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Selective production of hydrogen by steam reforming of bio-ethanol

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ABSTRACT

Experimental results of catalytic activity, selectivity and coking phenomenon on co-precipitated cobalt catalysts with the ZnO–Al_2O_3 support in the steam reforming of ethanol (SRE) are reported. The influence of the cobalt active phase content (9–41 wt.%) and the reaction temperature (350–600 °C) was the point at issue. From the point of view of activity and selectivity, temperatures 420 °C and higher favoured steam reforming of ethanol on supported cobalt catalysts. At these temperatures the conversion of ethanol reached 100%, simultaneously the hydrogen yield achieved the level of above 5 mol of H_2 formed from 1 mol of EtOH introduced to the reaction, as well as the selectivity of carbon monoxide formation was depressed to 2–3%. However, taking into account possibility of coking of catalysts, the optimum temperature of the SRE is 420 °C. The catalyst containing 24 wt.% of cobalt was the most effective one. The obtained results are very important in the aspect of electricity generation in fuel cells feed with a reformate gas.

1. Introduction

Nowadays it is crucial to find renewable, non-toxic and biomass-derived fuel. Hydrogen is considered to be clean energy carrier which reduces also energy dependence on fossil fuel. One of the most encouraging hydrogen reservoirs is bioethanol. From the environmental point of view, hydrogen generation from bioethanol will bring benefits in lowering carbon dioxide emission. In contrast to fossil fuel systems for hydrogen production the use of bioethanol has a significant advantage of being nearly carbon dioxide neutral. Though there are several possibilities of gaining hydrogen from bioethanol the one which was used in this work is the steam reforming of ethanol (SRE). The reformer with efficient catalyst producing hydrogen-rich gas connected to a low-temperature fuel cell could become an ecological power source. According to the stoichiometry of the SRE reaction $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 3CO_2$, the maximum yield of hydrogen is 6 mol with respect to 1 mol of ethanol reacted, what is very good point of this process. However, the final hydrogen yield/efficiency will depend on the intensity and the state of the equilibrium of the water gas shift reaction $H_2O + CO \leftrightarrow H_2 + CO_2$ as well as successful inhibition of non-selective transformations of ethanol to acetaldehyde, ethylene, methane, acetone and other by-products which are formed in side reactions [1]. Besides, some of those compounds act as coke precursors, leading to carbon deposits on the catalysts. A balanced, thermodynamic productivity of hydrogen, taking into account the participation of side reactions, is established to be about 5.5 mol of H_2/mol EtOH introduced [2].

The steam reforming of ethanol reaction has been studied for more than ten years, but till now there is no clear chemical formula for a catalyst assigned to this process. The development of a catalyst which could operate at relatively low temperature without by-products formation, which is also resistant to carbon deposition is currently goal of research in this area. As an active phase researches considered first of all noble metals [3–6], nickel [1,3–6] and cobalt [3–20]. As noble metals are expensive, an interest was paid to nickel-based and cobalt-based catalysts. However, similarly to noble-metal catalysts, nickel favours production of methane and, as consequence, it assures high hydrogen yields only at high temperatures. Very encouraging results of the SRE were obtained over supported cobalt catalysts [10,12,16]. An attention given to Co/ZnO [3–7,11,16–19] and CoZnAl systems [20] which are very effective in the steam reforming of ethanol is noticeable but the reports on this kind of catalysts are not very numerous.

Most of the Co/ZnO type of catalysts used so far in investigations of the SRE process contained c.a. 10 wt.% of cobalt [3–7,11]. Certain attention was given also to catalytic activity of unsupported cobalt oxide [12,24]. Tuti et al. [12] and Wang et al. [24] suggested that cobalt is an active phase for the SRE. The yield of hydrogen formed over unsupported Co_3O_4 was 4.6–5.6 [12,24] what is in agreement with that obtained over supported cobalt catalysts. As an example, Llorca et al. [16] gained hydrogen efficiency equal to 5.2–5.3 over catalysts with cobalt phase (10 wt.% Co) supported on zinc oxide. According to results gained by Llorca et al. [21,22] supported cobalt catalyst can break C–C bond and are appropriate for selective ethanol steam reforming. Llorca et al. [21] revealed mixture of metallic and oxidized cobalt species as an active phase for the SRE.

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Simultaneously, Batista et al. [10] showed that selectivity of the SRE can be improved by increasing of cobalt content in the Co/Al_2O_3 catalyst, from 8 to 18 wt.%. The increase of cobalt loading caused that the ethanol conversion achieved 99%, in parallel to advantages in carbon-containing products selectivity and stabilization of catalyst performance. Liquid organic products (CH_3CHO, $(C_2H_5)_2O$, $(CH_3)_2CO$) were almost eliminated, formation of carbon monoxide was decreased and at the same time the selectivity towards carbon dioxide raised. Nevertheless, the lack of scientific analysis of various amounts of cobalt active phase impact on the activity and selectivity of catalytic materials in the SRE is noticeable. There are no reports on the steam reforming of ethanol carried out on zinc oxide-supported cobalt-rich catalysts. In addition to the zinc oxide-supported also cobalt catalysts with numerous supports of active phase, including Al_2O_3, MgO, SiO_2, CeO_2, ZrO_2, CeO_2–ZrO_2, La_2O_3, Y_2O_3, were examined. However, those with zinc oxide as a cobalt support enabled production of hydrogen with high selectivity and yield, even in the range of moderate temperatures [16].

