

**UNIVERSITY OF PARDUBICE**  
**FACULTY OF CHEMICAL TECHNOLOGY**  
Department of Physical Chemistry

**Ing. Martin Kout**

**Analysis of the structure of active sites in the  
heterogeneous Ni based catalysts and its behaviour in  
oxidative dehydrogenation of ethane and dry reforming of  
methane**

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Author: **Ing. Martin Kout**

Supervisor: **Prof. Ing. Libor Čapek, Ph.D.**

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## **Abstract**

The main goal of the thesis is (i) to clarify of Ni-species presented in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts which are active and stable in the oxidative dehydrogenation of ethane and the dry reforming of methane and (ii) to clarify the performance of Ce as a promotor on the catalytic behaviour of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts.

The thesis describes preparation of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with different distribution of Ni-species. For the preparation of Ni based catalysts, there were used different procedures like different precursors of Ni-species, different temperature of pre-treatment or different impregnation order of Ni- and Ce-species on the alumina matrix. The effect of Ce as a promotor which affects the distribution of Ni-species, is analysed in detail. For analysis of distribution of Ni-species was used X-ray diffraction (XRD), diffuse reflectance UV-vis spectroscopy (DRS UV-vis) and temperature programmed reduction with hydrogen (H<sub>2</sub>-TPR). Prepared catalysts were tested in two different reactions, oxidative dehydrogenation of ethane and dry reforming of methane. In the thesis is discussed correlation between structural properties including distribution of Ni and Ce species, textural properties of catalysts and results of activity and selectivity.

## **Abstrakt**

Hlavním cílem disertační práce je (i) objasnění typů Ni-částic přítomných v Ni-Ce/Al<sub>2</sub>O<sub>3</sub> katalyzátorech, které jsou aktivní a stabilní v oxidativní dehydrogenaci ethanu a suchém reformování methanu a (ii) vysvětlení vlivu Ce jakožto promotoru na katalytické chování Ni-Ce/Al<sub>2</sub>O<sub>3</sub> katalyzátorů.

Disertační práce popisuje přípravu nanosených Ni-Ce/Al<sub>2</sub>O<sub>3</sub> katalyzátorů s rozdílnou distribucí Ni-částic. Pro účely přípravy Ni-katalyzátorů s rozdílnou distribucí Ni-částic byly použity různé postupy příprav, a to využití různých prekurzorů Ni-částic, odlišné teplotní předúpravy katalyzátorů či odlišný postup nanášení částic na Al<sub>2</sub>O<sub>3</sub> matici. V práci je sledován vliv Ce jako promotoru na rozdílnou distribuci Ni-částic. Pro účely analýzy rozdílné distribuce Ni-částic jsou využity charakterizační techniky: rentgenová difrakční analýza (XRD), difuzně-reflektanční UV-vis spektroskopie (DRS UV-vis), teplotně programovaná redukce (H<sub>2</sub>-TPR). Připravené katalyzátory jsou testovány ve dvou reakcích, a to v oxidativní dehydrogenaci ethanu (ODH) a suchém reformování methanu (DRM). Na základě takto získaných informací je diskutován vztah mezi strukturálními a texturními vlastnostmi Ni-Ce/Al<sub>2</sub>O<sub>3</sub> katalyzátorů a jejich aktivitou a stabilitou.

## **Keywords:**

oxidative dehydrogenation of ethane (ODH), dry reforming of methane (DRM), nickel, cerium, alumina

## **Klíčová slova:**

oxidativní dehydrogenace ethanu (ODH), suché reformování methanu (DRM), nikl, cer, alumina

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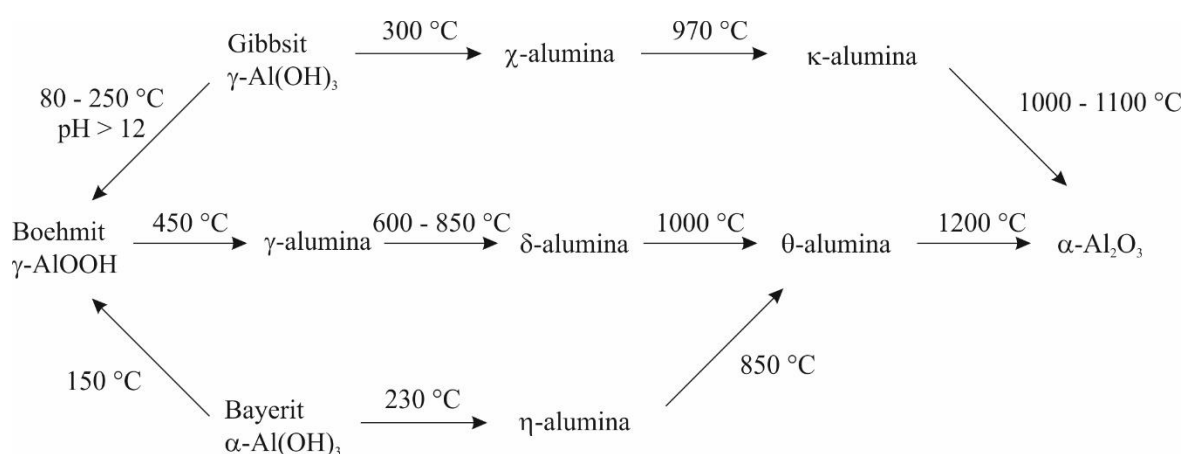
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# 1 Introduction

## 1.1 Catalytical system Ni-Ce/Al<sub>2</sub>O<sub>3</sub>

### 1.1.1 Transition alumina matrix

Crystalline aluminium oxide, commonly known as corundum or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, is prepared by thermal treatment of precursors like boehmite ( $\gamma$ -AlOOH), gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>) or bayerite ( $\alpha$ -Al(OH)<sub>3</sub>) [1–3]. As the temperature of treatment rises, there can be found several transition forms which are widely known as alumina. In Figure 1-1 is depicted which alumina is formed during thermal treatment. When the temperature of treatment is at least 1200 °C, crystalline aluminium oxide  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is formed. Although the crystalline aluminium oxide is thermally, mechanically and chemically highly resistant, it is not widely used as matrix nor as catalyst itself.



**Figure 1-1** – Evolution of transition alumina phases formation by thermal treatment of precursors

Transition forms of alumina are much attractive due to their textural properties. The most common is  $\gamma$ -alumina (or  $\delta$ - and  $\theta$ -alumina) because it has high specific surface area. It is used as catalyst in Claus process of sulphur production [4–6], dehydrogenation of ethane to ethylene or diethyl ether [7,8], as a sorbent and as a matrix for immobilization of metal particles in several processes, e.g. steam reforming of methane [9] or in petrochemistry [10]. Alumina based catalytical system are widely studied in many other chemical reactions, e.g. deoxygenation of vegetable oils [11,12], selective catalytic reduction of NO [13], transesterification of fatty acids [14], oxidative dehydrogenation of light alkanes [15] or dry reforming of methane [9,16].

Structure of  $\gamma$ -alumina and thermodynamics and kinetic of phase transformation are still not fully explained. It is expected that  $\gamma$ -alumina has similar structure like spinel MgAl<sub>2</sub>O<sub>4</sub> [5]. It has cubic structure where bivalent metal ions M<sup>2+</sup> are tetrahedrally coordinated by O<sup>2-</sup> anions whereas trivalent Al<sup>3+</sup> ions are octahedrally coordinated. In general, the basic unit of spinel should be M<sub>8</sub><sup>2+</sup>[Al<sub>16</sub><sup>3+</sup>O<sub>32</sub>] [1]. In the structure of alumina there are no bivalent metal ions and these sites are occupied by trivalent Al<sup>3+</sup> ions. This led to existence of cationic vacancies in octahedral and tetrahedral coordination [10].

Thermal treatment is sequence of several steps. In general, during thermal treatment of alumina precursors, collapse of structure, where recombination of surface –OH group occurs, can be observed. The recombination of surface –OH group is followed by H<sub>2</sub>O desorption and Al cations are connected by O-bridge [17]. Temperature of thermal treatment decreases the amount of surface –OH group. Moreover, the calcination affects textural properties like specific surface area, pore volume and pore width. With increasing temperature of calcination, the specific surface area decreases, pore volume decreases and pore width increases [18].

Transition alumina phases are prepared by thermal treatment of precursors. These precursors can be natural or prepared by several synthesis procedures. Simple method is precipitation of aluminium salts in the presence of basic agent. Textural properties can be adjusted by control of drop rate of precipitation agent, pH, temperature, pressure or aging period. Nowadays, the mostly used method is sol-gel technique. This technique is advantageous because the textural properties can be controlled much more precisely and specific surface area can reach 700 m<sup>2</sup>.g<sup>-1</sup> [19,20]. For the preparation of jelly precursor, there are used aluminium alkoxides as a source of aluminium dissolved in anhydrous solvents. Structure directing agents are used for adjustment of textural properties. Commonly, there are used polyethylene oxide based copolymers (Pluronic P123, Triton<sup>TM</sup> X-114). More information about preparation of transition alumina phases can be found in literature [19,21,22].

It is well known that temperature of calcination is crucial for structure and textural properties of alumina. It can be expected that  $\gamma$ -alumina is not thermally stable phase and it can undergo phase transformation. In literature high effort is given to enhance thermal stability of  $\gamma$ -alumina. One of the possibilities, how to enhance the thermal stability, is doping  $\gamma$ -alumina by rare-earth metal ions. Commonly, Ce and La are used. The mechanism of phase stabilization is still not well described. Ozawa et al. [23] expected that the phase stabilization could be enhance by the formation of well dispersed La<sub>2</sub>O<sub>3</sub> which strongly interact with alumina and prevent phase transformation to  $\alpha$ -alumina.

### 1.1.2 Ni- and Ce-species

Distribution of different Ni- and Ce-species is strongly affected by the procedure of preparation of Ni-Ce/alumina catalysts. In the literature, many procedures of catalysts preparation can be found. Impregnation is one the mostly used method, where the precursors of Ni- and Ce-species are deposited from the solution of salts on the surface of matrix where crystalize. Another technique is precipitation or coprecipitation, where all the substances are dissolved in appropriate solvent and precipitating agent is added dropwise. It can be controlled pH, temperature and some structure directing agent could be added. Another technique is the preparation of hydrotalcite-like precursors. The final catalysts are formed during calcination.

There can be controlled parameters which can affect the final distribution of different Ni- and Ce-species, e.g. specific surface area of matrix and amount of metal in the final catalysts (together determines the amount of metal atoms per nm<sup>2</sup>), different

metal precursors, different solvent, alumina phase, presence of other promoters and finally the temperature profile of calcination process.

In general, it can be expected the formation of following Ni-species in Ni-Ce/alumina catalysts: (i) bulk NiO without interaction with alumina matrix, (ii) NiO with weak interaction with alumina matrix, (iii) octahedrally coordinated Ni<sup>2+</sup> ions migrated into cationic vacancies in alumina structure, (iv) tetrahedrally coordinated Ni<sup>2+</sup> ions migrated into cationic vacancies in alumina structure, (v) bulk nickel aluminate NiAl<sub>2</sub>O<sub>4</sub> in stoichiometric and nonstoichiometric form.

When the cerium is presented in Ni-Ce/alumina catalysts, it can be expected presence of following Ce-species: (i) Ce<sup>4+</sup> in the form of CeO<sub>2</sub>, (ii) Ce<sup>3+</sup> in the form of Ce<sub>2</sub>O<sub>3</sub> and (iii) Ce<sup>3+</sup> in the form of CeAlO<sub>3</sub>.

When Ni and Ce precursors are impregnated together in one step on the alumina or Al-Ce-O mixed oxide matrix, Ni-species can migrate in the structure of CeO<sub>2</sub> and Ni-Ce-O mixed oxide is formed.

### **1.1.3 Effect of Ce as promotor on the structure of Ni-Ce/alumina catalysts**

In the literature there can be found many works dealing with the study how cerium affects the structure and catalytic performance of Ni-Ce/alumina catalysts.

Addition of cerium in Ni-Ce-O mixed oxides led to the enhance of specific surface area [24]. Moreover, there can be seen that the average crystallite size of NiO decreased. Ni-Ce-O mixed oxides contain new types of sites which are able to adsorb oxygen [25]. In general, CeO<sub>2</sub> is able to adsorb or desorb oxygen very quickly [26]. It is given by its redox properties where cerium can easily change state between Ce<sup>4+</sup> and Ce<sup>3+</sup>. Moreover, high mobility of O<sup>2-</sup> species was observed in bulk CeO<sub>2</sub> [27]. This phenomena is called “oxygen storage capacity” in the literature.

