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Operando FT-IR study on basicity improvement of Ni(Mg, Al)O hydrotalcite-derived catalysts promoted by glow plasma discharge

To cite this article: R DEBEK *et al* 2019 *Plasma Sci. Technol.* **21** 045503

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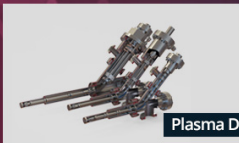
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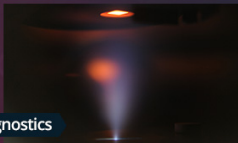
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Operando FT-IR study on basicity improvement of Ni(Mg, Al)O hydrotalcite-derived catalysts promoted by glow plasma discharge

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Received 6 October 2018, revised 29 November 2018

Accepted for publication 10 December 2018

Published 31 January 2019



CrossMark

Abstract

CO₂ adsorption on the surface of hydrotalcite-derived mixed oxide catalysts was investigated under low pressure glow discharge plasma in *operando* conditions via FT-IR spectroscopy. Nickel catalysts were promoted with various transition metal species (Ce, Fe, La, Zr) to influence their physico-chemical properties. Fe and Zr species were successfully incorporated into hydrotalcite brucite layers. After calcination formed a single phase with Ni(Mg, Al)O mixed oxide, while La and Ce species formed separate phases. This had a consequence in the distribution of surface basic sites as well as in the affinity to CO produced upon CO₂ dissociation in plasma. Plasma treatment activated the surface of prepared materials and changed their properties via the generation of strong basic sites associated with low coordinated surface oxygen anions. Moreover, the CO₂ adsorption capacity of prepared materials increased after plasma treatment.

Keywords: plasma, glow discharge, basicity, hydrotalcite, carbon dioxide

(Some figures may appear in colour only in the online journal)

1. Introduction

Application of hybrid plasma-catalytic processes has recently gained much attention due to the fact that non-thermal plasmas are able to induce various chemical reactions at both atmospheric pressure and room temperature [1–4]. Non-thermal plasmas produce the abundance of highly energetic species including electrons, ions etc that allow chemical reaction initiation. The role of a catalyst in such a process is mainly to properly shape the selectivity of the overall process [5, 6]. Taking into account the continuous increase of carbon dioxide emissions, the application of both plasma technologies and

catalysis has been intensively considered for CO₂ chemical utilization [2, 7, 8]. Many recent studies report that CO₂ can be dissociated to CO and O in various type of plasmas [3, 8–12]. Several studies concerning different CO₂ consuming reactions and catalytic systems have been carried out in the last decades [13–17]. The possibility of obtaining reactive and excited CO₂ species capable to promote a chemical reaction is a very attractive fact since CO₂ is a highly stable and non-reactive molecule. Hence, usually high temperatures and/or highly active catalysts are required to initiate a chemical reaction involving CO₂, such as dry reforming of methane or hydrogenation of carbon dioxide [15–17].

Table 1. Summary of characterization of prepared materials.

Sample	Cations in brucite layers ^a	Ni (wt%)	M ^b (wt%)	S _{BET} ^c (m ² g ⁻¹)	Basicity ^d (μmol m ⁻²)	Ni particle size ^e (nm)	T _{max} ^f red. (°C)
MgAl	Mg ²⁺ , Al ³⁺	—	—	95	2.43 ^g	—	—
Ni	Mg ²⁺ , Ni ²⁺ , Al ³⁺	19.6	—	115	0.90	6	835
NiCe	Mg ²⁺ , Ni ²⁺ , Al ³⁺	17.9	3.7	102	0.89	8	810
NiFe	Mg ²⁺ , Ni ²⁺ , Al ³⁺ , Fe ³⁺	20.0	1.5	169	0.66	7	798
NiLa	Mg ²⁺ , Ni ²⁺ , Al ³⁺ , La ³⁺	21.2	1.8	165	0.84	9	820
NiZr	Mg ²⁺ , Ni ²⁺ , Al ³⁺ , Zr ⁴⁺	17.3	2.5	229	0.22	6	858

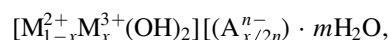
^a Cations introduced into hydrotalcite brucite layers at the co-precipitation stage.^b Content of the second metal/promoter.^c Specific surface area.^d Determined via CO₂-TPD experiments for *in situ* reduced catalysts.^e Estimated by Scherrer equation for *ex situ* reduced catalysts.^f Maximum reduction temperature from the H₂-TPD profile.^g Determined for calcined sample.

The main advantages of the application of both plasma and catalyst are the synergetic effects resulting in the better performance of both together. It is important to underline that catalyst and plasma are interdependent and both influence each other. On one hand, plasma interacts with the catalyst and may change its morphology, structure and properties through several interactions including etching and sputtering, heating, charging and charge transfer, deposition and implantation or photon irradiation. On the other hand, catalyst properties (dielectric constant, morphology) may affect plasma properties near catalysts surface (electric field distribution, electron-energy distribution) or creation of micro-discharges within the pores of the catalyst [5, 18–21]. The interdependence of plasma and catalyst makes the overall process very complex, thus, it is important to gain knowledge about their interactions.

CO₂ consuming reactions, such as dry reforming of methane and CO₂ hydrogenation to methane, have been studied in plasma-catalytic systems [19, 20, 22–28]. Application of both plasma and catalysts resulted in a significant increase in CO₂ conversions, lower reaction temperatures and increase in selectivity of these CO₂ consuming reactions, proving synergetic effect between plasma and catalyst. However, mechanisms of the reaction in plasma-catalytic systems and the plasma-catalysts interactions remain an open question. To the best of our knowledge, there are only a few reports concerning mechanisms of CO₂ consuming reactions on the surface of the catalyst under plasma [20, 28–30]. Therefore, in this study CO₂ adsorption on the surface of hydrotalcite-derived catalysts during plasma discharge was investigated.

The selected catalysts for this research were proven to be efficient and promising materials to catalyze both dry reforming of methane and CO₂ methanation under thermal catalysis conditions [31–35]. The beneficial performance in CO₂ valorization reactions comes from the unique properties of materials derived from hydrotalcites. Hydrotalcite-like materials are layered double hydroxides which can be

described by the general formula [36, 37]:



where: M²⁺ and M³⁺—di- and tri-valent cations present in brucite-like layers, *x*—mole fraction of trivalent cations, Aⁿ⁻—anions and *m*—the number of water molecules present in the interlayer spaces. Apart from di- and tri-valent cations it is as well possible to introduce mono or tetra-valent cations e.g. Zr⁴⁺ [38]. Upon calcination layered structure of hydrotalcite collapse and periclase like the structure of MgO is obtained with isomorphic substituted cations from hydrotalcites brucite layers. This gives an opportunity to obtain homogeneous mixture of oxides with randomly distributed cations. As the layer's composition, both type and cations content, may be strictly controlled it allows tailoring catalytic properties of the final material.

CO₂ adsorption is an important and an essential step of the catalytic reaction. Therefore, it is crucial to understand how CO₂ adsorption is affected by plasma. In order to guarantee the plasma stability and to prolong the lifetime of species generated in the plasma, in this study low pressure glow discharge plasma was applied. The obtained results showed improvement of catalysts basicity via plasma treatment which might be considered an important and novel insight into mechanisms of mentioned CO₂ consuming reactions.