The strong disadvantage of zinc oxide as a catalyst support is its low thermal stability. It is known that the presence of small amounts of alumina improves resistance of various metal oxides to sintering. There are limited numbers of reports on the zinc oxide-supported cobalt catalysts stabilized with alumina. One of them concerns CoZnAl (Co/ZnO–Al_2O_3) system [20], where the aluminium content was 20 wt.%. However, acidic nature of the alumina surface brings about dehydrogenation of ethanol to ethylene, which is strong precursor for carbonaceous deposit formation on the Co/Al_2O_3 catalyst what results in its fast deactivation (24.6 wt.% of carbon was deposited on catalyst during 9 h of the SRE at 400 °C, when the $EtOH/H_2O$ molar ratio was equal to 1:3) [9]. Therefore, smaller amounts of alumina present in the zinc oxide-supported cobalt catalyst should ensure more selective and stable performance of the catalyst in the SRE.

Precise comparison of efficiency of various catalysts proposed for the hydrogen-rich gas production from bioethanol is often difficult as very different reaction mixtures are used in the studies reported in open literature. The most frequently, the $EtOH/H_2O$ molar ratios were varied from 1/3 to 1/13, what require distilled ethanol as a raw material.

The main aim of our studies was to evaluate influence of the cobalt phase content, varied in the wide range (9–41 wt.%), supported on zinc oxide stabilized with small amount of alumina (5 wt.% only), on the catalyst activity, selectivity, hydrogen yield and intensity of coking in the steam reforming of ethanol. An aqueous solution of ethanol (10.85 wt.%, the ethanol/water molar ratio equals to 1/21), simulating a fermentation broth, without its distillation, was used as a feed. The performance of catalysts in the SRE was measured in the wide range of the process temperatures, 350–600 °C. All varied parameters of catalysts and reaction conditions enabled us to accomplish the goals of this report, i.e. to establish the optimum content of cobalt in catalysts with alumina stabilized zinc oxide support, prepared by the co-precipitation method, as well as to establish the optimum temperature of the steam reforming of ethanol over such catalysts. The basic characterisation of catalysts is also given.

2. Experimental

ZnO-supported cobalt catalysts and the catalyst support were prepared by the co-precipitation method from $Zn(CH_3COO)_2$, $Al(NO_3)_3$ and $Co(CH_3COO)_2$ (except of the support preparation) aqueous solutions. The precipitation was accomplished at 40 °C by addition of $(NH_4)_2CO_3$ solution, drop by drop, up to pH equal to 8.5, under continuous stirring of suspension. After ageing of precipitate at 55 °C for 3 h, the suspensions were filtered. The filtrates were washed with an absolute ethanol, in order to remove water from precipitates (precursors of catalysts). The obtained solids were dried at 110 °C for 14 h and then calcined at 400 °C for 6 h. The catalysts were labelled as *x*Co/ZnO (where *x* is the content of cobalt expressed in wt.%). The ZnO-based support in all catalysts contained 5 wt.% of alumina.

Unsupported cobalt oxide Co_3O_4, used as a standard in Raman spectroscopy studies, was obtained by the calcination of cobalt nitrate $Co(NO_3)_2$ at 400 °C.

Contents of cobalt in catalysts were determined by the X-ray fluorescence technique, by means of an energy-dispersive XRF spectrometer (Canberra 1510) equipped with the liquid nitrogen-cooled Si(Li) detector.

The porosity and BET surface area of catalysts and those of the support were measured by the low-temperature (−196 °C) nitrogen adsorption in the ASAP 2405N v1.0 analyser (Micromeritics). The average pore diameter and the volume of pores were calculated from desorption data using Barret–Joyner–Halenda (BJH) method [23].

X-ray powder diffraction patterns of catalysts and the support were collected with the upgraded Zeiss HZG-4 diffractometer using Mn-filtered Cu Kα radiation. The average size of Co_3O_4 and ZnO crystallites was estimated from X-ray diffraction line broadening of the appropriate peaks corresponding to Co_3O_4 ($2\Theta = 36.9$) and ZnO ($2\Theta = 36.3$), using Scherrer equation. The raw data obtained from the X-ray diffractometer (scanned at 2θ intervals of 0.02° in the 2θ range of 35–38°) were put to a mathematical treatment with the PeakFit software (AISN Software Inc.). At first, a baseline (a background level of the apparatus) was subtracted. Next, the data were smoothed with the Savitsky-Golay filter and overlapping peaks were deconvoluted using Gauss–Lorentz amplitude algorithm.

The Raman spectra were recorded with the resolution of 2 cm^{-1} in the Raman microscope (inVia Reflex, Renishaw) with Raman dispersive system, using the 785 nm semiconducting laser. In order to avoid sample overheating 3 mW of laser power was used. In the case of the zinc oxide-alumina support the spectra were collected also with the 300 mW laser power.

The temperature-programmed reduction of catalysts and the support alone was carried out in the AMI-1 analyser (Altamira Instruments Inc.) using 0.05 g of the catalyst and support. The 6% H_2–Ar mixture was used at the flow rate of 30 cm^3/min with the linear temperature increase of 10 °C/min.

