Article

Effect of Support and Chelating Ligand on the Synthesis of Ni Catalysts with High Activity and Stability for CO₂ Methanation

Vetrivel Shanmugam *, Stefan Neuberg©, Ralf Zapf, Helmut Pennemann and Gunther Kolb *

Fraunhofer Institute of Microengineering and Microsystems, Division of Energy and Chemical Technology, Carl-Zeiss-Straße 18–20, 55129 Mainz, Germany; Stefan.Neuberg@imm.fraunhofer.de (S.N.); Ralf.Zapf@imm.fraunhofer.de (R.Z.); Helmut.Pennemann@imm.fraunhofer.de (H.P.)
* Correspondence: vetrivel.shanmugam@imm.fraunhofer.de (V.S.); gunther.kolb@imm.fraunhofer.de (G.K.);
Tel.: +49-6131-990-335 (V.S.); +49-6131-990-341 (G.K.)

Received: 6 March 2020; Accepted: 21 April 2020; Published: 1 May 2020

Abstract: Carbon dioxide methanation was carried out over Ni-based catalysts on different supports and chelating ligands in microreactors. To investigate the influence of chelating ligands and supports, the Ni catalysts were prepared using different support such as CeO₂, Al₂O₃, SiO₂, and SBA-15 by a citric acid (CA)-assisted impregnation method. The properties of the developed catalysts were studied by X-ray diffraction (XRD), Transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS) measurement, and the results show that the addition of CA in the impregnation solution improved the dispersion, refines the particle size, and enhanced the interaction of nickel species. The catalytic performance of the developed Ni catalysts were evaluated by CO₂ methanation in microreactors in the temperature range of 275 °C–375 °C under 12.5 bar pressure. All the catalysts exhibit high CO₂ conversion and extremely high selectivity to methane. However, the catalysts prepared via CA-assisted method exhibited excellent activity and stability, compared with Ni catalysts prepared by a conventional impregnation method, which could be attributed to highly dispersed nickel particles with strong metal–support interaction. The activity of CO₂ methanation followed the order of Ni/CeO₂-CA > Ni/SBA-15-CA > Ni/Al₂O₃-CA > Ni/SiO₂-CA > Ni/CeO₂. The Ni/CeO₂ catalysts have also been prepared using different chelating ligands such as ethylene glycol (EG), sucrose (S), oxalic acid (OA) and ethylene diamine tetra acidic acid (EDTA). Among the tested catalysts prepared with different support and chelating ligands, the Ni/CeO₂ catalyst prepared via CA-assisted method gave superior catalytic performance and it could attain 98.6% of CO₂ conversion and 99.7% methane selectivity at 325 °C. The partial reduction of the CeO₂ support generates more surface oxygen vacancies and results in a high CO₂ conversion and methane selectivity compared with other catalysts. The addition of CA as promoter favored the synergistic effect of Ni and support, which led to high dispersion, controls the size, and stabilizes the Ni nanoparticles. Furthermore, the Ni/CeO₂-CA catalyst yields high CO₂ conversion in a time-on-stream study due to the ability of preventing the carbon deposition and sintering of Ni particles under the applied reaction conditions. However, the Ni/Al₂O₃-CA and Ni/SBA-15-CA catalysts showed stable performance for 100 h of time on stream.

Keywords: ceria; chelating ligands; nickel; methanation; methane; microreactors

1. Introduction

Since the CO₂ emissions into the atmosphere cause greenhouse effects and hence global warming, its fixation has received much attention in recent years and has become a world challenge and
Priority [1]. Hence, intensive efforts have been devoted to mitigating CO₂ emissions through various strategies, such as CO₂ capture and storage [2,3] and chemical recycling [4-11]. Indeed, many industries consider CO₂ as a valuable resource rather than a waste [11-13]. However, it is necessary to find new paths enabling fuel production without releasing additional CO₂ in the atmosphere. In recent years, increased research efforts have been dedicated to the chemical conversion of CO₂ into useful chemicals such as methane, methanol, ethanol, and dimethyl ether through catalytic hydrogenation [14]. However, CO₂ methanation is considered to be one of the most promising ways of transforming CO₂ into methane, which is an important chemical feedstock as well as a fuel for power generation by gas turbines. However, the reaction temperature needs to be controlled since the exothermic character of methanation reaction makes the temperature control of methanation reactors difficult, especially under conditions of dynamic operation [15]. Plate heat-exchanger reactors offer benefits here of improved temperature control [16]. However, the amount of catalyst which can be incorporated into such a reactor is limited. Therefore, the development of catalysts of high activity is the key factor for the CO₂ methanation reaction at low temperature [17,18].

Though various catalysts have been developed for the catalytic hydrogenation of CO₂, especially metal catalysts containing Ru [19,20], Rh [21-23], Pd [24], Pt [25], and Ni [26-30] have been proved to have good catalytic activity in CO₂ methanation reaction. Among them, nickel-based catalysts have been widely investigated due to their high catalytic activity, high selectivity for methane, and relatively low cost [14,26,31-34]. Many researchers have reported that Ni catalysts were highly active for CO₂ methanation, including Ni/CeO₂-ZrO₂ [35-37], Ni/SiO₂ [31], and Ni/Al₂O₃ [15]. In general, most of the Ni-based catalysts were prepared by the conventional impregnation method, which has the advantages of a simple synthesis process, low cost, and an environmentally friendly procedure. However, large-size particles are usually formed through the traditional impregnation method, which leads to lower catalytic performance in the methanation reaction. Similarly, a strong metal-support interaction is also an important concern for Ni-based catalysts because the thermal sintering of metallic Ni active sites can easily take place under CO₂ methanation reaction conditions. In view of these challenges, preparing highly dispersed Ni catalyst on the supports with strong metal-support interaction can be considered to be the potential solution for effectively promoting the activity of CO₂ methanation, especially at low temperature [15]. Recent research shows that the addition of chelating ligands, for example citric acid (CA), enhances the promotion of the catalysts and resulted in the preparation of highly active Ni catalysts with small crystallite size and good dispersion [38,39]. Suárez-Toriello et al. [40] reported that the addition of CA to the impregnation solutions during the catalyst synthesis has led to a remarkable increased formation of the metal-support phase and as a result to increased catalytic activity. The Ni/SBA-15 catalyst prepared by the chelating ligand-assisted impregnation method yields the small size Ni particles and outstanding catalytic performance for CH₄ reforming with CO₂ [41]. In our previous work, we introduced sucrose as chelating ligand, which contributes majorly to the distribution of Ni species by preventing their sintering on SBA-15 silica support [42]. Therefore, size controlled and highly dispersed Ni crystallites with strong metal-support interaction need to be prepared for high CO₂ activation at low temperature.