2. Experimental

2.1. Catalyst preparation

The preparation procedure of materials investigated in this study has been reported in detail elsewhere [39–41]. Shortly, catalysts precursors—hydrotalcites were prepared via co-precipitation at constant pH of 10 at 65 °C under constant stirring. Depending on the desired hydrotalcite layers composition various nitrate solutions were prepared (table 1). The appropriate amounts of metal nitrates solution (total cations

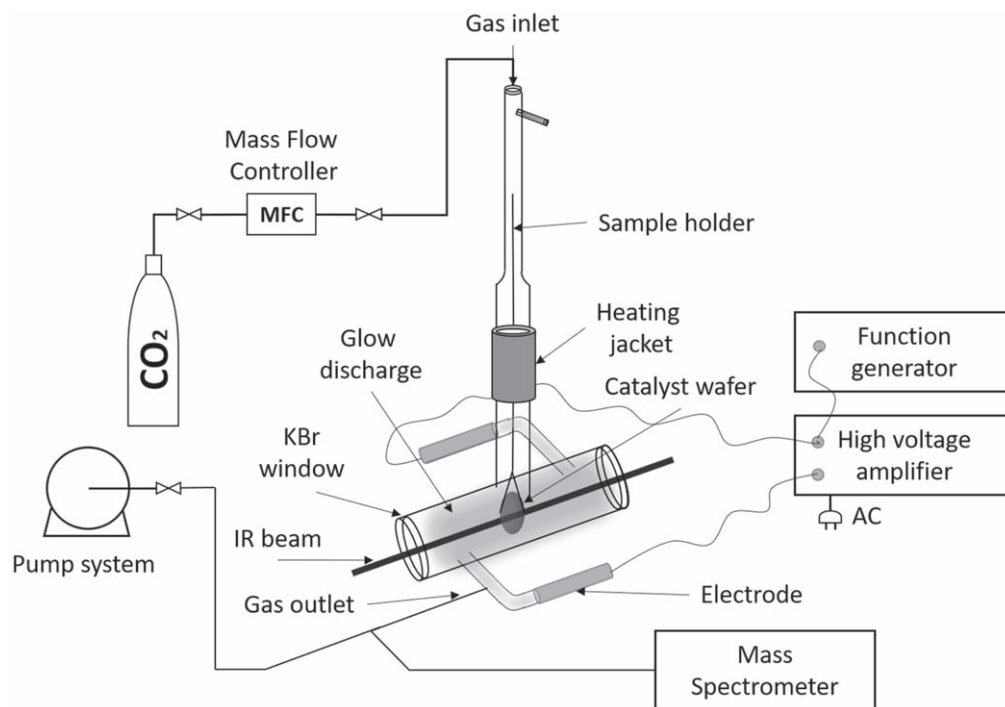


Figure 1. Scheme of operando IR reactor set up used for *in situ* measurements of CO₂ adsorption.

concentration equal to 1 M) and 1 M NaOH were added simultaneously to the solution of sodium carbonate. Co-precipitation in the Na₂CO₃ solution guarantees the introduction of carbonate anions into interlayer spaces. The addition of both solutions was controlled and adjusted to work with constant pH equal to 10. The obtained mineral suspension was kept at 65 °C for 1 h and was subsequently washed with warm distilled water (ca. 5 dm³) and dried overnight at 80 °C. In this way, Mg, Al and Ni, Mg, Al containing samples were prepared. In order to investigate the effect of various promoters, Ni-containing hydrotalcite sample was promoted with Ce, La, Zr and Fe species. La, Zr and Fe species were introduced into hydrotalcite structure (brucite-like layers) at the co-precipitation stage by addition of an appropriate amount of lanthanum, zirconium or iron nitrate to the nitrate's solution. On the other hand, due to the large ionic radii of Ce³⁺, it is impossible to incorporate them into brucite-like layers. Therefore, Ce species were introduced into the catalytic system via the adsorption of [Ce(EDTA)]⁻. The [Ce(EDTA)]⁻ complex solution was prepared by mixing of equimolar amounts of Ce³⁺ and EDTA⁴⁻ originating respectively form the solutions of cerium nitrate and disodium EDTA. The final concentration of cerium complexes was equal to 3 wt%. The prepared solution was subsequently aged for 24 h at room temperature. Adsorption was performed for 24 h at room temperature via constant stirring of Ni, Mg, Al containing hydrotalcite sample with a prepared complex solution. Modified hydrotalcite was further filtered and dried overnight at 80 °C.

The obtained hydrotalcites promoted with various species were calcined at 550 °C for 4 h in the flow of air (10 cm³ min⁻¹). The composition and designation of prepared catalysts are presented in table 1.

2.2. Physico-chemical characterization of catalysts

The crystallinity and structure of catalysts and their precursors were evaluated with the aid of an EMPYREAN diffractometer from PANalytical equipped with a Cu K_α radiation source. The composition of prepared samples was evaluated by means of x-ray fluorescence analyses performed in an energy dispersive XEPOS spectrometer from Spectro-Ametek. Temperature-programmed reduction experiments (H₂-TPR) were carried out in a BELCAT-M apparatus from BEL Japan equipped with a thermal conductivity detector. Catalyst sample (ca. 50 mg) was firstly degassed at 100 °C for 2 h. Then the sample was reduced between 100 °C and 950 °C at 7.5 °C min⁻¹ heating rate in 5% vol. H₂ in Ar. The same apparatus was used to perform CO₂-TPD experiments, in which the sample (ca. 60 mg) was firstly degassed at 500 °C for 2 h. After cooling down the sample mixture of 10% vol. CO₂ in He was introduced to the reactor for 1 h to adsorb CO₂. Subsequently, He was introduced into the reactor for 15 min to desorb weakly physically adsorbed CO₂. The samples were further heated up to 800 °C under He flow at a heating rate of 10 °C min⁻¹, while the evolution of CO₂ was measured with the aid of a TC detector. In the case of nickel-containing samples, *in situ* reduction at 900 °C in the stream of H₂ was performed prior to CO₂-TPD experiments.

2.3. Operando FT-IR spectroscopy setup

The experimental setup used in this study was described in detail in our previous work [29, 30] and is schematically shown in figure 1. Prepared catalysts were pressed (ca. 1.5 × 10⁸ Pa) into self-supported wafers (ca. 2 cm², 25–30 mg). Prior to wafers preparation, catalysts powders were reduced *ex situ* in the stream

of 5% vol. H_2 in Ar at 900 °C for 1 h. The materials were reduced in order to obtain nickel metallic phase, as it is active in CO_2 consuming reactions and it was important to investigate CO_2 adsorption under the same phase composition as during regular work of catalysts. Only MgAl wafer was prepared from the calcined material. The sample holder containing catalyst wafer was placed inside the reactor within the glow discharge zone perpendicularly to the IR beam. The plasma discharge was generated between two tungsten electrodes using a function generator (FI5350GA) coupled to a high voltage amplifier (Trek model 20/20C). With the function generator pulse signal was generated with the frequency of 66 Hz, peak to peak voltage of $3V_{pp}$ and cycle time 15 ms with the duty of 33% (5 ms ON and 10 ms OFF). The CO_2 was introduced into the reactor via Brooks mass flow controllers. The outlet of the reactor was connected to a vacuum pump and to a Quadrupole Mass Spectrometer (Pfeiffer Omnistar GSD 301) in order to analyze the composition of the gases leaving the reactor. The reactor was placed inside the compartment of a Bruker Vertex 80 v spectrometer with a mercury–cadmium–telluride MCT detector. The FT-IR spectra were recorded between 4000 and 1000 cm^{-1} at 0.2 cm^{-1} optical resolution.

Prior to CO_2 adsorption in glow discharge plasma experiments, the catalyst was activated at 450 °C during 12 h under secondary vacuum. Afterwards, the sample was cooled down to room temperature and CO_2 was introduced into the reactor with a volumetric flow rate of $2\text{ cm}^3\text{ min}^{-1}$ STP. The pressure measured inside the reactor in CO_2 flow was equal to 3.5 Torr. After introducing CO_2 to the reactor, FT-IR spectra were recorded until catalyst surface was saturated with CO_2 species and no difference between spectra was observed. Then plasma was turned on and spectra were again recorded until no difference between them was observed. In order to evaluate the changes in catalysts surface and to observe adsorbed species, FT-IR spectra were as well recorded after turning off the plasma and after turning off the CO_2 flow. The latter was performed under secondary vacuum.

3. Results and discussion

3.1. Physico-chemical characterization of the hydrotalcite-derived catalysts

A detailed discussion about the physico-chemical properties of materials studied in this work has been presented in our previous papers concerning catalysts for dry methane reforming [33–35, 39, 40] and for CO_2 methanation [31, 32, 41]. To elucidate the results in this paper, the main characteristics of prepared materials are listed in table 1, as well as in [appendix](#).