In Ni-Ce/Al<sub>2</sub>O<sub>3</sub>, it can be found that Ce presence is decreasing the average crystallite size of NiO and it can generate Ni-Ce-O mixed oxides with new types of sites as was mentioned above. Moreover, Ce can prevent  $\gamma$ -alumina against structure transformation to  $\alpha$ -alumina [28].

Frequently, there is published that cerium can prevent catalysts against coking. Coking is undesirable formation of carbon deposits on the surface of catalysts which could lead to block of active sites. This type of deactivation of catalysts is very common during the reaction of dry reforming of methane. Addition of cerium can prevent against or decrease the amount of carbon deposits in steam or dry reforming of methane [29].

## **1.2 Ethylene production**

Ethylene is one of the building blocks of chemical industry. In 2008, the annual production of ethylene was 120 mil. tons [30] whereas its production in 2012 was over 141 mil. tons of ethylene [31]. Cavani et al. [32] reported that the production of ethylene and propylene will be still increasing.



Ethylene is used for production of different alkanes, e.g. ethylbenzene (styrene and polystyrene), vinyl chloride (polyvinyl chloride), ethylene oxide or polyethylene.

### 1.2.1 Common processes of ethylene production

The mostly common process of ethylene production is pyrolysis of crude oil or natural gas in the presence of steam. The feed is preheated to 500 – 680 °C with steam. Then the reaction mixture is put into the reactor where the reaction temperature is 750 – 875 °C and the reaction time is 0,02 – 0,1 s. Then the reaction mixture is separated by distillation and adsorption. The efficiency is dependent on reaction time, reaction temperature and partial pressures of feed and steam. If the feed is ethane the yield of reaction is ca 50 % [30]. Pyrolysis has several disadvantages like (i) high energy inputs, (ii) generation of greenhouse gases, (iii) usage of special material for reactors and heating system and (iv) coking.

Secondly, catalytic dehydrogenation of ethane is used. It is carried out at 700 °C with conversion ca 40 % [30]. The most common catalysts are Cr based. Catalytic dehydrogenation suffers from disadvantages like (i) special catalysts geometry, (ii) high energy inputs, (iii) undesired reaction which led to coking.

In countries with high production of bioethanol, catalytic dehydration of ethanol is sometimes used. Reaction temperature is ca 300 °C and sulphuric acid or alumina are used as a catalyst. The reaction mixture is preheated, put into catalytic reactor and then separation of gaseous and liquid phase is done. Liquid phase is given back to reaction and gaseous phase is purified. Catalytic dehydration of ethanol is less energy dependent with lower production of greenhouse gases. Nevertheless, ethanol as a feed is not suitable.

## 1.3 Oxidative dehydrogenation of ethane

In previous text, existing processes of ethylene production with their disadvantages were mentioned. Oxidative dehydrogenation of ethane is alternative route for ethylene production. High effort is given to ODH due to its possibility to overcome some of these disadvantages. On the other hand, there are other limitation and ODH is still laboratory studied.

ODH is heterogeneously catalysed reaction which is carried out in the presence of oxidative agent (most common is O<sub>2</sub>). Hydrogen which is generated by the reaction reacts with oxygen and the product is water [33]. In general, ODH is exothermic reaction ( $\Delta H_r^{298K} = -105 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta H_r^{923K} = -149 \text{ kJ} \cdot \text{mol}^{-1}$  [30]). Typically, the ODH is carried out at 450 – 700 °C.

ODH is carried out at lower reaction temperatures than pyrolysis which is beneficial from economical point of view. Usually, the reaction is not limited by deactivation of catalyst by coking. On the other hand, there is still no catalysts which combines high conversion of ethane and high selectivity toward ethylene. ODH is liable to shift to subsequent reactions which produce CO and CO<sub>2</sub> which are undesirable products. Moreover, there are other typical chemical engineering aspects which have to be solved, e.g. heat transport, geometry of reactor, product separation etc.

Until today there were studied dozens of catalytic systems reported in literature. In general, the catalysts for ODH of ethane can be split into 3 groups: (i) transition metal based catalysts, (ii) alkali and rare-earth metal oxides and (iii) alkali and rare-earth chlorides. Comparison of performance was done in review written by Cavani et al. [32]. Major part of studied catalytic systems is transition metal based catalysts. Into these groups can be counted transition metal oxides, mixed oxides of transition metals and supported transition metals on matrix. There can be found articles dealing with catalysts based on vanadium [34,35], molybdenum [36,37], nickel [15,24], less frequent based on iron [38] or cobalt [38]. In the literature can be found that ODH of ethane over transition metal based catalysts goes through with Mars-van Krevelen mechanism [39,40].

### **1.3.1 Ni-based catalysts in ODH of ethane**

It is frequently reported that bulk and crystalline NiO is active in ODH of ethane. On the other hand, it is unselective toward ethylene. There are manuscripts where much effort is given to preparation of NiO with adjusted textural properties or defined crystallite size. Li et al. [41] published that mesoporous NiO is active with selectivity 53.2 % toward ethylene at reaction temperature 400 °C. Authors reported that the increased selectivity should be affected by presence of mesopores in NiO [41].

Zhang et al. [42] reported that supported Ni/alumina catalysts are less active than bulk NiO but their selectivity is much higher. In another work [43] they were focused on the effect of different alumina matrixes with different specific surface area. Authors reported that pore volume is a key factor affecting dispersion of NiO over surface of matrix, with increasing pore volume was increased dispersion of NiO over alumina surface, smaller NiO crystallites were formed and the strength of interaction between NiO and alumina was higher.

Čapek et al. [44] focused on the effect of Ni content over the same alumina matrix. They reported that strength of interaction is crucial for the productivity of ethylene over studied materials. Catalysts with higher relative population of octahedrally coordinated Ni<sup>2+</sup> species reached higher productivity than catalysts containing higher relative population of tetrahedrally coordinated Ni<sup>2+</sup> species.

Smoláková et al. [15] reported that active and selective catalysts contains NiO with average crystallite size smaller than 8 nm and/or with presence of nonstoichiometric NiO. Presence of large scale (22-32 nm) NiO crystallites led to catalysts with low activity and selectivity.

## **1.4 Production of synthesis gas**

Synthesis gas (mixture of H<sub>2</sub> and CO) is one of the major intermediates in chemical industry. It is widely used for separation of hydrogen (hydrogenation reaction, ammonia synthesis), in Fischer-Tropsch synthesis of long chain alkanes or in methanol synthesis.

### **1.4.1 Common processes of synthesis gas production**

Major part of synthesis gas is produced by steam reforming of methane (natural gas). The reaction is endothermic. Feed mixture is preheated to 450 – 650 °C and reaction is carried out at 800 – 950 °C. The reaction is catalysed by Ni-based catalyst which is beneficial for its low costs. The process is used mainly for production of synthesis gas suitable for hydrogen extraction. It is carried out in excess of steam and subsequent reaction (water gas shift reaction) which enhances the amount of hydrogen in product. Synthesis gas which is produced by steam reforming of methane is composed by H<sub>2</sub>:CO molar ratio 3-4,5:1 [9].

Minor part of synthesis gas is produced by partial oxidation of methane. The reaction is exothermic and it is carried out at 700 – 900 °C. It is catalysed by Ni-based catalysts. Synthesis gas contains H<sub>2</sub>:CO molar ratio 1,7-1,8:1 [9]. Partial oxidation of methane suffers from crucial disadvantages. Firstly, the reaction consumed oxygen and the separation from air is expensive. Secondly, the reaction can generate hot spots in catalyst, which could lead to uncontrollable reactions. Finally, partial oxidation produces coke which deactivates catalyst.

Autothermal reforming combines partial oxidation of methane and steam reforming of methane in one step. Addition of steam leads to decrease of thermal gradient in catalyst, decreases the amount of oxygen in reaction and decreases of coke generation. Moreover, it is possible to adjust composition of product. Synthesis gas produced by autothermal reforming contains H<sub>2</sub>:CO molar ratio 1,9-3,8:1 dependent on the amount of steam [9].

## **1.5 Dry reforming of methane**

Dry reforming of methane is alternative route of the synthesis gas production. It is formed by reaction between methane and carbon dioxide which is endothermic. The advantage of the reaction is that product contains H<sub>2</sub>:CO molar ratio ca 1:1. On the other hand, there are simultaneous reaction like reverse water gas shift reaction which decreases the amount of hydrogen in product, Boudouard reaction and methane decomposition which are responsible for coke deposition and deactivation of catalyst. Until today there is no industrial application of dry reforming of methane. Nowadays there is used only addition of CO<sub>2</sub> into reaction mixture for steam reforming of methane which leads to adjust the composition of product.

### **1.5.1 Catalysts for dry reforming of methane**

High effort has been given to develop the catalysts for dry reforming of methane. The requirement is to develop catalysts which combine high conversion of methane and carbon dioxide, do not suffer from simultaneous reaction leading to the deactivation and catalysts with high stability in order of thousands of hour TOS.

In general, the catalysts used for dry reforming can be split into 2 groups: (i) supported metal oxides and (ii) mixed oxides belong to pyrochlores A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> [45] or perovskites ABO<sub>3</sub> [46], where A are usually alkali or rare-earth metals and B are usually transition metals.

## 2 Experimental part

For preparation of catalysts, there was used conventional impregnation method. Impregnation was done by dissolving of nickel and cerium salts in water (nickel and cerium nitrates) or ethanol (nickel acetate and cerium nitrate) followed by addition of alumina powder and evaporation of solvent at 90 °C (water) or 65 °C (ethanol). The powder was dried overnight at 105 °C, granulated and calcined in flow of air.

It was prepared few sets of catalysts with different population of nickel species and the effect of cerium on different distribution of Ni-species was studied. It was prepared:

- Catalysts from two different precursors of Ni-species with the same content of nickel (10.5 wt. %) and the different content of cerium (0 – 4.5 wt. %) calcined at 500 °C. For detailed information of preparation see [47,48].
- Catalysts prepared from nickel nitrate and cerium nitrate with constant content of nickel (10.5 wt. %) and the different content of cerium (0 wt. % or 3.0 wt. %) calcined at different temperatures (500 – 1000 °C). For detailed information of preparation see [47,49].
- Catalysts prepared from nickel nitrate and cerium nitrate with the constant content of nickel (10.5 wt. %) and the constant content of cerium (3.0 wt. %). The catalysts were prepared by the different impregnation order (one-step or two-step impregnation) and calcined at 500 °C. For detailed information of preparation see [47].

Moreover, it was prepared reference materials: NiO, NiAl<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub>. Detailed information of preparation can be found in the thesis [47].

For the characterization of catalysts was used XRD, DRS UV-vis, H<sub>2</sub>-TPR, N<sub>2</sub>-BET, SEM and TGA-DTA. Experimental setup of all used techniques is described in thesis [47].

All prepared catalysts were tested in the reaction of oxidative dehydrogenation of ethane. ODH was carried out in quartz through-flow microreactor. The catalysts were activated in the stream of oxygen for 1 h at 450 °C before measurement. It was used several types of experimental conditions. Firstly, the reaction mixture (7.5 vol.% C<sub>2</sub>H<sub>6</sub>, 2.5 vol.% O<sub>2</sub> and 90 vol.% He) was kept at a total flow of 100 cm<sup>3</sup>.min<sup>-1</sup>. Temperature dependence was monitored in the range of 400 – 500 °C, atmospheric pressure and with 50 mg of catalyst diluted with 1 cm<sup>3</sup> of silicon carbide inert. Secondly, the activity of catalysts was compared at the constant value of conversion of ethane (X = 10 %). Constant value of conversion of ethane was achieved by changing of catalyst weight and constant total flow of reaction mixture. Thirdly, the reaction mixture (6.0 vol.% C<sub>2</sub>H<sub>6</sub>, 6 vol.% O<sub>2</sub> and 88 vol.% He) was kept at a total flow of 40 cm<sup>3</sup>.min<sup>-1</sup>. Temperature dependence was monitored in the range of 400 – 500 °C, atmospheric pressure and with 100 mg of catalyst diluted with 1 cm<sup>3</sup> of silicon carbide inert. Finally, the activity of catalysts was compared at the constant value of conversion of ethane (X = 10 %). Constant value of conversion of ethane was achieved by changing of catalyst weight and total flow of reaction mixture. Analysis of reaction mixture was carried out by online

gas chromatograph Shimadzu GC-17A with two columns (Carboxen<sup>TM</sup> 1010 PLOT and RT-S-PLOT) equipped with TCD and FID detectors.

