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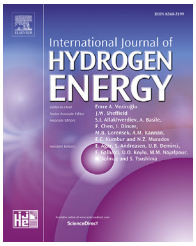

Role of metal type on mesoporous KIT-6 for hydrogen storage

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ABSTRACT

Hydrogen is envisaged to become an alternative clean energy source to fossil fuels that eventually lead to gradually increasing demand to design an efficient adsorbent for high storage capacity. Being inspired from the metal-doped adsorbents, mesoporous KIT-6 was functionalized with different metals namely Ce, Co, Cr, Cu, Ni, Pd, Pt, Sn and Ti with constant loading by wet impregnation method. Hydrogen adsorption performance showed that the metal doping improves the hydrogen storage capacity of KIT-6 except for K–Cu. Adsorbents K–Pd and K–Pt showed small hysteresis during adsorption/desorption analysis. Among all the metals, Pd-doped KIT-6 (K–Pd) showed the maximum uptake capacity (0.31 wt%) at atmospheric conditions. However, Sn-doped KIT-6 (K–Sn) showed the maximum uptake of 4.74 wt% at 77 K and 40 bar. This study provides a thorough insight in to the hydrogen adsorption/desorption behavior of the various metal–doped KIT-6 studied, which could be important first-hand information before designing the hydrogen storage material for the practical application.

Introduction

Global energy demand is gradually increased in the last few decades and expected to increase in future too [1]. Fossil fuels such as coal, crude oil and natural gas are the major sources of energy as well as an anthropogenic source of greenhouse gases [1], which promote the global warming across the globe. Therefore, the world is moving towards alternative sources for energy production. Renewable energy sources such as solar and wind have great potential but a lower efficiency of energy generation with the relatively higher production cost compared to fossil fuel sources [1]. Hydrogen has a large chemical energy (142 MJ/kg) and drawn great attention as a next-generation clean energy carrier for mobile and stationary power sources [2]. However, the major challenge is to store the hydrogen to set the targeted hydrogen storage capacity of 6.5 wt% for mobile applications at ambient condition [2].

Hydrogen can be stored in three possible ways namely, electrochemical, liquefaction, compressed hydrogen and adsorbed hydrogen in a solid porous material [3–6]. The various materials have already been tested for storing hydrogen electrochemically, but there is no solid strategy to pursue the most promising materials. Liquefaction and compression processes are highly energy intensive. Therefore, a large community of researchers is currently focused on to design solid storage materials for hydrogen. Recent reports suggest that the bare porous solid adsorbents have very low

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hydrogen storage capacities at ambient condition [7,8]. This is because hydrogen is adsorbed on the surface by van der Waals interactions (binding energy ~ 0.1 eV/H) [3]. However, according to literature, hydrogen storage performance of porous adsorbents can be improved by decorating the surface with transition metals [6–8]. Therefore, transition metal-doped porous sorbent with a high surface area and low bulk density has gained significant attention in hydrogen storage [4–30]. Chemical doping is the most commonly used method for decorating the porous material over ultrasonication and plasma assisted methods for its simplicity [6]. In last few years, through carbon-based materials [10–13] (graphene, and activated carbon) and metal organic frameworks (MOFs) [8,9] have been tested for hydrogen storage, there are only a few attempts on mesoporous silica. The transition metal present in the adsorbents/MOFs enhances the electrostatic interactions; induce chemisorption and spillover phenomena during hydrogen adsorption [6,18].

The hydrogen storage capacity of a porous material can be increased by physically mixing of active metals with the substrate. It is suggested that the improvement in hydrogen storage capacity is due to the atomic hydrogen spillover from the metal–doped adsorbent. Hence improved contacts between the spillover source and the secondary receptor would facilitate the hydrogen spillover, resulting in the enhanced hydrogen capacity. Fig. 1 display the schematic flow of the designing of hydrogen storage material by decorating with metal and spillover process in the adsorbent. In spillover approach, transition metal present in the low sorption capacity receptor interacts with hydrogen molecule by formation of Kubas dihydrogen complex and further it breaks the hydrogen molecule in to consecutive hydrogen atom, followed by migration to the substrate and diffusion in the bulk material [8]. A Kubas interaction, is consistent with a lengthening of the H–H bond without its breakage [19]. It also raises the average hydrogen enthalpy of the adsorbent. Furthermore, active metal does not only improve the hydrogen sorption capacity by spillover phenomena but also the sorption kinetics [20]. The Pd and Pt deposition already proved its efficiency towards hydrogen adsorption through enhancing the capacity by dissociation on metal sites [7,11,25,28,30,31]. Saha et al. [7] studied the hydrogen sorption performance of Pt, Pd, Ni and Ru-doped mesoporous carbon and observed that the sorption capacity increases with increase in metal loading except Ni. Carraro et al. [32] improved the adsorption performance up to ~1.2 wt% of SBA-15 by Ni loading. However, Acatrinei et al. [15] improved the hydrogen storage capacity of SBA-15 from 48 cc/g to 80 cc/g by Ti doping at 77 K and 1 bar. Additionally, they also showed the stable sorption capacity of Ti-doped SBA-15 upto 4 cycles. The enhancement in sorption capacity of metal-doped carbonaceous and non-carbonaceous receptor is by inducing the hydrogen dissociation on the metal surface [25,30].