XRD experiments (see figure A1, [appendix](#)) confirmed the successful synthesis of the hydrotalcite materials. Magnesium, nickel and aluminum species were successfully introduced into brucite layers of hydrotalcite, which guaranteed the formation of homogenous oxides mixture with periclase structure after decomposition of hydrotalcite precursor. For Zr and Fe promoted

materials, the successful incorporation of promoter species into hydrotalcite layers was as well confirmed [33]. Thus, after thermal decomposition, i.e. calcination, Fe and Zr promoted materials formed a single phase of periclase-like mixed oxides. In the case of La promoted sample, La species introduced at the co-precipitation stage formed a separate phase of lanthanum oxide upon calcination [41]. Similarly, a separate phase of Ce species was observed for Ce promoted material [35].

The introduction of various promoters influenced the final structure of catalyst as well as the partially shaped properties of final materials [31, 33, 40]. As can be observed in table 1, the presence of the different promoters had a significant influence on the final textural properties of the resulting catalyst (see figure A4, [appendix](#)). For instance, zirconia introduction resulted in materials having a high specific surface area with small pores (ca. 2 nm) and narrow pore size distribution. However, Ce species partially blocked the pores of Ni(Mg, Al)O mixed oxide resulting in the lower surface area and pore volume. The use of promoters has as well important consequences when it comes to the basicity of the different catalytic materials prepared, as well as on their reducibility. Since these catalysts were synthesized aiming to their application in CO_2 chemical utilization reactions, the reducibility of nickel species is a very important factor. In order to guarantee complete reduction of surface nickel species, samples were reduced at 900 °C, which was slightly above the maximum reduction temperature observed for all samples in H_2 -TPR experiments (see figure A2, [appendix](#)). As previously discussed, such high reduction temperatures are due to the formation of a Ni(Mg, Al)O mixed oxide phase [32, 34, 35]. Moreover, the presence of promoters influenced reducibility of nickel species, which had an effect of Ni particle size (table 1). These characteristics were confirmed by XRD and TEM analysis (see figures A1 and A3, [appendix](#)).

3.2. Non-catalytic CO_2 gas phase dissociation under plasma discharge

FT-IR spectra recorded using an empty reactor and in the flow of CO_2 ($2\text{ cm}^3\text{ min}^{-1}$ STP) are presented in figure 2(a) Before plasma ignition, the spectra exhibited typical absorption bands for the CO_2 present in the gas phase (bands at 3715, 3610, 2365 and 2335 cm^{-1}). After plasma ignition, the bands characteristic for CO gas phase appeared at 2176 and 2107 cm^{-1} , pointing to the occurrence of CO_2 dissociation. The production of CO and O_2 in plasma was as well observed by mass spectrometry (figure 2(b)).

The process of CO_2 dissociation under glow discharge plasma has been widely reported in the literature [3, 9, 10, 42, 43]. The highly energetic electrons generated by plasma at room temperature are able to initiate the highly endothermic CO_2 dissociation reaction ($\Delta H^0 = 280\text{ kJ mol}^{-1}$) (1) [11]. As the main electronic processes in the CO_2 plasma are excitation (2) and ionization (3), both processes may lead to the formation of CO and O_2 . However, several undesired reactions leading to

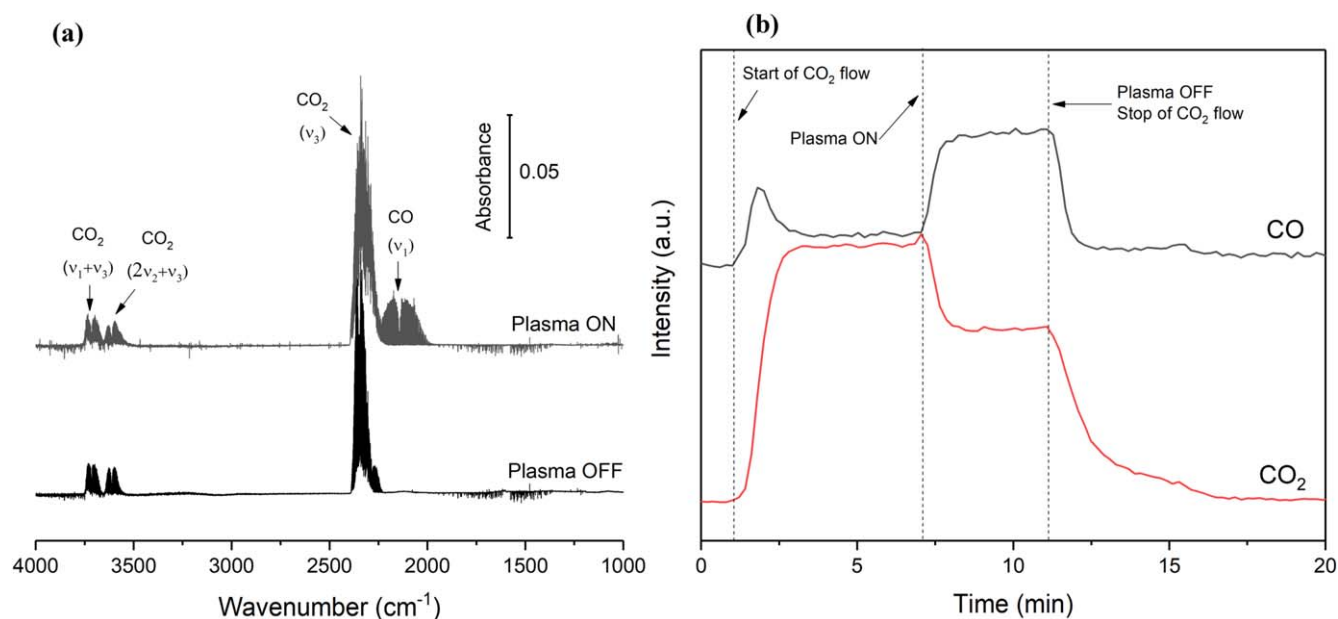


Figure 2. Spectra registered in the flow of CO_2 ($2 \text{ cm}^3 \text{ min}^{-1}$ STP) in an empty reactor with and without plasma (a) and corresponding data registered via mass spectrometer (b).

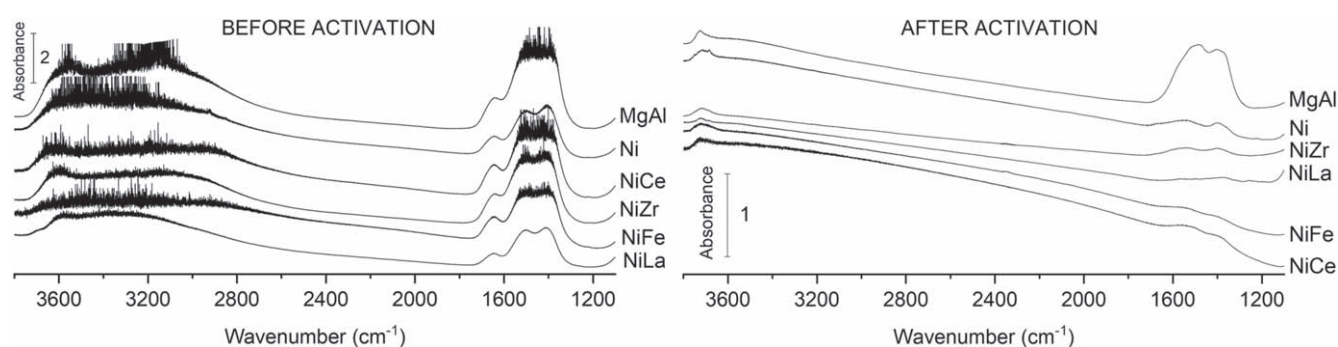
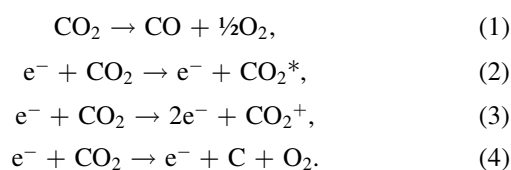


Figure 3. Spectra recorded for prepared catalyst before and activation of catalyst surface.

the formation of carbon deposits can be also observed (e.g. (4))



3.3. Off-plasma CO_2 adsorption on the catalysts surface

Prior to *operando* experiments with CO_2 adsorption in plasma, the surface of the catalyst was activated overnight (12 h) under secondary vacuum at 450°C . FT-IR spectra recorded before and after activation (figure 3) confirmed that all the adsorbed species were removed from the catalysts surface. After activation, all the materials (figure 3) exhibited small intensity adsorption bands at ca. 3720 and 3865 cm^{-1} , which may be attributed to the presence of surface hydroxyl groups in hydrotalcite-derived mixed oxides [44]. The absence of the broad adsorption band in the $4000\text{--}3600 \text{ cm}^{-1}$

region originating from the water molecules points to the good vacuum system operation. Additionally, bands at ca. 1540 and 1400 cm^{-1} were still present sometimes (e.g. samples MgAl and Ni) even after activation in a vacuum, which may be attributed to typical mixed-oxide structural bands.

