Multicomponent catalysts for steam reformation of ethanol

PhD Theses

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1. Introduction

Renewable energy sources have become increasingly important recently. Many efforts have been made in order to replace the fossil fuel-based energy sources to hydrogen-oriented ones. Environmental protection issues as well as the need of higher security of energy supply speeds this up. There are several advantages of using hydrogen as energy carrier: (i) it can be realized from a large variety of primary energy sources; (ii) it is completely environmental-friendly since the byproduct of energy production is only water; electrooxidation of hydrogen in fuel cells is more efficient than burning it in inner combustion engines. In addition, combustion of hydrogen in air can result in the formation of NOx\(^1\).

Nowadays hydrogen is mainly produced from natural gas (48%), oil (30%), coal (18%) and by electrolysis (4%)\(^2\). The dominance of fossil sources evidently indicates that the present H\(_2\) production methods are not sustainable yet. As a remedy for the problem, renewable electric energy based on solar, water or wind energy and/or biomass derived raw materials are proposed to use for hydrogen production. Bioethanol reforming can be a possible way for sustainable hydrogen production.

Steam reformation of ethanol is a complex catalytic process, leading to carbon-dioxide and hydrogen according to (R1) reaction.

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \quad \Delta H^{\circ}_{298} = +347.4 \text{ kJ/mol} \quad (R1)
\]

Noble metals have been proved to be suitable catalysts for this reaction, however, there are several problems with respect to their application. For example, they are expensive and their availability is limited. Nowadays, interest towards noble metal free catalyst compositions for steam reformation of ethanol has been increased\(^3\). Multicomponent, noble metal free catalysts, supported over MgAl\(_2\)O\(_4\) have been designed in our work. As emerges from reaction (R1), the formation of carbon-dioxide is unavoidable. However, if ethanol is derived from biomass, the reforming process would not increase the CO\(_2\) emission to air, because CO\(_2\) would have been consumed for the biomass source growth, resulting a nearly closed carbon loop.

Catalytic investigations were carried out in a 16-channel flow-through reactor. Our method uses the advantages of high-throughput approach: In laboratory scale, several catalysts can be investigated at the same time, under the same conditions in a single test.

2. Objectives

Most important goal of my work was to develop a noble metal free catalyst for steam reformation of ethanol, which has high performance on lower temperature. Fine tuning of the composition of catalysts and investigation of new modifiers were necessary for this. An other goal was the study of the effect of temperature on ethanol reforming reaction. Carbon deposition was investigated, because its formation is a harmful process under reforming of ethanol; analysis of lifetime and stability was carried out. Discovery of the mechanism of catalytic processes is crucial, because it is able to give important informations for optimization of reaction conditions and the composition of catalysts.

\(^1\) MacLean, H. L.; Lave, L. B. Prog. En. & Combust. Sci. 2003, 29, 1-69
\(^3\) Haryanto, A.; Fernando, S.; Murali, N.; Adhikari, S. Energy & Fuels 2005, 19, 2098-2106
3. State of the reformation of ethanol

3.1. Main reaction routes

Reforming of ethanol is a complex process, with several reaction steps. The overall reaction results in 2 mols of CO₂ and 6 mols of H₂, as described in the Introduction (R1).

Depending on the used catalysts and working at very low contact times, two reactions take place yielding acetaldehyde or ethylene, according to the following reactions⁴,⁵:

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4\text{CHO} + \text{H}_2 \quad \Delta H^\circ_{298} = +67.8 \text{ kJ/mol} \quad (R2)
\]

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O} \quad \Delta H^\circ_{298} = +44.7 \text{ kJ/mol} \quad (R3)
\]