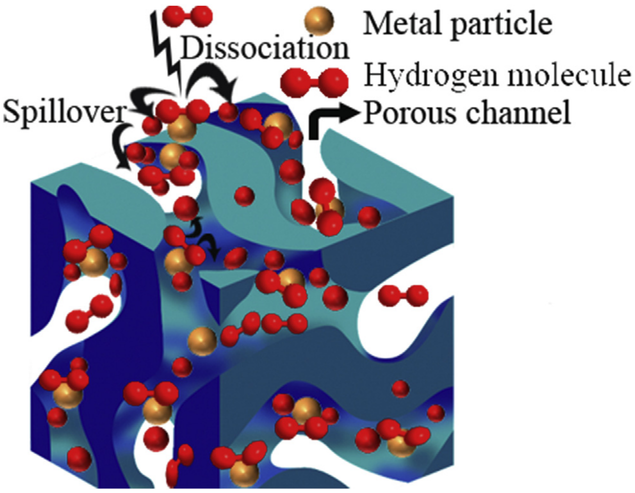

Fig. 1 – Schematic illustration of spillover phenomena on metal-doped KIT-6.

Selection of porous material, surface chemistry and type of active metal plays a significant role in designing the hydrogen storage material for practical application [7,8,12,26,27,31]. Moreover, easier way of synthesis of support is also desirable during designing of such an adsorbent. Mesoporous silica possesses such advantage as it can be synthesized in bulk more easily than other adsorbents like carbon-based sorbent and MOFs. Additionally, it shows high thermal, mechanical and hydrolytic stability in extreme external conditions and thus, makes it a potential candidate to explore as hydrogen storage material [24,28–30]. In addition to that, selection of metal and its behavior in wide operating conditions of temperature and pressure are also vitally important in designing the hydrogen storage material for the real application. Thus, the principal goal of this study is to promote the mesoporous silica as a hydrogen storage material and to understand the adsorption behavior towards different metals. Hence, in this work three dimensional mesoporous KIT-6 is doped with cerium (Ce), cobalt (Co), chromium (Cr), copper (Cu), palladium (Pd), platinum (Pt), nickel (Ni), tin (Sn) and titanium (Ti) metal fragment, in order to investigate the role of metal type and its interaction behavior with hydrogen adsorption/desorption performance and the storage capacity in wide range of temperature and pressure.

Experimental section

Materials

Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Sigma), tetraethylorthosilicate (TEOS, Sigma), Chloroplatinic acid hexahydrate (Sigma-Aldrich, $H_2Cl_6Pt{\cdot}6H_2O$, 37.5%), Palladium chloride (Sigma-Aldrich, $PdCl_2$, 99%), Nickel acetate tetrahydrate (Sigma-Aldrich, $Ni(OCOCH_3)_2{\cdot}4H_2O$, 98%), Tin chloride (Sigma-Aldrich, Cl_2Sn, 98%), Cerium nitrate hexahydrate (Sigma-Aldrich, $CeN_3O_9{\cdot}6H_2O$, 99%), Cobalt nitrate hexahydrate (Merck, $Co(NO_3)_2{\cdot}6H_2O$, 97%), Copper nitrate trihydrate (Merck, $Cu(NO_3)_2{\cdot}3H_2O$, 99%), Titanium oxide (Sigma-Aldrich, TiO_2, 99%), Chromium (III) nitrate (Loba chemie, $Cr(NO_3)_3{\cdot}9H_2O$, 97%), hydrochloric acid (Merck, HCl, 35%), n-butanol (Merck, 99%) were purchased. All the chemicals were used without any further purification. Millipore purified water was used during synthesis of material. High purity gases (99.999%) were used during analysis.

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