

Microscopic characterization of changes in the structure of KCo/CeO₂ catalyst used in the steam reforming of ethanol



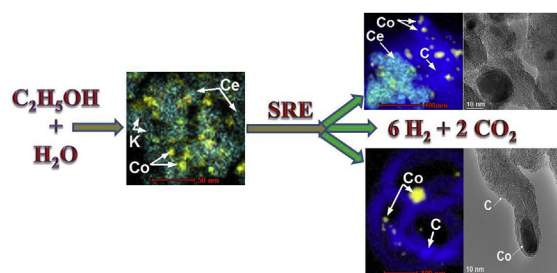
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HIGHLIGHTS

- CeO₂ and K promoter do not prevent cobalt catalyst from carbon formation in the SRE.
- Carbon deposit was present in three forms: fibrous, encapsulates, partly surrounding.
- Two types of carbon deposit structures: amorphous and hexagonal graphite were found.
- Metallic cobalt and ceria support crystallites are present with K in fibrous carbon.
- Cobalt active phase is present under SRE conditions as metallic Co and CoO.

GRAPHICAL ABSTRACT



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ABSTRACT

The cobalt catalyst with a support of CeO₂ and potassium promoted (KCo/CeO₂) was prepared by an impregnation method and used in the steam reforming of ethanol (SRE). The catalyst was characterized in its initial oxide form and after its work in the SRE by electron microscopy and EDS methods. Microscopic characterization of the catalyst allowed for identification of the active phase (in Co₃O₄ form) and the CeO₂ support phase (O-terminated), existing in the fresh catalyst, and also the active phase (at various forms, Co and CoO), support phase as well as various carbonaceous phases in the used catalyst. STEM-EDS studies allowed to determine the distribution of constituent elements in the catalyst before reaction and besides of them - also carbon deposit after the SRE. Microscopic studies of used catalyst proved that it was largely covered with carbonaceous deposit which was the main reason of deactivation of the catalyst. Carbon deposit growing during the reaction causes destruction of the support and the active phase into smaller particles which are sunk in the carbonaceous structures.

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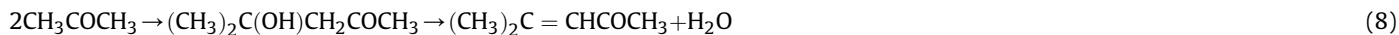
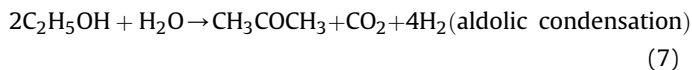
1. Introduction

Decreasing stocks of fossil fuels may be a serious energy problem in the future [1]. Therefore, interest in technologies using biomass energy grows [1,2]. Hydrogen is one of the clean energy sources, which does not emit neither CO₂ nor NO_x, and its role as a fuel in fuel cells is still indispensable. The steam reforming of lower

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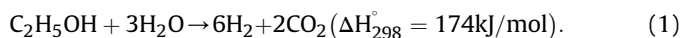
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organic compounds like methanol, ethanol and propane is considered to be an effective method of hydrogen production. Nevertheless, it is advisable from the environmental point of view if



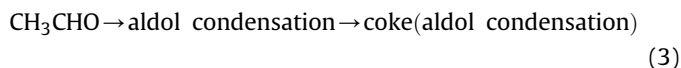
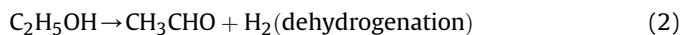
ethanol derived from biomass (e.g. cellulose, sugar cane, corn) fermentation will be applied. The aqueous solution of ethanol obtained by this method can be used for a steam reforming without removal of excess water. The application of ethanol derived from biomass sources is very beneficial for energy saving [1]. Hence, the steam reforming of ethanol (Eq. (1)) can be applied both in the chemical industry and for fuel cells to produce hydrogen from renewable and environmentally friendly energy sources [2–6]. There are many SRE pathways with parallel side reactions which leads to generation undesirable products (e.g. CO, CH₄, C₂H₄ and carbon) and which, depend on the reaction conditions as the ethanol/water ratio and the temperature and also on the catalytic properties of used catalyst [3,6–8].