It is also important to select the nature of support materials to improve the specific surface area of the active metal, reducibility of the catalyst, and dispersion of the active site, thereby affecting the catalytic performance of the CO₂ methanation reaction [43]. Since the morphology of the support has a significant influence in the catalytic properties, effective support with well-dispersed Ni particles must be prepared to meet these requirements. Alumina is known to be the most commonly employed support material due to its high thermal stability and strong resistance to attrition [44]. However, the resulting catalysts did not show superior catalytic stability especially at low reaction temperature mainly due to the sintering of Ni particles and deposition of carbon [45]. Indeed, nickel catalysts have been prepared on various supports such as Al₂O₃ [15,17,44], SiO₂ [46-49], MCM-41 [26], SBA-15 [27], ZrO₂ [28] and CeO₂ [29,32,50-52] and tested in methanation reaction. Among them, CeO₂ has recently emerged as the best support for metal-based catalysts and it has the capability of promoting the
dispersion of Ni species and change metal properties through strong metal–support interactions. Le et al. [53] also studied the CO\(_2\) methanation over Ni-based catalysts on some selected supports such as Al\(_2\)O\(_3\), SiO\(_2\), TiO\(_2\), CeO\(_2\), and ZrO\(_2\). Owing to its high oxygen storage capacity and thermal stability CeO\(_2\) could create the additional driving force for the CO\(_2\) conversion at low temperature [54].

Tada et al. [29] investigated the CO\(_2\) methanation over Ni catalysts loaded on different supports and found the following activity ranking: Ni/CeO\(_2\) > Ni/α-Al\(_2\)O\(_3\) > Ni/TiO\(_2\) > Ni/MgO. The formation of oxygen vacancies on the CeO\(_2\) support by the redox circulation existing in the Ce\(^{3+}\)/Ce\(^{4+}\) ion pairs can activate the CO\(_2\) molecules effectively to improve the CO\(_2\) methanation [55]. Although some reports are available on Ni-based catalysts for the methanation reaction, those catalyst had been prepared by conventional impregnation methods and poor stability of the catalysts was observed, which impaired their performance of the Ni-based catalyst at low temperatures due to the formation of mobile nickel sub-carbonyl, which has to be removed quickly to maintain the catalytic activity. Moreover, these investigations had been carried out in packed bed reactors, which have the drawback of poor heat and mass transfer. In this work, we prepared various metal oxide-supported Ni catalyst by the impregnation method modified with chelating ligands. The catalytic performance of these catalysts was investigated in CO\(_2\) methanation in microreactors and the results are presented.

2. Results and Discussion

2.1. Catalysts Characterization

X-ray diffraction was used to determine the crystalline structure of the developed catalysts and the results are shown in Figure 1. All the calcined samples exhibited the diffraction peaks at \(2\theta \approx 37.2^\circ\), 43.1°, 62.8°, 75.3° and 79.4°, which are attributed to (111), (200), (220), (311) and (222) facets of cubic crystalline structure of NiO, respectively [1,56]. However, the intensity of NiO peaks was too weak for the Ni/CeO\(_2\)-CA sample, while that can be highly visible in the other samples, indicating a high degree of metal dispersion over the support surface. The difference of the peak intensity can be attributed to the different size and morphology of NiO present on the different supports. It is reported that the relatively small particle size of highly dispersed NiO on the support may also lead to the weak intensity of diffraction peaks [57]. The average crystallite sizes of the NiO were estimated from the main peak of (200) plane using the Scherrer equation. The average crystallite sizes of NiO were determined for Ni/CeO\(_2\), Ni/CeO\(_2\)-CA, Ni/Al\(_2\)O\(_3\)-CA, Ni/SiO\(_2\)-CA and Ni/SBA-15-CA and their results presented in Table 1. Strong diffraction peaks appeared in the Ni/CeO\(_2\) and Ni/CeO\(_2\)-CA samples at \(2\theta \approx 28.3^\circ\), 33.1°, 47.2°, 56.2° and 79.0° corresponding to (111), (200), (220), (311) and (222), which are characteristic of the cubic fluorite structure of CeO\(_2\) [58]. Additional peaks appeared in Ni/Al\(_2\)O\(_3\)-CA samples at \(2\theta \approx 29.2^\circ\), 45.8° and 68.8° corresponding to (220), (400) and (440) diffractions of crystalline alumina [40]. Ni/SiO\(_2\)-CA and Ni/SBA-15-CA samples show no peaks corresponding to silica support due to amorphous nature of silica.

