

Article

CO₂ Adsorption and Methanation over Ni/ZSM-5 Catalysts: Mechanistic Insights from FTIR Spectroscopy

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Abstract

The development of materials capable of combining efficient CO₂ capture with catalytic conversion is an important objective in carbon utilization strategies. In this work, a series of Ni/ZSM-5 catalysts prepared by different methods and characterized by different nickel loadings and speciation was investigated by FTIR spectroscopy, complemented by structural characterization and catalytic CO₂ hydrogenation measurements, to establish the CO₂ coordination mode and the relationship between nickel speciation, molecular CO₂ adsorption, and catalytic performance. FTIR spectroscopy demonstrates that molecular CO₂ is preferentially adsorbed on Ni²⁺ cations. Detailed investigation of the low-loaded catalyst, in which nickel is predominantly present as highly dispersed, mainly exchanged Ni²⁺ cations, shows that adsorption initially proceeds through end-on Ni²⁺–CO₂ species, which progressively transform into geminal Ni²⁺(CO₂)₂ complexes with increasing coverage. The adsorption geometry was established by applying the isotopic linkage isomerism (ILI) approach using ¹³C¹⁶O₂–¹³C¹⁸O₂ isotopic mixtures. In contrast, CO₂ adsorption on Ni⁺ sites formed upon reduction with CO is negligible, whereas these sites strongly bind CO, a key intermediate in CO₂ hydrogenation. FTIR experiments performed under CO₂/H₂ mixtures reveal the formation of surface formate species at low temperatures, followed by the appearance of adsorbed and subsequently gaseous CO. For the catalysts containing larger amounts of nickel, in which less electrophilic and more readily reducible Ni species are additionally present, methane was also detected in the gas phase, and the onset of the reaction processes shifted to lower temperatures. The FTIR observations closely parallel the catalytic behaviour. Overall, the results demonstrate that isolated Ni²⁺ cations provide effective sites for molecular CO₂ adsorption, whereas its subsequent catalytic hydrogenation requires more readily reducible nickel species capable of generating metallic sites under reaction conditions.



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1. Introduction

The continued reliance on fossil fuels and other anthropogenic activities has resulted in steadily increasing CO₂ emissions, contributing significantly to global warming and climate change—one of the major environmental challenges facing modern society [1].

Consequently, considerable efforts have been devoted to the development of carbon capture, utilization, and storage (CCUS) technologies as an important component of future decarbonization strategies [2].

While efficient capture of CO₂ is an essential decarbonization step, considerable effort is also being devoted to the further conversion of captured CO₂ into valuable products whenever economically and energetically feasible [3]. Therefore, increasing attention is being directed toward materials capable of combining both functions within a single system, namely efficient CO₂ capture and subsequent catalytic transformation of the adsorbed molecules. The development of such integrated capture-and-conversion materials is regarded as a promising approach to improving the overall efficiency and economics of CO₂ mitigation pathways [4,5].

Among the various classes of porous materials investigated for CO₂ capture, zeolites occupy a prominent position because of their high thermal and chemical stability, well-defined pore systems, tunable acidity, and ion-exchange properties [6–8]. Their negatively charged aluminosilicate frameworks contain extra-framework cations that can act as adsorption sites for CO₂ through electrostatic interactions with the molecular quadrupole moment. Consequently, zeolites are among the most effective solid adsorbents for CO₂ capture [6,9]. Beyond their role as adsorbents, zeolites can also serve as catalyst supports or as active catalytic materials. In particular, transition-metal-containing zeolites are attractive candidates for integrated capture-and-conversion processes because they can combine sites for CO₂ adsorption with sites capable of promoting its subsequent transformation.

The ZSM-5 zeolite (MFI framework) is particularly attractive as a model system because of its high thermal stability, well-defined medium-pore architecture, and ability to accommodate transition-metal cations in different coordination environments [10,11]. In particular, Ni-containing ZSM-5 has been reported to exhibit higher CO₂ adsorption capacity than Na-ZSM-5 [12], indicating a beneficial role of nickel cations in CO₂ capture. At the same time, Ni-containing zeolites are established catalysts for CO₂ hydrogenation, particularly methanation [13–17], suggesting that Ni/ZSM-5 may combine CO₂ adsorption and catalytic conversion within the same material. Furthermore, the state of nickel in Ni/ZSM-5 can be varied through the preparation method, nickel loading, and pretreatment conditions, resulting in materials containing different proportions of exchanged Ni²⁺ cations and more readily reducible nickel species. These characteristics make Ni/ZSM-5 a suitable platform for investigating the interplay between CO₂ adsorption, nickel speciation, and catalytic conversion.

The interaction of CO₂ with zeolites has been extensively studied [9,18–22]. In ion-exchanged zeolites, CO₂ is usually adsorbed as molecular complexes coordinated to extra-framework cations, while the strength and geometry of adsorption depend on the nature of the cation, its coordination environment, and the local electric field [18,21]. Recent FTIR studies have further demonstrated that a single cationic site may accommodate more than one CO₂ molecule, leading to the formation of geminal or higher polyligand complexes [18,20]. Such multiple coordination is particularly relevant to CO₂ capture because it allows more than one molecule to be accommodated by a single adsorption site, and can thereby enhance the adsorption capacity. However, comparatively little is known about molecular CO₂ adsorption on nickel-containing ZSM-5, particularly regarding its adsorption geometry, the possible formation of polyligand complexes, and the role of different nickel species.

FTIR spectroscopy is particularly well suited to addressing these questions because it provides molecular-level information on the nature of adsorption sites and the structure of adsorbed species [23–25]. In nickel-containing zeolites, FTIR spectroscopy has revealed a variety of nickel carbonyl and dinitrogen complexes, demonstrating the ability of isolated

Ni cations to coordinate multiple ligands. In particular, Ni^+ cations in partially reduced Ni/ZSM-5 were shown to form $\text{Ni}^+(\text{CO})_x$ ($x = 1-3$), $\text{Ni}^+(\text{N}_2)_2$, and mixed $\text{Ni}^+(\text{CO})(\text{N}_2)$ complexes, while highly electrophilic Ni^{2+} sites were able to coordinate up to two CO molecules [26,27]. Whether analogous multiple coordination occurs with CO_2 is, however, unknown. Moreover, conventional analysis of the CO_2 vibrational frequencies does not allow an unambiguous distinction between possible adsorption geometries. In this respect, the isotopic linkage isomerism (ILI) approach provides direct structural information by distinguishing end-on from bridging CO_2 coordination through the characteristic behavior of mixed-oxygen isotopologues [22].

A further important question concerns the role of nickel speciation. Depending on the preparation method and treatment conditions, nickel may be present as isolated exchanged Ni^{2+} cations, Ni^+ species formed upon reduction, small nickel oxide clusters or nanoparticles, and metallic Ni particles. These species differ substantially in their adsorption, redox, and catalytic properties. Establishing how the individual nickel species interact with molecular CO_2 and how their roles in adsorption are related to their behavior during hydrogenation is therefore important for understanding the coupling between CO_2 capture and catalytic conversion. FTIR spectroscopy is particularly valuable in this respect because, in addition to characterizing the adsorbed CO_2 species, it allows the evolution of surface intermediates and accessible nickel sites to be followed during interaction with the reaction mixture.

In the present work, we investigate Ni/ZSM-5 materials prepared by different methods and characterized by different nickel contents and nickel speciation in order to establish how the nature of the nickel species governs molecular CO_2 adsorption and its subsequent catalytic hydrogenation. Particular attention is paid to the adsorption geometry and formation of polyligand CO_2 complexes, which are investigated using isotopically labelled CO_2 and the ILI approach, as well as to the different adsorption behavior of Ni^{2+} and Ni^+ sites. These molecular-level observations are correlated with the behavior of the materials during interaction with CO_2/H_2 mixtures and with their catalytic performance in CO_2 methanation. The findings provide a basis for understanding the different functions of nickel species in CO_2 adsorption and catalytic conversion and, consequently, for the rational design of materials combining these two functions.

2. Results

Three Ni/ZSM-5 catalysts prepared in different ways and with increasing nickel loading, denoted NiZ-IE, NiZ-SSE, and NiZ-DP, were investigated in this study. Their synthesis details are described in Section 3.1.1, while the main physicochemical characteristics of the catalysts and the corresponding parent zeolites are summarized in Table 1.

Table 1. Notations and basic physicochemical characteristics of the samples.

Sample	Notation	At. % Ni (EDS)	Origin/Support	Preparation Method	S_{BET} m^2/g
H-ZSM-5	H-Z(Z)	-	Zeolyst	Calcination of $\text{NH}_4\text{ZSM-5}$	368
H-ZSM-5	H-Z(D)	-	Degussa	-	399
Ni-ZSM-5	NiZ-IE	0.7	H-Z(Z)	Ion-exchange	370
NiO/ZSM-5	NiZ-SSE	2.5	H-Z(Z)	Solid-state ion-exchange	356
NiO/ZSM-5	NiZ-DP	24	H-Z(D)	Deposition-precipitation	280

2.1. Physicochemical Characterization

All samples were initially characterized by XRD, TEM, TPR, UV-Vis spectroscopy and BET measurements.

2.1.1. Powder X-Ray Diffraction

The XRD patterns of all Ni/ZSM-5 catalysts (Figure 1) are characteristic of the MFI framework, displaying the well-known reflections at $2\theta = 7-9^\circ$ (doublet) and $22-25^\circ$ (triplet) typical of ZSM-5 [21,28], and they agree well with the calculated reference pattern [29]. The positions of the most intense MFI reference reflections are included in Figure 1 for comparison. No signals attributable to additional zeolitic crystalline phases were detected.

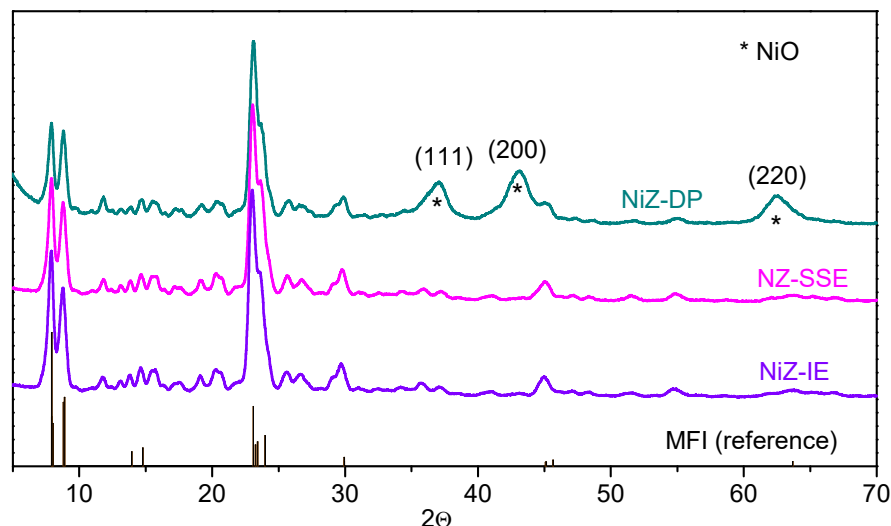


Figure 1. XRD patterns of the Ni/ZSM-5 catalysts. The most intense reflections of the calculated MFI reference pattern are shown as sticks at the bottom. Asterisks denote reflections of NiO.