Dehydrogenation of ethanol via reaction (R2) can take place on Cu and Ni catalysts⁴,⁵. On the other hand, acidic sites, existing for example on alumina, are responsible for the dehydration of ethanol via reaction (R3). At higher contact times, both, the initial and intermediate products can react further easily. Nevertheless, depending on the steam/ethanol ratio, the total conversion of ethanol at T>500 K can be predicted by thermodynamics⁶. The following additional reactions must also be considered:

\[
\begin{align*}
\text{CH}_3\text{CHO} & \leftrightarrow \text{CH}_4 + \text{CO} \quad \Delta H^\circ_{298} = -18.90 \text{ kJ/mol} \quad (R4) \\
\text{CH}_3\text{CHO CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ_{298} = -41.20 \text{ kJ/mol} \quad (R5) \\
\text{CH}_3\text{CHO} + \text{H}_2\text{O} & \leftrightarrow 2 \text{ CO} + 3 \text{ H}_2 \quad \Delta H^\circ_{298} = -186.96 \text{ kJ/mol} \quad (R6) \\
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^\circ_{298} = -206.11 \text{ kJ/mol} \quad (R7) \\
\text{CO} + \text{H}_2 & \leftrightarrow \text{H}_2\text{O} + \text{C} \quad \Delta H^\circ_{298} = -131.26 \text{ kJ/mol} \quad (R8) \\
2 \text{ CO} & \leftrightarrow \text{CO}_2 + \text{C} \quad \Delta H^\circ_{298} = -172.43 \text{ kJ/mol} \quad (R9) \\
\text{CH}_4 & \leftrightarrow 2\text{H}_2 + \text{C} \quad \Delta H^\circ_{298} = +74.85 \text{ kJ/mol} \quad (R10)
\end{align*}
\]

Accordingly, acetaldehyde gives methane and carbon monoxide by decarboxylation (R4), while steam reformation of acetaldehyde leads to CO and hydrogen (R5). The water-gas shift reaction (WGSR) (R6) results CO₂ and hydrogen. CO methanation (R7) is thermodynamically feasible below T < 700 K, while the reverse reaction (methane steam reforming) takes place at higher temperatures⁶,⁷. It has to be mentioned that, the presence of CO in the effluent gas should be suppressed when the produced hydrogen is used in fuel cells. In order to minimize CO formation, in case of high steam/ethanol ratios, temperatures at T>700 K are suitable, which facilitate WGSR⁶. There are many processes reported leading to coke deposition and removal, such as carbon gasification (R8), Boudouard reaction (R9) and methane decomposition (R10). According to thermodynamic calculations, the removal of carbonaceous deposits is favorable at higher temperatures and higher steam/ethanol ratios. It has been observed that, at water/ethanol ratios above 3, the graphitic carbon deposition is practically zero above 600 K⁶,⁷,⁸.

Beside thermodynamic issues discussed above, kinetic promotion and hindrance of different processes helps improve selectivity towards hydrogen. For this reason, different active metals, preparation methods, supports and additives have already been tested. The appropriate catalyst should work at as low temperature as possible, it should be active in WGSR, while it should inhibit reactions, such as coke formation, CO production and CO methanation.

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3.2. Active components and modifiers in reformation of ethanol

Noble metals have been proved to be active catalyst components for reformation of ethanol. Among the Al$_2$O$_3$ supported noble metal catalysts Rh containing ones have been proven to be the most active\cite{Breen2002, Aupretec2002}. Over Al$_2$O$_3$ supported noble metal catalysts, the rate of hydrogen formation decreased and that of ethylene increased in time, due to the accumulation of the surface acetate species, while the conversion was almost constant. This phenomenon is suppressed by increasing the water concentration, the metal content of the catalyst and the reaction temperature. The activity of Al$_2$O$_3$ supported catalysts decrease as Rh $>$ Pd $>$ Ni $>$ Pt. Upon using CeO$_2$ or ZrO$_2$ as support materials, the formation of ethylene is negligible and the order of the catalyst’s activity changes as Pt $\geq$ Rh $>$ Pd\cite{Erdohelyi2008}. Dehydration of ethanol can be depressed by adding K to neutralize the acidic support as it was found in case of the Pt/Al$_2$O$_3$\cite{Cavallaro2003}, or by using basic supports, for example, La$_2$O$_3$ and MgO\cite{Profeti2005}. Deposition of Rh on MgAl$_2$O$_4$ provides catalysts higher basicity to the catalysts than alumina-supported Rh, resulting in improved stability\cite{Choong2011}. Addition of Ca to Al$_2$O$_3$ also decreases acidity of the support\cite{Horvath2011}. Profeti et al.\cite{Profeti2005} studied addition of small amount (0.3w/w\%) of Pt, Ir, and Ru to Co/MgAl$_2$O$_4$ catalysts, resulting total conversion at 500 °C. Hydrogen productions were 41.6 % (Co/MgAl$_2$O$_4$) and 58.3 % (CoRu/MgAl$_2$O$_4$) of the maximum theoretical hydrogen yield.

