

Article

Hydrogen Production from Formic Acid and Methanol in a Fluidized Bed Made Out of Diatomaceous-Earth-Based Catalysts with Fast Chromatographic Hydrogen Detection

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Abstract

From the sedimentary rock moler, a specific fraction of diatomaceous earth suitable for fluidized-bed applications was isolated. Three heterogeneous catalysts were prepared by wet impregnation: Cu@diatomaceous-earth, Co₃O₄@diatomaceous-earth, and NiO@diatomaceous-earth. The new materials were characterized by XRD, SEM, BET, and ICP-OES analyses, and their minimum fluidization velocities were experimentally determined. The catalytic performance of the fluidized beds was evaluated in the conversion of formic acid and methanol to hydrogen. Cu@DE exhibited the highest hydrogen production, reaching 94% during formic acid decomposition at 377 °C and 96% during methanol conversion at 400 °C. The use of NiO@DE bed for methanol conversion allows for a reduction in the conversion temperature with a slightly lower hydrogen efficiency, 92% at 332 °C. For the first time, a combined FTIR–GC–PDHID analytical approach was applied for comprehensive identification of the process products. A method enabling the analysis of infrared-active species using Fourier-transform infrared spectroscopy was developed, while infrared-inactive hydrogen was separated on a chromatographic column and quantified using a Pulsed Discharge Helium Ionization Detector. Furthermore, a rapid sequential hydrogen-analysis procedure was established, allowing evaluation at a frequency of 0.05 Hz. The calculated TOF and GHSV values confirm the competitive performance of the Cu@DE fluidized-bed catalyst relative to previously reported fluidized-bed and fixed-bed reactor systems.



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1. Introduction

Nowadays, more than 90% of chemical manufacturing processes rely on catalysts [1]. Many functional catalysts based on synthetic mesoporous silica materials, such as MCM-41, have been developed. However, the high cost of production and the negative environmental impact of their production still hinder the commercialization of these solutions [2]. Li et al.

demonstrated the potential to replicate these advanced materials using diatomaceous earth. Two hierarchically porous diatomite carriers were coated with Pd nanoparticles and used in the Suzuki reaction. The authors demonstrated that the macroporous structure of diatomites reduces dead volume in the reactor, which increases catalytic efficiency in both batch and continuous processes [2]. Wang et al. deposited TiO_2 nanoparticles onto diatomaceous earth by impregnation [3]. The authors attributed the permanent bond between nanoparticles and diatoms to the formation of Ti–O–Si bonds at the interface of the phases. Catalytic activity was confirmed by photocatalytic degradation of Rhodamine B. Rabie et al. synthesized a diatomite-supported CaO/MgO composite and used it in the transesterification process of used cooking oil into biodiesel, achieving a 96.5% yield [4]. It was found that the Ca–O–Si bond is the main factor responsible for the high stability of the catalyst and its tolerance to water [5]. Chen et al. developed a lithium metasilicate (Li_2SiO_3) catalyst from diatomaceous earth [6]. Thanks to the use of diatomaceous earth, it was also possible to convert KOH from a homogeneous to a heterogeneous catalyst by immobilizing it on a solid support and applying it in the palm-oil conversion process [7]. Nazhipkyzy et al. demonstrated the potential of diatomite as a catalyst carrier for the synthesis of carbon nanotubes [8]. The good optical, thermal, chemical and mechanical properties of diatomite-derived biomimetic materials make them attractive for applications in environmental remediation, energy storage, microwave absorption [9], and geopolymer production [10]. Diatomite deposits occur worldwide, and researchers believe that the oldest ones have not yet been discovered [11]. According to a report by the National Minerals Information Center, 830,000 tons of diatomite were processed in 2023 alone, mainly in the United States [12]. Despite its general availability and promising applications, diatomaceous earth has not yet been investigated in the processes of converting liquid organic hydrogen carriers (LOHCs) to hydrogen. Developing processes that enable on-demand green hydrogen production has become particularly important for achieving climate neutrality as soon as possible.

In accordance with the development of the LOHC concept, the processes of dehydrogenation of liquids such as benzene [13], methylcyclohexane [14], 18H-dibenzyltoluene [15], diphenyl [16], methylindole [17], formic acid [18], methanol [19], and ethanol [20] have been widely studied. Methanol contains 126.17 g H_2 per kg and can be directly obtained from syngas [21]. Hydrogen from methanol can be obtained by thermal decomposition, steam reforming, or partial oxidation [22]. The issue of the use of formic acid as a hydrogen carrier was presented, among others, in a review paper [23]. Formic acid contains 43.79 g H_2 per kg HCOOH . On an industrial scale, formic acid is mainly produced from CO and methanol; however, alternative routes have also been reported, including direct synthesis from CO_2 and H_2 [24]. The resulting formic acid can be directly used to obtain hydrogen in processes using catalysts based on precious metals, such as Pd, Pt, Ru, and Au [25,26]. In the catalytic conversion of methanol and formic acid, transition metals such as Nickel, Copper, and Cobalt are also widely used. Their lower cost and the possibility of catalyst regeneration make heterogeneous catalysis a particularly attractive option. For example, Faroldi et al. investigated the catalytic decomposition of formic acid using Ni, Cu, and Ni–Cu composite catalysts doped with selected alkali metals and supported on graphene-based materials. The best performance was obtained for the K-doped Ni–Cu catalyst [27]. Dilsad Dolunay Eslek Koyuncu et al. carried out formic acid conversion using Ni- and Co-based catalysts supported on the mesoporous silica support KIT-6, and reported higher catalytic activity for the nickel-containing catalyst [28]. Lytkina et al. studied the influence of support structure (Zirconium dioxide) and Ni/Cu metal ratio on hydrogen production by methanol steam reforming. They concluded that the best results were achieved with a Ni_{0.2}–Cu_{0.8}/amorphous ZrO_2 catalyst [29].

Although numerous catalytic systems have demonstrated promising hydrogen production efficiencies at the laboratory scale, the current state-of-the-art still faces significant challenges related to process scale-up and commercialization. In this context, fluidized-bed reactors offer an attractive alternative due to their excellent heat and mass transfer, scalability, and suitability for continuous operation, although studies on hydrogen production from liquid organic hydrogen carriers in catalytic fluidized-bed systems remain limited, leaving a significant gap between laboratory-scale catalyst development and industrially relevant process implementation.

Fluidized-bed solutions based on core-shell catalysts made out of cenospheres for hydrogen production from LOHCs have been proposed in [30,31]. The cenosphere support was essential for achieving the low particle density required for fluidization. However, the limited availability of cenospheres and the need for repeated coating cycles during catalyst preparation hinder the large-scale implementation and commercialization of this approach.

To accelerate the implementation of the hydrogen economy, scientists are also working on the development of analytical methods. These methods include the analysis of gases with high and low hydrogen concentrations. Analysis of gases with high hydrogen concentrations is important for the control of hydrogen purity. The analysis of impurity content is performed using Fourier-transform infrared spectroscopy (FTIR) and chromatographic methods equipped with TCD [32], FID [33], and PDHID [34] detectors. Chromatographic methods are also used to determine hydrogen at low concentrations. In such cases, researchers typically aim to develop methods that provide a low limit of detection [35]. Chromatographic methods are characterized by high accuracy; although when a rapid measurement is important for safety reasons, sensors are used that operate on the principle of changes in the physical or optical properties of materials upon exposure to hydrogen [36]. The sensors do not require initial gas separation, although the presence of other gases may falsify the main result.

The main hypothesis of this work was that low-density diatomaceous-earth-supported catalysts based on inexpensive transition metals can serve both as an effective catalytic system and as a fluidizable bed material for hydrogen production from formic acid and methanol. In parallel, an additional hypothesis was that the integration of FTIR spectroscopy with GC-PDHID analysis would enable rapid and comprehensive monitoring of reaction products and catalyst performance under fluidized-bed conditions. Therefore, to match the sequential FTIR acquisition of gas-mixture spectra, a method for rapid chromatographic hydrogen detection at a frequency of 0.05 Hz was developed and validated.

Accordingly, the specific objectives of this work were: (i) to evaluate the applicability of diatomaceous earth as a low-cost, low-density catalyst support for fluidized-bed hydrogen production from methanol and formic acid, (ii) to investigate the performance of Cu-, Ni-, and Co-based catalytic systems, and (iii) to develop and validate a combined FTIR-GC-PDHID analytical approach enabling hydrogen detection with a chromatographic acquisition frequency of 0.05 Hz. To the best of the authors' knowledge, this is the first study employing diatomaceous-earth-based catalyst particles for hydrogen production from liquid organic hydrogen carriers in a catalytic fluidized-bed reactor.

2. Experimental Section

2.1. Materials

The following reagents were used for the production of catalysts:

- (I) The sedimentary rock "Moler" obtained from the northwestern coast of Denmark and now located on the islands of Fur, Mors and Nordsalling [37], which consists of 66 wt.% diatomaceous carapace and 33 wt.% smectite clay commercially sold under the name "Loose Red sorbent" from B2B Partner (Ostrava, Czech Republic);

- (II) Citric acid monohydrate pure, with a minimum purity of 99.0%, from Warchem (Warsaw, Poland);
- (III) Cobalt (II) chloride hexahydrate pure, with a minimum purity of 98.0%, from Warchem (Warsaw, Poland);
- (IV) Nickel (II) chloride hexahydrate pure, with a minimum purity of 97.0%, from Chempur (Piekary Śląskie, Poland);
- (V) Copper chloride dihydrate pure, with a minimum purity of 99.0%, from Chempur (Piekary Śląskie, Poland).

For the hydrogen-production tests in the catalytic fluidized bed, the following liquid hydrogen carriers were used:

- (I) Formic acid with a minimum purity of 99%, purchased from Acros Organics (Geel, Belgium).
- (II) Methanol with a minimum purity of 99.8%, supplied by Sigma-Aldrich (St. Louis, MO, USA).

