Structural, Textural, and Catalytic Properties of Ni-Ce$_x$Zr$_{1-x}$O$_2$ Catalysts for Methane Dry Reforming Prepared by Continuous Synthesis in Supercritical Isopropanol

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Received: 12 May 2020; Accepted: 15 July 2020; Published: 20 July 2020

Abstract: A series of 5%Ni-Ce$_x$Zr$_{1-x}$O$_2$ ($x = 0.3, 0.5, 0.7$) catalysts has been prepared via one-pot solvothermal continuous synthesis in supercritical isopropanol and incipient wetness impregnation of Ce$_x$Zr$_{1-x}$O$_2$ obtained by the same route. The textural, structural, red-ox, and catalytic properties in methane dry reforming (MDR) of Ni-modified Ce-Zr oxides synthesized by two routes have been compared. It was shown by XRD, TEM, and Raman spectroscopy that the method of Ni introduction does not affect the phase composition of the catalysts, but determines the dispersion of NiO. Despite a high dispersion of NiO and near-uniform distribution of Ni within Ce-Zr particles observed for the one-pot catalysts, they have shown a lower activity and stability in MDR as compared with impregnated ones. This is a result of a low Ni concentration in the surface layer due to segregation of Ce and decoration of nickel nanoparticles with support species.

Keywords: methane dry reforming; Ce-Zr oxide; synthesis in supercritical isopropanol; Ni loading

1. Introduction

The carbon dioxide reforming of methane-generating synthesis gas has now attracted considerable attention as the environmental friendly process transforming undesirable greenhouse gases into syngas [1]. Ni-based catalysts, due to their high activity and low cost, are very promising for the practical use. However, the major problem of nickel nanoparticles deposited on traditional supports is rapid deactivation caused by Ni sintering and coke formation [2]. CeO$_2$-based supports are considered as the promising ones for Ni-based MDR catalysts, because of their ability to store and release oxygen that prevents coke poisoning of Ni nanoparticles [3–13]. It is known that oxygen vacancies and mobile surface/subsurface lattice oxygen provide the activation of CO$_2$ and carbon oxidation near/at the metal-support interface, respectively. Besides this, a strong interaction of Ni with CeO$_2$-based supports ensures high Ni dispersion that helps to enhance the catalytic activity and resistance to coking [6,11,13]. Compared to CeO$_2$ itself, mixed Ce-Zr oxides show a higher thermal stability, improved oxygen mobility and better catalytic performance [3–5,7,9].
The performance of Ni-Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} catalysts in MDR depends on the methods of their synthesis: impregnation of supports [5,7,9,10] or one-pot routes (co-precipitation [4,7,8], sol-gel [3]), which affect Ni interaction with oxide matrix, its dispersion, and, to a large extent, the features of Ce-Zr oxides [3–13]. The MDR activity and stability of Ni/\text{Ce}_{0.75}\text{Zr}_{0.25}O\textsubscript{2} catalysts prepared by impregnation and co-precipitation with or without the surfactant (CTAB) have been studied elsewhere [4]. For the co-precipitated catalysts, Ni cations are embedded into the lattice of \text{Ce}_{0.75}\text{Zr}_{0.25}O\textsubscript{2} that leads to a stronger interaction of nickel species with the support and higher nickel dispersion in comparison with the impregnated catalysts. In addition, the large specific surface area and pore volume of the surfactant-assisted co-precipitated catalyst provide its highest activity [4]. Kumar et al. studied Ni-containing catalysts obtained by impregnation of Ce\textsubscript{y}Zr\textsubscript{1-x}O\textsubscript{2} solid solutions \((x = 0.4 – 0.92)\), which have been prepared by co-precipitation using alcosol or the surfactant CTAB [9]. Testing in the low-temperature MDR has revealed that the catalysts prepared with CTAB are very active and stable because of a higher dispersion of Ni species and enhanced reducibility of the supports [9]. In contrast, 5%\text{Ni}–\text{Ce}_{0.6}\text{Zr}_{0.4}O\textsubscript{2} catalyst prepared by impregnation of the surfactant-assisted precipitated support is not active in MDR, as has been reported in the recent work by Wolfbeisser [7]. This result has been explained by the inaccessibility of Ni particles due to their encapsulation by ceria–zirconia species after reduction at 600 °C, as revealed by TEM and H\textsubscript{2} chemisorption.

The dependence of MDR performance of Ni–Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} on the composition of Ce–Zr–O solid solution has been reported in a number of works but obtained results and their interpretation differ considerably [3,5,7,8,10]. The study of 5%\text{Ni}–\text{Ce}_{x}\text{Zr}_{1-x}O\textsubscript{2} with \(x\) varied from 0.28 to 0.75 shows superior MDR activity and a high coke resistance of zirconium-rich 5%\text{Ni}–\text{Ce}_{0.28}\text{Zr}_{0.72}O\textsubscript{2} catalyst [5]. The amount and type of coke formed in the course of MDR were not straightforwardly related to the activity but obviously depended on the Ce/Zr ratio. On the contrary, the remarkable performance of a Ce-rich \text{Ni}/\text{Ce}_{0.8}\text{Zr}_{0.2}O\textsubscript{2} sample and a low activity or fast deactivation of Ni supported on \text{Ce}_{0.5}\text{Zr}_{0.5}O\textsubscript{2} and \text{Ce}_{0.2}\text{Zr}_{0.8}O\textsubscript{2} carriers were observed in [8,10]. Makri et al. studied the carbon formation pathways and carbon reactivity during MDR over 5%\text{Ni}–\text{Ce}_{0.8}\text{Zr}_{0.2}O\textsubscript{2} and 5%\text{Ni}–\text{Ce}_{0.5}\text{Zr}_{0.5}O\textsubscript{2} catalysts using temperature-programmed methods and transient isotopic experiments [10]. The Ce-rich catalyst was found to be more active and selective despite a lower oxygen capacity. The authors have underlined that the rate of oxygen transfer from the support towards the Ni-support interface is more important parameter than the oxygen storage capacity itself. Roh et al. explained the better performance of co-precipitated Ni–\text{Ce}_{0.8}\text{Zr}_{0.2}O\textsubscript{2} by a proximate contact between finely dispersed Ni and support particles [8]. On the other hand, \text{Ni}/\text{Ce}_{0.6}\text{Zr}_{0.4}O\textsubscript{2} was considered as the most active MDR catalyst due to the ability of the Ce–Zr support to provide better transfer of oxygen species to Ni nanoparticles, thus accelerating the removal of carbon [9].