**Table 1. Structure parameters of different catalysts.**

| Catalysts   | \(S_{\text{BET}}\) (m\(^2\)/g\) | Crystallite Size of NiO from XRD (nm) | Crystallite Size of NiO from TEM (nm) |
|-------------|---------------------------------|--------------------------------------|--------------------------------------|
| Ni/CeO\(_2\) | 41                              | 10.8                                 | 10                                   |
| Ni/CeO\(_2\)-CA | 44                      | 5.8                                   | 6                                     |
| Ni/Al\(_2\)O\(_3\)-CA | 153                    | 7.4                                   | 8                                     |
| Ni/SiO\(_2\)-CA | 230                     | 6.4                                   | 7                                     |
| Ni/SBA-15-CA | 380                             | 4.9                                   | 4                                     |
Nitrogen adsorption-desorption isotherms of Ni/CeO$_2$-CA, Ni/Al$_2$O$_3$-CA, Ni/SiO$_2$-CA and Ni/SBA-15-CA are shown in Figure 2. The adsorption branches of isotherms for Ni/CeO$_2$-CA and Ni/SiO$_2$-CA resemble that of type V with H1 hysteresis loops and are associated with the existence of uniform pores with a narrow size distribution. The Ni/Al$_2$O$_3$-CA catalyst shows a type IV isotherm with H1 type hysteresis loops, suggesting there are mesopores in the sample. The Ni/SBA-15-CA catalyst also exhibited IV-type isotherms with a well-expressed H1-type hysteresis loop, which is corresponding to a well-developed mesoporous structure. However, this catalyst shows two hysteresis loops due to the presence of both cylindrical and ink-bottle shape pores. It is assumed that the pores were significantly blocked by nickel species during the impregnation procedure. The surface area obtained for Ni/CeO$_2$-CA, Ni/Al$_2$O$_3$-CA, Ni/SiO$_2$-CA and Ni/SBA-15-CA catalysts from the N$_2$ adsorption-desorption measurements and the results are presented in Table 1.
X-ray photoelectron spectroscopy (XPS) was used to investigate the nature and surface exposure of all the elements present in the developed catalysts. The oxidation states of Ni present on the support can be determined from the binding energy (BE) of Ni 2p XPS spectrum. As can be seen in Figure 3A, all the samples exhibited the Ni 2p3/2 BE between 855.2 and 855.7 eV along with the broad peak around 860.5 eV which are attributed to NiO species [38]. In case of the Ni/CeO2-CA, Ni/Al2O3-CA, Ni/SiO2-CA and Ni/SBA-15-CA catalysts, the main peak at 855.7 eV was slightly shifted to higher BE indicating that the nickel species might have strong interaction with the support. Figure 3B shows the XPS result of O 1s core electron levels for all the catalysts. The Ni/CeO2 catalyst exhibited the main peak at 529.1 eV with two shoulders at 530 eV and 531.1 eV implying the presence of different oxide species. The main peak appeared at 529.1 eV and the shoulder peak at 530 eV can be attributed to the lattice oxygen and weakly bonded oxygen species present in CeO2 [40]. The peak appearing at higher BE (531.1 eV) belongs to the surface absorbed oxygen. For the Ni/CeO2-CA sample similar observations indicate the combination of lattice oxygen and weakly bonded oxygen species and/or chemisorbed oxygen along with the shoulder peak (532.7 eV) corresponding to the adsorptive oxygen species present in this catalyst. The main peak appearing in the range between 530.5 eV and 532.2 eV for Ni/Al2O3-CA, Ni/SiO2-CA and Ni/SBA-15-CA samples could be attributed to adsorptive oxygen species, whereas the small peak at higher BE might be due the other oxygen species [39]. The presence of different oxygen species on all these supports due to their structure and chemical properties. The availability of high oxygen surface mobility by redox Ce4+/Ce3+ on CeO2 support could create more oxygen vacancies, which can enhance the catalytic reactions.

Figure 3. XPS (A) Ni 2p and (B) O 1s spectra of different catalysts.

TEM analysis was employed to investigate the distribution and size of NiO species, and the results are shown in Figure 4. The TEM images of Ni/CeO2-CA, Ni/Al2O3-CA, Ni/SiO2-CA and Ni/SBA-15-CA catalyst show that the small size NiO particles are well dispersed on the support. The average particle sizes of NiO nanoparticles are presented in Table 1 which was consistent with the particle sizes observed by X-ray diffraction (XRD). In the case of Ni/SBA-15-CA, the nickel particles arranged regularly in
the nanochannels of the mesoporous SBA-15 support with much smaller particle size, which has the advantages of enhance the resistance of sintering due to arising of confinement effect from the wall of mesoporous SBA-15 [22]. TEM image of Ni/CeO₂ catalyst prepared without CA shows that NiO particles of larger size (9 nm) are aggregated around the CeO₂ support (Figure S1). TEM-EELS images also confirm that the NiO particles are highly dispersed on the catalysts prepared by addition of CA (Figure 5) than on the Ni/CeO₂ catalyst prepared without CA (Figure 5A). The addition of CA as chelating ligand in the impregnation solution could form the chelated metal complexes and increase the viscosity of the solution, which prevents the particle aggregation and stabilizes the NiO species due to the presence of the steric hindrance effect [41]. This phenomenon proved that the presence of chelating ligand has increased the dispersion and controlled the size of the NiO particles. The TEM images of Ni/CeO₂ catalysts prepared with different chelating ligands such as sucrose, ethylene glycol, oxalic acid, and EDTA are presented in Figure S2. The Ni/CeO₂-S and Ni/CeO₂-OA catalysts show the uniform dispersion of NiO with average particle size of 8 nm, whereas the Ni/CeO₂-OA and Ni/CeO₂-EDTA catalysts possess the slight accretion of NiO with an average particle size of 11 nm.

Figure 4. TEM images of (A) Ni/CeO₂-CA, (B) Ni/Al₂O₃-CA (C) Ni/SiO₂-CA and (D) Ni/SBA-15-CA catalysts.
Figure 5. TEM-EELS images of (A) Ni/CeO₂, (B) Ni/CeO₂-CA, (C) Ni/Al₂O₃-CA, (D) Ni/SiO₂-CA, (E) Ni/SBA-15-CA and (F) spent Ni/CeO₂-CA catalysts.