The steam reforming of ethanol was carried out in a fixed-bed continuous-flow quartz reactor over catalysts (0.1 g, grain size of 0.15–0.30 mm) reduced *in situ* with hydrogen at 350 °C for 1 h prior to the reaction studies. The catalysts were diluted (at the weight ratio 1:10) with grains of quartz in order to ensure constant temperature in the catalytic layer. In a preliminary experiment it was found that the conversion of ethanol over quartz starts, to a small extent, at higher temperatures (>700 °C) than those at which the steam reforming of ethanol in the presence of catalysts was investigated. The aqueous solution of ethanol ($EtOH/H_2O$ molar ratio equal to 1:21, simulating a fermentation broth) was supplied by mass controller (Bronkhorst) to an evaporator (140 °C) and the reactants' vapours (at a flow rate of 0.27 mol/h, 100 cm^3/min), without diluting with any inert gas, were fed to the reactor. The reaction temperature measured in the center of the catalyst + quartz bed, was changed from 350 °C to 600 °C (350; 420; 480; 540; 600 °C). Analyses of the reaction products were conducted several times during 2 h of the reaction at each of the temperatures, and then results were averaged.

The analysis of the reaction mixture and the reaction products (all in gas phase) were carried out on-line by means of two gas chromatographs. One of them, Varian CP-3800 was equipped with two capillary columns, the first one contained a porous polymer

Porapak Q (for all organics, carbon dioxide and water vapour) and the second of them – an activated molecular sieve 5 Å (for methane and carbon monoxide analysis). Helium was used as a carrier gas and a TCD detector was employed. The hydrogen concentration was analysed by the second gas chromatograph, Chromatron GCHF 18.3, using a column packed with an activated charcoal, nitrogen as a carrier gas and a TCD detector. The sensitivity of the detectors to the analysed compounds (response factors) was determined by their calibration against external standards of single compounds or their certified (Praxair) mixtures in helium. The concentrations of the external standards were comparable with those of analysed products. The reproducibility of analysis of standard compounds was ±2%. Because of some tailing of chromatographic peaks of water, the reproducibility of its analysis was lower than other compounds, about ±5 relative percent.

The total conversion of ethanol X_{EtOH}, conversion of water $X_{\mathrm{H_2O}}$ and conversions 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 a gas volume during the reaction, from equations:

$$X_{\mathrm{EtOH}} = \frac{C^{\mathrm{in}}_{\mathrm{EtOH}} - C^{\mathrm{out}}_{\mathrm{EtOH}} \times K}{C^{\mathrm{in}}_{\mathrm{EtOH}}} \times 100\%,$$

$$X_{\mathrm{H_2O}} = \frac{C^{\mathrm{in}}_{\mathrm{H_2O}} - C^{\mathrm{out}}_{\mathrm{H_2O}} \times K}{C^{\mathrm{in}}_{\mathrm{H_2O}}} \times 100\% \quad \text{and}$$

$$X_{\mathrm{CP}} = \frac{C^{\mathrm{out}}_{\mathrm{CP}} \times K}{n/2 \times C^{\mathrm{in}}_{\mathrm{EtOH}}} \times 100\% \quad (\%)$$

where

$C^{\mathrm{in}}_{\mathrm{EtOH}}$ and $C^{\mathrm{in}}_{\mathrm{H_2O}}$ – are the molar concentrations of ethanol and water in the reaction mixture (mol%)
$C^{\mathrm{out}}_{\mathrm{EtOH}}$ and $C^{\mathrm{out}}_{\mathrm{H_2O}}$ – are the molar concentrations of ethanol and water in the post-reaction mixture (mol%)
$C^{\mathrm{out}}_{\mathrm{CP}}$ – is the molar concentration of carbon-containing product in the post-reaction mixture (mol%)
n – is the number of carbon atoms in the carbon-containing molecule of the reaction product
K – is the volume contraction factor ($K = C^{\mathrm{in}}_{\mathrm{C}}/C^{\mathrm{out}}_{\mathrm{C}}$ where $C^{\mathrm{in}}_{\mathrm{C}}$ and $C^{\mathrm{out}}_{\mathrm{C}}$ are the molar concentrations of carbon in ethanol fed to the reaction and in all carbon-containing compounds which were present in post-reaction gases, respectively).

The selectivity of ethanol conversion into individual carbon-containing products was expressed as: $X_{\mathrm{CP}}/X_{\mathrm{EtOH}} \times 100\%$. The carbon mass balances, based on the carbon selectivity at each of the reaction temperatures, were close to 100 ± 3%. The selectivity of hydrogen formation was determined from the equation:

$$H_2 \quad \text{selectivity} = \frac{C^{\mathrm{out}}_{\mathrm{H_2}}}{C^{\mathrm{out}}_{\mathrm{H_2}} + 2C^{\mathrm{out}}_{\mathrm{CH_4}} + 2C^{\mathrm{out}}_{\mathrm{C_2H_4}} + 2C^{\mathrm{out}}_{\mathrm{CH_3CHO}} + 3C^{\mathrm{out}}_{\mathrm{(CH_3)_2CO}}} \times 100\%$$

where

C^{out} – are the molar concentrations of the hydrogen-containing reaction products (mol%) [1].

The studies of the catalyst coking in the steam reforming of ethanol conditions were performed by the gravimetric method using the conventional TG121 microbalance system (Cahn), under dynamic conditions in a quartz reactor with a continuous flow of ethanol–water vapours. The sensitivity of the balance was 0.1 μg. Those experiments simulated the activity measurement tests but the catalyst sample was placed on a small quartz plate. The *in situ* reduced (with hydrogen at 350 °C for 1 h) samples (0.01 g, 0.15–0.30 mm) were cooled down to 300 °C in a flow of hydrogen. Then the reactor was flushed with nitrogen and the catalyst samples were heated up to the 600 °C in the stream of the ethanol and water vapour mixture (molar ratio of $\mathrm{EtOH/H_2O}$ = 1/4, 0.27 mol/h, without diluting with any inert gas) with the heating rate of 5 °C/min.

