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Interfacial Ni active sites strike solid solutional counterpart in CO₂ hydrogenation



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ABSTRACT

Ni enhanced CeO₂ based catalysts were tested in CO₂ hydrogenation reaction with the objective to investigate the importance and role of Ni⁰ and Ni⁰-NiO-CeO_{2-x} interfaces. Two materials were prepared: a 4 mol% NiO/CeO₂ interfacial oxide where CeO₂ supports NiO nanoparticles was produced by wet impregnation method and a Ce_{0.96}Ni_{0.04}O₂ mixed oxide was obtained by co-precipitation of Ce³⁺ and Ni²⁺ ions. Besides these materials, pure NiO and CeO₂ were also synthesized and tested, serving as reference materials. HRTEM, TPR, XRD, BET, EDS, Raman spectroscopy, and XPS were used for the characterization of the catalysts. The activity and selectivity strongly depended on metallic Ni content, which is tunable by the temperature of hydrogen pretreatment. The impregnated catalyst with significant metallic content exhibited high activity and high methane selectivity. The mixed oxide was more resistant to reduction, in the case of both the Ni²⁺ and Ce⁴⁺ species, thus it has low activity with high CO selectivity. The activity and methane selectivity increased considerably by increasing the metal content or higher hydrogen pretreatment temperature. *Operando* DRIFTS experiments suggested that bicarbonate and formate intermediates play important role in CO₂ hydrogenation in both types of catalysts. The reduced Ni particles help to produce the high amount of hydrogen needed for the hydrogenation of formate to methane. It turned out that the metallic Ni not only catalyzes the methane production from formate but also the bicarbonate-formate transformation. The most important factor in the high performance of these catalysts is the Ni⁰/NiO ratio in the Ni⁰-NiO-CeO_{2-x} interface.

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1. Introduction

Catalytic CO₂ hydrogenation is a promising method to reduce anthropogenic CO₂ in the atmosphere and also produce value-added liquid fuels and feedstock chemicals for the chemical industry (Centi et al., 2013; Sápi et al., 2019a,b; Wang et al., 2011). CO₂ conversion using H₂ produced from electrolysis of water powered by wind or solar energy produces carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), and other valuable chemical feedstock. This approach is considered to be promising to reduce the atmospheric concentration of CO₂ (Porosoff et al., 2016). Because of the chemical inertness and thermodynamic stability of CO₂, efficient and selective CO₂ conversion remains a challenge (Freund and Roberts, 1996; Kiss et al., 2019; Zheng et al., 2017). Another route for CO₂ conversion is the production of CO. The produced CO can be used as feedstock in the Fischer–Tropsch (FT) process to transform value-added chemicals or fuels (Daza and Kuhn, 2016; Luk et al., 2017). Synthesis of methane or synthesis gas over the other products through CO₂ hydrogenation requires relatively low temperature and takes place at atmospheric pressure. Various transition metals such as Co, Ni, Ru, Rh, Pt, and Pd supported on metal oxides such as Al₂O₃, TiO₂, SiO₂, ZrO₂, and CeO₂ have been investigated for CO₂ methanation reaction (Frontera et al., 2017; Sápi et al., 2018; Vogt et al., 2018; Wang et al., 2016). Likewise, for water gas shift reaction transition metals such as Cu, Pt and Rh supported on various oxides such as Al₂O₃, TiO₂, SiO₂, ZrO₂, and CeO₂ have been investigated (Daza and Kuhn, 2016). CeO₂ has been extensively used as a support due to its redox behavior and oxygen storage capacity (OSC) (Montini et al., 2016). The OSC of CeO₂ derives from the oxygen deficiency of the crystal lattice, which is a desirable trait of metal oxides concerning catalysis (Zu et al., 2019). However, the stoichiometry and physical chemical properties of CeO₂ change at high temperatures, resulting in decreased OSC and subsequent deactivation. Recently different ceria based solid solutions and ceria with interfacial particles were engineered and tested for CO₂ hydrogenation (Rajkumar et al., 2021). To improve catalytic activity and thermal stability, CeO₂ is doped with various metals such as Mn, Fe, Co, Ni, Cu, or Zr (Li et al., 2016; Selvamani et al., 2015; Zhang et al., 2018b; Zhou et al., 2010). CeO₂ supported NiO has been reported as an excellent catalyst for various reactions such as oxidation of methane and selective catalytic reduction (SCR) of NO_x with NH₃ compared to pure CeO₂ due to the synergetic effect between the CeO₂ and NiO (Maitarad et al., 2014; Zhang et al., 2018b). The metal-support interface is crucial in determining product selectivity (Sápi et al., 2019a,b; Zhang et al., 2018a). A fundamental understanding of the difference between interfacial and solid solution effects on CO₂ hydrogenation at the atomic level is necessary. In this study, the difference between interfacial and solid solution effect on CO₂ hydrogenation over NiO impregnated CeO₂ (labeled as 4 mol% NiO/CeO₂ and Ce_{0.96}Ni_{0.04}O₂ solid solution catalysts have been studied.

2. Materials and methods

2.1. Catalyst synthesis

2.1.1. Chemicals

Ce(NO₃)₃·6H₂O and NaOH were obtained from Sigma-Aldrich. Ni(NO₃)₂·6H₂O was obtained from Merck. All the chemicals were used without further purification. Distilled water was used for all synthesis and washing processes.

2.1.2. Synthesis of Ce_{0.96}Ni_{0.04}O₂ solid solution

The Ni²⁺ doped CeO₂ based solid solutions were prepared by the hydrothermal method according to the literature (Zhang et al., 2018a). In a typical synthesis, an appropriate amount of Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O were dissolved in distilled water. Then, NaOH solution was added dropwise into the solution until the pH reached 12. The obtained suspension was stirred constantly for 2 h before transferring into an autoclave, then kept at 200 °C for 24 h. When the hydrothermal reaction was finished, the product was washed with distilled water and dried in an oven at 80 °C overnight. Pure CeO₂ and NiO were also prepared with the same method.