For NiZ-IE and NiZ-SSE, no diffraction peaks attributable to crystalline nickel-containing phases were detected, indicating that nickel is highly dispersed or present in X-ray amorphous species. In contrast, the diffraction pattern of the highly loaded NiZ-DP catalyst contains reflections at 37.1° , 43.1° , and 62.4° , assigned to the (111), (200), and (220) planes of crystalline NiO, respectively [30]. The average NiO crystallite size, estimated from the (220) reflection using the Scherrer equation, was approximately 4.4 nm.

2.1.2. Electron Microscopy

The morphology of the Ni/ZSM-5 catalysts was examined by bright-field TEM (Figure 2). The NiZ-IE and NiZ-SSE samples consist of ZSM-5 crystals with sizes ranging from approximately 30 to 200 nm. The NiZ-DP catalyst exhibits a similar morphology but with a somewhat broader particle-size distribution.

The corresponding SAED patterns confirm the presence of both single-crystal spots and polycrystalline rings indexed to the ZSM-5 phase in all samples (for details see Supplementary Materials). In addition, diffraction features attributable to crystalline NiO are observed for NiZ-DP, in agreement with the XRD results. Local SAED analysis also revealed traces of NiAl_2O_4 in selected regions and minor amounts of metallic Ni, possibly produced by beam-induced reduction. Their low abundance is consistent with the absence of detectable diffraction peaks in the XRD patterns.

Elemental mapping (Figure S1) shows a homogeneous distribution of Si, Al, and O in all catalysts. For the lowest-loaded sample, NiZ-IE, nickel is also uniformly distributed throughout the zeolite crystals. In contrast, NiZ-SSE already exhibits localized nickel-rich domains, while in NiZ-DP these domains become considerably more pronounced,

indicating the formation of NiO nanoparticles on the external surface of the zeolite crystals. In the nickel-rich regions, the Si and Al signals are strongly attenuated because of the screening effect of the NiO particles. The elemental compositions determined by EDS are summarized in Table S1.

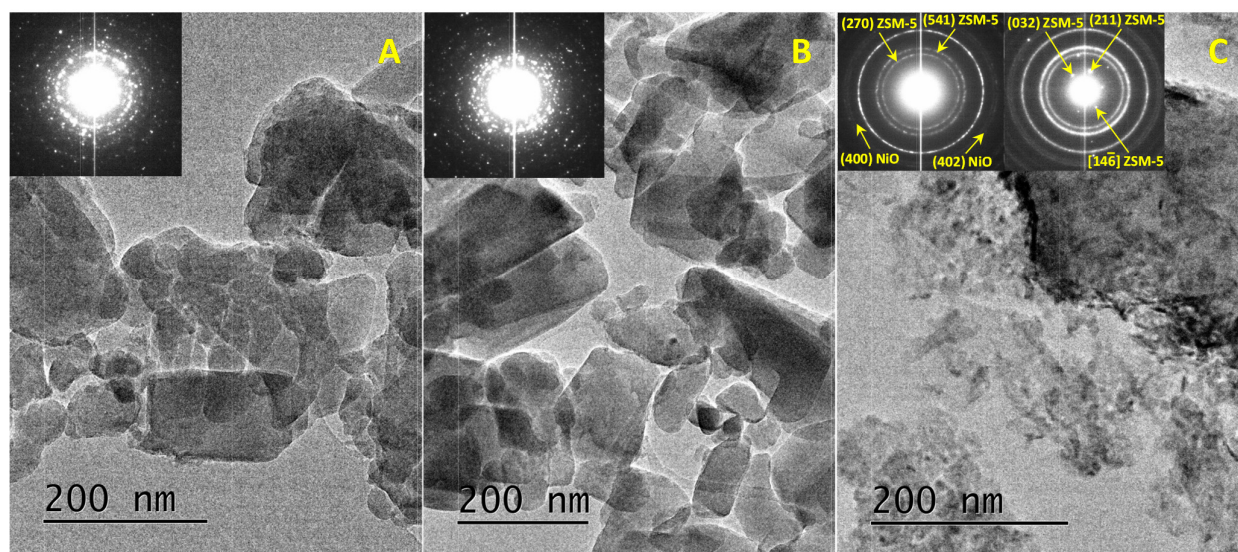


Figure 2. Bright-field TEM micrographs and selected-area electron diffraction (SAED) patterns (insets) of NiZ-IE (A), NiZ-SSE (B) and NiZ-DP (C) catalysts.

The TEM images of the NiZ-SSE catalyst (Figure S2) showed the presence of NiO particles with sizes ~ 3 nm (red circles) that are located on the external surface of the zeolite crystals. When sitting flat on the crystal edges, these NPs exhibited characteristic hemispherical morphologies that can be approximated as semi-octahedral, truncated-pyramidal (frustum), or semi-truncated octahedral shapes (Figure S2, circles 1, 2 and 3). Such morphologies are consistent with a relatively strong interaction between the NiO particles and the zeolite surface [31].

The representative HRTEM images of the NiZ-DP catalyst (Figures S3–S5) confirm the presence of crystalline NiO nanoparticles with sizes of approximately 3–5 nm on the external surface of the zeolite crystals, in excellent agreement with the crystallite size estimated from XRD. In addition to the external 3–5 nm NiO nanoparticles, occasional, considerably smaller NiO and metallic Ni nanodomains were observed within the ZSM-5 crystallites (Figure S5). HRTEM revealed local crystallographic alignment between these domains and the surrounding zeolite lattice.

Overall, the electron microscopy results indicate that nickel is highly dispersed in NiZ-IE, whereas increasing the nickel loading leads to the progressive formation of NiO nanoparticles that become abundant in NiZ-DP. The presence of these external NiO particles also provides a plausible explanation for the lower BET surface area of NiZ-DP (Table 1), owing to partial coverage of the external surface and reduced accessibility of the zeolite pores.

2.1.3. Diffuse Reflectance UV–Vis Spectroscopy

Diffuse reflectance UV–Vis spectroscopy was employed to obtain additional information on the coordination and chemical state of nickel in the catalysts (Figure 3). The spectra of the parent H-ZSM-5 supports exhibit the characteristic absorption bands below 350 nm associated with the zeolite matrix [32,33]. Upon nickel incorporation, additional absorption bands due to Ni^{2+} species appear.

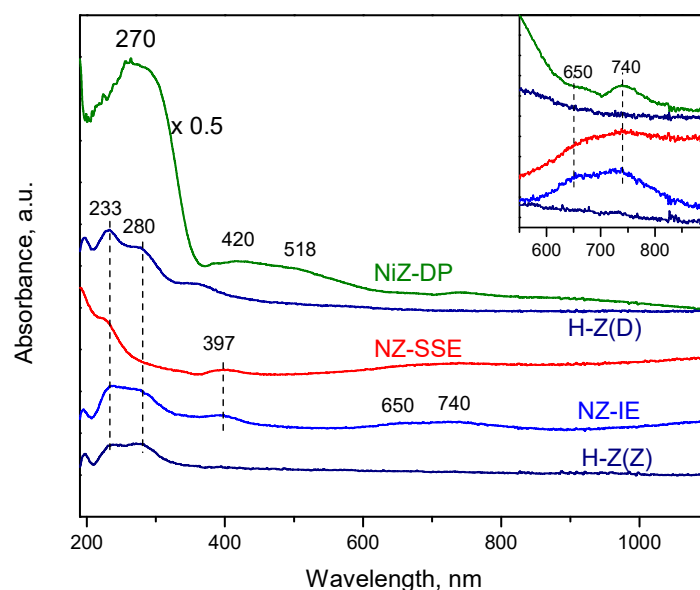


Figure 3. DR UV-Vis spectra of the H-Z supports and the Ni/ZSM-5 catalysts. The inset shows a magnification of the range between 550 and 900 nm.

The spectrum of NiZ-DP is dominated by intense absorption below 350 nm arising from $O^{2-} \rightarrow Ni^{2+}$ ligand-to-metal charge-transfer transitions, together with bands at approximately 420 and 740 nm, characteristic of octahedrally coordinated Ni^{2+} in NiO [34,35]. A broad absorption extending from 500 to 600 nm is also observed, indicating the presence of tetrahedrally coordinated Ni^{2+} species, consistent with small amounts of nickel aluminate [34–36].

The lower-loaded catalysts, NiZ-IE and NiZ-SSE, also exhibit bands at approximately 400 and 740 nm, evidencing the presence of octahedrally coordinated Ni^{2+} species. The broad 500–600 nm absorption is considerably weaker, indicating that nickel aluminate, if present, represents only a minor fraction of the nickel species. Overall, the UV-Vis spectra are consistent with the conclusions drawn from XRD and electron microscopy regarding the progressive formation of NiO with increasing nickel loading.

2.1.4. Temperature-Programmed Reduction

The H_2 -TPR profiles of the Ni/ZSM-5 catalysts are shown in Figure 4, while the corresponding total H_2 consumption values are summarized in Table S2. All samples exhibit broad reduction features characteristic of nickel species with different degrees of interaction with the zeolite. The reduction behaviour changes markedly across the series, indicating substantial differences in nickel speciation.

The NiZ-DP sample, with the highest Ni content, exhibits a dominant reduction peak centered at 409 °C, together with minor low- and high-temperature contributions. Reduction starts already at approximately 300 °C, indicating the presence of readily reducible NiO species. The position and the shape of the main peak are similar to those reported for NiO [37] and, in agreement with the XRD and TEM results, it is therefore assigned predominantly to the reduction of NiO to metallic nickel. The broad reduction profile is consistent with the presence of NiO particles with different degrees of dispersion.

The NiZ-IE sample, with the lowest Ni content, shows its main reduction feature at a considerably higher temperature. Such high-temperature reduction is characteristic of Ni^{2+} species strongly stabilized by the zeolite framework and is consistent with the predominant location of nickel at ion-exchange positions [38,39]. A similar high-temperature feature is observed for NiZ-SSE. Its higher intensity is consistent with the higher absolute concentration of exchanged Ni^{2+} cations in this sample, as independently indicated by

the FTIR results discussed below. The high-temperature feature can therefore also be associated predominantly with exchanged Ni^{2+} species. In addition, a weaker reduction feature appears at approximately 340 °C. Considering that reduction of NiO in NiZ-DP starts at approximately 300 °C, this low-temperature feature is attributed to more readily reducible, highly dispersed NiO species.

