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Sulfur tolerant Co–Mo–K catalysts supported on carbon materials for sour gas shift process — Effect of support modification

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ABSTRACT

The effect of steam gasification on the surface composition, surface area, pore size distribution as well as on the morphology of the carbon supports has been investigated. Materials have been characterized by nitrogen physisorption, mercury porosimetry, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Model samples of the Co–Mo–K catalysts with the same composition have been prepared on carbon supports differing in the temperature of steam gasification process. Catalytic activity measurements have been carried out in a gradientless reactor in a kinetic regime at low partial pressures of reagents. A relationship between textural parameters of the supports and the catalysts activity has been estimated. The highest activity in the SGS process has been determined for the Co–Mo–K/SRO/40.49 supported catalyst.

1. Introduction

The usefulness of carbon supports in catalysis results from their specific physicochemical properties, especially from a possibility of obtaining large specific surface areas up to >1000 m^2/g (or even >3000 m^2/g) [1], from their high stability within high temperature ranges, easy recovery of an active phase from spent catalysts through burning of the carbon support, from a relatively easy modifiability as well as from much weaker support-active phase interactions as a result of carbon surface specifics [2].

There have been several attempts to utilize the carbon-supported Co–Mo and Ni–Mo catalyst in hydrodesulphurization processes [3] and higher alcohols synthesis [4,5,6]. Moreover, the application of carbon-based catalysts in hydrodechlorination processes of chlorofluorocarbon compounds (CFC) seems to be also of interest [7]. While reports in the literature concerning the carbon-supported Co–Mo catalysts used in the HDS reactions are extensive [3,8] analogous examples on the application of these catalytic systems in the SGS process are relatively sparse [9,10]. To the best of our knowledge only two reports on carbon-supported catalysts in the SGS reaction are dedicated to the Co–Mo–K system.

Alkali-promoted Co–Mo catalyst is suitable for processing the products of coal or biomass gasification [11]. In spite of numerous advantages of carbon-based catalysts, their industrial application is strongly limited. Practically, only Co–Mo catalysts supported on Al_2O_3 or MgO–Al_2O_3 [12–20] have found the application in the SGS process, although there is a number of literature contributions on the utilization of other supports [21–24]. Recently, there has been an increasing interest in cesium-doped Co–Mo catalysts [25], which are very active even at low H_2S content in the process gas [26].

The limited applicability of carbon supports in industrial catalysis results from unquestionable disadvantages of raw carbon materials including, in particular, a high content of mineral impurities, unfavorable pore structure characterized by a relatively high micropore presence that generates diffusion resistances, facilitates the mechanical blocking and limits the active surface availability [2,27]. Furthermore, carbon materials exhibit relatively low mechanical strength and due to the potential methanation reaction they should not be used in the presence of hydrogen at temperatures exceeding 700 K [28]. Thus, a wider application of carbon materials as catalyst supports is strongly related to the improvement of active carbons properties and these materials are a subject of various modifications.

Our present contribution is strictly related to the subject area of the previous work [10]. Co–Mo–K catalysts prepared on modified active carbon had substantially higher activity than that supported on flash calcined alumina. Such effect was found even for Co–Mo K/NRO/1900

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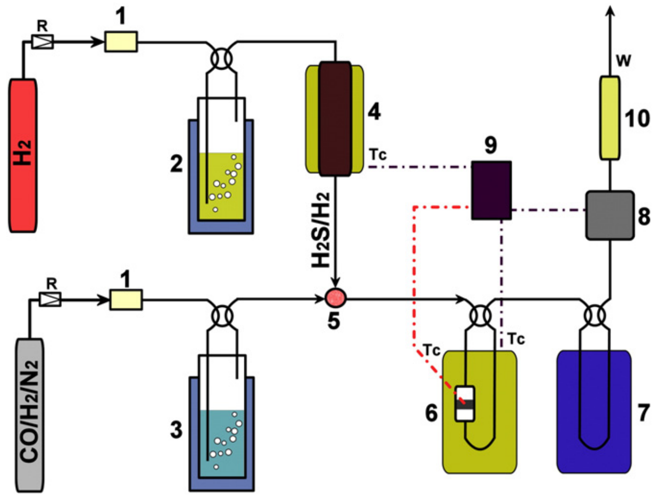

Fig. 1. Flow diagram of the reaction system for determination of the catalysts activity: 1 — gas steam regulators, 2 — H_2S generator, 3 — steam generator, 4 — reactor with Ni–Mo/Al_2O_3, 5 — mixer, 6 — gradientless reactor, 7 — dry ice cold trap, 8 — gas flow analyzer, 9 — PC, 10 — flowmeter.

catalyst, i.e. system which was supported on carbon with the lowest specific surface area and porosity. The highest activity in the SGS reaction was obtained for sulfided catalysts supported on NRO/1900/33.3 and can be related with specific surface area of carbon support.

As reported in our previous work [10] the removal of mineral impurities leading to the improvement of porous structure (more pores with a diameter > 2 nm) can be achieved by thermal treatment of raw carbons at high temperature (1900 °C) in helium atmosphere and subsequent partial gasification with steam. However, this processing may cause deterioration of the mechanical strength. The improvement of texture properties with maintaining high mechanical strength of carbon supports can be realized by the application of carbon black composites for the preparation of carbon materials [29,30].

