



CO₂ methanation with MOF-derived hierarchically porous spherical carbon nanocomposite incorporating cobalt nanoparticles

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ABSTRACT

In this work, a spherical and hierarchical carbon-based nanocomposite containing dispersed cobalt nanoparticles is introduced. The preparation of this material is based on a facile microwave-assisted synthesis of a cobalt-based metal-organic framework containing a 2,6-naphthalene dicarboxylic linker (labeled as NDC) and its subsequent carbonization at either 600 °C or 700 °C in an argon atmosphere. The resulting materials exhibit unique morphology and feature small Co nanoparticles with sizes of about 3.1 and 6.0 nm, respectively, evenly dispersed on the carbon matrix. In the methanation of carbon dioxide, these CoNDC-derived nanocomposites achieved a methane formation rate of up to 10.5 μmol_{CH₄} g_{cat}⁻¹ s⁻¹ at 350 °C, with 100% selectivity to methane. Such behavior is ascribed to a high content of accessible small metallic cobalt nanoparticles present in the hierarchical structure of CoNDC nanocomposite catalysts, highlighting their promising potential for CO₂ utilization in industry.

1. Introduction

The increasing carbon dioxide (CO₂) concentration in the atmosphere, primarily due to anthropogenic activities, poses significant environmental challenges, including climate change and global warming. As a result, the conversion of CO₂ into valuable chemicals and fuels has garnered considerable attention as a potential strategy for mitigating these issues while simultaneously addressing energy demands [1]. Methanation stands out among the various methodologies explored for CO₂ utilization via reaction with green H₂ as it produces methane, a convenient energy carrier [2]. This process contributes to carbon recycling and aligns with sustainable energy production principles [3–5], particularly in the context of the Power-to-gas (P2G) scenario [2,6].

CO₂ methanation is an exothermic process (CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH°_{298K} = −164 kJ mol⁻¹), but its performance becomes limited at elevated temperatures due to thermodynamic constraints. Although

the reaction offers several benefits, it also presents notable challenges. Because it is exothermic, high CH₄ yields are favored at lower temperatures. Yet, the inherent stability of the linear CO₂ molecule requires highly active catalysts to promote its activation under such mild conditions. In addition, the competing reverse water–gas shift (RWGS) reaction—which forms carbon monoxide (CO) and water—significantly hinders optimal CH₄ production at high temperature [7]. Efficient CO₂ methanation requires catalysts that combine high activity, high CH₄ selectivity, and long-term stability.

Cobalt-based catalysts have emerged as promising alternatives to noble metals for CO₂ methanation, particularly due to their relatively low cost, unique properties, and satisfactory catalytic performance. The catalytic activity of cobalt nanoparticles is influenced by several factors, including their oxidation states, particles size and dispersion, and the nature of the support material used during synthesis.

Recent studies have demonstrated that cobalt oxide (CoO) and

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metallic cobalt (Co) nanoparticles exhibit distinct catalytic behaviors, with the former being active in the hydrogenation of CO₂ to CO or hydrocarbons, and the latter in the hydrogenation to CH₄ [8–11].

Cobalt dispersion on various supports, such as titania and alumina, can lead to variations in catalytic activity and selectivity [9,12–14]. Smaller cobalt nanoparticles generally offer a higher density of active sites, which is essential for improving the overall reaction kinetics [12]. Furthermore, stabilizing these nanoparticles on appropriate supports helps mitigate deactivation processes, thereby extending catalyst lifetime and enhancing overall efficiency [4].

In this context, metal-organic framework (MOF)-derived cobalt carbon composite catalysts have emerged as a promising class of functional materials for various applications in electrochemistry [15–17], adsorption [18,19] and separation, and in particular in heterogeneous thermocatalysis [20,21]. For the CO₂ methanation reaction, MOF-derived catalysts have shown promising performance, thus contributing to carbon neutrality and renewable energy storage. The unique properties of MOFs, including their tunable porosity and high surface area, allow for the effective encapsulation and stabilization of small cobalt nanoparticles, which are essential for enhancing catalytic activity and selectivity in methanation processes.

Typically, the synthesis of cobalt carbon composites from MOFs involves pyrolysis, which converts the MOF structure into a carbon matrix while retaining the metal component. This process not only provides robust support for the cobalt nanoparticles but also enhances their dispersion and stability. For instance, Xu et al. demonstrated that MOF-derived carbon can effectively confine cobalt nanoparticles, preventing their aggregation and maintaining high catalytic performance during reactions [22]. Recent studies have highlighted the promising potential of cobalt-based catalysts derived from various MOFs, such as ZIF-67, which has been utilized to create cobalt nanoparticles embedded in a nitrogen-doped carbon framework [23–27]. This configuration not only promotes CO₂ adsorption but also enhances the overall catalytic activity for methanation [28,29]. Furthermore, the ability to tailor the morphology and composition of these composites allows for the optimization of their catalytic properties, making them suitable for specific reaction conditions [30]. In addition to their structural advantages, MOF-derived cobalt carbon composites exhibit excellent thermal stability and resistance to deactivation, which are essential for practical applications in CO₂ methanation [23,31]. The high surface area and porosity of these materials facilitate the accessibility of reactants to the active sites, thereby enhancing the reaction kinetics [32,33]. It has been demonstrated that the texture of cobalt carbon composite materials and cobalt nanoparticle size play important roles in catalytic activity and selectivity to CH₄ within CO₂ methanation reactions [14,34,35]. Despite these advances, the development of MOF-derived cobalt carbon composites with controlled morphology, hierarchical porosity, and highly dispersed small Co nanoparticles remains an important challenge, especially using facile and rapid synthesis approaches. Moreover, although these catalysts exhibit reasonable activity, achieving high selectivity toward CH₄ with correspondingly high yields remains a significant challenge.

Herein, we present a straightforward approach for the preparation of a Co-MOF-derived spherical nanocomposite catalyst for CO₂ methanation. Synthesis is based on microwave-assisted (MW) solvothermal preparation of cobalt MOF material from 2,6-naphthalene dicarboxylic acid (H₂NDC) resulting in CoNDC MOF serving as a parent precursor for carbon-based nanocomposites containing metallic cobalt nanoparticles. The Co(acac)₂ precursor was chosen due to its high solubility in organic solvents and its melting point temperature (ca. 165 °C), which is close to the boiling point of the DMF solvent. As demonstrated in this work, the fast MW-assisted heating allows obtaining spherical particles of Co/C with a unique hierarchically porous morphology and with a homogeneous dispersion of small cobalt nanoparticles. To the best of our knowledge, this kind of spherical nanocomposite was used in CO₂ methanation for the first time. It was confirmed that this simple

combination of well dispersed cobalt nanoparticles and carbon matrix possesses high catalytic activity in CO₂ methanation with high methane selectivity.

2. Experimental

2.1. Chemicals

2,6-naphthalene dicarboxylic acid (H₂NDC, 95 %, M_w = 216.19 g mol⁻¹), biphenyl-4,4'-dicarboxylic acid (H₂BPDC, 97 %, M_w = 242.23 g mol⁻¹), and cobalt(II) acetylacetonate Co(II)(acac)₂ (99 %, M_w = 257.15 g mol⁻¹) were supplied from Sigma Aldrich. N,N'-dimethylformamide DMF (p.a.), and chloroform (p.a.) were purchased from Penta (Czech Republic).

2.2. Synthesis of catalysts

The synthesis of CoNDC (where NDC is abbreviation for 2,6-naphthalene dicarboxylic linker) material in a microwave reactor was performed as follows: Co(II)(acac)₂ (0.395 g, 1.53 mmol) was dissolved in 60 mL of N,N'-dimethylformamide (DMF) in a Teflon reaction vessel under ambient atmosphere. After the dissolution of the cobalt precursor, 2,6-naphthalene dicarboxylic acid (H₂NDC, 0.446 g, 2.06 mmol) was added, and the Teflon reaction vessel with the reaction mixture was placed into a microwave reactor and tightly closed. The microwave power was set to 60 % (360 W), and the reaction mixture was heated to 160 °C under microwave irradiation. The reaction was stopped after 40 min. The microwave reactor record is illustrated in the Supplementary materials (Fig. 1S). Once the reaction mixture was cooled to 50 °C, the reactor was removed, and the resulting violet precipitate was filtered on a Büchner funnel and washed with chloroform. The violet powder product was dried at 80 °C in an oven and weighed. The yield of the CoNDC MOF-based product was 0.445 g. In the following step, the as-prepared product was carbonized in a tubular furnace at 600 °C or 700 °C for 2 h under the atmosphere of argon with a heating ramp of 5 °C min⁻¹. The resulting catalysts are denoted as CoNDC-600 and CoNDC-700.

The synthesis of CoBPDC (where BPDC is abbreviation for biphenyl-4,4'-dicarboxylic linker) material in a microwave reactor was performed according to the published procedure under the same conditions and in the same manner as in the case of CoNDC MOF preparation [36]. However, biphenyl-4,4'-dicarboxylic acid (H₂BPDC) was used as an organic linker to achieve different morphology of the products. To obtain the CoBPDC-700 catalyst, the as-prepared CoBPDC MOF was carbonized at 700 °C for 2 h under the atmosphere of argon with a heating ramp of 5 °C min⁻¹. This catalyst with platelet-like morphology was used for comparison purposes with the CoNDC-700 catalyst. The characterization data of CoBPDC-700 are given in the supplementary information.