It has been observed that Ni containing catalysts can be more active than supported noble metals\cite{Fatsikostas2002}. Ni has been evidenced to have high activity for C–C bond and O–H bond breaking, and also for hydrogenation of CO. The addition of alkali species modifies the character of interaction between adsorbed species and the metallic Ni, enhancing its steam reforming activity further. However, like Rh, Ni is less active for WGSR. Since Cu favors dehydrogenation and WGSR, the combination of Ni and Cu yields high steam reforming activity and high hydrogen selectivity\cite{Fatsikostas2002}. In addition, mixing Cu with noble metal, such as Rh may also improve hydrogen production due to the enhanced WGSR by Cu. Like other catalysts, Ni-based ones also suffer from coke formation as well as metal sintering, leading to a considerable decrease of performance during long-term operation. Thus, addition of properly selected additives is needed to improve the stability of catalysts. All of these results strongly indicate that ethanol reforming requires development of multi-component catalysts.

The Co catalysts also exhibit high activity and selectivity towards hydrogen at low temperature. Excellent results were obtained over ZnO supported Co catalysts by Llorca et al.\cite{Llorca2011}. Modification of Ni with Co is generally known to have a negative effect on the performance of ethanol steam reforming\cite{Choong2011}.

The selection of Ce as catalytic component is justified by high oxygen mobility of CeO$_x$, which can facilitate the removal of deposited carbon\cite{Choong2011}. Similarly to this, the effect of La on ethanol steam reforming in Ni/La$_2$O$_3$ catalyst has been explained by scavenging coke deposition due to the formation of surface lanthanum oxycarbonate species intermediate\cite{Choong2011}.

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\textsuperscript{18} Marino, F. J.; Baronetti, G.; Jobbagy, M.; Laborde, M. \textit{Appl. Catal. A: Gen.} 2003, 238, 41-54
Selection of Zr as catalyst component is explained by synergism between Ni and Zr reported by Fierro et al.\textsuperscript{23}. The improvement in intrinsic activity was ascribed to the enhancement of water adsorption/dissociation on the Ni–Zr interfaces developed on Ni/ZrO$_2$–Al$_2$O$_3$ catalysts.

### 3.3. Holographic Research Strategy

High-throughput experimental technique\textsuperscript{24,25} is a novel method for catalyst optimization. Although the weight of prepared samples is small, but the number of catalyst compositions can be very large. Key element of this method is the parallel preparation and test of a lot of samples. It works as a filter, consequently good compositions and modifiers can be identified relatively quickly in this way. Former experimental techniques do not provide this efficiency. High throughput method has other advantage too: it is usually applied with combinatorial methods. This is very important, because it allows us not only to find the best catalyst composition, but to reveal interactions between different modifiers, which is crucial to understand the working mechanism. 

HRS is an optimization algorithm, which additionally has unique visualization abilities\textsuperscript{26,27}. In HRS, variables are arranged along the perpendicular X and Y axes\textsuperscript{27}. Lines with different length represent the discrete levels of different variables. A given line represents one level of a variable and the length of that line is proportional to the number of data points displayed along the line. The visualization is based on wavelike arrangement of levels of independent variables along the X and Y axes. The level of each component increases gradually until its maximum, then decreases gradually again. Accordingly, when moving along any axis from an experimental point to the next one, only one level of a single variable is changed. This arrangement results in a 2D matrix where the adjacent points are neighbors in the original multidimensional space too.