It is well known that the Zr content strongly affect the structure of Ce–Zr mixed oxides. Only a cubic fluorite phase is detected in the Ce-rich samples, while three tetragonal phases \((t, t', t'')\) can form at intermediate Zr concentrations [14,15]. Except for the composition, the structural and morphological features of Ce\textsubscript{y}Zr\textsubscript{1-x}O\textsubscript{2} nanoparticles are determined by their synthesis method [16]. Mixed CeO\textsubscript{2}–ZrO\textsubscript{2} systems can be prepared using various methods including co-precipitation [4,5], sol-gel [3], microemulsion [17], high energy ball milling [18], and synthesis in supercritical fluids (SCS) [19–30]. The last one is highly attractive due to its usability and high productivity especially in a continuous mode.

Supercritical (SC) and near-critical (NC) fluids exhibit unique properties, which can be tuned by the reaction temperature and pressure. Along with these parameters, the morphology, crystallinity, dispersion of cerium and zirconium oxides, as well as their solid solutions prepared using SC fluids depend on the process mode (batch or continuous), nature of SC media (for example, water or alcohols), presence of complexing agents, heating rate, and reaction time [19–30].

The synthesis of CeO\textsubscript{2} and Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} nanoparticles using NC and SC water was presented in a number of articles [20–25]. It was shown that the rapid reaction kinetics in SC water makes possible the preparation of oxide nanoparticles using continuous process, which is easily scalable.
and attractive for industry [20,22–25]. The formation of highly crystallized oxide nanoparticles in hydrothermal conditions occurs at relatively low temperatures and does not require calcination that allows preparation of highly dispersed CeO₂ and CeₓZr₁₋ₓO₂ [22]. Some authors pointed out a higher specific surface area and thermal stability of samples produced by hydrothermal SCS in comparison with those synthesized by conventional co-precipitation method [23,24].

The ligand-assisted hydro- and solvothermal synthesis was developed to produce surface-modified ceria and Ce-Zr mixed oxides. The interaction between the surface hydroxyl groups and organic molecules results in a high dispersion of oxide nanoparticles in organic media and unusual morphology of individual crystals or secondary aggregates [25–28]. Except this, the usage of surface modifier leads to decrease in the particle size because of the inhibition of crystal growth [25,27].

Some reports suggest that alcohols can act as not only a reaction media, but also as ligand molecules modifying the surface with carboxylate-, alkoxide-, and alkyl- groups [26,29]. The solvothermal continuous synthesis (T = 300 °C, p = 24.5 MPa) of CeO₂ nanocrystals with different crystal size and textural properties was reported by Słostowski and co-workers [29,30]. Primary particles of CeO₂ (3 – 7 nm) aggregated in spherical agglomerates (20 – 100 nm) have demonstrated two types of thermal behavior depending on the alcohol used (MeOH, EtOH, PrOH, i-PrOH, ButOH, PentOH, or HexOH). First, a significant drop in the specific surface area and an increase in the crystallite size due to a thermal treatment are observed, if alcohol had nC ≤ 3. When alcohol with nC = 4 – 6 is used, CeO₂ nanoparticles show an increase in the specific surface area (up to 190 m²/g) and retention of crystallite size. The authors have concluded that the thermal resistance of CeO₂ samples depends on the thermal stability of organic grafts provided by different alcohols.

It has been demonstrated in our previous papers that solvothermal continuous synthesis using SC-i-PrOH along with a complexing agent allows to obtain homogeneous CeₓZr₁₋ₓO solid solutions, which provide the high MDR activity and stability of Ni/CeₓZr₁₋ₓO catalysts prepared by impregnation [31,32]. In the present work, for the first time, we have realized the one-pot solvothermal continuous synthesis of Ni-Ce-Zr-O oxides as precursors of the MDR catalysts. CeₓZr₁₋ₓO₂ and 5%Ni-CeₓZr₁₋ₓO with the different Ce/Zr ratio were prepared and characterized by the complex of physical-chemical methods. The textural, structural, red-ox, and catalytic properties of the Ni-modified Ce-Zr oxides obtained by one-pot route and impregnation technique were studied. The influence of the preparation method on the physicochemical properties of Ni-CeₓZr₁₋ₓO₂ and their catalytic performance in MDR has been discussed.

2. Materials and Methods

CeₓZr₁₋ₓO₂ and 5%Ni-CeₓZr₁₋ₓO catalysts were prepared by the solvothermal continuous synthesis using SC-i-PrOH along with acetylacetone as a complexing agent, which was added into the Zr solution at the 2:1 molar ratio to Zr. Zr(OBu)₄ (Alfa Aesar, 80% solution in n-butanol) and Ce(NO₃)₃·6H₂O (Vector, pure for analysis grade) i-propanol solutions, were used as Zr and Ce precursors. The mixture of Ce and Zr precursor’s solutions was fed into a U-shaped reactor (l = 75 cm, inner d = 4 mm) at a rate of 5 mL/min along with i-PrOH preheated to 150 °C, which flow rate was 8 mL/min. For one-pot synthesis of NiCeZrO samples, the required amount of Ni(NO₃)₂·6H₂O (Vector, pure for analysis) was additionally dissolved in the Ce(NO₃)₃ solution. The synthesis of CeₓZr₁₋ₓO₂ and NiCeZrO one-pot catalysts was carried out at 400 °C under a pressure of 120–130 bar using an installation described elsewhere [33]. The solid product separated from a mother liquid by decantation was dried and calcined at 600 °C for 2 h to obtain samples marked as CeₓZr₁₋ₓ or Ni-CeₓZr₁₋ₓ.op. Along with one-pot NiCeZrO samples, Ni was supported on Ce-Zr oxides by a wet impregnation using an aqueous solution of Ni(NO₃)₂. The obtained catalysts dried and calcined at 600 °C were denoted as Ni-CeₓZr₁₋ₓ.im.

XRD patterns of the samples were recorded on a D8 Advance diffractometer (Bruker, Germany) in the 2θ angle range of 20 – 85 ° using the CuKα radiation. The data were collected in a step-scanning mode with a step of 0.05 ° and a step-counting time of 3 s. In order to analyze the phase composition
of complex oxides, the full-profile analysis was done using the software TOPAS (Bruker, Germany). At first, the lattice constants for each phase contained in the samples have been refined to determine the unit cell volume. The chemical composition of the phases was evaluated from the literature data on the dependence of the cell volume versus the Ce content [14,15]. Then, we fixed the occupancies of Ce and Zr atoms in TOPAS to determine a weight ratio of two or three phases. The average particle sizes of nickel oxide were estimated by the Selyakov–Scherrer equation from the integral broadening of the most intensive (200) peak.