2.3. CO₂ methanation test

The CO₂ methanation performance was assessed using a continuous flow fixed-bed reactor (Stainless steel tube with internal diameter of 6 mm). 100 mg of the catalyst was introduced in the reactor and reduced in situ at 400 °C for 1 h under 20 mL/min of 50% (v/v) H₂ diluted in Ar, followed by purging for 1 h with Ar and cooling down to 200 °C. Subsequently, a reaction mixture with a total flow rate of 20 mL/min, containing 10% CO₂ and 40% H₂ diluted in Ar, was introduced into the reactor. The reaction was conducted at atmospheric pressure in step mode, with temperature increments of 50 °C from 200 °C to 400 °C. At each temperature step, at least four gas chromatography (GC) injections were performed after reaching a steady state. The outlet gases were analyzed using a SCION 456-GC chromatograph equipped with Haysep Q, Molsieve 5A, Porapak R, and SCION-1 columns. CO and CO₂ were quantified with a thermal conductivity detector, while CH₄ was detected

using a flame ionization detector. To prevent condensation of water by-product during the reaction, all gas transfer lines were maintained at 125 °C. CO₂ conversion (X_{CO_2}), CH₄ selectivity (S_{CH_4}), CO selectivity (S_{CO}), and CH₄ formation rate (r_{CH_4}) were calculated according to the following equations, where F , m_{cat} and m_{Co} are the molar flow rate, the mass of catalyst, and the mass of Co metal determined by ICP-OES, respectively:

$$X_{\text{CO}_2}(\%) = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \times 100\% \quad (1)$$

$$S_{\text{CH}_4}(\%) = \frac{F_{\text{CH}_4, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100\% \quad (2)$$

$$S_{\text{CO}}(\%) = \frac{F_{\text{CO}, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100\% \quad (3)$$

$$r_{\text{CH}_4} = \frac{F_{\text{CH}_4, \text{out}}}{m_{\text{cat}}} \text{ or } \frac{F_{\text{CH}_4, \text{out}}}{m_{\text{Co}}} \quad (4)$$

2.4. Instrumentation and characterization methods

2.4.1. MW synthesis

The CoNDC and CoBPDC MOF materials were synthesized under an ambient atmosphere in a PTFE-lined microwave reactor ERTEC Magnum II (600 W; 2.45 GHz). Microwave power was set to 60 % (360 W), and the reaction duration was 30 min.

2.4.2. Chemical/elemental analyses

Cobalt content in CoNDC and CoBPDC materials was determined by ICP-OES spectroscopy performed on an iCAP PRO XPS Duo spectrometer (Co spectral line $\lambda = 238.892$ nm).

2.4.3. Structural characterizations

The powder XRD patterns were collected on a Rigaku MiniFlex 600 diffractometer equipped with a CoK α ($\lambda = 1.7903$ Å) X-ray tube (40 kV, 15 mA). For the data processing and crystallite size calculations, Rigaku PDXL2 software was used. The average size of the crystallites was evaluated using Scherrer's formula, $D = K\lambda/\beta\cos\theta$, where D is the crystalline size, K is a grain shape-dependent constant (0.9), λ is the wavelength, θ is a Bragg reflection angle, and β is the full-width half-maximum. For the crystallite size calculation, the Co (111) diffraction line was used to apply the Scherrer equation.

2.4.4. Infrared and Raman spectroscopy

The FTIR spectra were recorded on a Thermo NICOLET 6700 spectrometer using an ATR technique with the diamond crystal (resolution 2 cm⁻¹, 4000–400 cm⁻¹). Raman spectroscopy was carried out on a Thermo Raman microscope Nicolet DXR equipped with a He–Ne laser with an emission wavelength of 633 nm (laser power 2 mW). The spectra were recorded from 50 to 2000 cm⁻¹.

2.4.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy measurements were performed on a spectrometer Axis Supra (Kratos Analytical) equipped with monochromatized Al-K α radiation (1486 eV). The pressure in the analysis chamber was around 10⁻⁶ Pa. The analyzed area was approximately 1.4 mm², and the pass energy was set at 150 eV. The C 1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale [37,38]. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK), and some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a nonlinear baseline [39].

2.4.6. Thermal analysis and carbonization

Thermogravimetric analyses were performed on a Setaram LabSys

Evo thermogravimeter with TG/DSC sensor in an atmosphere of air (heating ramp 5 °C min⁻¹, up to 800 °C, airflow 5 ml min⁻¹). Dried CoNDC powders were carbonized in a Nabertherm LE 4/11/R6 tubular furnace at 600 and 700 °C (5 °C min⁻¹) for 2 h in an atmosphere of argon.

2.4.7. Microscopy

The scanning electron microscopy and EDS analyses were performed on a Nova NanoSEM (FEI) with Schottky field emission electron source (0.02–30 keV) and TLD detector at 5 kV. For EDX analysis, an EDS platform Octane plus (SDD detector) by EDAX, AMETEK, Inc. was used. The scanning TEM energy-dispersive X-ray spectroscopy (STEM-EDS) analysis was performed using a Thermo Fisher Scientific TalosF200C instrument equipped with a Bruker Xflash 6T-30 detector. STEM imaging was conducted with a high-angular annular dark-field (HAADF) detector to provide atomic Z-contrast. The sample for STEM-EDS was dispersed in cyclohexane, and 4 μ l of this suspension were placed on a QuantiFoil R 2/2300 mesh copper grid and allowed to dry by evaporation at ambient temperature. Subsequently, the sample underwent low-pressure H₂/O₂ plasma cleaning for 80 s using a Gatan Solarus II apparatus to reduce the organic contamination.

2.4.8. Nitrogen adsorption/desorption

Nitrogen adsorption/desorption isotherms were recorded at a temperature of 77 K on a BELsorp Mini II (Japan). Within pretreatment, the samples were degassed in the BELsorp preparation unit at 300 °C for 20 h. Surface areas (S_A) and total pore volumes (V_{tot} at $p/p_0 = 0.99$) were determined by volumetric techniques [40,41]. The specific surface area was determined by multipoint Brunauer-Emmet-Teller (BET) analysis using at least five data points with relative pressures between 0.05 and 0.30 [40]. Pore size distributions were determined by NLDFT and BJH methods using the adsorption branch isotherm [42,43]. Micropore surface area was calculated by t-plot method [44].

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

H₂-temperature programmed reduction (H₂-TPR) was carried out on a BELCAT II analyzer (Microtrac). About 50 mg of catalyst was first pretreated under Ar flow of 50 mL/min at 200 °C for 1 h to eliminate physisorbed water and impurities. After cooling down to 100 °C, H₂-TPR measurement was performed as a function of temperature from 100 °C to 800 °C (10 °C/min) under 50 mL/min of 1% (v/v) H₂ diluted in Ar.

2.4.10. CO₂-temperature programmed desorption

CO₂-temperature programmed desorption (CO₂-TPD) was performed using a Hiden instrument equipped with an online QGA mass spectrometer (MS). About 100 mg of catalyst was first pretreated under 30 mL/min of 1% H₂/Ar at 400 °C for 1 h, followed by purging with Ar and cooling to 50 °C. The sample was then exposed to 30 mL/min of 15% CO₂/Ar for 1 h and subsequently flushed with Ar for 30 min. The CO₂-TPD measurement was performed from 50 °C to 800 °C at a heating rate of 10 °C/min under 30 mL/min Ar flow.

3. Results and discussion

3.1. Synthesis and materials characterization

The cobalt metal-organic framework material (Co-NDC) was synthesized through a microwave-assisted approach based on the reaction of Co(II)(acac)₂ and 2,6-naphthalene dicarboxylic acid in N,N'-dimethylformamide at 160 °C. For comparison of catalytic activity, a CoBPDC-derived platelet-like nanocomposite catalyst was prepared following our previously published procedure [36]. Characterization data for this sample are provided in the Supplementary Information (see below).

As-prepared CoNDC MOF material was characterized by FTIR spectroscopy (Fig. 2S), thermogravimetric analysis (Fig. 2S), and SEM-EDX