One of such material is *Sibunit*, prepared by pyrolysis of C1–C3 hydrocarbons at 850–950 °C. A detailed description of the *Sibunit* preparation process has been reported in work [31]. *Sibunit* is used as the support of catalysts for various processes [32]. Undoubtedly, *Sibunit* has a beneficial texture (in the range that could be important for the catalytic properties of support materials), high purity and higher thermal stability than conventional active carbons. It seems to be especially promising support of highly dispersed Co–Mo–S phase of type II, which is characterized by no Mo–O–S species [33,34]. Thanks to this feature a higher degree of reduction and sulphidation can be achieved that in consequence results in a higher catalytic activity compared to systems supported on alumina [35]. From the technological viewpoint of WGS process it is also preferred to decrease the process temperature (beneficial shift of the equilibrium), which requires the development of low-temperature catalysts.

In the present study a detailed characteristics of carbon supports was carried out in order to get a support with desired and defined properties for the preparation of highly active catalysts for the low temperature SGS process. The catalytic activity of several model carbon-supported Co–Mo–K samples with the same content of Mo, Co and K was evaluated in the SGS process at the temperature range 200–350 °C and in the presence of H_2S.

2. Experimental

2.1. Preparation

The commercial material *Sibunit* (denoted as SRO, in the form of balls of a diameter in the range 0.5–1.0 mm) was used as a starting material. Partial steam gasification of SRO was carried out in a tubular furnace in the presence of H_2O/Ar mixture generated by passing at 675, 800, 835 or 850 °C for 5 h the stream of argon at the total flow rate of 15 l/h through an evaporator filled with H_2O to achieve the steam flow of 19 ml/h. The obtained materials were washed with distilled water in order to remove the dust fraction and then dried at 120 °C for 24 h in air. The prepared materials were denoted as SRO/3.8, SRO/13.95, SRO/32.42 and SRO/40.49.

All catalysts were prepared using the impregnation method, according to the procedure described in our previous contributions [10,24]. The nominal content composition of the precursors was 16 wt% MoO_3 and 4 wt% CoO, the promoter content expressed as a K/Mo molar ratio was 0.1. The prepared catalyst samples were marked with the following

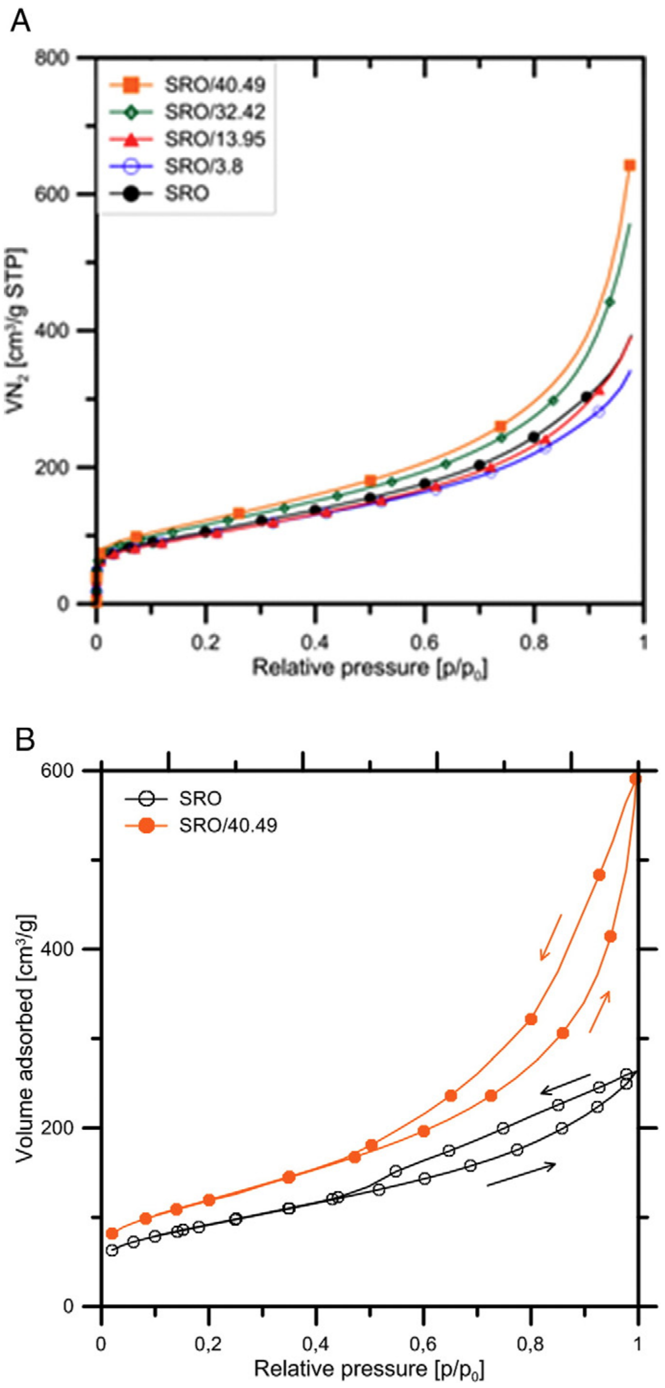

Fig. 2. Nitrogen adsorption–desorption isotherms of the initial carbon SRO and modified carbon materials.