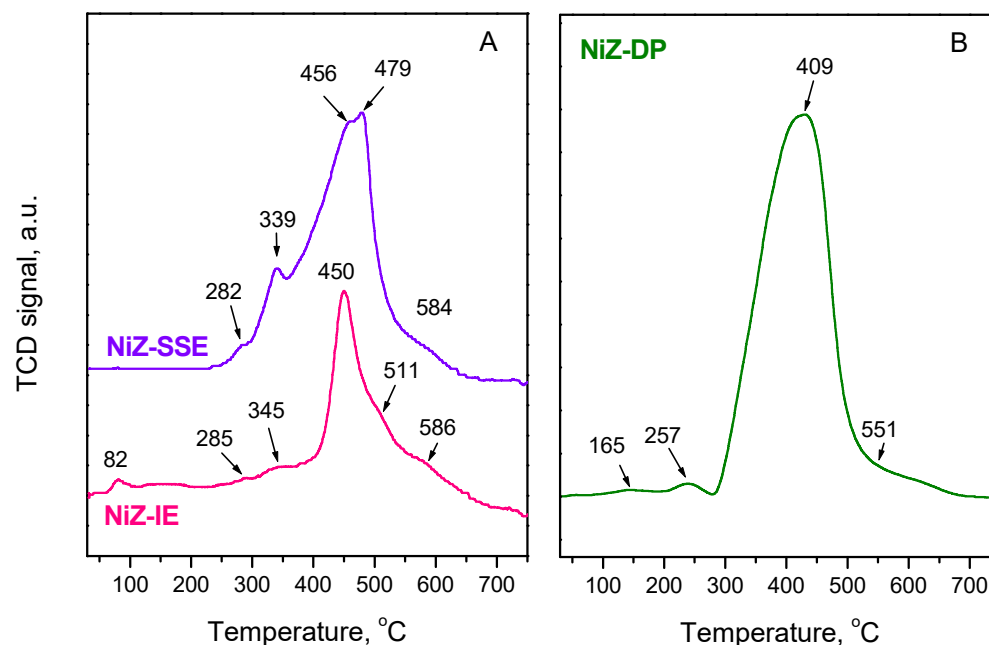


Figure 4. H₂-TPR profiles of the Ni/ZSM-5 catalysts. (A) Samples NiZ-IE and NiZ-SSE. (B) Sample NiZ-DP. The signal in this panel has been divided by a factor of 7 for better visualization.

Overall, the characterization results consistently reveal substantial differences in nickel speciation across the series. NiZ-IE contains predominantly highly dispersed nickel species, namely exchanged Ni^{2+} cations strongly interacting with the zeolite framework. In NiZ-SSE, exchanged Ni^{2+} species remain important and are present in higher absolute concentrations, while highly dispersed NiO species are also formed. In contrast, NiZ-DP contains abundant crystalline NiO nanoparticles, as evidenced by XRD, TEM, UV-Vis, and H₂-TPR. The lower BET surface area of NiZ-DP is consistent with the presence of these external NiO particles, which may partially cover the external surface and reduce the accessibility of the zeolite pores, while simultaneously lowering the overall specific surface area through a mass-dilution effect. These differences in nickel speciation provide the basis for interpreting the CO₂ adsorption and catalytic behaviour discussed below.

2.2. FTIR Spectra of the Samples and Adsorbed CO₂

2.2.1. Activated, Reduced and Deuterioxylated Samples

The FTIR spectra of the activated samples in the OH stretching region are shown in Figure 5. The two parent H-ZSM-5 supports exhibit very similar spectra, characterized by bands at 3745 cm^{−1} due to terminal silanol groups, 3612–3611 cm^{−1} assigned to bridging Si–OH–Al hydroxyls, and a broad band centered at approximately 3300 cm^{−1} arising from hydrogen-bonded hydroxyl groups [40,41]. Minor additional bands are observed for H-ZSM-5(Z) at 3664 cm^{−1}, assigned to aluminol groups [40], and for H-ZSM-5(D) at 3780 cm^{−1}, attributed to hydroxyl groups associated with extra-framework aluminum species [40,42].

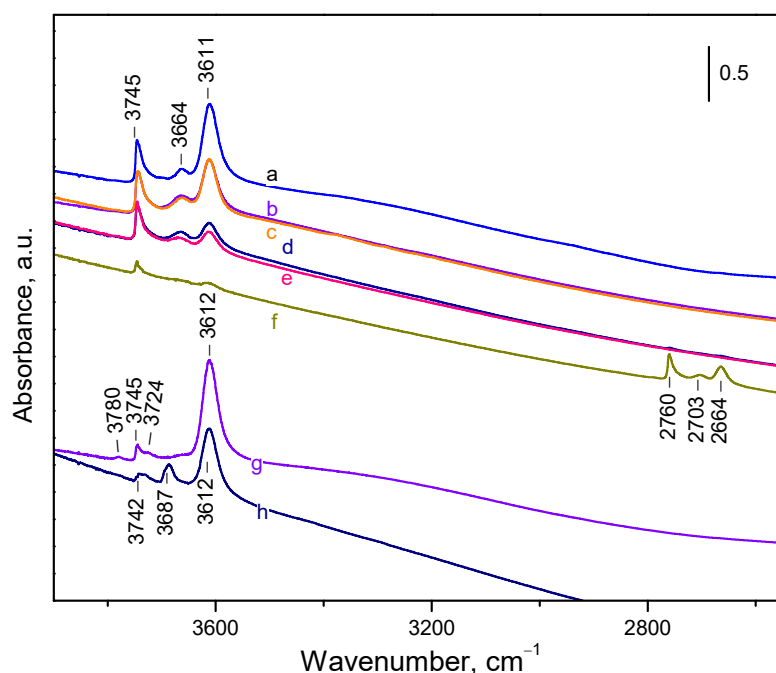


Figure 5. FTIR spectra of activated H-Z(Z) (a), H-Z(D) (g), NiZ-IE (b), NiZ-SSE (d) and NiZ-DP (h), CO-reduced NiZ-IE (c) and NiZ-SSE (e), and D₂O-exchanged NiZ-SSE (f). All spectra were normalized to the intensity of the Si-O overtone band at 1879 cm⁻¹.

Nickel incorporation produces a pronounced decrease in the intensity of the bridging hydroxyl band at 3611 cm⁻¹, accompanied by complete disappearance of the broad hydrogen-bonded OH band at ca. 3300 cm⁻¹, suggesting that ion exchange has occurred in all catalysts. Indeed, the CO adsorption experiments confirmed the presence of isolated ion-exchanged Ni²⁺ cations in all catalysts through the formation of characteristic carbonyls. No bands attributable to Ni-OH groups (3658–3636 cm⁻¹ [41,43]) are detected. Furthermore, no absorption bands are observed in either the CH stretching or carbonate regions, confirming the absence of residual organic species or carbonate contaminants after sample activation.

Reduction with CO has only a minor effect on the hydroxyl region (Figure 5, spectra c and e). After deuteroxylation of NiZ-SSE, the OH bands are almost fully converted into OD bands, as evidenced by their shift by the expected factor of ca. 1.357 [40] (Figure 5, spectrum f).

2.2.2. IR Spectra of ¹²C¹⁶O₂ + ¹³C¹⁶O₂ Co-Adsorbed on NiZ-IE

The adsorption of CO₂ was first investigated in detail on NiZ-IE, in which nickel is most homogeneously distributed. The remaining catalysts were subsequently examined mainly to assess the effects of increasing nickel loading and changes in nickel speciation.

Under the present conditions, CO₂ is adsorbed predominantly in molecular form, i.e., without loss of its molecular identity. The position of the ν₃ band (vide infra) indicates that the molecules retain an almost linear geometry. Upon adsorption, the molecular symmetry is lowered, leading to shifts in the vibrational frequencies and activation of the normally IR-forbidden ν₁ symmetric stretching mode.

Because the ν₃ band of ¹²CO₂ is very intense and often becomes saturated, adsorption studies are often based on the weaker ¹³CO₂ satellite. However, its low intensity limits the analysis at low coverages. To overcome this difficulty and to obtain information on possible vibrational interaction, experiments were performed using CO₂ enriched in ¹³CO₂ (¹²CO₂/¹³CO₂ ≈ 80/20).

Sequential adsorption of small doses of the $^{12}\text{CO}_2/^{13}\text{CO}_2$ mixture on activated NiZ-IE resulted in the development of a ν_3 band at 2361 cm^{-1} , which shifts to 2356 cm^{-1} with increasing coverage (Figure 6A). The corresponding $\nu_3(^{13}\text{CO}_2)$ bands are observed in the $2295\text{--}2290\text{ cm}^{-1}$ region. Since these bands are absent from the spectra of the parent H-ZSM-5 support, they are assigned to CO_2 species coordinated to Ni^{2+} sites. The pronounced red shift in the ν_3 band with increasing coverage indicates that the adsorption geometry or the coordination environment changes as the nickel sites become progressively occupied.