2.2. Catalyst Preparation

The diatomite was mechanically milled and subjected to wet sieving on sieves with nominal mesh sizes ranging from 50 to 125 μm . Wet separation prevents agglomeration of clay-based particles by weakening the interparticle binding forces [38]. During the mechanical milling process, nanosized fragments of the material were generated, which adhered to the larger grains (Figure 1a). The removal of these cohesive fines and the preparation of clean, dust-free carrier particles (Figure 1b) are important for eliminating fluidization disturbances and minimizing catalyst losses during the process. After the wet separation, the material was dried at 150 $^{\circ}\text{C}$ for 8 h. Three precursor solutions for the catalysts were prepared by dissolving citric acid and the respective cobalt, nickel, and copper salts in distilled water. The mass of each metal salt was adjusted so that the final catalyst contained 5 wt.% metal. Citric acid was added in a molar excess of 1.25 relative to the number of moles of the metal salt. Due to the low pore volume of DE (ca. 0.02 cm^3/g), the wet impregnation method was used in the catalyst preparation process, where 100 cm^3 of precursor solution was added to 70 g of diatomaceous earth support. The precursor solution was carefully and uniformly distributed over the diatomaceous earth support and manually mixed with a glass rod. Due to the high sorption capacity of the diatomaceous earth, mechanical stirring was not feasible, as the precursor solution was rapidly absorbed by the support. The prepared material was left at room temperature for 2 h before drying. The volume of the applied solution was approximately 70 times higher than the total pore volume of the support. The impregnated materials were dried at 150 $^{\circ}\text{C}$ for 120 min and subsequently calcined in air in a muffle furnace at 800 $^{\circ}\text{C}$ for 90 min.

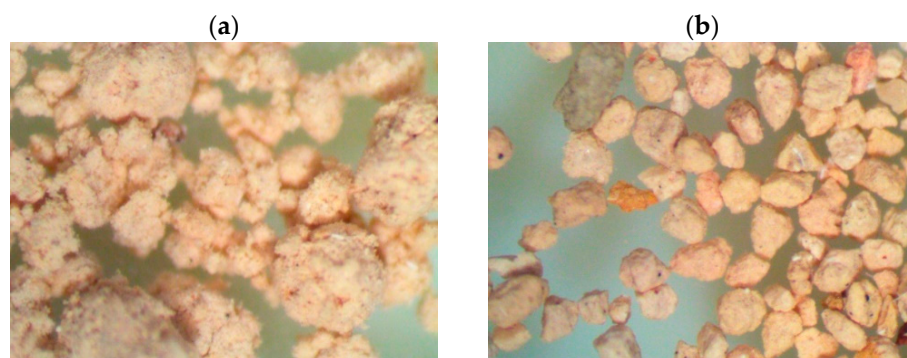


Figure 1. Optical microscope images of the diatomite particle fraction obtained after sieving to a nominal particle size of 0.15–0.25 mm: (a) without wet purification, (b) after wet purification.

The obtained metal-oxide–diatomite composite materials were reduced in situ in a stream of 0.4 L/min N_2 + HCOOH vapor with a formic acid concentration of approximately 16,000 ppm at 450 °C for 120 min.

The material thus prepared was used in catalytic tests. The catalysts after the processes of formic acid and methanol conversion were characterized using XRD, SEM, BET, and ICP-OES techniques. To minimize possible oxidation, samples were placed in 2 mL micro-centrifuge tubes, transferred to a desiccator, and subjected to analysis as quickly as possible.

2.3. Fluidized Bed Lab-Scale Setup

The experimental setup for the catalytic degradation of formic acid or methanol in a fluidized-bed technology is shown in Figure 2. A tube with an internal diameter of 34 mm and a height of 400 mm was used as the fluidized-bed reactor. The tube was made of borosilicate glass and equipped with the glass frit with G0 porosity, which served as both the gas distributor and the support plate. In each experiment, 40 g of catalyst with a particle size of 50–125 μm was introduced into the reactor. The reactor was mounted on a three-neck round-bottom flask. A pressure sensor was placed in one of the side necks and was used to determine the minimum fluidization velocity of the new catalysts. The second side neck was used for dosing the fluidizing gas. The fluidizing gas, a gaseous mixture of formic acid or methanol in nitrogen, was produced by passing a nitrogen stream (0.4 L/min) through a saturator (bubbler) containing either HCOOH or CH_3OH , depending on the experiment. The saturator was placed in a water bath whose temperature was controlled using a chiller (Steinberg, Essen, Germany) so that the temperature inside the bubbler was maintained at 2.5–3 °C.

For safety reasons, and to adjust the concentrations of hydrogen and other gases to the analytical ranges of the detectors, the gases leaving the reactor were diluted with an additional nitrogen stream before being introduced into the analytical block. The dilution streams were 10 L/min and 12 L/min for formic acid and methanol, respectively. The analytical block consisted of a series-connected FTIR spectrometer with a heated gas cell and a gas chromatograph equipped with a sampling loop, a chromatographic column separating hydrogen from the remaining gases, and a Pulsed Discharge Helium Ionization Detector (PDHID). The FTIR spectra obtained during the analysis were subsequently processed using a program written in MATLAB R2021a (MathWorks, Natick, MA, USA), which enabled the conversion of signals into concentration values expressed in ppm. The acquired data were used to determine the degree of compound conversion and to perform an elemental mass balance, allowing for the quantification of the carbon deposit formed during methanol catalytic conversion. Two complementary analytical methods were used to analyse the products of the catalytic conversion of liquid organic hydrogen carriers. The infrared-active products were quantified by recording IR spectra of the gases leaving the reactor. A portable FTIR spectrometer (atmosFIR, Protea) was employed. FTIR spectra were collected at a frequency of 0.05 Hz over the wavenumber range 900–5000 cm^{-1} with a high spectral resolution of 1 cm^{-1} . The gas cell, with a volume of approximately 300 cm^3 , was maintained at 180 °C to prevent condensation of any components. Infrared-inactive hydrogen was analysed using a PDHID detector after separating H_2 from other gases in a gas chromatographic system. The chromatographic parameters are summarised in Table 1. Two Mole Sieve 5A columns (each 4.5 m in length) connected in series were used. A 250 μL gas sample, introduced via a sampling loop, entered the columns in a nitrogen stream at a flow rate of 15 mL/min. A valve located between the columns enabled reversal of the flow direction in column 1. To reverse the gas flow and purge the retained non-hydrogen components from the first column, an additional carrier-gas source at 9 psi was used.

In this study, a newly applied backflush method enabled rapid (0.05 Hz), sequential hydrogen analyses at a frequency complementary to the FTIR spectral acquisition. This fast hydrogen analysis method, integrated with FTIR measurements, allowed precise evaluation of the process carried out between 450 and 150 °C under a controlled temperature decrease of 3 °C/min. The reactor temperature was controlled using a LUMEL RE72 controller (Poland) coupled with an RP7 power controller (Lumel, Zielona Góra, Poland). Data acquisition and temperature control were performed using MATLAB.

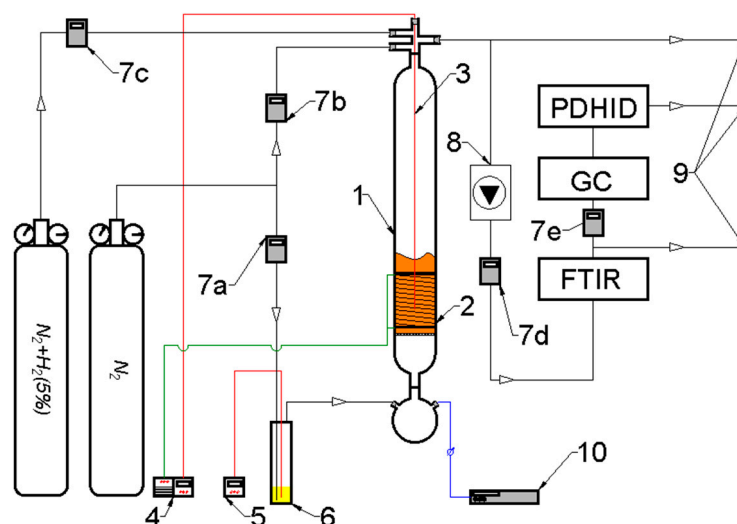


Figure 2. Lab-scale apparatus for studying the catalytic degradation of liquid hydrogen carriers in the fluidized bed system: 1—fluidized bed reactor, 2—heating mantle, 3—thermocouple, 4—temperature regulator, 5—temperature gauge 6—saturator with liquid hydrocarbon, 7a–7e—mass flow regulators, 8—gas pump, 9—ventilation, 10—pressure gauge.

Table 1. Parameters of chromatographic analysis.

Parameter	Specification
GC model	GC 8890
Injector	Gas loop
Injection volume	250 µL
Column 1	Molsieve 5 Å, 4.5 m × 0.32 mm × 1.5 µm
Column 2	Molsieve 5 Å, 4.5 m × 0.32 mm × 1.5 µm
Temperature program	Constant temperature 90 °C
Carrier gas	He, constant flow, 15 mL/min
Auxiliary gas	He, constant pressure, 9 psi
Detector type	PDHID
Detector temperature, °C	100
Method	Sequence consisting of 16 analyses
Target (retention times)	Hydrogen
Total run time	5.33 min

3. Results and Discussion

3.1. Structural Analysis of Catalysts

XRD patterns of the diatomite and the catalysts after the catalytical reactions are presented in Figure 3. The broad, diffuse halo band centred at $2\theta \approx 20\text{--}25^\circ$ indicates that amorphous silica is the dominant component of the diatomite [10] (Figure 3, DE). The presence of a crystalline quartz impurity is confirmed by a distinct reflection at $2\theta = 26.6^\circ$, corresponding to the (101) crystallographic plane. These features are also visible in the XRD patterns of the cobalt-, nickel-, and copper-based catalysts.

For the cobalt-based catalyst ($\text{Co}_3\text{O}_4@\text{DE}$), a cubic oxide phase ($\alpha = \beta = \gamma = 90^\circ$) with a lattice parameter of 0.838 nm ($a = b = c$) was identified. A characteristic reflection of cobalt oxide was observed at $2\theta = 35.4^\circ$, corresponding to the (311) crystallographic plane. The presence of a single reflection suggests that the sample is either monocrystalline or that the remaining reflections—which, for a lattice parameter of 0.832 nm, would appear at $2\theta = 18.3^\circ, 30.1^\circ, 43.1^\circ, 57.0^\circ$, and 62.1° —are masked due to their low intensity.

