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Oxidation states of active catalytic centers in ethanol steam reforming reaction on ceria based Rh promoted Co catalysts: An XPS study

Erika Varga, Zsuzsa Ferencz, Albert Oszkó, András Erdőhelyi, János Kiss*

Department of Physical Chemistry and Materials Science of the University of Szeged, Aradi vértanúk tere 1, H-6720 Szeged, Hungary

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ABSTRACT

X-ray photoelectron spectroscopic (XPS) investigations were carried out to study the oxidation states of CeO_2 and CeO_2 supported Co–Rh catalysts during the temperature programmed stream reforming of ethanol reaction (SRE). Gas chromatography also was used to analyze the product composition. An initial re-oxidation of the pre-reduced catalysts was observed by water reactant and our results revealed a tendency of the oxidized monometallic catalysts to promote aldol condensation-type reactions. It was found that Rh enhances the reduction of Co during the pretreatment, and the highest H_2 selectivity was obtained with the bimetallic catalyst in SRE reaction. Moreover, acetone formation was negligible on this sample. Enhanced C—C bond scission and hydrogen production were detected from 650 K. In contrast to pure ethanol decomposition, during the EtOH + H_2O reaction minor but important changes could be detected on the Ce 3d spectra. It was concluded that the accumulation of strongly bonded carbide species in the case of Co/CeO_2 catalyst can contribute to the decreasing activity. This type of carbon was absent in the presence of a trace amounts of Rh, therefore the catalyst was more stable.

1. Introduction

Sustainable development requires new alternative cheap and renewable sources of energy. Great efforts are currently made to produce hydrogen, e.g., for fuel cell applications by heterogeneously catalyzed processes. This demand inspired studies of the dehydrogenation of oxygenated hydrocarbons [1–3]. In particular, the light alcohol ethanol is an important candidate as a chemical hydrogen carrier. Noble metals, especially Rh, are proved to be excellent catalysts for the dehydrogenation reaction [4], but their prices are prohibitively high. As an alternative, the less expensive transition metal Co is considered to be a promising catalyst for the steam reforming of ethanol (SRE) [5–10]. In addition, a mixture of carbon dioxide and methane can serve as a feed for the catalytic production of hydrogen by dry reforming of methane (DRM) [11,12] where cobalt containing catalysts may have an important role. During SRE, acidic supports like Al_2O_3 favor dehydration and thereby increase the tendency for coke formation due to the polymerization of ethylene [13–15]. However, on ceria (CeO_2), which is considered to be a basic support, dehydration is limited and its redox properties hinder coke formation [5,16]. The oxygen exchange capacity of cerium oxide is associated with its ability to reversibly change the cerium oxidation states between Ce^{4+} and Ce^{3+} [17–19]. All these observations led to the outstanding attention to the catalytic properties of Co/ceria system in SRE.

Naturally, the surface properties of the metal and of the oxide support, and also the metal/oxide interface determine the formation and stability of the intermediates present in the ethanol transformation processes. It is generally accepted that the primary step in alcohol activation is the formation of alkoxide [20]. Depending on the particular metal, dehydrogenation and C—C bond scission lead to the formation of alkoxide, oxametallacycle, aldehyde, acyl and coke on the surface and mostly H_2, CH_4, CO, CO_2 and aldehyde in the gas phase [21–30]. Recent studies suggested that Co^{2+} sites are the active centers in SRE, and Co^0 sites are responsible for coke formation [29,30], while other authors considered metallic cobalt to play the key role in SRE [32]. High pressure X-ray photoelectron spectroscopic studies (HPXPS) demonstrated that at a constant ethanol (without water) pressure of 0.1 mbar the reduction of Ce^{4+} to Ce^{3+} increased significantly between 320 and 600 K due to a higher mobility of oxygen or Ce^{3+} centers at elevated temperatures. No coke formation was observed up to 600 K on CeO_2. During the reaction of ethanol with the Co/CeO_2(1 1 1) model catalyst the amount of Co^{2+} decreased drastically with increasing temperature, and at 600 K the majority of Co was metallic; this process was accompanied by a severe reduction of the ceria [33].