2.1.3. Synthesis of NiO impregnated CeO₂

CeO₂ supported NiO with 4 mol% loading was prepared by wet impregnation method. In a typical synthesis, an aqueous solution containing an appropriate amount of Ni(NO₃)₂·6H₂O was added dropwise to the CeO₂ support. The excess water was removed at 80 °C under magnetic stirring. The obtained sample was further dried in an oven at 80 °C overnight and calcined at 400 °C for 2 h in air.

2.2. Sample characterization

2.2.1. N₂ adsorption–desorption isotherm measurements

The specific surface area (BET method), the pore size distribution, and the total pore volume were determined by the BJH method using a Quantachrome NOVA 2200 surface analyzer by N₂ gas adsorption/desorption at –196 °C. Before the measurements, the samples were pretreated in vacuum (< ~0.1 mbar) at 200 °C for 2 h. Results are shown in the Supplementary Information.

2.2.2. Powder X-ray diffraction (XRD)

XRD studies of all samples were performed on a Rigaku MiniFlex II instrument with a Ni-filtered Cu-K α source in the range of $2\theta = 20\text{--}80^\circ$. Diffraction data are shown in the Supplementary Information. The XRD patterns of pure CeO₂, Ce_{0.96}Ni_{0.04}O₂, 4 mol% NiO/CeO₂, and NiO catalysts are shown in Fig. S3 of the Supplementary Information. Also, the XRD patterns of the spent catalysts are shown in Fig. S8 of the Supplementary Information.

2.2.3. Transmission electron microscopy (TEM)

Imaging of the synthesis products was carried out using a FEI TECNAI G2 20 X-Twin high-resolution transmission electron microscope operating at an accelerating voltage of 200 kV. The samples were drop-cast onto carbon film coated copper grids from ethanol suspension. The TEM images are shown in the Supplementary Information.

2.2.4. High angle annular dark field imaging (HAADF) and energy dispersive X-ray spectroscopy (EDX)

Pretreated catalyst samples were further investigated with a Thermo Fisher Scientific Themis TEM instrument equipped with Super-X EDX detectors. HAADF and EDX images were taken in STEM mode.

2.2.5. Raman spectroscopy

The Raman spectra were collected on a Bruker Senterra II equipped with a 532 nm wavelength laser source. The Raman spectra of pure CeO₂, Ce_{0.96}Ni_{0.04}O₂, 4 mol% NiO/CeO₂, and NiO catalysts are shown in Fig. S4 of the Supplementary Information.

2.2.6. H₂-temperature programmed reduction (H₂-TPR)

The temperature-programmed reduction (TPR) was carried out in a BELCAT-A analyzer using a reactor (quartz tube with 9 mm outer diameter) that was externally heated. Before the measurements, 50 mg of catalyst was pretreated in oxygen at 400 °C for 30 min and in N₂ at 400 °C for 15 min. Thereafter, the sample was cooled in flowing N₂ to 50 °C. The oxidized sample was flushed with N₂ containing 10% H₂, the reactor was heated linearly at a rate of 10 °C/min from 50 °C to 500 °C and the H₂ consumption was detected by a thermal conductivity detector (TCD). The result is showcased in section 6. of the Supplementary Information.

2.2.7. Energy-dispersive X-ray spectroscopy (EDS)

A field emission scanning electron microscope (Thermo Fisher Scientific Apreo C) equipped with an energy dispersive detector was used to characterize the elemental content of samples. The applied voltage was 20 kV and the spot size was 8. The data are presented in Table S2 of the Supplementary Information.

2.2.8. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Infrared spectroscopy measurements were carried out with an “Agilent Cary-670” Fourier transform infrared (FTIR) spectrometer equipped with a “Harrick Praying Mantis” diffuse reflectance attachment. The sample holder had two BaF₂ windows in the infrared path. The spectrometer was purged with dry nitrogen. The spectrum of the pretreated catalyst was used as background. At room temperature, a CO₂ to H₂ mixture with a molar ratio of 1:4 was introduced into the DRIFTS cell. The tubes were externally heated to avoid condensation. The catalyst was heated under the reaction feed linearly from room temperature to 400 °C, with a heating rate of 20 °C/min, and IR spectra were measured at 50 °C intervals.

2.2.9. In situ and ex situ X-ray Photoelectron Spectroscopy

The *in situ* X-ray photoelectron spectroscopy (XPS) measurements were performed in a Kratos Analytical XSAM800 instrument. Pretreatment and *in situ* sample preparations were done in the modified pre-chamber of the instrument. Pretreatment consisted of a cycle of oxidation (O₂, 1 atm, 300 °C, and 30 min) and reduction (H₂, 1 atm, 300 °C, 60 min). After this, the samples were introduced into the chamber to acquire spectra. Finishing data acquisition, CO₂ and H₂ (1:4 ratio) were introduced to the pre-chamber. The reaction time was 30 min at 400 °C and 1 atm. Thereafter spectra were collected once again. Also, the spent catalysts were removed from the quartz tube after cooling and were prepared for *ex situ* XPS. The data are presented in Fig. S11 of the Supplementary Information.

2.2.10. Hydrogenation of carbon dioxide in a continuous flow reactor

Before the catalytic reactions, the as-received catalysts were oxidized in O₂ atmosphere at 300 °C for 30 min to remove the surface contaminants and thereafter were reduced in H₂ at 300 °C for 60 min. In parallel, the samples were tested with 600 °C pre-reduction temperature also. Catalytic reactions were conducted at atmospheric pressure in a fixed-bed continuous-flow reactor (200 mm long with 8 mm id.), which was heated externally. The dead volume of the reactor was filled with quartz beads. The operating temperature was controlled by a thermocouple placed inside the oven close to the reactor wall. The samples were prepared as small fragments (about 1 mm) of slightly compressed pellets. Typically, the reactor filling contained 150 mg of the catalyst sample. In the reacting gas mixture molar ratio of CO₂: H₂ was 1:4 in all cases. The CO₂: H₂ mixture was fed with the help of mass flow controllers (Aalborg), and the total flow rate was 40 ml/min. The reacting gas mixture flow entered and left the reactor through externally heated tubing to avoid condensation. The