For the $\text{NiO}@\text{DE}$ catalyst, diffraction peaks characteristic of the oxide phase were identified at 2θ values (with corresponding hkl planes) of 37.3° (111), 43.3° (200), 62.9° (220), 76.4° (311), and 79.2° (222). The lattice parameters $a = b = c = 0.418$ nm together with $\alpha = \beta = \gamma = 90^\circ$ confirm the cubic crystal structure.

For the copper-based catalyst ($\text{Cu}@\text{DE}$), a metallic phase with a cubic structure ($\alpha = \beta = \gamma = 90^\circ$) and a lattice parameter of 0.362 nm ($a = b = c$) was identified. Characteristic diffraction peaks were recorded at 2θ values of $43.3^\circ, 50.4^\circ$, and 74.1° , corresponding to the (111), (200), and (220) crystallographic planes, respectively. The XRD pattern also displays peaks at 35.5° and 36.5° , which were already present in the sample before the in situ reduction and were attributed to plancheite—a copper silicate mineral with the structure $\text{Cu}_8(\text{Si}_4\text{O}_{11})_2(\text{OH})_4 \cdot \text{H}_2\text{O}$.

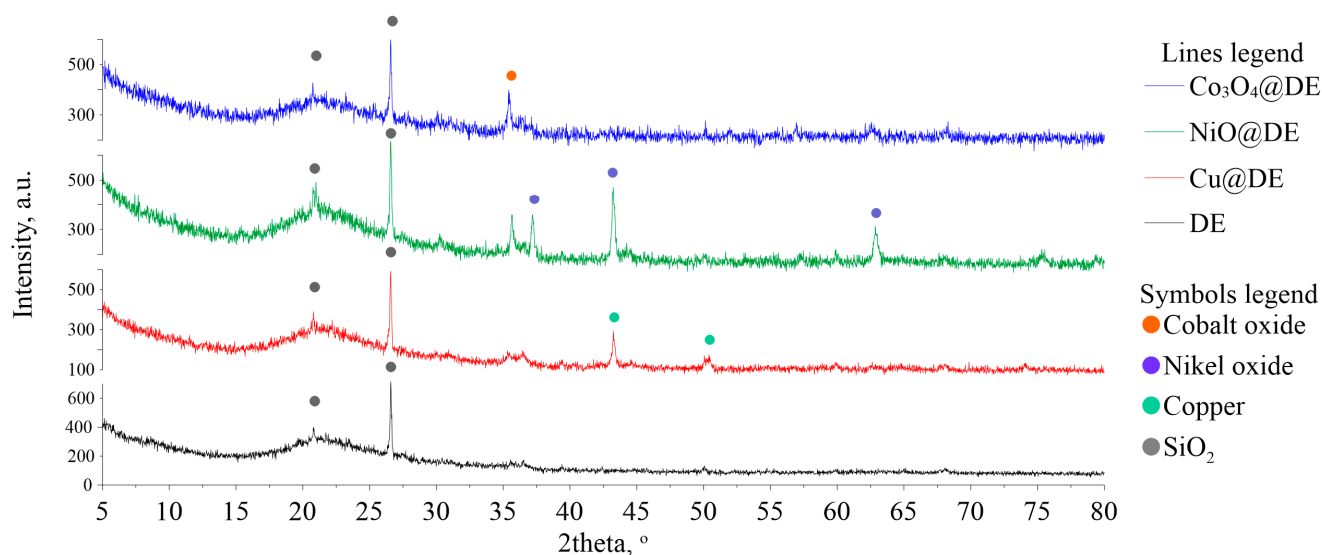


Figure 3. XRD patterns of the $\text{Co}_3\text{O}_4@\text{DE}$, $\text{NiO}@\text{DE}$, $\text{Cu}@\text{DE}$ and the DE support.

SEM images of the synthesized catalysts, taken at various magnifications, are presented in Figure 4. The images at $\times 500$ magnification reveal that the grains possess irregular edges. Individual particles larger than the nominal mesh size used during sieving can be observed. The absence of fine dust in the images indicates that no particle erosion occurred during the in situ reduction of the materials in the fluidized bed. The images taken at $\times 2500$ – 5000 magnification confirm the porous structure of the materials. The grains are composed of tightly bonded fragments of diatom frustules. This strong cohesion of the material results from post-depositional silica diagenesis [11]. In some regions, less degraded fragments of diatom frustules with the characteristic symmetry typical of diatomaceous organisms can be observed. For one such fragment present on the $\text{Cu}@\text{DE}$ catalyst, an image at $\times 20,000$ magnification was taken. The evenly spaced pores, which enabled gas exchange in the living organism, have diameters of approximately $1.5 \mu\text{m}$ ($\text{Cu}@\text{DE}$, $\times 20,000$). In addition to centric diatoms exhibiting radial symmetry, elongated diatoms are also visible on the catalysts. An image of such frustules, characterized by axial symmetry, is shown at $\times 160,000$ magnification for the $\text{Co}_3\text{O}_4@\text{DE}$ catalyst. The recorded cluster consists of rod-like structures with lengths of approximately 400 nm.

In areas where the grains are composed of heavily degraded frustule fragments, where no symmetry is preserved, the tightly interlocked structures appear to impart additional porosity to the material (NiO@DE, $\times 20,000$).

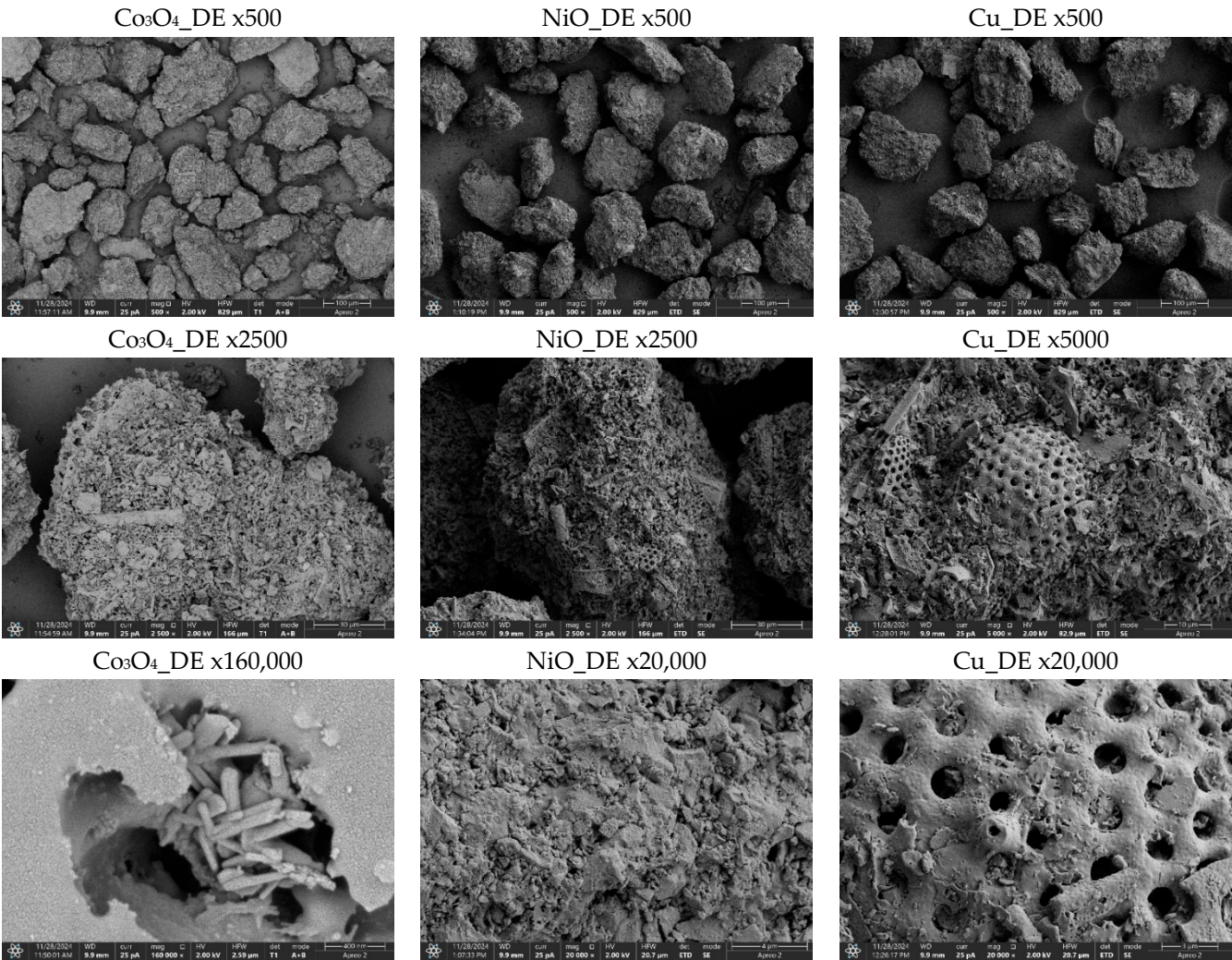


Figure 4. SEM images of the Co₃O₄@DE, NiO@DE and Cu@DE catalysts at various magnifications.

3.2. BET Analysis

The BET analysis was performed on the ASAP 2020 apparatus (Micromeritics, Norcross, GA, USA). The samples were degassed according to a temperature program consisting of heating at 10 °C/min up to 250 °C and soaking for 12 h under vacuum. Nitrogen adsorption measurements were carried out at −195.8 °C. Based on the nitrogen adsorption–desorption isotherms, the specific surface area was calculated using the BET method, and the pore volume and the average pore diameter were determined using the BJH method. Results are listed in Table 2.

Table 2. Porosity characterization of the materials.