Selected catalysts were tested in the dry reforming of methane (DRM). DRM was carried out in fixed-bed tubular reactor, using 20 mg of catalysts between two pompons of quartz wool. Reaction mixture (16 vol.% CH<sub>4</sub>, 16 vol.% CO<sub>2</sub> and 68 vol.% He) was kept at total flow 100 cm<sup>3</sup>.min<sup>-1</sup>. Two types of experimental condition were used. Firstly, the calcined catalysts were put in contact with reaction mixture without any pretreatment. Catalysts were heated from room temperature to 750 °C with heating rate 1 °C.min<sup>-1</sup> and holding the samples at 750 °C for 12 h. Secondly, all catalysts were reduced in flow of 5% H<sub>2</sub>/Ar (50 cm<sup>3</sup>.min<sup>-1</sup>) during 1 h at 750 °C. Then were the catalysts cooled down to room temperature and the catalytic reaction was accomplished under the conditions aforementioned. Analysis of reaction mixture was done by online gas chromatograph Varian CP-3800 with two in series columns (Molecular Sieve, 5A, Porapak Q) and equipped with TCD.

### 3 Results and discussion

The thesis is focused on the study of structure and catalytic performance of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts.

In the first part of the work is focused on the study of positive effect of Ce as a promotor in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts and its behaviour in ODH of ethane. Detailed discussion is given to effect of Ce on the Ni-species distribution and their effect in ODH of ethane. The results were published in Topics in Catalysis [48].

In the second part of thesis the effort was given to the preparation of catalysts with defined distribution of Ni-species which could be active in the reaction of ODH of ethane. For this goal different calcination temperature was chosen. The results were published in Industrial & Engineering Chemistry Research [49]. The defined distribution of Ni-species can be achieved with another routes. In the next part of thesis it was studied the effect of different type of preparation of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts. The results were not published in literature yet.

The preparation of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts was learnt. Therefore, the prepared catalysts were tested in the reaction of DRM. This part of research was done on the internship at Instituto de Ciencia de Materiales de Sevilla (CSIC-University of Seville) under leading of prof. Alfonso Caballero. Selected results were published in International Journal of Hydrogen Energy [50] and Reaction Kinetics, Mechanism and Catalysis [51].

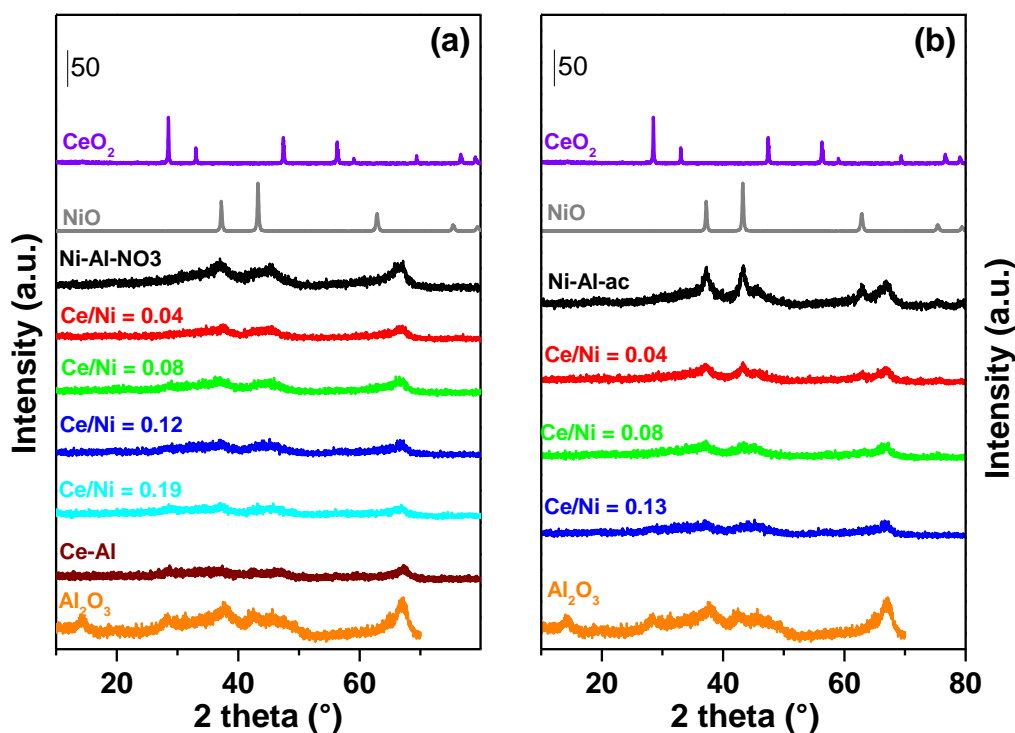
#### 3.1 Effect of Ce as a promotor and its amount on distribution of Ni-species in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts, catalytic performance in ODH of ethane

*The aim of the work: In this part of thesis the aim of the work was to observe the effect of Ce on the catalytic behaviour of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts in ODH of ethane. Question is if the Ce change catalytic behaviour itself or affecting the distribution of Ni-species in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts. There were prepared catalysts with different distribution of Ni-species and with the different content of Ce. For preparation of catalysts with the different distribution of Ni-species, there was used two precursors of Ni-species (nickel nitrate and nickel acetate).*

##### 3.1.1 Effect of Ce and its amount on the change of distribution of Ni-species

###### *XRD*

In Figure 3-1, XRD diffractograms of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> (A) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac (B) and reference materials (NiO, CeO<sub>2</sub> and commercial alumina matrix) are depicted. The diffractogram of commercial alumina contained diffraction lines at  $2\theta = 14.4^\circ, 37.6^\circ, 42.5^\circ, 45.8^\circ$  and  $67^\circ$  which should be attributed to  $\gamma$ -alumina [52]. Moreover, the intensity and width of diffraction lines showed that commercial alumina is mainly amorphous.



**Figure 3-1** – XRD diffractograms of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalysts (a) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts (b) with different Ce/Ni ratio and reference NiO, CeO<sub>2</sub> and commercial alumina matrix (a,b)

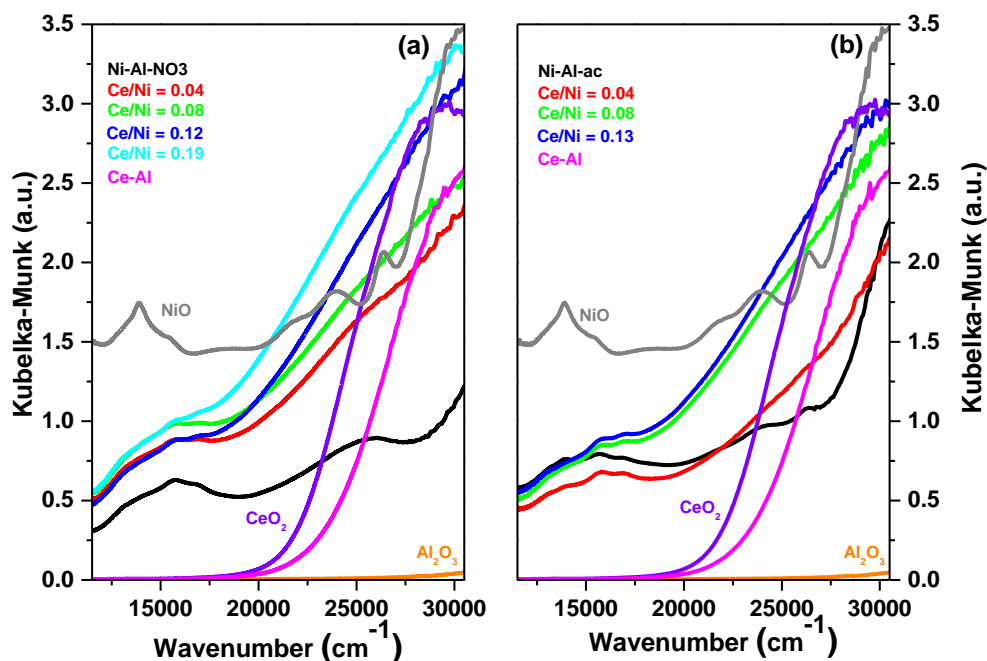
In the diffractogram of Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub>, the lines with low intensity at  $2\theta \approx 37^\circ$ ,  $43^\circ$  and  $67^\circ$  which could be attributed to small portion of crystalline  $\gamma$ -alumina were presented [52]. With addition of Ce in Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalysts, these lines disappeared.

In the diffractogram of Ni/Al<sub>2</sub>O<sub>3</sub>-ac, there were presented lines at  $2\theta = 37^\circ$ ,  $43^\circ$ ,  $63^\circ$ ,  $75^\circ$  and  $79^\circ$ . These lines correspond to the presence of crystalline NiO [25,53]. It was made calculation of average size of crystallites via Scherrer's equation and the size is  $D_{\text{NiO}} = 8$  nm. With addition of Ce in Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac the lines became more width and with low intensity which led to suggestion that average NiO crystallites size decreased.

Presence of crystalline CeO<sub>2</sub> was not confirmed. None of diffraction lines at  $2\theta = 28.6^\circ$ ,  $33.3^\circ$ ,  $47.5^\circ$  and  $56.4^\circ$  which correspond to crystalline CeO<sub>2</sub> [25] was detected.

### **DR UV-vis spectroscopy**

In Figure 3-2, there are shown DR UV-vis spectra of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> (A) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac (B) and reference materials (NiO, CeO<sub>2</sub> and commercial alumina matrix). Commercial alumina did not show any band and did not contribute to the overall background of catalysts.



**Figure 3-2** – DR UV-vis spectra of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalysts (a) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts (b) with different Ce/Ni ratio and reference NiO, CeO<sub>2</sub> and commercial alumina matrix (a,b)

In the spectra of Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub>, bands at ~ 14 080, 15 860, 16 830 cm<sup>-1</sup> and a broad band in the range of 21 500 – 27 500 cm<sup>-1</sup> can be found. The broad band could be attributed to the octahedrally coordinated Ni(Oh) species in alumina lattice [53,54]. Other bands at 14 080 cm<sup>-1</sup> and doublet at 15 860 and 16 830 cm<sup>-1</sup> could be attributed to the tetrahedrally coordinated Ni(Td) species in alumina lattice [53,54].

Spectra of Ni/Al<sub>2</sub>O<sub>3</sub>-ac was different. The bands corresponding to the presence of the tetrahedrally coordinated Ni(Td) species was presented, but the intensity was lower than in the case of Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub>. Broad band in the range of 21 500 – 27 500 cm<sup>-1</sup> was not presented. On the other hand, new bands appeared at ~ 13 900, 24 050 and 26 360 cm<sup>-1</sup>. These bands are attributed to the octahedrally coordinated Ni(Oh) species in NiO lattice [54].