After activation, the surface of catalysts was saturated with CO_2 (CO_2 stream $2 \text{ cm}^3 \text{ min}^{-1}$ STP). The FT-IR spectra recorded for the different catalysts under CO_2 flow are presented in figure 4. All the spectra exhibited common absorption bands. CO_2 was present in the gas phase (same bands as in figure 2(a)) [45]. Several overlapping bands were observed within the region of carbonates modes ($1200\text{--}1700 \text{ cm}^{-1}$), pointing to a somehow heterogeneous surface basicity. CO_2 adsorbed species, their vibrational modes and position of absorption bands are presented in table 2. According to literature, the bands appearing at $1200\text{--}1700 \text{ cm}^{-1}$ correspond to different bicarbonate, bidentate carbonates and monodentate carbonates species [46–48]. Thus, the presence of various sites with different basic character results in the formation of diverse surface carbonate species.

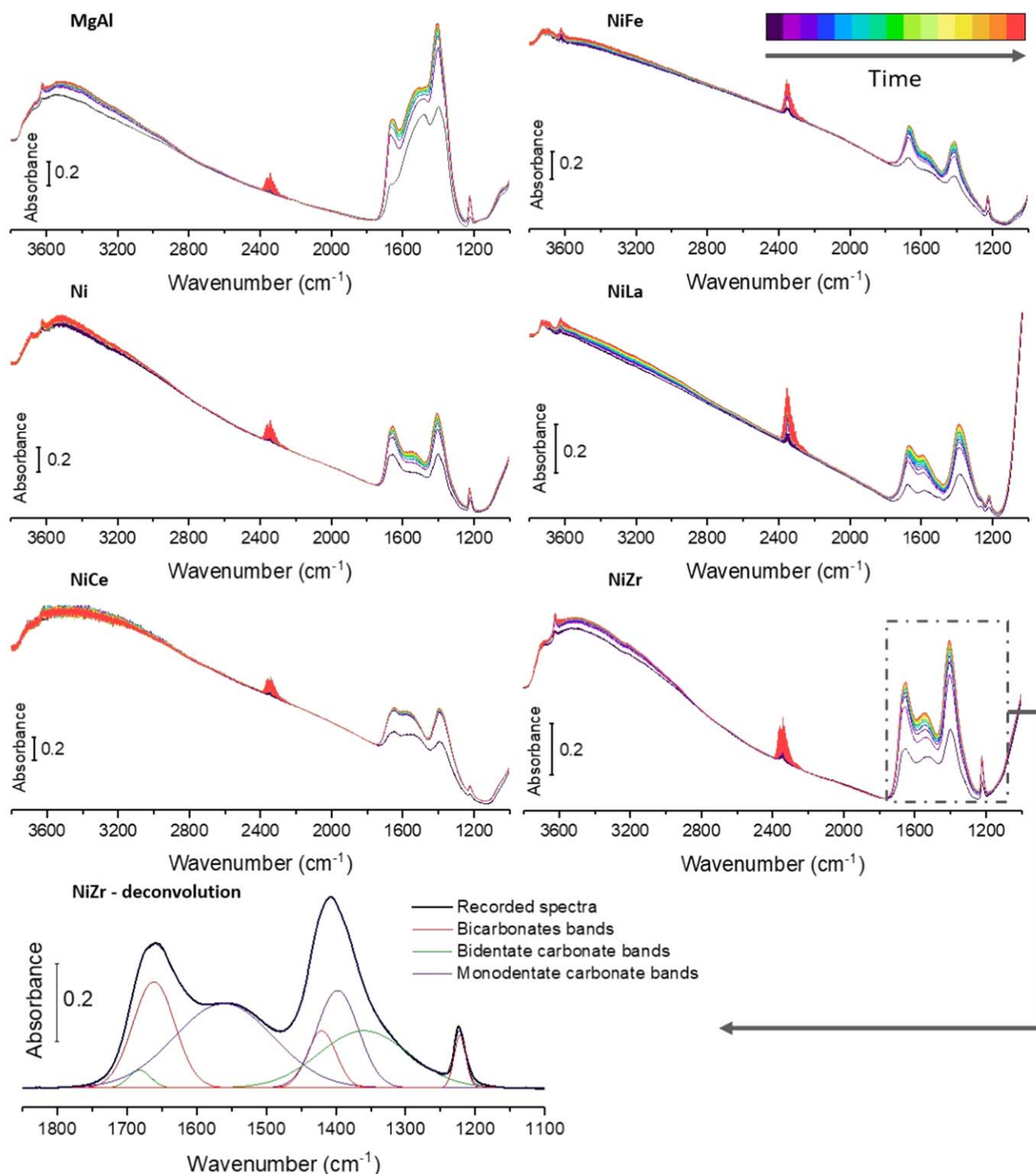


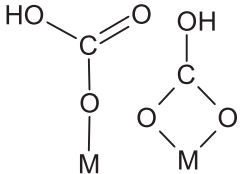
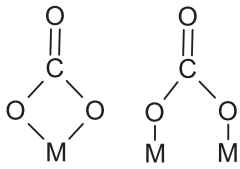
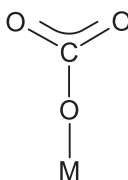
Figure 4. FT-IR spectra of the prepared catalysts in the stream of CO_2 ($2 \text{ cm}^3 \text{ min}^{-1}$ STP) recorded until the surface of samples were saturated with CO_2 species and exemplary deconvolution of overlapping bands in the carbonate region in the case of NiZr sample.

Bicarbonates are formed on surface hydroxyl groups (weak Brønsted basic sites), while carbonates are formed on surface oxygen atoms with different coordination degrees. Monodentate carbonates require oxygen species with the lowest coordination degree i.e. surface O^{2-} anions (strong Lewis base). Bidentate carbonates (both chelating and bridging) do not only require oxygen species but also adjacent cationic metal sites

(intermediate Lewis acid-base pairs) [49–52]. Additionally, a weaker band (results not shown) at $1050\text{--}1070 \text{ cm}^{-1}$ was also visible in all cases, which corresponds to the overlapping contributions of these three carbonate species [48].

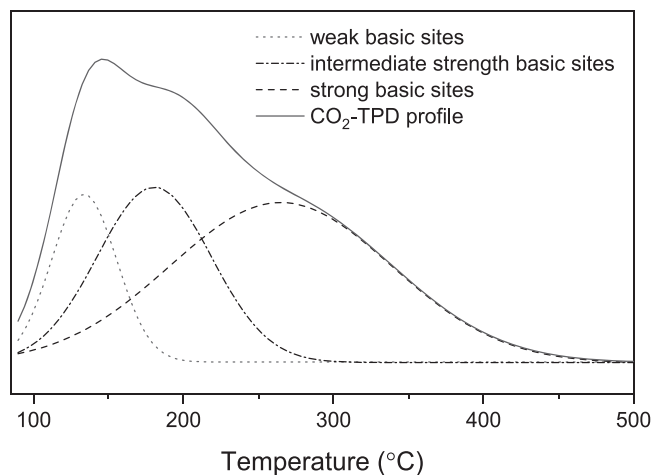
All examined catalysts showed the presence of bicarbonate, mono- and bidentate carbonate species. An example of deconvolution of this $1200\text{--}1700 \text{ cm}^{-1}$ spectral region for the

Table 2. Absorption bands and their position of CO₂ species adsorbed on the hydrotalcite-derived mixed-oxide surface.