Material	BET (m ² /g)	Vpore (cm ³ /g)	Pore Size BJH (nm)
DE	8.15	0.0196	11.4
Co ₃ O ₄ @DE	4.57	0.0099	11.0
NiO@DE	7.22	0.0184	12.4
Cu@DE	5.29	0.0127	11.4

The DE material itself is characterized by a specific surface area of $8.15 \text{ m}^2/\text{g}$ and a mesopore volume of $0.0196 \text{ cm}^3/\text{g}$, with an average pore diameter of 11.4 nm . Since the total pore volume is $0.0200 \text{ cm}^3 \text{ g}^{-1}$, approximately 98 vol.% of the pore volume is associated with mesopores, confirming the predominantly mesoporous character of the support. The introduction of catalytic phases on the DE carrier reduces the BET specific surface area to $4.57 \text{ m}^2/\text{g}$ for $\text{Co}_3\text{O}_4@\text{DE}$. This is because the metal/metal-oxide phases themselves have a lower specific surface area than the carrier and partially block the existing DE pores. Co_3O_4 forms the largest agglomerates, which leads to a two-fold decrease in pore volume. Nickel, on the other hand, exhibits the highest dispersion, thus maintaining parameters close to those of the carrier. The average BJH pore diameters indicate that surface modification with metals does not change the pore geometry; it only affects their accessibility. The regular shape of the nitrogen adsorption isotherms indicates that degassing at 250°C does not lead to changes in the porous framework, and that the $\text{Co}_3\text{O}_4@\text{DE}$, $\text{Cu}@\text{DE}$, and $\text{NiO}@\text{DE}$ materials maintain their thermal stability under the applied treatment conditions.

Although the BET values of the catalysts decrease compared with those of the parent diatomaceous earth, it should be emphasized that BET values are expressed per gram of the composite material. Thus, when compared with the bulk forms of Cu, NiO, and Co_3O_4 , deposition of these phases onto DE increases the accessible active surface area per unit mass of metal/oxide. It should also be noted that, under fluidized-bed operating conditions, catalytic performance is strongly influenced by mass-transfer phenomena. The predominantly mesoporous structure of the DE support facilitates reactant transport to the active sites, whereas intensive particle mixing in the fluidized bed promotes efficient gas–solid contact and reduces external diffusion limitations. Therefore, the relatively low BET surface area does not necessarily translate into reduced catalytic activity.

3.3. ICP-OES Analysis

A 0.5 g portion of the homogenized catalytic material was weighed into the pressure-vessel body, followed by the addition of 2 mL of concentrated HCl and 6 mL of concentrated $\text{HNO}_3(\text{V})$. The vessel was then placed in the rotor of the microwave digestion system. Digestion was performed in an Anton Paar Multiwave 5000 microwave digester using the 41HVT56 rotor (Anton Paar GmbH, Graz, Austria), according to a program consisting of heating to 175°C within $5 \text{ min } 30 \text{ s}$ and holding at 175°C for 10 min at 800 W , with a maximum pressure limit of 40 bar [39]. After digestion, the solutions were quantitatively transferred to 25 cm^3 volumetric flasks, diluted to volume with distilled water, and analysed by ICP-OES. The procedure was carried out separately for each of the three catalytic materials: $\text{NiO}@\text{DE}$, $\text{Cu}@\text{DE}$ and $\text{Co}_3\text{O}_4@\text{DE}$. The ICP-OES results showed that $4.2 \text{ wt.}\%$ Ni, $2.1 \text{ wt.}\%$ Cu and $3.6 \text{ wt.}\%$ Co were deposited on the corresponding materials, compared with the nominal loading of $5 \text{ wt.}\%$. The lower-than-nominal metal loading may be attributed to the limited penetration of the precursor solution into the low-pore-volume support and partial deposition of the precursor on the external surface of the diatomaceous earth particles.

3.4. Evaluation of Fluidization Properties of Diatomite-Supported Catalyst

In a fluidized bed reactor designed for the synthesis of hydrogen from formic acid and methanol (Figure 2), the ability of the new catalytic materials $\text{NiO}@\text{DE}$, $\text{Cu}@\text{DE}$, and $\text{Co}_3\text{O}_4@\text{DE}$ to undergo fluidization was investigated (Figure 5). About 40 g of $\text{NiO}@\text{DE}$ was placed in the reactor. In one of the side necks of the round-bottom flask, a pressure drop sensor was installed. The flow through the 7a flowmeter was controlled by gradually increasing the flow of the fluidizing gas (N_2) while registering the pressure drops below the sieve bottom that changed with the setpoint. The procedure was repeated for $\text{Cu}@\text{DE}$ and

Co₃O₄@DE materials. To eliminate the influence of the spatial properties of the measuring system, the pressure drop in the empty reactor was also measured. The measurement results for the catalytic materials, corrected to eliminate the influence of the reactor geometry, are presented as fluidization curves in Figure 5. To increase the versatility of the measurements, the volumetric flow rate of the fluidizing gas was divided by the cross-sectional area of the reactor and expressed as the superficial gas velocity, i.e., the gas flow rate per empty cross-section of the apparatus. Taking into account that a constant pressure drop despite increasing gas velocity indicates that the fluidized state has been achieved, the minimum fluidization velocities ($U_{mf,i}$) were determined, yielding values in the range of 0.74–0.86 cm/s.

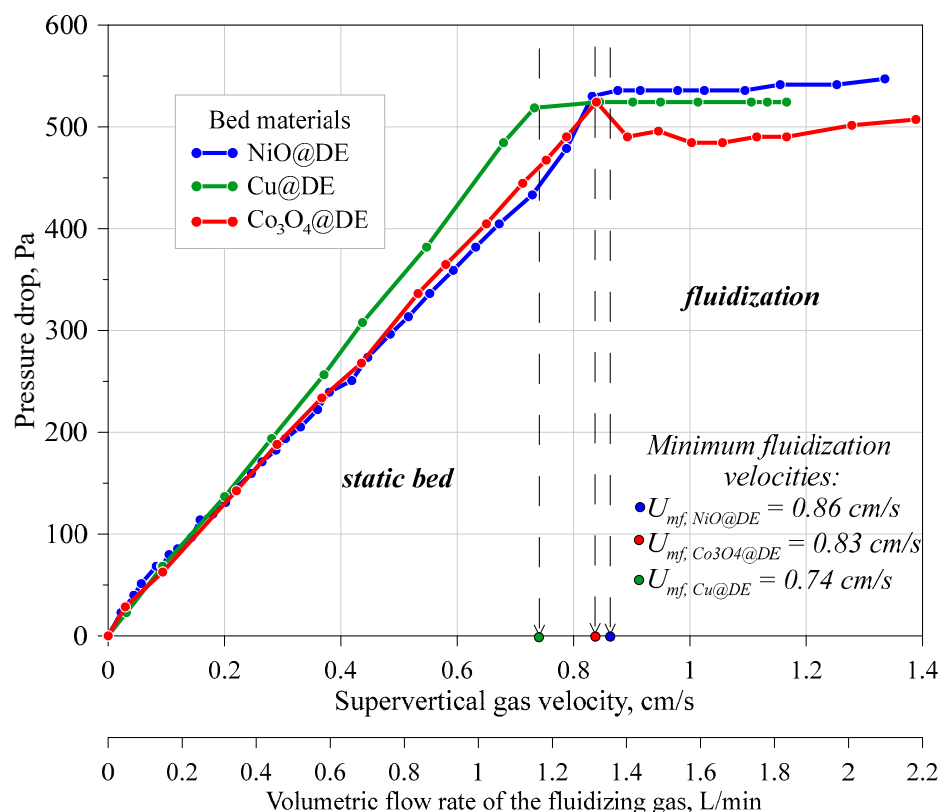


Figure 5. Fluidization curves for the NiO@DE, Cu@DE, and Co₃O₄@DE catalysts.

In addition to the experimentally determined minimum fluidization velocity ($U_{mf} = 0.74\text{--}0.86\text{ cm s}^{-1}$), the bulk density of the diatomaceous earth particles was measured according to PN-EN ISO 2811-1 [40] using a 100 cm³ aluminum pycnometer, yielding a value of 0.512 g cm^{−3}. After accounting for the density increase associated with the deposition of the active phase and assuming a bed porosity of 40 vol.%, the apparent (hydrodynamic) particle density was estimated to be approximately 0.896 g cm^{−3}. Using the Ergun equation, it was determined that, for the estimated particle density and the experimentally measured U_{mf} values, the bed voidage at minimum fluidization (ϵ_{mf}) is approximately 0.43 (Appendix A). This value provides a physically consistent description of the transition from the packed-bed to the fluidized state. The Ergun equation together with the calculated ϵ_{mf} was subsequently used to estimate the minimum fluidization velocity over the investigated temperature range. As the process temperature increased, U_{mf} decreased, reaching a value approximately two times lower at 500 °C than under ambient conditions (Table 3). Furthermore, particle terminal velocities (U_t) were calculated and found to be approximately 50 times greater than U_{mf} throughout the investigated temperature range. This demonstrates that fluidization can be safely conducted over a

wide range of gas flow rates without significant particle entrainment. To assess the Geldart classification of the material, the minimum bubbling velocity (U_{mb}) was also calculated. Since the condition $U_{mb}/U_{mf} > 1$ was satisfied, the material was classified as a Geldart Group A powder. This classification is consistent with the relatively low particle density and the observed fluidization behavior. As the process is conducted over the temperature range of 150–500 °C under a constant volumetric gas flow rate, the superficial-gas-velocity-to-minimum-fluidization-velocity ratio (U_0/U_{mf}) was determined to assess the fluidization regime. The ratio increased from 1.61 to 4.62, demonstrating that the degree of fluidization intensifies with increasing temperature.

Table 3. Characteristic velocities of the fluidization of DE catalysts (U_{mf} —minimum fluidisation velocity, U_{mb} —minimum bubbling velocity, U_t —terminal velocity, U_0 —experimental velocity).