microscopy (Figs. 3S and 4S). FTIR spectrum of as-prepared CoNDC sample (Fig. 2S) shows the absorption bands for carboxylic, aromatic ring, and DMF moieties with the most intense absorption band raised at 1394 cm^{-1} which is attributed to ν_{sym} modes of carboxylate groups characteristic for MOF materials [45]. TG curve of the CoNDC shows a mass loss of approximately 25% in the temperature range of $140\text{--}330\text{ }^{\circ}\text{C}$, which is attributed to the release of coordinated DMF (Fig. 2S). This corresponds well to the DMF loss observed in the TG curve of the $\text{Co}_3(\text{NDC})_3\text{DMF}_4$ MOF reported by Liu [46]. The subsequent mass loss (51 %) occurring between 360 and $440\text{ }^{\circ}\text{C}$ is assigned to the decomposition of the NDC linker. The residual mass at $800\text{ }^{\circ}\text{C}$ is 24%, and powder XRD analysis (Fig. 5S) indicates that this residue corresponds to Co_3O_4 (JCPDS card no. 073-1701). When this residual oxide mass is converted to the equivalent cobalt content, it corresponds to 17.6 wt% Co in the as-prepared CoNDC material. This value is consistent with the EDX elemental analysis (Fig. 3S), which indicates a cobalt content of 17 wt%. Based on the mass losses attributed to DMF and the NDC linker, as well as the residual cobalt content observed in the TG analysis, the composition of the CoNDC sample appears to correspond to the $\text{Co}_3(\text{NDC})_3\text{DMF}_4$ MOF structure [46] (molar mass $1111.68\text{ g mol}^{-1}$). The powder X-ray diffractogram (Fig. 1a) of the as-prepared CoNDC sample exhibits diffraction peaks confirming its crystalline nature, which is characteristic of MOF materials. According to published results, the diffractogram of as-prepared CoNDC MOF material matches the powder diffraction pattern of $\text{Co}_3(\text{NDC})_3\text{DMF}_4$ MOF reported by Liu et al. [46]. Moreover, it is also consistent with the pattern calculated from the single-crystal diffraction data of $\text{Co}_3(\text{NDC})_3\text{DMF}_4$ (.CIF file) available in Cambridge structural database (CCDC No. of structure 639913) (Fig. 6S) [46,47]. However, a distinctly different hierarchical morphology (Fig. 4S) is obtained when using the $\text{Co}(\text{acac})_2$ precursor, in contrast to the $\text{Co}(\text{NO}_3)_2$ precursor employed in Liu's study [46]. The resulting violet (magenta) CoNDC powder MOF (Fig. 4S) material obtained from $\text{Co}(\text{acac})_2$ was used as a precursor for the preparation of hierarchical carbon-based spherical nanocomposites containing metallic cobalt nanoparticles. Final nanocomposites (CoNDC-600, CoNDC-700) were obtained after carbonization of CoNDC powder at 600 or $700\text{ }^{\circ}\text{C}$ under an inert atmosphere of argon. To prove the presence of metallic cobalt nanoparticles in the nanocomposite structure, powder X-ray diffraction analysis was performed. As displayed in Fig. 1, the diffractograms revealed diffraction lines corresponding to the (111) facet and (200) facet of face-centered-cubic (fcc) Co (ICDD-PDF card 015-0806) characteristic for metallic cobalt nanocrystals. According to the Scherrer equation, the crystallite size calculated from (111) diffraction is about 3.1 and 6.0 nm for CoNDC-600 and CoNDC-700, respectively.

The nanocomposite morphology was investigated by electron

microscopy. As demonstrated in Fig. 2, 7S, and 8S, SEM images revealed a morphology of hierarchically ordered spherical microparticles ($\sim 10\text{ }\mu\text{m}$) formed by the aggregation of smaller particles ($\sim 1\text{ }\mu\text{m}$). It can be argued that microparticles have a hollow structure with a cavity inside (Fig. 9S). Based on a thorough literature survey, we put forward that such hierarchical spherical morphology of cobalt nanoparticle incorporated carbon nanocomposite has not been reported before.

To study the homogeneity of cobalt nanoparticle dispersion, the STEM-EDS technique was employed. As displayed in Fig. 3, cobalt nanoparticles are evenly distributed in the carbon matrix. This has to be related to the fact that Co NP actually emerge (during carbonization) from the homogeneously distributed Co species included in the parent MOF structure. The particle size estimated from the high-resolution HAADF STEM image of the CoNDC-600 sample (Fig. 4) was $5.3 \pm 1.8\text{ nm}$, which fairly correlates with the size calculated from the powder XRD pattern by Scherrer's formula (3.1 nm) with a relatively narrow particle size distribution (Fig. 10S). In the case of the CoNDC-700 sample, a population of larger cobalt nanoparticles ($20\text{--}30\text{ nm}$) was observed (Fig. 3) as well as bigger average particle size determined by STEM ($6.7 \pm 4.5\text{ nm}$) (Fig. 10S). Hence the broader size distribution of Co nanoparticles in CoNDC-700 sample is evidenced. The difference in the Co particle size of CoNDC-600 determined from PXRD and STEM may be explained by the fact that particles observed in STEM can be formed by the agglomeration of several nanocrystals.

The cobalt content in CoNDC-600 and CoNDC-700 was determined by SEM-EDS (Figs. 11S and 12S) and confirmed by ICP-OES (Table 1). Both methods are in good agreement, showing that both CoNDC-600 and CoNDC-700 contain $\sim 45\text{ wt\%}$ of Co.

Raman spectra of CoNDC-600 and CoNDC-700 nanocomposites (Fig. 5a) revealed the characteristic bands at 1318 and 1586 cm^{-1} , indicative of the vibrational modes of disordered carbon (D-band) and in-plane vibrations (E_{2g}) of ordered graphitic carbon (G-band), respectively [48,49]. The I_D/I_G band intensity ratio increased from 1.00 for CoNDC-600 to 1.14 for CoNDC-700, indicating a lower degree of graphitization at higher carbonization temperature. As previously reported, the variation of the D band intensity represents the evolution of defects and other disorder-induced structures [50]. In the case of carbonized MOF products and metal-containing carbonaceous materials the metal-induced defects in the structure of the products carbonized at different temperatures were reported [51,52]. Based on these works, the increased intensity of D band observed in the Raman spectrum of CoNDC-700 compared to CoNDC-600 leading to its higher value of I_D/I_G ratio, can be ascribed to cobalt-induced defects originating for example from change of cobalt nanoparticle size [52]. Furthermore, no Raman bands of cobalt oxide appeared in the spectra [53].

Nitrogen adsorption/desorption physisorption was employed for to

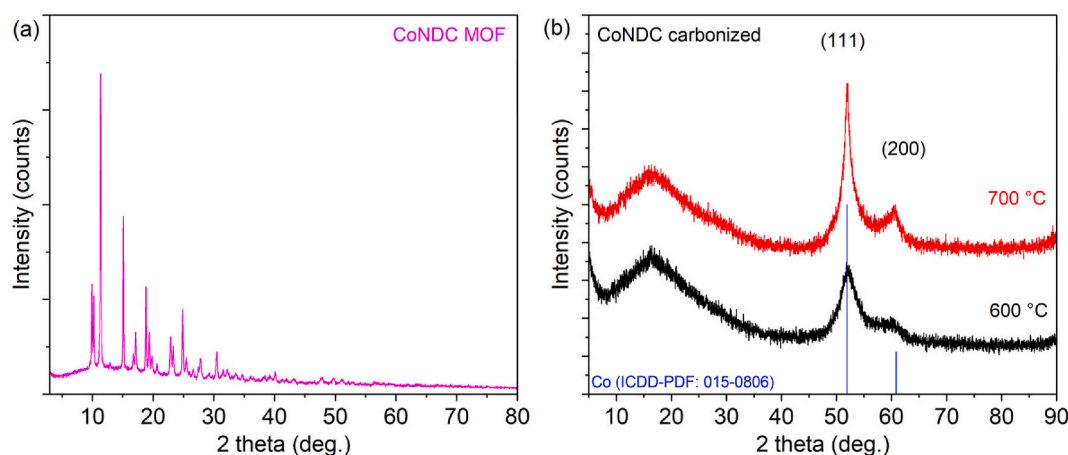


Fig. 1. (a) PXRD pattern of CoNDC as-prepared MOF material. (b) PXRD patterns of CoNDC-600 and CoNDC-700 nanocomposites obtained after carbonization of the parent as-prepared CoNDC MOF. The diffractograms were recorded with the use of a cobalt X-ray tube.

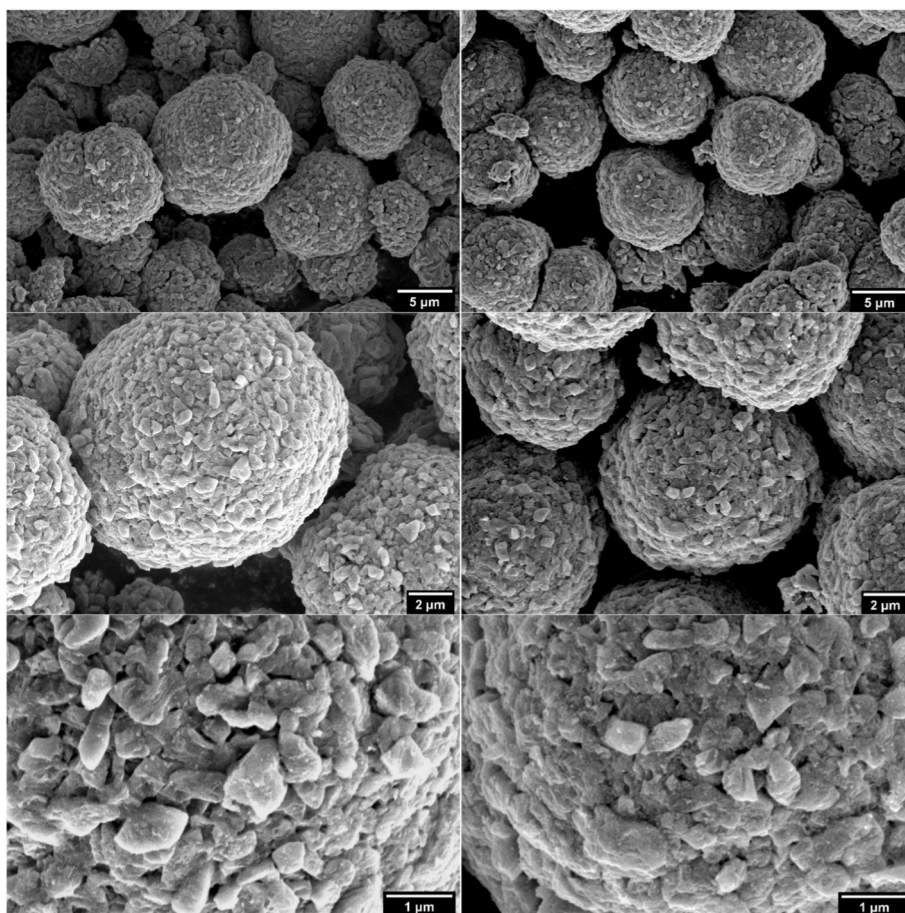


Fig. 2. SEM images of CoNDC-600 (left column) and CoNDC-700 (right column) nanocomposites.