Adsorbed species	Vibration mode	References			
		[46]	[47]	[48]	This work
Bicarbonates HCO ₃ [−]			3616		3620
	ν (OH)				
	ν_{as} (OCO)	1650–1670	1670	1685–1690	1640–1660
	ν_s (OCO)	1410–1440	1470		1400–1420
Bidentate carbonate <i>b</i> -CO ₃ ^{2−}					
	δ (COH)	1220	1230	1215–1225	1215–1225
	ν (C=O)		1570–1680		
	ν_{as} (OCO)	1610–1630	1250–1350	1645–1655	1670–1690
Monodentate carbonate <i>m</i> -CO ₃ ^{2−}					
	ν_s (OCO)	1320–1340	1040–1060	1300–1325	1300–1340
	$\Delta\nu$	290	210–290	330–345	330–370
	ν_{as} (OCO)	1510–1560	1500–1550	1575–1590	1530–1570
	ν_s (OCO)	1360–1400	1400–1450	1505–1530	1360–1390
	$\Delta\nu$	150–200	100	60–70	170–180

NiZr is also shown in figure 4. As observed in table 2, the position of the carbonate bands may be shifted. The spectral parameter $\Delta\nu_3$ is usually used to properly assign species modes. The $\Delta\nu_3$ parameter represents the splitting of the degenerate asymmetric ν_{OCO} vibration, which is caused by the lowered symmetry of adsorbed species with respect to free carbonate ion in inorganic salt. The value of this parameter depends on the nature of adsorbed species and therefore may be treated as a measure of the strength of the basic site, following the rule: the lower the splitting the stronger the basic site [44, 48].

The intensity of all the observed bands was increasing with time until complete saturation of catalyst surface occurred. The obtained results of FT-IR analysis agree, in fact, with the CO₂-TPD experiments (figure 5), since these CO₂-TPD profiles may be deconvoluted into three contributions of carbonate species. The comparison of the CO₂-TPD profiles of reduced and calcined materials, as reported in our previous work [39], showed that upon reduction the surface basicity is strongly modified. Upon reduction, nickel species are derived from the pristine structure of periclase and form separate metallic nickel phase, which may cover and partially block access to support and thus result in a decrease of total basicity. As the studied catalysts were reduced *ex situ*, partial oxidation of Ni sites may have occurred to a certain extent, leading to its passivation. Therefore, in order to avoid any misleading conclusions, the only CO₂-TPD profile of calcined MgAl sample was presented in this work and basicity of the

**Figure 5.** CO₂-TPD profile registered for MgAl sample after calcination at 550 °C for 4 h in the stream of air.

catalyst was compared via integration of the bands in the carbonate species region. The estimated surface basicity of different materials followed the sequence: MgAl > Ni > NiZr > NiCe > NiFe > NiLa. The highest basicity was shown by the support alone (MgAl sample), which may be explained by the highest content of highly basic magnesia. It is important to underline that due to the high stability of the CO₂ molecule, any CO₂ valorization processes require the presence of highly active metal. Therefore, catalyst activity is not

only the function of basicity but also various other parameters, including the size of nickel crystallites or the presence of promoters. The introduction of nickel as well as of the different promoters led to decreased surface basicity, indicating that the introduction of transition metal promoters to catalytic system affects its CO₂ adsorption capacity (as well confirmed by CO₂-TPD, see table 1).

The FT-IR study of CO₂ adsorption at room temperature on the hydrotalcite derived catalysts (figure 4) showed that although all samples confirmed the presence of weak, intermediate and strong basic sites, their presence and contribution to overall basicity is strongly dependent on the composition of prepared catalysts. The highest basicity was observed for the MgAl sample. Addition of nickel and other transition metal promoters changed the distribution of weak, intermediate and strong basic sites of each catalyst, which affects their final performance in CO₂ consuming reactions. E.g. for CO₂ methanation presence of intermediate strength basic sites was reported to greatly increase CO₂ conversion and CH₄ yield [32, 53, 54], while for dry reforming of methane strong basic sites were reported to improve catalyst stability [39, 55].

3.4. CO₂ adsorption under glow discharge plasma

After saturating the surface of prepared materials with CO₂, catalysts wafers were exposed to pulsed glow discharge plasma. The FT-IR spectra in the carbonate region recorded under plasma are presented in figure 6 (right side of the graph). For the ease of comparison, on the left side of figure 6 the FT-IR spectra recorded upon different gas/plasma configurations were presented: (i) black line—spectra recorded under flow of CO₂ (2 cm³ min⁻¹ STP), surface saturated with CO₂ species; (ii) blue line—first spectra recorded under plasma with CO₂ flow; (iii) red line—last spectra recorded under plasma and CO₂ flow and (iv) green line—spectra recorded under vacuum without CO₂ flow and after turning off the plasma. The FT-IR spectra in the region of the gas phase and linearly adsorbed CO₂ and CO are presented in figure 7. No difference in the 4000–2500 cm⁻¹ region was observed.

The comparison of the recorded spectra in the carbonate region (figure 6) clearly shows that right after plasma ignition significant changes occurred on the distribution of carbonate species (black and blue lines; figure 6). In all cases, the intensity of the bands associated with bicarbonate species notably decreased (bands at ca. 1650, 1420 and 1220 cm⁻¹). Bicarbonate species were consumed in plasma until steady-state conditions were reached and no changes were observed (red line). Similar observations consider the bands associated with bidentate carbonate species (shoulders at 1670, 1300–1340 cm⁻¹). The behavior of the various catalytic materials mainly differed in the intensity of bands associated with strong basic sites observed at ca. 1550 and 1380 cm⁻¹. Except for samples NiCe and NiLa, right after turning on the plasma, the band at ca. 1550 cm⁻¹ significantly increased, pointing to the increase in surface basicity (comparison of black and blue lines). This difference between prepared catalysts may come from the fact that NiCe and NiLa samples were characterized by strong surface basicity

before turning on the plasma (black line) when the intensity of bands associated to monodentate to other carbonate species is compared. As the intensity of the band at ca. 1550 cm⁻¹ increased with time under plasma conditions (apart from NiZr sample) and the band in the region 1420–1380 cm⁻¹ shifted towards lower wavenumbers, it may be stated that for all samples strong surface basicity is promoted. In case of NiZr sample, after an initial increase in surface basicity (black line and blue line) associated to the increase of the concentration of surface monodentate species, the intensity of all bands in the carbonate region decreases with time (comparison of the blue and red line). This behavior suggests that while plasma is turned on, it activates the surface and promotes CO₂ adsorption in the form of monodentate carbonate species. This effect seems to be however temporary since band intensity decreased with exposure time.

The most interesting conclusions may be driven when spectra before and during plasma treatment are compared with respect to the one recorded after plasma discharges and after catalysts surface was again saturated with CO₂ species (green line figure 6). One could expect that, after turning off plasma and introducing CO₂ stream, the catalyst surface should regenerate and go back to its original state (black line). However, observed results prove otherwise. In case of all samples increase in surface basicity after plasma discharges are observed (green lines). This clearly indicates that the surface of all catalysts underwent some changes, which promoted the creation of low coordinated oxygen species on the surface. It is well known that plasma interacts with solids and may change its surface properties [18, 21, 56]. In the presented case it seems that highly energetic plasma species through the collision with the surface modified surface sites making them available for CO₂ adsorption, which may explain the initial increase of the bands intensity after plasma ignition. Another possibility is that plasma species interact with adsorbed carbonates causing the change in their interactions with the surface and the surface itself. The exact understanding of how these process proceeds require additional research. However, at this point, it was clearly proven under *operando* conditions that plasma treatment modified the surface of hydrotalcite-derived mixed oxides and promoted the creation of strong basic sites.

Similarly, as in the experiments performed with an empty reactor, after turning on the plasma CO and O₂ production was observed, clearly pointing to the CO₂ dissociation under plasma conditions. Observation of the CO adsorption region in the FT-IR spectra not only confirmed CO production (figure 7) but also showed additional differences between catalysts surface. In figure 7, FT-IR spectra registered after CO₂ adsorption before and after plasma treatment are presented. In the case of samples NiCe and NiLa after plasma treatment, CO species adsorbed on the surface were observed (band at ca. 2200 cm⁻¹). Both catalysts in the previous discussion proved to have an initial high distribution of strong basic sites. What is more, in case of those materials, it was proven that Ce and La species formed a separate phase on the catalyst surface. Thus, it may explain their high affinity to CO species.