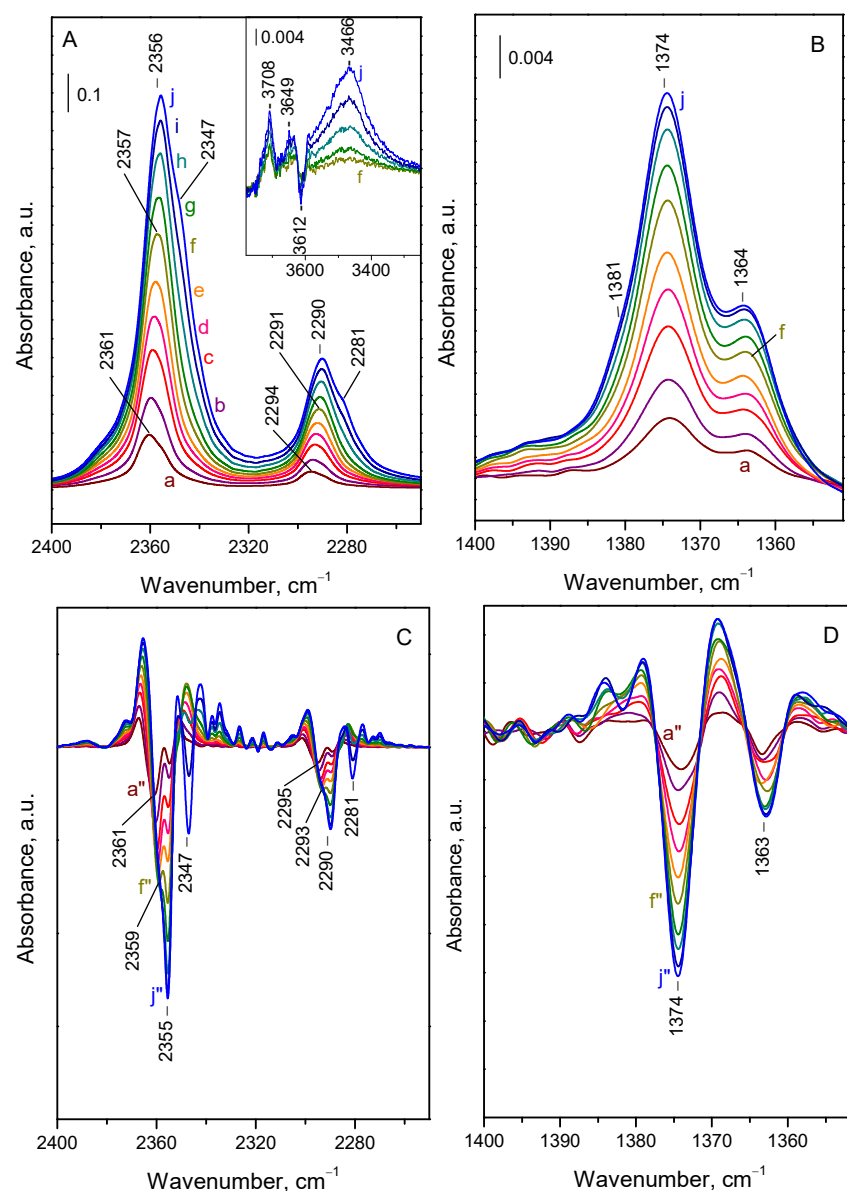


Figure 6. Successive adsorption of doses of $^{12}\text{CO}_2$ (80%) + $^{13}\text{CO}_2$ (20%) mixture on activated NiZ-IE catalyst (a–j). (A) $\nu_3(\text{CO}_2)$ region; (B) $\nu_1(\text{CO}_2)$ region. (C) Second derivatives of the spectra in panel (A) (a''–j''). (D) Second derivatives of the spectra in panel (B) (a''–j'').

At higher coverages, an additional band develops at approximately 2347 cm^{-1} . Simultaneously, the bridging hydroxyl band at 3612 cm^{-1} shifts to 3466 cm^{-1} ($\Delta\nu = -146\text{ cm}^{-1}$, see the inset of Figure 6A). A similar band has previously been observed for H-ZSM-5 [22], allowing us to assign it to $\text{OH}\cdots\text{CO}_2$ adducts. Thus, the H-bonded species can be clearly distinguished from those coordinated to Ni^{2+} sites. It should be noted that the band at 3708 cm^{-1} is not due to O–H vibrations but originates from the $(\nu_1 + \nu_3)$ combination

mode of adsorbed CO₂. The corresponding ¹³CO₂ band appears at 3649 cm^{−1} with lower intensity, as expected from its lower abundance.

Changes are also observed in the region of ν_1 symmetric modes: two bands at 1374 and 1364 cm^{−1} develop in parallel (Figure 6B) and are assigned to adsorbed ¹²CO₂ and ¹³CO₂ species, respectively. The band positions remain essentially unchanged with coverage, confirming that the ν_1 mode is less sensitive to the adsorption geometry than the antisymmetric ν_3 mode. At high coverage, a weak band at 1381 cm^{−1} appears and is assigned to OH...¹²CO₂ adducts, while the corresponding ¹³CO₂ band is not resolved because it overlaps with the band at 1364 cm^{−1}.

The isotopic shift factors also support these assignments. For a harmonic C–O oscillator, the expected ¹²C/¹³C shift factor is approximately 1.023. The experimentally observed values for the ν_3 modes (1.0287–1.0298) are somewhat larger, whereas the ν_1 modes exhibit a much smaller shift ($\approx$ 1.008). This difference reflects the different character of the two vibrations: the symmetric ν_1 mode involves a smaller contribution of carbon atom motion and is therefore less sensitive to isotopic substitution than the antisymmetric ν_3 mode.

The evolution of the individual adsorption bands becomes considerably clearer from the second derivatives of the spectra (Figure 6C,D). At low coverage, a band at 2361 cm^{−1} develops first, followed by a band at 2355 cm^{−1}. The former increases in intensity, reaches a maximum, and then decreases, whereas the latter continuously increases up to saturation. The different coverage dependence of the two bands indicates that they correspond to distinct adsorption states rather than a single evolving species. At higher coverages, a band at 2347 cm^{−1} appears, which is associated with CO₂ interacting with acidic hydroxyl groups.

In summary, the results indicate the presence of two nickel-bound CO₂ species (A and B), characterized by ν_3 bands at 2361 and 2355 cm^{−1}, respectively, and exhibiting distinctly different coverage dependencies. At higher coverages, additional CO₂ is adsorbed on acidic hydroxyl groups.

These observations can be explained by two alternative mechanisms: (i) species A is assigned to Ni²⁺–CO₂ end-on adducts, which, upon increasing coverage, is converted into geminal Ni²⁺(CO₂)₂ species (species B); (ii) species A corresponds to CO₂ bound in a bridging configuration, which, upon increasing coverage, converts into end-on adducts, for example due to competition for adjacent cationic sites. To discriminate between these possibilities, we applied the isotopic linkage isomerism (ILI) approach [22,44].

2.2.3. Identification of Adsorption Geometry by Isotopic Linkage Isomerism (ILI)

The isotopic linkage isomerism (ILI) approach is based on the fact that adsorption of ¹⁶O–C–¹⁸O produces two linkage isomers for end-on coordinated CO₂, giving rise to two ν_3 bands of comparable intensity. In contrast, for bridging coordination, the two possible linkage orientations are spectroscopically equivalent, and only one ν_3 band is therefore expected.

In a ¹³C¹⁶O₂–¹³C¹⁸O₂ isotopic mixture, rapid oxygen isotope scrambling occurs, leading to a statistical redistribution of ¹⁶O and ¹⁸O atoms. Consequently, a 1:1 mixture contains 25% ¹³C¹⁶O₂, 50% ¹³C¹⁶O¹⁸O, and 25% ¹³C¹⁸O₂.

Adsorption of a small dose of a ¹³C¹⁶O₂–¹³C¹⁸O₂ isotopic mixture (with experimental ¹⁶O:¹⁸O ratio of $\approx$ 55:45) leads to the appearance of three spectral envelopes (Figure 7, spectrum a). The high- and low-frequency envelopes are dominated by the ν_3 bands of ¹³C¹⁶O₂ and ¹³C¹⁸O₂ at 2296 and 2259 cm^{−1}, respectively. The central envelope, corresponding to adsorbed ¹³C¹⁶O¹⁸O, consists of two main bands of comparable intensity at 2283 and 2276 cm^{−1}. According to the ILI principle, this isotopic pattern provides direct evidence for the presence of two linkage isomers. Based on our previous studies [20,22], these bands are assigned to end-on Ni²⁺–¹⁸O–¹³C–¹⁶O and Ni²⁺–¹⁶O–¹³C–¹⁸O species, respectively.

The observation of two bands of comparable intensity in the $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ region therefore demonstrates that CO_2 is initially adsorbed in an end-on configuration on Ni^{2+} sites. This result highlights the unique ability of the ILI approach to distinguish adsorption geometries that cannot be resolved by conventional FTIR spectroscopy.

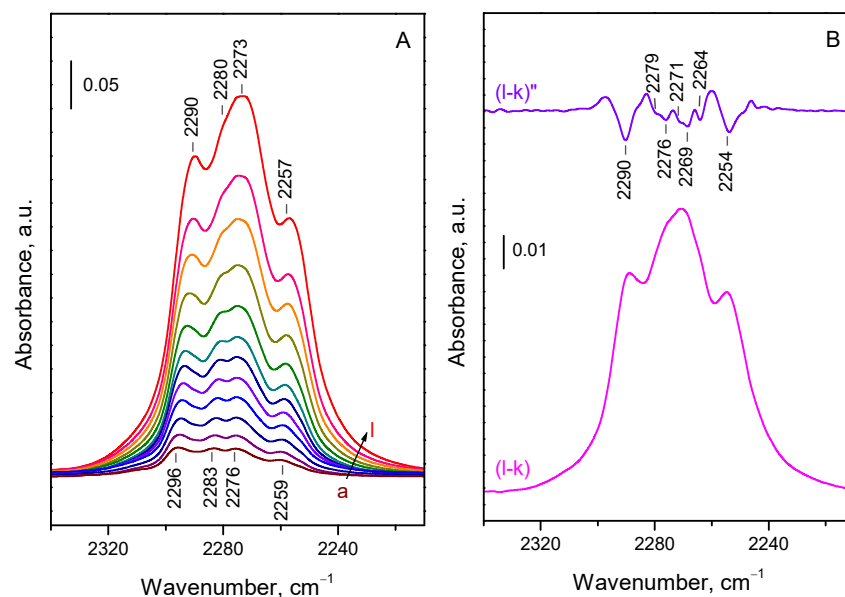


Figure 7. Adsorption of a $^{13}\text{C}^{16}\text{O}_2/^{13}\text{C}^{18}\text{O}_2$ isotopic mixture on NiZ-IE. (A) Successive addition of small doses (a–l). (B) Difference spectrum (l–k) and its second derivative (l–k)''.

Upon increasing the CO_2 coverage, the central spectral envelope becomes more complex, indicating either the appearance of additional adsorption species or the transformation of the pre-existing ones. To analyze this region in greater detail, a difference spectrum was examined, corresponding to the coverage range in which the lower-frequency ν_3 band component (supposed to arise from geminal species) mainly develops (Figure 7B). Its second derivative reveals that the central envelope consists of at least five components.

Although a complete theoretical description of the ILI pattern expected for geminal CO_2 complexes is not yet available, previous experimental results have shown that the coordination of two CO_2 molecules to the same cation produces additional splitting in the $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ region [22]. Accordingly, the increased complexity of the central envelope observed at higher coverages is consistent with the formation of geminal species.

The ILI experiment therefore resolves the ambiguity discussed in the previous section and demonstrates that species A corresponds to end-on $\text{Ni}^{2+}\text{--CO}_2$ adducts. Upon increasing coverage, they are progressively converted into geminal $\text{Ni}^{2+}(\text{CO}_2)_2$ complexes.

2.2.4. Reduced NiZ-IE Sample

It is well established that a fraction of the Ni^{2+} cations in Ni-ZSM-5 can be readily reduced to Ni^+ [26,45]. Indeed, probing the CO-reduced NiZ-IE sample with CO confirmed the formation of Ni^+ sites. Besides the band at 2212 cm^{-1} due to $\text{Ni}^{2+}\text{--CO}$ species, bands at 2137 and 2094 cm^{-1} , characteristic of $\text{Ni}^+(\text{CO})_2$ dicarbonyls, were observed. Upon evacuation, these bands were converted into a band at 2112 cm^{-1} assigned to $\text{Ni}^+\text{--CO}$ monocarbonyls [26,41].