2.2. Catalytic Performance Test

The effect of chelating ligand and different supports on the performance of the developed Ni-based catalysts was investigated for CO₂ methanation. The catalytic activity was tested under different reaction temperature on the catalytic conversion of CO₂ over Ni/CeO₂, Ni/CeO₂-CA, Ni/Al₂O₃-CA, Ni/SiO₂-CA and Ni/SBA-15-CA catalyst between 275 °C and 375 °C. All the catalysts were reduced with H₂ gas at 450 °C prior to the CO₂ methanation tests. Figure 6 displays the percentage of CO₂ conversion against the reaction temperature for all the catalysts. It can be seen that the CO₂ conversion increases with the reaction temperature gradually then reached a maximum value, except for the Ni/CeO₂-CA catalyst. It is worth mentioning that owing to thermodynamic limitations, no significant increase of the conversion could be observed above 375 °C with a maximal CO₂ conversion of 96.3% for all the catalysts. Methane was determined to be a major product for all the catalysts. In addition to methane, small quantities of carbon monoxide were also detected especially at low temperatures. Among all the tested catalysts, the Ni/CeO₂-CA catalyst exhibited the best CO₂ conversion of maximum 98.6% already at 325 °C when compared with the other catalysts. A further raise in temperature led to a slight decrease in CO₂ conversion due to the exothermicity of methanation reaction. Since the high temperature has a negative effect on CO₂ methanation reaction, 325 °C could be the optimum temperature to achieve maximum CO₂ conversion and high selectivity towards CH₄ for this catalyst under the conditions of this test. The Ni/CeO₂-CA catalyst yields highest CO₂ conversion of all samples at a low reaction temperature of 325 °C [34]. Among the catalysts investigated, the citric acid addition in Ni/CeO₂ catalyst preparation showed substantial improvement of the catalytic performance compared to the Ni/CeO₂ catalyst prepared without addition of CA. Apparently, the Ni/CeO₂-CA catalyst exhibited much higher CO₂ conversion than Ni/CeO₂. As confirmed by the TEM results (Figure 4), the Ni dispersion could be the critical factor to control the catalytic activity in these Ni catalysts. It implied that the addition of chelating ligand enhanced the dispersion of Ni species and control the particle size, resulting in more exposed active species, which was responsible for the superior catalytic activity [41]. The carboxylic groups of CA could deprotonate easily and generate the citrate ligands, which are capable of coordinating with nickel ions and prevents the aggregation of large-size Ni nanoparticles during the calcination process. Suárez-Toriello et al. [40] reported that the addition of CA drastically changed the chemical equilibria in the solution mixture and the deprotonation of the carboxylic acids...
groups increased the amount of citrate ligands, which is capable of forming Ni–citrate complexes. The catalytic performance of all the catalysts studied at different reaction temperatures is in the following order: Ni/CeO₂-CA > Ni/SBA-15-CA > Ni/Al₂O₃-CA > Ni/SiO₂-CA > Ni/CeO₂. As shown in Figure 6, ceria-supported Ni catalyst prepared by the CA modified method showed higher CO₂ conversion than Al₂O₃, SiO₂, and SBA-15-supported Ni catalysts. The higher catalytic activity of Ni/CeO₂-CA is associated with the medium basicity of CeO₂ support, compared to other supports used in this work, allowing stronger CO₂ adsorption. The adsorbed CO₂ on CeO₂ support can be reduced easily due to the sufficient amount of oxygen vacancies available on the CeO₂ support. Pan et al. [36] reported that Ce₀.₅Zr₀.₅O₂-supported Ni catalyst is highly active when compared with Ni/γ-Al₂O₃. Similarly, Tada et al. [29] investigated the catalytic performance of different supported Ni catalysts on CO₂ methanation and reported that the partial reduction of the CeO₂ surface, which was covered by CO₂-derived species are responsible to yield higher CO₂ conversion over Ni/CeO₂ compared with Ni/γ-Al₂O₃, Ni/TiO₂, and Ni/MgO. When compared with other supports the unique superiority of CeO₂ is that the existence of Ce³⁺/Ce⁴⁺ ion pairs on its surface can enhance the formation of the oxygen vacancies, which can promote the adsorption and activation of CO₂ [32,55]. The SBA-15-supported Ni catalyst with highest surface area of 380 m²/g showed however lower activity than Ni/CeO₂-CA with a lower surface area of 44 m²/g, indicating that the surface area of the developed catalyst has no significant effect on the catalytic activity. As seen in Figure 7, all the developed catalysts show high selectivity towards methane in the temperature range of 275–375 °C. Compared with Ni/CeO₂, Ni/CeO₂-CA exhibits higher selectivity towards methane. The maximum selectivity of methane was found to be 99.7% for Ni/CeO₂-CA.

| Temperature (°C) | Conversion of CO₂ (%) |
|------------------|-----------------------|
| 250              | Ni/CeO₂-CA            |
| 275              | Ni/Al₂O₃-CA           |
| 300              | Ni/SiO₂-CA            |
| 325              | Ni/SBA-15-CA          |
| 350              | Ni/CeO₂               |
| 375              | Equilibrium CO₂ curve |

Figure 6. Effect of temperature on CO₂ conversion over different catalysts: H₂:CO₂:CH₄ = 4:1:1, WHSV = 45 L/h g catalyst and pressure = 12.5 bar.
To investigate the influence of chelating ligands on catalytic performance, the methanation reaction was performed over Ni/CeO₂ catalysts prepared by using various chelating ligands such as sucrose (S), EG, OA, and EDTA and the obtained results are shown in Figure 8. The CO₂ conversion for Ni/CeO₂-S and Ni/CeO₂-EG increased with increasing reaction temperature up to 325 °C and remained then stable close to complete conversion with further increasing reaction temperature. The selectivity towards methane is very close to 100% for these catalysts at all reaction temperatures (Figure 8). Notably, the conversion of CO₂ and selectivity of methane was initially much lower and increased then with increasing reaction temperature for the Ni/CeO₂-OA and Ni/CeO₂-EDTA catalysts. Among the catalysts tested, Ni/CeO₂-S and Ni/CeO₂-EG exhibited much higher CO₂ conversions around 97.5% and 94.8%, respectively, at 325 °C. However, the CO₂ conversion obtained for these catalysts was slightly lower than for the Ni/CeO₂-CA (Figure 6). Ni/CeO₂-OA and Ni/CeO₂-EDTA catalysts showed poorer catalytic activity under the same conditions, indicating that the nature of chelating ligands had affected the dispersion of Ni species on the support which was confirmed by TEM measurement (Figure S2).

Figure 7. Effect of temperature on CH₄ selectivity over different catalysts: H₂:CO₂:CH₄ = 4:1:1, WHSV = 45 L/h g catalyst and pressure = 12.5 bar.

