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The influence of water vapour on the redox properties of $Co–CeO_2–ZrO_2$ catalysts

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ABSTRACT

Cobalt supported on ceria and zirconia catalysts were prepared by the impregnation method. High cobalt dispersion was achieved by the introduction of citric acid. The properties of catalysts were studied in model reaction mixtures containing water vapour. It was observed that the presence of water decreased reducibility of the samples at elevated temperatures. This effect was strongly manifested in the ceria containing catalysts. Surface and bulk oxidation was observed when samples were heated up in the inert gas saturated with water vapour. The strongest surface oxidation effect was observed in the composite $CeO_2–ZrO_2$ oxide supported catalysts.

1. Introduction

It is widely discussed that hydrogen can be used in the near future for power generation in the stationary and mobile fuel cell systems. Bio-ethanol is regarded as valuable, inexpensive and renewable energy carrier. Hydrogen productivity in the steam reforming of ethanol ($C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$) depends on the side and successive reactions [1–4]. This process has been studied over noble and transition metal catalysts, mainly based on nickel and cobalt. The properties of catalysts have been improved by the application of new preparation methods, introduction of promoters or different supports. The support may influence oxygen mobility, which relates the activity, selectivity, and resistance of the catalysts to coking. Our recent studies indicated that, the application of nano-powder ceria and ceria–zirconia supports may improve cobalt catalysts properties [4].

Ceria, zirconia and ceria–zirconia are oxygen storage materials. Noble and transition metal catalysts containing such supports have been widely used in the environmental clean-up processes [5]. The oxygen storage capacity and thermal stability of CeO_2 depend on its structure, crystallite size, physicochemical properties and composition. An addition of zirconium ions into the cerium framework may enhance valence change process and influence metal–support interactions in the supported catalysts. In order to increase selectivity to CO_2 and H_2, and to decrease coking rate, steam reforming of ethanol can be carried out in the large excess of water vapour. The reaction conditions, especially the presence of water vapour may induce dynamic changes in the oxidation state and dispersion of metal crystallites. Hence the detailed studies of the surface, redox and catalytic properties of the catalysts in model reaction conditions are still indispensable for further development.

The aim of the work was determination of the influence of water vapour on the reduction and oxidation of cobalt in the $CeO_2–ZrO_2$ supported catalysts.

2. Experimental

The Co/support and Co–Ce/support catalysts were obtained by the impregnation of the commercial (Aldrich) nano-dispersed CeO_2, ZrO_2 and mixed oxide supports of different composition with the solution of citric acid (CA) and cobalt (II) (Aldrich) and/or cerium (III) (Fluka) nitrate aqueous solutions. The relative molar ratio of Co/CA was equal 1/1. The samples after impregnation were dried at 110 °C, and calcined at 400 °C for 1 h. Nitrogen adsorption/desorption isotherms at −196 °C were determined volumetrically using ASAP 2405N analyzer (Micromeritics Corp., Norcross, GA). The BET specific surface area, S_{BET}, and the total pore volumes, V_t, were determined by applying the standard methods [6]. The calculation of pore size distributions followed the Barrett, Joyner and Halenda (BJH) procedure. X-ray powder diffraction (XRD) measurements were conducted with an upgraded Zeiss HZG-4 diffractometer using CuK_α radiation. The bulk contents of cobalt and cerium in the calcined catalysts were determined by the X-ray fluorescence spectroscopy technique, by means of an energy-dispersive XRF spectrometer (Canberra 1510) equipped with a liquid nitrogen-cooled Si(Li) detector. The surface area of

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Table 1
Catalysts characterisation results.

Catalyst	Composition (wt.%)		Total surface area (m^2/g)	Cobalt surface area (m^2/g)
	Co	Ce		
Co/CeO_2	7.9 ± 0.3	–	66.9	3.82
$Co/Ce_{0.75}Zr_{0.25}O_2$	9.6 ± 0.3	52.8 ± 0.1	118.2	2.55
$Co/Ce_{0.6}Zr_{0.4}O_2$	8.6 ± 0.3	41.4 ± 0.1	56.0	0.29
Co/ZrO_2	8.2 ± 0.3	–	40.5	0.20
$Co–Ce/ZrO_2$	9.1 ± 0.3	22.3 ± 0.1	63.5	1.79

cobalt active phase and mean size of the crystallites were calculated on the basis of the hydrogen chemisorption measurements (see Ref. [4]). The properties of the catalysts in the model reaction conditions were performed by the application of the temperature programmed reduction and oxidation methods using AMI-1 apparatus (Altamira Instruments Inc.). The samples in the TPR studies were heated up in the dry and saturated with water vapour hydrogen/argon mixtures (total flow rate $Q = 30$ ml/min). The temperature increase was 10 °C/min. Partial water vapour pressure ranged from 1.23 to 2.35 kPa. Water was removed from the stream (prior the TCD) in a cold trap with LN_2–methanol mixture. The oxidation of cobalt species in the catalysts was followed in the H_2O/Ar mixture ($xH_2O + M \rightarrow MO_x + H_2$). The pretreatment procedure was similar to that in the catalytic tests of the steam reforming of ethanol [4]. The samples were initially reduced in the flow of hydrogen (flow rate $Q = 30$ ml/min) with the rate of temperature increase 20 °C/min, next they were heated at 500 °C for 1 h, and then cooled down. Next, the samples were heated up with the ramp 10 °C/min in argon saturated with water vapour (2.35 kPa). Water was removed from the stream in a cold trap. Hydrogen production was analyzed by the thermal conductivity detector (TCD).

