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Effect of Active Phase Precursor on Structural, Textural and Catalytic Properties of the Model NiO_x/CeO₂ System Active in Dry Reforming of Methane

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Abstract: The current paper is devoted to the synthesis of ceria-supported nickel-based catalysts starting from different precursors of the nickel active phase. Thermal decomposition of metal-containing precursors, deposited onto stable supports by dry impregnation, belongs to the industrially preferred, simple ways of catalyst preparation. The synthesized series of NiO_x/CeO₂ catalysts have been tested in dry methane reforming (DMR), in which two greenhouse gases, i.e., CO₂ and CH₄, are simultaneously converted into syngas. Both reaction progress and stability of the catalyst strongly depend on nickel speciation, which in turn can be determined by the nature of the chosen precursor. Contrary to relatively many studies focused on the importance of synthetic methods and conditions on nickel speciation, the effect of precursor nature on structural, textural, and functional properties of catalytic systems has neither been discussed much nor fully understood. The main goal of this paper was to elucidate the effect of precursors on the properties of NiO_x/CeO₂. Consequences of the use of various nickel precursors (simple inorganic salts, organometallic complexes, and chelates) have been analyzed in detail from the viewpoint of their beneficial influence on the catalytic performance of NiO_x/CeO₂ system (containing 3 wt. % of Ni) tested in DMR.

Keywords: NiO_x/CeO₂; Ni precursor; structure and morphology; catalytic valorization of CO₂; dry reforming of methane



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1. Introduction

1.1. Main Challenges in CO₂ Valorization

Observed in the last 70 years, strongly growing emission of CO₂ from various stationary and mobile anthropogenic sources and a consequent increase in its content in the Earth's atmosphere [1,2] must be considered as fundamental motivations not only to postulate elimination of as many CO₂ emission sources as possible but also to search for new powerful strategies to control, convert, and utilize the emitted CO₂.

The problem of CO₂ emission control belongs to the most burning issues, which need to be efficiently tackled practically everywhere in the world. Emission control is strongly connected with technical and technological problems, such as CO₂ capture, purification, and sequestration, including the dilemmas related mainly to a local specificity of energy sectors, such as energy choices, generation efficiency, utilization and economics but also with the global issues of climate changes, environmental protection or adequate policy and regulations [2]. Only holistic, fully sustainable solutions can be opposed to such complex problems to stop the current growing trends in both CO₂ content in the atmosphere and the mean global temperature in the future.

In general, three main groups of CO₂ mitigation and/or removal strategies can be considered and adopted in practice: (i) reduction of fossil fuel exploitation for energy production, (ii) CO₂ capture, its separation, purification, and storage, and (iii) industrial valorization of CO₂, including the corresponding chemical, photo-, thermo-, bio-, or electrochemical pathways [2–6]. CO₂ can thus be used as a feedstock to produce a wide variety of chemical products, including hydrogen, synthesis gas, liquid fuels, formic and acetic acids, methanol, dimethyl ether, urea, carbonates (including cyclic carbonates and polycarbonates), polymers (e.g., polyurethane and polystyrene), pharmaceuticals (e.g., salicylic acid) [2,7–9]. In this paper, dry methane reforming (DMR) as a specific case of the catalytic valorization of the CO₂ supplied, e.g., from fossil-derived waste gases or captured from large-scale industrial processes will be described.

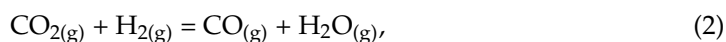
1.2. Catalytic Pathways of CO₂ Conversion

Due to the high thermodynamic stability of CO₂ molecules, large-scale production of this pollutant, and specific technological limitations, the chemical conversion of carbon dioxide is not easy. At the process level, CO₂ reduction and/or hydrogenation are generally costly and energy-consuming. The quite unique thermodynamic stability of the CO₂ molecules is mainly related to their linear geometry, non-polar character, and specific electronic structure. CO₂ is formed as the final product of the total oxidation of both fossil fuels and C-containing organic compounds. The formation of carbon dioxide is accompanied by a high energy loss by a reacting system, reflected in the relatively low heat of the formation of CO₂ molecules ($\Delta H^\circ_f = -394$ kJ/mol) [2]. The back reactions, including a reduction of CO₂, must thus be thermodynamically demanding.

From a chemical viewpoint, the most important way of CO₂ valorization is its reduction to CO. Such a product may be further chemically processed. The direct reduction of CO₂ described by the following equation:



is, however, thermodynamically extremely disfavored due to a high value of this process enthalpy ($\Delta H^\circ = +293$ kJ/mol) [2]. This reaction can occur at temperatures above 2000 °C and can be performed using concentrated solar furnaces or dedicated photocatalytic or photoelectrocatalytic systems [9]. A main route of CO₂ conversion is its catalytic coupling with highly energetic reactants, e.g., hydrogen. Catalytic hydrogenation, which can be expressed, e.g., by the following equation describing the so-called reverse water–gas shift reaction (RWGS):



The catalytic reduction with hydrogen as a co-reactant, even if it does not become favorable, is characterized by a distinctly lower energetic barrier, i.e., $\Delta H^\circ = +41.2$ kJ/mol [9]. The use of hydrocarbons, particularly methane, can be an alternative source of hydrogen (CO₂ reforming). Being at the center of our attention in this work, the so-called dry methane reforming (DMR, described below), is one such option. In general, the hydrogenation of CO₂ to obtain oxygenates (e.g., CH₃OH or DME on various types of Cu-based catalysts, HCOOH or C₂H₅OH over rhodium-based catalysts) or hydrocarbons (alkanes from syngas via Fischer–Tropsch process, olefins over Fe/Mn–Al₂O₃), are the most widely investigated areas in catalytic CO₂ conversion [9,10]. Methanation of CO₂, occurring via so-called Sabatier reaction:



requires more hydrogen, in comparison to oxygenates and thus it is not considered as a favorable route for the conversion of CO₂ to fuels using H₂ [9,10].

1.3. Dry Reforming of Methane

Dry reforming of methane is an interesting catalytic reaction permitting the simultaneous conversion of two greenhouse gases: carbon dioxide and methane into a syngas being a mixture of carbon monoxide and hydrogen, according to the equation:



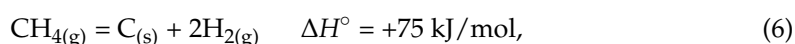
which may be considered as an alternative to the so-called steam reforming



The activity in DMR of Ni-, Co-, and Fe-based systems supported on various supports was confirmed by many authors [2,11,12]. The transition-metal-containing catalysts can be a reasonable alternative for such noble metals as Pd, Pt, Rh, and Ru [2,10] also tested in DMR. For more than 10 years, nickel has been considered as particularly promising component of DMR catalysts because it is relatively more active and more selective than the other transition metals [10]. Various types of Ni-based catalysts, including Ni/ γ -Al₂O₃, Ni/Na-Y, Ni/ZrO₂, Ni/CeO₂-ZrO₂, La-Ni/SBA-15, Ni-Co/ γ -Al₂O₃, La_xNi_yO_z/KTT-6, Ni-CaO-ZrO₂, Ni/MgO/ γ -Al₂O₃ have been reported as catalytic systems active in DMR [2,10–12].