An application of HRS is demonstrated on Figure 1. A, B, C and D, E, F are the variables along X and Y axes, which can be the applied amount of a catalyst modifier, or the reaction temperature. The main goal of this method is to optimize the reaction conditions. The matrix represents the experimental space, while the colours symbolize the level of the conversion (or other measurable catalytic outcome), where the light green fields belong to the worst and the dark blue fields belong to the best samples. In HRS optimization the initial experimental points (first catalyst generation) are fixed as small clusters (i) in the center, (ii) along the symmetry axes and (iii) in the corners of given multidimensional experimental space resulting in 48 different catalyst compositions (Figure 1a)\textsuperscript{26,27}. The next generations have been created by a rectangular-shaped 5×5 size experimental region around the best hit of the preceding generations (Figure 1c).

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\textsuperscript{23} Sanchez-Sanchez, M. C.; Navarro, R. M.; Fierro, J. L. G. \textit{Int. J. Hydr. En.} 2007, 32, 1462-1471  
\textsuperscript{24} Verdine, G.L. \textit{Nature} 1996, 384 supp., 11-13  
\textsuperscript{25} Broach, J.R.; Thorner, J. \textit{Nature} 1996, 384 supp., 14-16  
\textsuperscript{27} Vegvari, L.; Tompos, A.; Gobolos, S.; Margitfalvi, J. L. \textit{Catal. Today} 2003, 81, 517-527
The pattern of the Holographic Map can be changed (Figure 1a vs. 1b) as follows. If the position of the variables is changing, the position of the experimental points (the pattern of the map) will be changed (Figure 1a vs. 1b), but the new matrix will have the same information, because the continuity of the system is not injured. The working mechanism of the holograms is based on this property. The “variable position change” has an important practical advantage: The good experimental results are generally nearer to each other on the Holographic Map, making more exact experimental plan for the next catalyst generation (Figure 1c).

The above demonstrated experimental square on Figure 1 contains 576 experimental points. This is not large, experimental spaces with 50 000 or 100 000 experimental points frequently occur in case of a practical problem. Predicting experimental results of not measured samples is also crucial, because unnecessary preparations and measurements should be avoided. Holographic Mapping helps to find the best experimental points. The ANNs and the PLS regression are complementary methods for HRS to predict unknown results.

4. Experimental methods

A very effective method, the high-throughput experimental technique was chosen in my work. A new inert 16-channel reactor was used for it, of which development (see Figure 2) was also a part of my work. This apparatus was used for catalytic tests, Temperature Programmed Ethanol Reforming (TPER) and stability measurements on 350, 400 and 450 °C for 6 hours. Temperature Programmed Oxidation (TPO) and Reduction (TPR) was carried out on the previously tested catalysts for determining the amount of carbon deposition. Holographic Research Strategy method was chosen for the experimental optimization, as well
as Partial Least Square Regression (PLSR) and Artificial Neural Networks (ANNs) were used for expansion and completion of the experimental space.

Complex surface spectroscopic characterization was carried out on the best samples. Distribution of elements and crystalline surface species were studied by HR-TEM analysis. XPS measurements were also carried out to identify the chemical environment and concentration of elements on the surface of freshly prepared catalysts, activated catalysts (350 °C 1h H₂, 30 ml/min) and after application of the catalysts, i.e. after 20 and 60 min ethanol reforming. Reaction intermediates and surface species were identified by in situ FT-IR spectroscopy.

5. Summary of results

5.1. Holographic Research Strategy

Composition of MgAl₂O₄ supported catalysts was optimized by Holographic Research Strategy. 189 samples were examined in 5 generations, as well as 10 different modifiers were tested under preparations: Pt, Pd, Au, Ni, Co, Cu, Zn, La, Ce, Zr (Pt was used as reference only). Results are visualized by Holographic Map of hydrogen production in Figure 3. Stability measurements were executed on 350, 400 and 450°C for 6 hours. Best hits and the molar flow rates of different products and by-products are shown in Table 1.