Thermodynamic point of view of SRE was frequently mentioned in the literature [3,4,6,9]. The reaction demonstrate strongly endothermic properties and if ethanol reacts in the most desirable way only H₂ and CO₂ are generated [3,6,9,10]. Stoichiometrically, the general steam reforming of ethanol (C₂H₅OH) reaction can be written as follows [6,11]:

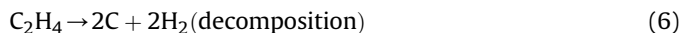
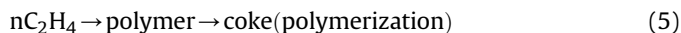
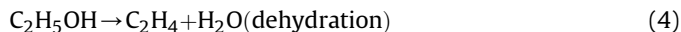


When water-ethanol vapors are introduced into reactor, the ethanol can be also decomposed into another carbonaceous species. Formed compounds may participate in the reaction with steam over the catalyst and form a mixture of H₂ with other compounds, to which belong CO, CO₂, CH₃CHO, C₂H₄, CH₄ and CH₃COCH₃ [3]. It may be also noticed that there are several sources of carbonaceous deposit formation over catalyst surface. The undesired reactions taking place in the SRE process, that contribute to catalyst deactivation by coke formation, are presented below:

- C₂H₅OH dehydrogenation to CH₃CHO (acetaldehyde) [3,4,6,12] and coke formation [9]:



- C₂H₅OH dehydration to ethylene (C₂H₄), followed by easily polymerization and decomposition of C₂H₄ causing formation of the coke [3,4,6,9,11,13]:



- Acetone and coke formation via aldolic condensation of acetaldehyde, followed by dehydrogenation [9]:

- Boudouard reaction [2,4,6,9,13]:



- Decomposition of CH₄ [2–4,9,13]:



- Reverse of carbon gasification [9]:



In the SRE, the catalyst has an essential role in achieving selective and complete ethanol conversion, as well as it is crucial for the process to be economically profitable. Supported catalysts with an active phase containing noble metals (such as Pd, Pt, Ru and Rh) exhibit high activity in the SRE, but the high cost of these systems restricts their application. The catalysts with the cobalt active phase seems to be a much cheaper alternative [14]. Another alternative for noble metal-based catalysts can be also nickel supported catalysts which are also active and selective during the production of hydrogen [7]. However, they produce much more of methane than cobalt catalysts.

Ceria have been used in various multicomponent systems like catalysts or fuel cells [15]. One of the key roles of cerium oxide in those systems is to provide surface active sites and to act as a high oxygen transport and storage center, by shifting between Ce³⁺ and Ce⁴⁺ under reductive/oxidizing conditions [16,17]. Cerium oxides show unique activity in various catalytic reactions such as water gas shift reaction, oxidation of methane and other hydrocarbons or oxidation of CO, soot oxidation, etc. [15,17].

Therefore, the Co/CeO₂ catalyst in view of the high effectiveness of ceria, which is used as a support, and cobalt as the active phase can form a highly active and selective catalytic system for ethanol steam reforming towards hydrogen production [18]. In spite of many advantages of this system, it shows a major problem associated with deactivation of catalysts during SRE, caused by the formation of carbon deposits [19]. However, it was noted that addition of promoters with alkaline properties (e.g. Li, Na, K, Mg) is effective in improving the performance of catalysts in the SRE [20–25]. The main effect of alkali dopants is their assistance in removal of carbon or inhibition its formation by favoring water adsorption or neutralizing acid sites of the catalyst, responsible for ethylene formation and its polymerization [9].

The composition of very specific catalytically active sites and precise atomic nanostructure influence on the efficiency of catalytic system. Hence, the chemical and nanostructural characterization at the atomic level becomes very important requirement in order to identify relationships between nanostructure and performance existing in heterogeneous catalytic systems [26–28]. The performance of catalytic system depends on a different parameters such as particle shape and size, local composition, chemical bonding,

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