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Cogeled copper–silica aerogel as a catalyst in hydrogen production from methanol steam reforming

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ABSTRACT

In this work, the copper–silica aerogel catalyst was prepared by cogelation of copper and silica precursors in a sol–gel process followed by chemical surface modification and ambient pressure drying. The results of characterizations by XRD, BET, FE-SEM, TEM, FTIR and TPR showed the prepared catalysts had high surface area and pore size distribution in the range of 1–10 nm. Also, uniform nanostructural morphology with particle size of 5–20 nm was observed. The copper loading and calcination temperature influenced the morphology and texture of the catalyst and the nature of copper species. So, copper existed within the silica matrix as highly dispersed isolated copper ions or CuO crystallite clusters which have good interaction with the matrix. Catalytic performance for hydrogen production from methanol reforming was evaluated at 300 °C in the methanol feed rate of 12–65 mmol g^{-1} h^{-1}. The catalyst activity was increased by increasing the copper loading and calcination temperature. In comparison with $CuO/ZnO/Al_2O_3$ commercial catalyst which showed 6–11% CO selectivity, no CO formation was detected using the prepared Cu/SiO_2 aerogel catalysts.

Introduction

Hydrogen fuel cells are a promising alternative to the internal combustion engines in the transportation application. Due to the safety and mechanical problems of the distribution and storage of hydrogen, the on-board hydrogen production from liquid hydrocarbons can be a practical option for the development of the fuel cell powered systems. Steam reforming of methanol has received particular attention to supply the hydrogen feed of the fuel cell [1–4].

In addition to the main products, hydrogen and carbon dioxide, a small amount of CO as undesired by-product can also be produced in MSR process. The presence of CO in the fuel cell feed causes poisoning of the platinum anodes of the fuel cell. Thus, the reformer gas requires further purification processes such as water–gas shift reaction followed by preferential CO oxidation. But, in these processes some of the produced hydrogen will be consumed and an excessive amount of oxygen is required. Also, the number of unit, complexity and cost of process will be increased. Therefore, development of new and more efficient catalysts with high selectivity and high hydrogen production rate is of interest to

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minimize the CO production, simplify the process and compact the fuel processing unit [5–8]. Various researchers have attempted to develop an efficient catalyst to this reaction. Copper containing catalyst show the highest activity and selectivity for MSR [5,9]. Silica-supported copper catalyst was used for MSR and shows good activity and significantly low CO selectivity [10,11]. Taking this into consideration, and due to the remarkable properties of the aerogels as catalytic applications including large surface area, good thermal stability, high open porosity and no mass transfer limitation of reactants [12–14], copper–silica aerogel catalyst was prepared for methanol steam reforming process.

Many investigations have been done on catalytic application of silica aerogels in which silica aerogel composites are generally derived through sol–gel process followed by supercritical drying of wet gels using silicon alkoxides as silica source [12–26]. However, alkoxides precursors are more costly and harmful. Also, supercritical drying is quite energy intensive, requires high temperature and pressures, and involves the heating and evacuation of highly flammable solvents, which is dangerous. These two factors restrict the commercial production of aerogels. So it is necessary to fabricate the silica aerogels using a low-cost precursor in combination with a cheap and safe drying method. Sodium silicate is perhaps the cheapest industrial silica source, its chemical stability is long, easy to handle and has no flammability hazard like silicon alkoxides. Moreover, for drying step the ambient pressure drying (APD) method was proposed instead of supercritical method [27–29]. Hence, in this work the copper–silica aerogel nanocatalyst was synthesized using the sodium silicate as silica source and by simple drying at ambient pressure through the solvent exchange and surface modification of the wet gels.

Various methods such as kneading and ion exchange [30–33], deposition–precipitation [32,34], co-precipitation [32], impregnation [33,35–37] and sol–gel process [10,36,38,39] have been used for introducing the copper to the silica matrix in conventional silica-supported copper catalyst. In this work, wet gels were formed through sol–gel process by cogelation of active metal precursor and silica precursor. This method provides controllable loading of metal, higher dispersion, stronger anchoring of metal particles in the support and more stable catalysts than other methods [25,36,40,41].