Table 1

Oxidation state distribution of Ce and Ni in pretreated and spent catalyst samples of 4 mol% NiO/CeO₂ and Ce_{0.96}Ni_{0.04}O₂

Samples	Ce ³⁺	Ce ⁴⁺	Ce ³⁺ /Ce ⁴⁺	Ni ⁰	Ni ²⁺	Ni ⁰ /Ni ²⁺
4 mol% NiO/CeO ₂ after pretreatment	18.66%	81.32%	0.23	32.01%	67.99%	0.47
4 mol% NiO/CeO ₂ after reaction	26.93%	73.06%	0.37	77.03%	22.97%	3.35
Ce _{0.96} Ni _{0.04} O ₂ after pretreatment	21.48%	78.52%	0.27	0.0%	100%	–
Ce _{0.96} Ni _{0.04} O ₂ after reaction	15.43%	84.57%	0.18	36.69%	63.31%	0.58

analysis of the products and reactants was performed with an Agilent 6890N gas chromatograph using an HP-PLOTQ column. The gases were detected simultaneously by thermal conductivity (TC) and flame ionization detectors (FID). The CO₂ was transformed by a methanizer into methane and it was also analyzed by FID. CO₂ conversion was calculated from carbon balance:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}}{\text{CO}_2 \text{ inlet}} \times 100\%$$

CH₄ selectivity and CO selectivity were calculated as the following:

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{\text{CH}_4 \text{ outlet}}{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}} \times 100\%$$

$$\text{CO selectivity (\%)} = \frac{\text{CO outlet}}{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}} \times 100\%$$

Where CO₂ inlet and CO₂ outlet represent the CO₂ concentration in the feed and effluent, respectively, and CH₄ outlet and CO_{outlet} represent the concentration of CH₄ and CO in the effluent, respectively.

3. Results and discussion

3.1. In situ XPS

XPS was performed for both pretreated and spent catalysts to determine the chemical state and the relative proportion of elements on the surface. High resolution Ce 3d spectrum regions were fit with the method described by Eric Beche et al. thus four peaks represent the Ce³⁺ oxidation state and six peaks represent the Ce⁴⁺ oxidation state (Beche et al., 2008). The conventional peak labels suggested by Burroughs et al. were used to denote components of the Ce 3d region, where v and u denote the 5/2 and 3/2 doublet components respectively (Burroughs et al., 1976). We also collected spectra of the synthesized pure CeO₂ where the Ce³⁺/Ce⁴⁺ ratio had been proved to be ~0.11, which is in accordance with the literature (Varga et al., 2015). Collected and fit spectra are presented in the Supplementary Information (Fig. S9, S10).

Fig. S9 compares the Ce 3d spectra of 4 mol% NiO/CeO₂ and Ce_{0.96}Ni_{0.04}O₂ catalysts after pretreatment and after reaction. Comparing the observed 3d envelope with those previously reported for Ce⁴⁺ and Ce³⁺ indicates that both the pretreated and spent catalysts contain mixed valence states of Ce⁴⁺ and Ce³⁺ ions (Ferencz et al., 2014; Ovari et al., 2013). The percentages of Ce³⁺ and Ce⁴⁺ ions were calculated based on the integrated peak areas as shown in Table 1. The Ce³⁺/Ce⁴⁺ ratio is higher on the 4 mol% NiO/CeO₂ spent catalyst than that on the other catalysts. This indicates higher OSC, which favors high CO₂ conversion and CO₂ consumption rate.

The low concentration of Ni present in the samples made the detection a serious challenge. (Because of the overlap of Ni 2p 1/2 and Ce 3d 3/2 peaks and lower Scofield RSF value of Ni compared to Ce.) To acquire data about Ni only the Ni 2p 3/2 spectrum region was fit. Two peaks were distinguished during the procedure, a metallic Ni⁰ peak at ~852.6 eV, which was fit with an asymmetric peak shape (Biesinger et al., 2011) and an oxide peak at ~855.4 eV. This binding energy is higher than the binding energy observed for pure NiO (~853.4 eV) (Lian et al., 1992) and is characteristic of oxide structures where another metal is present beside Ni²⁺ ions (McIntyre and Cook, 1975). The ratio of Ni⁰/Ni²⁺ species is presented in Table 1. In the case of the 4 mol% NiO/CeO₂ sample, Ni is mostly present as Ni⁰, which serves as an active site for H₂ spillover, promoting CH₄ production. The Ce³⁺/Ce⁴⁺ of Ce_{0.96}Ni_{0.04}O₂ decreases from pretreatment to reaction, indicating that Ce³⁺ and Ni²⁺ are competing for the reduction, thus slowing down the reduction of Ni²⁺ species.

3.2. HAADF and EDX

According to the HAADF and EDX imaging (Fig. 1) of the catalysts, after reduction the dispersion of Ni is more homogeneous in the Ce_{0.96}Ni_{0.04}O₂ sample, which is accounted for the formation of nanoclusters. It is hard to determine their exact size due to the homogeneity, according to the image the particles have ~5 nm diameter. Also, it is important to note that single-atom catalysis is ruled out since those are usually created with less than 0.05 wt% of the supported material (DeRita et al., 2017). In the 4 mol% NiO/CeO₂ sample locally grouped Ni atoms are observed, creating separated inclusions in the form of nanoparticles, which have ~10 nm diameter.