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* Corresponding author. Tel.: +36 62 544803; fax: +36 62 544106.
E-mail address: jkiss@chem.u-szeged.hu (J. Kiss).

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Very recently we have found that trace amounts of rhodium promoter (0.1%) dramatically altered the reaction pathways of SRE on Co/ceria catalysts. In contrast to Co/ceria, on rhodium containing Co/ceria catalysts acetone was not observed. Addition of a small amount of Rh as promoter to the Co/CeO_2 catalyst, however, resulted in a significant increase in the hydrogen selectivity [34]. These very important findings motivated us to establish the oxidation state of the catalytically active sites before and after the catalytic reaction of ethanol + water (SRE) on pure ceria, Co/ceria and Rh + Co/ceria catalysts by X-ray photoelectron spectroscopy (XPS).

2. Experimental procedure

The catalysts preparation and characterization methods were detailed elsewhere [34]. The ceria supported Co catalysts were prepared by impregnating the support CeO_2 (Alfa Aesar, 43 m^2/g) with the aqueous solution of $Co(NO_3)_2$ to yield a nominal metal content of 2 wt% (0.056 mol%). The impregnated powders were dried at 383 K, calcined at 973 K and pressed to pellets. The Rh–Co bimetallic samples were prepared by sequential impregnation (impregnation with Co first, then the same procedure after impregnation with 0.1 wt% Rh −0.0017 mol%). After calcined at 973 K the BET surface areas of the CeO_2 support, the 2% Co/CeO_2 and of the 0.1% Rh + 2% Co/CeO_2 catalysts were 21.5 m^2/g, 7.4 m^2/g and 7.6 m^2/g, respectively, while the average pore sizes were between 14.4 and 12.3 nm, which is consistent with a mesoporous material [9,34]. Before the measurements, fragments of catalyst pellets were oxidized at 673 K in flowing O_2 for 20 min and reduced at 773 K in flowing H_2 for 60 min in the catalytic reactor.

Catalytic reactions were carried out in a fixed-bed continuous-flow reactor (200 mm long with 8 mm i.d.), which was heated externally. The dead volume of the reactor was filled with quartz beads. The operating temperature was controlled by a thermocouple placed inside the oven close to the reactor wall, to assure precise temperature measurement. For catalytic studies small fragments (about 1 mm) of slightly compressed pellets were used. Typically, the reactor filling contained 50 mg of catalyst. In the reacting gas mixture the ethanol:water molar ratio was 1:3. The ethanol–water mixture was introduced into an evaporator with the help of an HPLC pump (Younglin; flow rate: 0.007 ml liquid/min); the evaporator was flushed with Ar flow (60 ml/min). Argon was used as a carrier gas (60 ml/min). The reacting gas mixture-containing Ar flow entered the reactor through an externally heated tube in order to avoid condensation. The space velocity was 72,000 h^{-1}. The samples were heated in the gas mixture from 373 to 773 K at a rate of 3 K/min.

The analysis of the products and reactants was performed with an Agilent 6890 N gas chromatograph using HP-PLOT Q column. The gases were detected simultaneously by thermal conductivity (TC) and flame ionization (FI) detectors. To increase the sensitivity of CO and CO_2 detection a methanizer was applied before the detectors.

The amount and the reactivity of surface carbon formed in the catalytic reactions were determined by temperature-programmed hydrogenation. After performing the reactions of ethanol–water mixture at 823 K for 120 min the reactor was flushed with Ar at the reaction temperature; then the sample was cooled to 373 K, the Ar flow was changed to H_2, and the sample was heated up to 1173 K with a 10 K/min heating rate. The formed hydrocarbons were determined by gas chromatography.

