

# **The catalytic conversion of ethanol on supported Rh catalysts**

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## Introduction and objective

In the last few decades increasing attention is being paid to pollution-related environmental and public health problems. Particularly, as one of the major contributors to the atmospheric pollution, the automotive sector had to work hard on its pollution control. A possible way is to use hydrogen produced as renewable energy source. The catalytic conversion of bioethanol produced by the fermentation of biomass is available for various high efficiency fuel cell uses. A fuel cell is a device that converts the chemical energy to electric energy. However, hydrogen is dangerous to store in large quantities, it is safer when produced directly onboard in high purity. Hydrogen can be produced from bioethanol with high selectivity using supported noble metal catalysts.

In the present work we examine the decomposition, reforming, and partial oxidation of ethanol on supported Rh catalysts. The aim of these experiments was mainly to identify the products formed using different catalysts under various conditions. Another aim was the identification of the products that form in these reactions and the further examination of the interaction between ethanol and the catalytic surfaces that greatly influence the whole process.

## Experimental

The catalysts were prepared by impregnating the supports ( $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$  ( $5 \text{ m}^2/\text{g}$ ),  $\text{CeO}_2$  ( $75 \text{ m}^2/\text{g}$ ),  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ) with the aqueous solutions of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ . The metal content of the catalysts was 1 m/m% in most cases. The same method was used to impregnate the titanate nanowire (TiONW) and nanotube (TiONT) with the mixtures of calculated volumes of  $\text{HAuCl}_4$  and  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  solutions to yield 1 m/m% metal content (ratio of the two metals of 1:1 molar ratio). Before each experiment the catalysts were pre-treated by oxidation and reduction.

The catalytic tests were carried out in a fixed bed continuous flow reactor. 50 mg catalyst was used in each experiment. The pure ethanol or the mixtures of ethanol and water of 1/3 and 1/9 molar ratios were fed with the aid of an infusion pump by 0.3 ml/h into 80 ml/min of argon stream. The products were analysed by gas chromatography. For the partial oxidation of ethanol an ethanol/oxygen molar ratio of 2/1 was used. We used 10 mg catalyst in the reaction of  $\text{CO}_2$  and  $\text{H}_2$ . The  $\text{CO}_2$  and  $\text{H}_2$  total flow rate was 50 ml/min, wherein the stoichiometric ratio of the two gases was 4/1. The products have been identified by gas chromatography.

The amount of surface carbonaceous deposit formed during the reaction was determined on the basis of temperature programmed reduction (TPR) peak area. The catalysts were heated from 373 to 1173 K with 5 K/min heating rate in 40 ml/min of H<sub>2</sub> stream. The products formed in these experiments were also analysed by gas chromatography.

IR spectroscopy was used to identify the surface species formed during the adsorption of ethanol onto the catalyst. In these experiments the samples were treated in ethanol after the pre-treatments, and then evacuated and the IR spectra of the surface were registered. By heating the samples to different temperatures the stability of these species could also be examined. The changes in the gas phase of the IR cell were monitored by a mass spectrometer. The surface species formed during the catalytic reactions were monitored by an IR spectrometer equipped with a diffuse reflectance infrared cell (DRIFTS).

The interaction of ethanol and the catalysts was studied by temperature programmed desorption (TPD) and temperature programmed oxidation (TPO). The adsorption of ethanol was performed by bubbling the carrier gas through the ethanol at 273 K for 30 minutes in the presence of the catalyst. The amount of adsorbed ethanol was followed by measuring the weight changes with a microbalance. After ethanol adsorption the sample was flushed again by He-flow at 300 K for 15 min, and then the catalyst was heated with a rate of 20 K/min up to 900 K in He (for TPD) or O<sub>2</sub> (for TPO) stream.

## **Novel results**

### **T1. The decomposition and steam reforming of ethanol on supported Rh catalysts**

#### **T1.1**

In the catalytic decomposition of ethanol at 723 K the conversion decreased over time except on the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst. Ethylene or acetaldehyde was the main product of the decomposition. The dehydration of ethanol produces ethylene and the oxidative dehydrogenation of ethanol produces acetaldehyde.

#### **T1.2**

In the catalytic steam reforming of ethanol the conversion decreased over time except on the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst. In the reaction of ethanol and water the selectivity of H<sub>2</sub> and CO decreased during the observation while the ethylene or acetaldehyde production gradually increased. Increasing the relative amount of water in the feed the ethanol conversion and the production of H<sub>2</sub> showed a slower decrease.

### T1.3

After the decomposition of ethanol and the catalytic reaction of the ethanol + water mixture at 723 K, the amount and the reactivity of surface carbonaceous deposit have been determined using Temperature Programmed Reduction (TPR) technique on the Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/CeO<sub>2</sub> catalysts. It has been found that neither the composition of the reaction mixture nor the support material influenced the reactivity and amount of the surface carbonaceous deposit. The acquired data clearly show that the amount of carbonaceous residues decreased with the increasing amount of water in the reaction mixtures. This has been interpreted by the reaction of water and the surface reactants that are responsible for the formation of carbonaceous deposit.