Raman spectra were recorded on a LabRAM HR Evolution spectrometer (Horiba, Japan) in the backscattering configuration excited by 488 nm line of an Ar-ion laser.

The texture of Ce$_x$Zr$_{1-x}$O$_2$ or Ni-Ce$_x$Zr$_{1-x}$O$_{0.5}$ samples was studied by low-temperature N$_2$ adsorption technique using an ASAP-2400 instrument (Micromeritics, USA). Prior to analysis, the samples were degassed at 150 °C under vacuum for 16 h. The micropore volume was determined by t-plot analysis. The mean pore size was evaluated as 4V/A. The specific surface area of Ni-Ce$_x$Zr$_{1-x}$im catalysts was estimated with a SORBI N.4.1 apparatus by the four-point BET method. Prior to measurements, samples were pretreated at 200 °C for 1 h in vacuum.

The TEM-EDX studies were performed using a JEM-2010 instrument (JEOL Ltd., Japan) operated at acceleration voltage of 200 kV and lattice resolution of 0.14 nm. The samples were prepared by depositing drops of the powders dispersed in ethanol onto copper–carbon grids. EDX mappings and line scan spectra were provided using a JEM-2200FS microscope (JEOL Ltd., Japan).

X-ray photoelectron spectroscopy (XPS) study was carried out with a spectrometer from SPECS Surface Nano Analysis GmbH (Germany) using the monochromatic AlKα radiation. The charge correction was performed by setting the Ce3d$_{3/2}$-u” peak at 916.7 eV. The samples were analyzed in the calcined and reduced state. After ex-situ reduction at 500 °C, they were transferred to the analysis chamber under an ambient atmosphere. The relative element concentrations were determined from the integral intensities of the core-level spectra using the cross-sections according to Scofield [34]. For the detailed analysis, the spectra were fitted into several peaks after the background subtraction by the Shirley method. The fitted procedure was performed using the CasaXPS software.

The reducibility of catalysts was studied by H$_2$-temperature-programmed reduction (TPR). The sample (200 mg) was heated at a rate of 10 °C/min to 900 °C in an installation equipped with a thermal conductivity detector under a H$_2$ (10%)-Ar mixture with a flow of 40 mL/min. To analyze the TPR data, the Asymmetric Gauss Decomposition method (AGDM) was applied.

The catalytic performance in MDR was studied in a conventional fixed-bed quartz microreactor in the feed of 5% CO$_2$+5% CH$_4$ (He – balance) at the contact time of 7.5 ms and 700 °C. All tests were conducted for 3 h. Before the reaction, 15–20 mg of the catalyst (depending on its poured bulk density) was pretreated in-situ at 600 °C for 30 min in the feed of 10% O$_2$ in He. Due to a fast in-situ NiO reduction in the reaction media at 650 °C [30], the pretreatment in H$_2$ flow was not required. The reaction products were analyzed at each 30 min using a Test-201 gas analyzer (Boner, Russia) equipped with optical, IR, and electrochemical sensors.

### 3. Results

#### 3.1. Textural Properties of Supports and Catalysts

The N$_2$ adsorption and desorption isotherms for Ce$_x$Zr$_{1-x}$O$_2$ supports and Ni-containing catalysts prepared by one-pot synthesis are shown in Figure 1. According to the classification adopted by the IUPAC, all isotherms belong to IV type with H3 shaped hysteresis loop at P/P$_0$ ~ 0.4–0.7, which is associated with open-ended mesopores [35]. A similar shape of isotherms was obtained for CeO$_2$ prepared by the continuous synthesis in supercritical C$_4$-C$_6$ alcohols, while only micro- or macropores were found when C$_1$, C$_3$, or iso-C$_3$ alcohols were used [30]. It is probable that the formation of mesopores in our Ce$_x$Zr$_{1-x}$O$_2$ mixed oxides prepared using supercritical isopropanol is due to the presence of zirconium butoxide and acetylacetone in the reaction solution.
The Ce0.2–0.9, three different tetragonal phases could be distinguished according to the literature: the stable phase t, metastable phase t’ obtained through a diffusionless transition, and t” - intermediate between t’ and cubic (c) phases [36]. The t” phase has the cubic cation sublattice, but the oxygen atoms are shifted from their ideal fluorite sites along c-axis [36].

The specific surface area (SSA), pore and micropore volume of Ce-Zr mixed oxides and Ni-Ce-Zr1-x op catalysts increase at increasing Ce content, whereas the mean pore size is not directly related to Ce/Zr ratio (Table 1). The introduction of Ni leads to decrease in SSA and pore volume of all samples. In the case of one-pot catalysts, this could be caused by the influence of nickel cations on the formation of Ce4+O2− framework during the SC-synthesis, while for the impregnated ones, this could be due to blocking a part of pores with NiO particles formed after calcination at 600 °C.

Table 1. Textural characteristics of the Ce0.5Zr0.5O2 and Ni-containing catalysts.

| Sample            | SSA (m² g⁻¹) | V_pore (cm³ g⁻¹) | V_micropore (cm³ g⁻¹) | D (nm) |
|-------------------|--------------|------------------|-----------------------|--------|
| Ce0.3Zr0.7        | 32           | 0.052            | 0.0013                | 9.9    |
| Ce0.5Zr0.5        | 42           | 0.047            | 0.0002                | 5.6    |
| Ce0.7Zr0.3        | 66           | 0.090            | 0.0033                | 7.3    |
| Ni-Ce0.3Zr0.7im   | 20           | n.d.             | n.d.                  | n.d.   |
| Ni-Ce0.5Zr0.3im   | 23           | n.d.             | n.d.                  | n.d.   |
| Ni-Ce0.3Zr0.7op   | 30           | 0.045            | 0.0011                | 9.8    |
| Ni-Ce0.5Zr0.5op   | 25           | 0.045            | 0.0011                | 16.9   |
| Ni-Ce0.7Zr0.3op   | 36           | 0.060            | 0.0018                | 8.9    |

1 Mean mean pore size.

3.2. Structural Properties of Supports and Catalysts

XRD data for the initial Ce₅₀₇Zr₀₅₀₋ₒ₂ supports with a different Ce/Zr ratio are presented in Table 2 and Figure 2. XRD patterns of all Ce-Zr oxides show rather broad reflections typical for the fluorite-like structure [15,22]. The positions of reflections shift to lower angles at increasing Ce content due to a larger size of Ce⁴⁺ cation (ionic radius r = 0.97 Å) as compared with that of Zr⁴⁺ (r = 0.84 Å). For Ce₅₀₋ₓZrₓO₂ solid solutions with x = 0.2–0.9, three different tetragonal phases could be distinguished according to the literature: the stable phase t, metastable phase t’ obtained through a diffusionless transition, and t” - intermediate between t’ and cubic (c) phases [36]. The t” phase has the cubic cation sublattice, but the oxygen atoms are shifted from their ideal fluorite sites along c-axis [36].