3. Results and discussion

3.1. Catalyst characterisation

The total surface area, volume of pores and their average diameter for the ZnO support and all catalysts are presented in Table 1. In general, the total surface area and pore volume decreased after cobalt loading and with increasing content of cobalt phase.

The XRD patterns (Fig. 1a) of the $\mathrm{ZnO–Al_2O_3}$ catalyst support shows the only visible crystalline phase of zinc oxide; alumina oxide was amorphous or strongly dispersed. In the case of all unreduced catalysts intense peaks of ZnO and $\mathrm{Co_3O_4}$ are present. The XRD lines of $\mathrm{Co_3O_4}$ phase are poorly displayed. Simultaneously, the presence of $\mathrm{CoAl_2O_4}$ or $\mathrm{Co_2AlO_4}$ cannot be excluded since their diffraction reflections coincide with those from cobalt oxide (at $2\Theta = 44.9°$, 55.7°, 59.3° and 65.3°). It makes impossible to unquestionable, precise determine of the mean size of crystallites of cobalt oxide on the basis of those diffraction peaks. Therefore, for the evaluation of the mean size of crystallites peaks of $\mathrm{Co_3O_4}$ and ZnO from the 2Θ range of 35–38° were chosen (Fig. 1b). In addition, even though $\mathrm{Co_3O_4}$ characteristic diffraction lines at $2\Theta = 44.9°$, 55.7°, 59.3° and 65.3° are often very well visible by other authors in the Co/ZnO type of catalysts, e.g. by Llorca et al. [16], they were all very broad and weakly stressed in the diffraction patterns of our catalysts containing less than 30 wt.% of cobalt. It proves that the precipitation method of catalyst preparation and the presence of small amount of alumina as the structural stabilizer ensure much higher dispersion of cobalt oxide (zinc oxide also) phase than that observed in catalysts without alumina stabilizer obtained by the incipient wetness impregnation, used by Llorca et al. As the zinc oxide and cobalt oxide peaks in the diffraction range of 35–38° overlap, and in the case of smaller contents of cobalt oxide in catalysts the $\mathrm{Co_3O_4}$ diffraction line brings only about asymmetrisation of the ZnO peak, the deconvolution procedure with the Gaussian–Lorentzian amplitude algorithm (from the PeakFit software) was applied (Fig. 1b). Even after deconvolution procedure, diffraction peaks corresponding to $\mathrm{Co_3O_4}$ ($2\Theta = 36.8–36.9°$) can be clearly seen only in the case of catalysts containing high amounts of cobalt (32Co/ZnO and 41Co/ZnO). For catalysts with lower content of cobalt, diffraction peaks of $\mathrm{Co_3O_4}$ are very broad and small and slightly moved towards higher diffraction angles (Fig. 1b and Table 1). Analysis of the ZnO diffraction line ($2\Theta = 36.3°$) broadening proves that the mean size of ZnO crystallites increased (from 10 to 26 nm) with increasing amount of $\mathrm{Co_3O_4}$ in catalysts (Table 1). The mean size of cobalt oxide crystallites increased from 6.9 to 26 nm when the cobalt content was increased from 9 to 41 wt.% (Table 1). We assume that values of mean sizes of metallic cobalt crystallites in reduced catalysts are similar to those of cobalt oxide in fresh catalysts and they form similar order of their changes with the cobalt content. Because of pyrophoricity of reduced catalysts, even carefully passivated, it was impossible to evaluate directly the mean size of metallic cobalt crystallites in the *ex situ* measurements. The significant influence of crystallite size on the catalytic properties is usually observed in many reactions when the crystallites are smaller than 5 nm. In our catalysts the size of cobalt phase crystallites is in the range of 7–26 nm, i.e. they should not be crucial for the activity and selectivity of catalysts in the steam reforming of ethanol.

Table 1
Catalysts and support alone characterisation results.

	ZnO support	9Co/ZnO	17Co/ZnO	24Co/ZnO	32Co/ZnO	41Co/ZnO
BET surface area (m^2/g_{cat})[a]	104	112	74	95	45	27
Volume of pores (cm^3/g_{cat})[a]	0.56	0.66	0.40	0.58	0.29	0.13
Average pore diameter (nm)[a]	19.1	18.2	16.4	19.3	21.6	14.6
Cobalt content (wt.%)[b]	–	8.8	16.6	23.5	31.6	40.5
Mean size of Co_3O_4 crystallites (nm)/2Θ[c]	–	6.9[d] (36.93)	12.0[d] (36.82)	14.2[d] (36.94)	19.8 (36.83)	26.0 (36.84)
Mean size of ZnO crystallites (nm)/2Θ[c]	11.8 (36.29)	10.3 (36.27)	14.8 (36.28)	11.8 (36.31)	21.5 (36.27)	26.2 (36.26)

[a] Determined by the low-temperature N_2 adsorption.

[b] Determined by the XRF technique.

[c] Determined by the XRD technique.

[d] Due to small intensity of Co_3O_4 peaks and their strong overlapping with ZnO lines the determination of mean size of cobalt oxide crystallites was possible after deconvolution procedure only.