Adsorption of CO_2 on the reduced NiZ-IE sample at an equilibrium pressure of 5 mbar produced a spectrum very similar to that obtained for the activated sample (Figure 8A). The ν_3 region was dominated by a band at 2348 cm^{-1} assigned to $\text{OH}\cdots\text{CO}_2$ adducts, together with high-frequency shoulders at approximately 2366 and 2355 cm^{-1} due to

CO₂ coordinated to Ni²⁺ sites. The corresponding ν_1 bands were observed at 1381 and 1375 cm⁻¹, respectively (Figure 8C).

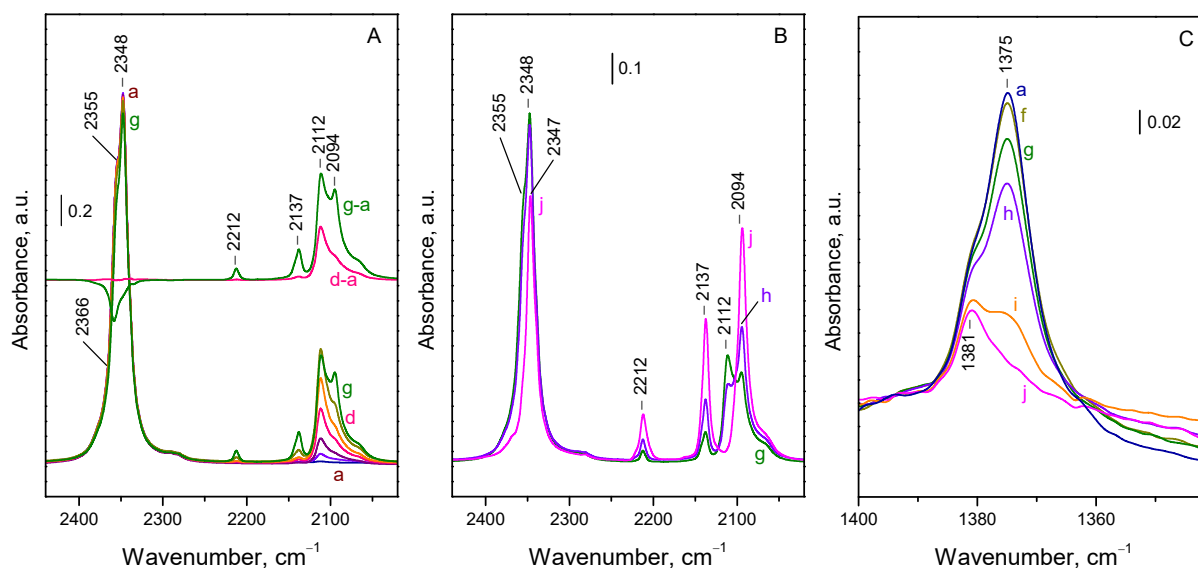


Figure 8. FTIR spectra recorded during the successive admission of small doses of CO to NiZ-IE with preadsorbed CO₂ (a–j). (A) Low coverage, $\nu(\text{CO})$ and $\nu_3(\text{CO}_2)$ regions. (B) High coverage, $\nu(\text{CO})$ and $\nu_3(\text{CO}_2)$ regions. (C) All coverages, $\nu_3(\text{CO}_2)$ region.

Subsequent stepwise admission of CO produced no measurable changes in the CO₂ spectra during the first several doses (Figure 8A, spectra b–d). In contrast, the carbonyl region showed the progressive development of the 2112 cm⁻¹ band due to Ni⁺–CO species. Comparison with separate CO adsorption experiments indicates that, under these conditions, a significant fraction of the Ni⁺ sites is occupied by CO. Nevertheless, no spectral changes attributable to CO₂ adsorbed on Ni⁺ cations were detected, indicating that CO₂ adsorption on these sites is negligible under the present conditions. This behaviour is readily understood in view of the lower electrophilicity of Ni⁺ compared with Ni²⁺.

A further increase in the CO pressure gradually converts Ni⁺–CO monocarbonyls into Ni⁺(CO)₂ dicarbonyls, as evidenced by the growth of the bands at 2137 and 2094 cm⁻¹ at the expense of the 2112 cm⁻¹ band (Figure 8B). Simultaneously, the intensity of the Ni²⁺–CO band at 2212 cm⁻¹ increases, accompanied by a progressive decrease in the $\nu_3(\text{CO}_2)$ band at 2355 cm⁻¹ and the $\nu_1(\text{CO}_2)$ band at 1375 cm⁻¹, both assigned to CO₂ coordinated to Ni²⁺ sites (Figure 8B,C). At a CO equilibrium pressure of approximately 1 mbar (Figure 8, spectrum j), these bands are largely suppressed, demonstrating that CO effectively displaces CO₂ from Ni²⁺ cations. No evidence for the formation of mixed Ni(CO)(CO₂) complexes was obtained.

In contrast, the OH...CO₂ adducts, characterized by the bands at 2347 and 1381 cm⁻¹, remain essentially unaffected throughout the experiment. Only a slight increase in the intensity of these bands was observed, which can be attributed to a small increase in the gas-phase CO₂ concentration following displacement of CO₂ from Ni²⁺ sites.

Overall, these results demonstrate that CO readily replaces CO₂ adsorbed on Ni²⁺ cations, whereas CO₂ does not compete effectively for Ni⁺ sites. The weak interaction of Ni⁺ with CO₂ suggests that these sites are unlikely to contribute significantly to molecular CO₂ adsorption. In contrast, they readily form stable carbonyl complexes with CO, a key intermediate in CO₂ hydrogenation.

2.2.5. FTIR Spectra of CO₂ Adsorbed on Ni/ZSM-5 (NiZ-SSE and NiZ-DP)

The spectra of CO₂ adsorbed on NiZ-SSE and NiZ-DP at an equilibrium pressure of 5 mbar are shown in Figure 9A. In the $\nu_3(\text{CO}_2)$ region, both samples exhibit a main band peaking at 2355–2354 cm^{−1}. Second-derivative analysis (Figure 9B) reveals the complex structure of these bands. Based on the assignments established for NiZ-IE, the components at 2360–2357 cm^{−1} are assigned to CO₂ coordinated to Ni²⁺ sites, whereas those at 2356–2355 cm^{−1} are associated with geminal Ni²⁺(CO₂)₂ species. The band at 2347 cm^{−1} is due to hydrogen-bonded CO₂ and is barely detectable for NiZ-SSE, consistent with the low concentration of bridging hydroxyl groups in this material. The band at 2351 cm^{−1}, which was absent for NiZ-IE, is tentatively assigned to CO₂ adsorbed on a second family of less electrophilic Ni²⁺ sites, most likely associated with NiO nanoparticles. The small shoulder at 2339 cm^{−1}, revealed by the second derivative analysis in Figure 9B, is related to CO₂ species physisorbed in the zeolite channels.

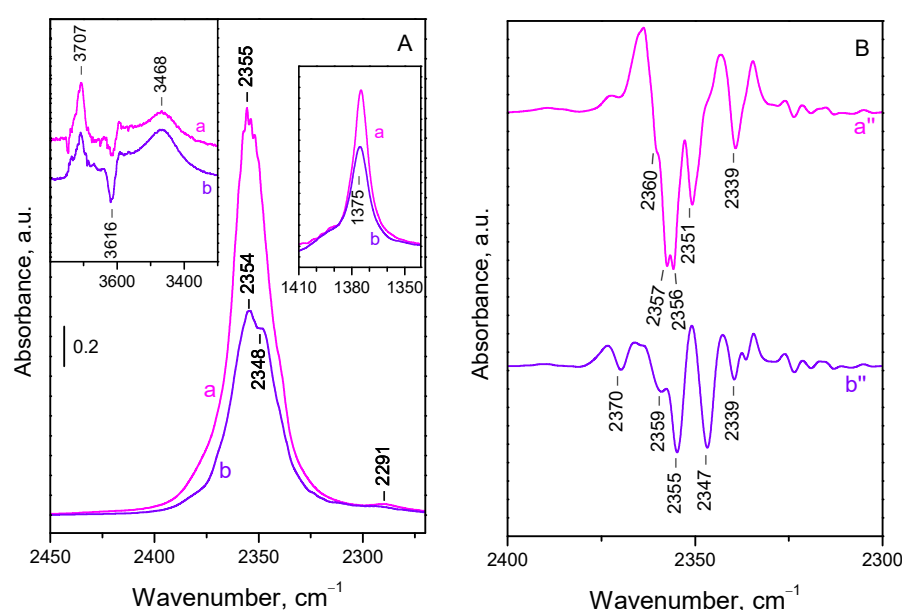


Figure 9. (A) FTIR spectra of CO₂ adsorbed on activated NiZ-SSE (a) and NiZ-DP (b) at ambient temperature and under 5 mbar CO₂ equilibrium pressure. (B) Second derivatives of the spectra.

Overall, the spectra indicate that increasing the nickel loading does not alter the fundamental adsorption mechanism established for NiZ-IE but leads to the appearance of an additional family of less electrophilic Ni²⁺ sites, most probably located on NiO nanoparticles.

2.3. FTIR Study of the Interaction Between CO₂ and H₂

2.3.1. NiZ-IE

To obtain mechanistic insight into CO₂ hydrogenation over Ni/ZSM-5, the interaction of CO₂ and H₂ with the catalysts was investigated by in situ FTIR spectroscopy at stepwise increasing temperatures. After each interaction step, the sample was cooled to room temperature, and separate spectra of the adsorbed species and the gas phase were recorded.

Consider first the NiZ-IE catalyst (Figure 10). After interaction with a CO₂/H₂ mixture at 100 °C, the spectrum is dominated by a $\nu_3(\text{CO}_2)$ band with two components at approximately 2356 and 2347 cm^{−1} (Figure 10A, spectrum a), accompanied by the much weaker $\nu_1(\text{CO}_2)$ band at 1377 cm^{−1}. Small amounts of adsorbed water are already formed, as evidenced by the $\delta(\text{H}_2\text{O})$ band at 1623 cm^{−1} together with OH stretching bands at 3654 and 3478 cm^{−1}. Simultaneously, the Brønsted hydroxyl band at 3615 cm^{−1} slightly decreases in intensity, indicating the formation of hydrogen-bonded species. This

assignment is further supported by the appearance of a broad band in the 3600–3000 cm^{-1} region with the characteristic ABC pattern [40]. In addition, a weak band at 1443 cm^{-1} is detected and is tentatively assigned to the $\nu_s(\text{CO}_3^{2-})$ vibration of carbonate species; the corresponding antisymmetric vibration is probably obscured by the intense water deformation band, as indicated by the spectra of the deuterioxyated sample (see below).