The results of full-profile analysis presented in Table 2 have shown that only the Ce₀.₃Zr₀.₇ sample comprises a single phase solid solution of the stable tetragonal t structure with c/a’ equal to 1.015. The Ce₅₀₋ₓZrₓ samples with a larger Ce concentration along with a main tetragonal phase showing c/a’ = 1.005 contain admixtures of other phases. The Ce₀.₅Zr₀.₅ sample includes minor impurities of c and t phases enriched by Ce and Zr, respectively, while Ce₀.₇Zr₀.₃ contains the admixture phase
with composition close to pure CeO₂. The mean crystallite size of the CeₓZr₁₋ₓO₂ main phases was estimated to be 10–14 nm independent on their composition (Table 2).

### Table 2. Lattice parameters and phase composition of CeₓZr₁₋ₓO₂ and Ni-CeₓZr₁₋ₓO₂op samples.

| Sample      | a (Å)    | c (Å)    | c/a ¹ | V    | D (nm) | Ni(Ce) ² | W ³ (%) |
|-------------|----------|----------|-------|------|--------|----------|---------|
| Ce₀.₃Zr₀.₇ | 3.686(7) | 5.291(1) | 1.015 | 71.9 | 14     | 0.34     | 100     |
| Ce₀.₅Zr₀.₅ | 3.754(1) | 5.335(2) | 1.005 | 75.19| 14     | 0.59     | 93      |
| Ce₀.₇Zr₀.₃ | 3.674(3) | 5.272(1) | 1.014 | 71.16| 10     | 0.28     | 4       |
| Ni-Ce₀.₃Zr₀.₇op | 3.780(1) | 5.372(2) | 1.005 | 76.75| 14     | 0.71     | 86      |
| Ni-Ce₀.₅Zr₀.₅op | 3.748(1) | 5.326(1) | 1.005 | 74.8 | 14     | 0.56     | 98      |
| Ni-Ce₀.₇Zr₀.₃op | 3.78(2)  | 5.36(7)  | 1.003 | 76.6 | 14     | 0.70     | 86      |

¹ a·√2; ² Ce occupancy in CeO₂–ZrO₂ oxide; ³ phase content.

![Figure 2](image.png)

**Figure 2.** XRD patterns of CeZrO supports (a) and NiCeZrO catalysts prepared by impregnation (b) and one-pot method (c): 1—Ce₀.₃Zr₀.₇; 2—Ce₀.₅Zr₀.₅; 3—Ce₀.₇Zr₀.₃. #—reflections of NiO phase.

The XRD patterns of all catalysts are mainly similar to the patterns of CeₓZr₁₋ₓ supports showing the broad reflections of CeO₂–ZrO₂ complex oxides (Figure 2). The reflections of NiO have been observed only for the impregnated catalysts (Figure 2b). The size of NiO crystallites is within the value of 18–20 nm not depending on the support. The absence of NiO reflections in the case of catalysts prepared by the one-pot method evidences high NiO dispersion. The full-profile analysis of XRD patterns for Ni-CeₓZr₁₋ₓop catalysts has shown that their phase composition, like that of CeₓZr₁₋ₓ samples, depends on the Ce content (Table 2). Thus, only the tetragonal t phase is observed in Ni-Ce₀.₃Zr₀.₇op likewise for the pure Ce₀.₃Zr₀.₇, while for Ni-Ce₀.₅Zr₀.₅op and Ni-Ce₀.₇Zr₀.₃op admixtures of cubic phases enriched by Ce are present along with the main tetragonal phase.

It is known that the reflections broadening due to a high dispersion of CeₓZr₁₋ₓO₂ makes it difficult to distinguish between the cubic and metastable tetragonal phases [14]. In this context, Raman spectroscopy characterizing the anion sublattice can be applied to get the additional information on the structural features of samples [14,37]. Raman spectra of CeₓZr₁₋ₓO₂ samples calcined at 600 °C are presented in Figure 3. In the spectrum of Ce₀.₃Zr₀.₇, five broad bands of a low intensity correspond to the stable tetragonal t phase [37,38] confirming the XRD data. A band at around 465 cm⁻¹ due to the
F$_2g$ Raman active mode is a characteristic of CeO$_2$ cubic fluorite-like structure [14,22,37]. The bands at ~300–308 cm$^{-1}$ and ~610 cm$^{-1}$ are usually observed in the spectra of CeO$_2$–ZrO$_2$ oxides with the t’ or t” metastable phases [22,37]. The band near 600–610 cm$^{-1}$ is associated with structure defects (oxygen vacancies) arising due to the substitution of Zr$^{4+}$ into the ceria lattice. A weak band in the region of 300–315 cm$^{-1}$ could be related to the displacement of the oxygen atoms from their ideal positions in the fluorite lattice [14,37]. Taking into account the axial ratio c/a’ $\approx$ 1 calculated from the XRD data, well-defined symmetric band at 466 cm$^{-1}$, and two broad bands of a low intensity at ~300–308 cm$^{-1}$ and ~610 cm$^{-1}$ observed in the spectra of Ce$_{0.5}$Zr$_{0.5}$ and Ce$_{0.7}$Zr$_{0.3}$, the t’ tetragonal phase should be considered as the main phase for both these samples. In contrast to Ce-Zr supports, the Raman spectra of Ni–Ce$_x$Zr$_{1-x}$-op catalysts with Ce occupancy $\geq$ 0.5 give evidence of a larger tetragonality of anion sublattice. Therefore, the t’ phase rather than the t” one prevails.

