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Hydrophobicity and Phase Changes of Pd/SiO_2 Organic-inorganic Hybrid Materials Calcined in Air Atmosphere

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Abstract

Pd/SiO_2 organic-inorganic hybrid material was prepared by sol-gel method, in which $PdCl_2$ was added into methyl-modified silica sol. The Pd/SiO_2 sol particle size distribution, the hydrophobicity and phase changes of Pd/SiO_2 hybrid materials calcined at 200, 350, 500, 600 and 750 °C in air atmosphere were discussed. The Pd/SiO_2 sol system exhibits moderate dispersion and the mean particle size of Pd/SiO_2 sol is 2.70 nm. When the calcination temperature is raised to 350 °C, metallic palladium of high crystallinity is formed in the Pd/SiO_2 sample. PdO occurs in minor quantities in the Pd/SiO_2 sample calcined at 500 °C, which increases in amount in the samples calcined at 600 and 750 °C. With the increase of calcination temperature, the Si-CH_3 and Si-OH bands in Pd/SiO_2 materials are found to decrease in absorption intensity and the hydrophobicity on Pd/SiO_2 film surfaces increases. The water contact angle on the Pd/SiO_2 film surface achieves the maximum value as the calcination temperature is up to 350 °C and the particle sizes of the formed metallic Pd are about 15∼20 nm. The optimal calcination temperature for hydrophobic Pd/SiO_2 membrane materials is about 350 °C.

Keywords: Sol-gel Method; Palladium Doping; Hydrophobicity; Phase Change

1 Introduction

With the excessive use of carbon based fossil fuels, the world is now facing several great challenges, such as poor air quality, greenhouse gas emissions and high energy consumption rate. Nowadays, it is generally acknowledged that hydrogen would become an environmentally benign alternative to the conventional fossil fuels [1, 2]. However, hydrogen does not exist naturally and has to be produced from hydrogen-containing compounds [3]. Current methods for H_2 separation are solvent adsorption, pressure swing adsorption, cryogenic distillation and membrane separation. Compared with other methods, membrane separation technologies have sufficient selectivity, high permeation flux, minimized unit operations and economic potential in reducing operating costs

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[4, 5]. For these reasons, the development for effective hydrogen membranes has engendered considerable interest in academia and industry.

Intensive researches have been conducted on the development of hydrogen separation membranes, including Pd and Pd-alloy membranes, zeolite membranes, carbon molecular sieve membranes, and silica membranes [1, 2, 6]. Pd and Pd-alloy membranes possess ideal H_2 permselectivity from mixed gas streams but suffer from high cost and rapid performance degradation when they get in touch with CO or H_2S [2, 7, 8]. Carbon molecular sieve membranes have excellent H_2 separation properties. However, they are very brittle and fragile and difficult to be prepared as thin supported membranes [6, 9]. Zeolite membranes possess great hydrothermal stability and chemical resistance but show low H_2/CO_2 selectivity, because of the existence of intercrystalline micro defects and the relatively large zeolitic pores [6]. Nowadays other non-Pd-alloy membrane materials, such as Ti-Ni-V, Nb-Ti-Ni, Ni-Nb-Ta and Ta-Ti-Ni alloys, etc., have been investigated by many research groups [7, 10, 11]. However the drawbacks of the alloy membranes are the poor H_2 permeability and the sensibility of hydrogen embrittlement [10]. The maximum hydrogen permeability of the $Ni_{60}Nb_{30}Ta_{10}$ alloy membrane was 4.13×10^{-8} mol/m·s·$Pa^{1/2}$ at 673 K [10]. Silica membranes tend to be cheaper and economically more attractive. There has been much advancement in controlling the structural formation of microporous silica membranes to deliver high-purity H_2 separation applications [1, 12, 13]. Amorphous silica membranes can be prepared by sol-gel and Chemical Vapour Deposition (CVD) methods [1, 14]. The methods generally show a trade-off in terms of permeability and selectivity. It is well known that silica materials are instable after prolonged exposure to water vapor, which will result in pore blocking and reduced gas permeability [15]. A tremendous amount of work has been done to improve the hydrothermal stability of silica membrane materials, including incorporation of hydrophobic groups [16], heat treatment [17] and introducing some inorganic oxides such as Al_2O_3, MgO, ZrO_2, Co_3O_4, NiO, and Nb_2O_5 [18-23]. From the reports published in the literature [16-23], it has been known that an increase in selectivity is commonly at the expense of a decrease in membrane permeation. Kanezashi *et al.* reported that the Ni-doped silica membranes (Si/Ni=2/1) showed a permeance of 11.2×10^{-7} mol·m^{-2}·Pa^{-1}·s^{-1} for He and 4.5×10^{-8} mol·m^{-2}·Pa^{-1}·s^{-1} for H_2 with a high selectivity of 950 (He/N_2) and 370 (H_2/N_2) when operated at 500 °C and 90 kPa.

Based on the material functional superposition effect, we put forward a new membrane material preparation method, including hydrophobic modification and metallic palladium doping. In this work, Pd/SiO_2 organic-inorganic hybrid material was prepared by sol-gel method, in which $PdCl_2$ was added into methyl-modified silica sol. The influence of calcining temperature on the hydrophobicity and phase changes of Pd/SiO_2 hybrid material in air atmosphere were investigated by X-ray Diffraction (XRD), fourier transform infrared spectroscopy (FTIR), Thermogravimetric-differential thermogravimetric (TG-DTG) analysis, contact angle and Scanning Electron Microscopy (SEM) measurements. The contact angle measurements were used to quantify the degree of hydrophobicity of Pd/SiO_2 materials.

2 Experimental

2.1 Pd/SiO_2 Sol Preparation

The Pd/SiO_2 sol was prepared using tetraethylorthosilicate (TEOS, p.a. grade), methyltriethoxysilane (MTES, grade 98%), absolute ethanol (EtOH, grade 99.9%), hydrochloric acid (HCl,