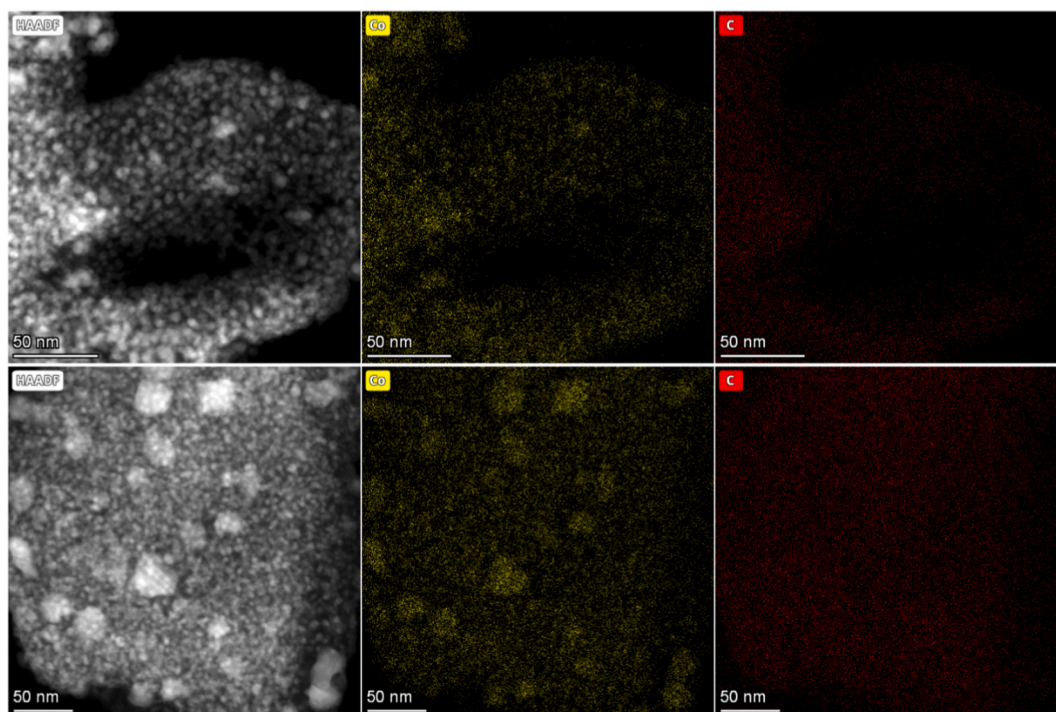


Fig. 3. HAADF and STEM-EDS images of CoNDC-600 (upper row) and CoNDC-700 (bottom row) catalysts (Co – yeallow, C – red).

characterize the sample texture (Table 1, Fig. 5b). According to the IUPAC classification, the isotherms exhibited the shape of Type IV with

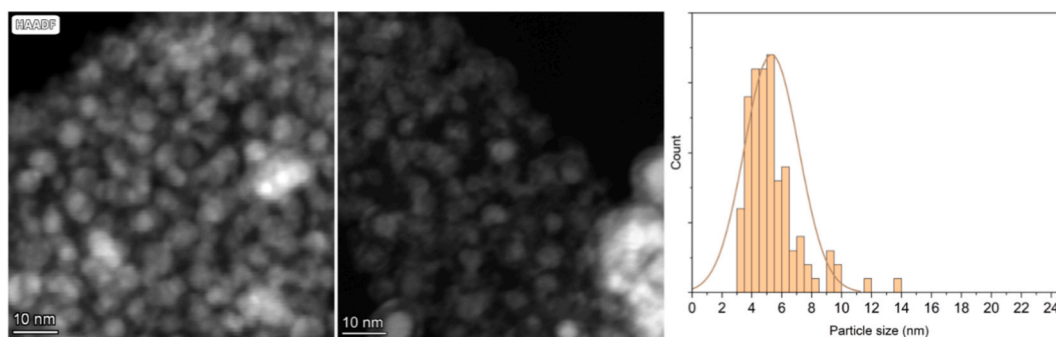


Fig. 4. HR-HAADF images of CoNDC-600 catalyst and particle size distribution of Co nanoparticles.

Table 1

Contents of cobalt in the catalyst samples, nanoparticle size, and surface area values.

catalyst	Co wt. %		Crystallite size ^a [nm]	Particle size ^b [nm]	SA _{BET} [m ² g ⁻¹]	Micropore SA ^c [m ² g ⁻¹]	Total pore volume [cm ³ g ⁻¹]	Micropore volume ^b [cm ³ g ⁻¹]
	SEM-EDS	ICP-OES						
CoNDC-700	43.4	45.9	6.0	6.7 ± 4.5	207	179	0.16	0.083
CoNDC-600	44.1	46.5	3.1	5.3 ± 1.8	212	181	0.17	0.084

^a determined by the Scherrer equation;

^b calculated from STEM HAADF images.

^c determined by t-plot.

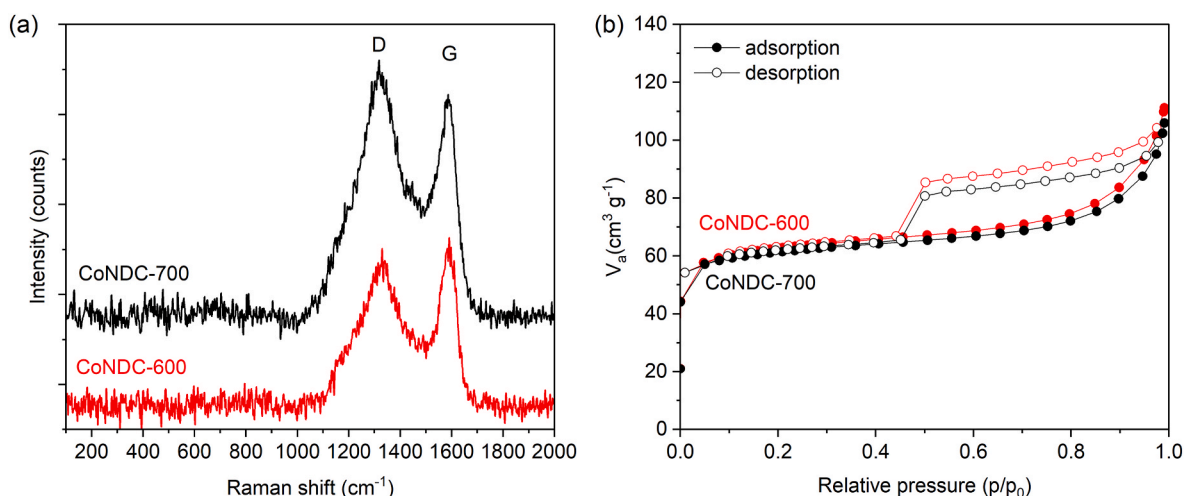


Fig. 5. Raman spectra (a) and N₂ adsorption/desorption isotherms (b) of CoNDC-600 and CoNDC-700 nanocomposite catalysts.

the hysteresis loop starting in the middle of the relative pressure branch corresponding to small mesopores or pore mouths below 3.8 nm [54, 55]. However, in a more realistic scenario involving a random distribution of pores and an interconnected pore network, the adsorption and desorption branches of the isotherm exhibit different behavior. In particular, this leads to a forced closure of the hysteresis loop around a relative pressure of $p/p_0 \approx 0.45$ (for N₂ at 77 K). This phenomenon is commonly referred to as the Tensile Strength Effect [54]. The surface areas determined by the BET method are 212 and 207 m² g⁻¹ for CoNDC-600 and CoNDC-700 materials, respectively. The total pore volume (Table 1) of the CoNDC-600 and CoNDC-700 samples was 0.17 and 0.16 cm³ g⁻¹, respectively. Since nitrogen adsorption occurs at low relative pressures, the micropore population in the samples was evaluated using the t-plot method. This analysis revealed micropore surface areas of 181 and 179 m² g⁻¹ for CoNDC-600 and CoNDC-700, respectively. Furthermore, based on the t-plot results, the external surface areas of CoNDC-600 and CoNDC-700—31 and 28 m² g⁻¹, respectively—can be attributed to the presence of small mesopores. Pore size

distribution was calculated using both the NLDFT method [56] and the BJH method, based on the adsorption branch in each case. As illustrated (Fig. 13S), the samples are characterized by the presence of micropores with the diameters around 1.1 nm and mesopores predominantly in the 2–5 nm range.