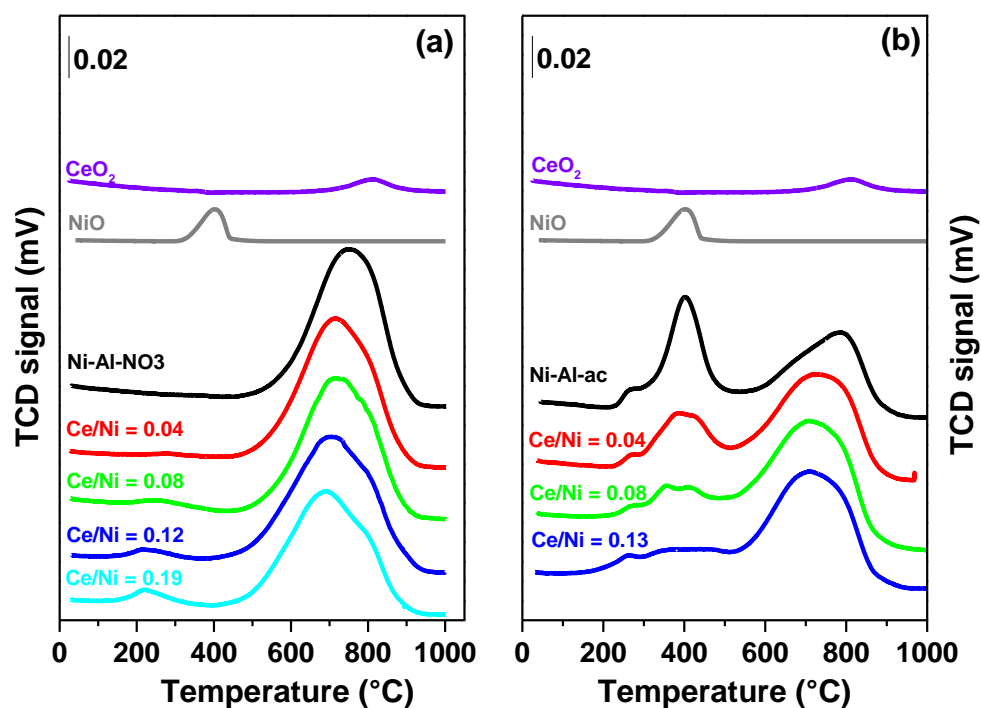
Spectra of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac is affected by the presence of Ce-species which contribute to overall background of spectra. The discussion of presence aforementioned Ni-species is not clear. Therefore, the effect of Ce on the distribution of Ni-species could be done on the basis of combination of DR UV-vis spectroscopy and H<sub>2</sub>-TPR.

### ***H<sub>2</sub>-TPR***

In Figure 3-3, there are shown H<sub>2</sub>-TPR patterns of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> (A) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac (B) and reference materials (NiO, CeO<sub>2</sub>). Reduction of Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> showed one broad reduction peak with maximum at 755 °C. This reduction peak corresponded to Ni-species which strongly interacted with alumina matrix. In the



literature, this peak is attributed to the reduction of the octahedrally coordinated Ni(Oh) and/or the tetrahedrally coordinated Ni(Td) species in the alumina lattice [55]. This is in accordance with UV-vis spectra where bands corresponding to presence of the octahedrally and the tetrahedrally coordinated Ni-species are present. Moreover, diffraction lines corresponding to the presence of the crystalline NiAl<sub>2</sub>O<sub>4</sub> was not detected, which means that the species are amorphous or under detection limit of XRD. There was not shown reduction peaks in low temperature area which is characteristic for presence of NiO. This is again in agreement with XRD where no diffraction lines of NiO was evident.



**Figure 3-3** – H<sub>2</sub>-TPR pattern of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalysts (a) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts (b) with different Ce/Ni ratio and reference NiO and CeO<sub>2</sub> (a,b)

There can be found some differences in the reduction pattern of Ni/Al<sub>2</sub>O<sub>3</sub>-ac catalyst. In the reduction pattern two major reduction peaks with maximum at 403 and 785 °C could be found. The low temperature reduction peak had shoulder peak at 265 °C. Reduction in this temperature range is attributed to the reduction of NiO with weak interaction with alumina matrix [53,56]. This is in agreement with the presence of diffraction lines of NiO in XRD and the presence of characteristic band in UV-vis spectra. Reduction in high temperature area could be attributed to the reduction of Ni<sup>2+</sup> strongly interacting with alumina matrix [55]. The high temperature reduction peak was shifted to higher temperature in contrast with Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalyst. In the literature, it is generally accepted that the reduction of octahedrally coordinated Ni(Oh) species is carried out at lower temperature than the reduction of the tetrahedrally coordinated Ni(Td) species. It could be suggested that Ni/Al<sub>2</sub>O<sub>3</sub>-ac catalyst contained higher population of the tetrahedrally coordinated Ni(Td) species. Moreover, it is in agreement with the presence of characteristic bands in UV-vis spectra where was presented bands of Ni(Td) species whereas the bands of Ni(Oh) species was not evident.

Different effect of addition of Ce into Ni-Ce/Al<sub>2</sub>O<sub>3</sub> was observed. In the reduction pattern of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> appeared new reduction peak in the range of 120 – 400 °C. Intensity of this reduction peak increased with the increasing content of Ce in catalysts. In the literature, it can be found that this peak is attributed to the reduction of adsorbed oxygen species in NiO-CeO<sub>2</sub> mixed oxide [25]. Moreover, it was observed that high temperature reduction peak was shifted to lower temperatures about 40 °C. This behaviour is in accordance with published results [57,58] and with UV-vis spectra of catalysts. Intensity of bands corresponding to the presence of Ni(Td) species decreased. It could be suggested that addition of Ce affected redistribution of octahedrally and tetrahedrally coordinated Ni-species in alumina lattice.

Different behaviour was observed in Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts. Low temperature reduction peak attributed to the reduction of NiO weakly interacting with alumina matrix broadened, the intensity decreased and the total area decreased with increasing Ce content. It could be suggested that the population of large scale NiO decreased and the dispersion increased. In XRD diffractograms, there was observed that the addition of Ce led to the decrease of average size of NiO crystallites. Nevertheless, it could be assumed that species of NiO-CeO<sub>2</sub> mixed oxide was formed and adsorbed oxygen in the low temperature area was reduced. In the case of high temperature reduction peak was observed that the total area of this peak increased. It means that the population of octahedrally and/or tetrahedrally coordinated Ni-species increased. Moreover, the maximum of this peak was shifted to lower reduction temperature from 785 °C to 708 °C. It could be suggested that Ni/Al<sub>2</sub>O<sub>3</sub>-ac catalyst contained predominantly tetrahedrally coordinated Ni(Td) species whereas in the case of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts the population of Ni(Oh) species increased with increasing content of Ce.

### **3.1.2 Activity and selectivity of catalysts in ODH of ethane**

Activity and selectivity of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from different precursor of Ni-species and with different content of Ce was done by two types of experiments. Firstly, the effect of reaction temperature on the conversion of ethane was observed with constant amount of catalysts diluted with silicon carbide inert and constant flow of reaction mixture. Secondly, the yield and selectivity of catalysts was observed at constant conversion of ethane ( $X = 10\%$ ) at 500 °C. Details of experiments are described in thesis more deeply [47].

The first type of experiment showed that Ce had positive effect on the conversion values of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts (not shown in this work). Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts achieved higher conversion of ethane than the corresponding Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The conversion of ethane increased with increasing content of Ce and the maximum was observed at catalysts contained 3.0 wt.% of Ce (atomic ratio Ce/Ni = 0.12 or 0.13 respectively). The catalytic behaviour of Ce/Al<sub>2</sub>O<sub>3</sub> (3 wt. % of Ce) was tested. Ce itself is not active or selective in the reaction of ODH of ethane. This catalyst achieved 1.3 % of conversion of ethane and 24.9 % of selectivity toward ethylene. Catalysts which was prepared from nickel acetate achieved higher conversion of ethane than corresponding catalysts prepared from nickel nitrate.

For the comparison of activity and selectivity was done experiments at constant conversion of ethane. In Table 3-1 are summarized results of conversion of O<sub>2</sub>, selectivity toward ethylene and CO<sub>2</sub>, yield of ethylene and productivity.

**Table 3-1** – conversion of O<sub>2</sub>, selectivity toward ethylene and CO<sub>2</sub>, yield of ethylene, productivity and relative productivity of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts at constant conversion of ethane (X = 10 %)

Catalyst	Ce/Ni	W (mg)	X (%)		S (%)		Y (%)		Productivity (g <sub>C2=</sub> ·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	P <sub>rel</sub> <sup>a</sup>
			O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>			
Ni-Ce/Al <sub>2</sub> O <sub>3</sub> -NO <sub>3</sub>	-	453.8	23.8	84.2	15.0	8.5	0.11	1.0		
	0.04	118.7	27.7	86.0	13.0	8.5	0.40	3.7		
	0.08	89.1	34.5	80.2	19.3	7.9	0.49	4.6		
	0.12	42.4	34.8	82.1	17.5	8.1	1.01	9.5		
	0.19	44.7	37.5	78.5	20.9	7.8	0.92	8.7		
Ni-Ce/Al <sub>2</sub> O <sub>3</sub> -ac	-	87.5	26.0	80.6	18.7	7.7	0.49	1.0		
	0.04	57.6	27.8	80.9	16.2	8.5	0.76	1.6		
	0.08	41.3	33.4	82.8	16.8	8.2	1.04	2.1		
	0.13	31.3	37.3	75.4	24.1	7.5	1.30	2.7		

<sup>a</sup> relative productivity of catalysts compared with appropriate Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (P<sub>Ni-Ce/Al<sub>2</sub>O<sub>3</sub></sub>/P<sub>Ni/Al<sub>2</sub>O<sub>3</sub></sub>)

### *Yield and productivity of ethylene*

Results in Table 3-1 show that Ni/Al<sub>2</sub>O<sub>3</sub>-ac catalyst achieved higher productivity of ethylene (P = 0.49 g<sub>C2=</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>) in comparison with Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalyst (P = 0.11 g<sub>C2=</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>). Addition of Ce increased productivity of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts and the maximum was observed at catalysts with Ce content 3 wt.% (atomic ratio Ce/Ni = 0.12 or 0.13 respectively). Higher productivity was observed at catalysts prepared from nickel acetate. Productivity of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> was 1.01 g<sub>C2=</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> and productivity of Ni-Ce(0.13)/Al<sub>2</sub>O<sub>3</sub>-ac was 1.3 g<sub>C2=</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.

### *Selectivity*

Based on the results in Table 3-1, it was found that the higher selectivity toward ethylene was achieved over Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalyst (S = 84 %) against Ni/Al<sub>2</sub>O<sub>3</sub>-ac (S = 81 %). Effect of Ce addition was not dramatic but the slight decrease of the selectivity to ethylene in comparison with appropriate Ni/Al<sub>2</sub>O<sub>3</sub> catalysts was observed. The catalysts which achieved the highest conversion of ethane showed selectivity toward ethylene 82 % (Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub>) and 75 % (Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-ac) respectively. Similar results were published by Bortolozzi et al. [59] which reported that Ce addition lead to increase of conversion of ethane but decrease of selectivity toward ethylene.

### **3.1.3 Effect of Ce on the catalytic activity and selectivity of catalysts in ODH of ethane**

One of the crucial roles for catalytic behaviour of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts played formed adsorbed oxygen species. These oxygen species were resulted from presence of Ce as a promotor in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts.

Secondly, it was proved that Ce as a promotor can affect distribution of Ni-species in Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts and subsequently the productivity of ethylene and selectivity toward ethylene.

From the results of H<sub>2</sub>-TPR it was mentioned that Ce as a promotor can increase the reducibility of Ni-species. Jalowiecki-Duhamel et al. [60] reported that Ni-species could be easily reduced and reversibly re-oxidized in the presence of Ce. On the other the shift of reduction maximum could be related to the change of Ni-species distribution. In another word the Ce can lead to higher formation of octahedrally coordinated Ni(Oh) species in alumina lattice and decrease of tetrahedrally coordinated Ni(Td) species.

Ni/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> catalyst contained higher relative population of Ni(Td) species. These Ni(Td) species are less active (lower productivity of ethylene) but more selective than octahedrally coordinated Ni(Oh) species. Ce addition led to the decrease of relative population of Ni(Td) species. It could be suggested that these Ni(Td) species were replaced by another more active species. Firstly, it could be caused by the fact that Ce could occupied the same position which could lead to formation of Ni(Td) species. In such case, these centres are blocked resulting in formation of more active Ni(Oh) species that after that interact with Ce. Secondly, the replacement of less active Ni(Td) species by more active species resulted from Ce-Ni interaction as it is evident from decrease of reduction maximum of high temperature reduction peak.

On the other hand, Ni/Al<sub>2</sub>O<sub>3</sub>-ac catalyst contained crystalline NiO with average diameter 8 nm. The average diameter decreased with Ce addition and its content. Smoláková et al. [15] reported that average diameter of crystalline NiO plays crucial role for activity and selectivity of catalysts in ODH of ethane. Decrease of average diameter of crystalline NiO and formation of Ni(Oh) species in alumina lattice is critical for enhanced productivity of Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts.

In the thesis, there was observed that the role of Ce differed at Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-NO<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub>-ac catalysts and it was dependent on the type of Ni-species presented in catalysts.