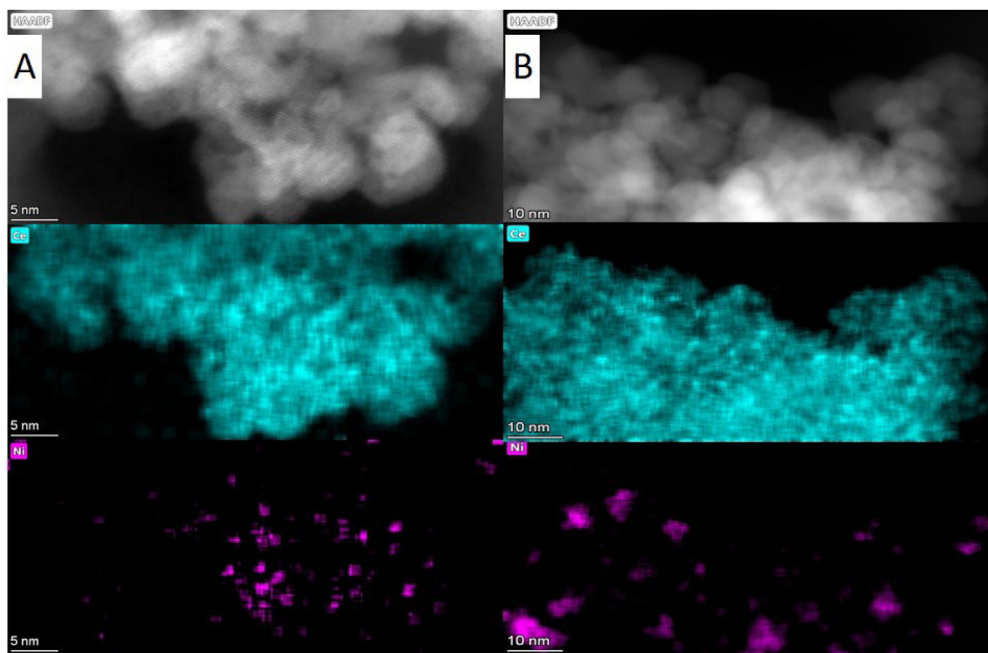


Fig. 1. 1. HAADF and EDX images of the (A) solid solution and (B) impregnated catalysts after pretreatment at 300 °C.

3.3. Catalytic performance

Catalytic performance of the prepared samples was tested in CO₂ hydrogenation reaction. Fig. 2 displays the CO₂ consumption rate as a function of reaction temperature for the catalysts. CO₂ conversion and selectivity of the catalysts are summarized in Table 2. Pure CeO₂ favors the formation of methanol and ethanol at low temperatures. Modification by Ni species suppressed the formation of alcohols. When the pre-reduction temperature was 300 °C the CO₂ conversion for 4 mol% NiO/CeO₂ was 65% (CH₄ selectivity = 94.71% at 400 °C) at 400 °C which is 10 times higher than the Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst which had a CO₂ conversion of 6.39% (CH₄ selectivity = 4.48% at 400 °C). This indicates that NiO present on the surface of CeO₂ is more active than Ni²⁺ ions in the lattice. CH₄ was formed as the major product and CO as a minor product on the interfacial catalyst (4 mol% NiO/CeO₂ catalysts) while CO was formed as the major product and CH₄ as a minor product on the Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst. This indicated that Ni present on the surface of CeO₂ produces selectively CH₄ due to the stronger hydrogenation ability of Ni. However, Ni present in the solid solution does not expose during the hydrogenation reaction, hence does not contribute to the CH₄ formation. It is observed that CO₂ conversion was zero at low temperatures over the Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst and improved at higher temperatures. This could be attributed to the absence of potential active surface sites for the CO₂ adsorption on the Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst. In addition, *in situ* XPS analysis of the spent catalysts revealed that the Ce³⁺/Ce⁴⁺ ratio in 4 mol% NiO/CeO₂ was 0.37 compared to the value of 0.18 in Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst (Table 1.), which is marginally higher than the value of 0.11 characteristic to pure CeO₂. The high Ce³⁺/Ce⁴⁺ ratio over 4 mol% NiO/CeO₂ boosted its CO₂ conversion and consumption rate. It is important to note that a lower BET surface area (Table S1 of the Supplementary Information) was obtained for 4 mol% NiO/CeO₂ (86.12 m²g⁻¹) compared to Ce_{0.96}Ni_{0.04}O₂ (123.18 m²g⁻¹), implying that the impact of the specific surface area is a lesser contributing factor to CO₂ conversion.

The catalytic performance is further investigated based on the CO₂ consumption rate of the catalysts during reaction. It is important to note, that according to the *in situ* XPS results, no Ni⁰ is forming in the Ce_{0.96}Ni_{0.04}O₂ solid solution catalyst until the reaction temperature passes 300 °C. Fig. 2 illustrates the impact of the reduction of Ni²⁺ to Ni⁰ between 300 °C and 400 °C, significantly increasing the consumption rate of the Ce_{0.96}Ni_{0.04}O₂ catalyst.

Also at this temperature we achieve the highest CO₂ consumption rate (31.82 μmol/gs) with the 4 mol% NiO/CeO₂ sample. In comparison, the Ce_{0.96}Ni_{0.04}O₂ solid solution counterpart has CO₂ consumption rate of 0.87 μmol/gs at 400 °C. To further emphasize the importance of Ni⁰ species and the interface it creates with the Ce_{2-x} we calculated the CO₂ consumption rate specific to surface Ni⁰ species (Fig. 4) which proves to be 2.7 times higher for 4 mol% NiO/CeO₂ compared to Ce_{0.96}Ni_{0.04}O₂.