X-ray photoelectron spectroscopy (XPS) was employed to identify the elemental composition (Table 1S), chemical states, and functional groups on the surface of the CoNDC-700 and CoNDC-600 nanocomposite catalysts collected after carbonization of parent CoNDC MOF. The survey spectra over the whole binding energy region are given in supplementary information (Figs. 14S and 15S). The Co 2p_{3/2} spectrum (Fig. 6) reveals the major presence of Co⁰ species associated with oxidized Co²⁺ species. As displayed, the main contribution represented with asymmetric peak at 778.6 eV is related to Co⁰ confirming the major presence of metallic cobalt [57], which is most evident in the case of CoNDC-600 sample. This peak is accompanied by two plasmon loss peaks at 3.0 eV, and 5.0 eV of low intensity above the main peak. The other components constituting the observed peak, centered at 780.5 eV, can be attributed

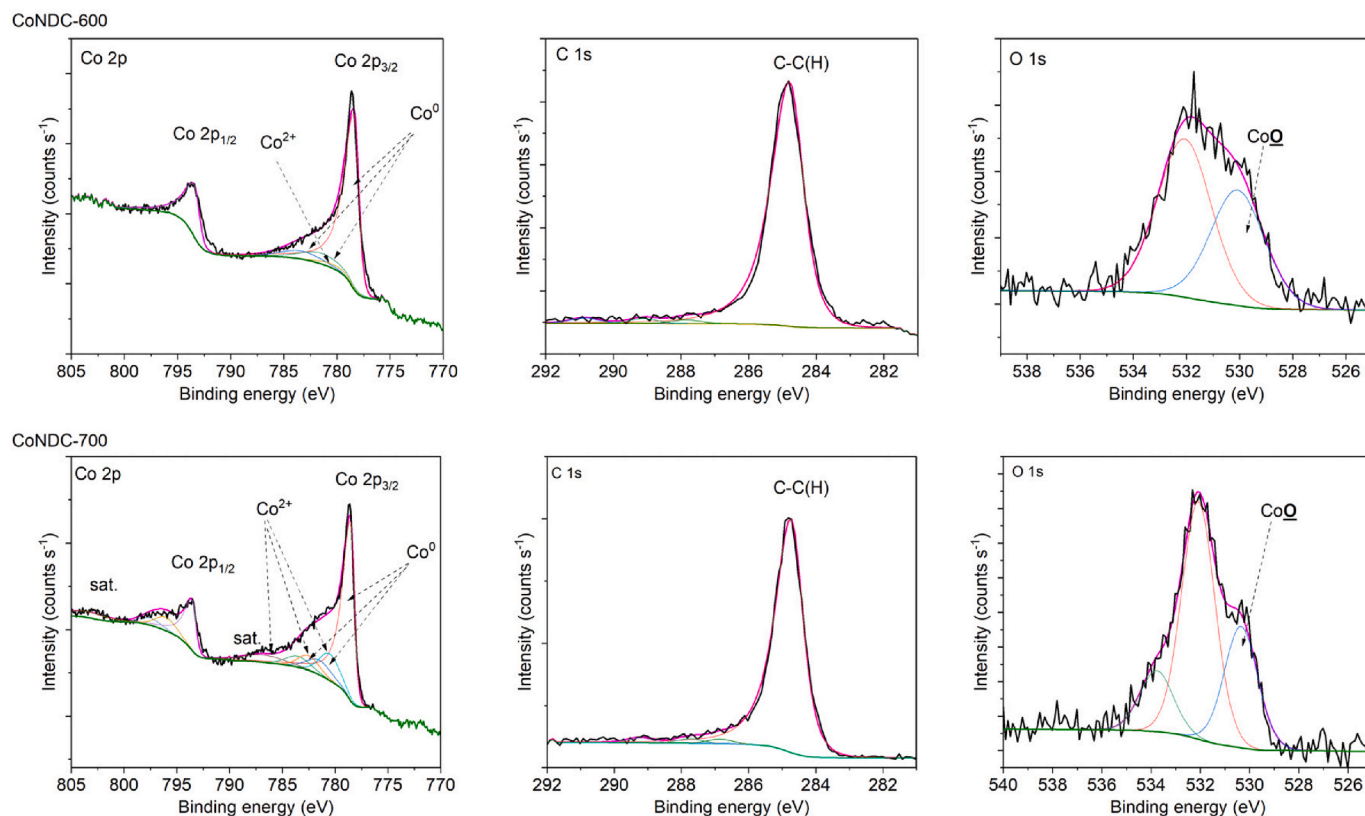


Fig. 6. Co 2p, C 1s, and O 1s XPS spectra of CoNDC-600 and CoNDC-700 catalysts.

to Co^{2+} in CoO and are accompanied by a satellite peak at approximately 786.8 eV, which is more pronounced in the spectrum of the CoNDC-700 sample. According to the literature, a contribution from a higher Co oxidation state of Co_3O_4 at 779.6 eV is also expected, accompanied by corresponding peaks at 780.9 eV and 782.2 eV, and satellites at 785.2 eV and 789.5 eV [57]. This variety of overlapping signals makes the curve fitting procedures difficult; therefore, only the main components are presented in Fig. 6. This observation also aligns with the published data for metallic cobalt particles and the Co^{2+} valence in CoO oxide [25,36,57,58]. The C 1s XPS spectra of CoNDC-600 as well as CoNDC-700 samples displayed in Fig. 6 show the most intense peak with binding energy 284.8 eV characteristic for sp^2 -hybridized C=C in graphitic-like materials [59]. Particularly, the slight asymmetry of the main component in the high BE side is associated with the presence of conductive graphitic-like compounds, presenting intrinsic asymmetry of the C 1s peak [60]. The presence of oxidized carbon species cannot be confirmed, as no quantifiable components indicate organic carbon moieties (C–O, C=O, and O–C=O) manifested in the binding energy range from 286 to 289 eV, in ascending order. Hence, the detected components in the high BE side of the O 1s peak at 532.1 and 533.8 eV (Fig. 6) correspond most likely to chemisorbed and physisorbed hydroxyls, respectively, being attributable to the presence of Co oxides and hydroxides. Although a small contribution of oxidized carbon organic moieties cannot be excluded, it was not confirmed in the C 1s line analysis. The O 1s peak at 530.3 eV is assigned to oxygen in CoO or Co_3O_4 [60]. The presence of multiple O 1s signals associated with the progress of Co surface oxidation was also demonstrated in the literature [61]. In contrast, the bulk contains metallic Co as shown by PXRD. The XRD probes the bulk and confirms that Co^0 was formed and remained in the bulk, while XPS probes only the top few nanometres of the surface and shows that Co on the surface oxidizes to some extent, gaining possibly also hydroxyl groups or even physisorbed water molecules upon exposure to air. The surface elemental composition determined by

XPS is provided in the supplementary information (Table 1S). Notably, the cobalt content on the surface is 16.0 wt% for CoNDC-700 and 14.2 wt% for CoNDC-600 nanocomposites. Moreover, quantitative analysis of the XPS signals (Table 1S) indicated a higher carbon-to-cobalt ratio compared to that determined for the bulk material by ICP-OES analysis of the overall composition. At the same time, EDS confirmed the bulk concentration at its micrometre-scale probing depth. Therefore, only a very top surface graphitic carbon enrichment can be deduced.

To evaluate the distinctive reducibility of CoNDC-600 and CoNDC-700 catalysts, the H_2 -TPR technique was employed. The H_2 -TPR

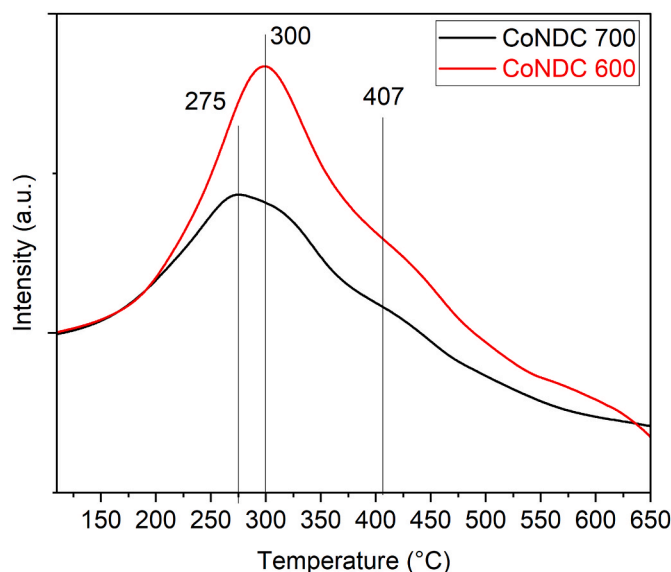


Fig. 7. H_2 -TPR profiles of CoNDC-700 and CoNDC-600 catalysts.

profiles (Fig. 7) revealed hydrogen consumption peaks at ca. 275, 300, and 407 °C. These peaks indicate two reduction steps from Co_3O_4 to CoO at 275–300 °C and from CoO to Co^0 at 400 °C [13,62]. This observation is in accordance with O 1s and Co 2p XPS results where the contribution of the Co^{2+} state was observed (Fig. 6).

3.2. CO_2 methanation catalytic tests

The catalytic activity of MOF-derived CoNDC nanocomposites in CO_2 methanation was tested in a continuous-flow fixed-bed reactor. Before the catalytic reaction, the catalysts were pre-reduced in H_2 at 400 °C to ensure the availability of Co^0 sites, as they were reported to primarily promote CO_2 methanation, whereas CoO sites favor the RWGS reaction [11,63]. Then, the catalytic reaction was performed under atmospheric pressure in step mode, with temperature increments of 50 °C from 200 °C to 400 °C. The CO_2 methanation test was also performed with a catalyst without a pre-treatment step. As illustrated in Fig. 8, the CoNDC-700 catalyst with pre-treatment under H_2 shows higher performance in CO_2 methanation, likely due to the increased availability of metallic Co active sites. With increasing temperature, the CO_2 conversion logically elevates. CoNDC-700 reached 63% conversion at 350 °C. This corresponds to a specific methane formation rate (i.e. productivity) of $9.5 \mu\text{mol}_{\text{CH}_4} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$ or $20.7 \mu\text{mol}_{\text{CH}_4} \text{g}_{\text{Co}}^{-1} \text{s}^{-1}$. To investigate the effect of lower carbonization temperature on catalytic activity, CO_2 methanation over the CoNDC-600 catalyst was performed. As demonstrated in Fig. 8, CoNDC-600 was more active, reaching 70% conversion at 350 °C and 68% conversion of CO_2 at 400 °C (approaching equilibrium conversion). The higher activity of CoNDC-600 can be attributed to the higher population of smaller Co nanoparticles than that observed for the CoNDC-700 catalyst. This observation is in line with previous works on Co-based methanation catalysts [26,64]. The highest conversion level measured for CoNDC-600 and 350 °C corresponds to a specific methane formation rate of $10.5 \mu\text{mol}_{\text{CH}_4} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$ or $22.5 \mu\text{mol}_{\text{CH}_4} \text{g}_{\text{Co}}^{-1} \text{s}^{-1}$. Interestingly, full selectivity toward CH_4 was observed for both CoNDC-600 and CoNDC-700 catalysts in the temperature range 200–350 °C (no CO was detected). The catalytic performance of CoNDC-600 at 300 °C also compares favorably with reports from the literature on similar catalytic systems as discussed below.