For XPS studies, the powder samples were pressed into pellets with ca. 1 cm diameter and a few tenth of mm thickness. Sample treatments were carried out in a high-pressure cell (catalytic chamber) connected to the analysis chamber via a gate valve. The samples were pre-treated in the same way as described above. After the pre-treatment, they were cooled down to room temperature in flowing nitrogen. Then, the high-pressure cell was evacuated; the sample was transferred to the analysis chamber in high vacuum (i.e., without contact to air), where the XP spectra were recorded. As the next step, the sample was moved back into the catalytic chamber, where it was treated with the reacting gas mixture at the reaction temperature under the same experimental conditions as used for the catalytic reaction. XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer, using Al K_α radiation ($h\nu = 1486.6$ eV). The X-ray gun was operated at 210 W (14 kV, 15 mA). The analyzer was operated in the FAT mode, with the pass energy set to 20 eV. The takeoff angle of electrons was 20° with respect to surface normal. Typically five scans were summed to get a single spectrum. For data acquisition and evaluation both manufacturer's (SpecsLab2) and commercial (CasaXPS, Origin) software were used. The binding energy scale was corrected by fixing the Ce 3d u‴ peak (see below) to 916.6 eV.

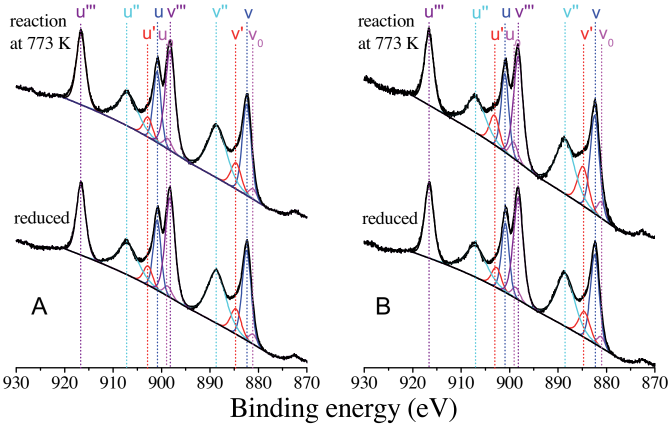

Fig. 1. Ce 3d spectra before and after SRE reaction on reduced ceria (A) and on 0.1% Rh + 2% Co/ceria catalysts.

3. Results and discussion

Based on former studies [34,35], it can be concluded that the oxidized and reduced ceria is not fully inactive either in the decomposition of ethanol or in the SRE reaction. On the CeO_2 support (without cobalt and rhodium), initially only acetaldehyde was formed (at 3–5% ethanol conversion), but between 650 and 800 K (where the ethanol conversion was ∼25–30%) the main product was ethylene besides the less amount of acetone and CO_2.

The Ce 3d spectra of reduced ceria before and after SRE reaction at 773 K are shown in Fig. 1A. Generally, the Ce 3d region of CeO_2 is rather complex, i.e., it is composed of three doublets, (u‴, v‴), (u″, v″) and (u, v) corresponding to the emissions from the spin-orbit split $3d_{3/2}$ and $3d_{5/2}$ core levels of Ce^{4+}. The three doublets are assigned to different final states: u‴ (916.6 eV) and v‴ (898.4 eV) are due to a $Ce^0 3d^9 4f^0$ O $2p^6$ final state, u″ (907.7 eV) and v″ (889.0 eV) to a Ce $3d^9 4f^1$ O $2p^5$ final state, and u (900.9 eV) and v (882.5 eV) to a Ce $3d^9 4f^2$ O $2p^4$ final state [36,37]. A minor reduction of Ce^{4+} to Ce^{3+} is best detectable as the small intensity increase of the u′ (903.9 eV) and v′ (885.3 eV) peaks and also the weaker u_0 (899.3 eV) and v_0 (880.2 eV) components, which are characteristic of Ce^{3+}. Interestingly, this spectral feature of ceria did not change after the reaction with ethanol–water mixture at 773 K (Fig. 1A). To quantify the amount of Ce^{3+}, the ratio of the integrated peak areas of Ce^{3+} spectral contributions to the total Ce 3d spectrum, i.e., $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ was used. The Ce^{3+} content was 11%