mail address: [mahuya@iitg.ernet.in](mailto:mahuya@iitg.ernet.in) (M. De).

spillover mechanism for hydrogen adsorption [25,26,29–31]. The hydrogen spillover involves dissociative chemisorption of hydrogen molecules on metal site with subsequent migration of hydrogen atoms on adjacent support surface sites through surface diffusion [23]. Alam et al. [25] have shown that Pt-doped zeolite templated carbon can store hydrogen up to 4.8 wt% at  $-196\text{ }^{\circ}\text{C}$  and 20 bar. Mesoporous carbons are particularly important for doping with metals. The mesoporous carbons are expected to accommodate the dopants more uniformly [32]. Limited studies are reported for doped mesoporous templated carbon. Oh et al. [29] observed hydrogen storage of 2.2 wt% for Pt-doped silica templated carbon at  $-196\text{ }^{\circ}\text{C}$  and 20 bar.

These zeolite or silica templates are quite costly and may contribute to higher production cost [33]. Therefore, preparation of templated carbons using cheaper inorganic templates will lower the cost. The present study has explored in this direction and alumina based templates were investigated. Alumina is usually mesoporous material having both amorphous and crystalline structure depending on preparation conditions. In this study alumina and surfactant modified alumina were prepared and investigated for hydrogen storage studies. The comparison of physicochemical properties and hydrogen storage capacity of alumina based templated carbons with that of zeolite and silica gel based templated carbons were carried out. The effect of platinum and nitrogen doping on physicochemical properties and hydrogen uptake capacity of alumina templated carbons were investigated and also compared with that of doped zeolite and silica gel templated carbons. The templated carbons were analyzed using Thermal gravimetric analysis (TGA), Surface area and pore analysis, X-ray diffraction (XRD), Raman spectroscopy, Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and energy dispersive analysis X-ray (EDAX) techniques to evaluate thermal stability, textural properties, degree of graphitization, structure and elemental characteristics.

## 2. Experimental

### 2.1. Reagents and materials

The  $\text{NH}_4\text{Y}$ -zeolite (Product No. 334413, Sigma-Aldrich) and silica gel (Sigma-Aldrich, High Purity Merck Grade 10180) were used as templates in as received condition without any further pre-treatment. Alumina and surfactant modified alumina templates were prepared from aluminium nitrate nonahydrate (Merck,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) precursor using ammonia solution (Merck,  $\text{NH}_4\text{OH}$ , 30%) as the precipitating agent. Sodium dodecyl sulfate (Merck, SDS, 90%) was used for preparation of surfactant modified alumina. The nitrogen-doped carbons were synthesized using these different templates by chemical vapor deposition (CVD). Acetonitrile (Merck,  $\text{CH}_3\text{CN}$ , 99.9%) was used as carbon as well as nitrogen precursor. The platinum-doped templated carbons were synthesized using chloroplatinic acid hexahydrate (Sigma-Aldrich,  $\text{H}_2\text{Cl}_6\text{Pt} \cdot 6\text{H}_2\text{O}$ , 37.50%) as precursor for the precious metal. Hydrofluoric acid (Merck, HF, 48%) was used to remove the templates from the carbon-template composite.

### 2.2. Preparation of alumina based templates

Alumina templates were prepared by precipitation method with and without surfactant. To prepare 3 gm of alumina required amount of aluminium nitrate (22.05 gm) was dissolved in 250 ml of deionised water. The solution was stirred for 15 min at room temperature then precipitation was carried out by addition of 30% ammonia solution. The pH was maintained at 10.5. After completion of precipitation, the mixture was stirred for 60 min at room

temperature followed by aging under reflux at  $75\text{ }^{\circ}\text{C}$  for 6 h. After aging, the mixture was cooled to room temperature. The precipitate was filtered and washed repeatedly. The precipitate was dried at  $120\text{ }^{\circ}\text{C}$  for 12 h in hot air oven and then calcined at  $550\text{ }^{\circ}\text{C}$  for 4 h in static air.

For preparation of the surfactant modified alumina, aluminium nitrate and sodium dodecyl sulfate solutions were prepared by dissolving required amount in deionised water. Molar composition of both the aluminium nitrate precursor and surfactant solutions was taken as 0.1 M each. Mixture was stirred for 15 min at room temperature then precipitation was carried out by gradual addition of 30% ammonia solution at pH of 10.5 as described earlier. The subsequent steps of aging, filtering, washing, drying and calcination were same as described earlier. The preparation steps of alumina and surfactant modified alumina are shown in [Supplementary Fig. S1](#).

### 2.3. Preparation of nitrogen-doped templated carbons

For synthesis of nitrogen modified templated carbon by CVD, required amount of templates were placed in a quartz boat in horizontal furnace. The templates were heated to the deposition temperature in flow of the argon carrier gas using heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . On reaching the target deposition temperature of  $800\text{ }^{\circ}\text{C}$ , the template was maintained at the same temperature for predetermined deposition time of 3 h for all the synthesized templated carbons. The acetonitrile vapor was carried to the heated template by passing a fraction of the carrier gas through a flask contains acetonitrile at  $30\text{ }^{\circ}\text{C}$ . The total flow rate of carrier gas was maintained at 50 ml/min. Under given conditions obtained acetonitrile concentration in carrier gas was 70 ppm. The concentration of acetonitrile was measured by Gas Chromatography (NUCON-5765). After completion of deposition time, the carbon-template composite was further treated for 2 h in inert carrier gas at  $800\text{ }^{\circ}\text{C}$ . Thereafter the sample was cooled down to the room temperature in the same flow of carrier gas. After vapor deposition the carbon-template composite was collected from the furnace and treated with 40 ml of 48% aqueous HF solution at room temperature for 24 h to remove the templates. The templates were dissolved in hydrofluoric acid during the treatment and thereby separated from the carbon. To ensure complete removal of dissolved template, the residual carbon was washed and filtered several times with deionised water. The carbon sample was finally dried overnight at  $150\text{ }^{\circ}\text{C}$  in air oven. The synthesized samples are denoted as Al-N, AIS-N, SG-N and Z-N. The Al, AIS, SG and Z indicated as alumina, alumina-SDS, silica gel and zeolite respectively. Whereas, N represented nitrogen.

### 2.4. Preparation of platinum and nitrogen co-doped templated carbons

Co-doped templated carbon was prepared using alumina, alumina-SDS, silica gel and zeolite as templates. Pt was introduced in the template by incipient impregnation method and N was incorporated by vapor deposition as described in above section. In impregnation method, the required amount of platinum precursor was dissolved in deionised water. Equal amount of Pt precursor corresponding to 0.0045 mg Pt/g of template was used for all templates. The metal precursor solution was added drop wise to templates. This wet sample was dried at  $120\text{ }^{\circ}\text{C}$  for 12 h. Then, dry platinum doped sample was transferred to a quartz boat and placed in a horizontal quartz tube. Thereafter, acetonitrile vapor was carried to doped template using a similar procedure as described earlier. The synthesized samples are represented as Pt/Al-N, Pt/

Download English Version:

<https://daneshyari.com/en/article/6532545>

Download Persian Version:

<https://daneshyari.com/article/6532545>

[Daneshyari.com](https://daneshyari.com)