Figure 8. Cont.
Owing to the highly exothermic nature of CO$_2$ methanation, the development of Ni catalyst must be stable enough against the thermal sintering to avoid deactivation of the catalyst. The catalytic stability of the Ni/CeO$_2$-CA, Ni/SBA-15-CA, Ni/Al$_2$O$_3$-CA and Ni/SiO$_2$-CA catalysts was investigated for duration of 100 h at 325 °C. As shown in Figure 9, the Ni/CeO$_2$-CA catalyst exhibited highest CO$_2$ conversion. However, the conversion decreased slowly with time and ended up with a value of 85% CO$_2$ conversion after 100 h on stream. It is well known that the methanation catalysts are also subject to carbon deposition on the active sites of the Ni nanoparticles that leads the deactivation of the catalysts. To investigate the carbon deposition on these spent catalysts, TEM and Thermogravimetric analysis (TGA) were performed, and their results are presented in Figure 10. From TEM images, a thin layer of carbon was identified on the surface of these catalysts. However, the TGA result shows no weight loss curve of carbon. Therefore, carbon deposition seems to be very less and that could not be the main reason for the catalytic deactivation. The TEM-EELS image (Figure 5F) of spent Ni/CeO$_2$-CA catalyst confirms that the Ni particles were not much agglomerated under this reaction conditions. This result indicates that the Ni/CeO$_2$-CA catalyst presented comparatively better activity under this reaction conditions. As seen in Figure 8, Ni/Al$_2$O$_3$-CA and Ni/SBA-15-CA catalysts show considerably stable performance than Ni/CeO$_2$-CA catalyst for 100 h of time on stream. However, the overall CO$_2$ conversion was found to be maximum 70%, which is lower when compare with Ni/CeO$_2$-CA catalyst. The conversion over the Ni/SiO$_2$-CA decreased drastically with time on stream. According to TEM and TGA results, the Ni/Al$_2$O$_3$-CA and Ni/SBA-15-CA catalysts are resistant against high coke formation and shows stable performance which is attributed to the strong metal–support interaction and lower sintering under methanation reaction conditions, thereby leading to long-term catalytic stability.
The Ni catalysts supported on different supports such as CeO$_2$, Al$_2$O$_3$, SiO$_2$, and SBA-15 were prepared by a impregnation method modified with different chelating ligands such as CA, ethylene glycol (EG), sucrose (S), oxalic acid (OA) and EDTA. Ni(NO$_3$)$_2$·6H$_2$O was used as the metal oxide precursor and the commercial CeO$_2$ (99.9%, Sigma-Aldrich, Steinheim am Albuch, Germany), Al$_2$O$_3$ (99.99%, Sigma-Aldrich, Steinheim am Albuch, Germany) and SiO$_2$ (99.8%, Sigma-Aldrich, Steinheim am Albuch, Germany) were used as supports. The SBA-15 support was prepared by a method describing in the literature [42]. To prepare 20 wt. % Ni catalysts, 2.92 g of Ni(NO$_3$)$_2$·6H$_2$O and 2.89 g of citric acid (Ni:CA = 1:1.5 ratio) were dissolved in 20 ml of water. Then, 3 g of the support were added and then the mixtures were stirred at a constant speed for 5 h. The mixtures were dried at 80 °C for 6 h and 120 °C for 12 h. The brownish power was carbonized at 500 °C for 4 h in N$_2$ followed by calcination at the same temperature for 3 h in the presence of air. All other Ni catalysts on different supports were prepared using CA by fixing the molar ratio of Ni to CA to 1:1.5. Similarly, Ni/CeO$_2$ catalysts with different chelating ligands such as EG, S, OA, and EDTA were also prepared by following the same procedure with fixed molar ratio of Ni to chelating ligands to 1:1.5.

Figure 9. Stability test over different catalysts: Reaction temperature = 325 °C, H$_2$:CO$_2$:CH$_4$ = 4:1:1, WHSV = 45 L/h g catalyst and pressure = 12.5 bar.

Figure 10. TEM images of different spent (A) Ni/CeO$_2$-CA, (B) Ni/Al$_2$O$_3$-CA (C) Ni/SiO$_2$-CA and (D) Ni/SBA-15-CA catalysts (left) and TGA results of different spent catalysts (right).

3. Materials and Methods

3.1. Catalysts Preparation

The Ni catalysts supported on different supports such as CeO$_2$, Al$_2$O$_3$, SiO$_2$, and SBA-15 were used as supports. The SBA-15 support was prepared by a method modified with different chelating ligands.
To make the catalysts suspension to fill in the microreactors, 1.25 g of Polyvinyl alcohol (PVA) was dissolved in water under constant stirring at 65 °C for 3 h. Then, 2.5 g catalyst powder and 0.19 g of acetic acid was added under the same conditions and continued the stirring for another 3 h. After stirring the mixture for three days at room temperature a homogenous suspension was obtained, which was then filled in the microchannels of the microreactors and dried at room temperature and calcined at 450 °C for 6 h in air [59].

3.2. Catalysts Characterization

XRD patterns were recorded on a Stoe Stadi P diffractometer using Cu Kα 1 radiation from a sealed tube x-ray source operating at 40 kV and 30mA. N₂ adsorption-desorption isotherms of the developed catalysts were obtained from Sorptomatic 1900 analyzer. To remove the moistures the catalysts were degassed at 150 °C for a few hours before the measurement. Specific surface areas were obtained by the Brunauer–Emmett–Teller (BET) method in the relative pressure range of P/P₀ = 0.0–1.0. The surface nature of the developed catalysts was investigated by XPS using a multi-chamber Ultra high vacuum (UHV) system (PREVAC, Poland). The system equipped with a monochromated Al source (XM 650 X-ray monochromator) source and operated at 360 W. The constant pass energy of 200 eV was fixed to collect the survey scans. High–resolution scans of the separate regions were measured at 50 eV. The background pressure for ultra–high vacuum chamber was fixed as 5 × 10⁻⁸ mbar and the calibration was done at 284.7 eV by setting the position of the C1s carbon line. CasaXPS (ver. 2.3.16 PR 1.6) software was used to process the recorded spectra. A LIBRA 120 microscope was used to collect the TEM images by suspending a small amount of catalysts in ethanol/water and placed onto the copper grids. Thermogravimetric analysis was carried out in a Mettler Toledo, TGA/DSC 1100.

3.3. Catalytic Activity Measurements

The CO₂ methanation tests were carried out in a microchannel reactor in the temperature range between 275 °C and 375 °C. The reaction mixture of H₂:CO₂:CH₄ (molar ratio of 4:1:1) was introduced into the test microreactors through mass flow controllers. The flow rate of the reaction mixture was fixed to 45 L/h g catalyst and experiments were performed at a pressure of 12.5 bar. The sandwich type of three microchannel platelets of microreactors were coated with the developed Ni catalysts and subsequently sealed by laser welding along with inlet and outlet capillaries [60]. Before starting the experiment, the catalysts were reduced by passing H₂ gas at 400 °C for 2 h, then the microreactor was by-passed by reaction mixture until a stable feed composition were reached. The obtained product composition was analyzed by on–line Gas chromatography (GC, Agilent Technologies 7890A GC System).