One of the main problems associated with DMR is related to its high-temperature character. Temperatures above 650 °C result very often in catalyst instability connected with sintering, segregation of its components, and, first of all, catalyst deactivation due to the formation of carbon deposits (confirmed by scanning electron microscopy (SEM) and temperature-programmed oxidation (TPO)), formed in two main reactions:

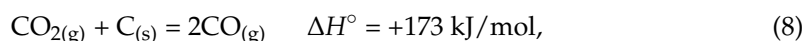
decomposition of methane (methane cracking):



and reverse coal gasification:

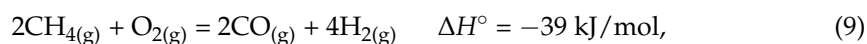


The coke deposit could potentially be removed in the reverse Boudouard reaction:



but unfortunately, despite its endothermic character, this reaction is usually not efficient enough to solve the problem of catalyst deactivation by coke deposition. Usually, the Boudouard reaction is thus considered as contributing to the coke formation [12].

Another problem is related to lower selectivity to syngas due to such side-reactions as the RWGS reaction mentioned earlier (Equation (2)) or partial oxidation of methane:



competing with DMR.

The CO/H₂ concentration ratio produced in DMR should be nominally equal to 1, but RWGS is responsible for CO₂ conversion greater than that of methane resulting in the effective content ratio CO/H₂ > 1. The favorable CO/H₂ ratio between 0.5 and 1 is considered as optimal for producing synthetic alkanes via the Fischer–Tropsch process [2,9]. A variety of other possible products may be synthesized starting from syngas too. It is thus worthy to study and optimize the conditions of the DMR as it offers a rare possibility to use CO₂ for the production of attractive final products.

1.4. Synthetic Parameters Controlling the Catalytic Performance of Supported Oxide Systems Active in DMR

Several synthetic parameters may influence the efficiency of supported oxide systems tested in DMR. The nature of both support and active phase oxides, the loading of active components, adopted preparation route, calcination conditions, etc., belong to the crucial factors determining the catalytic behavior of the catalysts regarding their activity in DMR, selectivity to syngas, and stability. Especially, the influence of those synthetic parameters on high-temperature catalyst stability and coke formation remains particularly important. Homogeneity of ceria-based supports, e.g., of CeO₂-ZrO₂ binary system, frequently applied in DMR due to their thermal stability, activating character towards deposited oxometallic phases, relatively high specific surface area, and resistance to chemical corrosion, also remains of vital importance to avoid temperature-induced segregation. Many preparative routes have already been described and discussed in the literature in relation to Ni-containing systems [13–15]. Similarly, the effect of nickel content on DMR progress has also been reported [16]. Contrary to this, even if some authors suggested that the nature of active phase precursor may belong to the vital activity-controlling parameters of ceria- and ceria-zirconia-supported nickel catalysts active in redox reactions [17–19], this effect is rather far from being sufficiently studied and convincingly elucidated. It is worth noting that mainly nickel chelates were mentioned as beneficial precursors stabilizing nickel in DMR catalysts.

This work is thus devoted to more systematic studies of a series of NiO_x/CeO₂ samples, containing the same loading of nickel (3 wt. %) but obtained from precursors of various chemical characteristics. The content of 3 wt. % of nickel has been chosen as optimal based on our earlier studies [16]. Three series of precursors have been studied: (i) simple inorganic salts, (ii) organic acid salts, and (iii) chelating precursors. Our main goal was to confirm the precursor effect on the catalytic activity and stability of the model NiO_x/CeO₂ catalysts tested in dry methane reforming and to rationalize the observed changes in catalytic behavior in terms of structural and morphological modifications of ceria-supported nickel induced by the kind of the chosen precursor.

2. Materials and Methods

2.1. Synthesis of Catalysts

The used ceria support was synthesized by the Pecchini method. Cerium(III) nitrate hexahydrate (Merck, Rahway, NJ, USA) and citric acid monohydrate (POCH, Gliwice, Poland), mixed in a molar ratio equal to 1/1, were dissolved in a minimal amount of deionized water. Then ethylene glycol was added to the solution to obtain a cerium/citric acid/ethylene glycol molar ratio equal to 1/1/2.2. The final solution was mixed and heated to obtain a dark yellow gel. The resulting gel was filtrated on the Büchner funnel and washed with distilled water to obtain a neutral pH. Samples were dried at 110 °C overnight, then ground in an agate mortar and calcined at 800 °C for 6 h. The ceria support was dry-impregnated with aqueous solutions of nickel(II) chloride (POCH), nickel(II) nitrate (Sigma-Aldrich, St. Louis, MO, USA), nickel(II) sulfate (Acros, Geel, Belgium), nickel(II) formate (Alfa Aesar, Haverhill, MA, USA), nickel(II) acetate (Aldrich), nickel(II) lactate (Alfa Aesar), nickel(II) citrate (Alfa Aesar), and nickel(II) EDTA complex (POCH) with appropriate concentrations to achieve 3 wt. % of metallic nickel in the final catalysts. As it is generally known in dry impregnation the material of support was contacted with an appropriate amount of precursor solutions. In the next step, the solvent was removed by drying [20]. All samples were dried at 100 °C for 12 h and subsequently calcined in air at 400 °C for 3 h. The simplified structures of the more complex precursors of our NiO_x/CeO₂ catalysts have been shown in Figure 1 below.

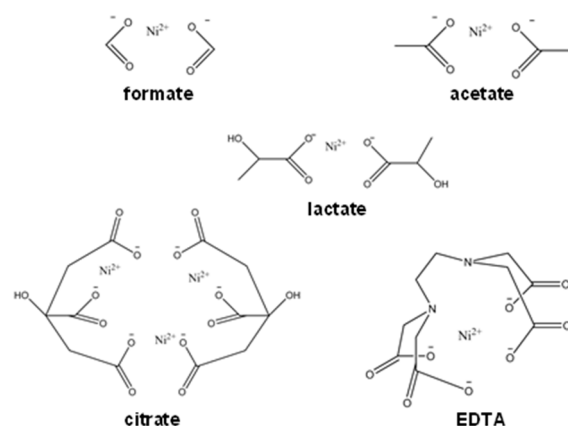


Figure 1. Schematic structures of the more complex precursors of nickel as catalytically active components.