Temp. °C	U_{mf} cm/s	U_{mb} , cm/s	U_t , cm/s	U_0 cm/s	U_t/U_{mf}	U_0/U_{mf}	U_{mb}/U_{mf}	$U_{mb}/U_{mf} > 1$	Geldart's Group
20	0.86	1.47	39.2	0.73	45.58	0.85	1.70	true	A
150	0.66	1.39	32.9	1.06	49.84	1.61	2.10	true	A
300	0.53	1.32	27.6	1.43	52.07	2.69	2.50	true	A
500	0.42	1.25	22.9	1.94	54.52	4.62	2.98	true	A

3.5. Chemical Products of the Catalytic Degradation Process in a Fluidized Bed

The primary data of the catalytic degradation of organic compounds in a fluidized bed included a set of FTIR spectra of the registered products and a set of chromatograms. The high resolution of the recorded FTIR spectra allowed for their analysis with particular attention to the details of the absorbance bands. Examples of gaseous spectra of process products recorded during the decomposition of formic acid on the catalyst NiO@DE and the decomposition of methanol on a bed formed from Cu@DE grains are shown in Figure 6 (black graphs). To illustrate, spectra recorded in processes carried out at intermediate temperatures were selected to capture as many reactants as possible, including raw materials, intermediates and products of complete decomposition. In the process carried out with formic acid as a raw material (Figure 6a), the spectra indicated increased absorbance values in the wavenumber ranges of 980–1260, 1700–1833, 2050–2400, 2800–3050, and 3450–3750 cm^{-1} . The structure of formic acid induces four of these absorbance bands. In the fingerprint region, below 1500 cm^{-1} , the band maxima at 1085, 1106 and 1122 cm^{-1} are the result of stretching vibrations of single C–O bonds and the bending vibrations of O–H groups. The double bond of the C=O aldehyde group causes an increase in absorbance in the range of 1700–1833 cm^{-1} . The C–H bond results in an absorbance signal in the range of 2800–3050 cm^{-1} . The non-gaseous OH group absorbs radiation in the last of the recorded wavenumber ranges of 3450–3750 cm^{-1} . The absorption band in the range of 2050–2400 cm^{-1} is mainly the result of the presence of CO and CO₂ in the gas mixture [41]; the C–O bond in formic acid also delicately marks its presence here, raising the absorbance lines resulting from CO (Figure 6b). Using the least-squares optimization method (appendix [42]), the reference spectra were given appropriate multipliers so that after they were added together, the recorded spectrum could be reproduced with the highest possible accuracy. The calculated multipliers allowed assignment of the values of concentrations in the mixture to individual components. The multiplier-corrected reference spectra for the deconvolution of the spectrum selected in Figure 6a are shown in Figure 6b, and their sum, shown in the blue graph in Figure 6a, well reflects the experimental/deconvoluted spectrum. In the spectra recorded when the raw material was methanol (Figure 6c), the shape of the absorption bands was characteristic in the ranges of 950–1550 cm^{-1} and 2780–3200 cm^{-1} . In the example spectrum shown, the dominant surface of the bands in these ranges is caused by the transition product dimethyl ether (DME), which gives signals

from the ethereal stretching vibrations of C-O-C and C-H in the wavenumber ranges of lower and higher values, respectively (Figure 6d). As a result of the deconvolution of this spectrum, CO₂, CO, methane, and trace amounts of methanol were detected in the mixture in addition to DME. The sum of the component spectra reconstructs the recorded spectrum well, proving the correctness of the applied infrared analysis methodology (Figure 6a,c).

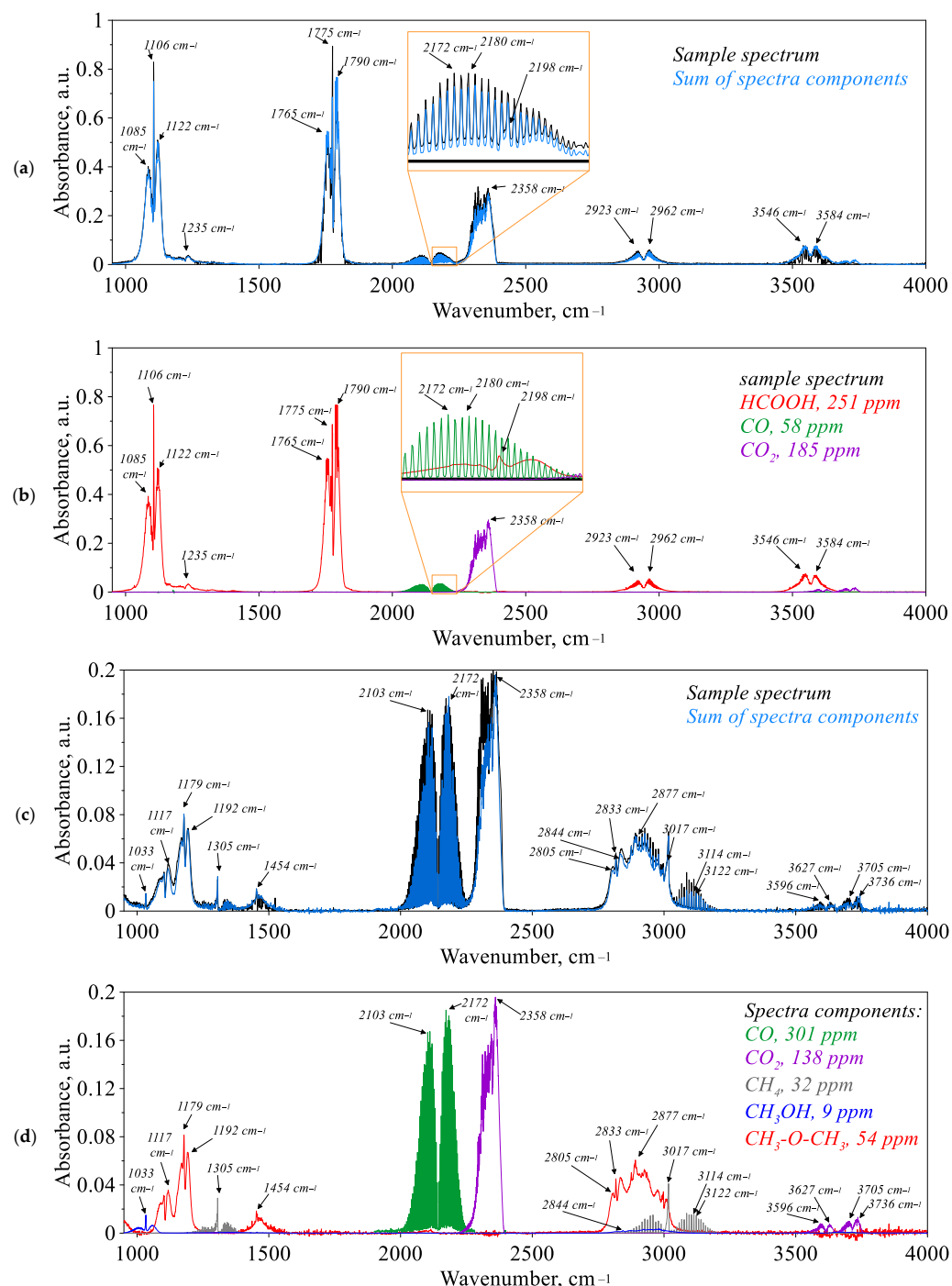


Figure 6. FTIR spectral analysis. (a) Comparison of the spectrum recorded during formic acid decomposition over the NiO@DE catalyst with the spectrum reconstructed from the component spectra. (b) Component spectra obtained from the deconvolution of the spectrum shown in part A. (c) Comparison of the spectrum recorded during methanol decomposition over the Cu@DE catalyst with the spectrum reconstructed from the component spectra. (d) Component spectra obtained from the deconvolution of the spectrum shown in part C.

Example chromatogram of hydrogen peaks recorded during the decomposition of HCOOH in a fluidized bed of $\text{Co}_3\text{O}_4\text{@DE}$, in the temperature range of 400–450 °C, is shown in Figure 7a as the blue curve. According to the adopted methodology, the chromatogram consists of 16 successive, well-resolved hydrogen peaks. Each analysis in the sequence lasts 20 s, of which 7.8 s is performed in the mode of constant helium flow through columns 1 and 2, and the remaining 12.2 s in the backflush mode at constant pressure. The time-dependent position of the valve responsible for switching the gas flow direction is shown in Figure 7a as the green curve. The 0 and 1 positions of the ten-port valve are illustrated in Figure 7b. In position 0: (I) the gas sample flows freely through the sample loop; (II) the backflush gas at 9 psi flows through column 1; and (III) the carrier gas at 15 mL/min flows through column 2 to the detector. In position 1: (I) the helium carrier gas flows through the sample loop, directing the gas sample onto columns 1 and 2 and then to the PDHID detector. Within the set sequence, the first PDHID signal with an intensity of approx. 550,000,000 a.u. was recorded at a retention time of 10.8 s (Figure 7a). The peak is narrow and symmetrical. The absence of tailing confirms a lack of analyte interaction with the stationary phase. The small molecular diameter of H_2 (2.89 Å) results in negligible adsorption on 5 Å molsieve columns and rapid elution of the analyte as sharp, well-shaped peaks. The detector is not overloaded.