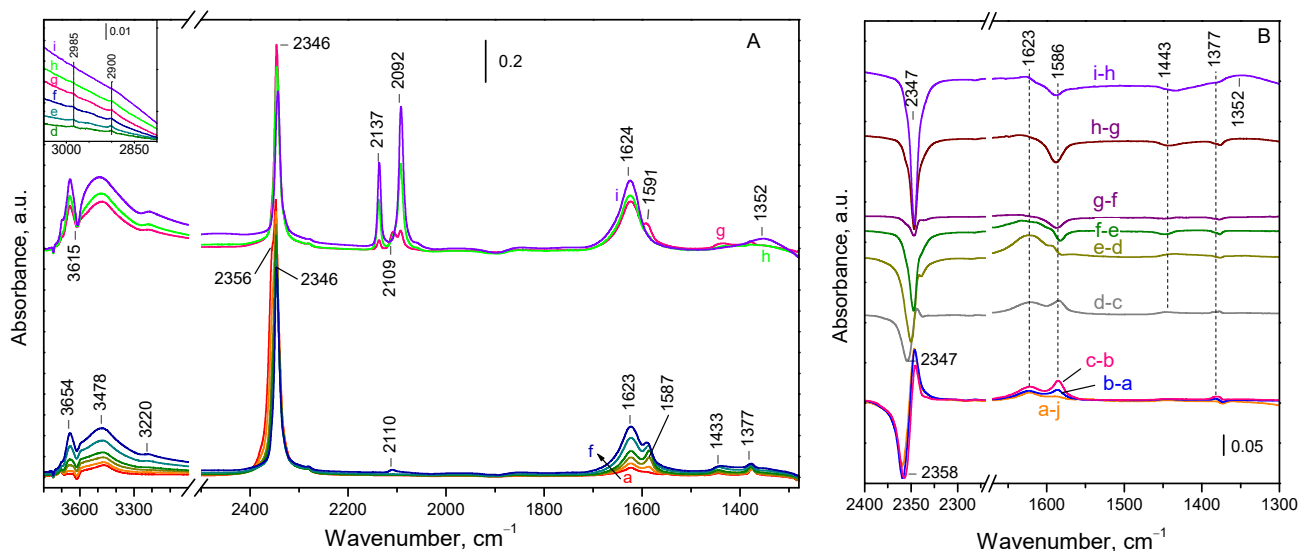


Figure 10. (A) FTIR spectra of surface species produced after 15 min interaction of CO_2 (5 mbar) and H_2 (20 mbar) over NiZ-IE catalyst. Temperature of interaction: 100 °C (a), 125 °C (b), 150 °C (c), 175 °C (d), 200 °C (e), 225 °C (f), 250 °C (g), 275 °C (h), and 300 °C (i). The spectra are collected at ambient temperature, and are background and gas phase corrected. (B) Difference FTIR spectra relative to Panel (A). Spectrum (j) refers to interaction at room temperature.

The evolution of the surface species with increasing reaction temperature is clearly illustrated by the incremental difference spectra shown in Figure 10B, where, from each spectrum, the previous one is subtracted, thus showing only the spectral changes in the respective temperature window.

Water is formed throughout the investigated temperature range, as indicated by the continuous growth of both the OH stretching and the $\delta(\text{H}_2\text{O})$ bands.

In contrast, the amounts of both adsorbed and gaseous CO_2 gradually decrease with increasing temperature, reflecting the progressive occupation of the adsorption sites by water and the consumption of CO_2 under reaction conditions. At the initial stages of the interaction (Figure 10B), the band at 2347 cm^{-1} developed due to increasing hydroxyl coverage of the sample.

The first evidence of CO formation is obtained after interaction at 225 °C, when a band at 2110 cm^{-1} assigned to Ni^+-CO monocarbonyls appears (Figure 10A, spectrum f). At higher temperatures, this band progressively gives rise to the characteristic $\text{Ni}^+(\text{CO})_2$ dicarbonyl bands at 2137 and 2092 cm^{-1} , reflecting the increasing CO concentration (Figure 10A, spectra g–i). Their appearance also demonstrates partial reduction of Ni^{2+} to Ni^+ under the reaction conditions. CO in the gas phase is first detected after interaction at 275 °C, and its concentration increases markedly after treatment at 300 °C.

Formate species are among the first reaction intermediates formed, in agreement with literature data [46–48]. Their characteristic bands at 1586 and 1377 cm^{-1} , assigned to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ vibrations of monodentate formates, respectively, are already detected after interaction at 100 °C. The corresponding C–H stretching vibration appears near 2900 cm^{-1} , while the band at 2985 cm^{-1} is attributed to a Fermi resonance associated with the formate species (see the inset in Figure 10A). The intensities of the formate bands

In contrast to NiZ-IE, both higher-loaded catalysts also produce methane, readily detected in the gas phase at 3018 cm^{-1} [46] (see the insets in Figure 11). The amount of CH_4 formed over NiZ-DP after interaction at $275\text{ }^\circ\text{C}$ is approximately one order of magnitude higher than that observed for NiZ-SSE, consistent with its substantially higher catalytic activity (see below). As in the case of NiZ-IE, the formation of surface formate species and adsorbed water is also observed, indicating that the same general reaction pathway operates on all catalysts.

To support the band assignments, analogous experiments were performed with deuterioxylated NiZ-SSE using CO_2 and D_2 (Figure S6). The observed isotopic shifts are fully consistent with the proposed assignments. In particular, the red shift of the $\delta(\text{H}_2\text{O})$ band at 1628 cm^{-1} after deuteration uncovers weak bands in this spectral region. It is thus evident that the bands at 1445 and 1430 cm^{-1} evolve in parallel with bands at 1677 and 1647 cm^{-1} , respectively, providing additional support for the assignment of the $\sim 1445\text{ cm}^{-1}$ band to carbonate species.

2.3.3. H-ZSM-5

Control experiments performed with the parent H-ZSM-5 samples showed behaviour qualitatively similar to that of NiZ-IE. However, only adsorbed water was detected as a surface reaction product, while CO was observed exclusively in the gas phase. Moreover, the onset of CO formation occurred at approximately $300\text{ }^\circ\text{C}$, about $25\text{ }^\circ\text{C}$ higher than for NiZ-IE, suggesting that isolated nickel cations facilitate CO_2 activation even though they exhibit only limited methanation activity.

Overall, the FTIR results demonstrate that all samples exhibit common surface intermediates, suggesting that increasing nickel loading accelerates the same general sequence of processes. Formate intermediates are formed already at low temperatures, whereas CO appears only above a certain temperature. The progressively earlier appearance of surface carbonyls, gas-phase CO, and methane is fully consistent with the catalytic behaviour of the three samples. These results further indicate that isolated Ni^{2+} and Ni^+ cations possess only limited activity for CO_2 methanation, whereas readily reducible NiO nanoparticles, acting as precursors of active reduced Ni sites, are crucial for efficient methane formation [16,46].

2.4. Catalytic Performance in CO_2 Hydrogenation

To relate the nickel speciation and CO_2 adsorption properties established above to catalytic behaviour, the Ni/ZSM-5 catalysts were evaluated in CO_2 hydrogenation. Importantly, the catalysts were tested in their activated state without prior reduction, allowing their ability to develop the catalytically active nickel phase directly under the CO_2/H_2 reaction atmosphere to be assessed. This approach is also relevant to the concept of integrated CO_2 capture and subsequent conversion, where a separate reduction step after CO_2 adsorption would be undesirable. The catalytic performance was evaluated in the temperature range of $240\text{--}480\text{ }^\circ\text{C}$ (Figure 12). In addition to the forward run, in which the temperature was increased stepwise, backward measurements were performed during cooling after the maximum temperature had been reached. CO and CH_4 were the only carbon-containing products detected throughout the experiments, and the carbon balance was maintained at $98 \pm 4\%$.

All catalysts were active for CO_2 hydrogenation (Figure 12A). However, both the CO_2 conversion and its temperature profile strongly depended on the nickel loading. The highest activity was observed for NiZ-DP, which reached approximately 85% CO_2 conversion at $420\text{ }^\circ\text{C}$, close to the thermodynamic equilibrium under the employed reaction conditions. NiZ-SSE exhibited intermediate activity, reaching 65% conversion at $450\text{ }^\circ\text{C}$, whereas NiZ-IE attained only 15% conversion even at $480\text{ }^\circ\text{C}$. Thus, the catalytic activity

follows the order NiZ-DP > NiZ-SSE >> NiZ-IE and closely correlates with the amount of reducible nickel species available for hydrogen activation, in agreement with previous studies on Ni-based methanation catalysts [10,51]. This trend is consistent with the increasing amount of reducible nickel species and their higher accessibility in the catalysts with higher nickel loading.

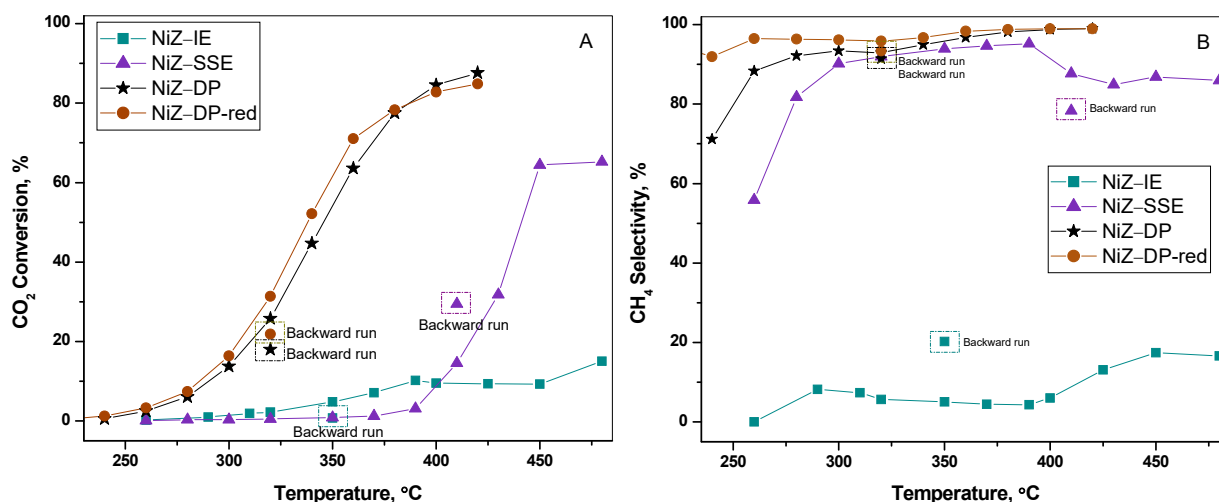


Figure 12. Catalytic activity (A) and selectivity (B) of the samples as a function of reaction temperature ($\text{H}_2/\text{CO}_2 = 4/1$; GHSV = 12,000 mL $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$).