2.2. Characterization of the Synthesized Ni-Based Catalysts

X-ray diffraction patterns (XRD) of a series of investigated samples were recorded using a *Panalytical* (Malvern, UK) X'pert Pro diffractometer equipped with PW3050/60 goniometer and Cu_{Kα} lamp ($\lambda = 1.5406 \text{ \AA}$). Anode voltage and anode current values were set to 40 kV and 30 mA, respectively. The diffraction patterns were collected in the range of 2θ angles 10–90° with a step of 0.026°. The size of crystallites has been estimated based on the Scherrer equation [21]:

$$d_{\text{XRD}} = (K \times \lambda) / (\beta \cos \theta), \quad (10)$$

where K is a dimensionless shape factor equal to 0.93, λ stands for the X-ray wavelength (0.15406 nm), β is the line broadening at half of the maximum intensity (FWHM), and θ stands for the corresponding Bragg angle.

The specific surface area and pore volume of the catalysts were determined by low-temperature ($-196\text{ }^{\circ}\text{C}$) nitrogen adsorption and desorption measurements using a 3Flex (Micromeritics) (Unterschleißheim, Germany) adsorption analyzer. The samples, prior to the analysis, were degassed under vacuum (0.2 mbar) at $350\text{ }^{\circ}\text{C}$ for 24 h. The specific surface area (S_{BET}) of the catalysts was calculated using the Brunauer–Emmett–Teller (BET) model.

Scanning electron microscope (SEM) images were recorded using a Hitachi S-4700 (Kokyo, Japan) field emission apparatus (FE-SEM) working at 20 kV. The samples were placed on carbon adhesive discs and coated with gold.

The diffuse reflectance ultraviolet/visible (UV/Vis-DR) spectra of the investigated samples were recorded using a Perkin-Elmer (Waltham, MA, USA) Lambda 650 UV/Vis spectrophotometer with Praying Mantis (Harrick, Pleasantville, NY, USA) accessory. The measurements have been performed in the range of 200–900 nm with a resolution of 1 nm. The electronic spectra were recorded under ambient conditions and their final intensities were transformed according to the Kubelka–Munk equation [22]. Deconvolution of spectra was carried out using PeakFit4 software. Energy in eV was calculated based on the formula: $1240/\lambda$, where λ stands for wavelengths expressed in nm. The dependence of $[ExF(R)]^2$ on E (where E stands for energy, and $F(R)$ is the Kubelka–Munk function) was plotted. Estimation of the straight line, tangent to the corresponding curve, permitted us to determine the band gap. A similar method has also been adopted for Ni^{2+} doped CeO_2 samples by the other authors cf. [23].

For the temperature-programmed reduction by hydrogen (H_2 -TPR) measurements, 50 mg of the sample was put into the fixed-bed quartz reactor and degassed in an inert gas (He, 300 °C, 30 min, 50 mL/min). Then the gaseous mixture was changed to 5% H_2 /Ar and the reactor was heated from room temperature to 920 °C at a rate of 5 °C/min. Outlet gases were monitored by the thermal conductivity detector (TCD).

2.3. Activity Tests

A mixture of reaction gases CH_4/Ar and CO_2/Ar with a total flow of 100 mL/min ($\text{Ar} = 95 \text{ mL/min}$, $\text{CH}_4 = 2.5 \text{ mL/min}$, $\text{CO}_2 = 2.5 \text{ mL/min}$) was fed into a quartz reactor. The total flow was adjusted with flowmeters and a mass flow controller (Brooks Industry, Oklahoma, OKC, USA). The quartz reactor was placed in the oven, where temperature was controlled with a temperature programmer. A mass of 100 mg of a tested catalyst (sieve fraction from 0.2 to 0.3 mm) was placed into the fix-bed reactor. Reactants were analyzed by GC chromatograph (Agilent Technologies 7890A GC System, Santa Clara, CA, USA). Firstly, a catalyst was pre-reduced at 850 °C with 5% H_2 in Ar (50 mL/min) for 120 min. After reaching a temperature of 500 °C 5% H_2/Ar flow was switched off and the other gaseous reactants were turned on. Gas chromatographic measurements have been performed in the temperature range 500–800 °C with a 50 °C step. Additionally, one backpoint measurement at 650 °C has been performed.

3. Results and Discussion

3.1. Catalytic Activity of the Investigated Ni/CeO₂ Samples

Even at first glance, the catalytic activity in DMR of the $\text{NiO}_x/\text{CeO}_2$ samples obtained from various precursors of the structures presented in Figs. 2AB below distinctly differs. This result clearly confirms that the nature of nickel precursor belongs to the important parameters determining the catalytic behavior of the model $\text{NiO}_x/\text{CeO}_2$ system. Both temperature dependences of the catalytic activity and activity thresholds were different for the samples obtained from various precursors of the nickel active phase. Unfortunately, not all investigated samples were active in DMR. Those synthesized from chloride, sulfate, and acetate precursors were not or just weakly active. Contrary to this, the $\text{NiO}_x/\text{CeO}_2$ samples obtained from nitrate, lactate, citrate, and EDTA precursors showed quite high conversions of CO_2 . The sample synthesized from formate precursor exhibited rather medium activity in the investigated reaction. In all cases, where satisfactory conversions were observed, the progress of DMR reaction correlated with temperature increase. The highest conversions of both reactants, i.e., CO_2 and CH_4 were observed at 750–800 °C.

The conversion of methane followed the same trend as it was determined for the conversion of CO_2 , which followed the same trend as it was determined for the conversion of CO_2 but with lower values. And so, the conversion of methane has been about 30% lower for most active samples. The H_2/CO content ratio for all active samples was lower than 1 (ranging from 0.8 to 0.9).

Based on these results, the following decreasing activity sequence of the investigated $\text{NiO}_x/\text{CeO}_2$ samples in DMR can be proposed, taking into account active phase precursors: nitrate $\approx$ EDTA > citrate > lactate > formate > acetate > chloride $\approx$ sulfate. At the highest reaction temperatures, the investigated $\text{NiO}_x/\text{CeO}_2$ catalysts showed the maximal conversion of CO_2 (95–98%) and of CH_4 (65–70%) for the three most favorable cases, mentioned earlier. The observed activities were quite satisfactory, even if the decrement in catalytic activity observed in the back point at 650 °C can be significant for the partial deactivation of our catalysts. As it was stated in the Section 1, the lower conversion of CH_4 in comparison to that of CO_2 is quite characteristic of DMR and related to the RWGS parallel reaction occurring simultaneously [9]. It can be inferred from Figure 2B that samples obtained from EDTA and citrate precursors showed better stability under catalytic conditions in comparison to the other investigated $\text{NiO}_x/\text{CeO}_2$ samples.

