Evolution of the structure of unpromoted and potassium-promoted ceria-supported nickel catalysts in the steam reforming of ethanol

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A B S T R A C T

Unpromoted and potassium-promoted Ni/CeO_2 catalysts, fresh, reduced and used in the SRE were characterized by TEM (as a leading method), SEM, XRD, hydrogen chemisorption, H_2-TPR and Raman spectroscopy. The evolution of the nature and the size of the nickel active phase (different in both catalysts) as well as distribution of potassium is disclosed. The promoter does not protect the catalyst against formation of carbonaceous deposit and does not improve its stability in the SRE. More important is high dispersion of nickel. Smaller nickel crystallites in Ni/CeO_2 ensure its better stability. In both catalysts, fragments of nickel (devoid of potassium in the case of KNi/CeO_2) are pushed from ceria by carbonaceous fibres formed. Their nature is different in both catalysts. On the Ni/CeO_2 amorphous (disordered) long and thick as well as short and thin graphitic fibres are formed. The KNi/CeO_2 produces very large amount of only graphitic fibres, longer and thicker than those in unpromoted catalyst. Much intensive production of graphitic fibres, which with time-of-stream can encapsulate greater number of nickel crystallites, is considered as responsible for faster deactivation of KNi/CeO_2 catalyst in the SRE.

1. Introduction

Hydrogen is considered as a high-energy and alternative energy source, which can play an important role in reducing emission to the environment. One of the most efficient methods of the production of hydrogen is the steam reforming of ethanol (SRE). If the process runs in the most desirable way, it is possible obtaining 6 mol of hydrogen from 1 mol of ethanol (according to the reaction $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$) [1–3]. Otherwise, the decrease in the efficiency of hydrogen production takes place by production of undesirable products such as acetaldehyde, acetone, methane and ethylene. These side products can also lead to carbon formation and catalyst deactivation [3–6]. For these reasons, in the steam reforming of ethanol, suitably selected catalyst plays an important role in achieving selective and complete ethanol conversion, as well as it is essential for the process to be economically profitable [2,3,6]. Active catalysts should maximize hydrogen selectivity, inhibit coke formation and by-products production [7]. Therefore, a high efficiency in conversion of ethanol, a high selectivity to hydrogen and, at the same time, a high resistance to deactivation under the SRE process conditions are important factors in designing the catalyst for the steam reforming of ethanol. The most commonly used metallic active phases in the catalytic steam reforming of ethanol are very active and efficient noble metals and, as a significantly less expensive alternative, transition metals, such as nickel or cobalt [2].

Reports are very often presented on catalysts with the nickel active phase [5,8,9,10]. The nickel-based catalysts were reported to be more active in the steam reforming of ethanol, they have better properties in the cleavage of C−C bonds [11,12] but they have a higher selectivity to carbon monoxide and methane formation than cobalt-based catalysts [13]. However, the use of nickel as the active phase in the catalytic system has also some other drawbacks, which include escalated production of the carbon deposit which leads to falling-off activity and selectivity of the catalyst in the SRE process [6]. In order to reduce these negative effects various improvements were proposed. One of them is synthesis of very small nickel crystallites, and then their stabilization by using an oxide support material with redox properties, such as CeO_2, which would also affect the catalytic properties by a strong interaction with the active metal [14]. An another improvement is addition of the promoter with alkaline properties which would have a positive impact on the stability and reactivity of such catalytic system. The addition of the alkali promoter (e.g. potassium) can improve catalytic properties of the nickel-based system; the electron enrichment of nickel by the presence of alkali can also modify interaction between

adsorbed intermediate reaction products and the metallic active phase [15]. Frusteri et al. [15] showed that addition of the alkali metal (Li, Na, K) to the nickel catalyst increases its ability to prevent carbon formation and increases the catalyst activity and stability in the SRE process [15]. Another method for elimination or reduction of the carbon deposit formation is mentioned above suitable choice of the catalyst support. In the recent years many studies showed a high resistance of ceria to formation of carbonaceous deposits [16–20]. It was suggested that the catalyst with the CeO_2 support has a high oxygen storage capacity and mobility what enables a more efficient gasification of carbon atoms adsorbed on the surface of the catalyst.

Beside of selection of the appropriate support and application of the alkaline promoter, catalytic properties of catalysts depend also on their features, such as their structure, morphology and crystallites size of the active phase. The dispersion as well as the average crystallites size of the active metal belong to the most decisive parameters characterizing supported catalysts [21,22], which are important for the activity, selectivity and stability of the catalyst in the catalytic processes. The catalytic activity of the heterogeneous catalysts depends on the dispersion of the metallic active phase and its active surface area [21–23], and it usually increases with increasing dispersion of the active metal and decreasing of its crystallites size [21,23]. Moreover, the crystallites shape and the size distribution are closely related to the mechanism of a catalytic reaction, which dependents on exposed crystal planes available for reactants [21,24]. The share of various individual active sites on the active phase is closely related to its crystallites size [25–27].