4. Conclusions

In this work, Ni catalysts supported on different supports were prepared by chelating ligand-assisted impregnation method and their catalytic activity was investigated by CO₂ methanation at different temperatures. A CeO₂-supported Ni catalyst was determined to be the most active for CO₂ methanation compared with Ni catalysts supported on different support such as Al₂O₃, SiO₂, and SBA-15. The formation of chelated metal complexes by strong interaction of CA chelating ligand with nickel ions inhibited the accumulation of the nickel particles and contributed to the well-dispersed Ni particles. The Ni/CeO₂-CA catalyst exhibited the highest CO₂ conversion among all the catalysts with 99.7% of CH₄ selectivity. The higher catalytic performance was closely related to the enhanced metal–support interactions between Ni and Ce species, the size of Ni nanoparticles, and the synergistic effect of the nickel and ceria supports. Furthermore, the medium basicity of CeO₂ is beneficial for strong adsorption of CO₂ and resulted in high catalytic activity. In the stability test, the Ni/CeO₂-CA catalyst yields high CO₂ conversion even though there is slight deactivation during 100 h of time on stream. The CO₂ conversion was above 85% at the end of 100 h of time on stream. From the observed results, it can be concluded that ceria-supported Ni catalyst prepared via the citric acid-assisted method.
can be applied to keep the metal active at lower reaction temperatures in any other thermodynamically controlled exothermic reactions.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/5/493/s1, Figure S1: TEM image of Ni/CeO$_2$ catalysts and Figure S2: TEM image of (A) Ni/Fe$_2$O$_3$S and (B) Ni/Fe$_2$O$_3$-EG (C) Ni/Fe$_2$O$_3$-OA and (D) Ni/Fe$_2$O$_3$-EDTA catalysts.

**Author Contributions:** Conceptualization, V.S., H.P., G.K. and S.N.; methodology, V.S. and R.Z.; formal analysis, C.H.; investigation, VS.; writing—original draft preparation, VS.; writing—review and editing, VS. and G.K.; visualization, H.P.; supervision, H.P. and G.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

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

**References**

1. Ocampo, F.; Louis, B.; Kiwi-Minsker, L.; Roger, A.C. Effect of Ce/Zr composition and noble metal promotion on nickel based Ce$_x$Zr$_{1-x}$O$_2$ catalysts for carbon dioxide methanation. *Appl. Catal. A Gen.* 2011, 392, 36–44. [CrossRef]

2. Wu, Y.; Chan, C.W. A data analysis decision support system for the carbon dioxide capture process. *Expert Syst. Appl.* 2009, 36, 9949–9960. [CrossRef]

3. Walspurer, S.; Boels, L.; Cobden, P.D.; Eizinga, G.D.; Haij, W.G.; Van den Brink, R.W. The crucial role of the K$^+$–aluminium oxide interaction in K$^+$-promoted alumina- and hydrotalcite-based materials for CO$_2$ sorption at high temperatures. *ChemSusChem* 2008, 1, 643–650. [CrossRef] [PubMed]

4. Song, C. Global challenges and strategies for control, conversion and utilization of CO$_2$ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* 2006, 115, 2–32. [CrossRef]

5. Omae, I. Aspects of carbon dioxide utilization. *Catal. Today* 2006, 115, 33–52. [CrossRef]

6. Weatherbee, G.D.; Bartholomew, C.H. Hydrogenation of CO$_2$ on group VIII metals: I. Specific activity of NiSiO$_2$. *J. Catal.* 1981, 68, 67–76. [CrossRef]

7. Peebles, D.E.; Goodman, J.M.; White, J.M. Methanation of carbon dioxide on nickel (100) and the effects of surface modifiers. *J. Phys. Chem.* 1983, 87, 4378–4387. [CrossRef]

8. Olah, G.A.; Goeppert, A.; Prakash, G.K.S. Chemical recycling of carbon dioxide to methanol and dimethyl ether: From greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *J. Org. Chem.* 2009, 74, 487–498. [CrossRef] [PubMed]

9. Kilo, M.; Weigel, J.; Wokaun, A.; Koeppel, R.A.; Stoeckli, A.; Baiker, A. Effect of the addition of chromium and manganese oxides on structural and catalytic properties of copper/zirconia catalysts for the synthesis of methanol from carbon dioxide. *J. Mol. Catal. A* 1997, 126, 169–184. [CrossRef]

10. Melian-Cabrera, I.M.; Lopez Granados, M.; Fierro, J.L.G. Reverse topotactic transformation of a Cu–Zn–Al catalyst during wet Pd impregnation: Relevance for the performance in methanol synthesis from CO$_2$/H$_2$ mixtures. *J. Catal.* 2002, 210, 273–284. [CrossRef]

11. Olah, G.A.; Goeppert, A.; Prakash, G.K.S. *Beyond Oil and Gas: The Methanol Economy*; Wiley-VCH, Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006.

12. Centi, G.; Perathoner, S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal. Today* 2009, 148, 191–205. [CrossRef]

13. Ritter, S.K. What can we do with carbon dioxide. *Chem. Eng. News* 2007, 85, 11–17.

14. Ashok, J.; Ang, M.L.; Kawi, S. Enhanced activity of CO$_2$ methanation over Ni/Fe$_2$O$_3$-ZrO$_2$ catalysts: Influence of preparation methods. *Catal. Today* 2017, 281, 304–311. [CrossRef]

15. Rahmani, S.; Rezaei, M.; Meshkani, F. Preparation of highly active nickel catalysts supported on mesoporous nanocrystalline g-Al$_2$O$_3$ for CO$_2$ methanation. *J. Ind. Eng. Chem.* 2014, 20, 346–1352. [CrossRef]

16. Neuberg, S.; Pennemann, H.; Shanmugam, V.; Thiermann, R.; Zapf, R.; Gac, W.; Greluk, M.; Zawadski, W.; Kolb, G. CO$_2$ methanation in microstructured reactors—Catalyst development and process design. *Chem. Eng. Tech.* 2019, 42, 2076–2084. [CrossRef]
17. Hwang, S.; Lee, J.; Gi Hong, U.; Gil Seo, J.; Chul Jung, J.; Jun Koh, D.; Lim, H.; Byun, C.; Kyu Song, I. Methane production from carbon monoxide and hydrogen over nickel–alumina xerogel catalyst: Effect of nickel content. *Ind. Eng. Chem. 2011*, 17, 154–157. [CrossRef]

18. Yamasaki, M.; Komori, M.; Akiyama, E.; Habazaki, H.; Kawashima, A.; Asami, K.; Hashimoto, K. CO₂ methanation catalysts prepared from amorphous Ni–Zr–Sm and Ni–Zr–misch metal alloy precursors. *Mater. Sci. Eng. A 1999*, 267, 220–226. [CrossRef]

19. Sharma, S.; Hu, Z.; Zhang, P.; McFarland, E.W.; Metiu, H. CO₂ methanation on Ru-doped ceria. *J. Catal.* 2011, 278, 297–309. [CrossRef]