The observed fact that the use of Ni precursors with strongly chelating ligands led to the higher activity of the final $\text{NiO}_x/\text{CeO}_2$ samples in DMR is not surprising and can be explained by an isolating effect of strongly complexing and spatially demanding ligands. The promoting effect of $[\text{Ni}(\text{EDTA})]^{2-}$ complexes as precursors of active sites in DMR has already been described [17,18,24]. The other authors suggested that the deposition of nickel–EDTA complexes may result in a stabilization of small crystallites or aggregates of nickel oxide on the catalyst surface, positively influencing CO_2 conversion in dry reforming with CH_4 [18]. Such an explanation can be adopted also in the case of our nickel complexes

with citrate or lactate ligands. Contrary to this, the observed high activity in DMR of the $\text{NiO}_x/\text{CeO}_2$ sample obtained from nitrate precursor seems to be a bit more specific case and will be discussed in terms of rather anomalous band gap value.

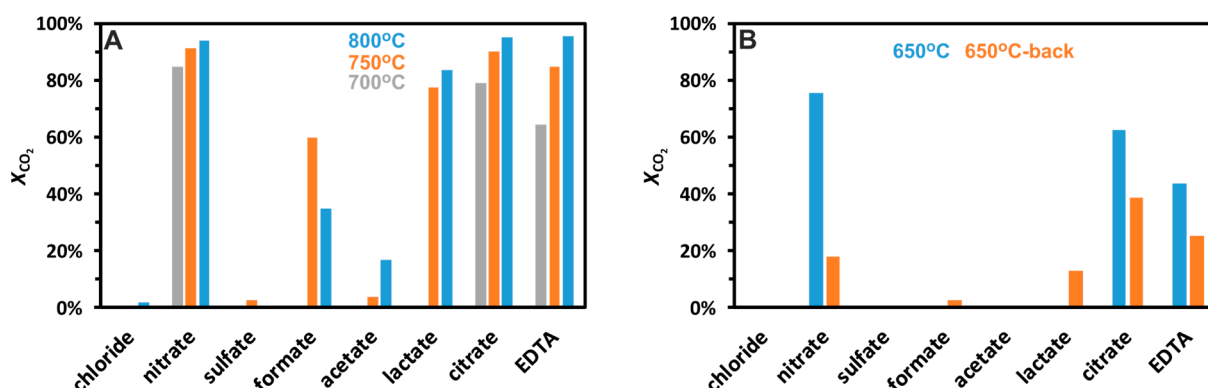


Figure 2. (A) Conversions of CO_2 at 700, 750, and 800 °C; (B) comparison of CO_2 conversions at 650 °C before and after a high-temperature test in DMR on $\text{NiO}_x/\text{CeO}_2$ catalysts prepared from various precursors of nickel active phase.

The catalytic results reported above confirmed the promising activity of the investigated series of $\text{NiO}_x/\text{CeO}_2\text{-ZrO}_2$ samples in dry reforming of methane, permitting to obtaining the $\text{H}_2:\text{CO}$ products ratio, which is the most suitable for synthetic fuel production. Moreover, the $\text{CeO}_2\text{-ZrO}_2$ supports obtained via continuous synthesis in a supercritical medium substantially enhanced the thermal stability of the studied catalysts, making them applicable in such demanding reactions as DMR [25,26]. Catalytic activity can be ascribed to nickel sites initially stabilized within oxide and hydroxide surface complexes.

3.2. Structural Properties

As it can be seen in Figure 3 below, XRD patterns collected for a series of investigated $\text{NiO}_x/\text{CeO}_2$ samples, calcined in air at 400 °C for 3 h, are quite similar and all are predominated by the Bragg reflections characteristic of well-crystalline CeO_2 support (Figure 3A). All visible diffraction maxima matched quite well to those registered for pure ceria of regular structure (ICDD: 01-081-0792). The diagnostic patterns, characteristic of CeO_2 , were identified at 2θ positions of ca. 28.5, 33.5, 48, and 57°, originating from (111), (200), (220), and (311) crystallographic planes, respectively. In all investigated cases, the support was a single phase of quite high homogeneity. It can be inferred from the recorded XRD patterns, that after deposition of Ni-containing active phases and after thermal treatment of our final samples at 400 °C, the structure of CeO_2 was well preserved. Even if a formation of a $\text{Ce}_{1-x}\text{Ni}_x\text{O}_{2-y}$ substitutional solid solution is potentially possible [27], no stabilization of Ni sites within the cationic sublattice of CeO_2 matrix can be suggested in the case of our calcined samples, based on the recorded XRD patterns. As the presence of the solid solution may influence the activity of the $\text{NiO}_x/\text{CeO}_2$ in DMR, the formation of $\text{Ce}_{1-x}\text{Ni}_x\text{O}_{2-y}$ should be a subject of further, more advanced structural studies.

Bragg reflections confirming the occurrence of a nanostructural three-dimensional (3D) NiO are absent or weak in the diagnostic 2θ region from 35 to 45°, as it can be seen in Figure 3B. Only in the case of the $\text{NiO}_x/\text{CeO}_2$ sample synthesized from nickel chloride as a precursor of the NiO active phase, more intense Bragg maxima can be distinctly observed in the recorded XRD pattern at 2θ ca. 37.5 and 43.5° (Figure 3B(a)). The traces of NiO nanocrystals were identified also in the cases of catalysts obtained from nitrate, citrate, formate, and acetate precursors. However, in all these samples the structure of NiO was just weakly crystalline or quite well dispersed. The use of such precursors as EDTA complexes, lactates, or sulfate of Ni(II) resulted in the $\text{NiO}_x/\text{CeO}_2$ samples, which did not exhibit any crystalline NiO phases manifested in the corresponding XRD patterns (Figure 3B(c,f,h)). This means that in the vast majority of the analyzed cases, a rather strong

interaction between surface nickel-containing entities and the CeO_2 support occurs. This fact was confirmed also by the other authors studying the $\text{Ni(111)/CeO}_{2-x}\text{(111)}$ system [28]. Moreover, they suggested that such strong interaction between nickel centers and the CeO_2 support can strongly determine C-H bond activation in CH_4 molecules during DMR at relatively low temperatures. Based on our XRD results, the high dispersion of nickel species on the surface of CeO_2 support can be confirmed.

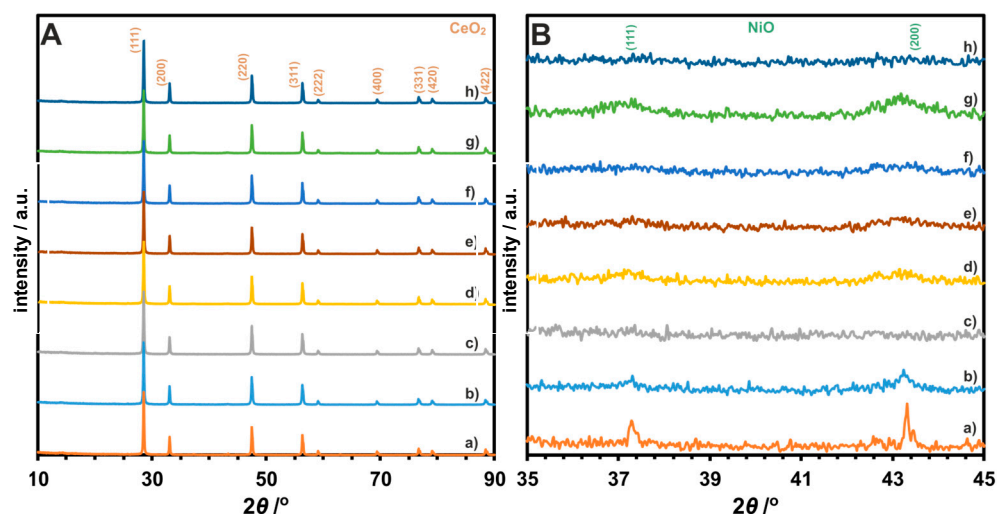


Figure 3. (A) XRD patterns of the investigated samples of $\text{NiO}_x/\text{CeO}_2$ synthesized from various nickel precursors; (B) the magnified 2θ range characteristic for NiO. Precursors: chloride (a), nitrate (b), sulfate (c), formate (d), acetate (e), lactate (f), citrate (g), EDTA complex (h) of nickel(II).