However, there are a few studies concerning the copper–silica composite aerogels. Hair et al. [42] prepared copper–silica aerogel, but used silicon alkoxide, as Si source and drying by supercritical method. The influence of preparation condition on the structure of copper-doped silica composite aerogel was investigated by Li GuiAn et al. [43]. However, in their work in addition to using alkoxide precursor the drying control chemical additive (DCCA) was used to preserve the wet gel structure and avoid the collapse of the gel during the ambient drying. DCCA is usually used to manipulate pore size and decrease the capillary drying stresses and to convert the wet gel into a monolithic xerogel; in order to achieve the aerogel the addition of DCCA is followed by supercritical drying [44–46]. On the other hand, literature shows that the most common and successful preparation method for APD derived silica aerogels is the hydrophobication of gels through silylation of their pore surface by silylating agents such as TMCS and HMDS [27–29,47,48]. Hence, in the present work, after obtaining the wet gels by cogelation of active phase and support precursors, the mentioned method was used to dry the wet gels. The prepared copper–silica aerogels were characterized by AAS, BET, XRD, TPR, SEM, TEM and FTIR techniques and their catalytic performance was evaluated in the MSR process to hydrogen production.

Experimental

Catalyst preparation

Initially, the sodium silicate solution (SiO_2 contents 8 wt%, Na_2O: SiO_2 mole ratio 1: 3.3, Merck) was diluted with the deionized water by 1:4 volume ratio, then this diluted solution was mixed by an ion exchange resin (IR-120, Merck) to replace the Na^+ ions present in the water-glass by the H^+ ions. Collecting the ion exchanged solution results in silicic acid (SA). The desired amount of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) was dissolved in deionized water by ultrasound stirring. This copper nitrate aqueous solution was added to SA and mixed vigorously. In order to achieve gelation, the resulting mixture was transferred into the air tight PTF beakers and aged at 60 °C for 12 h. The resulting gel was immersed in equivolume isopropyl alcohol for 18 h. Then the pore liquid was exchanged with hexane two times during a 48 h period. Hexane was removed from beaker and for surface modification the gel was immersed in an equivolume solution of 20% HMDZ (Merck) in hexane at 60 °C for 24 h. After the completion of surface modification reaction the resulting liquid was removed from the beaker and the obtained wet gel was dried at 60 °C for 4 h, 90 °C for 2 h and 120 °C for 2 h. For calcination, the as prepared catalysts were heated up (4 °C/min) to the desired calcination temperature (300, 450 and 700 °C) and kept at the final temperature for 3 h in a muffle furnace.

Catalyst characterization

Atomic absorption spectrometry (AAS, Analytic Jena novAA 300, Germany) was used for obtaining the Cu contents in the aerogel catalysts. The BET surface area and pore size distribution of the catalysts were measured using instrument by nitrogen adsorption–desorption method (Belsorp mini II, Japan and Quantachrome Instruments CHEMBET – 3000, USA). X-ray diffraction (XRD) patterns were obtained with a BrukerAxs D8, Germany, diffractometer using Cu Kα radiation. Fourier transform infrared (FT-IR) spectra of the samples were obtained with a Mattson 1000 FTIR spectrometer, Unicam, UK. Spectra were recorded in the range of 4000–400 cm^{-1}. The samples were diluted with IR-grade KBr.

Microstructural studies of the copper–silica aerogel catalysts were performed by Field Emission Scanning Electron Microscopy (MIRA3 FE-SEM, Tescan, Czech) and Transmission Electron Microscopy (CM30, Philips). Temperature programmed reduction (TPR) experiments were carried out using BELCAT, Japan, apparatus equipped with a thermal conductivity detector (TCD). 0.23 g of catalyst was placed in the reactor, then heated and reduced in a flow of 7.25% H_2/Ar mixture with a flow rate of 50 ml/min. The samples were heated from room temperature to 850 °C and the heating rate was kept at 10 °C/min.