![Figure 3](image-url) Visualization of hydrogen production in Holographic Maps obtained upon combination of HRS with ANNs. Color codes of hydrogen yield values (given in %): 5.8+, 5.8-11.6, 11.6-17.4, 17.4-23.3, 23.3-29.1, 29.1-34.9, 34.9-40.7, 40.7-46.5, 46.5-52.3, 52.3<.
Table 1. Best three hits at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Composition w/w % to MgAl₂O₄ support</th>
<th>Conv. %</th>
<th>Molar flow rate μmol/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt  Ni  Co  La  Ce</td>
<td></td>
<td>CH₄  CO  CH₃CHO  CO₂  H₂</td>
</tr>
<tr>
<td>350</td>
<td>0  10  10  0  7</td>
<td>100</td>
<td>22.7  7.3  0.6  20.1  52.9</td>
</tr>
<tr>
<td>400</td>
<td>3  10  10  0  7</td>
<td>100</td>
<td>16.9  3.1  0.5  30.3  80.3</td>
</tr>
<tr>
<td>450</td>
<td>3  10  10  0  0</td>
<td>100</td>
<td>13.9  2.5  0.4  33.9  94.0</td>
</tr>
</tbody>
</table>

Concentration of Pd, Au, Cu, Zn and Zr are zero. Reaction conditions: \( F^{\text{ini} \text{EtOH}} = 25.8 \mu\text{mol/min} \), \( F^{\text{ini} \text{H₂O}} = 220 \mu\text{mol/min} \), \( W_{\text{cat}} = 30 \text{ mg} \).

5.2. High-throughput temperature programmed tests

More detailed examinations were executed on five catalysts. The modifiers were Ni, NiCo, NiCoCe, NiCoCeMo, and PtNiCoCe on these samples. The sample modified only with Ni was the base catalyst. The NiCo sample was important because of the synergy effect between the modifiers as well as the analysis of carbon deposition. The NiCoCe/MgAl₂O₄ composition was found the best in relation to the properties considered and listed above. Mo has gotten attention because of hindering the formation of carbon deposition\(^{28} \). Pt containing sample was used as reference.

TPER analysis of different catalysts has shown that there is considerable methanization on Pt catalyst. Application of Ni, Co and Ce modifiers with Pt remarkably decreased methane formation and the least CH₄ formation was detected on Pt free catalysts. It is interesting, that addition of Pt to NiCoCe system did not result more intensive hydrogen production.

Modification of Ni catalyst by Co and Ce decreased the formation of CH₄ and, paralley, increased hydrogen production. Methanization of CO and Water Gas Shift Reaction (WGSR) was pushed to the background in 320-370 °C temperature interval by application of Mo as fourth component (Figure 4). There was not any remarkable difference between catalysts above 450 °C (Figure 5).

![Figure 4 Comparison of CH₄ formation by TPER](image1)

![Figure 5 Comparison of H₂ formation by TPER](image2)

Acetaldehyde and CO production were analysed on Ni, NiCo, NiCoCe and NiCoCeMo catalysts. It was found, that the activity of Mo modified samples were lower in the decomposition of acetaldehyde, and the maximum value of CO formation was shifted to higher temperatures with 50 °C. Catalysts with two and three components were more active in WGSR than samples containing Ni only. By this reason, the CO formation is supposed to be less by application of NiCo and NiCoCe.

Temperature Programmed Oxidation (TPO) measurements (Figure 6) were carried out on catalysts directly after TPER. Goal of these examinaiions were to determine the amount of carbon deposition, which can be formed on the surface of the samples decreasing considerably the lifetime of catalysts. In this measurement the carbon deposition oxidizes to CO₂, which is able to be detected by MS exactly. The amount of carbon can be calculated from the molar flow rate of CO₂. Intensive formation of carbon deposition was obtained between 320 and 370 °C on those catalysts, which were active under TPER. Carbon formation can be described by the previously introduced reverse carbon gasification (R8), Boudouard reaction (R9), and the decomposition of methane (R10).