It is noteworthy that according to the literature [29–36], investigated nickel precursors can be analyzed in three main groups based on their decomposition temperatures: EDTA and citric complexes undergo thermal decomposition at a temperature range of 310–320 °C [29,30], nickel nitrate, lactate, formate, and acetate at distinctly lower temperatures from 238 °C to 250 °C [31–34], whereas NiCl_2 and NiSO_4 remain stable (neglecting dehydration of the corresponding hydrates) far above 400 °C. Thermal stability well corresponds to the ligation strengths/anion bonding characteristic of the investigated precursor. It also explains the observed catalytic behavior in DMR. Most probably, Ni active sites are strongly agglomerated in the case of catalysts obtained from NiCl_2 and NiSO_4 , and thus catalytically not very active. The evident presence of three-dimensional NiO was confirmed by XRD patterns. Decomposition of nickel nitrate, lactate, formate, and acetate is much easier in comparison to nickel(II) chloride or sulfate, but calcination of our $\text{NiO}_x/\text{CeO}_2$ catalysts at 400 °C for 3 h and their subsequent pre-reduction at 850 °C in the stream of 5% H_2 in Ar for 2 h was responsible for at least partial agglomeration of active sites. As it was stated earlier, the case of nitrate precursor is slightly different as the catalytic activity of the corresponding $\text{NiO}_x/\text{CeO}_2$ sample was slightly higher than expected, regarding the other sample obtained from precursors belonging to the same group. The most complex chelating ligands: citrates and EDTA (cf. Figure 1), seem to favor higher dispersion of nickel in the final $\text{NiO}_x/\text{CeO}_2$ catalysts and thus are beneficial for their activity in DMR. The corresponding precursor starts to be decomposed at temperatures high enough to facilitate partial isolation of nickel particles on the surface of the final catalysts.

Because the reactivity of the investigated $\text{NiO}_x/\text{CeO}_2$ samples in the DMR reaction is strongly dependent on their electronic properties, UV/Vis-DR spectra were recorded for all calcined $\text{NiO}_x/\text{ZrO}_2$ to provide deeper insight into essential functional features of the studied system. The deconvoluted electronic spectrum collected for the $\text{NiO}_x/\text{CeO}_2$ sample obtained from the nickel(II) nitrate precursor is presented as a representative example in Figure 4A. Both ligand-to-metal $\text{Ce}^{3+} \leftarrow \text{O}^{2-}$ and $\text{Ce}^{4+} \leftarrow \text{O}^{2-}$ charge transfer transitions at ca. 230 nm and 275 nm, respectively, as well as an interband transition (at ca. 340 nm)

were observed in the UV/Vis-DR spectra recorded for the investigated samples [37,38]. In the same spectrum of the $\text{NiO}_x/\text{CeO}_2$ sample ex nitrate, the transitions attributed to NiO can also be observed in all recorded spectra: d-d transitions between adjacent Ni^{2+} centers at ca. 400 nm, 3d-3d interatomic transitions at ca. 300 nm, ligand-to-metal $\text{Ni}^{2+} \leftarrow \text{O}^{2-}$ charge transfer transitions at ca. 270 nm, and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ transitions of Ni^{2+} centers in octahedral symmetry at ca. 725 nm [39–41]. The diffused band shifted in the discussed spectrum to higher wavelengths, ascribed to the transitions within the bulk of NiO, was more intense for Ni/CeO_2 than for other analyzed samples.

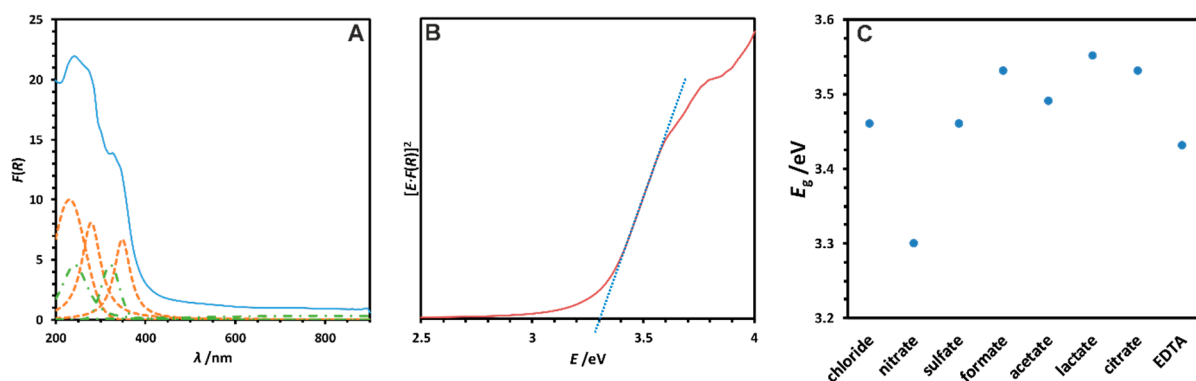


Figure 4. (A) Deconvoluted UV/Vis-DR spectrum of $\text{NiO}_x/\text{CeO}_2$ sample obtained from nickel(II) nitrate as a precursor; (B) the corresponding Tauc plot for this spectrum; (C) energy gap values for all investigated $\text{NiO}_x/\text{CeO}_2$ samples synthesized from various precursors.