The Raman spectra (Fig. 2) give more information on the surface composition of the catalysts. The spectra of cobalt catalysts (Fig. 2b) show strong peaks at 190, 478, 518, 616 and 681 cm^{-1}, which are close to that of calcined Co_3O_4 (Fig. 2a) 199, 484, 524, 622, 693 cm^{-1} as well as 197, 483, 524, 619 and 690 cm^{-1} reported in the literature [9,24]. For cobalt oxide phase supported on ZnO–Al_2O_3 all bands are shifted into lower wave numbers with respect to unsupported Co_3O_4 powder. Additional band at 207 cm^{-1} is also observed for all catalysts. According to results of Gao et al. [25] this band can be associated with presence of $CoAl_2O_4$. Another broad, weak band at 583 cm^{-1} observed in spectra of all catalysts, except that for the 41Co/ZnO, matches the presence of a high dispersed cobalt oxide [26]. The spectrum of alumina stabilized zinc oxide support presented in Fig. 2b was obtained with the same laser power (3 mW) as used in the case of catalysts investigations while that in Fig. 2c presents bands corresponding to the maximum laser power (300 mW). The spectrum of the support was fine fitted to that of pure ZnO spectrum. The most intensive ZnO base bands were 204, 337, 442, 539, 585, 659 and 806 cm^{-1}. Comparison of Raman spectra of the support and those of catalysts showed no coincidence between them. No bands corresponding to ZnO or alumina are present in Raman spectra of catalysts.

Results of the XRD and Raman measurements prove that the strongly dispersed (especially if the cobalt content is lower than 30 wt.%) cobalt oxide is spread over ZnO–Al_2O_3 support and that the higher is content of cobalt in the catalyst (particularly if the cobalt content is higher than 30 wt.%) the higher are amounts of crystalline Co_3O_4, weakly interacting with the support.

The temperature-programmed reduction profiles show that the reduction of catalysts occurred in two main temperature regions (Fig. 3). The first occurs between 200° and 390 °C. It is assigned to reduction of cobalt oxides weakly interacting with the zinc oxide support to metallic cobalt $Co_3O_4 \rightarrow CoO \rightarrow Co$. The second, wide bands, with maxima at about 600 °C and higher temperatures, can be associated with the reduction of cobalt oxide strongly and very strongly interacting with the support as well as with the reduction of some part of ZnO, facilitated by the presence of metallic cobalt. The ZnO support alone, without cobalt phase, undergoes reduction with strong difficulty (Fig. 3).

3.2. *Activity and selectivity of cobalt catalysts in the ethanol steam reforming*

The temperature of 350 °C was too low for the complete conversion of ethanol in its steam reforming over all catalysts studied (Fig. 4). At that temperature the highest, 95% conversion of EtOH was reached in the case of catalyst containing 24 wt.% of cobalt. The lowest activity possessed the 9Co/ZnO catalyst; the complete conversion of ethanol over this catalyst was achieved only at 480 °C. The cobalt-rich catalysts, when the cobalt content was equal to or higher than 17 wt.% enabled us to achieve complete conversion of EtOH at as low temperature as 420 °C.

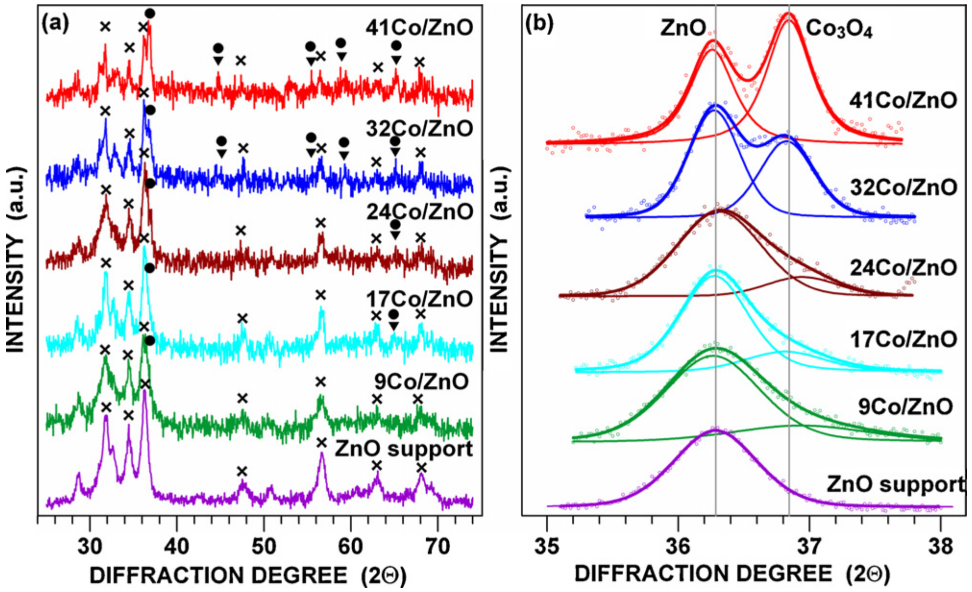

Fig. 1. Diffraction patterns of *x*Co/ZnO catalysts and ZnO–Al_2O_3 support, where (×) ZnO, (●) Co_3O_4, (▼) $CoAl_2O_4$: (a) in the 2Θ range of 25–75°, (b) in the 2Θ range of 35–38° with deconvoluted peaks.

