Adsorption and transformations of ethanol over ceria based model catalysts

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ABSTRACT

In this contribution a model system consisting of Ni particles grown onto epitaxial CeO$_2$ films deposited on CaF$_2$-buffered Si(111) is presented for molecular level study of the transformations of ethanol under steam reforming conditions. The adsorption behaviour of ethanol and other stable compounds thought to be important in ethanol reforming is explored by means of photoelectron spectroscopy. Acetic acid adsorbs dissociatively and relatively strongly on both fully oxidized and slightly reduced ceria surfaces. Acetaldehyde, a key intermediate of ethanol reforming, interacts weakly with CeO$_2$(111) while on the reduced surface stronger adsorption and a transformation towards acetate were observed. In case of ethanol, low temperature molecular adsorbates transform into ethoxy moieties around 200–250 K along with considerable surface reduction. A competitive behaviour between O$_2$ and ethanol emphasize the role of oxygen vacancies in the stabilization of the ethoxy groups. On the Ni-free ceria surface strongly bound ethoxy adsorbates show signs of oxidation at elevated temperatures. In the presence of Ni a certain part of the ethoxy adsorbates oxidizes towards acetate even at room temperature, which transform to carbonate upon annealing. At the same time, a significant amount of graphitic species appears on the surface, which are removed by either lattice oxygen during annealing in vacuum, resulting in heavy surface reduction or by hydroxyl groups upon annealing in water vapour. In the latter case the acetate-carbonate forming pathway becomes also suppressed, indicating that surface hydroxyl species from adsorbed water influence the decomposition route of ethanol, contribute to the elimination of carbonaceous deposits and maintain the oxidation state of ceria at the same time.

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1. Introduction

Although at present it is difficult to predict the role of ethanol in a future energy economy [1], the molecule itself offers many favorable features such as lack of toxicity, easy handling, high hydrogen content and availability from renewable resources. As a result, considerable industrial and legislative efforts are involved in utilization of ethanol in the energy supply chain [2]. While the chemical energy of ethanol can be exploited by combustion, a particularly powerful option is to extract its hydrogen content for use as feedstock for fuel cells. The reaction of choice for hydrogen release from ethanol is steam reforming:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$
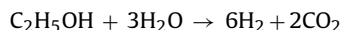
which, according to thermodynamic calculations [3], is indeed feasible at high water/ethanol ratios and temperature ranges of 700–800 K, in spite of the endothermic nature of the reaction.

A detailed analysis of the ethanol steam reforming process reveals that hydrogen generation occurs as a result of a complicated network of elementary reaction steps [1,4,5]. The numerous side processes can lead to enrichment of less favorable products such as carbon monoxide or methane; accordingly, appropriate catalysts are needed for sufficient hydrogen selectivity under practical conditions [1,6].

The practical importance of the ethanol steam reforming reaction as well as its prototype role among processes for hydrogen generation from oxygenated hydrocarbons resulted in a very substantial literature ranging from understanding fundamental steps

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of the reaction up to optimization of sophisticated catalysts; some of the more relevant aspects are summarized in several important reviews [1,7–9]. According to the available information, the most active catalysts for the ethanol steam reforming process are oxide supported near noble metals [10,11], especially rhodium, which is particularly capable for breaking the C—C bond [12–14]. The stability of these catalysts against deactivation by coke formation is also remarkable. Nevertheless, a search for cheaper and hopefully better alternatives identified Ni as a very promising replacement for the near noble metals [15,16]. However, these Ni-based catalysts often suffer from rapid deactivation due to either deposition of carbonaceous overlayers or sintering, which can be compensated by addition of further modifying compounds like rare earth oxides [17–19].

The beneficial behaviour of rare earth oxides in the ethanol steam reforming process is indicated by the fact that CeO_2 is among the most appropriate supports for transition metal based reforming catalysts [20–23]. Therefore, it is not surprising that the Ni/CeO_2 system, as a combination of a particularly appropriate oxide support and metal, indeed exhibits good activity, hydrogen selectivity and stability [1,24].

Significant efforts has been spent on unveiling the mechanistic aspects of the ethanol steam reforming reaction, which are very well summarized in recent reviews [1,7–9]. Based on *in situ* spectroscopic observations, it is generally agreed that ethanol dissociatively adsorbs on the oxide supported catalyst surface in the form of ethoxy groups. Under favourable conditions the ethoxy moieties transform into acetaldehyde, which dehydrogenate into acetyl adsorbates; further dehydrogenation and C—C bond cleavage results in CH_x and CO adsorbates on the metallic elements. The carbon monoxide may react with hydroxyl groups arising from dissociative adsorption of water, resulting in CO_2 release, while the CH_x species can dehydrogenate into surface carbon atoms, which may either oxidize or form graphitic deposits. The unwanted side process of ethylene formation is the result of dehydration of the initial ethoxy adsorbates.