In the case of reactions with 600 °C pre-reduction, both catalysts exhibit similar activity, as is shown in Fig. 3B. This is mainly due to the high pre-reduction temperature, where hydrogen could successfully reduce the catalysts, creating lattice defects and allowing a significant increase in the reduction of Ni²⁺ species. *Ex situ* XPS measurements (Fig. S11, Table S7) of the spent samples confirm, that 67% and 51% of Ni is present as Ni⁰ in Ce_{0.96}Ni_{0.04}O₂ and 4 mol% NiO/CeO₂,

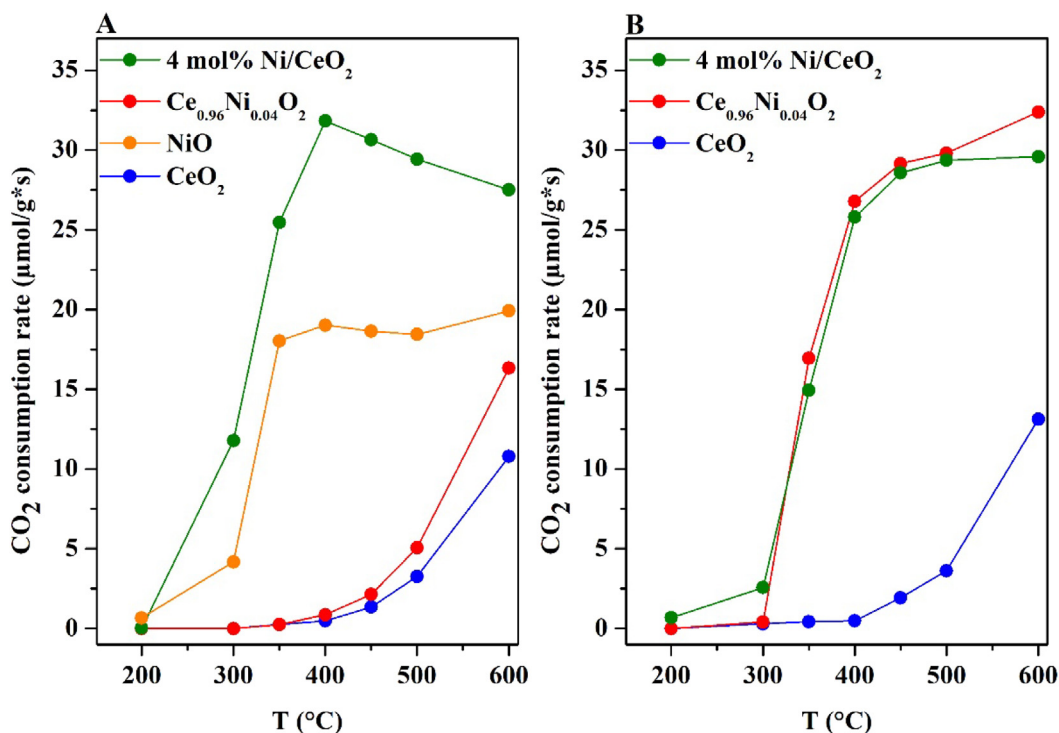


Fig. 2. CO₂ consumption rate as a function of temperature over CeO₂, Ce_{0.96}Ni_{0.04}O₂ solid solution, and 4 mol% NiO impregnated CeO₂ and NiO catalysts. (A) Pre-reduced in H₂ at 300 °C (B) Pre-reduced in H₂ at 600 °C.

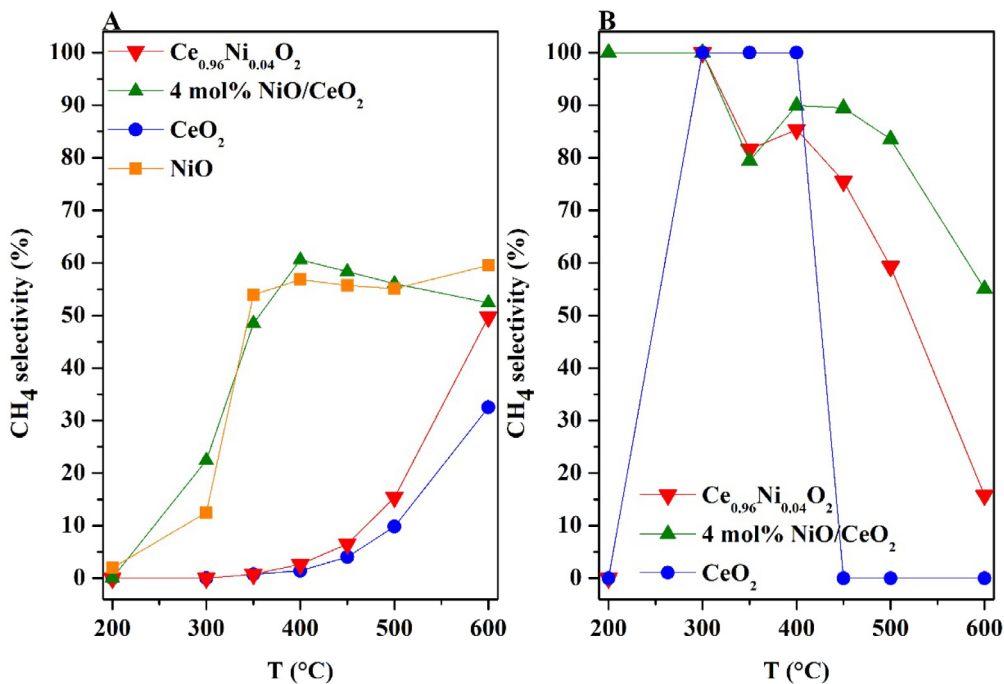


Fig. 3. Methane selectivity of the investigated catalysts, with different pretreatment temperatures. (A) Pre-reduced in H₂ at 300 °C (B) Pre-reduced in H₂ at 600 °C.

respectively. As for selectivity, a significant decrease is observed in methane selectivity after 400 °C. This is accounted for the formation of CO being the thermodynamically favored process instead of the formation of CH₄.

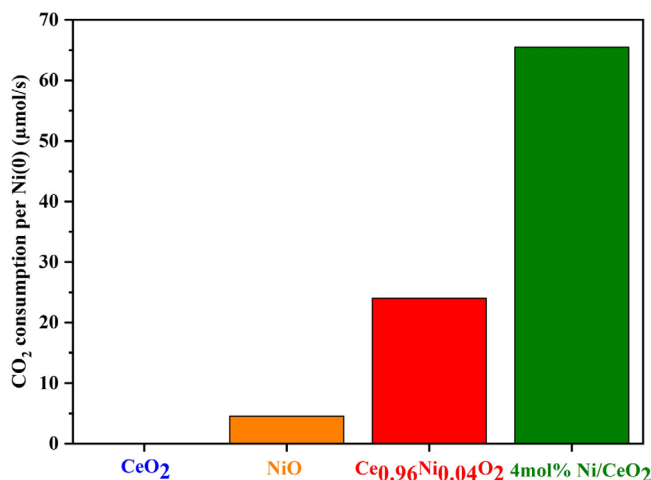


Fig. 4. CO₂ consumption rates calculated as a function of available Ni⁰ species on the surface at 400 °C.