The principle of TPR is similar to TPO, because the goal is the removal of carbon deposition also. However, heating under TPR takes place in H₂ flow instead of O₂, and the methane production is detected in the end of the process. It was found, that carbonaceous deposits can be removed above 450 °C by H₂ flow (Figure 7). By this reason, cleaning the surface of the catalysts on higher temperature is promoted by the formation of hydrogen during TPER.

![Figure 6](image6.png) Analysis of carbonaceous deposits by TPO

![Figure 7](image7.png) Analysis of carbonaceous deposits by TPR

5.3. Characterization of catalysts
5.3.1. HR-TEM analysis

NiCoCe modified catalyst was found the best noble metal free Ni/MgAl₂O₄ based catalyst. By this reason, this sample was analysed by HR-TEM. Elementary maps of different modifiers were also taken by Electron Energy Loss Spectroscopy (EELS). These images show, that modifiers appears on the whole surface of the sample, as well as their distribution is even. More intensive accumulation was detected in case of Ce, which is able to aggregate on the surface as oxide.
Presence of carbonaceous deposits was possible, because ethanol reforming was previously carried out on the sample, and indeed, small amount of carbon nanolayers was identified by HR-TEM.

The layer distances were analysed on HR-TEM images to identify differently arranged structures of the surface (Figure 8). The 4.65 Å was the most frequent layer distance, which may belong to Mg-, Ni- and CoAl₂O₄ (111) surfaces as well. By this reason, formation of layer spinel is supposed. It can be an explanation for the even distribution of Ni and Co atoms, and verifies that they are in close proximity (atomic distance). The latter is essential for synergy. Ce did not become the part of the frame, since it occurred in oxide form; the 3.12 Å belongs to CeO (111) surface. Frames of NiO and CoO (111) also occurred in the sample, their layer distance was 2.41 Å.

5.3.2. XPS measurements

XP spectras of MgAl₂O₄, Ni/MgAl₂O₄, NiCo/MgAl₂O₄ and NiCoCe/MgAl₂O₄ catalysts were taken in C 1s, Ni 2p - Ce 3d, and Co 2p range. Results have shown, that both, Mg and Al are present in highly oxidized states. Nevertheless, the slight increase of the Mg and Al concentration along with a small decrease of oxygen concentration suggest that upon reduction and catalytic reaction, the samples became slightly oxygen deficient in comparison to the freshly prepared state. Formation of oxygen vacancies in the reduced samples is very likely, which may have crucial importance in catalytic activity.

According to C 1s spectras of different catalysts after ethanol reforming, surface acetate species was not found (Figure 9). Spectras have shown that, there was remarkable carbon deposition on NiCo/MgAl₂O₄ sample, as well as considerable graphitization. This observation is in good accordance with earlier TPO results, where significant carbon content was detected on NiCo catalyst (Figure 6) also. Other result was that the carbonate content of Ce modified sample was higher than in case of Ce free catalysts shown by C 1s spectras after reactions.

Considerable difference was not detected between catalysts in Ni 2p – Ce 3d spectral range after pretreatment with hydrogen or after ethanol reforming. It indicates the stability of the surface of the catalysts. Comparison of different catalysts after ethanol reforming has shown, that certain amount of metallic Ni was grown in presence of Co and Ce. It was indicated by the decrement of the rate of formation of oxidized Ni component on spectras (Figure 10). As detected previously, the catalytic activity becomes more intensive at 350°C in reactions of CO by Co and Ce modifiers. By this reason, the increment of catalytic activity was probably due to the presence of surface metallic Ni. Co contributes to the reduction of Ni and keeps it in reduced form.
Comparison of Co 2p range in case of different catalysts after ethanol reforming has shown, that the peaks of oxidized components appeared on higher binding energy values than they were predicted. It indicates a formation of mixed oxide phase, which is in good agreement with HR-TEM results. Co oxidized back in case of Ce modified samples.