Absorption edges determined for the investigated catalysts from their UV/Vis-DR spectra do not differ too much and can be localized at around 3.3 eV. Only in the case of the sample obtained with the use of nickel(II) nitrate absorption started a bit earlier (at about 3.0 eV) as it can be seen in Figure 4B above. The observed lack of substantial differences in absorption edges suggested that except for the case of the nitrate-originating sample, oxo-nickel species formed on ceria support are quite similar in size. The determined band gap values for Ni-containing species stabilized on CeO_2 support ranged from 3.30 to 3.55 eV (Figure 4C) and were comparable to or slightly lower than the values reported by other authors [42]. The band gap of bare NiO crystallites ranges from 3.4 to 4.0 eV, which originates from O 2p to Ni 3d electronic transitions [43]. The corresponding E_g value determined for the sample synthesized from nitrate precursor was distinctly lower (about 3.30 eV). This effect can explain the surprisingly high activity of this sample in DMR. Unfortunately, the stability of this sample was not as high (Figure 2B) as it was observed in the case of $\text{NiO}_x/\text{CeO}_2$ catalysts obtained from citrate or EDTA precursors. The anomalous E_g value determined in the case of the nitrate-originating $\text{NiO}_x/\text{CeO}_2$ sample can be a consequence of a modification of ceria support by NO_x liberated during the thermal decomposition of $\text{Ni}(\text{NO}_3)_2$ precursor [44]. Partial oxidation of the ceria surface by NO_x can in turn change the interactions between CeO_2 support and the deposited oxo-nickel species. Such changes can manifest themselves in the lower value of E_g .

Catalytically relevant functional properties of the investigated $\text{NiO}_x/\text{CeO}_2$ samples revealed by UV/Vis-DR spectroscopy can be confronted with the reducibility of these catalysts studied by TPR. However, it has to be kept in mind that, contrary to information provided by UV/Vis-DR, TPR results reflect to a much higher extent the bulk properties of the studied samples than those characteristic of their surfaces. The TPR profiles collected for the most active and for the least active samples are presented in Figure 5 below.

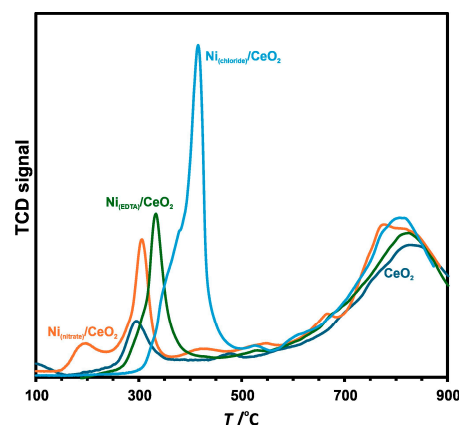


Figure 5. TPR profiles collected for CeO_2 support and for $\text{NiO}_x/\text{CeO}_2$ samples, which were the most active (ex nitrate and ex EDTA complexes of Ni(II)) and the least active (ex chloride) in DMR.

Analyzing the reduction temperatures of both support and the selected $\text{NiO}_x/\text{CeO}_2$ samples, which exhibited the highest and the lowest catalytic activity in DMR, it was clear that the bulk of CeO_2 is reducible at much higher temperatures (above 500 °C) than the ceria-supported nickel-containing samples. Moreover, the $\text{NiO}_x/\text{CeO}_2$ samples ex nitrate and ex EDTA complexes of Ni(II), which exhibited the most promising catalytic activity in DMR, were much more easily reducible than that (ex chloride), showing the lowest catalytic activity. It is thus evident that, not surprisingly, the catalytic activity of the investigated $\text{NiO}_x/\text{CeO}_2$ catalysts correlated with the reducibility of nickel entities. The effect of precursors has also been well-pronounced, reflecting differences in nickel speciation. The $\text{NiO}_x/\text{CeO}_2$ sample synthesized from nitrate precursor showed two reduction steps, corresponding to the maxima in the recorded thermogram at about 190 °C and 300 °C, whereas that ex EDTA complexes of Ni(II)—just one maximum at 330 °C. The $\text{NiO}_x/\text{CeO}_2$ sample ex chloride gave rise to a strongly asymmetric reduction maximum of around 400 °C, typical of the reduction of bulky NiO to metallic nickel [45].

The observed multistep reduction of CeO_2 support was well described in the literature as typical of this oxide [46]. The reduction maxima visible in the thermogram below 500 °C (one more intense at ca. 290 °C and another weaker at ca. 485 °C) can be attributed to the reduction of Ce^{4+} to Ce^{3+} centers in various surface surroundings, whereas the broad maximum around ca. 800 °C corresponds to bulk reduction as it was mentioned earlier. The low-temperature reduction maximum visible in the thermogram of $\text{NiO}_x/\text{CeO}_2$ ex nitrate can be attributed to the strongly dispersed NiO entities, which are able to be partially incorporated in the subsurface region of CeO_2 support, most probably forming Ni-O-Ce groups of higher oxygen mobility [47,48]. Whereas the maxima at about 300–330 °C visible in the TPR profiles of both $\text{NiO}_x/\text{CeO}_2$ ex nitrate and ex EDTA complexes of Ni(II) can be attributed to NiO reduction in smaller crystallites [47,48]. As confirmed by XRD, more bulky 3D nanocrystals of NiO stabilized on CeO_2 in the case of $\text{NiO}_x/\text{CeO}_2$ sample ex chloride were reduced at even higher temperatures, i.e., around 400 °C [45,47].

It can be inferred, based on the TPR results reported above, that the nature of the used precursor strongly influences NiO_x speciation over ceria support, altering mainly dispersion and agglomeration of the NiO entities. In the case of $\text{NiO}_x/\text{CeO}_2$ sample ex nitrate, the highest dispersion and rather strong interaction with CeO_2 (including partial incorporation of nickel in the subsurface region) resulted in the easy reduction of nickel, confirming its high reactivity, which also manifested itself in the DMR.

3.3. Textural Properties

The specific surface area of the parent CeO_2 support, determined by the BET method, was found to be rather low and equal to 5.37 m²/g. It increased after the deposition of nickel, reaching SSAs from 7.26 m²/g for the EDTA complex of nickel(II) as a precursor to

27.10 m²/g for nickel(II) chloride as an active phase precursor. Surface areas determined for all synthesized samples have been summarized in Table 1 below.

Table 1. Morphological parameters determined for investigated samples: BET surface areas, total pore volumes, and average pore diameters.

Sample/Ni Precursor	SSA/m ² g ^{−1}	V _{pore} /cm ³ g ^{−1}	d _{pore} /Å
Nitrate	6.01	0.019	127.91
EDTA	7.26	0.032	175.91
Formate	9.61	0.027	112.77
Sulfate	9.63	0.029	119.85
Acetate	9.84	0.032	130.38
Lactate	10.47	0.032	121.60
Citrate	13.78	0.036	103.48
Chloride	27.09	0.041	61.32