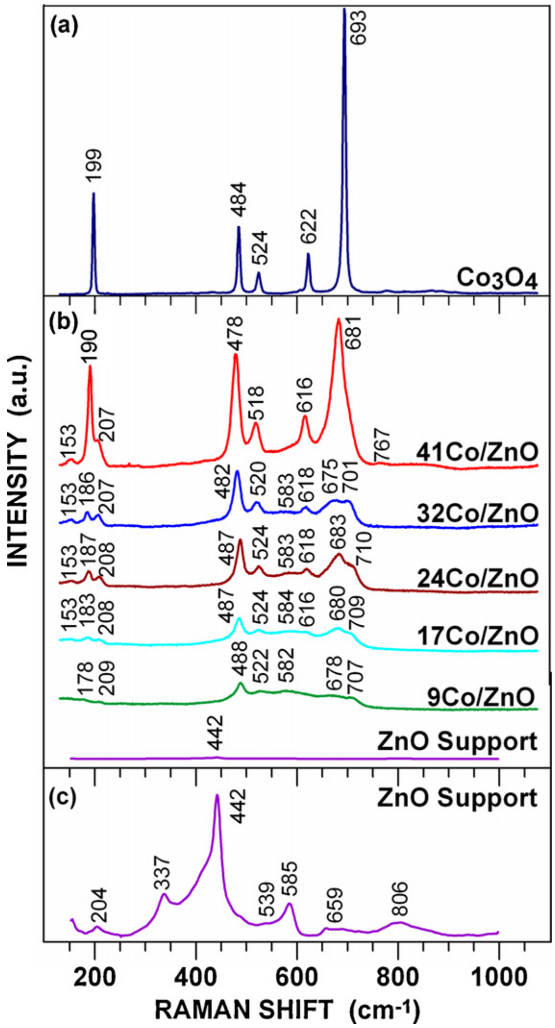

Fig. 2. Raman spectra of: (a) Co_3O_4 powder – laser power 3 mW, (b) *x*Co/ZnO catalysts – laser power 3 mW and (c) $ZnO–Al_2O_3$ support – laser power 300 mW.

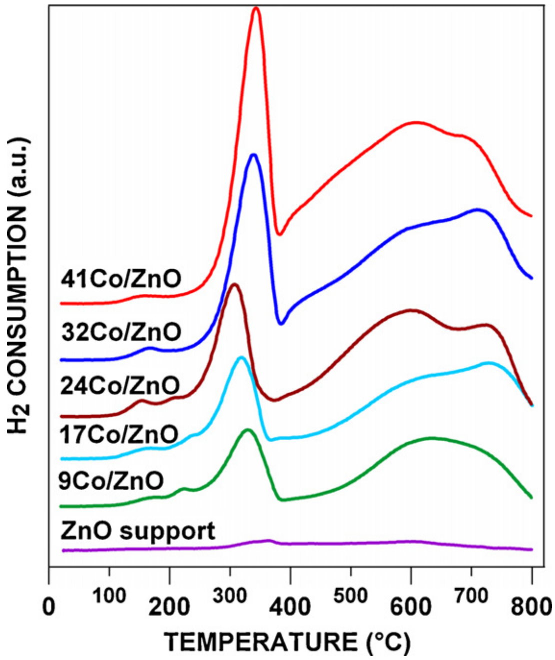

Fig. 3. TPR-H_2 profiles of *x*Co/ZnO catalysts and support alone.

The degree of water conversion seems to be low, but due to the large excess of water in relation to the stoichiometry of the SRE reaction, its highest conversion could be only equal to 14–15%. The dependences of water conversion on the cobalt contents in the catalysts and on the temperature of the SRE are similar to those of ethanol conversion.

Conversion of ethanol, without participation of water, led to its non-selective transformations. As a result, at 350 °C large amounts of acetaldehyde, small amounts of acetone, as well as carbon monoxide and methane were formed in side reactions (Fig. 4). At higher temperature of the SRE, i.e. at 420 °C, when not only ethanol complete conversion but also maximum conversion of water were achieved over catalysts containing 17 and more wt.% of cobalt, the acetaldehyde and acetone formation was eliminated (Fig. 4).

Hydrogen is the most desirable product of the SRE. The selectivity of its formation was below 80% at 350 °C but at higher temperatures it increased even to 98% (Fig. 4). At 420 °C and above, the amount of cobalt phase content did not greatly influence that selectivity (at 420 °C it is true only above 17 wt.% of cobalt).

The other most desirable product of the SRE is carbon dioxide. High selectivity of its formation proves that the SRE process is selective one in the sense of suppression of by-products formation. It can be clearly noticed that improved selectivity towards carbon dioxide was achieved at temperatures above 420 °C over catalysts with minimum 17 wt.% of cobalt content (simultaneously to strong limitation of acetaldehyde and carbon monoxide production (Fig. 4)).

Since carbon monoxide is a poison of platinum anodes in the low-temperature FCs, suppression or even total elimination of its formation is a very important issue. The advantage of Co/ZnO catalysts containing 24 wt.% or more of cobalt is their low selectivity of carbon monoxide formation, below 5% at 420–480 °C, simultaneously with high (90–95%) selectivity of hydrogen formation. The restriction of the carbon monoxide formation with the increase of cobalt content can be seen especially at 420 °C, where the selectivity to carbon monoxide dropped to 3% for catalysts containing 24 and above wt.% of cobalt (Fig. 4).

The only disadvantageous properties of cobalt-rich catalysts used in the steam reforming of ethanol carried out at 420 °C is the highest selectivity of methane formation in comparison with both lower and higher temperatures of the SRE (Fig. 4). It probably results from the most intense methanation reaction at that temperature. However, when the SRE is considered as a source of hydrogen-rich gas for fuel cells application, the presence of methane in the reformate gas is not very inconvenient as methane does not bring about disruption in electricity production.

The yield of hydrogen formed from one molecule of ethanol supplied to the SRE process, which reflects both catalyst activity and selectivity of ethanol conversion, reached the high level (5 and more moles of hydrogen formed from one mole of ethanol) above 420 °C over catalysts containing 17 and more wt.% of cobalt (Fig. 4). Taking into account the high selectivity and high hydrogen yield at temperatures equal to and above 420 °C, the Co/ZnO catalyst with approximately 24 wt.% of cobalt content is the most promising for generation of hydrogen-rich gas from bioethanol.

