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Precursor suitability and pilot scale production of super activated carbon for greenhouse gas adsorption and fuel gas storage

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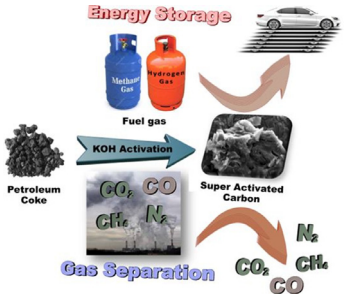
HIGHLIGHTS

- Physical properties define the suitability of coke as activated carbon precursor.
- Super activated carbon showed superior adsorption property for fuel gas (H_2 & CH_4).
- Low cost and excellent adsorbent for CO_2 sequestration and separation.
- Pilot scale production and pelletizing are demonstrated for commercial application.
- Mechanically strong carbon pellets showed enhanced CH_4 storage (112 cm^3 cm^{-3}).

GRAPHICAL ABSTRACT



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ABSTRACT

Raw and calcined petroleum cokes of Indian origin were characterized and screened as a carbon precursor for the preparation of activated carbon on medium and pilot scale by chemical activation method. Raw petroleum coke (RPC) was found more suitable precursor for preparation of activated carbon, whereas the enhanced graphitic arrangement limits the applicability of calcined petroleum coke. The suitability of petroleum coke as activated carbon precursor was correlated with its physical properties. Super activated carbon (SAC) obtained from RPC exhibited very high specific surface area (3578 m^2 g^{-1}) with ultra-microporosity ranges from 0.4 to 0.7 nm. The equilibrium adsorption of CO_2, CH_4, CO, and N_2 measured on powder SAC at different temperatures evidenced its applicability for gas separation through high adsorption capacity and selectivity. SAC also showed the high fuel gas storage capacity, H_2 (26.67 mmol g^{-1} at 77 K and 3000 kPa) and CH_4 (10.87 mmol g^{-1} at 303 K and 3700 kPa) due to its high specific surface area and microporous textural property. The production of SAC was also demonstrated for pilot scale and examined for CH_4 storage. The transformation of powder SAC into pellets using bentonite clay as a binder to provide better mechanical strength with enhanced CH_4 adsorption (on a volume basis) made it viable for practical application.

1. Introduction

Various raw materials such as coal [1], bio-waste [2], tire char [3], and polymer materials [4] have been studied as a precursor

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for preparation of activated carbon. Petroleum coke (PC), a carbonaceous material produced by the thermal decomposition and polymerization of a heavy liquid fraction of hydrocarbons derived from crude oil has been extensively used as raw material for the preparation of activated carbon due to its low cost and easy accessibility [5]. Mainly two types of activation techniques, chemical [2] and physical activation method [6] have been used for the preparation of activated carbon. Different combination of the carbon precursor and activating agents along with varying activation conditions have been studied to obtain activated carbon with the high specific surface area and controlled porosity [7]. Super activated carbon (SAC) possessing high specific surface area (>2500 $m^2 g^{-1}$) was first produced by AMOCO (Standard Oil Company, Indiana) in 1978 with chemical activation method using PC/coal [8]. Such activated carbons are especially suited for applications like gas storage, liquid phase adsorption, and carbon capacitors [7,9,10]. Various protocols have been used for the enhancement in the specific surface area of activated carbon. The properties of the activated carbon mostly depend on the activation method and precursor used [7]. Hence, the quality or structural properties of precursor also plays an important role in the porosity formation and surface properties of the activated carbon. In most of the cases, the suitability of activated carbon precursors has been tested with their direct application. As PC is one of the most used precursors for activated carbon, no specific protocol has been developed to describe its applicability from its physicochemical properties. The relation between the structural properties of PC and its suitability as activated carbon precursor is not yet well disclosed. Herewith we have tested the two types of PC (raw and calcined) samples with different structural properties and established the physicochemical properties based promising preliminary screening method for selection of PC as a suitable activated carbon precursor. In this paper, we have focused on the initial screening of the PC samples as a suitable precursor for activated carbon on the basis of their physicochemical properties.

Capture and storage of toxic and greenhouse gases released from the industries are urgently needed to reduce the climate change and health hazards [11]. The separation of CO_2 and CO is a very important task to minimize their environmental hazards and to enhance their reuse as feedstocks for a different process. Adsorption based separation is still considered as most practical, economical, and extensively used technique for gas separation. Various materials including zeolite [12], metal organic framework [13], synthetic clay [14], and carbon nanomaterials [15] have been studied as an adsorbent material for the separation of gases. The cost of material along with its adsorption capacity and selectivity decides its applicability as an adsorbent for gas sequestration and separation. Activated carbon is one of the promising and commercially utilized adsorbent for the gas adsorption and separation processes [16].