In the following step, the CoNDC-700 nanocomposite was compared to the CoBPDC-700 sample derived from the biphenyl-4,4'-dicarboxylic acid linker, disclosed and described in a previous report [36] and tested here in the CO_2 methanation reaction. The characterization of this sample is given in the supplementary information (Figs. 16S–24S). The CoBPDC-700 catalyst exhibits a platelet-like layered disc morphology (Fig. 17S) with microporous characteristics (Fig. 18S) and contains

cobalt nanoparticles averaging 3.6 and 3.9 ± 1.1 nm in size according to Scherrer equation and STEM (Figs. 19S and 20S, Table 2S), respectively. Its cobalt content, at 43 wt%, closely matches that of the CoNDC catalysts. As seen in Fig. 9, the conversion of CO_2 achieved with this catalyst was 45% at 400 °C with a maximal conversion of 50% at 300 °C, which is lower than in the case of the CoNDC-700 catalyst. Similarly, the selectivity toward CH_4 decreased at temperatures above 250 °C due to increased CO production via the reverse water-gas shift reaction on the CoBPDC-700 catalyst.

Based on the XPS experiments, the C/Co wt.% ratios for CoNDC-700 and CoBPDC-700 are 4.8 and 12.5, respectively (Fig. 6; Figs. 15S, 22S and 23S, and Table 1S). It shows a higher content of cobalt nanoparticles on the surface of the CoNDC-700 catalyst compared to that of the CoBPDC-700 catalyst. It could mean the Co nanoparticles in microporous CoBPDC-700 catalyst are more embedded in the carbon matrix and not accessible to the reaction on the surface. In other words, the improved activity of Co-NDC catalysts can be attributed to the better accessibility of CO_2 to Co nanoparticles on the surface of Co-NDC, as well as the presence of mesopores in their structure. Furthermore, the correlation between catalytic activity and the degree of graphitization, determined from the D-to-G band intensity ratio (I_D/I_G) in the Raman spectra (Fig. 5a), indicates that the higher graphitization degree (and lower I_D/I_G value) observed for the CoNDC-600 catalyst is consistent

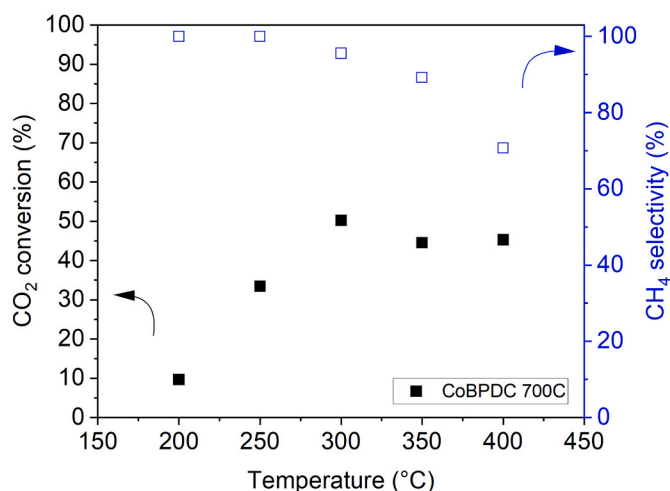


Fig. 9. CO_2 conversions and CH_4 selectivities for the catalytic reaction performed with the CoBPDC-700 catalyst.

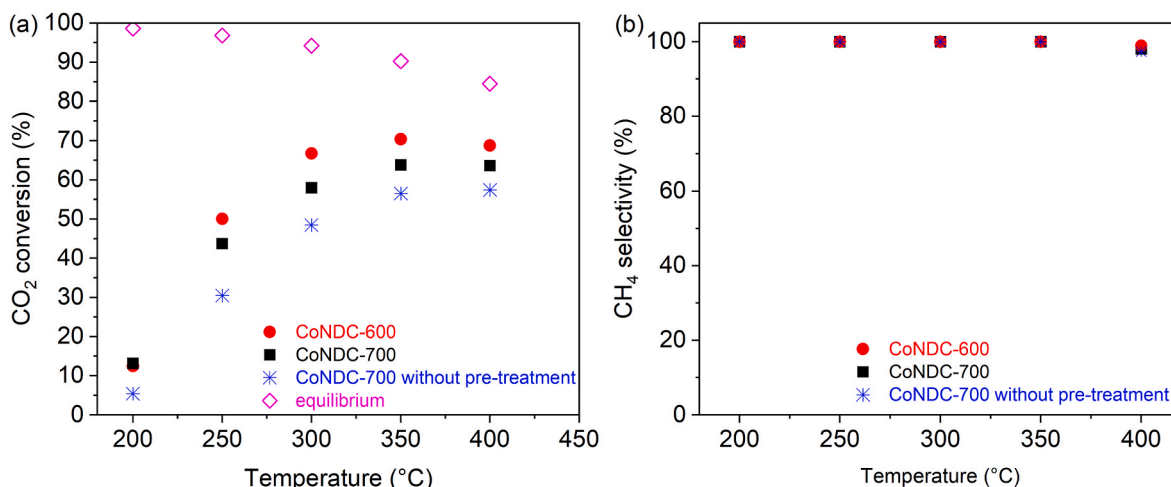


Fig. 8. CO_2 conversions (a) and CH_4 selectivities (b) for the catalytic reaction performed with CoNDC-700 and CoNDC-600 catalysts.

with its better catalytic performance. In contrast, the CoNDC-700 and CoBPDC-700 catalysts – which reached lower catalytic performance – showed higher I_D/I_G ratios (1.14 and 1.10, respectively) (Figs. 5a and 16S), which is characteristic of a lower degree of graphitization. This observation is consistent with the correlation between higher catalytic performance and a higher degree of graphitization reported by Gómez-Pérez et al. [65].

To study the surface basicity of the prepared catalysts, CO₂ temperature-programmed desorption (CO₂-TPD) analysis was conducted. As displayed in Fig. 25S, the peaks for weak, medium, and strong basic sites at 100–200, 200–450, and 450–700 °C, respectively, are revealed in CO₂-TPD profiles [23,27,66]. Compared to CoBPDC-700, the CoNDC-based samples have a higher adsorption capacity in the region of moderately strong basic sites in region 250–350 °C (Fig. 25S). After the deconvolution of the peaks, the numbers of basic sites were quantified and summarized in the Table 2. It is evident that CoNDC-600 catalyst exhibited the highest number of basic sites, particularly medium-strength sites. It has been reported that weak and medium basic sites facilitate the formation of surface carbonate or formate species, which can subsequently undergo hydrogenation on adjacent metallic cobalt sites towards CH₄, while CO₂ adsorbed on strong basic sites does not participate in the hydrogenation reaction tested at 200–400 °C [64, 67]. Thus, the improved catalytic activity observed for CoNDC catalysts with a higher density of medium-strength basic sites can be attributed to enhanced CO₂ adsorption and activation on the catalyst surface.

The stability of the CoNDC-600 catalyst was assessed by performing a 50 h catalytic reaction test at 300 °C. As illustrated in Fig. 10, no significant on-stream deactivation was observed. During the 50 h, the CO₂ conversion remained stable with an average value of 66 %, also maintaining full selectivity to methane.