The morphology of Ni–Ce$_x$Zr$_{1-x}$O$_2$ catalysts is similar to the supports except for higher density of aggregates agglomerated into chains (Figure 4c). HRTEM-EDX and HAADF-STEM-EDX were used to study the influence of the preparation method on the distribution of elements in the fresh catalysts. The TEM images of Ni-Ce$_{0.3}$Zr$_{0.7}$ and Ni-Ce$_{0.7}$Zr$_{0.3}$ catalysts prepared by the one-pot method and by impregnation are presented in Figure 7 and in Supplementary Materials Figures S1–S3. In the case of impregnated catalysts, NiO particles (20–30 nm size) epitaxially bounded with the surface of the support (Figure 7a) as well as separate NiO particles (50–150 nm size) with (111) and (200) planes are clearly resolved (Figure 7c, Figure S1). The elemental mapping of Ni-Ce$_{0.5}$Zr$_{0.5}$im demonstrates non-uniform distribution of Ni (Figure 8) that is typical for other impregnated catalysts.

For the one-pot catalysts, the TEM images of NiO particles are fuzzy, and they do not enable to measure the NiO interplanar spacing (Figure 7b,d, Figure S2 and S3). However, EDX data evidencing the presence of Ni and the dark spots visible on the images obtained in the phase contrast mode allow us to suppose that NiO species are decorated by Ce$_x$Zr$_{1-x}$O$_2$ particles. The elemental mapping

![Figure 3. Raman spectra of Ce$_x$Zr$_{1-x}$O$_2$ supports and Ni-Ce$_x$Zr$_{1-x}$-op catalysts: 1—Ce$_{0.3}$Zr$_{0.7}$, 2—Ce$_{0.5}$Zr$_{0.5}$, 3—Ni-Ce$_{0.5}$Zr$_{0.5}$-op, 4—Ni-Ce$_{0.7}$Zr$_{0.3}$-op, and 5—Ce$_{0.7}$Zr$_{0.3}$.](image-url)
for Ni-Ce\textsubscript{0.7}Zr\textsubscript{0.3}op catalyst shows a high NiO dispersion and uniform distribution of Ni within the catalyst particles (Figure 9) that could be due to a strong interaction with the support and formation of Ni-Ce-Zr-O solid solution \[6,13,39,40\]. Moreover, the line scanning along Ni-Ce\textsubscript{0.7}Zr\textsubscript{0.3}op particles showing the decrease of Ni concentration in the surface layers confirms the decoration of NiO species (Figure 6d).

Figure 4. TEM images of Ce\textsubscript{0.3}Zr\textsubscript{0.7} support (a), Ni-Ce\textsubscript{0.3}Zr\textsubscript{0.7}im (b), and Ni-Ce\textsubscript{0.3}Zr\textsubscript{0.7}op (c) catalysts.

Figure 5. STEM-EDX images for Ce\textsubscript{x}Zr\textsubscript{1−x} supports: a—Ce\textsubscript{0.3}Zr\textsubscript{0.7}, b—Ce\textsubscript{0.7}Zr\textsubscript{0.3}.

Figure 6. The variation of Ce/Zr (a, b, c) and Ni/(Ce+Zr) concentration ratios (d) along different agglomerates (different colors of lines mean different aggregates) calculated from STEM-EDX data: a—Ce\textsubscript{0.3}Zr\textsubscript{0.7}, b—Ce\textsubscript{0.5}Zr\textsubscript{0.5}, c—Ce\textsubscript{0.7}Zr\textsubscript{0.3}, and d—Ni-Ce\textsubscript{0.7}Zr\textsubscript{0.3}op.

The morphology of Ni–Ce\textsubscript{x}Zr\textsubscript{1−x}O\textsubscript{2} catalysts is similar to the supports except for higher density of aggregates agglomerated into chains (Figure 4c). HRTEM-EDX and HAADF-STEM-EDX were
Figure 5. STEM-EDX images for CexZr1-x supports: a—Ce 0.3Zr0.7, b—Ce 0.7Zr0.3.

Figure 6. The variation of Ce/Zr (a, b, c) and Ni/(Ce+Zr) concentration ratios (d) along different agglomerates (different colors of lines mean different aggregates) calculated from STEM-EDX data: a—Ce0.3Zr0.7, b—Ce0.5Zr0.5, c—Ce0.7Zr0.3, and d—Ni-Ce0.7Zr0.3op.

Figure 7. TEM images of Ni-CexZr1-x catalysts prepared by one-pot method and by impregnation: (a) Ni-Ce0.3Zr0.7im, (b) Ni-Ce0.3Zr0.7op, (c) Ni-Ce0.7Zr0.3im, and (d) Ni-Ce0.7Zr0.3op.
The Ni2p3/2 peak at 854 eV and peaks of shake-up satellites at 856.0 and 860.9 eV (Figure 10). These satellites are observed (Figure 10). Such spectra are characteristic of Ni2+ in the state, which is different from that due to diffusion of Ni2+ cations into the fluorite lattice [46].

The spectra of reduced catalysts, except for Ni-Ce 0.7Zr0.3im, are similar to ones of the fresh catalysts. The Zr3d and Ce3d core-level spectra for all the catalysts are typical for Ce x Zr1-xO2 oxides (Figs. 42–44), while being absent for Ni0 and Ni3+ compounds [42]. The intensive satellite at 856.0 eV observed only in the spectra of NiO [44] evidences that in the case of impregnated catalysts nickel is mainly located in the NiO structure. In the spectra of the fresh catalysts prepared by the one-pot method, the main peak at 855.1–855.5 eV and the peak of shake-up satellite at 861.2–861.5 eV are observed (Figure 10). Such spectra are characteristic of Ni2+ in the state, which is different from

3.4. XPS Analysis

The Zr3d and Ce3d core-level spectra for all the catalysts are typical for Ce x Zr1-xO2 oxides (Figures S4, S5). The Ni2p3/2 spectra of the fresh catalysts prepared by impregnation show the main peak at 854 eV and peaks of shake-up satellites at 856.0 and 860.9 eV (Figure 10). These satellites caused by the multielectron processes [41] are typical for Ni2+ compounds, such as NiO, Ni(OH)2, NiSiO3, etc. [42–44], while being absent for Ni0 and Ni3+ compounds [42]. The intensive satellite at 856.0 eV observed only in the spectra of NiO [44] evidences that in the case of impregnated catalysts nickel is mainly located in the NiO structure. In the spectra of the fresh catalysts prepared by the one-pot method, the main peak at 855.1–855.5 eV and the peak of shake-up satellite at 861.2–861.5 eV are observed (Figure 10). Such spectra are characteristic of Ni2+ in the state, which is different from
that in NiO (Ni*). According to the literature, the peak at 855.5 eV could arise because of the strong interaction between NiO₅₆ species and the support [45] or the formation of Ni-Ce-Zr-O solid solution due to diffusion of Ni²⁺ cations into the fluorite lattice [46].