An evident increase in the determined SSA values correlates to some extent with the formation of three-dimensional NiO nanocrystallites on the CeO₂ surface. Another correlation observed is with changes in the porous structure of our NiO_x/CeO₂ catalysts. The presence of the largest pores (av. of 175.91 Å in diameter) was confirmed in the case of nickel complexes with EDTA as ligands, which were used as a nickel precursor. Not surprisingly, the corresponding NiO_x/CeO₂ catalyst exhibited just a weakly developed surface area. Contrary to this, the catalyst synthesized ex NiCl₂ as nickel precursor of the highest SSA, showed the lowest pore diameter (av. 61.32 Å). As mentioned earlier, the case of the NiO_x/CeO₂ sample synthesized from nitrate is quite peculiar. For this system, the low specific surface area is accompanied by the occurrence of relatively large pores, but at the same time, pore volume is the lowest. It is however worth mentioning, that the reported average pore diameters cannot be considered as a fully informative measure of the porosity. A more in-depth analysis of pore size distributions confirmed that for all analyzed samples strongly polymodal mesopore structure can be observed. All range of mesoporosity is covered. The differences between the studied NiO_x/CeO₂ samples manifested themselves in specific mesopore distribution. And so, in all samples, the narrow mesopores of ca. 20–30 Å and of 33–45 Å in diameter were detected. In the case of catalysts ex acetate, formate, sulfate, and citrate of Ni(II) the pores of about 60 Å have also been detected. The presence of mesopores of ca. 80–100 Å was confirmed in the case of catalysts ex lactate, formate, sulfate, and acetate of Ni(II). Pores larger than 100 Å were typical of NiO_x/CeO₂ samples obtained from lactate, formate, sulfate, citrate, nitrate, and EDTA complexes of Ni(II) as precursors of the catalytically active phase. Only in the case of NiO_x/CeO₂ with deposited Ni-containing phase ex chloride, the mesopores larger than 100 Å were not observed. Contrary to this, in the case of the catalyst, where EDTA complexes of Ni(II) were used as an active phase precursor, the pores of diameters exceeding 100 Å were mainly present. Both latter facts remain in agreement with other parameters reported in Table 1. The pore structure of the NiO_x/CeO₂ sample synthesized from nitrate was rather specific and strongly different from those typical of all remaining samples. In the diameter ranges 55–90 Å and 100–400 Å a continuum of not very abundant mesopores was identified. It is thus obvious that the nature of the used precursor influences the textural properties of the final NiO_x/CeO₂ catalysts. The mesoporous character of the studied samples can be also confirmed by the N₂ adsorption–desorption isotherms presented in Figure 6 below.

Rather narrow sigmoidal hysteresis loops of H3 type are characteristic of all analyzed samples. The narrowest shape was observed in the case of NiO_x/CeO₂ sample ex chloride as active phase precursor (Figure 6h). This type of N₂ adsorption–desorption curve is usually observed in the case of non-rigid aggregates of plate-like particles with a grooved-pore network consisting of macropores that are not completely filled with adsorbate [49]. The adsorption branch of the loop resembles a type II isotherm (according to IUPAC classification) and the lower limit of the desorption branch is located at the cavitation-induced p/p₀ [50]. The average size of CeO₂ crystallites, estimated from XRD patterns, was

equal to 43.3 ± 2.1 nm and practically did not change after impregnation with precursors of nickel. Average diameters of NiO nanocrystallites ranged from 10.9 ± 1.4 nm in the case of NiO_x/CeO₂ catalyst obtained by CeO₂ impregnation with citrate nickel(II) complex to 73 ± 16 nm in the case of catalyst obtained by impregnation of ceria support with NiCl₂ as nickel precursor.

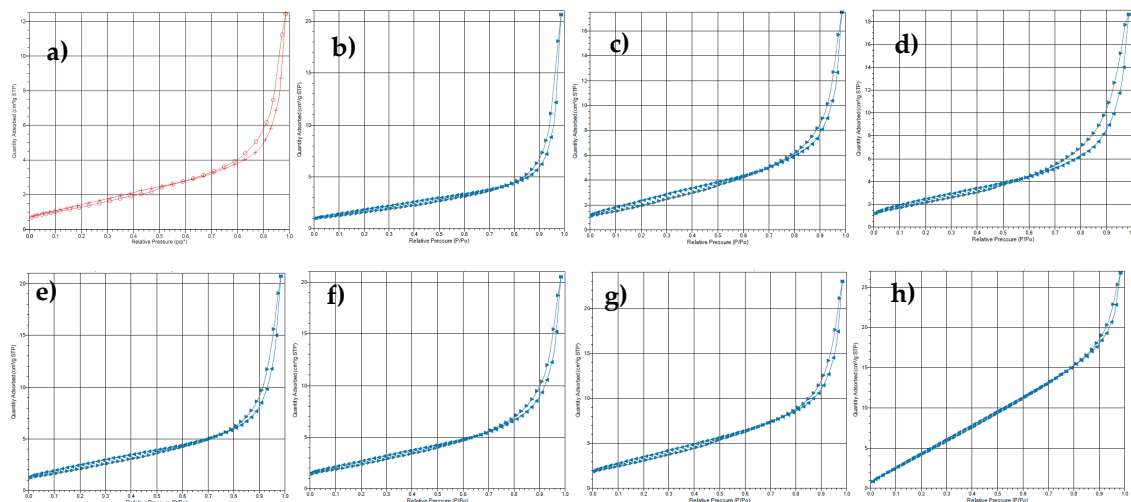


Figure 6. N₂ adsorption-desorption isotherms measured for the investigated samples of NiO_x/CeO₂ synthesized from various nickel precursors: nitrate (a), EDTA complex (b), formate (c), sulfate (d), acetate (e), lactate (f), citrate (g), chloride (h) of nickel(II).

SEM images of fresh catalysts (Figure 7) suggested rather strong agglomeration of the individual crystallites to form much larger polyhedral slightly elongated grains, partially sharp-angled with visible tiny plates in some cases. The progress of agglomeration was evidently non-uniform and strongly depended on the kind of nickel precursor. That remains in good agreement with the textural studies described above.