20. Eckle, S.; Anfang, H.-G.; Behm, R.J. Reaction intermediates and side products in the methanation of CO and CO₂ over supported Ru catalysts in H₂-rich reformate gases. *J. Phys. Chem. C 2011*, 115, 1361–1367. [CrossRef]

21. Karelovic, A.; Ruiz, P. CO₂ hydrogenation at low temperature over Rh/γ-Al₂O₃ catalysts: Effect of the metal particle size on catalytic performances and reaction mechanism. *Appl. Catal. B Environ.* 2012, 113–114, 237–249. [CrossRef]

22. Beuls, A.; Swalus, C.; Jacquemin, M.; Heyen, G.; Karelovic, A.; Ruiz, P. Methanation of CO₂: Further insight into the mechanism over Rh/γ-Al₂O₃ catalyst. *Appl. Catal. B Environ.* 2012, 113–114, 2–10. [CrossRef]

23. Swalus, C.; Jacquemin, M.; Poleunis, C.; Bertrand, P.; Ruiz, P. CO₂ methanation on Rh/γ-Al₂O₃ catalyst at low temperature: “In situ” supply of hydrogen by Ni/activated carbon catalyst. *Appl. Catal. B Environ.* 2012, 125, 41–50. [CrossRef]

24. Park, J.-N.; McFarland, E.W. A highly dispersed Pd–Mg/SiO₂ catalyst active for methanation of CO₂. *J. Catal.* 2009, 266, 92–97. [CrossRef]

25. Yu, K.-P.; Yu, W.-Y.; Kuo, M.-C.; Liou, Y.-C.; Chien, S.-H. Pt/titania-nanotube: A potential catalyst for CO₂ adsorption and hydrogenation. *Appl. Catal. B Environ.* 2008, 84, 12–18. [CrossRef]

26. Du, G.; Lim, S.; Yang, Y.; Wang, C.; Pfefferle, L.; Haller, G.L. Methanation of carbon dioxide on Ni-incorporated MCM-41 catalysts: The influence of catalyst pre-treatment and study of steady-state reaction. *J. Catal.* 2007, 249, 370–379. [CrossRef]

27. Lu, B.; Kawamoto, K. Preparation of the highly loaded and well-dispersed NiO catalyst in CO₂ methanation catalysts prepared from amorphous Ni–Zr alloys. *Ind. Eng. Chem. Res.* 2009, 48, 10883–10888. [CrossRef]

28. Yamasaki, M.; Habazaki, H.; Asami, K.; Izumiya, K.; Hashimoto, K. Effect of tetragonal ZrO₂ on the catalytic activity of Ni/ZrO₂ catalyst prepared from amorphous Ni–Zr alloys. *Catal. Commun.* 2006, 7, 24–28. [CrossRef]

29. Tada, S.; Shimizu, T.; Kameyama, H.; Haneda, T.; Kikuchi, R. Ni/Co₂ catalysts with high CO₂ methanation activity and high CH₄ selectivity at low temperatures. *Int. J. Hydrog. Energy* 2012, 37, 5527–5531. [CrossRef]

30. Jwa, E.; Lee, S.B.; Lee, H.W.; Mok, Y.S. Plasma-assisted catalytic methanation of CO and CO₂ over Ni–zeolite catalysts. *Fuel Process Technol.* 2013, 108, 89–93. [CrossRef]

31. Aziz, M.A.A.; Jalil, A.A.; Triawiyono, S.; Mukti, R.R.; Taufiq-Yap, Y.H.; Saizegar, M.R. Highly active Ni-promoted mesostructured silica nanoparticles for CO₂ methanation. *Appl. Catal. B Environ.* 2014, 147, 359–366. [CrossRef]

32. Zhou, G.; Liu, H.; Cui, K.; Jia, A.; Hu, G.; Jiao, Z.; Liu, Y.; Zhang, X. Role of surface Ni and Ce species of Ni/Co₂ catalyst in CO₂ methanation. *Appl. Surf. Sci.* 2016, 383, 248–252. [CrossRef]

33. Takano, H.; Kirihata, Y.; Izumiya, K.; Kumagai, N.; Habazaki, H.; Hashimoto, K. Highly active Ni/Y-doped ZrO₂ catalysts for CO₂ methanation. *Appl. Surf. Sci.* 2016, 388, 653–663. [CrossRef]

34. Ocampo, F.; Louis, B.; Roger, A. Methanation of carbon dioxide over nickel-based Ce₀.7Zr₀.28O₂ mixed oxide catalysts prepared by sol–gel method. *Appl. Catal. A Gen* 2009, 369, 90–96. [CrossRef]

35. Aldana, P.A.U.; Ocampo, F.; Kobl, K.; Louis, B.; Thibaut-Starzyk, F.; Daturi, M.; Bazin, P.; Thomas, S.; Roger, A.C. Catalytic CO₂ valorization into CH₄ on Ni-based ceria-zirconia. Reaction mechanism by operando IR spectroscopy. *Catal. Today* 2013, 215, 201–207. [CrossRef]

36. Pan, Q.; Peng, J.; Sun, T.; Wang, S.; Wang, S. Insight into the reaction route of CO₂ methanation: Promotion effect of medium basic sites. *Commun. Catal.* 2014, 45, 74–78. [CrossRef]

37. Zhu, H.; Razzaz, R.; Li, C.; Muhmmad, Y.; Zhang, S. Catalytic methanation of carbon dioxide by active oxygen material Ce₆Zr₁-xO₂ supported Ni-Co bimetallic nanocatalysts. *AiChE J.* 2013, 59, 2567–2576. [CrossRef]

38. Bian, Z.; Xin, Z.; Meng, X.; Tao, M.; Lv, Y.H.; Gu, J. Effect of citric acid on the synthesis of CO methanation catalysts with high activity and excellent stability. *Ind. Eng. Chem. Res.* 2017, 56, 2383–2392. [CrossRef]
39. Yu, C.; Hu, J.; Zhou, W.; Fan, Q. Novel Ni/CoO2-Al2O3 composite catalysts synthesized by one-step citric acid complex and their performance in catalytic partial oxidation of methane. *J. Energy Chem.* 2014, 23, 235–243. [CrossRef]

40. Suárez-Torrello, V.A.; Santolalla-Vargas, C.E.; de los Reyes, J.A.; Vázquez-Zavala, A.; Vrinat, M.; Geantet, C. Influence of the solution pH in impregnation with citric acid and activity of Ni/W/Al2O3 catalysts. *J. Mol. Catal. A Chem.* 2015, 404–405, 36–46.