That results of the steam reforming of ethanol carried out over cobalt-rich catalysts with alumina-stabilized zinc oxide support show that the optimum content of cobalt active phase is higher than those used and reported so far in the literature. The important issues will be also stability of good effects of the SRE. The above results were maintained during 2 h of the SRE performed at each temperature from the range of 420–600 °C. Only the lowest temperature, 350 °C, did not guarantee stable catalysts performance in the steam reforming of ethanol.

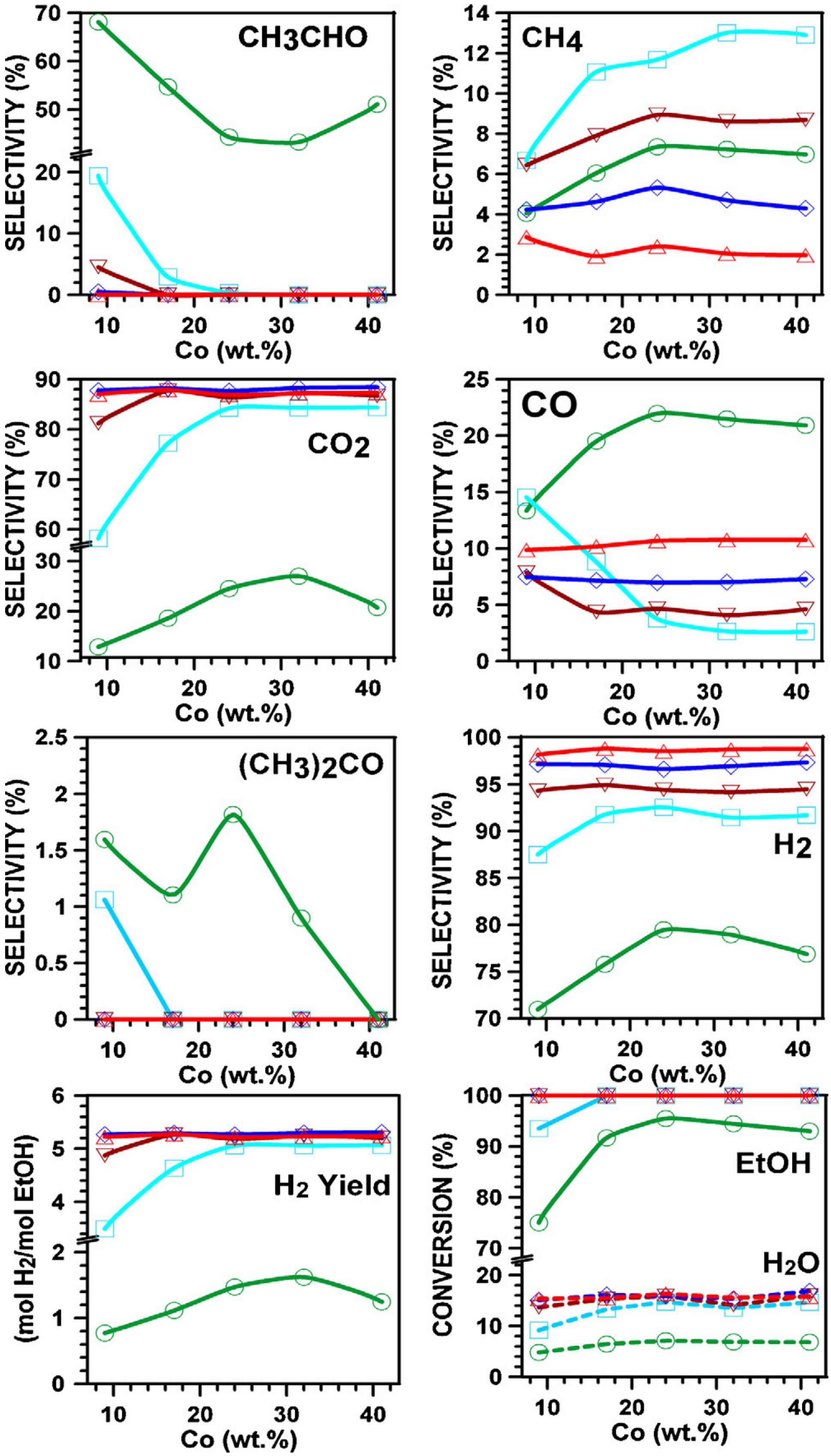

Fig. 4. Effect of cobalt content on activity, selectivity and hydrogen yield of *x*Co/ZnO catalysts in the steam reforming of ethanol (EtOH/H_2O = 1/21 mol/mol): (○) 350 °C, (□) 420 °C, (▽) 480 °C, (◊) 540 °C, (△) 600 °C.

Table 2
Coke formation on cobalt catalysts in the steam reforming of ethanol ($EtOH/H_2O = 1/4$ mol/mol) in temperature-programmed experiments.

	9Co/ZnO	17Co/ZnO	24Co/ZnO	32Co/ZnO	41Co/ZnO
The temperature of beginning of coke formation (°C)	455	405	390	365	350
Coke formation up to 420 °C (mg C/1 g_{cat})	–	13.4	76.9	281.9	334.8
Coke formation up to 560–570 °C (mg C/1 g_{cat})	182	588	877	2034	2775

3.3. Coking of the catalysts in the ethanol steam reforming

The catalysts coking measurements in the ethanol–water vapours stream (with the 1/4 molar ratio, i.e. with much lower concentration of water when compare to the reaction mixture used in the activity/selectivity tests, in order to increase a rate of that potential, disadvantageous phenomenon) were carried out to investigate influence of the cobalt content on the intensity of carbonaceous deposit formation over Co/ZnO catalyst surface (Fig. 5). The coke deposition began at 350–455 °C and that phenomenon was quite intensive (Table 2), with maximum at 560–570 °C for every catalyst. Moreover, the amount of coke deposit increased with the amount of cobalt phase content. Because cobalt is the main active phase in Co/ZnO catalysts used in the SRE process, it is obvious that the total amount of carbonaceous deposit grows with the increase in the cobalt content in catalysts.