3. Results and discussion

An average size of nanodispersed ceria, zirconia and ceria–zirconia particles is relatively small, in the range of 20–25 nm [4]. The $Co/Ce_{0.75}Zr_{0.25}O_2$ catalyst shows the largest total surface area (118 m^2/g), while the Co/ZrO_2 displays the lowest one (40.5 m^2/g) (Table 1). The increase was observed when simultaneous deposition of cobalt with Ce over ZrO_2 support was carried out. The catalyst based on the $Ce_{0.6}Zr_{0.4}O_2$ support shows rather low surface area, even lower that the Co/CeO_2 system.

The catalysts contain similar amounts of cobalt (~8–9 wt.%). The crystallites are strongly dispersed over the support. Their size was not able to determine with the help of the XRD method. The deposition of cobalt on the ceria support leads to the formation of high active surface area (3.82 m^2/g). Large number of the sites accessible to hydrogen is also observed for the $Co/Ce_{0.75}Zr_{0.25}O_2$ (2.55 m^2/g) and $Co–Ce/ZrO_2$ (1.79 m^2/g) catalysts. The samples containing pure zirconia or zirconia-reach support $Co/Ce_{0.6}Zr_{0.4}O_2$ show smaller values of hydrogen chemisorption.

The temperature programmed reduction curves of Co/CeO_2 catalyst in different reduction mixtures are presented in the Fig. 1. Reduction of cobalt oxide can be divided into two stages. The first one, which covers the region of 100 – 350 °C (in the case of measurements performed in the dry carrier gas) can be ascribed to the reduction of Co_3O_4 to CoO. The peaks above 350 °C are interpreted as consumption of hydrogen in the reduction of CoO to Co. The increase of hydrogen consumption above 700 °C is connected with partial reduction of the support. The irregular shape of the first reduction peak indicates the presence of cobalt oxide species, which demonstrate different interactions with the support.

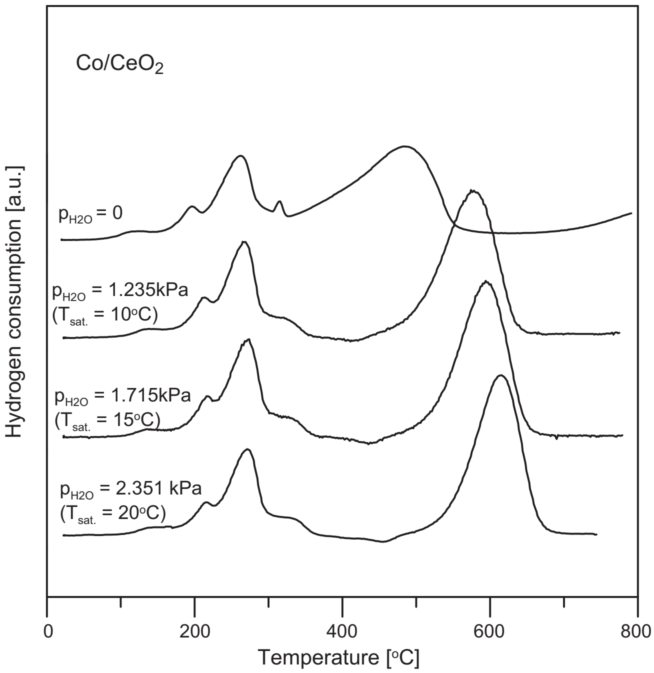

Fig. 1. TPR curves of the Co/CeO_2 catalysts in the dry and saturated with water vapour reduction mixture.

An introduction of water vapour to the reduction mixture does not strongly influence the reduction processes at the temperatures below 350 °C. However, it can be observed that very small amounts of water vapour in the carrier gas may shift the second reduction region (350–600 °C) to high temperatures (450–650 °C). An increase of water partial pressure leads to the gradual increase of temperature of the second peak maximum. The reduction of the support is not observed in such conditions. Similar phenomena are visible for the remaining catalysts (Fig. 2). The retardation of the reduction is related to the support composition. The weak-