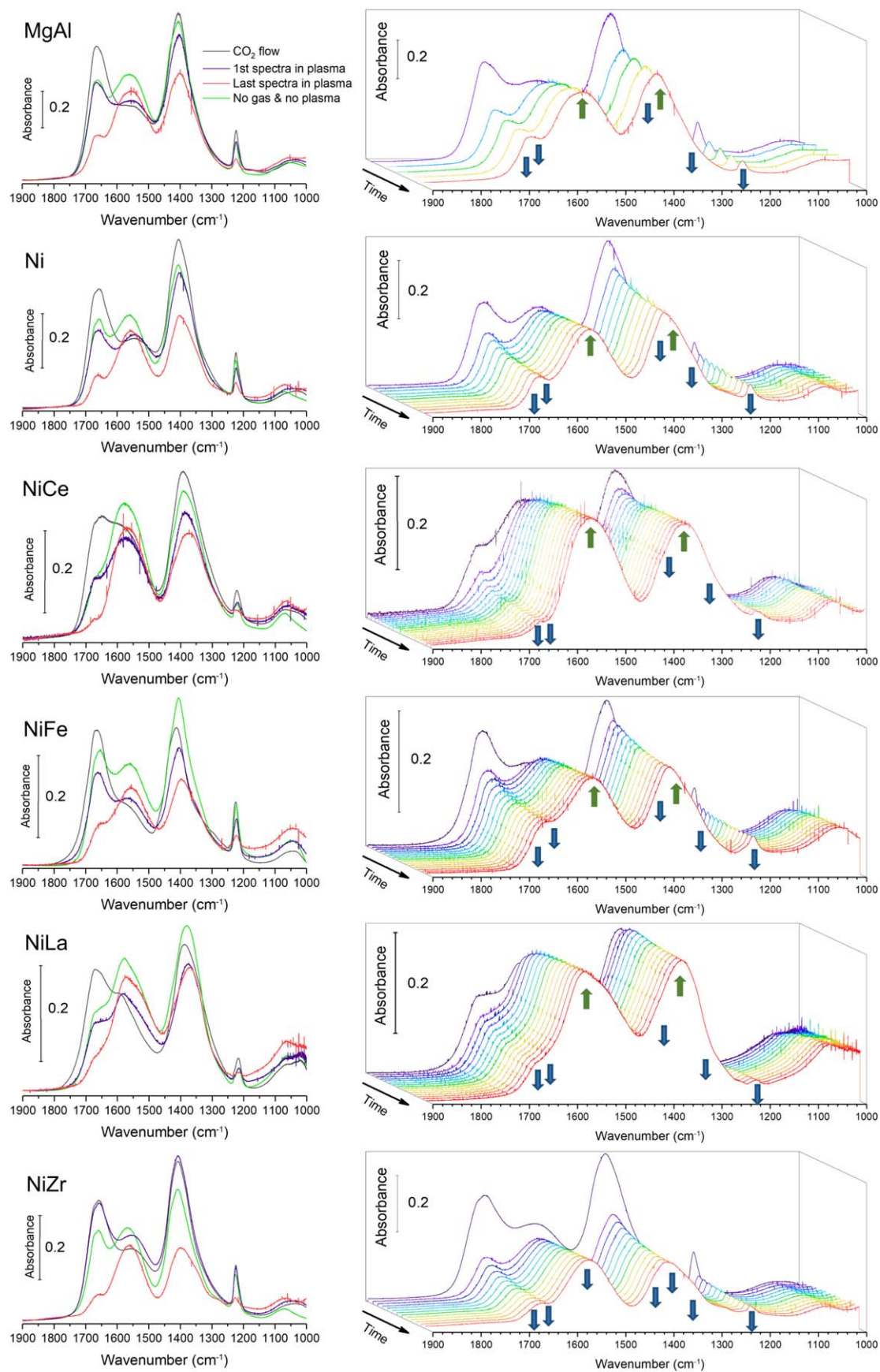


Figure 6. FT-IR spectra recorded during CO₂ adsorption in the glow discharge plasma.

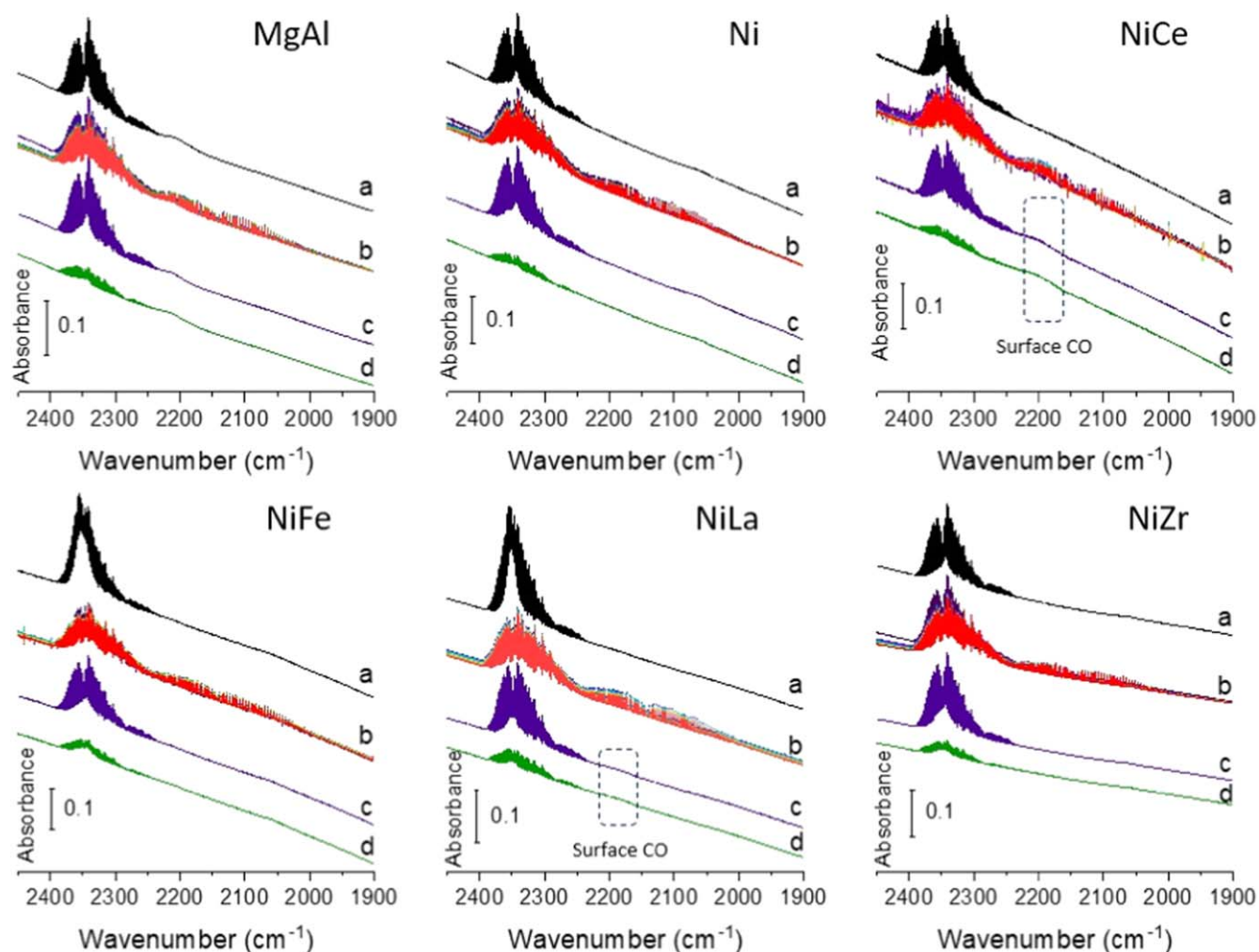


Figure 7. FT-IR spectra (2450–1900 cm^{-1} region) registered for catalysts: (a) under a flow of CO_2 ($2 \text{ cm}^3 \text{ min}^{-1}$ STP), and (b) plasma conditions; (c) under a flow of CO_2 after turning off the plasma and (d) after turning off the plasma and CO_2 flow after plasma treatment.