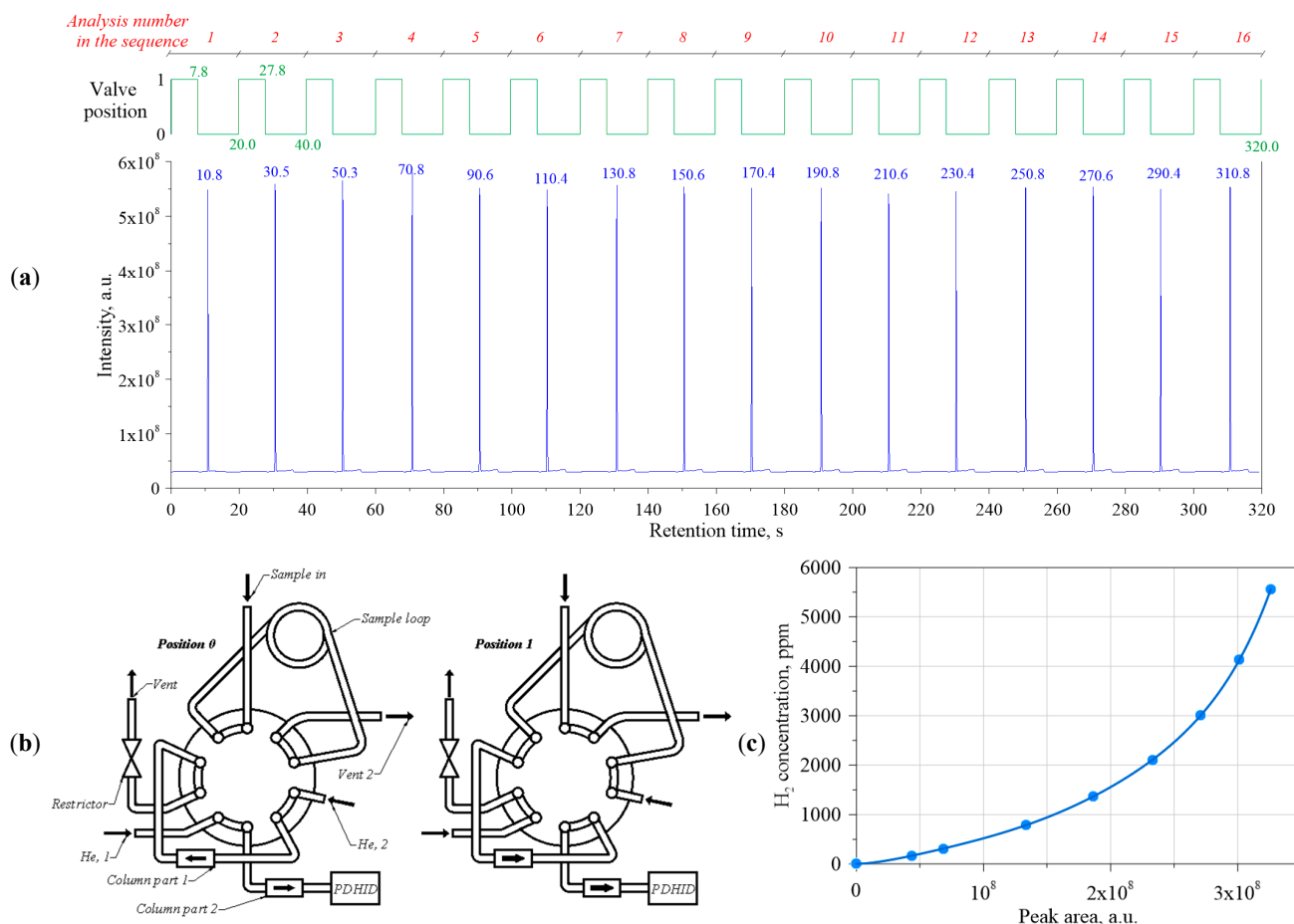


Figure 7. Chromatographic analysis. (a) Example chromatogram of the 16 hydrogen peaks in the sequence together with the valve position. (b) Gas flow paths through the ten-port valve in positions 0 and 1. The arrows indicate the direction of gas flow. (c) Calibration curve for hydrogen.

The total amount of analyte was determined based on the peak areas using a calibration curve. For calibration, hydrogen-containing gas mixtures of known concentration were obtained by diluting a commercial mixture of 5 vol.% H_2 in N_2 using the setup with

an empty fluidized reactor. The highest concentration of 5555 ppm was achieved by mixing 4 L/min of nitrogen with 0.5 L/min of the mixture, while the lowest concentration, 166 ppm, was obtained by mixing 14 L/min of nitrogen with 0.05 L/min of the mixture. The resulting nine-point calibration curve is shown in Figure 7c. It was fitted with a sixth-degree polynomial, yielding an R^2 value of 1, as displayed in Figure 7c. Due to the non-linear response of the PDHID detector over the investigated hydrogen concentration range, a polynomial calibration function was employed. A comparative analysis of several fitting models demonstrated that a sixth-order polynomial provided the best fit to the experimental calibration data, as evidenced by the highest coefficient of determination (R^2) and the lowest residual errors, particularly at the concentration extremes. To minimize the risk of overfitting, the calibration was performed using multiple calibration points distributed across the entire working range. The resulting calibration function was applied exclusively within this range, without extrapolation. Repeated calibration measurements confirmed the good reproducibility and stability of the detector response.

The H_2 concentrations obtained from the analysis of the recorded chromatograms were synchronized with the concentrations of the remaining gaseous products derived from the deconvolution of the successively acquired FTIR spectra. In this way, complete information was obtained on the time-dependent concentrations of all gaseous products formed in the process carried out at 200–450 °C. The experimental results are presented in the form of degrees of conversion (Figure 8) of formic acid (Figure 8a–c) or methanol (Figure 8d–f) to the respective products. The degree of conversion was defined as the ratio of the number of moles of a given gaseous product to the number of moles of the feed introduced, where “a” denotes the stoichiometric coefficient.

Regardless of the type of catalyst used, formic acid begins to decompose at approximately 150 °C, while the temperatures required to reach full or near-complete conversion depend strongly on the particular catalyst. For the Cu@DE catalyst (Figure 8a), the lowest temperature of complete formic acid conversion was observed, amounting to 228 °C. In the process carried out with this catalyst, the highest degree of conversion to hydrogen—exceeding 94%—was achieved at 377 °C. During catalytic conversion over the NiO@DE bed (Figure 8b), the temperature of complete conversion was slightly higher than for Cu@DE and reached 238 °C. The maximum degree of conversion to hydrogen, 77%, was obtained at 400 °C. In experiments with NiO@DE, a small conversion to methane was detected, not exceeding 2%, along with higher CO yields compared with the Cu@DE catalyst. The highest temperature of complete HCOOH conversion, 280 °C, was recorded for the Co_3O_4 @DE catalyst (Figure 8c). During formic acid catalytic conversion over this catalyst, the maximum degree of conversion to hydrogen reached 78% at 400 °C.

The use of methanol as a feedstock for hydrogen production (Figure 8d–f) requires higher temperatures compared with formic acid. Full conversion of the alcohol was observed in the process carried out over NiO@DE at temperatures above 361 °C (Figure 8e), while for the Cu@DE (Figure 8d) and Co_3O_4 @DE (Figure 8f) fluidized beds, complete conversion occurred at 378 °C and 394 °C, respectively. In the methanol-based processes, in addition to H_2 , CO, CO_2 , and CH_4 , the presence of dimethyl ether (DME) was also detected. DME is considered a promising alternative to conventional fossil fuels and is being evaluated as an environmentally friendly substitute for LPG [43]. The highest degree of conversion to DME, 27%, was achieved in the Cu@DE fluidized bed heated to 311 °C. Significantly lower amounts were observed for the Co_3O_4 @DE and NiO@DE beds, not exceeding 7% and 4%, respectively. If the aim of the process is to generate H_2 from methanol, the Cu@DE catalyst also provides the most favorable performance. The maximum degree of methanol conversion to H_2 , 96%, was recorded at 400 °C. A slightly lower value—by 4%—was obtained over the Co_3O_4 @DE bed at a similar temperature

(406 °C) and over the NiO@DE catalyst at 332 °C. Above 332 °C, the maximum hydrogen fraction in the product mixture decreases due to the increasing formation of methane. The methane concentration increased with rising process temperature, reaching a maximum conversion of 17% at 425 °C. In contrast, for Co₃O₄@DE (Figure 8e) and Cu@DE beds, methane conversions did not exceed 2% and 4%, respectively.

In addition to hydrogen-containing products, attention should also be paid to the molar fractions of carbon oxides. In processes carried out using formic acid, CO₂ concentrations exceed those of CO over the entire temperature range studied, whereas in the case of methanol, the situation is reversed and CO dominates. After separation, CO can be utilized as a fuel in a combustion step, providing an additional source of energy [30].