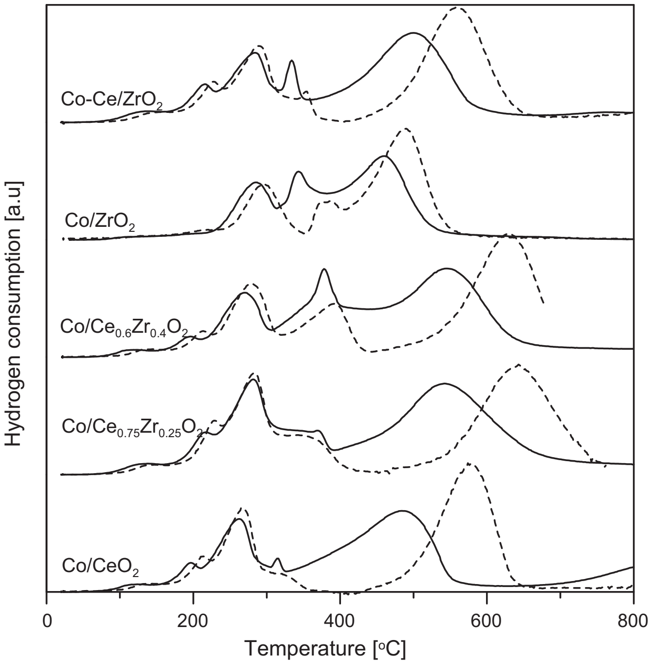

Fig. 2. TPR curves of the catalysts in the dry (solid lines) and saturated with water vapour reduction mixture (dashed lines).

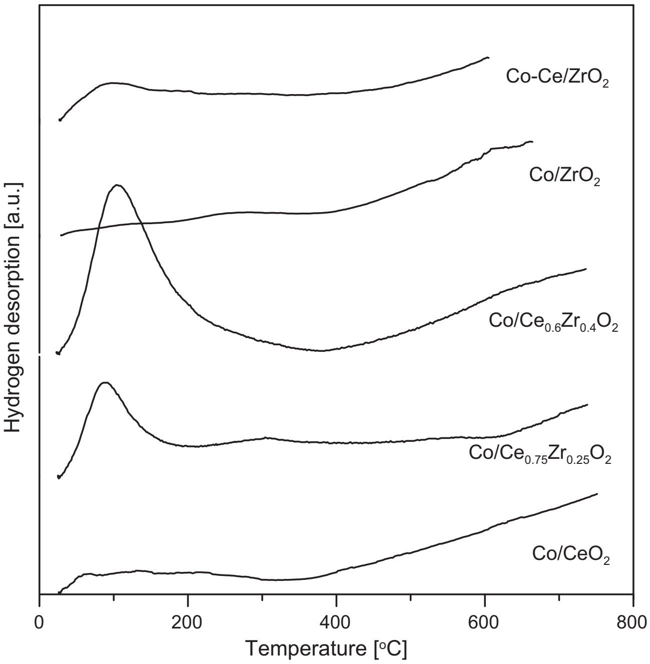

Fig. 3. TPO curves of the catalysts heated up in the flow of H_2O/Ar mixture.

est changes are observed for the Co/ZrO_2 catalyst. The obtained results indicate that cobalt oxide species in the reaction of the steam reforming of ethanol may be not completely reduced or easily reoxidised at elevated temperatures.

Cobalt crystallites can be oxidised by water vapour in the absence of hydrogen or in hydrogen lean mixtures. The TPO curves presented in the Fig. 3 reveal two main regions of the oxidation. The formation and then desorption of hydrogen at low temperature can be connected with the oxidation of the surface atoms of cobalt species (according to the equation: $xH_2O + M \rightarrow xH_2 + MO_x$). Low temperature oxidation is observed for the Co/$Ce_xZr_{1-x}O_2$ supported catalysts. Such effect is very weak for pure CeO_2 and ZrO_2 supported catalysts. The extent of oxidation at higher temperatures is not directly related to the low temperature process. However, the pronounced oxidation in most catalysts starts above 400 °C. TPO studies underline the advantage of the use of mixed ceria–zirconia supports, which facilitate dissociative adsorption of water and/or surface oxidation of cobalt crystallites. Such properties can be correlated with the number of defect in the materials. It is well known that an introduction of cations into the CeO_2 lattice can lead to the formation of defects, which are responsible for high oxygen mobility. Under reduction atmosphere ceria forms oxygen deficient, nonstoichiometric CeO_{2-x} oxides with anion vacancy and/or lattice expansion, resulted from larger radius of Ce^{3+} ions. Such phases can be reoxidised under mild oxidation conditions. The course of reduction of pure ceria depends on the size of the crystallites. The large-surface area materials may exhibits larger number of surface defects and imperfections.

The obtained results are in accordance with the studies of catalysts activity [4]. Good catalytic performance of the Co/$Ce_xZr_{1-x}O_2$ catalysts (high activity and selectivity to CO_2 and H_2) was observed in the temperatures of 450–550 °C. In such region the oxidation state of cobalt species is strongly related to the steam concentration in the feed, and it can be influenced by the local or temporal changes in the reaction composition mixture.

4. Conclusions

The oxidation state of cobalt crystallites in the Co–CeO_2–ZrO_2 catalysts may change in the ethanol steam reforming reaction conditions. The presence of water vapour and hydrogen may induce dynamic changes of the active sites. The dissociative chemisorption of water, surface or bulk oxidation of cobalt crystallites depend on the support composition, metal–support interactions, the size of the crystallites, water vapour and hydrogen concentration in the reaction mixture.

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