5.3.3. FT-IR measurements

Steam reforming of ethanol was analysed with using in situ FT-IR spectroscopy to identify reaction intermediates and surface species. TPER was carried out in a DRIFT cell on MgAl$_2$O$_4$ support and on Ni, NiCo and NiCoCe modified samples. Ethanol adsorbed on room temperature, C-H stretching vibrations were obtained on higher (3200-2600 cm$^{-1}$), while deformation vibration of ethoxy group on lower (1364 cm$^{-1}$) wavenumbers. The C=O stretching vibration of acetaldehyde was visible below 200 °C (1660-1630 cm$^{-1}$), however peaks, which appeared on higher temperatures, belong to surface acetates, formiates and carbonates. They are probably formed by oxidation of ethoxy group, the OCO stretching vibration was obtained at 1420 and 1575 cm$^{-1}$. If there were indeed acetates on the surface, peak of C-H stretching vibration should have been appeared at 2900 cm$^{-1}$. There was only a little peak and the simmetric CH$_3$ deformation vibration at 1320 cm$^{-1}$ was also negligible. By this reason, species, which were formed on the surface of the catalyst, are supposed to be carbonates.

Although the primary adsorbates are ethoxy and hydroxyl groups, formation of acetyl species was observed in presence of metallic Ni even at room temperature (Figure 11), i.e. at much lower temperatures than in the case of the bare support. This behavior indicates that the ethoxy species, which are probably mobile, diffuse to the metallic sites, where the $\alpha$-C-H bond breaks, and the rate determining step in the aldehyde formation route is much easier than on the bare support.

While decomposition of acetyl species was observed only around 300 °C in case of the empty support, their signals disappeared from the IR spectra of the Ni-containing sample around 200 °C. At the same time, results of high-throughput temperature programmed tests indicated considerable acetaldehyde release up to 300-350 °C, suggesting that the lifetime of adsorbed acetyl become too short for spectroscopic determination in this temperature range.
5.3.4. Surface processes

F-centers, i.e. oxygen vacancies in MgAl₂O₄ support play a crucial role in the activity of my samples. In oxygen vacancies, electrons are trapped in the vicinity of lattice cations. In case of the bare support, an F-center is represented by two species, M₁ and M₂, corresponding to a cation and a trapped electron, respectively, see Figure 12. Eventually, formation of an oxygen vacancy leads to separated charges, which are localized. Initial steps in ethanol reforming process are shown schematically in Figure 12. Oxygen vacancies mean favorable adsorption sites for protic molecules such as water and ethanol. Upon adsorption of ethanol and water, as a first step in ethanol reforming, surface ethoxy and hydroxyl species anchored to the cations are formed, while electrons, trapped in oxygen vacancies, reduces the protons to hydrogen. In the next redox reaction steps, the surface hydroxyl groups oxidize the ethoxy groups leading first to surface acetal/acetaldehyde.

In general, a separation of charges, that is presence of partially positively and negatively charged surface species in close atomic contact are required for the different steps in ethanol steam reforming and high hydrogen yield.

\[ \text{Absorbance (\%)} \]

\[ \text{Wavenumber (cm}^{-1}) \]

\[ 25 \text{ °C} \]

\[ 200 \text{ °C} \]

\[ 300 \text{ °C} \]

\[ 350 \text{ °C} \]

\[ 400 \text{ °C} \]

\[ 500 \text{ °C} \]

\[ 600 \text{ °C} \]

\[ 0,1 \]

\[ 0,2 \]

\[ 0,5 \]

\[ 0,1 \]

\[ 2356 \]

\[ 2320 \]

\[ 600 \text{ °C} \]

\[ 300 \text{ °C} \]

\[ 200 \text{ °C} \]

\[ 25 \text{ °C} \]

\[ 2982 \]

\[ 2938 \]

\[ 2887 \]

\[ 2948 \]

\[ 25 \text{ °C} \]

\[ 200 \text{ °C} \]

\[ 300 \text{ °C} \]

\[ 350 \text{ °C} \]

\[ 400 \text{ °C} \]

\[ 500 \text{ °C} \]

