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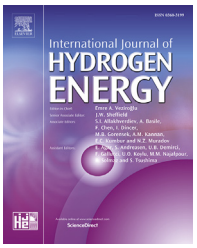

Optimizing parameters affecting synthetize of CuBTC using response surface methodology and development of AC@CuBTC composite for enhanced hydrogen uptake

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ABSTRACT

CuBTC, a widely studied metal-organic framework, is a promising candidate for industrial applications owing to its easy synthesis procedure and excellent textural properties. In this research CuBTC was synthesized by solvothermal method with the purpose of hydrogen uptake. Response surface methodology (RSM) was employed in order to determine the optimum synthesis condition with the highest hydrogen capacity. Amount of ligand, volume of solvent, synthesis temperature, and synthesis time were chosen as independent variables, while the amount of hydrogen uptake was selected as the response. Subsequently, activated carbon (AC) was incorporated within the optimized CuBTC structure as a "void space filling agent" and adsorption behavior of AC@MOF composite was evaluated from the view point of different AC contents. It was observed that the hydrogen uptake of AC@CuBTC composite was increased compared to bare CuBTC samples. This finding could be attributed to effective utilization of micropore volume of CuBTC structure by AC incorporation.

Introduction

Nowadays, growing consumption of fossil fuels which results in higher emission of greenhouse gases becomes an environmental threat worldwide and therefore, development of clean and carbon-free energy resources is somewhat crucial for future generations. Hydrogen is known as an ideal energy carrier which produces almost zero pollution during combustion. Methane steam reforming (MSR), coal gasification, and water electrolysis are well-stablished methods for hydrogen production [1–6]. Along with conventional hydrogen applications as a reactant in chemical and petroleum industries such as ammonia production and crude oil processing [7,8], hydrogen has the potential to be used for developing the environmentally friendly fuel cells [9–11]. However, finding efficient and cost-effective hydrogen storage materials with the ability of reversible application might be the major concern of hydrogen economy. Besides, enhanced hydrogen storage performance at near-ambient temperatures and safe pressures is always attractive for hydrogen storage materials. Carbonaceous materials (such as ACs and carbon

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nanotubes) and zeolites are well-known traditional porous solids for hydrogen storage [12,13]. Nevertheless, zeolites are difficult to regenerate and carbon-based materials have relatively low adsorption capacities [14,15].

Metal-organic frameworks (MOFs) are a group of porous solids with favorable textural properties for gas storage and separation purposes. MOFs are typically constructed by interconnection of secondary building units (SBUs) via organic linkers (ligands), forming various sizes of open windows appropriate for penetration of guest molecules with different sizes [15,16]. High specific surface area (SSA), high pore volume, and tunable structure are of most important characteristics of MOFs.

Although, the accessible micropore volume usually governs the sorption capacity of adsorbent rather than the internal surface area [17], however, the large void space in MOFs is not completely utilized for storage applications [16]. Recently, composite materials comprise of carbonaceous species - such as ACs, carbon nanotubes (CNTs), and graphene oxides (GOs) - incorporated within MOFs have attracted much attention [18–22]. It is revealed that, carbonaceous species can play the role of a "void space filling agent" which reduces the un-utilized void space within the MOF matrix and thereby enhances the adsorptive behavior of bare MOF [23]. In the case of AC/MOF composites (AC@MOFs), Somayajulu Rallapalli et al. [24], evaluated the potential of incorporating microporous ACs in MIL-101 structure with the purpose of higher hydrogen uptake at 77 K and high Pressures. Lee and Park [25], doped platinum on AC@MOF-5 in order to improve the hydrogen storage capacity of this hybrid composite. Bajaj et al. [23], revealed higher methane adsorption within AC@CuBTC in comparison to the bare CuBTC. Prabhakaran and Deschamps [26] demonstrated the higher hydrogen adsorption of MIL-101 modified by AC and lithium doping. Furthermore, Nasiri Azad et al. [27], employed AC@CuBTC composite for dyes removal process in aqueous solution.

Generally, there are three strategies of experimentation to find the optimum condition in an experimental investigation and therefore to optimize parameters affecting a phenomena: (a) best guess approach (trial and error), (b) one-factor-at-a-time approach (OFAT), and (c) factorial approach. Among these approaches, OFAT and factorial approaches are frequently used for various purposes including engineering and scientific investigations. In OFAT approach, the level of a specific factor is systematically changed while levels of all other factors are held intact. With this method the influence of each factor is investigated individually and optimal level of the factor under consideration is then selected. In contrast to OFAT, in factorial design approach, all possible combinations of factor levels are considered (multi-factor design), and the interactions of different factors on the overall response(s) are investigated [28]. Although OFAT is easy to implement, more economical, and more easily to understand than factorial approaches, it does not provide adequate information around interactions of different factors and consequently, factorial approach becomes the most valuable method for experimentation nowadays.

Response surface methodology (RSM) is a statistical method of factorial design approach which depicts interactions among independent variables by means of a quadratic polynomial equation. Central Composite Design (CCD), a method of RSM, is a reliable and prevalent design method which requires a smaller number of experiments, enhances the statistical understanding, and determines whether parameters interact or not [29,30].

During the synthesis procedure of CuBTC, numerous parameters influence final structure of porous solid. Hence, prediction of how input variables interact is a crucial knowledge in order to determine the most appropriate synthesis condition. For this purpose, a method so-called design of experiment (DOE) is employed wherein a statistical planning of experiment results in valid, objective, and meaningful conclusions. With regard to synthesis of CuBTC, DOE not only consists of designing the different synthesis procedures, but also comprises of an analysis of variance (ANOVA) to elucidate the accuracy of as-designed experimentation, as well as a regression analysis to find out the mathematical model which is useful to determine the simultaneous interactions of various parameters.

In this research, Design Expert® (version 7.0, State Ease, Inc., Minneapolis, MN, USA) was used as the computer statistical analysis program and RSM method of factorial design was employed to design the matrix of runs. Amount of ligand (g), volume of solvent (ml), synthesis temperature (°C), and synthesis time (h) were selected as independent variables of CuBTC synthesis procedure. Afterward, as-designed experiments were taken under account for synthesis of CuBTC samples, and hydrogen adsorption measurements were carried out by means of a volumetric apparatus to create responses. Finally, ANOVA statistical approach and regression analysis were used in order to find the optimal response (so-called stationary point). Subsequent to RSM procedure to recognize the optimum synthesis condition resulted in the highest hydrogen uptake, various amounts of AC (synthetized from walnut-shell as precursor by chemical activation) were incorporated in the optimum CuBTC sample as a filling agent. Finally, the effect of AC content was evaluated on the adsorption behavior of AC@CuBTC composite materials.

Material and methods

Chemicals

Copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), benzene–1,3,5-tricarboxylic acid (trimesic acid or H_3BTC), Sodium hydroxide (NaOH), nitric acid (HNO_3, 65 %wt), ortho-Phosphoric acid (H_3PO_4, 85 %wt), and ethanol were purchased from Merck (Germany) and were used as received without further purification. The purity of H_2 was 99.999%.

Material synthesis and preparation

Synthesis of CuBTC

CuBTC was synthesized according to the solvothermal procedure reported elsewhere [31]. Copper (II) nitrate trihydrate (metal salt) and H_3BTC (organic ligand) were dissolved in pure ethanol (solvent) and stirred for 30 min to form a homogenous solution. The solution then was transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was

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