In spite of the growing understanding of the mechanistic details, there are still several controversial points. For example, acetate species are often observed during ethanol steam reforming but their role is unclear as they may represent an important channel in the ethanol reforming pathway [7], although acetate formation clearly competes with more direct ways of acetaldehyde reforming.

Due to the good performance of the Ni/CeO_2 reforming catalysts and because of the relative simplicity of the preparation of high quality $CeO_2(111)$ surfaces on single crystalline metal supports [25,26], the $Ni/CeO_2(111)$ system has recently attracted attention in connection with studies in fundamental aspects of hydrogen generating reactions such as ethanol reforming or water-gas shift. The growth mode of Ni on fully oxidized ceria as well as on CeO_{2-x} has been clarified and the occurrence of charge transfer from Ni towards ceria was established [27], which is regarded as the sign of electronic strong metal-support interaction, influencing heavily the chemical properties of the supported metals [28]. Very similar behaviour was observed for the closely related $Co/CeO_2(111)$ system [29]. Studies dealing with the interaction between ethanol and these $Ni/CeO_x(111)$ model surfaces are still infrequent; the conclusions of a very recent work pointed to the possible role of Ni_3C in the formation of carbon deposits leading to deactivation and to the importance of surface —OH species in removal of the carbonaceous material [30]. A near ambient pressure XPS study of the transformation of ethanol on a $Co/CeO_2(111)$ model system reported the influence of the ethanol exposure on the chemical state of Ce and Co; at the same time, significant coke formation was observed at elevated temperatures [31].

In this contribution we present our observations on transformations of ethanol on $Ni/CeO_2(111)$ model surfaces. Possible electronic and chemical disturbance from the underlying catalytically active single crystalline metal support was avoided by depositing the epitaxial $CeO_2(111)$ overlayer on CaF_2-buffered Si(111) [32,33]. Our approach was to analyze the surface species appearing during exposure to the reactants by means of photoelectron spectroscopy. In order to be able to identify the surface adsorbates, experiments with the assumed key intermediates of the reforming process were also performed. In particular, we put emphasis on elucidating the role of acetate in the steam reforming process, as well as on the behaviour of carbonaceous species in the low temperature limit.

2. Experimental details

2.1. Materials

The $Ni/CeO_2(111)$ model catalysts investigated in this work were prepared by thin film technology tools on CaF_2-buffered Si(111). The single side polished Si wafers (p-type, 1–10 Ωcm) were obtained from Siegert Consulting e.K. (Germany). Ce (99.9%) and CaF_2 (99.99%) pieces were purchased from Sigma-Aldrich; Ni wire (1.5 mm diameter, 99.99%) was purchased from MaTeck GmbH (Germany).

Chemicals for pretreatment of the Si(111) surface (CH_2Cl_2 (99.9%), ethanol (99.0%), acetone (99.5%), NH_4OH (28–30%), H_2O_2 (30%) and HF (48%)) were obtained from Sigma-Aldrich.

Ethanol (96%) was purchased from Reanal (Hungary). Acetaldehyde (99.5%) and acetic acid (99.7%) were obtained from Sigma-Aldrich. These chemicals were purified before introducing into the vacuum system by several freeze-pump-thaw cycles.

Double distilled water prepared in our laboratory was used as the source of water vapour as well as solvent when needed.

2.2. Preparation of the $Ni/CeO_2(111)$ model surfaces

In preparation of the $CeO_2(111)$ model surface, the method described in [32,33] was followed. Si(111) pieces cut into adequate size were first cleaned by a variant of the RCA cleaning cycle (degreasing in mixture of 4 part CH_2Cl_2 : 1 part ethanol : 2 part acetone, short dip into 1:20 HF-water mixture and treatment in hot (75 °C) mixture of 1 part H_2O_2 : 1 part NH_4OH : 5 part water [34]) then washed in double distilled water, dried and loaded into the surface analysis system on standard direct current heating Omicron sample plates. After flashing for 1–1.5 min above 1000 K and cooling down, a very sharp 7×7-reconstructed LEED pattern was obtained. A CaF_2 layer of 2–4 nm thickness was deposited on this surface at around 600 K, resulting in a very strong 1×1 LEED pattern. The CeO_2 layer was grown by slow evaporation of Ce from a Mo crucible in 5×10^{-8} mbar O_2 at a sample temperature of 400 K; the evaporation was finished when no signal from the CaF_2 layer could be detected, resulting in a nominal CeO_2 thickness of 6–8 nm. The LEED pattern, the Ce 3d XPS and the valence band spectra of the model surfaces used in this study are shortly discussed in Supporting material (Figs. S1 and S2). Ni loading of the CeO_2 surface was achieved by electron beam induced evaporation of a nickel wire. In this work the Ni deposition was carried out at room temperature with a rate around 1 monolayer (ML)/min. No further annealing of the $Ni/CeO_2(111)$ model catalysts was performed before the vapour exposure experiments.

According to the literature [33] as well as to our own findings, the CaF_2 buffered CeO_2 system is thermally stable up to 600 K; above this temperature incorporation of F into the ceria starts to become evident, especially under reductive conditions, which