The selectivity toward CH₄ could be related to the oxidation state and particle size of cobalt nanoparticles. It has been reported that CoO sites favor CO production via the RWGS reaction, whereas metallic Co sites primarily promote CH₄ production through CO₂ methanation. Although there is no exact consensus on the reaction pathway over cobalt-based catalysts, CO₂ hydrogenation on cobalt oxide is thought to follow a hydrogen-assisted pathway, in which the formate (HCOO*) intermediate adsorbed on CoO sites serves as the key species for CO formation. Importantly, such formate intermediates may be formed during CO₂ hydrogenation; however, on oxidized CoO sites they are more often associated with the RWGS pathway and CO desorption rather than full hydrogenation to CH₄. In contrast, CO₂ hydrogenation on metallic cobalt mainly proceeds via CO₂ dissociation into adsorbed CO species. Metallic cobalt sites also accelerate H₂ dissociation, facilitating the subsequent hydrogenation of adsorbed CO into CH₄ [8,11,68]. Furthermore, studies have shown that single-atom Co or very small Co nanoparticles (~1.6 nm), which are more susceptible to oxidation under CO₂ hydrogenation conditions, tend to favor the RWGS reaction, resulting in higher CO selectivity. Conversely, larger metallic Co nanoparticles (~3 nm) promote methanation, leading to higher CH₄ selectivity [63,69]. Based on reported literature and observed methane selectivity, it can be inferred that CoNDC-based catalysts, containing metallic (due to H₂ pre-reduction) Co nanoparticles larger than 3 nm,

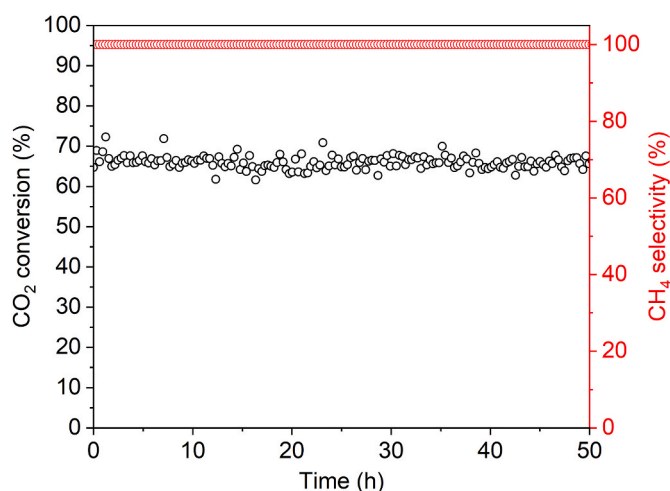


Fig. 10. Catalytic performance of the CoNDC-600 catalyst during 50 h of catalytic reaction at 300 °C.

favor methanation over the RWGS reaction. This behavior can be attributed to (i) the predominance of metallic Co sites that facilitate CO₂ dissociation and H₂ activation and (ii) the fast hydrogenation of surface intermediates towards CH₄ compared to CO desorption. It should be noted that the discussed reaction pathways are inferred from literature reports; further in-situ DRIFTS studies and theoretical investigations would be valuable for identifying the nature of active sites and reaction intermediates, as well as clarifying the reaction mechanism over these catalysts.

For a better insight into CoNDC-based catalyst performance, its activity in CO₂ methanation at 300 °C was compared with the activity of previously reported catalysts based on carbon- or silica-supported Co nanoparticles (Table 3). While the comparison is difficult due to the various conditions that are applied (cobalt loading, space velocity, pressure, and reagent ratios) in the different studies, CoNDC-based catalyst activity appears to be in line with or better than the performance obtained with other Co-based catalysts. Following the thorough literature survey, it can be concluded that the catalysts most similar to those that can be used for direct comparison are catalysts derived from ZIF MOFs. For example, the Co/C(L) and Co/C(67) catalysts containing about 39 wt% of cobalt provided lower CO₂ conversion and selectivity in the same reaction conditions (Table 3). A slightly higher content of cobalt may play a role in the increased catalytic activity of CoNDC-derived catalysts. When normalized by Co loading, CH₄ formation rate at 300 °C for CoNDC-600 catalyst ($21.1 \mu\text{molCH}_4 \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$) remains significantly higher than that of Co/C(L) ($14.1 \mu\text{molCH}_4 \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$) and Co/C(67) ($6.9 \mu\text{molCH}_4 \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$) catalysts. This improvement can be explained by the smaller size of Co nanoparticles contained in the CoNDC-derived catalyst compared to Co/C(L) and Co/C(67) catalysts [23]. It is worth mentioning that catalysts derived from ZIF MOFs contain nitrogen, which is considered as a component that increases Lewis basicity and positively contributes to the catalytic activity by promoting the adsorption of CO₂ [23,27,70]. Furthermore, as illustrated in Fig. 25S, basic sites in CoNDC-derived catalysts were detected by the CO₂-TPD method. As listed in Table 3, the Co/(0.01)PC-600 catalyst [26] exhibits higher conversion of CO₂ than the other catalysts but applying 3 MPa of pressure instead of 0.1 MPa here. Unfortunately, due to the difference in operating pressure and the lack of available data (for CH₄ formation rate calculation) in the referenced work, a rigorous comparison between the CoNDC and Co/(0.01)PC-600 catalysts is not possible [26]. This comparison demonstrates that CoNDC-600 achieved better performance than Co/(0.01)PC-600 catalyst at lower temperatures and even milder conditions.

Table 2

The number of basic sites for CO₂ adsorption.

Catalyst	The number of basic sites (mmol g^{-1}) ^a			
	Weak	Medium	Strong	Total
CoNDC 600	0.01	0.20	0.15	0.36
CoNDC 700	0.00	0.18	0.09	0.27
CoBPDC 700	0.03	0.12	0.07	0.22

^a The number of basic sites were calculated from deconvoluted CO₂-TPD profiles (Fig. 25S) using Gaussian peak fitting. Deconvoluted peaks centered at 100–200, 200–450, and 450–700 °C were assigned to weak, medium, and strong basic sites, respectively.

Table 3Catalytic performance comparison for CoNDC-600 and other reported catalysts in CO₂ methanation at 300 °C.

catalyst	Co loading [wt. %]	P [MPa]	Space velocity [cm ³ g _{cat} ⁻¹ h ⁻¹]	CO ₂ conversion [%] ^a	CH ₄ selectivity [%] ^a	CH ₄ formation rate [μmolCH ₄ g _{cat} ⁻¹ s ⁻¹]	Reference
Co/meso-SiO ₂	20	0.1	22000	43.5	78.7	9.3	[71]
Co/KIT	20	0.1	22000	51	98.9	13.8	[71]
Co/(0.01)PC-600	32.5	3.0	72000	80	99	n.a. ^b	[26]
Co/C derived from ZIF-67 (Co-5H ₂ /Ar)	48.2	0.1	45000	48.5	97.1	n.a. ^b	[27]
Co/GNPs	15	0.1	5850	50	100	5.6	[72]
Co/C (L)	39.1	0.1	12000	44	84	5.5	[23]
Co/C (67)	39.9	0.1	12000	33	56	2.7	[23]
CoNDC-700	45.9	0.1	12000	57	100	8.5	This work
CoNDC-600	46.5	0.1	12000	66	100	9.8	This work

^a CO₂ conversion and CH₄ selectivity values obtained from figure or table.^b Not available due to insufficient data for calculation.

3.3. Studies of the spent catalysts

After the catalytic reactions, the spent catalysts were analyzed to assess their stability and structural changes. SEM images (Fig. 11) reveal that the hierarchical morphology of the catalysts remains intact following CO₂ methanation.

STEM-EDS images of the spent catalysts are presented in Fig. 12. For the CoNDC-600 spent catalyst, the dispersion of Co nanoparticles appears homogeneous. The particle size determined from STEM images is 9 ± 2 nm (Figs. 26S–29S), which is slightly larger than that of the fresh catalyst (5.3 ± 1.8 nm in Fig. 4). Compared to the fresh CoNDC-600 catalyst (Fig. 3), the morphology of the spent catalyst also appears more densely packed, likely due to sintering and particle growth. In contrast, the spent CoNDC-700 catalyst exhibits a mixture of larger Co particles alongside smaller nanoparticles, in agreement with observations for the fresh CoNDC-700 catalyst. Based on STEM analysis, the Co nanoparticle size in the spent CoNDC-700 catalyst is 16 ± 9 nm (Figs. 26S, 27S and 29S).

Powder XRD patterns of the spent catalysts, shown in Fig. 13a, display diffraction peaks corresponding to metallic cobalt nanocrystals. Based on the Scherrer equation, the crystallite sizes are approximately 7 nm for CoNDC-600 and 14 nm for CoNDC-700, which aligns well with the Co particle sizes estimated from STEM images (Figs. 26S–29S). Compared to the fresh catalysts (Figs. 3, 4 and 10S), the Co nanocrystals in the spent catalysts are noticeably larger. Additionally, extra diffraction peaks are observed in the PXRD patterns, which correspond to the CoO crystalline phase. The presence of CoO suggests an oxidation of Co nanoparticles on the catalyst surface during the catalytic reaction.

The XPS analysis further confirms a high degree of surface oxidation (Figs. 13b–c and 30S). The Co 2p spectra (Fig. 13b–c) of the spent catalysts reveal a significant presence of Co²⁺ species. For the CoNDC-600 spent catalyst, only Co²⁺ species are detected, likely because small metallic Co nanoparticles can be easily oxidized by the water byproduct present in the reaction stream. In contrast, the CoNDC-700 spent catalyst exhibits contributions from both Co⁰ and Co²⁺ species in its XPS

spectrum. It is worth noting that the extensive surface oxidation of Co metallic nanoparticles on the catalyst surface has been reported by Lancelot et al. [73] and Munnik et al. [74]. Moreover, smaller nanoparticles tend to be more dynamic and are likely more susceptible to structural changes during reactions. These factors can significantly enhance the tendency of smaller cobalt nanoparticles to undergo oxidation. These findings were reported by Zhou et al. [63]. The oxidized surface species also have been detected in C 1s and O 1s XPS spectra of spent CoNDC-derived catalysts, specifically, in higher BE regions of spent CoNDC-600 XPS spectra (Fig. 30S).

In contrast to the observations for CoNDC-based samples, the analysis of the spent CoBPDC-700 catalyst (Figs. 31S–35S) indicated a lower tendency for surface oxidation of cobalt metallic nanoparticles during the methanation reaction. As shown in the PXRD pattern of the CoBPDC-700 spent catalyst (Fig. 33S), no CoO diffraction peaks were detected, and the Co crystallite size according to the Scherrer equation is 3.7 nm showing no significant increase of the nanocrystal size compared to fresh catalyst (Figs. 16S and 22S, Table 1S). This behavior could be attributed to the limited accessibility of the CO₂ substrate, resulting from the reduced content of cobalt nanoparticles on the surface of the microporous CoBPDC-700 catalyst (Figs. 18S and 20S) and their higher proportion embedded within the carbon matrix, where they are not accessible for surface reactions. Contrary to CoNDC-derived catalysts, the lower content of surface oxidized species in Co 2p (Fig. 34S) and C 1s (Fig. 35S) XPS spectra of spent CoBPDC-700 was observed hence supporting the fact that only a small population of cobalt is accessible for catalytic reaction.

