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Sputtering processed tungsten catalysts for aqueous phase reforming of cellulose

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ABSTRACT

In the present study we show that over some types of heterogeneous tungsten catalysts cellulose can be efficiently converted to hydrogen. Highly active for aqueous phase reforming of cellulose at the temperature of 260 °C are catalysts prepared by magnetron sputtering of tungsten coating on oxidized Si wafers with the thickness of metallic tungsten about 185–200 nm. The catalysts were characterized by X-ray diffraction, transmission electron microscopy, chemisorption of CO and N_2-adsorption. The TEM and XRD images have shown uniform morphology of deposited tungsten layers in the form of nano-columns, while the contents of metallic α- and β-W phases in the films changed with the thickness of coating. Since in the most active catalysts the content of metastable β-W phase is always high, we suggest that this phase is closely related to APR activity. In our study (at not optimized conditions) tungsten catalyst prepared by magnetron sputtering achieved turnover frequency for H_2 production of 18.1 min^{-1}, which was 11.3 times more active than Pt/C catalyst. Moreover, the platinum catalyst is strongly deactivated by nitrogen and sulphur containing compound (2-mercaptobenzothiazole). In contrast, the tungsten catalysts prepared by magnetron sputtering display stable performance, i.e. retain their original activity.

Introduction

The declining availability of oil and gas resources initiates the development of effective technologies to convert renewable biomass as feedstock into hydrogen. Hydrogen, as an important chemical raw material and emerging clean energy carrier, has received significant attention in the last years [1,2]. Novel types of photocatalysts for conversion of solar energy to hydrogen have been studied [3,4].

Nowadays, three main processes for the transformation of renewable and available biomass to hydrogen are developing: the gasification, reforming in supercritical water and the aqueous phase reforming. Aqueous phase reforming (APR) introduced by Dumesic and co-workers [5–10] attracted a lot of attention because it is realized under relatively mild conditions in water which avoid drying of the biomass. Intensive studies have been conducted in the APR of ethylene glycol and glycerol [8,11–18]. In recent years APR of other types of feedstocks were also published [19,20]. Cellulose and sugar alcohols were also investigated and revealed much more complicated process chemistry than ethylene glycol or glycerol comprising many chemical reactions and intermediates [21–27].

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Among the different noble and other transition metals and their mixtures [28–33], Pt supported on Al_2O_3 or three-dimensionally bimodal mesoporous carbon showed the highest hydrogen selectivity (>90%). Recently Beller and co-workers [34] described hydrogen generation from monosaccharides, disaccharide and lignocellulose substrates by using a pincer-type iridium catalyst. Applying ppm amounts of this catalyst, hydrogen is produced at temperatures lower than 120 °C and catalyst turnover number is to about 3000.

Tungsten catalysts have never been employed before for APR reaction of cellulose and polyols, but it is expected to show a good activity for C–C bond breaking, due to its adsorption properties induced by tungsten metal atoms. These types of catalysts were extensively studied for conversion of cellulose and polyols to ethylene glycol [35–37].

In this communication, we demonstrate new catalytic properties of tungsten catalysts for aqueous phase reforming of cellulose to hydrogen. It was noteworthy that the catalytic activity of supported tungsten catalysts prepared by magnetron sputtering was significantly higher than of Pt/C catalyst, and moreover, these catalysts were not deactivated by the presence of S- and N-containing compound (2-mercaptobenzothiazole). According to our best knowledge, there are no data available in open literature regarding the use of tungsten catalysts for the aqueous phase reforming of cellulose or polyols.

Experimental

Materials and catalysts

Cellulose (Sigma Aldrich, particle sizes 20 and 50 μm) was used as the feedstock. 2-Mercaptobenzothiazole, purchased from Istrochem, Slovakia, was purified by crystallization from toluene. 5%Pt/C catalyst was purchased from Johnson Matthey. Powdered metallic tungsten (denoted metallic tungsten) with grain sizes < 25 μm and a specific surface area of 0.85 $m^2\ g^{-1}$ was obtained from Sigma–Aldrich.