## **3.2 Effect of calcination temperature and presence of Ce as promotor on distribution of Ni-species, catalytic performance in ODH of ethane**

*The aim of the work: In the next part of thesis the aim of the work was to extend the knowledge of the effect of Ce presence on the distribution of Ni-species. For this purpose, there were prepared Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts, which were calcined at different temperatures in the range of 500 – 1000 °C. The catalysts were prepared from nickel nitrate, because in previous part of thesis there was observed more dramatic change of catalytic behaviour in comparison with catalysts prepared from nickel*

acetate. Different calcination temperature lead to catalysts with different structure but mainly affect the distribution of octahedrally and tetrahedrally coordinated Ni-species.

### 3.2.1 Effect of calcination temperature on distribution of Ni-species

#### *XRD*

In the diffractograms (not shown in this work) of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500, 600 and 750 °C were evident poorly resolved and not intensive diffraction peaks at  $2\theta = 37.3^\circ$ ,  $44.5^\circ$  and  $66.8^\circ$  which are attributed to  $\gamma$ -alumina [61]. With increasing temperature of calcination to 900 and 1000 °C there was not evident change of structure and formation of  $\alpha$ -alumina. The aforementioned diffraction lines became more evident. New diffraction peaks appeared at  $2\theta = 19.1^\circ$ ,  $31.8^\circ$ ,  $37.3^\circ$ ,  $45.4^\circ$ ,  $60.2^\circ$  and  $66.4^\circ$ . These diffraction peaks are attributed to crystalline NiAl<sub>2</sub>O<sub>4</sub> [62]. Moreover, Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 900 and 1000 °C showed diffraction lines at  $2\theta = 28.6^\circ$ ,  $33.2^\circ$ ,  $47.4^\circ$  and  $56.4^\circ$  which are attributed to crystalline CeO<sub>2</sub> [25].

#### *DR UV-vis spectroscopy*

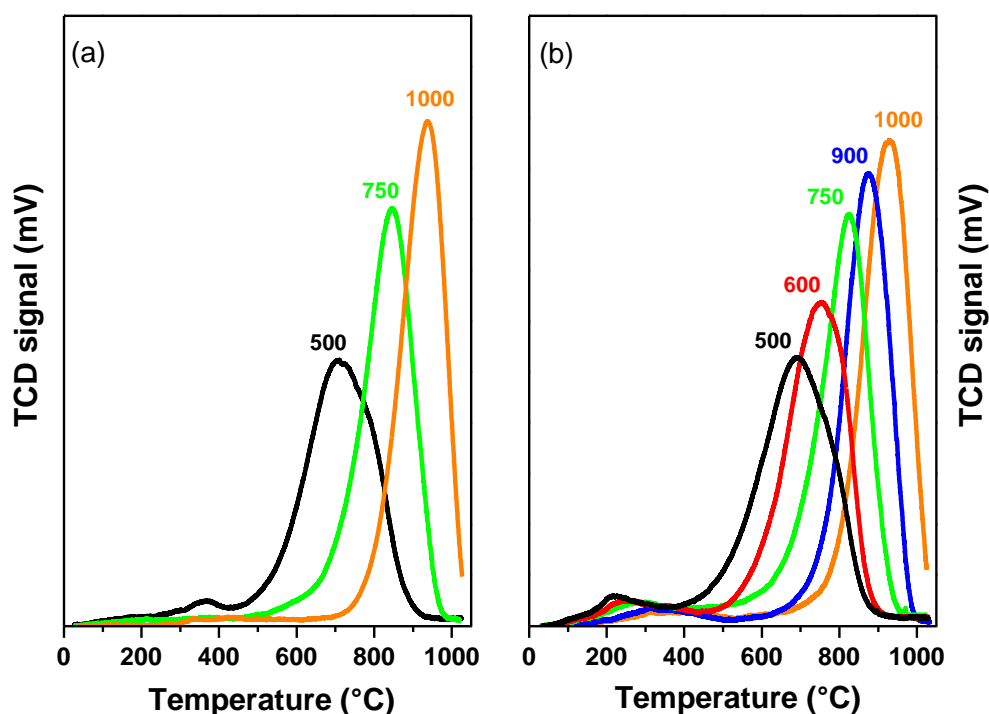
UV-vis spectra of Ni/Al<sub>2</sub>O<sub>3</sub>-500 (not shown in this work) showed presence of characteristic bands at  $\sim 13\ 100$ ,  $\sim 15\ 770$ ,  $\sim 16\ 690$  and broad band in range  $21\ 500 - 28\ 000\ \text{cm}^{-1}$ . Low intensive bands at  $15\ 770$  and  $16\ 690\ \text{cm}^{-1}$  are characteristic for presence of Ni(Td) species [53,54]. On the other hands, bands at  $13\ 100$  and broad band at  $21\ 500 - 28\ 000\ \text{cm}^{-1}$  are attributed to Ni(Oh) species in alumina lattice [53,54]. Moreover, in the spectra was observed high intensity background which some authors attributed to non-stoichiometric NiO [54]. As the temperature calcination increased the intensity of background decreased which led to lower population of non-stoichiometric NiO. Moreover, the broad band became narrower with maximum at  $27\ 000\ \text{cm}^{-1}$ . Heracleous et al. [53] attributed this band to the presence of inverse spinel. In the diffractogram of Ni/Al<sub>2</sub>O<sub>3</sub>-1000 was observed diffraction lines corresponding to presence of crystalline NiAl<sub>2</sub>O<sub>4</sub>. Moreover, the increase of calcination temperature led to increased intensity of doublet at  $15\ 770$  and  $16\ 690\ \text{cm}^{-1}$  which is characteristic for presence of Ni(Td) species.

In the UV-vis spectra of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-500 catalyst could be found low intensive characteristic doublet at  $15\ 770$  and  $16\ 690\ \text{cm}^{-1}$  attributed to presence of Ni(Td) species. Unfortunately, the presence of any other bands could not be discussed due to high intensity of absorption caused by the presence of Ce-species.

#### *H<sub>2</sub>-TPR*

In the Figure 3-4 are shown H<sub>2</sub>-TPR profiles of Ni/Al<sub>2</sub>O<sub>3</sub> (A) and Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> (B) catalysts. The reduction pattern of Ni/Al<sub>2</sub>O<sub>3</sub>-500 showed two reduction peaks, one low intensive with maximum at  $369^\circ\text{C}$  and second intensive with maximum  $712^\circ\text{C}$  and shoulder peak with maximum at ca  $800^\circ\text{C}$ . Low temperature reduction peak is attributed to NiO weakly interacting with alumina support [53,56].

Intensity of this peak was very low. No diffraction lines of crystalline NiO were detected in XRD diffractogram. It could be suggested that this NiO was amorphous or under detection limit of XRD. High temperature reduction peak with maximum at 712 °C and shoulder peak with maximum at ca 800 °C are attributed to the reduction of octahedrally or tetrahedrally coordinated Ni<sup>2+</sup> ions strongly interacting with alumina support [55]. As the calcination temperature increased the low temperature reduction peaks decreased total area whereas the maximum of high temperature reduction peak was shifted to higher reduction temperature. This mean that the interaction of Ni<sup>2+</sup> species became stronger. It is generally accepted that tetrahedrally coordinated Ni(Td) species are less reducible than octahedrally coordinated Ni(Oh) species. It should be suggested that higher calcination temperature increased relative population of tetrahedrally coordinated Ni(Td) species. This is fully in accordance with results of DR UV-vis spectroscopy. In the spectra increased intensity of characteristic doublet at 15 770 and 16 690 cm<sup>-1</sup> which is attributed to Ni(Td) species in alumina lattice and with XRD where the diffraction lines of crystalline NiAl<sub>2</sub>O<sub>4</sub> was evident.



**Figure 3-4** – H<sub>2</sub>-TPR pattern of Ni/Al<sub>2</sub>O<sub>3</sub> (a) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> (b) catalysts prepared by calcination at different temperature

The differences could be found in the reduction patterns of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts. In the low temperature reduction area appeared new reduction peak with maximum at 217 °C which is attributed to the reduction of adsorbed oxygen species in NiO-CeO<sub>2</sub> mixed oxide [25]. As the calcination temperature increased the maximum was shifted to higher temperature. Presence of Ce in the Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts affected the maximum of high temperature reduction peak which was shifted to lower temperature. On the other hand, as the calcination temperature increased the maximum

shifted to higher reduction temperature and the difference between corresponding Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> decreased.

### 3.2.2 Activity and selectivity of catalysts in ODH of ethane

Comparison of activity and selectivity of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from the same precursor of Ni-species and with constant content of Ce calcined at different temperatures was done by two types of experiments. Firstly, the effect of reaction temperature on the conversion of ethane was observed with constant amount of catalysts diluted with silicon carbide inert and constant flow of reaction mixture (not discussed in this work). Secondly, the yield and selectivity of catalysts was observed at constant conversion of ethane (X = 10 %) at 500 °C. Details of experiments are described in thesis more deeply [47].

For the comparison of activity and selectivity was done experiments at constant conversion of ethane. In Table 3-2 are summarized results of conversion of O<sub>2</sub>, selectivity toward ethylene and CO<sub>2</sub>, yield of ethylene and productivity.

**Table 3-2** – conversion of O<sub>2</sub>, selectivity toward ethylene and CO<sub>2</sub>, yield of ethylene, productivity and relative productivity of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts at constant conversion of ethane (X = 10 %)

Catalyst	T <sub>C</sub> (°C)	W/F (g <sub>cat</sub> .s/cm <sup>3</sup> )	X (%)			Y (%)		Productivity (g <sub>C2=</sub> .g <sub>cat</sub> <sup>-1</sup> .h <sup>-1</sup> )
			O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>		
Ni/Al <sub>2</sub> O <sub>3</sub>	500	0.18	10.7	84.0	13.0	8.4	0.14	
	750	0.27	10.5	81.5	14.1	8.2	0.08	
	1000	-	-	-	-	-	-	
Ni-Ce(0.12)/Al <sub>2</sub> O <sub>3</sub>	500	0.03	16.0	76.1	23.2	7.6	0.70	
	600	0.03	14.2	76.7	22.7	7.7	0.61	
	750	0.06	15.3	76.8	22.8	7.7	0.33	
	900	0.16	19.8	56.6	41.7	5.7	0.09	
	1000	0.28	26.6	28.5	62.1	2.9	0.03	

#### *Yield and productivity of ethylene*

Catalytic results showed (Table 3-2) that Ce as a promotor had a positive effect on the productivity of ethylene. Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> achieved higher productivity than corresponding Ni/Al<sub>2</sub>O<sub>3</sub> catalysts compared at constant conversion of ethane. Calcination temperature had crucial effect on the catalytic behaviour of all catalysts. As the calcination temperature increased the productivity of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts decreased. Moreover, Ni/Al<sub>2</sub>O<sub>3</sub>-1000 catalysts did not achieve 10% conversion of ethane. The highest productivity achieved Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 catalyst (0.7 g<sub>C2=</sub>.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>).

### ***Selectivity toward ethylene***

Ni/Al<sub>2</sub>O<sub>3</sub> catalysts achieved higher selectivity toward ethylene than corresponding Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>. As the calcination temperature of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts increased the selectivity toward ethylene decreased and higher amount of CO<sub>2</sub> was formed. On the other hand, Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500, 600 and 750 °C achieved almost the same value of selectivity. Major decrease of selectivity toward ethylene was observed over catalysts calcined at 900 and 1000 °C.

### **3.2.3 Effect of Ce and heat treatment on catalytic behaviour of catalysts in ODH of ethane**

Major decrease of selectivity toward ethylene and productivity of ethylene were observed over Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 900 and 1000 °C. It could be suggested that this effect could be caused by the presence of crystalline NiAl<sub>2</sub>O<sub>4</sub>. Moreover, it was showed that increasing calcination temperature led to catalysts with increasing relative population of Ni(Td) species which could led to catalysts with lower productivity of ethylene.

More crucial effect of calcination temperature could be connected with decreasing population of adsorbed oxygen species in NiO-CeO<sub>2</sub> mixed oxide. It was discussed that increasing calcination temperature caused that reduction peak of oxygen species was less intensive and the total area of this peak decreased. Moreover, CeO<sub>2</sub> species was formed in Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 900 and 1000 °C. Thus the interaction Ce-Ni could be dramatically decreased.

It should be concluded that decrease of ethylene productivity over catalysts calcined at 900 and 1000 °C could be given by several factors. However, it was unable to distinguish which factor is limiting for catalysts deactivation.