Table 2

Conversion and selectivity for CO₂ hydrogenation over various catalysts.^a

Catalysts	CO ₂ Conversion (%)	Selectivity (%)		
		CO	CH ₄	C ₂ H ₆
CeO ₂	9.92	100	0	0
Ce _{0.96} Ni _{0.04} O ₂	6.39	95.52	4.48	0
4 mol% NiO/CeO ₂	65.16	5.29	94.71	0
NiO	67.86	8.14	91.86	0

^aReaction conditions: T = 400 °C, CO₂/H₂ = 1/4, catalyst weight = 0.15 g.

3.4. Operando DRIFTS study

To identify the possible reaction intermediates and the composition of the gas phase in the CO₂ hydrogenation reaction, *operando* DRIFTS measurements were performed under reaction conditions. The *operando* DRIFT spectra were recorded from 50 °C to 400 °C for CeO₂ (Fig. S12), 4 mol% NiO/CeO₂, and Ce_{0.96}Ni_{0.04}O₂ catalysts pretreated at different temperatures (Fig. 5). The types of intermediate species and their corresponding DRIFT vibrational frequencies obtained on pure CeO₂, modified CeO₂, and NiO are summarized in the Supplementary Information (Table S7.)

It is generally observed in CO₂ hydrogenation reactions that the activated CO₂ (CO₂^{*}) forms (vibrationally or electronically) in the first step (Cheng and Lo, 2016; Freund and Roberts, 1996; Sápi et al., 2018). In the case of ceria based catalysts, the most important active sites for CO₂ activation are the lattice defects (Ce³⁺), which is proven by experimental data and density functional theory calculation combining microkinetic analysis (Cheng and Lo, 2016). The activated CO₂ species transform further in different ways according to the nature and oxidation state of modifiers. CeO₂ performs complex DRIFT spectral features. Its comprehensive analysis is important to draw a conclusion from the IR spectra obtained on Ni enhanced ceria. The DRIFT spectra obtained during CO₂ hydrogenation on unmodified CeO₂ are displayed in Fig. S12 A and the detailed analysis and conclusion are discussed in Supplementary Information. Only the main results, which are important for understanding the characteristic feature of the reaction, are summarized in this paragraph. The overtones of gas-phase CO₂ and OH bond modes appeared between 3600 and 3727 cm⁻¹. The activated bent CO₂^{δ-} formed on vacancy sites reacts with OH groups giving bicarbonate or carboxylate species (Collins et al., 2006). Peaks at ~1650 cm⁻¹ and 1287 cm⁻¹ can be assigned to ν₃(O-C-O)_a and ν₃(O-C-O)_s respectively of carboxylate (CO₂⁻) vibrational modes (Baltrusaitis et al., 2011; Su et al., 2008).

The bands centered at ~1614, ~1370, 1212 cm⁻¹ can be assigned to the ν₂(O-C-O)_a, ν₃(O-C-O)_s, and δ₄(C-OH) vibration modes respectively which were ascribed to the bicarbonate species (Fig. 12SA) (Sápi et al., 2018). The bicarbonate and carboxylate could convert to formate species, which play an important role in CO₂ hydrogenation on ceria based catalysts. Several different carbonates are also formed during the CO₂ adsorption and its hydrogenation, which do not participate in the process on CeO₂. Bridge bonded carbonates (two or three oxygen bonds to ceria surface) and bridge bonded hydrogen carbonate appear in a broad range at ~1212–1232 cm⁻¹ (Vayssilov et al., 2011) They are present even at 400 °C with high intensity. This very stable carbonate may be inactive in the CO₂ hydrogenation and it could contribute to the inhibition of the reaction. The characteristic vibrations (symmetric and asymmetric O-C-O and C-H modes) of formate appeared at 1560–1600, 1350–1380, and 2837 cm⁻¹ (Guo et al., 2018; Lin et al., 2018; Raskó et al., 2004; Wang et al., 2016). On pure

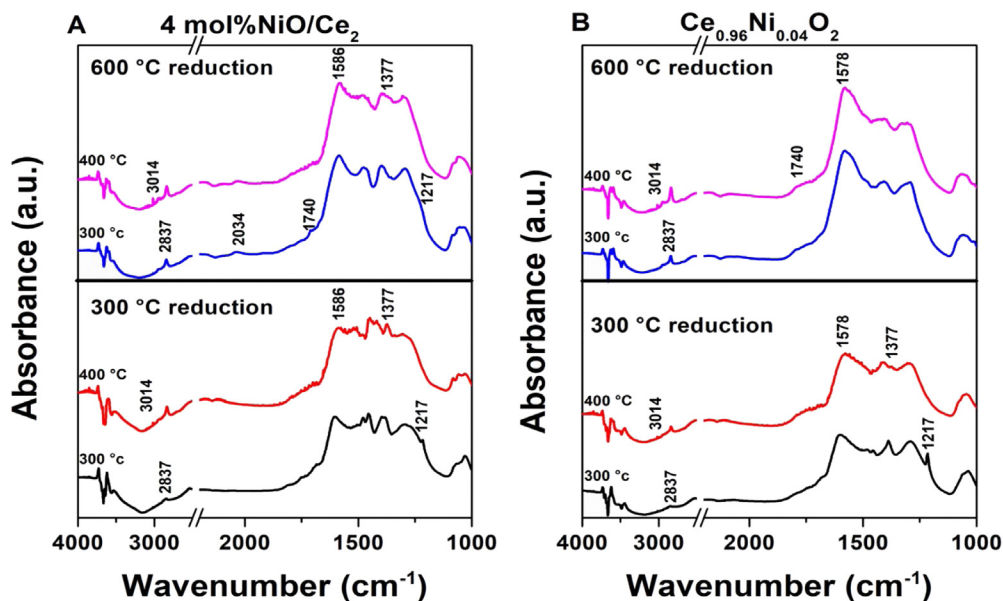


Fig. 5. DRIFTS spectra of (A) 4 mol% NiO/Ce₂O₃ and (B) Ce_{0.96}Ni_{0.04}O₂ obtained during CO₂ hydrogenation after different pre-reduction temperatures.