For the samples prepared by magnetron sputtering the tungsten coating was deposited on oxidized Si wafers with the thickness of 0.6 mm (the surface silicon oxide thickness was 10 nm) and with a surface roughness of 0.6 nm, at the substrate temperature of −50 °C, by using a DC magnetron, in a cryo-pumped apparatus with the base pressure of 10^{-5} Pa. The substrate–target distance was 70 mm; the sputtering rate of 100 nm min^{-1} was kept constant and the deposition rate was adjusted by the velocity of the substrate movement over the W target. The W deposition was done in an argon atmosphere at a pressure of 5 Pa. The as-prepared W/SiO_2/Si samples were cut to plates of about 4.5 × 10 mm. The samples with a thickness of W coating of 100 (denoted as W-MS(100)), 185, 200 and 400 nm were prepared. The metal loadings on these catalysts were calculated on the bases of specific weight of tungsten, taking into account the porosity of the film and the density of β-W phase (see Part 3.1.) present in the tungsten coating (Table 1). In this paper the turnover rates are reported at reaction temperature of 260 °C.

Catalyst characterization

X-ray diffraction (XRD) data were collected with a Cu-Kα source using a Stadi Stoe apparatus in Bragg–Brentano geometry and a Bruker D8 Discover diffractometer in parallel beam geometry with parabolic Goebel mirror in the primary beam. The Scherrer equation was used to estimate the W crystal size. Transmission electron microscope (TEM) images were collected using a JEOL 1200EX at accelerating voltage of 120 kV. The number of surface W or Pt atoms on each catalyst was determined from the irreversible chemisorption of CO at 30 °C. For CO chemisorption, the surface reaction was assumed to occur with a 1:1 stoichiometry.

Catalytic tests

The reactions of APR of cellulose were carried out in high pressure stainless steel tubes (i.d. 15 mm, volume 10 mL) equipped with valves, served as reactors. In a typical experiment, cellulose (100 mg) and the catalyst were added to 5 mL of water in the reactor. Before the reaction, the tube was sealed, closed and purged three times with nitrogen to remove the air inside. The tubes were placed into a preheated aluminium block which could hold up eight tubes. The temperature was measured inside the reference steel tube (accuracy ± 1.5 °C). The aluminium block filled with reactors was mounted on a swinging device that could oscillate in a large diameter of circle. After heating of tubes to the desired temperature (usually it lasted 8–10 min) and switching on the swinging device the reaction started. In specified time intervals the tubes were withdrawn from the heating block and then quickly cooled down with water. Reactions were conducted at 260 °C for 2 h. The gas produced was collected in a gas burette filed with water and the volume was measured by displacement of water. The gaseous products were analysed using gas chromatographs equipped with FID and TCD. Standard gas samples comprising CO_2, CO, N_2, H_2, CH_4 were used to calibrate the GC. The products detected in the gas phase were H_2, CO_2, CO, CH_4 and traces of propane. In the liquid phase formation of glycols was analysed by GC. The selectivity to reaction products was calculated based on total moles produced in the gas phase, without considering water. The hydrogen selectivity was calculated as follows: selectivity to hydrogen = (moles of H_2 produced/moles of C atoms in gas phase) (1/RR) × 100, where RR is the H_2/CO_2 stoichiometric reforming ratio, for cellulose it is 2. The hydrogen yield is defined as the moles of hydrogen produced per gram of dry feed.

Results and discussion

Catalyst characterization studies

Physical–chemical characterization of catalysts is in Table 1. The metallic tungsten can form one of two crystal structures: alpha (bcc), and the metastable beta-W phase. The type of W phase in the catalysts was evaluated by XRD analysis. As is evident from images in Fig. 1 the crystal structure of the

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