41. Zhang, Q.; Long, K.; Wang, J.; Zhang, T.; Song, Z.; Lin, Q. A novel promoting effect of chelating ligand on the dispersion of Ni species over Ni/SBA-15 catalyst for dry reforming of methane. *Ind. J. Hydrog. Energy* 2017, 42, 14103–14114. [CrossRef]

42. Shanmugam, V.; Neuberg, S.; Zapf, R.; Hessel, V.; Kolb, G. Novel route to control the size, distribution and location of Ni nanoparticles in mesoporous silica for steam reforming of propylene glycol in microchannel reactor. *Catal. Commun.* 2016, 83, 43–47. [CrossRef]

43. Pandey, D.; Deo, G. Effect of support on the catalytic activity of supported Ni–Fe catalysts for the CO2 methanation reaction. *J. Ind. Eng. Chem.* 2016, 33, 99–107. [CrossRef]

44. Lu, D.; Gao, J.; Ping, Y.; Jia, L.; Gu, F.; Su, F. Enhanced investigation of CO methanation over Ni/Al2O3 Catalysts for synthetic natural gas production. *Ind. Eng. Chem. Res.* 2012, 51, 4875–4886. [CrossRef]

45. Muroyama, H.; Tsuda, Y.; Asakoshi, T.; Masitah, H.; Okanishi, T.; Matsui, T.; Eguchi, K. Carbon dioxide methanation over Ni catalysts supported on various metal oxides. *J. Catal.* 2016, 343, 178–184. [CrossRef]

46. Lakshmanan, P.; Kim, M.S.; Park, E.D. A highly loaded Ni@SiO2 core–shell catalyst for CO methanation. *Appl. Catal. A Gen.* 2016, 513, 98–105. [CrossRef]

47. Yan, X.; Liu, Y.; Zhao, B.; Wang, Z.; Wang, Y.; Liu, C.J. Methanation over Ni/SiO2: Effect of the catalyst preparation methodologies. *Int. J. Hydrog. Energy* 2013, 38, 2283–2291. [CrossRef]

48. Wu, H.C.; Chang, Y.C.; Wu, J.H.; Lin, J.H.; Linc, I.K.; Chen, C.S. Methanation of CO2 and reverse water gas shift reactions on Ni/SiO2 catalysts: The influence of particle size on selectivity and reaction pathway. *Catal. Sci. Technol.* 2015, 5, 4154–4163. [CrossRef]

49. Chen, X.; Jin, J.; Sha, G.; Li, C.; Zhang, B.; Su, D.; Williams, C.T.; Liang, C. Silicon–nickel intermetallic compounds supported on silica as a highly efficient catalyst for CO methanation. *Sci. Technol.* 2014, 5, 53–61. [CrossRef]

50. Fukuhara, C.; Hayakawa, K.; Suzuki, Y.; Kawasaki, W.; Watanabe, R. A novel nickel-based structured catalyst for CO2 methanation: A honeycomb-type Ni/CoO2 catalyst to transform greenhouse gas into useful resources. *Appl. Catal. A Gen.* 2017, 532, 12–18. [CrossRef]

51. Ratchahat, S.; Sudoh, M.; Suzuki, Y.; Kawasaki, W.; Watanabe, R.; Fukuhara, C. Development of a powerful CO2 methanation process using a structured Ni/CoO2 catalyst. *J. CO Utilization* 2018, 24, 210–219. [CrossRef]

52. Atzori, L.; Cutrufoello, M.G.; Meloni, D.; Cannas, C.; Gazzoli, D.; Monaci, R.; Sini, M.F.; Rombi, E. Highly active NiO-CoO2 catalysts for synthetic natural gas production by CO2 methanation. *Catal. Today* 2018, 299, 183–192. [CrossRef]

53. Le, T.A.; Kim, M.S.; Lee, S.H.; Kim, T.W.; Park, E.D. CO and CO2 methanation over supported Ni catalysts. *Catal. Today* 2017, 293–294, 89–96. [CrossRef]

54. Trovarelli, A.; Deleitenburg, C.; Dolcetti, G.; Lorca, J.L. CO2 methanation under transient and steady-state conditions over Rh/CoO2 and CeO2-promoted Rh/SiO2: The role of surface and bulk ceria. *J. Catal.* 1995, 151, 111–124. [CrossRef]

55. Zhou, G.; Liu, H.; Cui, K.; Xie, H.; Jiao, Z.; Zhang, G.; Xiong, K.; Zheng, X. Methanation of carbon dioxide over Ni/CoO2 catalysts: Effects of support CeO2 structure. *Int. J. Hydrog. Energy* 2017, 42, 16108–16117. [CrossRef]

56. Shanmugam, V.; Zapf, R.; Neuberg, S.; Hessel, V.; Kolb, G. Effect of ceria and zirconia promoters on Ni/SBA-15 catalysts for coking and sintering resistant steaming for propylene glycol in microreactors. *Appl. Catal. B Environ.* 2017, 203, 859–869. [CrossRef]

57. Razzag, R.; Zhu, H.; Jiang, L.; Muhammad, U.; Li, C.; Zhang, S. Catalytic methanation of CO and CO2 in coke oven gas over Ni–Co/ZrO2–CeO2. *Ind. Eng. Chem. Res.* 2013, 52, 2247–2256. [CrossRef]

58. Shanmugam, V.; Zapf, R.; Hessel, V.; Pennemann, H.; Kolb, G. Nano-architected CeO2 supported Rh with remarkably enhanced catalytic activity for propylene glycol reforming reaction in microreactors. *Appl. Catal. B Environ.* 2018, 226, 403–411. [CrossRef]
59. Shanmugam, V.; Neuberg, S.; Zapf, R.; Pennemann, H.; Kolb, G. Hydrogen production over highly active Pt based catalyst coatings by steam reforming of methanol: Effect of support and co-support. *Int. J. Hydrog. Energy* 2020, 45, 1658–1670. [CrossRef]

60. Kolb, G.; Zapf, R.; Hessel, V.; Löwe, H. Propane steam reforming in micro-channels—results from catalyst screening and optimisation. *Appl. Catal. A Gen.* 2004, 277, 155–166. [CrossRef]