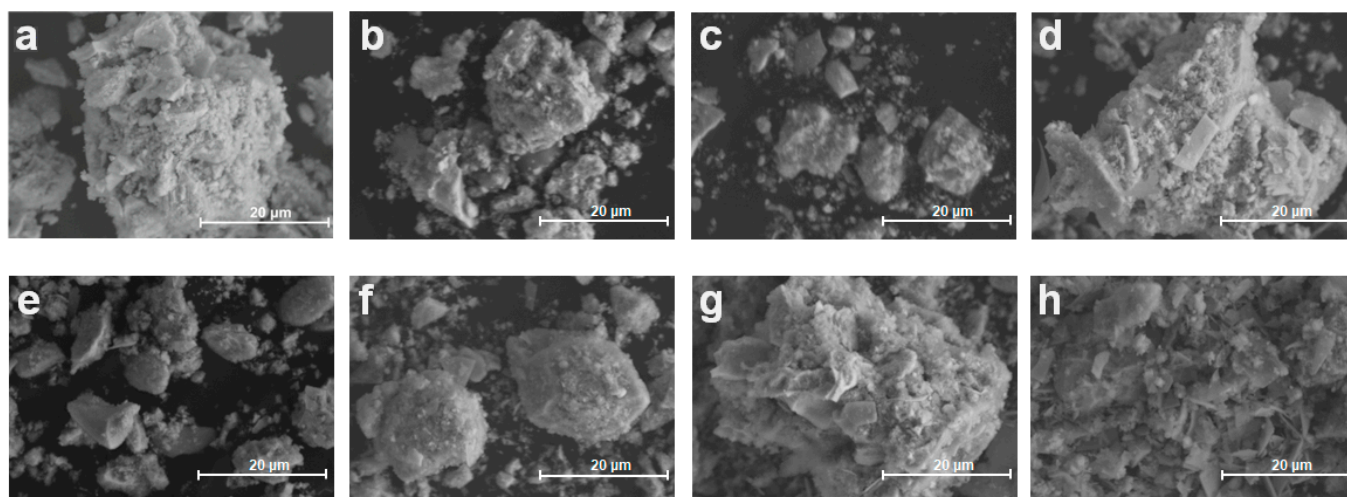


Figure 7. Selected SEM images of the investigated samples of NiO_x/CeO₂ synthesized from various nickel precursors: nitrate (a), EDTA-complex (b), formate (c), sulfate (d), acetate (e), lactate (f), citrate (g), chloride (h) of nickel(II).

The effect of the precursor was visible also in grain morphology and grain size distribution. And so, in the case of NiO_x/CeO₂ ex NiCl₂ as a precursor, a strong agglomeration makes it difficult to localize all edges of the individual grains (Figure 7h). The agglomerates were not transformed by liberation of gaseous products of decomposition during the thermal treatment of precursors, thus individual plates of ca. 2 nm are visible. Even if

the observed material was relatively dense and quite compact, the profiles of plate-like grains remained well visible. Such morphology corresponds well to a relatively high SSA value and to the other textural parameters reported above (*cf.* Table 1). Plate-like grains were visible also in the case of catalyst ex nickel(II) citrate as a precursor (Figure 7g). The morphological characteristics of this sample were however different from that described in the previous case. Citrate precursor facilitates the formation of plate-like grains coexisting with bigger, strongly transformed particles of $\text{NiO}_x/\text{CeO}_2$. These plates resembled initial structures protruding from the centers of those bigger grains. Most probably citrates as strong ligands are able to prevent some parts of the precursor material from fast thermal decomposition and some internal fragments were not transformed at the same time as the external parts. The grain size distribution was rather high in this case, and numerous small grains, of sizes far below $10\ \mu\text{m}$, were identified together with the larger grains of even $25\text{--}30\ \mu\text{m}$ in diameter. The coexistence of numerous small grains with individual relatively big, transformed ones was typical also for the remaining samples. In the case of $\text{NiO}_x/\text{CeO}_2$ catalysts ex acetates even the single grains of $90\text{--}100\ \mu\text{m}$ in size, with oval traces of decomposition can be observed. In the cases of catalysts ex sulfate or EDTA complexes of Ni(II) the transformed crystalline grains exposed not only smoothed edges but also many sharp-edged grains can be observed independently on their sizes. It is noteworthy, that in the case of $\text{NiO}_x/\text{CeO}_2$ synthesized from EDTA complexes of Ni(II) as precursors, the most fragmented grains (of even $3\text{--}5\ \mu\text{m}$ in size) were observed, which explains the highest porosity of that sample. As it can be inferred from SEM images recorded for $\text{NiO}_x/\text{CeO}_2$ samples after catalytic tests in DMR (not shown here), besides partial sintering, there were no significant changes in the grain morphology. For the most active samples characteristic forms of deposited carbonaceous residuals can be observed, morphologically similar to those described in more detail in our earlier paper [16]. One of the representative examples is the carbon deposit visible in the SEM image taken for the $\text{NiO}_x/\text{CeO}_2$ sample ex citrate, presented below (Figure 8A). As it can be inferred from the EDX profiles (Figure 8B,C), carbon deposits were non-uniformly distributed on the catalyst grain surface. There is no doubt that such a high content of carbon deposits can be responsible for DMR catalyst deactivation at temperatures above $600\ ^\circ\text{C}$.

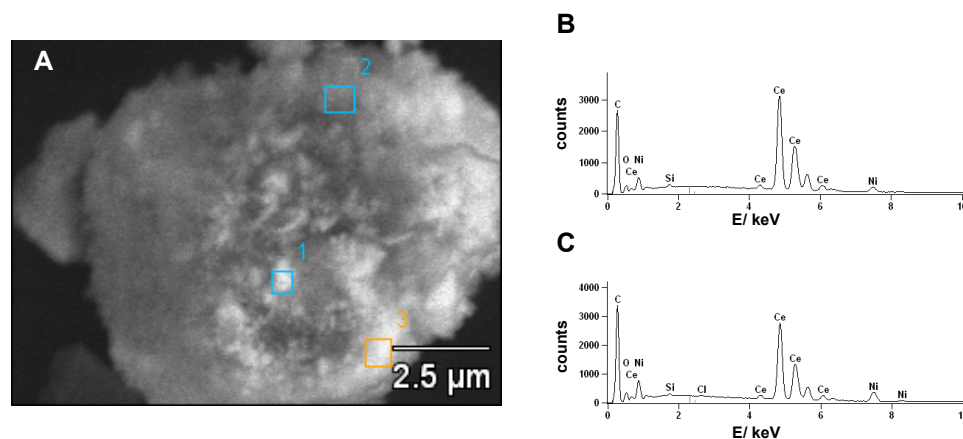


Figure 8. The selected SEM image of the $\text{NiO}_x/\text{CeO}_2$ sample synthesized ex citrate after catalytic test in DMR (A) with indicated analytic areas 1 and 2, showing the presence of increased carbon contents as it can be inferred from the corresponding EDX profiles (B and C, respectively). (In area 3 visible in the image carbon content was lower, EDX profile not shown).

4. Conclusions

The results reported for a series of $\text{NiO}_x/\text{CeO}_2$ catalysts, containing 3 wt. % of Ni and obtained by dry impregnation of ceria support with aqueous solutions of various nickel(II)-containing precursors: (i) simple inorganic salts: nitrate, sulfate, chloride), (ii) organic acid salts: acetate, formate, lactate and (iii) chelates: citrate, EDTA complexes of Ni(II) clearly confirmed that structural, textural and functional properties of our samples depend on the

nature of the used precursor. Due to the higher stability of the parent nickel(II) complexes and the resulting better dispersion of nickel and suitable morphological properties, the synthesis of NiO_x/CeO₂ catalysts from nickel(II) precursors with chelating ligands can be more beneficial the use of such systems in DMR. The obtained results showed also that nickel(II) nitrate as a precursor of NiO_x/CeO₂ catalyst can also boost its activity in DMR most probably due to the high reducibility confirmed by TPR and the observed distinct lowering in the band gap value. These effects can be associated with the partial oxidation of the ceria surface by NO_x liberated during precursor decomposition and with subsequent modification of the intimate interactions of the nickel species with the CeO₂ support.

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