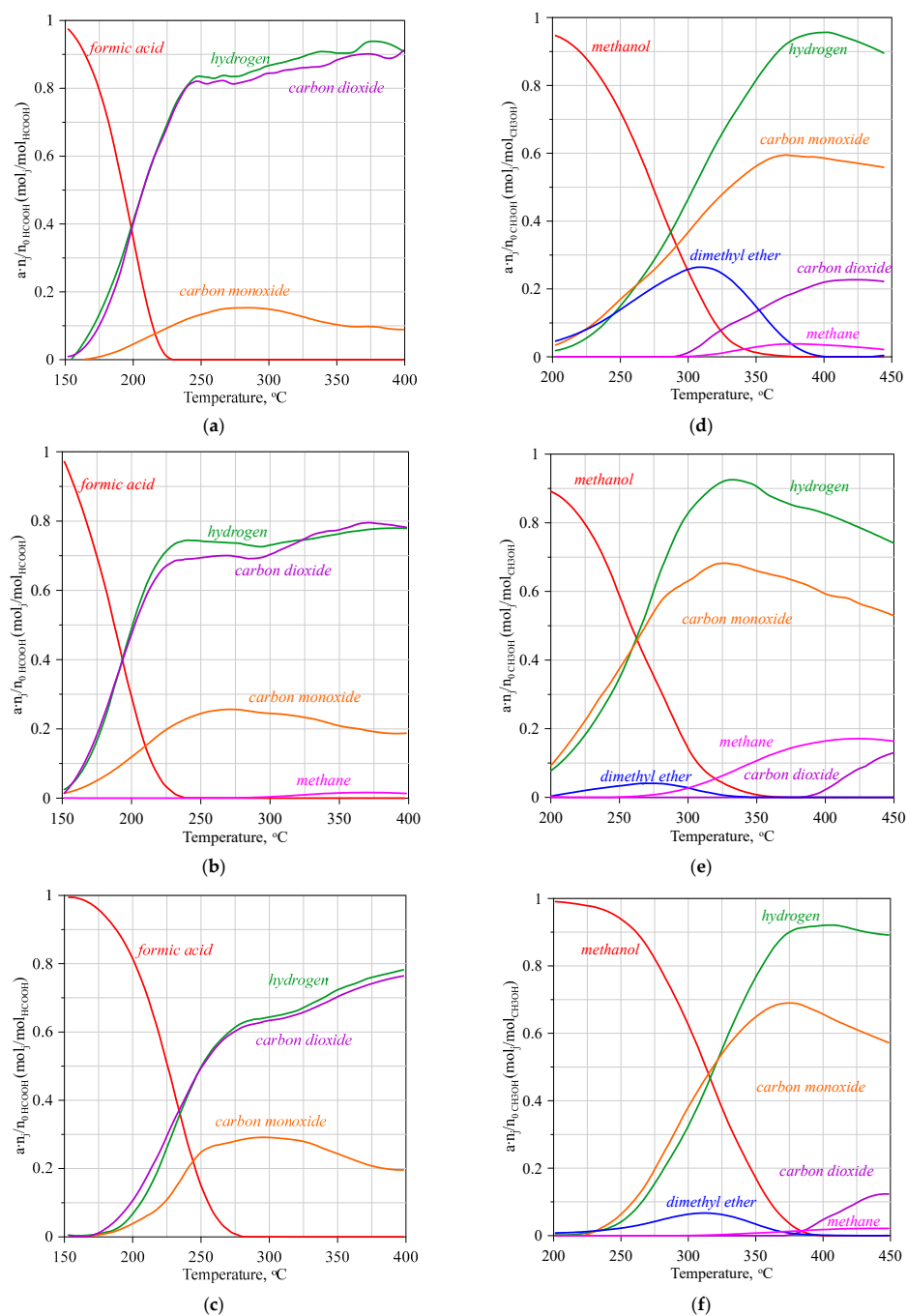


Figure 8. Molar fractions of products formed during catalytic conversion of: (a) HCOOH over Cu@DE, (b) HCOOH over Ni@DE, (c) HCOOH over Co₃O₄@DE, (d) CH₃OH over Cu@DE, (e) CH₃OH over Ni@DE, (f) CH₃OH over Co₃O₄@DE.

The reaction products formed are determined both by the acidic Si–OH sites present on the diatomaceous earth support and by the metallic component. During formic acid catalytic conversion, the Si–OH groups (Brønsted acidic sites) act as proton donors (H^+), thereby promoting the dehydration pathway, which contributes to CO formation. However, the desired dehydrogenation pathway leading to H_2 and CO_2 is primarily governed by the metallic active phase. The influence of the metallic phase depends on its electronic structure and the availability of electron vacancies. Copper, with the electronic configuration Cu: $[Ar] 3d^{10}4s^1$, exhibits the ability to chemisorb atomic hydrogen (H^*), thereby favoring the dehydrogenation pathway. In contrast, nickel and cobalt, with electronic configurations Ni: $[Ar] 3d^84s^2$ and Co: $[Ar] 3d^74s^2$, respectively, possess partially filled d orbitals that enable the adsorption of both H^* and OH^* species, directing the reaction toward the formation of CO and H_2O . Methanol dehydration to dimethyl ether proceeds via protonation on acid sites (Si–OH), followed by formation of surface methoxy intermediates and bimolecular coupling to DME [43]. In contrast, Cu-based catalysts promote the dehydrogenation pathways, where methanol is converted into CO and H_2 via CH_3O^* and HCHO intermediates. This behavior is attributed to the electronic structure of Cu (filled d-band), which favors cleavage of O–H and C–H bonds [44]. However, Ni catalysts exhibit strong adsorption of CO^* , H^* and CH_x^* intermediates, enabling stepwise hydrogenation and efficient methane formation via the Sabatier mechanism [45,46]; consequently, high CH_4 selectivity is observed for Ni-containing systems.

To compare the processes utilizing the acid and the alcohol, two parameters were calculated from the experimental results: (I) the number of moles of hydrogen produced per unit volume of the liquid feedstock and (II) the mass of carbon deposit formed per unit volume of the liquid feedstock. The parameters varying with temperature are presented in Figure 9.

The parameter nH_2 per cm^3 of feed is particularly important from the perspective of using formic acid and methanol within the concept of Liquid Organic Hydrogen Carriers (LOHCs) [47]. The parameter describing carbon deposition was introduced because a discrepancy in the carbon balance was observed in the methanol-based process. The highest yield of 0.25 mol H_2 per cm^3 of HCOOH was achieved in experiments using the Cu@DE catalyst (Figure 9a), which is approximately 25% higher than the yields obtained during formic acid catalytic conversion over the other two fluidized beds.

An advantage of using formic acid compared with methanol is that its catalytic conversion can be carried out without the formation of carbon deposits (Figure 9c). Its drawback, however, is the lower hydrogen yield per unit volume of feedstock (Figure 9a,b). Considering the maximum hydrogen production rates, methanol catalytic conversion (Figure 9b) enables the generation of 0.047 mol H_2 per 1 cm^3 of CH_3OH , which is about 80% higher than when HCOOH is used. The application of the NiO@DE catalyst allows for a reduction in the temperature at which this maximum is achieved.

Carbon deposition during methanol catalytic degradation begins above specific temperatures: 246 °C for the NiO@DE bed and 263 °C for Cu@DE. Thus, methanol catalytic conversion can be carried out to produce H_2 or DME without carbon deposition, but only at incomplete conversion of the feed, reaching up to 39% for NiO@DE, 41% for Cu@DE, and 54% for Co_3O_4 @DE. Under such operating conditions, the unconverted methanol would need to be recycled back to the reactor. If the process is to be operated in a manner that ensures 100% feed conversion and maximum hydrogen yields, a mitigation strategy for carbon deposition is required. This can be achieved through periodic reactor operation or by incorporating an additional fluidized-bed regeneration unit, as implemented in catalytic cracking processes [48]. The amount of carbon deposit depends on the catalyst used and

may reach as high as 0.082 g C per cm^3 CH_3OH , as observed in the process carried out with the Co_3O_4 @DE catalyst.

Due to quite elevated temperature of the process of catalytic conversion, a heat balance analysis was performed to evaluate the energetic implications. For example, for 1 mol methanol conversion at Cu@DE at 375 °C, the atom-balanced product distribution was represented as 1.86 mol H_2 , 0.60 mol CO, 0.04 mol CH_4 , 0.02 mol dimethyl ether, 0.19 mol CO_2 and 0.13 mol of solid carbon deposit. The carbon deposit was assumed to remain in the reactor and was not transferred to the combustion step. Based on the calculation presented in a previous paper [31], heat demand for conversion of liquid methanol at 20 °C to the product mixture at 375 °C was approximately $121.1 \text{ MJ}\cdot\text{kmol}^{-1}$. After H_2 separation, catalytic combustion of the remaining combustible gases (CO, CH_4 and DME) with stoichiometric air at 400 °C released approximately $203.9 \text{ MJ}\cdot\text{kmol}^{-1}$. Additional heat recovery from cooling the separated H_2 stream from 375 to 120 °C and the flue gases from 400 to 120 °C amounted to approximately $40.2 \text{ MJ}\cdot\text{kmol}^{-1}$ in total. These calculations indicate that the high-temperature methanol-based route should be considered together with heat recovery and combustion of flammable byproducts. It can substantially offset the thermal demand of the reactor and may lead to an overall exothermic integrated process. Therefore, realistic scale-up will require optimized heat recovery, effective management of carbon deposition, and verification of catalyst durability. Catalyst lifetime is strongly influenced by attrition of particles within the fluidized bed; therefore, extending the catalyst service life requires operation under conditions where the superficial-gas-velocity-to-minimum-fluidization-velocity ratio (U_0/U_{mf}) is maintained as close to unity as possible.

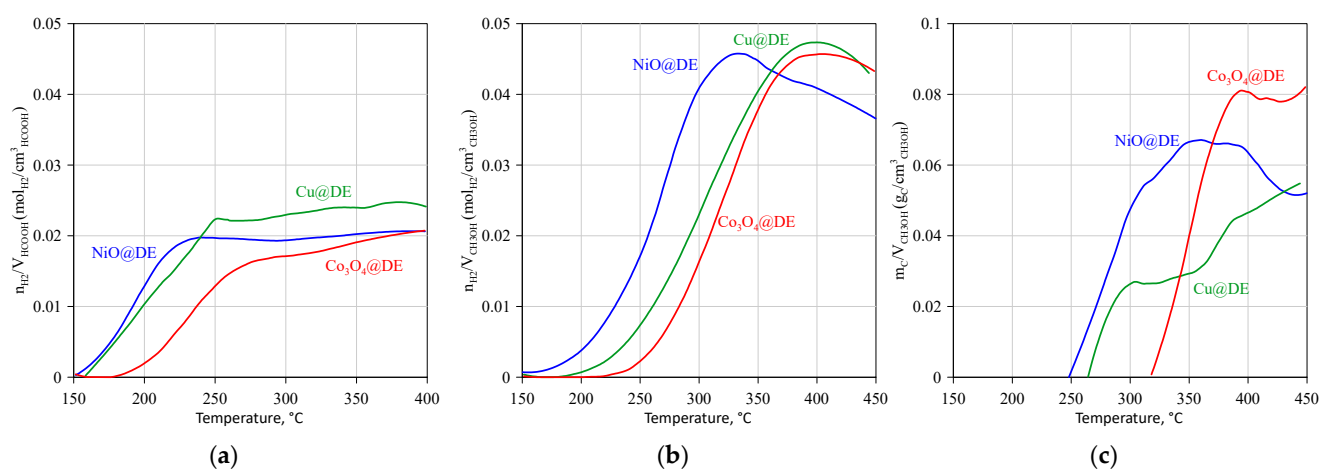


Figure 9. Hydrogen yield (a,b) and carbon-deposit formation (c) per unit volume of methanol or formic acid as a function of the catalyst used and the process temperature.