NiO, the IR bands obtained during CO₂ hydrogenation are identical to the published data earlier (Sapi et al., 2018) and are listed in Table S6.

Ni enhanced CeO₂ catalysts and their DRIFT spectra have different features during CO₂ hydrogenation. The dominant intermediate is the bicarbonate on both impregnated and solid solution samples at a low temperature range. The main IR bands for bicarbonate were detected at 1602–1611, 1408–1430, and 1216 cm⁻¹ (Table S6). These peaks disappeared around 250–350 °C. The peak around 1280–1292 cm⁻¹ is attributable to bidentate carbonate (Baltrusaitis et al., 2011; Guo et al., 2018; Lee et al., 2019). We should note that the very stable bridge bonded carbonates (at ~1212–1232 cm⁻¹) could not be detected on Ni enhanced CeO₂ catalysts. The important bands for formate are visible at ~1574–1585, 1398–1374, and 2837–2844 cm⁻¹ above 200 °C (Fig. 5 A and B). It should be mentioned that formate was found also as a key intermediate during CO₂ methanation on Ni containing ceria catalyst prepared with simple impregnation or with a modified hydrothermal method, published recently (Yu et al., 2021). In addition, Lee et al. (2019) presumed that, besides formate, a monodentate carbonate could be another intermediate in methane formation, especially at higher temperatures. In our case, this species is detected at 1387–1395 cm⁻¹.

Fig. 5A and B present the most important information about the reaction intermediates formed during CO₂ hydrogenation on the impregnated NiO/CeO₂ and the Ce_{0.96}Ni_{0.04}O₂ catalysts after different pre-treatments (300 °C and 600 °C). It is demonstrated in the figures, that the pre-reduction temperatures influence the amount and the thermal stability of formate. The results are compared at the same (~4%) Ni content. The figures present some selected spectra obtained at 300 and 400 °C.

Based on the literature and our data, we may conclude that the formate species originate from bicarbonate species. Bicarbonate disappeared when the formate bands showed up:



The further reaction of formate species likely determines the final products, and the type of modifiers may alter the reaction routes of formate. On pure ceria the formate decomposition only produced CO above 300 °C. A similar reaction mechanism was suggested for other similar catalytic systems (Laszlo et al., 2019; Sapi et al., 2018; Wang et al., 2017; Zhao et al., 2019).



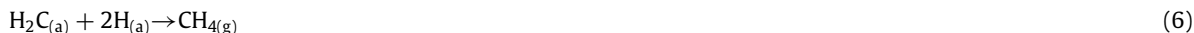
CO formation in CO₂ hydrogenation can be also explained via carboxylate (COOH) intermediate as it was suggested previously on clean ceria catalysts, too (Cheng and Lo, 2016):



These reaction sequences could be valid for the explanation of CO production in both types of Ni containing catalysts to a certain extent.

In Fig. 5 A at 300 °C pre-reduction the intensity of bicarbonate (1216 cm⁻¹) drastically decreased at 300 °C, and at the same time formate bands are developed (2844, ~1585–1590, and 1377 cm⁻¹). By increasing the temperature, the intensity of formate increased and the bands for gas phase methane and CO also intensified. At these temperatures, polydentate (1447 cm⁻¹) and monodentate (1508 cm⁻¹) carbonates are also present. Some features between 1100 and 900 cm⁻¹ may correspond to these carbonate-like species.

The catalytic measurements strongly indicate that the methane is formed with high selectivity on mixed oxides. XPS experiments revealed that metallic particles are produced and the Ce³⁺ concentration notably increased by hydrogen pre-treatment. The high methane selectivity on Ni modified ceria catalysts can be explained by the Ni⁰ particle assisted reaction between formate and hydrogen. The main role of Ni⁰ and support CeO₂ were to dissociate H₂. This conclusion was also drawn in similar Ni⁰ containing systems (Cheng and Lo, 2016; Yu et al., 2021). The reduced Ni particles help to produce the high amount of hydrogen needed to convert formates, which are located mainly at the Ni-ceria interface (Ni⁰ – NiO – CeO₂):



When hydrogen pretreatment was carried out at 600 °C, we obtained qualitatively the same picture (Fig. 5 A). Some differences can be attributed to the increased amount of metallic Ni, since Pre-reduction at 600 °C results in higher Ni⁰ concentration. Consequently, we detected a higher methane yield. The other remarkable difference is that the formate appeared at a lower temperature (200 °C) and in higher concentration at 300–400 °C than it was observed after 300 °C reduction (Fig. 5 A). The bicarbonate bands disappeared at lower temperatures (200 °C) in this case. This means that metallic Ni could catalyze not only the formate-hydrogen reaction but helps the bicarbonate-formate transformation, too (step 2).

After careful analysis of the spectra obtained during the reaction, a very weak band for adsorbed CO at ~2034 cm⁻¹ was detectable. Its intensity was much higher when a higher number of Ni⁰ particles are present (Fig. 5 A at 600 °C reduction). Adsorbed CO formation was also detected on almost similar systems previously (Lee et al., 2019; Yu et al., 2021). The origin of adsorbed CO can be attributed to the decomposition of formate or carboxylate (steps 3, 4). The other realistic scenario for adsorbed (or gas phase) CO formation is the transformation of formate to formaldehyde-like species, H₂CO. This species may decompose to CO at elevated temperatures. Indeed, our spectra show a weak band at 1740 cm⁻¹ above 350 °C. This band can be tentatively attributed to formaldehyde or formyl-like species, also derived from formate, which was reported on Ru/CeO₂ and NiO catalysts during the CO₂ hydrogenation (Sági et al., 2018; Wang et al., 2016). The formation and decomposition of formyl to CO could alter the methane selectivity in CO₂ hydrogenation.