## **T2 The interaction of ethanol and supported Rh catalysts using IR and TPD (Temperature Programmed Desorption)**

### T2.1

After the adsorption of ethanol on several oxide supported Rh catalysts at room temperature molecularly adsorbed ethanol, mono- and bidentate- ethoxy groups has been identified by IR spectroscopy. We were able to recognize ethanol molecules bound to the catalyst's surface OH groups by hydrogen bonds. The stability of these forms is decreasing by increasing the temperature. We found that except the Rh/SiO<sub>2</sub> catalyst, even above 773 K the presence of acetate groups was detectable in the case of the other supports.

### T2.2

Room temperature ethanol adsorption followed by TPD measurements showed that above 600 K high amounts of CO<sub>2</sub> desorbed from the oxide supported Rh catalysts. The source of the desorbed CO<sub>2</sub> was neither the adsorbed CO nor the carbonates but the surface bound acetates based on our IR data. We assumed that these surface bound acetates are responsible for the decreasing selectivity of the catalysts by the obstruction of access of OH groups to the Rh active centres. The increased amount of water in the reaction mixture could maintain the activity and selectivity of the catalysts by promoting the degradation of surface bound acetates.

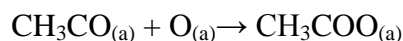
### **T3 Partial oxidation of ethanol on supported Rh catalysts**

#### **T3.1**

During the partial oxidation of ethanol at 493 K after 200 minutes the catalytic activity of the catalysts decreased in the order of Rh/CeO<sub>2</sub> (75 m<sup>2</sup>/g) > Rh/TiO<sub>2</sub> > Rh/CeO<sub>2</sub> (5 m<sup>2</sup>/g) > Rh/Al<sub>2</sub>O<sub>3</sub> > Rh/SiO<sub>2</sub>. The main products were identified as acetaldehyde and CO<sub>2</sub>.

#### **T3.2**

During the partial oxidation of ethanol on supported Rh catalysts we were able to identify the intermediate formate and acyl groups. Both of these species are unstable at low temperature. The formation of formate groups can be interpreted by the dissociation of formic acid. The formic acid is the reaction of acetaldehyde and oxygen is formed. The presence of acyl group as a product of the partial oxidation of ethanol might be the precursor of the acetate formation:



#### **T3.3**

X-ray photoelectron spectroscopic (XPS) and IR studies revealed that Rh is in a partially oxidized state except on Rh/SiO<sub>2</sub> catalyst.

### **T4 Ethanol decomposition on titanate nanowire supported Au and Rh catalysts**

The ethanol decomposition was studied at 603 K on Au, Rh and Au–Rh catalysts supported on titanate nanowire, titanate nanotube and TiO<sub>2</sub> (Degussa P25). The main products were acetaldehyde, but ethylene, diethyl ether and acetic acid were also detectable. It has been found that the catalytic activity decreased in the Rh>Au+Rh>Au order regardless of the support material. From IR and low energy ion scattering spectroscopy (LEIS) data we concluded that gold does not block entirely the adsorption and the active sites of Rh in a core–shell structure. The ethanol or the CO produced in the ethanol decomposition may also induce the segregation of Rh thus the supported Au + Rh is a more effective catalyst in the decomposition of ethanol.

## **T5 Hydrogenation of carbon dioxide on Rh, Au and Au–Rh bimetallic clusters supported on titanate nanotubes, nanowires and TiO<sub>2</sub> catalysts**

### **T5.1**

The CO<sub>2</sub> and H<sub>2</sub> formed during the complex reaction of steam reforming of ethanol likely also react with each other. It has been found that the catalytic performance decreased in the Rh>Au+Rh>Au order regardless of the supporting material. The supported Au catalysts were practically inactive in CO<sub>2</sub> hydrogenation. The main product of the CO<sub>2</sub> + H<sub>2</sub> reaction at 493 K on these catalysts was CH<sub>4</sub> in all cases but small amounts of CO has been detected, too.

### **T5.2**

The CO<sub>2</sub> + H<sub>2</sub> reaction has been studied by IR spectroscopy on different supported Rh catalysts; adsorbed CO and formate species were identified. However, we found a difference in the IR spectra of CO compared to the ones recorded after CO<sub>2</sub> adsorption. On different supported Rh and Au+Rh samples in a CO<sub>2</sub> flow at the reaction temperature linearly bonded CO band was found. During the CO<sub>2</sub> + H<sub>2</sub> reaction an intensive band was detected in all cases which could be assigned to the formation of Rh carbonyl hydride as found earlier. During the CO<sub>2</sub> + H<sub>2</sub> reaction a band was detected due to the formation of tilted CO that is bonded to Rh and interacts with a nearby oxygen vacancy of the support.

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