### **3.3 Effect of pre-treatment on distribution of Ni-species of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts and its activity and stability in DRM**

*The aim of the work: It was found that it is possible to prepare Ni based catalysts with targeted distribution of Ni-species. Due to that fact the catalysts were tested in dry reforming of methane. For this reaction, the key factor is the reducibility of catalysts and the formation of Ni<sup>0</sup> species. The aim was to find out how to transform different Ni-species to Ni<sup>0</sup> species.*

#### **3.3.1 Characterization of reduced catalysts**

In previous chapter, characterization of as-prepared catalysts for ODH of ethane, where the active form of catalysts is oxidic form, was discussed. In the reaction of DRM the active phase is metallic Ni<sup>0</sup>. In the following part will be discussed results of characterization of reduced Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts. Reduction of catalysts before reaction was done in-operando in flow of 5% H<sub>2</sub>/Ar at 750 °C for 1 h.



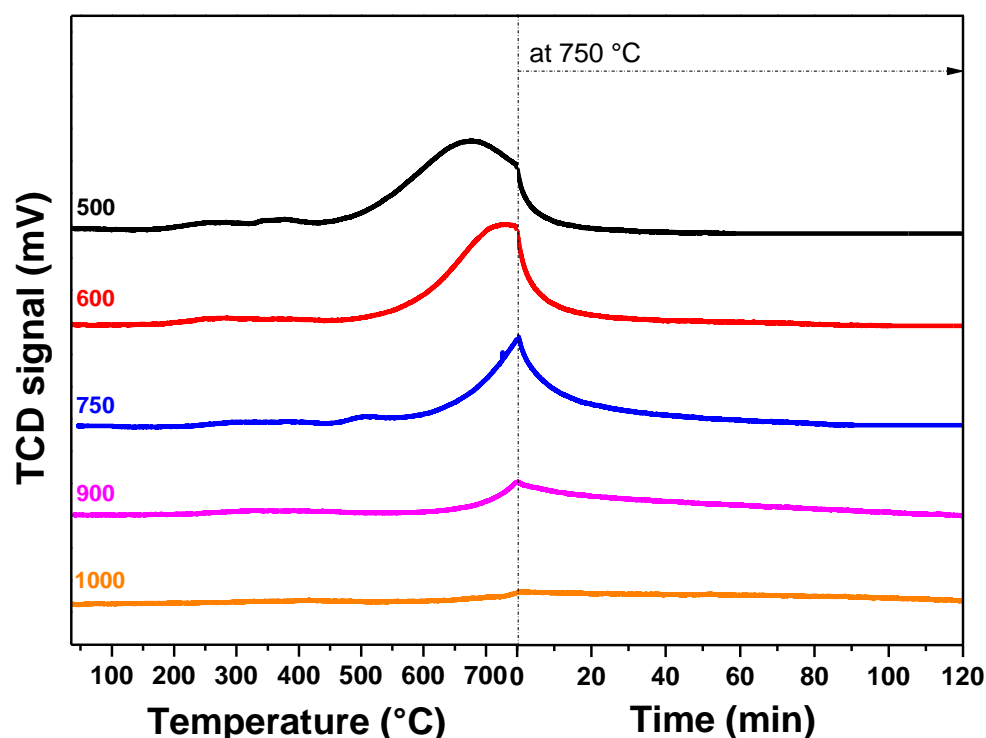
## XRD

The reduction of catalysts changed the diffractograms (not shown in this work). In the diffractograms appeared new diffraction peaks at  $2\theta = 44.5^\circ$ ,  $51.9^\circ$  and  $76.4^\circ$ . These diffraction lines are attributed to the metallic  $\text{Ni}^0$  [63]. Moreover, Ni-Ce(0.12)/ $\text{Al}_2\text{O}_3$  catalysts calcined at 900 and 1000 °C contained after reduction aforementioned diffraction lines of crystalline  $\text{NiAl}_2\text{O}_4$  and  $\text{CeO}_2$ .

The average diameter of  $\text{Ni}^0$  crystallites was calculated based on Scherrer's equation. It was found that the average size increased with increasing calcination temperature from 5 nm to 25 nm.

## Reduction degree of Ni-species, $\text{H}_2$ -TPR

Due to the fact that DRM requires reduced form of catalysts the reduction degree of Ni-Ce(0.12)/ $\text{Al}_2\text{O}_3$  catalysts was determined. Two  $\text{H}_2$ -TPR experiments were made. The first one was typical  $\text{H}_2$ -TPR experiment made in the range 25 – 1050 °C. The second experiment was done in the range 25 – 750 °C followed by isothermal reduction at 750 °C for 1 h. This type of experiment simulated the condition of in-operando reduction of catalysts. The reduction degree was determined as a percent portion of hydrogen consumption  $n_{\text{H}_2,\text{EXP}2}/n_{\text{H}_2,\text{EXP}1}$ . The  $\text{H}_2$ -TPR patterns are shown in the Figure 3-5.



**Figure 3-5** –  $\text{H}_2$ -TPR pattern of Ni-Ce/ $\text{Al}_2\text{O}_3$  catalysts calcined at different temperatures after 2 h of reduction at 750 °C

The reduction degree was the highest at Ni-Ce(0.12)/ $\text{Al}_2\text{O}_3$ -500 catalyst and it was achieved 90 %. As the calcination temperature of as-prepared catalysts increased

the reduction degree decreased and Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 achieved only 12 % reduction. It means that the majority of Ni(Td) species in alumina lattice was preserved after reduction. Transformation to Ni<sup>0</sup> underwent other oxidic Ni-species. Nevertheless, Figure 3-5 showed that after 2 h of reduction was not stable baseline and the reduction is not finished at this temperature.

### 3.3.2 Activity and stability of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts in DRM

Activity and stability of catalysts were studied for as-prepared catalysts and reduced catalysts. The activity of catalysts was observed in temperature range of 25 – 750 °C and the stability in 12 h TOS experiment at 750 °C. In the Table 3-3 are summarized results of test.

In general, the results showed that conversion of methane decreased for catalysts with increasing temperature of calcination. Catalysts which were reduced before reaction achieved 55% methane conversion earlier than not-reduced analogues. It could be suggested that this behaviour was caused by the presence of metallic Ni<sup>0</sup> particles in reduced Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts before reaction. On the other hand, metallic Ni<sup>0</sup> particles in not-reduced catalysts had to form in flow of reaction mixture.

Moreover, the results showed that reduced form of catalysts achieved higher methane conversion at 750 °C than not-reduced form of catalysts. The lowest difference was observed over Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-500 catalyst which contained the easiest reducible Ni-species. It could be suggested that the lowest temperature at which the methane conversion increased is dependent on reducibility of Ni-species.

Similar behaviour was observed for catalysts which were calcined at 600 and 750 °C and was compared in not-reduced and reduced form. Not-reduced form of catalysts achieved 55% methane conversion at higher reaction temperature than the reduced form of catalysts. On the other hand, not-reduced form of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> which were calcined at 900 and 1000 °C showed initial methane conversion after some induction period of reaction at 750 °C which was 4 and 8 hours respectively at 750 °C. After that induction period the dramatic increase of methane conversion was observed. Similar behaviour was reported in literature [64] but there is still no explanation of this behaviour.

Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts which were reduced before the reaction achieved higher methane conversion than the not-reduced form of catalysts. It is evident that these results could be connected in straight way with higher value of degree of reducibility and with absolute amount of metallic Ni<sup>0</sup>. However, it is remarkable that high difference in degree of reducibility do not correlate with relatively small difference in conversion. It was mentioned that Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-500 catalyst showed 90% degree of reducibility whereas Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 showed only 12% degree of reducibility. A quick calculation shows that 12% degree of reducibility in 11wt.% Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> yielded only 1.3 wt.% of metallic Ni<sup>0</sup> as effective catalytic active sites at the beginning of reaction. Similar results were reported. Al-Fatish et al. [65] reported 80% methane conversion over 1 wt.% Ni supported on  $\alpha$ - and  $\gamma$ -alumina. It is surprising that Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 catalyst containing relatively small amount of Ni<sup>0</sup> species with

relative big diameter (23 nm) achieved similar methane conversion as other studied catalysts. It could be suggested that these Ni<sup>0</sup> particles seemed to be very active in DRM.

All catalysts in not-reduced and reduced form underwent stability test at 750 °C over 12 h TOS. All reduced catalysts achieved high stability over this period (Table 3-3). On the other hand, not-reduced form of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts showed different values of stability. Catalysts calcined at 500, 600 and 750 °C continuously increased methane conversion which could be explained by continuous auto-reduction by H<sub>2</sub> in product. Catalysts which were calcined at 900 and 1000 °C in first step dramatically increased methane conversion but then the conversion continuously decreased.

**Table 3-3** – activity and stability of not-reduced and reduced Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at different temperatures

Catalyst	T <sub>c</sub> (°C)	T <sub>55</sub> <sup>a</sup> (°C)	Initial conversion <sup>b</sup> (%)		Final conversion <sup>c</sup> (%)		Stability <sup>d</sup>
			CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	
Not-reduced Ni-Ce(0.12)/Al <sub>2</sub> O <sub>3</sub>	500 <sup>e</sup>	675	81.8	85.9	86.0	89.2	1.05
	600 <sup>e</sup>	735	61.9	70.2	68.4	75.7	1.11
	750	75 min at 750	5.5	7.8	52.8	61.4	9.6
	900	5 h at 750	2.3	2.2	46.3	58.8	20.1
	1000	9 h at 750	2.3	2.1	60.3	71.4	26.2
Reduced Ni-Ce(0.12)/Al <sub>2</sub> O <sub>3</sub>	500 <sup>f</sup>	630	87.1	90.0	86.9	89.9	0.998
	600 <sup>f</sup>	630	85.7	89.6	85.4	89.0	0.996
	750	645	82.5	87.2	82.2	86.4	0.996
	900	660	77.2	83.0	77.1	82.9	0.999
	1000	675	74.6	80.6	74.5	80.8	0.999

<sup>a</sup> temperature at 55% of methane conversion

<sup>b</sup> methane conversion at initial time of reaction at 750 °C

<sup>c</sup> methane conversion after 12 h TOS experiment at 750 °C

<sup>d</sup> stability = final methane conversion/initial methane conversion

<sup>e</sup> catalysts calcined at lower temperature than reaction temperature

<sup>f</sup> catalysts calcined at lower temperature than reduction and reaction temperature

### 3.3.3 Characterization of spent catalysts

#### *XRD*

In the diffractograms of spent not-reduced and reduced catalysts (not shown in this work) were found new diffraction lines at  $2\theta = 26.0^\circ$  and  $43.1^\circ$  which could be attributed to crystalline form of carbon [66]. These diffraction lines were evident in all diffractograms of reduced form of catalysts and not-reduced form of catalysts calcined at 500 and 600 °C after reaction. In diffractograms of not-reduced catalysts calcined at 750, 900 and 1000 °C after reaction were not these lines evident.

## **SEM**

In the SEM images (not shown in this work) of reduced catalysts calcined at 500 and 1000 °C after reaction and not-reduced catalyst calcined at 500 °C after reaction was found filamentous carbon which is in agreement with XRD results. On the other hand, not-reduced catalysts calcined at 1000 °C did not contained any filaments of carbon after reaction.

## **TGA-DTA**

For quantitative analysis of carbon deposits over Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts the thermogravimetric analysis was done. TGA-DTA results (not shown in this work) showed decrease in weight of samples in two regions. Catalysts which were reduced before reaction and not-reduced catalysts calcined at 500 and 600 °C after reaction showed weight decrease at 400 – 700 °C. This region is attributed to the oxidation of filamentous carbon [66]. On the other hands, not-reduced form of catalysts calcined at 750, 900 and 1000 °C after reaction showed weight decrease at 300 – 500 °C which is attributed to oxidation of amorphous carbon [67]. These results are fully in agreement with XRD.

Reduced forms of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts showed methane conversion with relatively small difference. It is worth to note that Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 catalyst contained the lowest amount of carbon deposits after reaction.

### **3.3.4 Effect of calcination temperature and reduction of catalysts on the catalytic behaviour in DRM**

It was observed that calcination temperature and the pre-reduction played important role on the catalytic activity and stability of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts in DRM.

It is worth to note that the average crystallite size of Ni<sup>0</sup> species (calculated from XRD by Scherrer's equation) is significantly lower in reduced forms of catalysts. This fact could be one of the possible explanations of higher methane conversion achieved over reduced forms of catalysts.