Another factor significantly increasing coking of cobalt-rich (32Co/ZnO and 41Co/ZnO) catalysts can be large (above 20 nm) crystallites of cobalt active phase, much larger than they are in catalysts with smaller cobalt loading (9Co/ZnO, 17Co/ZnO and 24Co/ZnO), where they were in the range of 7–14 nm. It is very probable and reasonable that resistant to coking catalysts for the SRE should have small crystallites of the cobalt active phase. On the surface of cobalt activation of ethanol, while on the surface of zinc oxide – activation of water may occur. The intimate contact of both catalyst components and a short-enough distance from their border to the center of the surface of cobalt crystallites may have a great influence on the effects of the SRE, including carbonaceous deposit formation. The intimate cobalt–zinc oxide contact ensures reagents and their intermediates chemisorbed on the cobalt and on the zinc oxide support to interact together to form not only desirable products of the SRE, i.e. hydrogen and carbon dioxide but also to avoid carbon deposition or to enable gasification of the surface carbonaceous deposit. When the distance from the cobalt-support border is too long (as in the case of a center of large crystallites of cobalt) the nonselective ethanol transformations take place, without possibility of by-products and carbonaceous deposit to react with activated water from the support surface.

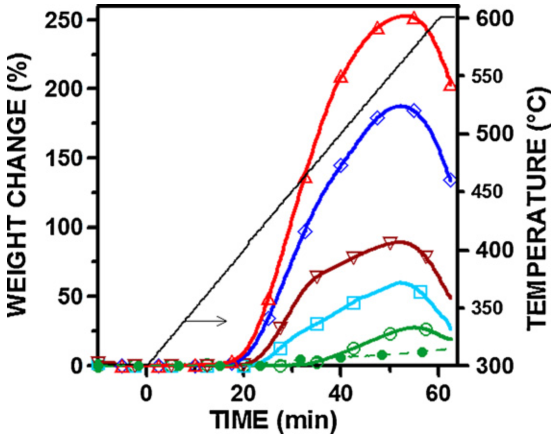

Fig. 5. Coking of supported cobalt catalysts in the steam reforming of ethanol ($EtOH/H_2O = 1/4$ mol/mol): (○) 9Co/ZnO, (□) 17Co/ZnO, (▽) 24Co/ZnO, (◊) 32Co/ZnO, (△) 41Co/ZnO. Dashed line present the result obtained for the Co/ZnO catalyst (8.9 wt.% of Co) without alumina stabilizer (symbols are used only for catalysts differentiate, they are not experimental points).

Another question is the influence of alumina stabilizer on the coking resistance of catalysts. In Fig. 5 there is included a result of coking studies for the Co/ZnO catalyst which did not contained of Al_2O_3 addition [27]. The rate of coking and amount of carbon deposit were somewhat lower than in the case of the 9Co/ZnO–Al_2O_3 catalyst with similar cobalt content. However, the influence of small amount of alumina stabilizer on the catalyst coking phenomenon requires more detailed studies, as alumina change also other structural and catalytic properties of catalyst.

In spite of the influence of reactants/products, amounts of cobalt active phase and its dispersion, the diffusion to and from catalysts' grains in the microbalance used in those experiments may also govern the observed course of catalytic reaction and amounts of coke deposit. Nevertheless, it is evident that it is necessary to employ some promoter or modifier of the catalyst to depress coke formation. The coking of Co/ZnO–Al_2O_3 catalysts may be a serious problem if lower concentration of water in the ethanol–water feed will be used instead of a fermentation broth.

Taking possibility of coking of catalyst into account, together with the activity and selectivity in the steam reforming of ethanol, the Co/ZnO–Al_2O_3 catalyst with moderate cobalt loading, i.e. 24 wt.%, and containing some promoter which will increase resistance of catalyst to coking, seems to be the more advantageous for hydrogen production from ethanol.

4. Conclusions

The presented results show that the optimum content of the cobalt active phase is approximately equal to 24 wt.%, and that the temperature of 420 °C for the steam reforming of ethanol performed over such cobalt catalyst with alumina-stabilized zinc oxide support is the most advantageous for hydrogen-rich gas production. At that temperature the conversion of ethanol reached 100%, simultaneously the hydrogen yield achieved the level higher than 5 mol of hydrogen formed from 1 mol of EtOH introduced to the reaction, while selectivities towards hydrogen and carbon dioxide were very high, the selectivity of carbon monoxide formation was depressed to 2–3% and organic by-products were eliminated from the reaction products. Allowing of the potential possibility of catalyst coking in the steam reforming of ethanol conditions, it is advisable to employ some promoter or modifier of the catalyst, which will increase resistance of catalyst to that undesirable phenomenon, particularly if lower concentration of water in the ethanol–water feed will be used instead of a fermentation broth. The use of the reformate gas obtained over the most efficient 24Co/ZnO–Al_2O_3 catalyst (after additional preferential oxidation of small amounts of carbon monoxide) to feeding low-temperature fuel cells in order to generate electricity and energy in scattered applications is possible.

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