4. Conclusions

CO_2 *operando* adsorption experiments under plasma conditions were performed to understand CO_2 activation in hybrid plasma-catalytic process. The CO_2 adsorption on hydrothermalite-derived mixed oxides materials containing nickel and promoted with various transition metal species was investigated. Such materials were proven to be interesting and potential catalysts for chemical CO_2 valorization processes. Therefore, understanding interactions between the surface of such materials and CO_2 under plasma conditions is an important step to properly design plasma-catalytic process for CO_2 utilization via e.g. dry reforming of methane or CO_2 hydrogenation.

The performed study showed that the surface of the catalysts and their affinity to CO_2 are dependent on the material composition i.e. promotion with different transition metal species, as well as on plasma treatment. In all cases, plasma treatment promoted strong basicity associated with low coordinated surface oxygen anions. Therefore, it may be concluded that highly energetic plasma species interact with

the catalyst surface via directly modifying CO_2 adsorption sites transforming surface hydroxyl groups to surface oxygen species or via interaction with adsorbed CO_2 species. The effect of plasma treatment is as well dependent on the composition of the material, as e.g. in the case of NiZr sample, the initial increase in CO_2 adsorption capacity was observed after plasma ignition. The abundance of plasma species and various possibilities in which they may interact with the surface of catalyst require additional studies in order to clearly understand how surface basicity is modified by plasma treatment. However, the presented study put in evidence the modification of the surface by plasma and therefore is a valuable piece of information for future plasma-catalytic studies about CO_2 valorization.

Acknowledgments

R Dębek, D Wierzbicki and M Motak would like to acknowledge AGH grant 11.11.210.373. Authors would like

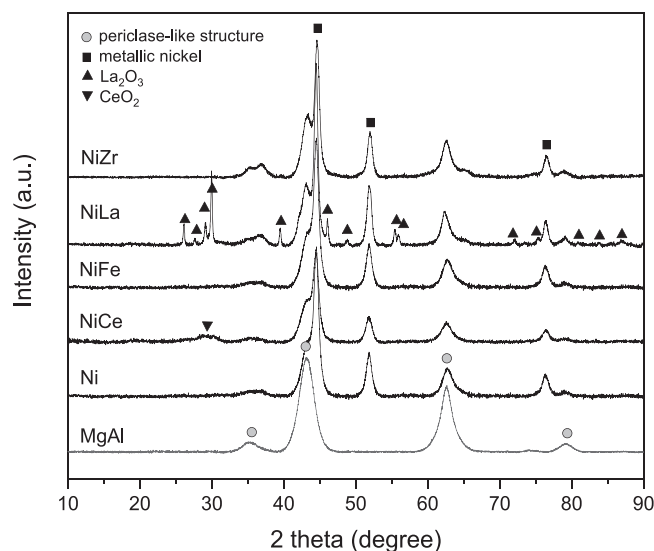


Figure A1. XRD patterns recorded for prepared reduced Ni(Mg, Al) O samples promoted with various transition metals.

to thank LCS staff: Yoann Levaque for technical support and glass-blower Adrien Lanel.

Appendix. Physio-chemical characterization of prepared materials

A.1. X-ray diffraction

Figure A1 presents XRD patterns recorded for prepared, reduced samples. Nickel-containing samples were reduced *ex situ* for 1 h at 900 °C in order to characterize phase composition of the samples in the similar state as during regular catalyst operation in CO₂ methanation or CO₂ reforming of CH₄. All samples exhibited reflections at 2θ equal to ca. 35°, 43°, 63° and 79° characteristic for the periclase-like structure of mixed oxides. This is typical for products of hydrotalcite thermal decomposition [36]. Additionally, all nickel containing samples showed the presence of reflections originating from the diffraction on metallic nickel crystal planes (reflections at 2θ equal to ca. 44°, 51° and 76°), based on which Ni crystal size was estimated (see table 1). It is important to underline that for Fe, and Zr promoted samples no additional phases were detected, pointing to successful incorporation of Zr⁴⁺ and Fe³⁺ cations into brucite-like layers. On the other hand, La and Ce promoted samples showed reflections characteristics for La₂O₃ and ceria phase, respectively. This clearly shows that it was not possible to introduce La³⁺ and Ce³⁺ into hydrotalcite structure. Instead, they formed separate phases. Such an effect may be associated with the ionic radii of Ce³⁺ and preparation method. The latter when appropriately modified may result in the incorporation of lanthanum cations into the periclase-like structure [57].

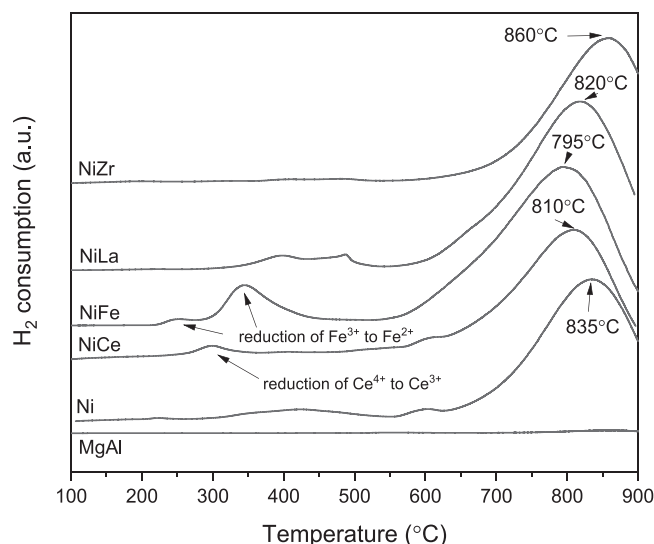


Figure A2. H₂-TPR profiles registered for prepared materials.

A.2. Temperature-programmed reduction with H₂

In order to investigate reducibility of nickel species temperature programmed reduction with H₂ experiments were performed and their results are presented in figure A2. In the case of all nickel containing samples one asymmetric reduction peak with the maximum in the range, 795 °C–860 °C was observed. This peak may be associated with the reduction of nickel species strongly interacting with periclase-like support. The differences between samples may be seen in the position of that peak, which is dependent on the presence of various promoters, influencing in this way reducibility of nickel species as well as the size of nickel crystallites formed upon reduction. Based on the results of H₂-TPR experiments temperature of samples reduction was selected and established to be 900 °C, which guarantees reduction of NiO to metallic nickel. Some additional reduction peaks were observed in the case of Ni, NiCe, NiFe and NiLa samples. In the case of Ni and NiLa samples small reduction peaks observed in the range 400 °C–500 °C may be associated with the reduction of weakly bonded with the support surface NiO. On the other hand, additional reduction peaks observed at ca. 250 °C and 360 °C for NiFe are attributed to the reduction of Fe³⁺ to Fe²⁺ [58]. In the case of the NiCe sample, a reduction peak at 300 °C was observed. Reduction of Ce⁴⁺ to Ce³⁺ usually occurs in three stages and 3 reduction peaks may be observed at ca. 300 °C, 600 °C and 900 °C associated respectively to the reduction of surface oxygen or oxygen capping species, reduction of surface lattice oxygen and finally total bulk reduction [59]. In the case of the NiCe sample, the two latter peaks may overlap with peak originating from nickel oxide reduction and thus cannot be clearly observed. Obtained results suggest that the presence of various promoters influences reducibility of Ni species and thus has an influence on the size of Ni particles formed upon reduction process (see table 1 or figure A3).