The hydrogen chemisorption data for the reduced catalysts further reveal that the catalytic activity is influenced not only by the total nickel loading but also by the dispersion and accessibility of the active metal sites (Table S3). The H_2 isotherms show a rapid increase in hydrogen uptake at low equilibrium pressures, followed by a gradual increase with increasing pressure (Figure S7). The differences in hydrogen uptake among the catalysts primarily originate from the different nickel loadings, while the normalized chemisorption data reveal significant differences in the fraction of exposed metallic Ni sites available for chemisorption [52]. The highest nickel dispersion and metal-specific surface area were determined for NiZ-IE (3.32% and 22.11 $\text{m}^2 \text{g}_{\text{metal}}^{-1}$, respectively), followed by NiZ-SSE (2.19% and 14.56 $\text{m}^2 \text{g}_{\text{metal}}^{-1}$) and NiZ-DP (1.88% and 12.52 $\text{m}^2 \text{g}_{\text{metal}}^{-1}$). Since catalytic reactions occur on exposed metal sites, the high nickel dispersion of NiZ-IE contributes to its measurable catalytic activity of around 10% at 400 °C despite its low nickel content. While the predominant formation of isolated Ni^{2+} cations can be assumed for NiZ-IE, the presence of NiO species dominates in NiZ-DP, leading to lower metal dispersion in the reduced catalysts. These results are in good agreement with XRD, TPR, and FTIR data, demonstrating that the catalytic performance results from a balance between nickel loading and nickel dispersion, which controls the fraction of the accessible metal sites.

A comparison between the NiZ-DP catalyst pre-reduced at 500 °C and the sample activated directly under the reaction mixture showed only a slight increase in activity for the pre-reduced catalyst (Figure 12A). This observation indicates that reduction of the nickel oxide species proceeds readily under the CO_2/H_2 reaction atmosphere and that the catalytically active phase is efficiently generated in situ.

The increase in catalytic activity is accompanied by a simultaneous increase in methane selectivity (Figure 12B). For NiZ-DP and NiZ-SSE, methane selectivity exceeded 90% already at approximately 320 °C, whereas NiZ-IE remained poorly selective throughout the investigated temperature range, reaching only about 17% at the highest temperature. Above 430 °C, the methane selectivity of NiZ-SSE gradually decreased to approximately 85%, whereas that of NiZ-DP remained essentially constant.

The backward experiments revealed different behaviour for the three catalysts. NiZ-DP showed only a slight decrease in CO₂ conversion while maintaining essentially unchanged methane selectivity, indicating good catalytic stability under the investigated conditions. NiZ-IE exhibited similarly small changes in conversion, accompanied by an increase in methane selectivity. In contrast, NiZ-SSE displayed a pronounced increase in CO₂ conversion during the backward run accompanied by a slight decrease in methane selectivity. This behaviour is consistent with the H₂-TPR results, which show that a substantial fraction of the nickel species in NiZ-SSE is reduced only at temperatures close to those reached during the catalytic experiment. This interpretation was further supported by experiments with NiZ-SSE pre-reduced at 500 °C, for which the activity profile shifted toward lower temperatures. In addition, NiZ-DP exhibited stable catalytic activity and methane selectivity during a 5 h time-on-stream test at 380 °C (Figure S8).

The catalytic results correlate well with the FTIR observations obtained under comparable activation conditions. Methane formation was detected by FTIR above approximately 225 °C for NiZ-SSE and NiZ-DP, whereas no methane was observed for NiZ-IE, even after treatment at 300 °C. In contrast, adsorbed CO species appeared at lower temperatures on all catalysts, with the onset temperature decreasing for the samples containing larger amounts of more readily reducible nickel species. The simultaneous observation of adsorbed CO and gas-phase methane for NiZ-SSE and NiZ-DP supports the involvement of CO as an intermediate during methanation.

At higher reaction temperatures, CO was detected together with CH₄ in the reactor effluent for all catalysts. The increase in methane selectivity observed for NiZ-IE above 400 °C suggests a larger contribution of CO hydrogenation under these conditions [51]. Conversely, the gradual decrease in methane selectivity observed for NiZ-SSE at high temperatures, despite increasing CO₂ conversion, indicates an increasing contribution of the reverse water–gas shift reaction.

Hydrogen chemisorption measurements provide additional information on the dispersion and accessibility of the metallic Ni sites formed upon reduction (Table S3, Figure S7). Although Ni dispersion decreases in the order NiZ-IE > NiZ-SSE > NiZ-DP, the absolute amount of accessible metallic Ni sites increases strongly with increasing nickel content, as reflected by the H₂ uptake and metal surface area per gram of catalyst. Further insight into the catalytic behaviour is provided by the TOF values normalized to the number of accessible Ni sites determined by H₂ chemisorption. Interestingly, although the overall CO₂ conversion follows the order NiZ-DP > NiZ-SSE >> NiZ-IE, the TOF shows the opposite trend, decreasing from 0.12 s^{−1} for NiZ-IE to 0.10 s^{−1} for NiZ-SSE and 0.06 s^{−1} for NiZ-DP. Thus, the high overall activity of NiZ-DP is associated with the much larger number of accessible metallic Ni sites, whereas the activity per accessible Ni site differs substantially among the catalysts.

CO₂ adsorption measurements provide further evidence that adsorption capacity does not directly determine the overall catalytic performance (Figure S9). NiZ-IE adsorbs approximately 2.6 and 2.0 mmol CO₂ g^{−1} at 0 and 25 °C, respectively, compared with 2.1 and 1.7 mmol g^{−1} for the much more catalytically active NiZ-DP. These results further demonstrate that efficient CO₂ adsorption and catalytic hydrogenation are governed by different characteristics of the nickel sites.

Although catalyst optimization was not the primary objective of this study, comparison with literature data obtained under comparable conditions (Table S4) shows that NiZ-DP exhibits competitive catalytic performance [53–58]. At 400 °C and a GHSV of 12,000 mL g_{cat}^{−1} h^{−1}, it achieves 85% CO₂ conversion with 98% CH₄ selectivity, comparing favorably with previously reported Ni-containing zeolite catalysts. Direct comparison

should nevertheless be made with caution because the reported catalysts were evaluated under different reaction conditions.

Overall, the catalytic, adsorption, and spectroscopic results demonstrate that catalytic performance is governed by the amount, nature, reducibility, and accessibility of the nickel species rather than by nickel loading alone. The higher overall activity of the catalysts containing larger amounts of readily reducible nickel is associated with the greater number of accessible metallic sites generated under reaction conditions, whereas the TOF results demonstrate substantial differences in the activity per accessible Ni site. Importantly, the absence of a direct correlation between CO₂ adsorption capacity and catalytic activity further supports the conclusion that molecular CO₂ adsorption and its subsequent hydrogenation are favored by different types of nickel sites.

3. Materials and Methods

3.1. Materials

3.1.1. Catalysts

Different preparation techniques were used to prepare three Ni/ZSM-5 catalysts with increasing nickel loading. Two H-ZSM-5 zeolite materials were used. The first was supplied by Degussa (Essen, Germany) and had a SiO₂/Al₂O₃ molar ratio of 26.8 and a specific surface area of 399 m² g^{−1}. The second was obtained by calcining NH₄-ZSM-5 supplied by Zeolyst International (Conshohocken, PA 19428, USA, CBV 3024E; SiO₂/Al₂O₃ molar ratio of 30) at 500 °C and had a specific surface area of 368 m² g^{−1}. Two low Ni-loaded (≤2.5 at. %) Ni/ZSM-5 samples were prepared using the Zeolyst support. The first catalyst, NiZ-IE, was synthesized through ion exchange by mixing 1 g of H-ZSM-5 and 0.2 M Ni²⁺ solution (50 mL) obtained from Ni(NO₃)₂·6H₂O and refluxing for 3 h. This procedure was repeated three times. The as-prepared sample was washed with distilled water, dried at 120 °C and calcined at 400 °C for 2 h. The second, NiZ-SSE catalyst was prepared by a solid-state ion exchange by mixing 1.194 g of H-ZSM-5 and 0.08411 g of NiCl₂. The mixture was mechanically ground in an agate mortar for 30 min. The homogenized material was placed in a quartz boat and dried in a He flow (50 mL min^{−1}) at 100 °C for 1 h. The temperature was then stepwise raised to 640 °C and kept at this level for 6 h. The obtained sample was cooled to room temperature in the same He flow. The third, NiZ-DP catalyst was obtained by deposition-precipitation technique using the Degussa support. In this procedure, 2 g of H-ZSM-5 were mixed with 200 mL of a 0.1 M Ni²⁺ solution of Ni(NO₃)₂·6H₂O and NH₃ (25%) was added until reaching pH = 12. The mixture was stirred continuously for 1 h at room temperature. The precipitate was washed thoroughly with distilled water, dried at 120 °C and finally calcined at 400 °C for 1 h.

3.1.2. Gases

The gases used in this work were carbon dioxide (Linde, Woking, UK, 99.9993%), carbon monoxide (Merck, Darmstadt, Germany, 99.5%), oxygen (Messer, Bad Soden, Germany, 99.999%), hydrogen (Messer, >99.999%), deuterium (Messer, >99.9%), and helium (Messer 99.999%). The CO₂ isotopologues used in FTIR studies were ¹³C¹⁶O₂ provided by Sigma-Aldrich (St. Louis, MO, USA) with isotopic purity of >99 at. % ¹³C and >97 at. % ¹⁶O, and ¹³C¹⁸O₂ purchased from CortecNet (Les Ulis, France) having isotopic purity of 99% ¹³C and 95% ¹⁸O. D₂O (purity 99.9%) originated from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Before use, CO, O₂ and He were additionally purified by passing through a liquid nitrogen trap. For the TPR experiments gas mixtures provided by Messer were used: 5% O₂/He (O₂ 99.95%) and 5% H₂/Ar (H₂ 99.95%). The ¹²CO₂/¹³CO₂ (80:20) and ¹³C¹⁶O₂/¹³C¹⁸O₂ (55:45) isotopic gas mixtures were prepared in advance by mixing the corresponding isotopologues and were stored in glass reservoirs.

3.2. Methods

3.2.1. X-Ray Diffraction

Powder X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation and a LynxEye position-sensitive detector (Bruker AXS, Karlsruhe, Germany). XRD patterns were recorded over a 2θ range of $5.3\text{--}80^\circ$, with a step size of 0.02° and a counting time of 17.5 s per step. The average NiO crystallite size was calculated using Bruker Topas v.4.2 software based on the Scherrer equation.

3.2.2. Electron Microscopy

The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2100 transmission electron microscope (TEM, Tokyo, Japan) operated at an accelerating voltage of 200 kV and equipped with an Oxford Instruments (Abingdon, UK) X-MAX N 80 T X-ray energy-dispersive spectrometer and a Gatan (Pleasanton, CA, USA) ORIUS 1000 11-MP CCD camera. Before examination, each sample was suspended in ethanol solution and drop-cast onto a standard holey carbon-coated Cu grid. The measurements of lattice-fringe spacing recorded in HRTEM micrographs were made using digital image analysis of reciprocal space parameters. The data analysis was carried out by the Digital MicrographTM software (Version 3.7.4) from Gatan.