Based on the analysis of the spent CoNDC-based catalysts, it can be concluded that both catalysts maintained good stability, as their morphology and Co nanoparticle dispersion remained nearly the same as in the fresh samples. Although, surface oxidation was evident, primarily indicated by the presence of the CoO crystalline phase in PXRD and oxidized cobalt species in XPS, no significant on-stream deactivation or change in selectivity toward CH₄ was observed. This behavior can be ascribed to the porous structure of CoNDC-derived nanocomposites.

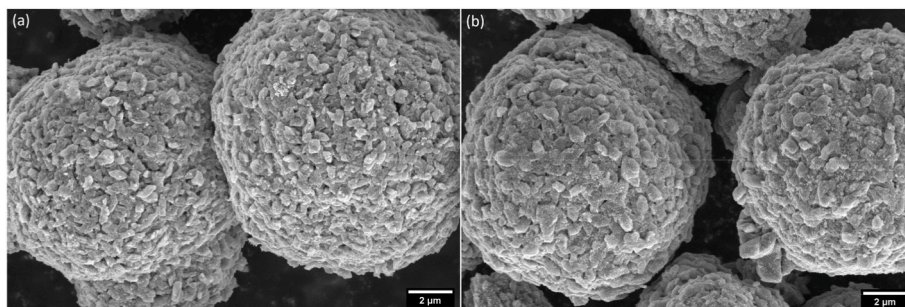


Fig. 11. SEM images of spent CoNDC-600 (a) and CoNDC-700 (b) catalysts.

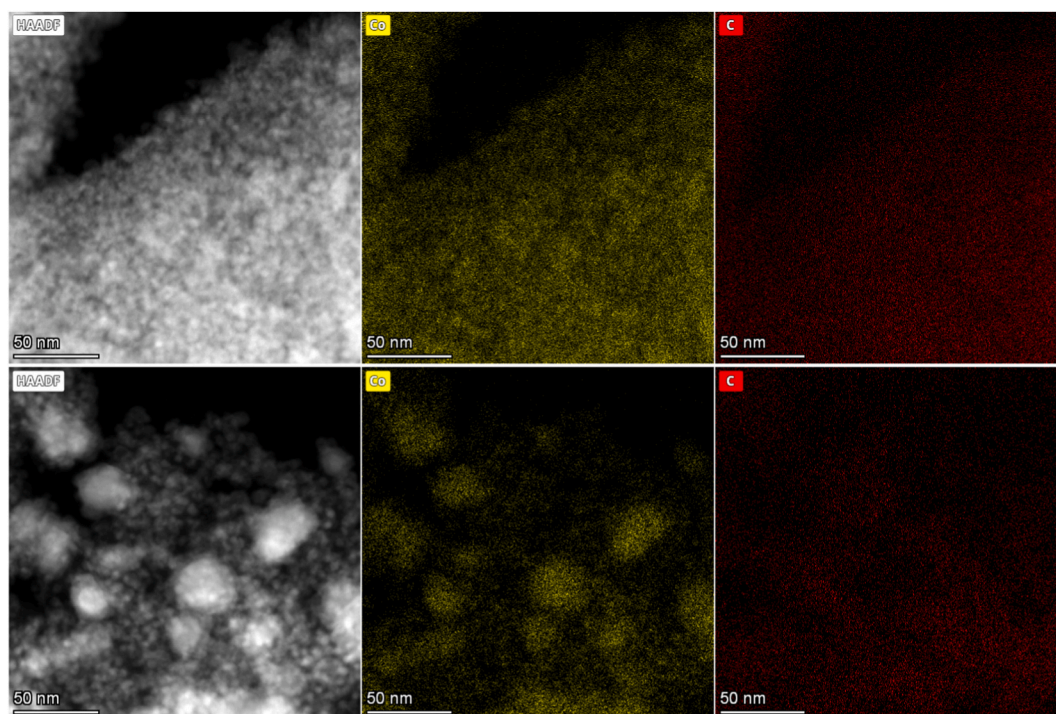


Fig. 12. STEM-EDS images of spent CoNDC-600 (upper row) and spent CoNDC-700 (bottom row) catalysts.

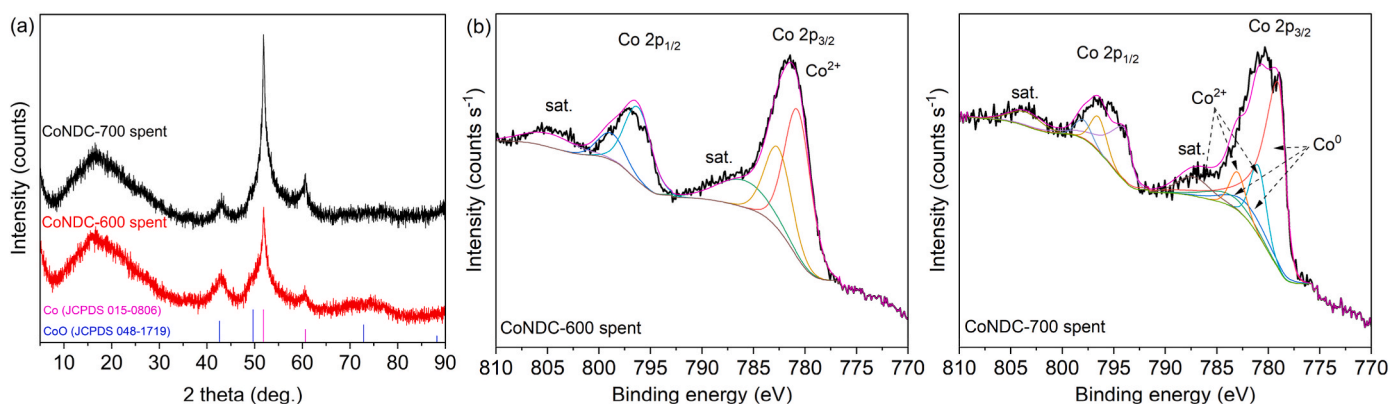


Fig. 13. Powder XRD patterns (a) and Co 2p XPS spectra (b) of spent catalysts.

Since XPS detects only surface species, we can conclude—based on the STEM-EDS and PXRD results—that small metallic Co nanoparticles remain present and accessible inside the pores and cavities of the hollow microspherical catalyst structure, thereby retaining their high catalytic activity.

4. Conclusion

A new CO₂ methanation catalyst with a hierarchically porous carbon-based structure and spherical architecture containing dispersed cobalt nanoparticles was developed. The preparation of this catalyst is based on the microwave-assisted synthesis of a cobalt metal-organic framework from cobalt(II) acetylacetonate and 2,6-naphthalene dicarboxylic acid in N,N-dimethylformamide. As demonstrated, MW irradiation provides fast heating of the reaction mixture, and CoNDC MOF material is obtained after 30 min. After the carbonization of CoNDC MOF at 600 and 700 °C, the unique morphology of nanocomposites featuring porous structure with cavity inside is revealed. The small size and homogeneous dispersion of Co nanoparticles in the carbon matrix

were evidenced by STEM-EDS microscopy and PXRD analysis. The CoNDC-600 and CoNDC-700 nanocomposite catalysts were tested for the CO₂ methanation reaction. It was found that CoNDC-derived catalysts exhibit high activity and full selectivity to CH₄. In our testing conditions, the CoNDC-600 catalyst achieved 70% conversion of CO₂ with 100% selectivity to CH₄ at 350 °C (corresponding to a specific methane production rate of 10.5 μmol_{CH₄} g_{cat}⁻¹ s⁻¹), while the CoNDC-700 reached 63% conversion (9.5 μmol_{CH₄} g_{cat}⁻¹ s⁻¹). This behavior is assigned to a beneficial effect caused by a better dispersion of small Co nanoparticles in the CoNDC-600 catalyst, confirmed by STEM-EDS and XRD analyses. Moreover, the highest number of basic sites according to CO₂ TPD was observed in the case of CoNDC-600 catalyst. Further comparison with platelet CoBPDC-700 nanocomposite or with other relevant Co-based carbon-based nanocomposites derived from MOF structures proved that CoNDC-based catalysts exhibit higher (or comparable) CO₂ methanation performance. The ongoing research into optimizing cobalt nanoparticles for CO₂ methanation addresses the pressing need for effective carbon capture and utilization strategies and opens pathways for innovative energy solutions that align with global

sustainability goals.

CRediT authorship contribution statement

David Skoda: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Plaifa Hongmanorom:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Barbora Hanulíková:** Writing – review & editing, Investigation. **Alžběta Dubravová:** Investigation, Data curation. **Martin Cvek:** Investigation, Data curation. **Iaroslav Doroshenko:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation. **Tomas Pokorný:** Investigation, Formal analysis, Data curation. **Jan Varada:** Investigation, Data curation. **Lucie Simoníková:** Investigation, Formal analysis. **Ivo Kuritka:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **Damien P. Debecker:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtchem.2026.103470>.

Data availability

The data that support the findings of this study are openly available in the Zenodo repository at <http://doi.org/10.5281/zenodo.18769372>.

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