![Graph showing Ni₂p3/2 spectra for fresh and reduced catalysts](image)

**Figure 10.** Ni₂p₃/2 spectra for the fresh (a) and reduced (b) catalysts prepared by impregnation and one-pot method.

The spectra of reduced catalysts, except for Ni-Ce₀.7Zr₀.3im, are similar to ones of the fresh catalysts that could be a result of metallic Ni oxidation during its transfer through the air. The spectrum of Ni-Ce₀.7Zr₀.3im is complex evidencing the presence of both Ni²⁺ states: NiO and Ni* with the ratio of 80/20, respectively. The surface concentrations of elements calculated for Ni-containing samples using the XPS spectra are presented in Table 3. The surface of both fresh Ni-Ce₀.₃Zr₀.₇ catalysts is enriched with Zr (Ce/Zr < 0.43), while for Ni-Ce₀.₇Zr₀.₃ samples the Ce/Zr ratio show the surface enrichment with Ce (Ce/Zr > 2.33). Higher [Ni]/([Ce]+[Zr]) ratios were obtained for the impregnated catalysts in comparison with those for the one-pot ones (0.19 against 0.06–0.1) that shows decoration of NiO particles in accordance with TEM data. After the ex-situ reduction, the decrease in the surface Ni content and the Ce/Zr ratio is observed for Ni-Ce₀.₇Zr₀.₃im catalyst.

| Catalyst            | Ce/Zr | [Ni]/([Ce]+[Zr]) | C(NiO)/C(Ni*) |
|---------------------|-------|-----------------|---------------|
| Ni-Ce₀.₃Zr₀.₇im     | 0.33  | 0.19            | 100/0         |
| Ni-Ce₀.₇Zr₀.₇im reduced | 0.37 | 0.21            | 100/0         |
| Ni-Ce₀.₃Zr₀.₇op     | 0.22  | 0.06            | 0/100         |
| Ni-Ce₀.₇Zr₀.₇op reduced | 0.27 | 0.05            | 0/100         |
| Ni-Ce₀.₇Zr₀.₃im     | 2.7   | 0.19            | 100/0         |
| Ni-Ce₀.₇Zr₀.₃im reduced | 1.9  | 0.15            | 80/20         |
| Ni-Ce₀.₇Zr₀.₃op     | 3.4   | 0.10            | 0/100         |

**Table 3.** Surface characteristics of NiCeZrO catalysts.

3.5. **H₂-TPR Analysis**

H₂-TPR profiles and the values of hydrogen consumption for CeₓZr₁₋ₓO₂ samples are presented in Figure 11 and Table 4. The H₂-TPR curves of supports showing the intensive asymmetric peak below ~ 700 °C and the high-temperature broad profile are typical for CeₓZr₁₋ₓO₂ solid solutions prepared by different routes [3,4,47–51]. The low-temperature peak is usually assigned to the removal of the surface oxygen either regular (main peak) or defect one (a shoulder), while the high-temperature hydrogen consumption is related to reduction of bulk oxygen [3,47–51]. At increasing Ce content in the solid
solution, the position of the main peak is shifted to lower temperature showing the increase in oxygen reactivity. A high temperature peak in Ce0.7Zr0.3 profile could be related to the reduction of the cubic phase with a composition close to CeO2 contained in this sample according to the XRD data (Table 2).

Figure 11. Temperature-programmed reduction (TPR) curves of Ce-Zr oxides: (a) Ce0.3Zr0.7; (b) Ce0.5Zr0.5; (c) Ce0.7Zr0.3.

Table 4. H2 consumption during TPR calculated by asymmetric Gauss decomposition method (AGDM).

| Sample          | H2 Consumption (mmol·g⁻¹) |
|-----------------|---------------------------|
|                 | 100–300 °C | 300–700 °C | 100–700 °C | 100–900 °C | CeO2-ZrO2¹ |
| Ce0.3Zr0.7      | 0          | 0.93      | 0.93      | 1.07       |             |
| Ce0.5Zr0.5      | 0          | 0.94      | 0.94      | 1.40       |             |
| Ce0.7Zr0.3      | 0          | 0.70      | 0.70      | 1.40       |             |
| Ni-Ce0.3Zr0.7im | 0.08       | 1.59      | 1.67      | 1.83       | 0.98        |
| Ni-Ce0.5Zr0.5im | 0.08       | 1.46      | 1.75      | 2.04       | 1.19        |
| Ni-Ce0.7Zr0.3im | 0.25       | 1.41      | 1.66      | 2.22       | 1.37        |
| Ni-Ce0.3Zr0.7op | 0.24       | 1.59      | 1.83      | 2.09       | 1.24        |
| Ni-Ce0.5Zr0.5op | 0.68       | 1.23      | 1.9       | 2.38       | 1.53        |
| Ni-Ce0.7Zr0.3op | 0.64       | 0.97      | 1.7       | 2.17       | 1.32        |

¹ Total H2 (100–900 °C) = 0.85 mmol·g⁻¹ (NiO).

To analyze the TPR data, Asymmetric Gauss Decomposition method (AGDM) has been applied (Figure 11, Figure 12, Table 4). The calculated value of the total hydrogen consumption increases with the increase in Ce content but is not straightforwardly related to it: Ce0.3Zr0.7 < Ce0.5Zr0.5 = Ce0.7Zr0.3. The larger share of hydrogen consumed in the high-temperature region for Ce0.7Zr0.1 is due to the presence of a cubic phase with the composition close to CeO2 (Table 2).

The H2-TPR spectra of Ni-Ce0.3Zr1−x catalysts prepared both by impregnation and one-pot methods are presented in Figure 12. In general, the reduction of all the catalysts starts at a lower temperature, as compared with the pure supports due to hydrogen spillover from Ni species facilitating reduction of CeO2-ZrO2 solid solution [3–6,13]. The H2-TPR curves of the catalysts shift to lower temperatures at increasing Ce content similarly to the pure supports. The spectra of impregnated catalysts show a broad peak with a double maximum in the region of 314–435 °C (Figure 12). Besides, the shoulder at 460 °C and a broad peak at 820 °C are observed in the spectrum of Ni-Ce0.7Zr0.3im.