3.2.3. Temperature-Programmed Reduction with H_2

Temperature programmed reduction with hydrogen (H_2 -TPR) was carried out using ChemBET TPR/TPD (Quantachrome Instruments, Anton Paar brand, Boynton Beach, FL, USA) apparatus equipped with a thermal conductivity detector. A cold trap with ethanol cooled to -60 to -65°C was used to eliminate water vapor from the gas flow. Before the TPR runs, the samples (50 mg) were pretreated in a flow of 5 vol.% O_2 in He ($20\text{ cm}^3\text{ min}^{-1}$) from RT to 400°C , held for 10 min, cooled to RT in the same flow and then purged with helium. The H_2 -TPR was conducted in a flow of 5 vol.% H_2 in Ar with a rate of $20\text{ cm}^3\text{ min}^{-1}$ from RT to 750°C at a heating rate of $10^\circ\text{C min}^{-1}$.

3.2.4. Nitrogen Physisorption

The specific surface area (S_{BET}) of each sample was determined by nitrogen adsorption at a nominal temperature of 77.4 K using a static volumetric Quantachrome NOVA 1200e apparatus (Quantachrome Instruments, Anton Paar brand, Boynton Beach, FL, USA). The samples were degassed under vacuum at 205°C for 16 h before the measurements. The S_{BET} values were calculated using the BET method.

3.2.5. Diffuse Reflectance UV-Vis Spectroscopy

DR UV–Vis spectra were recorded using a Thermo Scientific Evolution 300 DR UV–Vis spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) in the wavelength range of 200–1100 nm.

3.2.6. FTIR Spectroscopy

FTIR spectra were acquired with a Thermo Scientific Nicolet 6700 FTIR Spectrometer equipped with an MCT/A detector (Thermo Fisher Scientific, Waltham, MA, USA) at a spectral resolution of 2 cm^{-1} and accumulating 64 scans. Self-supporting pellets (ca. 15 mg cm^{-2}) were prepared from the sample powders and were directly treated in a purpose-made IR cell connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-4} Pa . Before the experiments, the samples were activated by heating in 100 mbar of O_2 for 30 min at 673 K, followed by 30 min evacuation at the same temperature and cooling to room temperature. Reduced samples were obtained by treating the pellets

with 100 mbar CO at 330 °C for 20 min, followed by evacuation at the same temperature for 30 min. Deuterioxyated NiZ–SSE was obtained by treating the activated sample with D₂O vapor (1 mbar) for 1 h at 373 K, followed by evacuation at 673 K. All spectra were recorded after cooling the samples to room temperature. The Omnic software (Thermo Fisher Scientific, Waltham, MA, USA) was used for treating the spectra.

3.2.7. Hydrogen Chemisorption

Hydrogen chemisorption experiments were performed using a Quantachrome Instrument AUTOSORB iQ-C-MP-AG-AG (Quantachrome Instruments, Anton Paar brand, Boynton Beach, FL, USA). 200 mg of the sample was loaded into a U-shaped quartz reactor and placed between quartz wool plugs. The sample was pretreated first under nitrogen flow (50 mL/min) at 500 °C for 30 min with a heating rate of 10 degrees per minute, cooled down to 50 °C, and then reduced in situ under a flow of pure hydrogen (50 mL/min) at 500 °C for 1 h with a heating rate of 10 degrees per minute. After reduction, the sample was evacuated for 30 min at 500 °C. Afterwards, the material was cooled down to 40 °C, and evacuated for 30 min. The exposed active metal surface was calculated based on the hydrogen uptake. A H/Ni adsorption stoichiometric factor of 2 was used.

3.2.8. CO₂ Adsorption Experiments

Static adsorption experiments were performed using an AUTOSORB iQ-MPAG instrument (Quantachrome Instruments, Anton Paar brand, Boynton Beach, FL, USA) with pure CO₂ as the adsorbate at 0 °C and 25 °C. After evacuation, the sample holder vessel was filled with CO₂ to a specific pressure. Once equilibrium was reached, the amount of CO₂ adsorbed by the sample was determined. The adsorption isotherms were plotted as the equilibrium amount of CO₂ adsorbed versus the relative pressure ($p/p_0 = 0.001\text{--}0.03$).

3.2.9. Catalytic Experiments

The catalytic activity and methane selectivity in CO₂ hydrogenation reaction over Ni/ZSM-5 catalysts were tested in a fixed-bed flow reactor catalytic setup operating at atmospheric pressure [59]. The reactor itself was a quartz tube of a 15 mm inner diameter, with a catalyst bed fixed at the middle. The catalyst bed contained 150 mg sample (particle size 0.2–0.8 mm) diluted with 100 mg glass beads of the same size (previously checked to be inactive). A thermocouple positioned in the catalyst bed allowed accurate measurements of reaction temperature. The reactant gases CO₂ and H₂ (1:4 ratio) were fed in the reactor at a total flow rate of 30 cm³ min^{−1}, GHSV = 12,000 cm³ h^{−1} g_{cat}^{−1}. Prior to the catalytic tests, all samples were treated in situ in air atmosphere (60 cm³ min^{−1}) at 400 °C for 30 min. The tests were performed with a stepwise increase in temperature (forward run) in the range 240–480 °C, followed by a backward run in which the temperature was decreased to evaluate changes in catalytic performance. GC- on-line analysis of the reaction products was performed on NEXIS GC-2030 ATF with a Supelco Carboxen 1006 PLOT Fused Silica Capillary column (Supelco, Bellefonte, PA, USA), Cat.# 25461 Serial# 274379-07 (30 m × 0.53 mm × 20.0 μm).

4. Conclusions

A series of Ni/ZSM-5 catalysts prepared by different methods and characterized by different nickel contents and speciation was investigated by combining structural characterization, FTIR spectroscopy, and catalytic CO₂ hydrogenation measurements. The results establish a direct relationship between nickel speciation, molecular CO₂ adsorption, and catalytic behaviour and reveal distinct functions of the different nickel species in CO₂ capture and conversion.

FTIR spectroscopy showed that molecular CO₂ is preferentially adsorbed on Ni²⁺ cations. Detailed investigation of the ion-exchanged catalyst demonstrated that, at low coverage, adsorption proceeds through end-on Ni²⁺–CO₂ complexes, whereas increasing coverage leads to the formation of geminal Ni²⁺(CO₂)₂ species. The adsorption geometry was established unambiguously by applying the isotopic linkage isomerism (ILI) approach, which provides direct discrimination between end-on and bridging adsorption configurations. Importantly, the formation of geminal complexes allows more than one CO₂ molecule to be accommodated at a single Ni²⁺ site and therefore contributes to enhanced adsorption capacity. These findings provide molecular-level information on CO₂ coordination that cannot be obtained unambiguously from conventional analysis of the vibrational frequencies alone.

Reduction of the catalysts by CO generates Ni⁺ sites that readily coordinate CO but exhibit negligible affinity toward molecular CO₂, demonstrating markedly different adsorption properties of Ni²⁺ and Ni⁺ cations. During the interaction of the ion-exchanged catalyst with CO₂/H₂ mixtures, FTIR spectroscopy revealed the formation and evolution of several surface species, including formates, carbonyls, and adsorbed water, while CO was also detected in the gas phase. For the catalysts containing larger amounts of readily reducible nickel species, these transformations occurred at lower temperatures and methane was additionally detected in the gas phase. Importantly, the catalysts were not pre-reduced before these experiments or the catalytic tests, demonstrating that the active reduced nickel species can be generated in situ under the CO₂/H₂ reaction atmosphere. The spectroscopic observations are thus consistent with the catalytic behaviour and support the involvement of CO as an intermediate in CO₂ methanation.

The combined FTIR and catalytic results demonstrate that efficient molecular CO₂ adsorption and its subsequent catalytic conversion require different types of nickel sites. Isolated Ni²⁺ cations provide effective sites for molecular CO₂ adsorption, whereas the hydrogenation steps require more readily reducible nickel species capable of generating metallic sites under reaction conditions. Chemisorption measurements further show that catalytic performance is governed not only by the amount of reducible nickel but also by the dispersion and accessibility of the metallic sites formed during reduction. Thus, optimization of integrated capture-and-conversion materials requires an appropriate balance between the density of sites capable of efficiently adsorbing CO₂ and the accessible metallic sites responsible for its catalytic hydrogenation.

The molecular-level understanding obtained in this work provides a basis for the rational design of Ni-containing materials that integrate efficient CO₂ capture with catalytic conversion. In addition, the methodology employed here, particularly isotopic linkage isomerism, should be broadly applicable to investigations of molecular CO₂ adsorption on other catalytic and adsorbent systems.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16090808/s1>. Figure S1: EDS and elemental mapping images of the Ni/ZSM-5 catalysts. Figure S2: TEM bright field micrograph of the NiZ–SSE catalyst. Figure S3: Experimental HRTEM image and Fourier filtered HRTEM images (A–C) of the NiZ–DP catalyst. Figure S4: Experimental HRTEM image and Fourier filtered HRTEM images (A–C) of the NiZ–DP catalyst. Figure S5: HRTEM image of NiZ–DP showing small intracrystalline NiO (A) and metallic Ni (B) nanodomains. The enlarged regions show lattice spacings assigned to the NiO(111), Ni(111), and ZSM-5 (112) and (120) planes. Figure S6: FTIR spectra and difference (incremental) spectra recorded after successive 15 min interactions of deuterioxyated NiZ–SSE with CO₂ (5 mbar) and D₂ (20 mbar). Temperature of interaction: 100 °C (a), 125 °C (b), 150 °C (c), 175 °C (d), 200 °C (e), 225 °C (f), 250 °C (g) and 275 °C (h). Spectrum (i) refers to interaction at ambient temperature. Figure S7: Pressure dependence of hydrogen uptake on the studied Ni/ZSM-5 samples. Figure S8:

Catalytic activity (A) and selectivity to methane (B) as a function of time on stream on the NiZ-DP catalyst at 380 °C, H₂:CO₂ = 4:1; GHSV = 12,000 mL gcat^{−1} h^{−1}. Figure S9: CO₂ adsorption–desorption isotherms on the samples at 0 °C (A) and 25 °C (B). Table S1: Averaged atomic contents and ratios for the Ni/ZSM-5 catalysts. Table S2: Hydrogen consumption in the 200–750 °C temperature range during TPR, normalized to 1 g of sample. Table S3: Chemisorption data and catalytic activity calculated as TOF for the studied samples. Table S4: Comparison of the catalytic performance of supported nickel catalysts in CO₂ methanation reported in the literature.

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