For determination of the crystallites size of metallic active phase usually X-ray diffraction (XRD), hydrogen chemisorption and transmission electron microscopy (TEM) are used [21,22,28], but sometimes for the same catalyst different results are founded from different methods. The differences in measurements of the crystallites size usually results from method limitations. In the case of XRD measurements such limitation may be the fact that this method does not measure very small crystallites. The measurement limitations can also concern hydrogen chemisorption which can be diminished by strong interactions between metal and its support [21,29]. Furthermore, our previous work [21] and others papers [30–32] showed that the temperature of hydrogen chemisorption measurements can significantly influence obtained value of the mean size of metal crystallites. Despite the fact that the hydrogen chemisorption is a simple, common and cheap method, it requires a suitable temperature of measuring. In order to obtain objective measurements of the average size of metal crystallites on the basis of hydrogen chemisorption it is important to find a correlation between this method and other methods allowing precisely estimating the crystallites size of the active phase. In this case, the most objective and reliable method of measuring the crystallite size becomes the transmission electron microscopy which gives a direct view of the crystallites size and shape, their dispersion, and simultaneously allows to observe the structure and morphology of the catalyst and relations between the active phase, the support and the promoter [29].

This work shows studies of the structure and morphology changes of unpromoted and potassium-promoted nickel catalysts with the ceria support during their three-stage functioning (fresh, reduced and used in the SRE). The key role in these studies plays the high resolution electron microscopy which allowed us to directly observe all changes in the structure and morphology of both catalysts in those individual stages. The HRTEM with FFT and the STEM-EDS characteristics allow us to identify phases, to determine crystallites size and dispersion of the active phase as well as distribution of elements in the catalysts. The scanning electron microscopy enabled characterization of the nature of carbonaceous deposits formed in the SRE. These studies were supplemented with XRD, hydrogen chemisorption, TPR studies, Raman spectroscopy and catalytic tests, which together with electron microscopic studies give a full view on to structural-performance relationships and on changes taking place within the both catalytic systems during their operation stage. As the dispersion of the nickel active phase plays an important role in behaviour of the catalysts in the SRE it was determined by three independent methods. The measurements of the average nickel crystallites size performed by XRD and TEM were compared with those from data of the total and strong hydrogen chemisorption. On the basis of these results the most suitable chemisorption temperatures for unpromoted and promoted with potassium nickel catalysts were indicated, which allow determining the proper crystallites size of the nickel active phase, compatible with the crystallites size determined by the most direct and objective method which is the transmission electron microscopy. The paper presents also the influence of addition of the potassium promoter to the nickel catalyst as well as the influence of the crystallites size of the nickel active phase on the catalytic activity, selectivity and resistance to production of various kinds of carbon deposits during the ethanol conversion process.

2. Materials and methods

2.1. Catalyst preparation

The Ni/CeO_2 and KNi/CeO_2 catalysts were prepared by impregnation of the cerium oxide support. Prior to impregnation, the ceria support (Aldrich) was dried at 110 °C for 3 h. For the Ni/CeO_2 catalyst, an aqueous solution of nickel nitrate with citric acid CA (Ni/CA = 1/1 mol/mol) was used for impregnation. In the case of preparation of the potassium promoted KNi/CeO_2 catalyst, an aqueous solution of potassium nitrate was applied for the second impregnation of the Ni/CeO_2 catalyst. After each impregnation, the catalyst precursors were dried at 110 °C for 12 h, then calcined at 420 °C with the heating rate of 2.2 °C/min up to the calcination set point and maintained for 1 h at this temperature. Before all measurements the catalysts were reduced with hydrogen at 420 °C for 1 h. The in situ XRD, the HRTEM with FFT and the electron diffraction measurements confirmed complete reduction of nickel oxide to metallic nickel at these conditions. The total surface area of the reduced Ni/CeO_2 catalyst was equal to 56.3 m^2/g and the active (nickel) surface area was 22.6 m^2/g while in the case of the KNi/CeO_2 catalyst − they were equal to 31.6 m^2/g and 7.9 m^2/g, respectively.

2.2. Steam reforming of ethanol studies

The reaction of ethanol conversion (SRE) was carried out at 420 °C under atmospheric pressure, in a fixed bed continuous-flow quartz reactor, using 0.1 g (0.15-0.30 mm) of the catalyst diluted (1/10 w/w) with 0.15-0.30 mm grains of quartz. The flow rate of the reaction mixture vapours was 100 ml/min. The reaction mixture was composed of ethanol and water vapours with the 1/12 ($EtOH/H_2O$) mol/mol ratio. This $EtOH/H_2O$ ratio is low enough to clearly show all changes in the morphology of the catalyst under SRE conditions. The products of the reaction were analyzed with two on-line gas chromatographs. The first of them, Bruker 450-GC, equipped with three columns: CP-Molsieve 5A, Molsieve 5A, Porapak Q and a TCD detector was used for analysis of carbon-containing products. The carrier gas in this system was helium. The second of the chromatographs, Bruker 430-GC, was used for analysis of hydrogen. This system was equipped with Molsieve 5A column and a TCD detector. In this case the carrier gas was argon.

The total conversion of ethanol X_{EtOH}, conversion of water X_{H2O} and conversion of ethanol into particular carbon-containing products, X_{CP}, were calculated on the basis of their concentrations before and after the reaction, with a correction introduced for the change in the gas volume during the reaction, from Eq. (1):

$$X_{EtOH} = \frac{C_{EtOH}^{in} - C_{EtOH}^{out}K}{C_{EtOH}^{in}} \cdot 100\%; \quad X_{H2O} = \frac{C_{H2O}^{in} - C_{H2O}^{out}K}{C_{H2O}^{in}}$$

$$\cdot 100\%; \quad X_{CP} = \frac{C_{CP}^{out}K}{(n/2)C_{EtOH}^{in}} \cdot 100\%$$

$$(1)$$

where C_{EtOH}^{in} and C_{H2O}^{in} represent molar concentrations of ethanol and