The spectra of one-pot catalysts differ from those of impregnated ones. For all one-pot samples, the first clearly marked narrow peak is shifted to lower temperature and the rather resolved peak with the maxima at ~ 500 °C appears (Figure 12). Further, AGDM analysis has been done to describe H2-TPR spectra of the catalysts (Figure 12, Table 4). All the peaks were grouped into three zones for more clear interpretation of TPR data [6,39]. Each zone is related to the predominant reduction of different species. The peaks at temperatures below 300 °C can be assigned to reduction of the surface oxygen species located on clusters of Ni and Ce cations [6,39,52,53], hydrogen consumed at 300–700 °C is related to the co-reduction of Ce0.5Zr1−xO2 near-surface layers, and NiO particles having different dispersion and degree of interaction with the support [5,6,39,53]. The reduction of the support
bulk occurs at the temperatures higher than 700 °C. In all cases, the sum of hydrogen consumed below 700 °C exceeds the value required for complete reduction of Ni2+ contained in the catalysts (0.85 mmol/gcat) (Table 4). In the region of 100–700 °C, the hydrogen consumption evaluated for the one-pot catalysts only slightly exceeds that obtained for the impregnated ones, but the distribution between deconvoluted peaks is various for different series. Thus, for all one-pot catalysts, the hydrogen consumption below 300 °C is substantially larger. Meanwhile, the deconvoluted peaks corresponding to hydrogen consumption in the region of 300–700 °C are shifted to the higher temperatures (500 °C) as compared with impregnated ones (415–470 °C) (Figure 12, Table 4). This indicates more difficult reduction of Ni2+ in the one-pot catalysts that could be explained by stronger interaction of Ni with the supports due to a high NiO dispersion and Ni incorporation into the bulk of Ce-Zr-O solution as XPS data have shown. The correlation between the existence of Ni* state (Figure 10) and more pronounced low-temperature reduction in the case of one-pot catalysts (Table 4) could be because of Ce-Zr-O lattice distortion and generation of additional oxygen vacancies, due to Ni incorporation into the support structure.

![TPR curves of Ni-CeₓZr₁₋ₓ catalysts](image)

**Figure 12.** TPR curves of Ni-CeₓZr₁₋ₓ catalysts: (a) Ni-Ce₀.3Zr₀.7im; (b) Ni-Ce₀.5Zr₀.5im; (c) Ni-Ce₀.7Zr₀.3im; (d) Ni-Ce₀.3Zr₀.7op; (e) Ni-Ce₀.5Zr₀.5op; (f) Ni-Ce₀.7Zr₀.3op.

### 3.6. Catalytic Properties

The time dependence of the CH₄ conversion and H₂/CO ratio over the impregnated and one-pot catalysts during MDR conducted at 700 °C are presented in Figure 13. In general, both of these parameters are higher over the impregnated catalysts as compared with the one-pot ones. However, for all samples, the CH₄ conversions are somewhat lower than those of CO₂, and the H₂/CO ratio is below 1 (0.8–0.88). The carbon balance is close to 100% in all cases.

All impregnated samples, except for Ni-Ce₀.3Zr₀.7im (Ce/Zr = 0.43) demonstrating a minor decrease in CH₄ conversion, show a stable catalytic behavior during all testing. In contrast, the activity of all one-pot samples decreases with time-on-stream by 6–10% depending on the support composition. Ni-Ce₀.5Zr₀.5op shows the minimal decrease in the methane conversion as compared with other one-pot samples (Figure 13b).

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which was synthesized via co-precipitation in the presence of CTAB as a surfactant.

In our case, the one-pot catalysts are active in MDR that evidences only a partial Ni partial decoration. Moreover, estimation of the efficient first-order rate constants $k$ for the initial activity of Ni-Ce$_0.3$Zr$_0.7$ catalysts prepared by both methods (Figure 13a) using well-known integral equation for the ideal plug-flow reactor $-\ln(1-x) = k \tau$ with a due regard for XPS estimation of the surface concentration of Ni (Table 3) and time $[29, 30]$ with a due regard for XPS estimation of the surface concentration of Ni (Table 3) and impregnated and one-pot samples, respectively (the detailed description of the estimation approach is given in Supplement). As follows from the comparison with H$_2$ TPR data (Table 4), this specific effect was observed for 5%Ni/Ce$_0.6$Zr$_0.4$O$_2$ catalyst prepared by impregnation of the mixed oxide, which was synthesized via co-precipitation in the presence of CTAB as a surfactant [7]. It was supposed that this catalyst was not active at all for MDR because of the encapsulation of Ni particles by Ce-Zr oxide particles. In our case, the one-pot catalysts are active in MDR that evidences only a partial Ni particle oxide particles. In our case, the one-pot catalysts are active in MDR that evidences only a partial Ni

It is known that concurrently with MDR (Equation (1)) such reactions as reverse water gas shift (RWGS) (Equation (2)), methane decomposition (Equation (3)), and Boudouard reaction or CO disproportionation (Equation (4)) could occur influencing H$_2$/CO ratio and carbon formation on the catalyst surface [2,3,7]. Among these processes only RWGS leads to a higher conversion of CO$_2$ as compared with that of CH$_4$ and also to H$_2$/CO ratio below 1. Therefore, our catalytic data demonstrating $X$(CH$_4$) < $X$(CO$_2$) and H$_2$/CO ratio lying in the range of 0.80–0.88 evidence the contribution of RWGS process in the overall reaction.

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2, \Delta H_0 = 248 \text{ kJ}\cdot\text{mol}^{-1} \tag{1}$$

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \Delta H_0 = 41 \text{ kJ}\cdot\text{mol}^{-1} \tag{2}$$

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2, \Delta H_0 = 75 \text{ kJ}\cdot\text{mol}^{-1} \tag{3}$$

$$2\text{CO} \rightarrow \text{C} + \text{CO}_2, \Delta H_0 = -172 \text{ kJ}\cdot\text{mol}^{-1} \tag{4}$$

It is suggested in the literature that MDR over Ni-Ce$_x$Zr$_{1-x}$O$_2$ occurs through a bifunctional mechanism when CH$_4$ is activated only on the Ni surface, while CO$_2$ activation proceeds also on oxygen vacancies at/near the Ni-support interface [2,10]. Thus, a high Ni dispersion as well as high oxygen mobility of the support enhance the catalytic activity and resistance to coking. In view of this, a lower activity and stability of the one-pot catalysts with a high dispersion and uniform distribution of Ni is an unexpected result. This could be due to decoration of Ni by support species resulting in a low Ni concentration in the surface layers as TEM and XPS data show (Figure 6d, Table 3). The same effect was observed for 5%Ni/Fe$_{0.6}$Zr$_{0.4}$O$_2$ catalyst prepared by impregnation of the mixed oxide, which was synthesized via co-precipitation in the presence of CTAB as a surfactant [7].