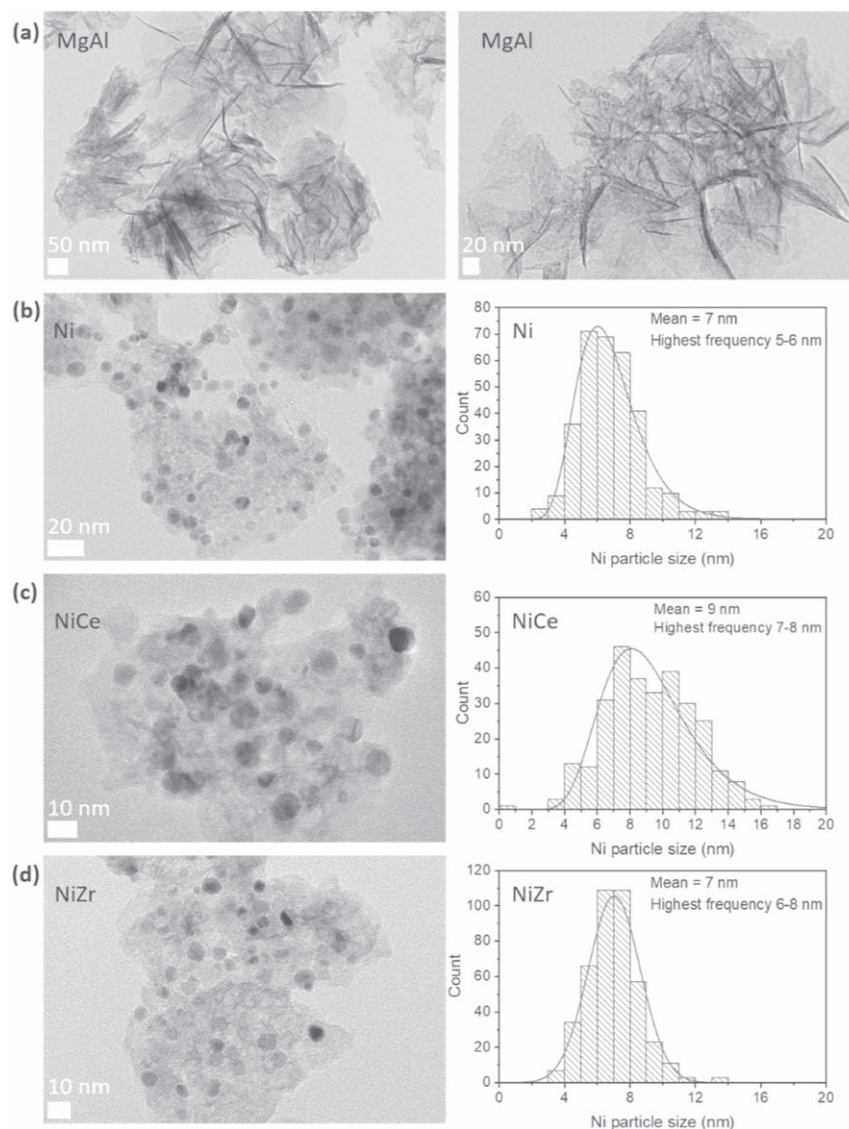


Figure A3. TEM pictures registered for selected samples and the corresponding distribution of Ni particle size calculated from TEM images: (a) MgAl, (b) Ni, (c) NiCe and (d) NiZr.

A.3. Transmission Electron Microscopy Images recorded for reduced samples

Figure A3 presents TEM micrograph registered for MgAl support and selected, a reduced nickel containing samples (Ni, NiCe, and NiZr). For the latter, based on the obtained micrographs, histograms of Ni particle size were prepared as well. It is important to underline that the results of the Ni particles size analysis stay in line with XRD results. The MgAl sample exhibited morphology typical for periclase-like structure derived from hydrotalcite materials. Upon reduction, nickel species are derived from brucite-like layers, forming a separate phase of metallic nickel. As already confirmed by XRD and H_2 -TPR analysis, the size of the formed Ni particle size is dependent on the presence of promoters which influences nickel-support interactions and thus reducibility of nickel species.

A.4. Low-temperature N_2 sorption experiments

Adsorption–desorption isotherms of low-temperature N_2 sorption experiments are presented in figure A4. The obtained isotherms may be classified as type IV with H4 hysteresis loop according to IUPAC which is characteristic for mesoporous materials and stays in line with the results described in the literature for hydrotalcite-derived materials [5, 6].

The corresponding values of specific surface areas, obtained from the registered isotherms, are in the rang of $90\text{--}230\text{ m}^2\text{ g}^{-1}$. The presence of promoters, especially Fe, La and Zr greatly improved textural parameters, resulting in the increase of specific surface area. E.g. $220\text{ m}^2\text{ g}^{-1}$ registered for NiZr versus $95\text{ m}^2\text{ g}^{-1}$ registered for MgAl. The increase of S_{BET} may be explained by the introduction of additional porosity by separate phase in case of NiLa, while for NiZr and NiFe samples it may be associated with

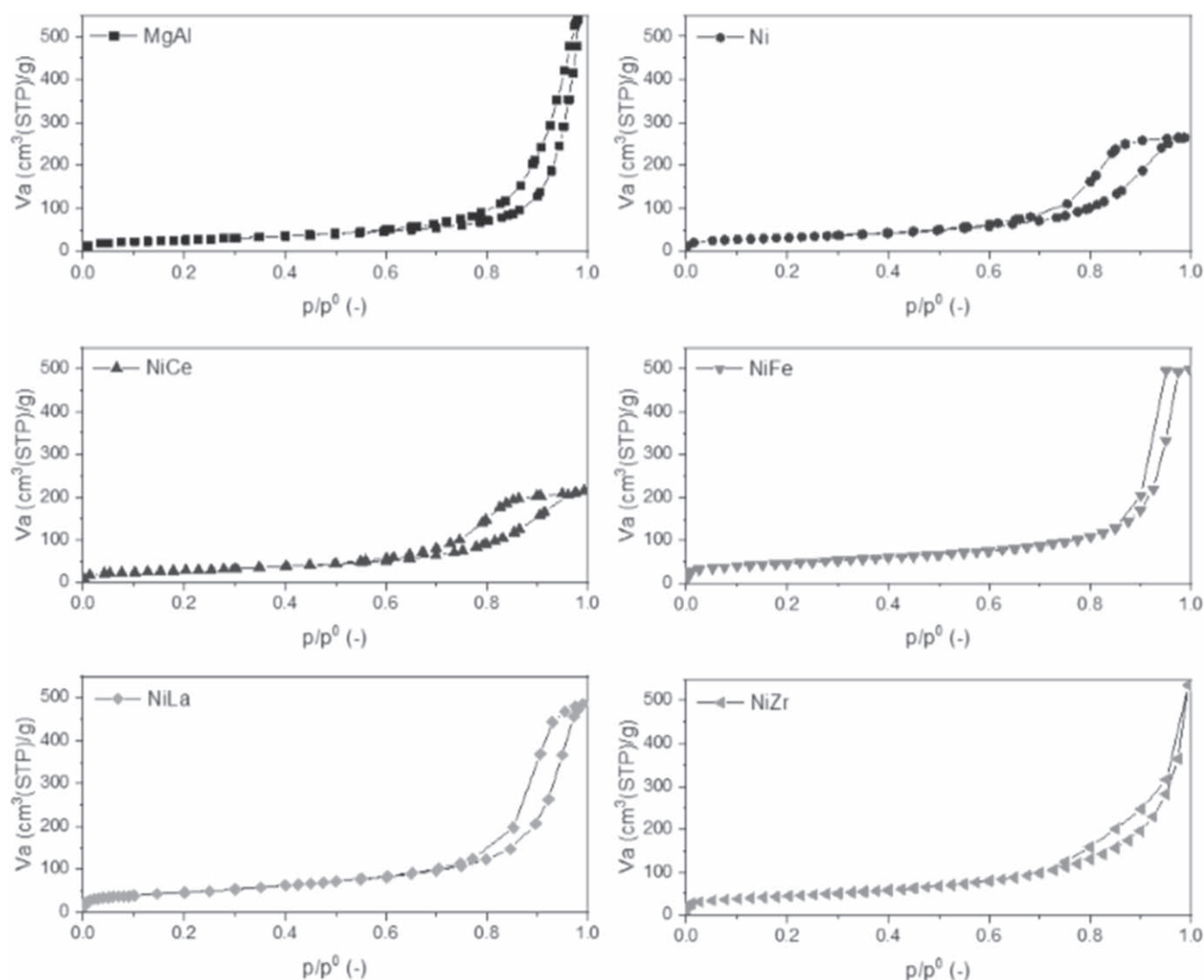


Figure A4. N₂ adsorption–desorption isotherms registered at –196 °C for prepared hydrotalcite-derived materials.

changes in crystallinity of obtained hydrotalcite-derived materials.

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