\[ 600 \text{ °C} \]

\[ 0,1 \]

\[ 0,2 \]

\[ 1320 \]

\[ 1423 \]

\[ 1575 \]

\[ 2356 \]

\[ 2320 \]

\[ 600 \text{ °C} \]

\[ 300 \text{ °C} \]

\[ 200 \text{ °C} \]

\[ 25 \text{ °C} \]

\[ 2982 \]

\[ 2938 \]

\[ 2887 \]

\[ 2948 \]

\[ 25 \text{ °C} \]

\[ 200 \text{ °C} \]

\[ 300 \text{ °C} \]

\[ 350 \text{ °C} \]

\[ 400 \text{ °C} \]

\[ 500 \text{ °C} \]

\[ 600 \text{ °C} \]

\[ 0,1 \]

\[ 0,2 \]

\[ 1320 \]

\[ 1423 \]

\[ 1575 \]

Figure 11 In situ DRIFT spectra of TPER on Ni/MgAl₂O₄ catalyst
Figure 12 Initial reaction steps in ethanol reforming. $M_1$ and $M_2$ represent surface species. $M_1$ – positively charged species of the support or Co$^{2+}$, $M_2$ – electron trapped in an oxygen vacancy, which is in close contact with metal/metal oxide sites in multicomponent catalysts.

6. Theses

1. Novel noble metal free MgAl$_2$O$_4$ supported catalyst has been developed for ethanol reforming by utilizing the advantages of high-throughput experimental technique. Catalysts have been found capable to work on 350 °C. Up to 65% of the maximum theoretical hydrogen yield has been reached on 450 °C. Composition of the best sample contains 10%Ni, 10%Co, 7%Ce/MgAl$_2$O$_4$. [1]

2. Combination of different chemometric tools (HRS, ANNs, PLS) were useful not only to develop the best catalyst composition, but also to determine the effect of different modifiers and their interactions. Many important relations were revealed by these methods. Synergism between Ni and Co, as well as between Ni, Co and Ce, and the hindering effect at simultaneous presence of Ni and Cu have been found. [2]

3. Intensive formation of carbonaceous deposits under catalytic tests was caused by the reactions of CO. The presence of metallic Ni is dominant in these reactions. Remarkable increase of hydrogen production and hindering of carbon deposition are caused by addition of Ce to NiCo/MgAl$_2$O$_4$ catalyst. Application of Mo and Pt as further modifiers also causes a decrease of carbon deposition. [3]

4. The complex surface spectroscopic characterization of the best NiCoCe catalyst has revealed that the Co modifier tends to keep Ni in metallic state under reaction conditions. This Co-assisted increased metallic character was identified as the key point in the synergism between Ni and Co. The ensemble of an oxygen vacancy with trapped electron and metallic site is proposed to be the active structural element of the catalyst. [4]
5. A model has been developed for the mechanism of the NiCoCe catalytic activity based on the results of complex surface spectroscopic characterization. Formation of acetaldehyde, its steam reforming and subsequent water-gas shift reaction are the main reaction steps in this mechanism. [3]

7. **Opportunities of application**

There are two very frequent problems in catalysis, which have impact on ethanol reforming. Catalysts contain noble metal, which makes them very expensive, or they are efficient only on higher temperatures, which means additional cost for application. I could contribute to the knowledge of this scientific area with a successful development of noble metal free catalyst, which is able to work on lower temperatures. Large-scale preparation of NiCoCe/MgAl$_2$O$_4$ may be promising one for the industry. Mechanism of catalytic processes investigated can be discovered by cooperative application of different analytic methods, however these are the tasks of further research.

High-throughput experimental technique, which was applied in my research, occurs in many areas of chemical industry nowadays, for example in pharmaceutical, or different refining related hydrocarbon industrial techniques. Continuous development in computer sciences helps combinatorial methods to spread, because obtaining the most information from the largest number of samples under the shortest period is essential interest for any firm.

8. **Articles and presentations**

8.1. **Publications in the subject of the dissertation**


8.2. Presentations