![Figure 13. Conversion of methane and H$_2$/CO during methane dry reforming (MDR) over Ni-Ce$_x$Zr$_{1-x}$O$_2$ catalysts: (a) Ni-Ce$_0.3$Zr$_0.7$; (b) Ni-Ce$_0.5$Zr$_0.5$; (c) Ni-Ce$_0.7$Zr$_0.3$; (d) dependence of initial (filled symbols) and final (empty symbols) CH$_4$ conversion on Ce/Zr ratio.](image-url)
decoration. Moreover, estimation of the efficient first-order rate constants k for the initial activity of Ni-Ce$_{0.3}$Zr$_{0.7}$ catalysts prepared by both methods (Figure 13a) using well-known integral equation for the ideal plug-flow reactor (-ln(1 - x) = kτ, where x is the CH$_4$ conversion, τ is the contact time [29,30] with a due regard for XPS estimation of the surface concentration of Ni (Table 3) and relating k to the unit of Ni surface revealed that it is equal to 47 s$^{-1}$m$^{-2}$Ni and 83 s$^{-1}$m$^{-2}$Ni for impregnated and one-pot samples, respectively (the detailed description of the estimation approach is given in Supplementary Materials). As follows from the comparison with H$_2$ TPR data (Table 4), this specific catalytic activity related to the unit of nickel surface perfectly correlates with the amount of reactive surface oxygen removed by H$_2$ at temperatures below 300 °C, the most probably associated with small surface clusters of Ni cations strongly interacting with support.

3.7. TEM Analysis of Used Catalysts

The TEM images of used catalysts are presented in Figure 14 and Figure S1–S3. For impregnated samples, Ce-Zr-O agglomerates observed in the initial catalysts break into smaller particles (Figure S1b,d). The well-resolved NiO particles of different size bounded with the support (Figure S1) or detached from the surface by carbon nanofibers are observed (Figure 14d). Such detachment during reduction by CH$_4$ or MDR is typical for the catalysts containing NiO particles slightly bounded with the support (Figure 7c). However, despite incapsulation a part of Ni particles with carbon (Figure S1h), the high MDR activity and stability of the impregnated catalysts is provided by small Ni particles strongly bound with the support surface and Ni species localized on the nanofibers, but not surrounded by them (Figure 14d). It was shown in previous studies [54–56] that the metal particles can keep the contact with reagents being on the top of filament thus ensuring the activity of the catalyst.

In the case of one-pot catalysts, Ce-Zr-O agglomerates are retained after their using in the reaction (Figure S2b and S3b). The micrographs of the spent one-pot samples show fuzzy images of Ni(NiO) particles that is due to the presence of thin well-resolved Ce-Zr-O species on their surface. Only amorphous carbon can be found on the surface of Ni-Ce$_{0.3}$Zr$_{0.7}$op, and no carbon deposition is observed in TEM images of Ni-Ce$_{0.7}$Zr$_{0.3}$op (Figure 14a,b, Figure S2 and S3). The absence of carbon nanotubes in the one-pot samples having very small Ni particles/surface clusters and a stronger metal–support interaction can be explained as follows. The oxygen mobility of ceria or Ce-Zr oxides is reported to play the main role in the elimination of CH$_x$ fragments by oxygen species originating from dissociation of CO$_2$. The CO$_2$ activation proceeds on Ni-support interface or nearby region of support and correlates with labile oxygen content of these catalysts [10,57]. To facilitate the removal of carbon species from the metal surface, the metal–support interface must be extended that can be provided by highly dispersed metal particles.

Thus, the TEM results (Figure 14, Figure S2 and S3) as well as TPO profiles (Figure S6) prove that the decrease in activity, which one-pot samples demonstrate with TOS, is not related to carbon accumulation. On the other hand, the migration of reduced ceria moieties onto the surface of Ni particles is widely known [47,58,59]. Due to the extremely small size of Ni particles in one-pot catalysts (fuzzy dark spots of 5–10 nm in TEM images), their surface could be easily covered by Ce-Zr-O support fragments in the conditions of MDR, as Figure 14b and Figure S2 and S3 demonstrate. Therefore, we suggest that a capping effect of the support is a main reason of one-pot catalysts deactivation.
was not influenced by the addition of Ni and synthesis method of the catalysts, while the latter
The admixtures of Ce- or Zr-enriched phases and the formation of Ce-Zr-O aggregates with Ce-enriched

Figure S6: TPO profiles for Ni-Ce$_{0.3}$Zr$_{0.7}$op.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/14/3728/s1,
Figure S1: TEM images of Ni-Ce$_{0.7}$Zr$_{0.3}$im catalyst before (a,c,e,g,i) and after MDR tests (b,d,f,h,j) at different magnification.
Figure S2: TEM images of Ni-Ce$_{0.7}$Zr$_{0.3}$op catalyst before (a,c,e,g) and after MDR tests (b,d,f,h).
Figure S3: TEM images of Ni-Ce$_{0.7}$Zr$_{0.3}$op catalyst before (a,c,e,g) and after MDR tests (b,d,f,h).
Figure S4: XRD spectra for the fresh catalysts prepared by impregnation and one-pot method, Figure S5: Ce 3d core-level spectra for the fresh catalysts prepared by impregnation and one-pot method, Figure S6: TPO profiles for Ni-Ce$_{0.3}$Zr$_{0.7}$op after MDR. Text describing approaches to estimation of specific rate constants.
Author Contributions: Conceptualization, S.P. and M.S.; methodology, M.S., S.P., and V.S.; validation, S.P., M.S., A.-C.R., and V.S.; formal analysis, A.B., S.C., A.I., and A.S.; investigation, A.B., S.C., A.I., V.R., and A.S.; data curation, V.K., V.A., and S.C.; writing—original draft preparation, S.P. and M.S.; visualization, A.B., V.R., V.K., and A.I.; supervision, A.-C.R. and V.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NICE project of ERA Net Rus Plus Call and the budget project for Boreskov Institute of Catalysis SB RAS, project no. 0303-2016-0013, registration no. AAAA-A17-117041110045-9.

Acknowledgments: The studies were conducted using the equipment of the Center of Collective Use «National Center of Catalyst Research» at the Boreskov Institute of Catalysis. The authors also acknowledge the resource center “VTAN” (Novosibirsk State University) for the access to experimental equipment (HRTEM).

Conflicts of Interest: The authors declare no conflict of interest.

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