Secondly, the reduced forms of catalysts showed much higher ability against sintering of Ni<sup>0</sup> into higher clusters than not-reduced catalysts. The resistance against sintering increased with increasing calcination temperature. High calcination temperature led to formation of strongly interacting Ni-species with alumina in oxidised state but this strength could stabilize Ni<sup>0</sup> species after reduction. This stabilization could be responsible for high activity of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub>-1000 catalyst. On the other hand, not-reduced catalysts did not contain metallic Ni<sup>0</sup> on the beginning of reaction and these species were formed in-situ in flow of reaction mixture. The average size of Ni<sup>0</sup> crystallites (24 – 78 nm) showed that there is no stabilization effect.

It was mentioned that the calcination temperature and the reduction before reaction had significant effects on the catalytic activity and stability of Ni-Ce(0.12)/Al<sub>2</sub>O<sub>3</sub> catalysts in DRM. On the other hand, Juan-Juan et al. [68] reported that

activity of catalysts in DRM is not dependent on calcination nor reduction treatment before reaction.

### 3.4 Activity and stability of Ni-Ce/alumina catalysts in ODH and DRM

*The aim of the work: One of the factors affecting activity of Ni-catalysts in ODH of ethane is the type of Ni-species in oxidised form. The type of Ni-species affects the transformation into  $Ni^0$  species and its average size. In previous parts, it was mentioned that the formation of the tetrahedrally coordinated Ni(Td) species is dependent on the accessibility of centres which could be or could not be blocked by the Ce. The aim of this part was to prepare catalysts with different impregnation order of Ni- and Ce-species which could be important for behaviour of Ni-Ce/alumina catalysts and its performance in ODH of ethane and DRM.*

#### 3.4.1 Characterization of as-prepared catalysts

##### ***XRD***

In the diffractograms of as-prepared Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (not shown in this work) is evident diffraction peak at  $2\theta = 67.2^\circ$  which is attributed to  $\gamma$ -alumina [69]. All catalysts with content of Ce showed diffraction peaks at  $2\theta = 28.6^\circ$  and  $67.2^\circ$ . Diffraction line at  $2\theta = 28.6^\circ$  is attributed to crystalline CeO<sub>2</sub> [25] and the diffraction line at  $2\theta = 67.2^\circ$  is attributed to  $\gamma$ -alumina [69]. There were no diffraction peaks attributed to crystalline NiO nor NiAl<sub>2</sub>O<sub>4</sub>.

##### ***DR UV-vis spectroscopy***

The UV-vis spectrum of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (not shown in this work) showed bands at ca.  $\sim 15\,860$ ,  $\sim 16\,830$  and shoulder at  $\sim 14\,080\text{ cm}^{-1}$  which are attributed to tetrahedrally coordinated Ni(Td) species in alumina lattice and a broad band at  $19\,400 - 27\,100\text{ cm}^{-1}$  which is attributed to octahedrally coordinated Ni(Oh) species in alumina lattice [53,54].

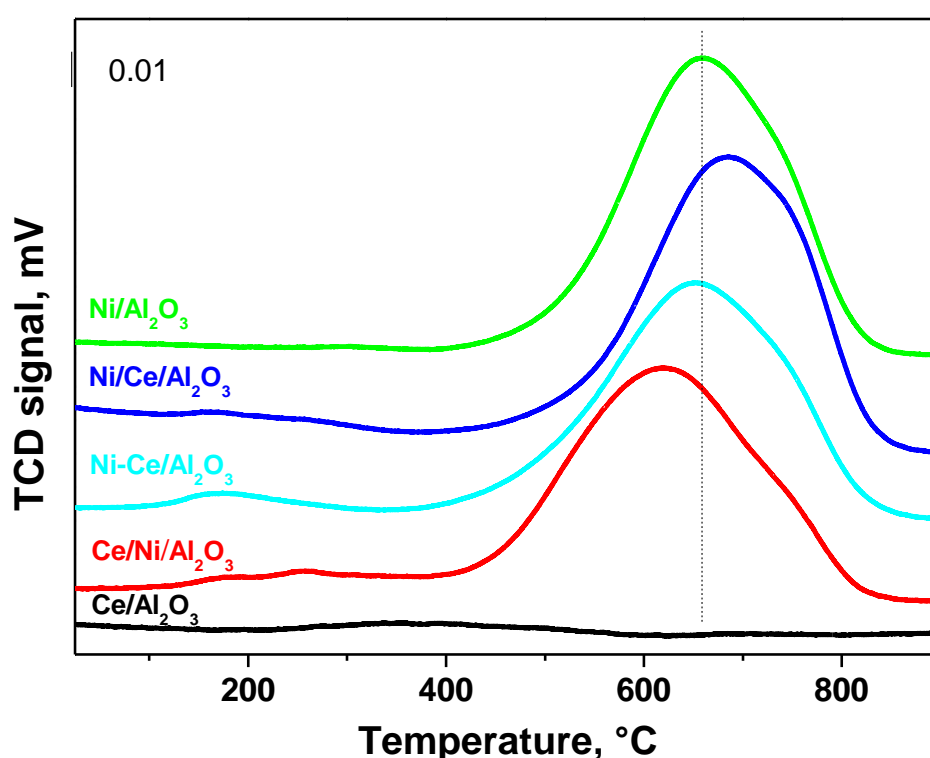
In the spectra of Ni-Ce/alumina catalysts, it is not possible to distinguish the presence of broad band corresponding to Ni(Oh) species in alumina lattice due to the presence of absorption band of Ce-species. On the other hand, the characteristic doublet of Ni(Td) species in alumina lattice at  $15\,860$  and  $16\,830\text{ cm}^{-1}$  is evident. The intensity of this doublet was higher at Ni/Al<sub>2</sub>O<sub>3</sub> and Ce/Ni/Al<sub>2</sub>O<sub>3</sub> catalysts whereas Ni/Ce/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> showed lower intensity of this doublet.

None of the catalysts did not show characteristic bands of Ni(Oh) species in NiO lattice which is in accordance with the absence of diffraction lines of crystalline NiO in XRD diffractograms.

## H<sub>2</sub>-TPR

In the Figure 3-7, there are shown reduction patterns of Ni/Al<sub>2</sub>O<sub>3</sub> and all Ni-Ce/alumina catalysts. All catalysts contained intensive reduction peak at 400 – 900 °C which is attributed to the reduction of octahedrally and/or tetrahedrally coordinated Ni-species with strong interaction with alumina support [55]. The maximum of the reduction peaks differed for individual catalysts. Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed maximum at 656 °C and with shoulder at 747 °C. If the Ni- and Ce-species were impregnated in one step (Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst), the maximum of reduction peak was shifted to 646 °C which showed better reducibility of Ni-species. Ni/Ce/Al<sub>2</sub>O<sub>3</sub> showed higher shift and the maximum was at 616 °C. On the other hand, Ce/Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed shift of reduction maximum to higher temperature. Shift of the reduction maximum is clearly connected with the different distribution of octahedrally and tetrahedrally coordinated Ni-species.

In the reduction patterns of catalysts with content of Ce was observed reduction at 150 – 400 °C which could be attributed to the reduction of adsorbed oxygen species in NiO-CeO<sub>2</sub> mixed oxide [25]. Reduction of NiO weakly interacting with alumina is not probable because no diffraction lines in XRD nor characteristic bands in UV-vis were presented.



**Figure 3-7** – H<sub>2</sub>-TPR pattern of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/alumina catalysts prepared by different impregnation order

### 3.4.2 Activity and selectivity of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by different impregnation order in ODH of ethane

Catalytic activity and selectivity were tested in two experiments. The first one was typical experiment with constant amount of catalysts diluted with silicon carbide inert in constant flow of reaction mixture and in temperature range 400 – 500 °C. The second test was made for comparison of productivity of catalysts and selectivity in the ODH of ethane at constant value of conversion ( $X = 15\%$ ) at 500 °C. Different values of conversion were achieved with change of weight of catalyst and flow of reaction mixture.

In the first experiment (data are not shown in this work), there was observed that addition of Ce as a promotor dramatically increased conversion of ethane. Conversion of ethane increased in order: Ce/Al<sub>2</sub>O<sub>3</sub> < Ni/Al<sub>2</sub>O<sub>3</sub> < Ce/Ni/Al<sub>2</sub>O<sub>3</sub> < Ni-Ce/Al<sub>2</sub>O<sub>3</sub>  $\approx$  Ni/Ce/Al<sub>2</sub>O<sub>3</sub>.

The experiment at constant value of conversion showed that the highest selectivity was achieved over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Catalysts with content of Ce achieved lower selectivity, the decrease in selectivity toward ethylene was in order: Ni/Ce/Al<sub>2</sub>O<sub>3</sub> > Ni-Ce/Al<sub>2</sub>O<sub>3</sub> > Ce/Ni/Al<sub>2</sub>O<sub>3</sub>.

The most important parameter which shows the activity of catalysts is the productivity to ethylene. Values of productivity to ethylene showed again to the positive effect of Ce. The catalysts achieved productivity in order: Ni/Al<sub>2</sub>O<sub>3</sub> (0.09 g<sub>C2=</sub>.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>) < Ce/Ni/Al<sub>2</sub>O<sub>3</sub> (0.28 g<sub>C2=</sub>.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>) < Ni-Ce/Al<sub>2</sub>O<sub>3</sub> (0.54 g<sub>C2=</sub>.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>)  $\approx$  Ni/Ce/Al<sub>2</sub>O<sub>3</sub> (0.64 g<sub>C2=</sub>.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>).

### 3.4.3 Characterization of reduced Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts

#### *XRD*

In the diffractograms of reduced Ni-Ce/alumina catalysts (not shown in this work), there were evident diffraction peaks at  $2\theta = 28.2^\circ, 33.2^\circ, 37.1^\circ, 44.5^\circ, 47.4^\circ, 51.9^\circ, 56.4^\circ, 67.2^\circ$  and  $76.3^\circ$ . Diffraction lines at  $2\theta = 37.1^\circ$  and  $67.2^\circ$  are attributed to  $\gamma$ -alumina [69]; at  $2\theta = 28.2^\circ, 33.2^\circ, 47.4^\circ$  and  $56.4^\circ$  are attributed to crystalline CeO<sub>2</sub> [25]; at  $2\theta = 44.5^\circ, 51.9^\circ$  and  $76.3^\circ$  are attributed to metallic Ni<sup>0</sup> species [63].

There was made calculation of average size of Ni<sup>0</sup> crystallites. In all catalysts was found crystallites with average size around 4 -5 nm which is on the detection limit of the techniques and no adequate information was taken from these results.

### 3.4.4 Activity and stability of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by different impregnation order in DRM

The activity and stability of catalysts were studied over 12 h TOS experiment at 750 °C. In the Table 3-4 are shown results of initial conversion of methane and CO<sub>2</sub>, conversion of methane and CO<sub>2</sub> after 12 h TOS and stability calculated as ratio of methane conversion after 12 h TOS experiment and initial methane conversion. The

highest initial conversion of methane was achieved over Ni/Al<sub>2</sub>O<sub>3</sub> (X = 92 %) and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> (X = 87 %) followed by Ce/Ni/ Al<sub>2</sub>O<sub>3</sub> (X = 79 %).

After 12 h TOS experiment, there were calculated the stability of observed value of conversion and the highest stability was achieved over Ni-Ce/Al<sub>2</sub>O<sub>3</sub> (99 %). All other catalysts achieved stability 95 – 97 %.

**Table 3-4** – conversion of methane and CO<sub>2</sub> at 0 h and 12 h TOS and stability of catalysts

Catalyst	Conversion <sup>a</sup> (%)		Conversion <sup>b</sup> (%)		Stability <sup>c</sup>
	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	
Ce/Al <sub>2</sub> O <sub>3</sub>	1.2	0.4	0.9	0.3	0.75
Ce/Ni/Al <sub>2</sub> O <sub>3</sub>	79.4	84.3	76.8	82.2	0.97
Ni/Al <sub>2</sub> O <sub>3</sub>	92.4	94.2	87.8	90.7	0.95
Ni/Ce/Al <sub>2</sub> O <sub>3</sub>	92.2	93.8	88.9	91.2	0.96
Ni-Ce/Al <sub>2</sub> O <sub>3</sub>	87.1	90.0	86.9	89.9	0.99

Reaction conditions: T<sub>R</sub> = 750 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1, GHSV = 300 000 L.kg<sup>-1</sup>.h<sup>-1</sup>

<sup>a</sup> conversion of methane and CO<sub>2</sub> at time 0 h at 750 °C

<sup>b</sup> conversion of methane and CO<sub>2</sub> at time 12 h at 750 °C

<sup>c</sup> stability = conversion of methane at 12 h TOS/ conversion of methane at 0 h TOS

### 3.4.5 Characterization of spent catalysts

#### *XRD*

In the diffractograms of spent catalysts (not shown in this work), there was observed new diffraction peaks at 2θ = 26.0 ° and 43.1 ° which are attributed to crystalline carbon [66]. Diffraction lines of metallic Ni<sup>0</sup> species were still presented. Calculation of average crystallite size showed minor increase of diameter of Ni<sup>0</sup> species but it was still on the detection limit of XRD.