Since past decades, the usage of natural gas as a fuel increase rapidly due to the unstable price and massive requirement of crude oil [17]. In view of environmental aspects, natural gas is much advantageous than gasoline. Adsorbed natural gas is the upcoming technology for natural gas storage due to its distinct advantages including low capital cost, room temperature storage, and ease of refilling [18]. Various adsorbents have been developed and tested for methane gas (CH_4) adsorption [19]. Lozano-Castelló et al. [20] showed the applicability of powder and extruded activated carbon as an adsorbent material for the CH_4 storage. Due to the fast depletion of fossil fuels and its serious pollution effects, hydrogen gas (H_2) is considered as a clean and ideal substitute for fossil fuels [21]. The onboard storage of H_2 is the major difficulty for its applications as a transportation fuel. Various methods of H_2 storage including high-pressure storage, liquid H_2, complex hydrides, intercalation in metals and adsorption on porous materials are currently under consideration [22]. None of the current H_2 storage technology satisfies all of the needs suggested by the end users and producers.

In view of the above, SAC obtained from raw petroleum coke (RPC) using chemical activation method was utilized as low-cost adsorbent for the fuel gas (H_2 and CH_4) storage and greenhouse gas (CO_2) adsorption. The equilibrium adsorption of pure CO_2, CH_4, CO, and N_2 up to 113 kPa pressure at 288, 303, and 318 K was also investigated. The production of SAC was further extended to pilot scale with 10 kg batch sizes. To confirm the practicability of SAC, the obtained powder sample was pelletized using bentonite clay as a binder and used as an adsorbent for the CH_4 adsorption.

2. Experimental

2.1. Preparation of super activated carbon

PCs (raw and calcined), provided by Corporate R & D Center, Bharat Petroleum Corporation limited, Greater Noida, India were ground using an electrical grinder to obtain the finely powdered samples. Potassium hydroxide (KOH) and hydrochloric acid (LR grade) were used as received from SD Fine Chemicals, India. As per previous reports, the precursor to KOH ratio of 1:4 and preparation time of 3 h is a most suitable protocol for the laboratory-scale preparation of activated carbon using PC [7]. Hence, medium scale preparation of SAC was carried out by mixing the finely powdered PC (100 g), KOH (400 g) and water (200 mL) in SS316 tray and heated at 1073 K for 3 h under nitrogen gas flow (300 mL min^{-1}) in a muffle furnace at a heating rate of 20 K min^{-1}. The reaction mass was removed after natural cooling and washed with aqueous hydrochloric acid (5% v/v) and distilled water till filtrate pH is ~7. The sample was dried for overnight at 120 °C.

2.2. Characterization

2.2.1. Characterization of petroleum coke and super activated carbon

The crystallographic phase identification of PC and carbon products was done by X-ray diffraction (XRD) analysis (Rigaku, MPD system) using Cu $K\alpha_1$ (λ = 1.54056 Å) radiation at a scanning rate of 2° min^{-1} over the 2θ range, 2–80°. The textural properties such as specific surface area and porosity were determined by nitrogen sorption isotherm at 77 K using volumetric adsorption system (ASAP 2020, Micromeritics Inc., USA). The texture property and particle size/shape were investigated by scanning electron microscopy (SEM, Leo 1430) using aluminum stuff as the sample holder. Transmission electron microscopy (TEM, JEOL JEM-2100 TEM) was carried out on SAC loaded holey carbon coated copper grid prepared using finely dispersed SAC in ethanol using ultra-sonication. The elemental composition of the samples was determined by CHN/S analyzer (Perkin-Elmer, Series II, 2400). The Fourier Transform infrared (FT-IR) spectroscopy (Perkins Elmer Spectrum GX 2500 FT-IR spectrophotometer) was used to characterize the surface functionalities. Thermogravimetric analysis (TGA) was done using Mettler Toledo TGA/SDTA 851 equipment under nitrogen flow (50 mL min^{-1}), at a heating rate of 10 K min^{-1}.

2.2.2. Equilibrium adsorption of CO_2, CH_4, CO and N_2

The ultra-pure grade gases (CO_2, CH_4, CO, and N_2), procured from INOX Ltd., Baroda, India were used for adsorption studies. The equilibrium adsorption of pure gases on SAC was performed using volumetric adsorption system ASAP 2020 (Micromeritics Inc., USA) up to 113 kPa. Samples were activated at 573 K under vacuum for 5 h prior to the surface area measurement and equilibrium adsorption study. The adsorption temperature was main-