Formaldehyde formation in HCOOH decomposition was observed previously on Pt supported TiO₂ (Raskó et al., 2004), and the formation and decomposition of formaldehyde on TiO₂ supported Rh and Au catalysts were studied earlier (Kecskés et al., 2004).



The CO₂ hydrogenation was also followed by DRIFTS on the solid solution sample at the same Ni quantity pre-reduced at two temperatures (Fig. 5B). The bicarbonate species were present up to 300–350 °C when the catalyst was pre-reduced at 300 °C. When the bicarbonate diminished, the formate showed up. From 300 °C its intensity increased continuously. The reaction proceeds with low conversion and high CO selectivity. In this case, the significant amount of formate decomposes via step 3, where the product is mainly CO. A new band was also developed at 1740 cm⁻¹ above 350 °C due to the formation of formyl-like species, which decomposes also to CO as it was discussed in previous cases (steps 5, 7).

When the catalyst was pre-reduced at 600 °C, more metallic Ni is formed, and the conversion of the reaction increased with high methane selectivity. The bicarbonate band disappeared already at 200 °C and the formate appeared at 200 °C, its intensity increased up to 350–400 °C (Fig. 5B). In these circumstances, the methane formation proceeds mainly via hydrogenation of formate. These results underline the importance of the role of Ni⁰ in the CO₂ methanation. It is turned out again that the metallic Ni catalysis first the bicarbonate-formate transformation (step 2) and then the hydrogenation of formate to methane (step 5,6). The catalytic measurements showed that the activities of impregnated and mixed oxide catalysts perform nearly the same activity and selectivity if the pre-reduction happens at 600 °C. Conversely, the TEM results indicate that the particle sizes are somewhat different (2–3 nm in the mixed oxide and ~5 nm in the impregnated sample) despite this fact the activities do not differ significantly. These experimental data suggest that the size effect does not play a decisive factor in this range. The most important factor is the Ni⁰/NiO ratio in the Ni⁰-NiO-CeO_x interface.

4. Conclusions and summary

Ni/NiO enhanced CeO₂ based catalysts were tested in CO₂ hydrogenation with the objective to demonstrate the importance of metallic Ni and Ni⁰-NiO-CeO_{2-x} interface. Two catalysts, a NiO-CeO₂ solid solution (labeled as Ce_{0.96}Ni_{0.04}O₂) and CeO₂ supported NiO nanoparticles, impregnated catalysts (labeled as 4 mol% NiO/CeO₂) were prepared. Differing from solid solutions, the catalytic behavior of impregnated catalyst retaining an interface was significantly better regarding conversion and product selectivity due to the formation of Ni⁰-NiO-CeO_{2-x}, the hydrogen spillover phenomena, and the

more reduced state of the CeO₂. The metallic Ni content was tunable by the temperature of hydrogen pretreatment. The impregnated catalyst with significant metallic content exhibited high activity and high methane selectivity. The mixed oxide was more resistant to reduction, in the case of both the Ni²⁺ and Ce⁴⁺ species. This type of catalyst has low activity with high CO selectivity. The activity and methane selectivity increased considerably by increasing the metal content or higher hydrogen pretreatment temperature. The 4 mol% NiO/CeO₂ catalyst showed a CO₂ conversion of 65% with the methane selectivity of 95% at 400 °C which is 10 times higher compared to the Ce_{0.96}Ni_{0.04}O₂ solid solution counterpart (CO₂ conversion = 6.39%, CO selectivity = 95% at 400 °C), indicating that Ni/NiO/CeO₂ interfacial catalyst is more active than the solid solution where the Ni²⁺ ions are built into the crystal lattice. XPS showed that the Ce³⁺/Ce⁴⁺ ratio is higher on the 4 mol% NiO/CeO₂ spent catalyst than that on the other catalysts. The reason for the higher activity of the interfacial sample is the synergistic effect of the higher Ni⁰ concentration on the sample surface (also confirmed by XPS), the reducibility of the CeO₂ support, which provides catalytically active sites for the O = C = O bonds to be broken, facilitating the conversion to methane. Ni⁰ supplies a significant amount of hydrogen atoms, which react with formate intermediates located at the Ni⁰-NiO-CeO_{2-x} interface. The critical concentration of metallic Ni helps to create the proper interface, which also plays an important role in methanation. In the case of the Ce_{0.96}Ni_{0.04}O₂ counterpart, the Ni distribution is rather uniform, supposing a lower particle size than the impregnated sample (confirmed by HAADF STEM), therefore the proper interface did not develop after 300 °C reduction. High temperature reduction (~600 °C) is necessary to reach the same active interface in these types of catalysts. *Operando* DRIFT spectral results show that the bicarbonate species is the origin of formate surface intermediates, which play important role in methane formation. It is concluded that metallic Ni catalyzes not only the methane production from formate but also the bicarbonate-formate transformation. The most important factor in the high performance of the catalysts is the Ni⁰/NiO ratio in the Ni⁰-NiO-CeO_x interface.

CRedit authorship contribution statement

Ákos Szamosvölgyi: Conception and design of study, Writing – original draft. **T. Rajkumar:** Conception and design of study. **András Sági:** Conception and design of study, Writing – original draft. **Imre Szent:** Analysis and/or interpretation of data. **Marietta Ábel:** Analysis and/or interpretation of data. **Juan Fernando Gómez-Pérez:** Writing – review & editing. **Kornélia Baán:** Acquisition of data. **Zsolt Fogarassy:** Acquisition of data. **Erzsébet Dodony:** Acquisition of data. **Béla Pécz:** Writing – original draft. **Seema Garg:** Analysis and/or interpretation of data. **János Kiss:** Acquisition of data, Writing – review & editing. **Ákos Kukovecz:** Writing – original draft. **Zoltán Kónya:** Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2022.102747>.

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