#### *TEM*

Images of TEM (not shown in this work) showed that the selected catalysts Ni/Al<sub>2</sub>O<sub>3</sub> and Ce/Ni/Al<sub>2</sub>O<sub>3</sub> contained filamentous after DRM. Formation of filamentous carbon is in agreement with results of XRD where was observed diffraction lines of crystalline carbon.

#### *TGA-DTA*

Thermogravimetric analysis of spent Ni-based catalysts showed that oxidation of samples was carried out at 400 – 700 °C. This area of oxidation is attributed to filamentous carbon species [66] and is fully in agreement with XRD and TEM results.

On the other hand, Ce/Al<sub>2</sub>O<sub>3</sub> catalysts contained amorphous carbon which was oxidised at 300 – 500 °C [67].



### **3.4.6 Effect of Ce-Ni interaction on catalytic performance of Ni-Ce/alumina catalysts in ODH of ethane and DRM**

Different impregnation order had effect on the different distribution of Ni-species in Ni-Ce/alumina catalysts. The major difference was in the relative population of Ni(Oh) and Ni(Td) species. It should be suggested that Ce could occupy the same centres which led to formation of Ni(Td) species. If the Ce was impregnated in first step the defect centres in alumina should be occupied by Ce and lower concentration of Ni(Td) was formed. Thus, the relative population of Ni(Td) species was observed in Ni/Ce/Al<sub>2</sub>O<sub>3</sub> catalyst in comparison with Ni/Al<sub>2</sub>O<sub>3</sub> and Ce/Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

The relative population of Ni(Oh) and Ni(Td) species could affect the catalytic behaviour in ODH of ethane. It was found that Ce as a promoter significantly increase the conversion of ethane. The productivity of ethylene was the highest over Ce/Ni/Al<sub>2</sub>O<sub>3</sub> catalyst which has the lowest reduction maximum and thus it could be suggested that this catalyst contained the highest relative population of Ni(Oh). By another word, the reducibility of this catalyst was the highest. The values of productivity followed the trend: the highest reducibility the highest productivity.

The different impregnation order could affect the activity and stability of catalysts in DRM. It could be suggested that the key factor is reducibility of catalysts. As the position of reduction maximum is shifted to lower temperature the higher initial conversion of methane was achieved.

## 4 Conclusions

The thesis deals with the preparation of Ni-alumina catalysts with different distribution of Ni-species and with the description of the effect of Ce as a promotor on change of distribution of Ni-species. For the preparation of Ni-alumina catalysts, there were used different precursors of Ni-species, different calcination temperature or effect of impregnation order of Ni- and Ce-species. For study of Ni-species distribution, XRD, H<sub>2</sub>-TPR and DR UV-vis spectroscopy were mainly used. Ni-alumina catalysts were used in reaction of oxidative dehydrogenation of ethane and dry reforming of methane.

The main conclusions could be summarized:

- Ce as a promoter could change the distribution of Ni-species in Ni-Ce/alumina catalysts.
- Ce increased the reducibility of Ni-species with strong interaction with alumina support. It was found that the relative population of Ni(Td) species decreased.
- Ce can affect the dispersion of NiO species over alumina support. It was found that the average size of NiO crystallites decreased when Ce was presented in catalysts.
- Different distribution of Ni-species and interaction Ce-Ni led to increase of catalytic activity and stability in ODH of ethane and DRM.
- The best catalytic performance in ODH of ethane was observed for catalysts prepared from nickel acetate with 10.5 wt.% of Ni and 3.0 wt.% of Ce which was calcined at 500 °C.
- On the other hand, catalysts prepared from nickel nitrate was affected by presence of Ce much more.
- Increasing temperature of calcination led to catalysts with higher population of Ni(Td) species.
- Calcination at 900 and 1000 °C led to the formation of crystalline NiAl<sub>2</sub>O<sub>4</sub> which is not active/selective in ODH of ethane and the formation of crystalline CeO<sub>2</sub>. In these catalysts, the enhance of reducibility was not significant and catalytic activity and selectivity in ODH of ethane was not preserved.
- On the other hand, higher calcination temperature led to formation of less reducible Ni-particles but stronger interaction between reduced Ni<sup>0</sup> species was formed which is one of the key factors for high stability of Ni-catalysts in DRM.
- Impregnation order of Ni- and Ce- species could affect the reducibility of Ni-species. Ce could occupy the same centres in alumina support which led to formation of Ni(Td). If the Ce is impregnated first then could block these centres and Ni ions have to occupy other centres which led to formation of Ni(Oh) species.

## 5 References

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## 6 List of published works and conference contributions

### *Published articles connected to the topic of dissertation thesis*

- L. Smoláková, **M. Kout**, L. Čapek; *The Role of Ni Species Distribution on the Effect of Ce as a Promoter in C2-ODH Reaction*; Topics in Catalysis 58 (2015) 843 – 853
- L. Smoláková, **M. Kout**, E. Koudelková, L. Čapek; *Effect of Calcination Temperature on the Structure and Catalytic Performance of the Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Oxidative Dehydrogenation of Ethane*; Industrial & Engineering Chemistry Research 54 (2015) 12730 – 12740
- L. Smoláková, **M. Kout**, L. Čapek, A. Rodriguez-Gomez, V. M. Gonzalez-Delacruz, L. Hromádka, A. Caballero; *Nickel catalyst with outstanding activity in the DRM reaction prepared by high temperature calcination treatment*; International Journal of Hydrogen Energy 41 (2016) 8459 – 8469
- H. Drobná, **M. Kout**, A. Soltyssek, V. M. Gonzalez-Delacruz, A. Caballero, L. Čapek; *Analysis of Ni species formed on zeolites, mesoporous silica and alumina supports and their catalytic behavior in the dry reforming of methane*; Reaction Kinetics, Mechanism and Catalysis 121 (2017) 255 – 274

### *Published articles without connection to the topic of dissertation thesis*

- L. Smoláková, Š. Botková, L. Čapek, P. Priecel, A. Soltyssek, **M. Kout**, L. Matějová; *Precursors of active Ni species in Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for oxidative dehydrogenation of ethane*; Chinese Journal of Catalysis 34 (2013) 1905 – 1913

### *Active oral presentation at international conferences*

- **M. Kout**, L. Smoláková, L. Čapek; *Ni-alumina catalysts in oxidative dehydrogenation of ethane and enhanced catalytic behavior after cerium addition*, 12<sup>th</sup> Pannonian Symposium on Catalysis, Třešť, Czech Republic, 16. – 20. 9. 2014
- **M. Kout**, L. Smoláková, V. M. Gonzalez-Delacruz, A. Caballero, L. Čapek; *Ni-Ce/Al<sub>2</sub>O<sub>3</sub> Catalysts in Dry Reforming of Methane and Oxidative Dehydrogenation of Ethane: Effect of Impregnation Order*, 3<sup>rd</sup> International Conference on Chemical Technology, Mikulov, Czech Republic, 13. – 15. 4. 2015
- **M. Kout**, L. Smoláková, V. M. Gonzalez-Delacruz, A. Caballero, L. Čapek; *Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts in oxidative dehydrogenation of ethane and dry reforming of methane: effect of impregnation order*, 42<sup>nd</sup> International Conference of Slovak Society of Chemical Engineering, Tatranské Matliare, Slovakia, 25. – 29. 5. 2015
- **M. Kout**, L. Smoláková, L. Čapek; *Potential of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts in the oxidative dehydrogenation of ethane*, 5<sup>th</sup> Czech-Polish doctoral seminar, Ostrava, Czech Republic, 27. 11. 2015

### ***Active oral presentation at national conferences***

- **M. Kout**, *Analýza Ni-částic aktivních v ODH ethanu* 2. katalytický seminář, Pardubice, 30. 1. 2013
- **M. Kout**, L. Smoláková, L. Čapek, *Vliv Ce na strukturu a aktivitu Ni-alumina katalyzátorů v C2-ODH a suchém reformování*, 3. doktorský seminář, Ostrava, 17. 4. 2014
- **M. Kout**, *Vliv ceru na aktivitu Ni-alumina katalyzátorů*, Workshop – Analysis of active sites in heterogeneously catalysed reaction, Pardubice, 1. 6. 2014

### ***Active poster presentation at international conferences***

- **M. Kout**, L. Smoláková, P. Prieceľ, Š. Botková, P. Kutálek, L. Čapek; *Analysis of Ni Species Active in the ODH of Ethane and Propane*, 11<sup>th</sup> Pannonian Symposium on Catalysis, Obergurgl, Austria, 3. – 7. 9. 2012
- **M. Kout**, L. Smoláková, P. Prieceľ, Š. Botková, L. Čapek, *Analysis of Ni Species Active in Oxidative Dehydrogenation of Ethane and Propane*, 44<sup>th</sup> Symposium on Catalysis, Prague, Czech Republic, 5. – 6. 11. 2012
- **M. Kout**, L. Smoláková, P. Prieceľ, Š. Botková, A. Soltýsek, L. Čapek, *Analysis of Ni-species in Ni-alumina catalysts by using of UV-vis, H<sub>2</sub>-TPR and XRD*, School of Molecular Sieves: Characterization, Prague, Czech Republic, 10. – 12. 3. 2013
- **M. Kout**, L. Smoláková, A. Soltýsek, L. Čapek, *The role of NiO species on the catalytic behaviour of Ni-alumina catalysts in the oxidative dehydrogenation of ethane and propane*, 5<sup>th</sup> Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis, Segovia, Spain, 16. – 19. 6. 2013
- **M. Kout**, L. Smoláková, K. Jenišťová, L. Čapek, *Influence of NiO in the oxidative dehydrogenation of ethane*, 45<sup>th</sup> Symposium on Catalysis, Prague, Czech Republic, 4. – 6. 11. 2013
- **M. Kout**, L. Smoláková, A. Soltýsek, L. Matějová, L. Čapek, *Analysis of Ni-species in NiCe-alumina catalysts and its catalytic behaviour in ODH of ethane*, School of Molecular Sieves: Catalysis, Prague, Czech Republic, 17. – 18. 3. 2014
- **M. Kout**, L. Smoláková, L. Čapek, *Effect of cerium addition to Ni-alumina catalysts and its catalytic behaviour in oxidative dehydrogenation of ethane*, 2<sup>nd</sup> International Conference on Chemical Technology, Mikulov, Czech Republic, 7. – 9. 4. 2014
- **M. Kout**, L. Smoláková, V. M. Gonzalez-Delacruz, A. Caballero, L. Čapek, *Effect of Calcination Temperature of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> Catalysts on the Structure of Ni-Species and Catalytic Activity in Dry Reforming of CH<sub>4</sub>*, 67. Zjazd Chemikův, Horný Smokovec, Slovakia, 7. – 11. 9. 2015
- **M. Kout**, L. Smoláková, L. Čapek, *Ni-species supported on Al-Ce-O mixed oxides: Characterization and catalytic behavior in ODH of ethane*, 4<sup>th</sup> International Conference on Chemical Technology, Mikulov, Czech Republic, 25. – 27. 4. 2016

- **M. Kout**, L. Smoláková, V. M. Gonzalez-Delacruz, A. Caballero, L. Čapek, *Analysis of the role of Ce species as promoter on the structure and catalytic properties of Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts in oxidative dehydrogenation of ethane and dry reforming of methane*, 17<sup>th</sup> Nordic Symposium on Catalysis, Lund, Sweden, 14. – 16. 6. 2016

### ***Internship abroad***

- Instituto de Ciencia de Materiales de Sevilla (CSIC-University of Seville) under leading of prof. Alfonso Caballero, Seville, Spain, 22. 9. – 18. 12. 2014
- European Synchrotron Radiation Facility under leading of prof. Alfonso Caballero, Grenoble, France, 21. – 27. 1. 2015