The hydrogen production process carried out in fluidized beds of diatomite-based catalysts was compared with processes in which the fluidized bed consisted of cenospheres coated with a catalytic layer, as well as with results reported by other authors for liquid-phase systems. A summary for the process using formic acid is presented in Table 4, highlighting the process temperature, feed conversion, hydrogen selectivity, turnover frequency (TOF), and the space–time performance expressed as the number of moles of hydrogen produced per hour per 1 cm^3 of reactor volume. TOF is a commonly used comparison metric and is defined as the ratio of the number of moles of hydrogen generated per hour to the number of moles of the active component in the catalyst. This parameter is particularly important when minimizing the use of the active phase is necessary, for example in systems employing expensive catalysts used in liquid-phase processes. When a low-cost catalyst can be used and the process is intended for industrial-scale implementation, the reactor

space–time performance becomes a more relevant measure. In the solutions proposed in this work, the TOF values range from 27.18 h^{-1} to 60.79 h^{-1} . These values are comparable to our earlier results obtained using fluidized-bed technology with a cenosphere-based catalytic bed [13], but lower than those typically reported for HCOOH conversion in the liquid phase [49,50]. The hydrogen yields normalized to the reactor volume are comparable both to our previous experiments performed in the fluidized-bed reactor and to the yields reported for liquid-phase processes. This indicates that, from the perspective of this parameter, the gas-phase process carried out in a fluidized-bed reactor can successfully replace liquid-phase systems that rely on noble-metal catalysts. An additional advantage of operating in the fluidized phase is the possibility of continuous reactor operation. This is more difficult in liquid-phase processes—for example, when the feed is not high-purity formic acid, only HCOOH undergoes decomposition, while water and other impurities accumulate in the reaction space.

Table 4. Comparison of H_2 synthesis with HCOOH on diatomaceous earth-based catalysts with literature solutions.

Phase	Catalyst	HCOOH, $\text{mL} \cdot \text{h}^{-1}$	Temp., $^{\circ}\text{C}$	Selectivity to H_2 , %	Substrate Conversion	TOF, h^{-1}	$\text{mmol}_{\text{H}_2} \cdot \text{cm}^{-3} \cdot \text{h}^{-1}$	Ref.
Gas	NiO@DE *	80.84	238	74	100	27.69	7.96	this work
Gas	Cu@DE *	80.84	228	75	100	60.79	8.09	this work
Gas	Co_3O_4 @DE *	80.84	280	62	100	27.18	6.62	this work
Gas	Co@cenosphere	56.293	218	75	100	18.28	15.22	[13]
Gas	Ni@cenosphere	49	233	67	100	25.53	16.23	[30]
Liquid	5 wt.% Pd/g- C_3N_4	1	30	100	55.5	1043	17.95	[49]
Liquid	PdRu/ C_3N_4 5 wt.%	1.88	60	100	2.9	30.57	0.01473	[51]
Liquid	5 wt.% Pd/C	1.66	60	100	84.8	684.6	3.731	[50]

* TOF values calculated using the actual active metal loadings determined by ICP-OES.

In the literature on methanol conversion, the authors compare processes mainly using the gas hourly space velocity (GHSV). GHSV is expressed as the volume of methanol gas passed through the catalytic bed over a period of 1 h per one gram of active substance in the catalyst. Table 5 compares the results of methanol catalytic degradation studies using diatomaceous earth catalysts with other processes, including steam reforming and partial oxidation. Assuming that the fluidized bed gas is pure methanol, high GHSV values of $28571\text{--}57142 \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ are achieved, comparable to steam reforming solutions using expensive metals [52] or nanoparticles [53]. The advantage of the proposed solution, in addition to the use of cheaper catalysts, is that there is no need to generate steam, while the disadvantage is the formation of a carbon deposit. Steam reforming using lanthanides allows the process temperature to be reduced to $230\text{--}280 \text{ }^{\circ}\text{C}$ [54] but is characterized by low GHSV values.

Table 5. Comparison of H_2 synthesis with CH_3OH on diatomaceous earth-based catalysts with literature solutions.

Type of Process	Catalyst	CH_3OH , $\text{mL} \cdot \text{h}^{-1}$	Temp., $^{\circ}\text{C}$	H_2 Selectivity, %	Substrate Conversion, %	GHSV $\text{mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	Ref.
catalytic degradation	NiO@DE *	86.68	361	87	100	28,571	this work
catalytic degradation	Cu@DE *	86.68	378	93	100	57,142	this work
catalytic degradation	Co_3O_4 @DE *	86.68	394	92	100	33,333	this work
catalytic degradation	Co@cenosphere	61.72	372	96	100	9471	[13]
steam reforming	CuPd/ ZrO_2	0.70	260	87	80	24,000	[52]
steam reforming	CuMnOx	2.17	400	n.d.	75	12,000	[55]
steam reforming	Cu-Sm/ Al_2O_3	0.3	280	99.9	100	3322	[56]

Table 5. Cont.

Type of Process	Catalyst	CH ₃ OH, mL·h ^{−1}	Temp., °C	H ₂ Selectivity, %	Substrate Conversion, %	GHSV mL·g ^{−1} ·h ^{−1}	Ref.
steam reforming	(La ₂ CuO ₄) _{0.7} (CNZ) _{0.3}	0.46	230	75	98	664	[54]
steam reforming	CuO + SiO ₂ nanoparticles	x	400	78	97	24,000	[53]
partial oxidation	5%Cu/CeO ₂ nanorods	0.96	280	55	50	21,262	[57]
steam reforming	CuO/ZnO/Al ₂ O ₃	424.02	350	100	92	11,739	[58]

* GHSV values calculated using the actual active metal loadings determined by ICP-OES.

4. Conclusions

This study demonstrates that molar-type diatomaceous earth is a promising catalyst support for fluidized-bed applications. The material can be easily coated by wet impregnation and possesses suitable fluidization properties, making it attractive for continuous catalytic applications. It was experimentally determined that diatomaceous-earth grains containing 2–4 wt.% of catalytic metal and sized 50–125 µm can be brought into a fluidized state using a gas with a minimum linear velocity of approximately 0.8 cm/s. Studies have shown that NiO@DE, Cu@DE, and Co₃O₄@DE materials exhibit catalytic activity in the conversion of methanol and formic acid to hydrogen. At temperatures up to 450 °C, CuO is reduced to Cu, which means that further catalytic activity stems from the Cu@DE material.

It has been demonstrated that chromatographic analysis can be efficiently combined with infrared gas analysis, enabling comprehensive monitoring of process products at a frequency of 0.05 Hz. Fast, sequential hydrogen detection is made possible by two series-connected 5A molsieve columns and a backflush function between them.

Comparison with literature-reported systems indicates that the proposed diatomaceous-earth-based catalysts achieve competitive TOF and GHSV values relative to previously reported fluidized-bed and fixed-bed hydrogen-production systems, especially for the Cu@DE catalyst, while relying on inexpensive natural supports and non-noble active phases.

Among the investigated catalysts, Cu@DE exhibited the highest hydrogen-production performance, achieving up to 94% conversion of formic acid to hydrogen, whereas NiO@DE enabled efficient hydrogen production at lower operating temperatures. Consequently, catalyst selection should depend on whether the primary objective is maximizing hydrogen production or minimizing process energy demand. Furthermore, the hydrogen-rich gas stream obtained over Cu@DE may improve the economic performance of downstream purification technologies, such as pressure swing adsorption (PSA), thereby improving the overall process efficiency. Although the process requires relatively high operating temperatures, this disadvantage may be mitigated through heat recuperation.

An important limitation of methanol catalytic degradation over the investigated catalysts is carbon-deposit formation under high-temperature conditions. While formic acid decomposition proceeded without measurable coke formation, carbon deposition could not be avoided during catalytic methanol conversion. This phenomenon may limit long-term catalyst stability and continuous operation, necessitating periodic catalyst regeneration through the combustion of accumulated carbon deposit.

Author Contributions: Conceptualization, W.Ż., G.B.-P. and P.M.; methodology, W.Ż.; software, W.Ż. and P.M.; validation, G.B.-P., J.A. and J.W.; investigation, P.M., J.A., J.W., A.M., A.P. and M.K.; resources, W.Ż., J.A. and J.W.; data curation, P.M. and G.B.-P.; writing—original draft preparation, W.Ż., G.B.-P. and P.M.; writing—review and editing, W.Ż., G.B.-P. and P.M.; visualization, P.M. and

G.B.-P.; supervision, W.Ż.; funding acquisition, W.Ż., J.W. and J.A. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

DE	diatomaceous earth
Co ₃ O ₄ @DE	tricobalt tetraoxide on diatomaceous earth catalyst
Cu@DE	copper on diatomaceous earth catalyst
NiO@DE	nickel(II) oxide on diatomaceous earth catalyst

Appendix A

MATLAB Script for Estimating the Bed Voidage at Minimum Fluidization Using the Ergun Equation

```
clear; clc;
```

```
%% Input data
```

```
rho_bulk0_g = 0.512;           % g/cm3
```

```
cat_factor = 1.05;
```

```
eps_bulk = 0.40;
```

```
rho_pyc_g = 2.08;             % g/cm3
```

```
T = 298.15;                   % K
```

```
p = 101,325;                  % Pa
```

```
M_g = 0.028;                  % kg/mol
```

```
R = 8.314;                    % J/(mol K)
```

```
g = 9.81;                     % m/s2
```

```
dp = 125e-6;                  % m
```

```
Utarget = 0.0086;             % m/s
```

```
%% Gas properties
```

```
mu = 2e-7 * T0.7558;
```

```
rho_g = M_g * p / (R * T);
```

```
%% Bulk density after catalytic correction
```

```
rho_bulk_cat_g = rho_bulk0_g * cat_factor;
```

```
%% Apparent particle density
```

```
rho_p_g = rho_bulk_cat_g / (1 - eps_bulk);
```

```
rho_p = rho_p_g * 1000; % kg/m3
```

```
%% Ergun equation constants
```

```
S = (rho_p - rho_g) * g;
```

```
C1 = 150 * mu * Utarget / dp2;
```

```
C2 = 1.75 * rho_g * Utarget2 / dp;
```

```

%% Solution of the cubic equation by bisection
lo = 0.30;
hi = 0.80;

for i = 1:200
    mid = (lo + hi)/2;
    f = S * mid3 + C1 * mid - (C1 + C2);

    if f < 0
        lo = mid;
    else
        hi = mid;
    end
end

eps_mf = (lo + hi)/2;

%% Verification of the Ergun equation terms
term_viscous = 150 * (1 - eps_mf) * mu * Utarget/(eps_mf3 * dp2);
term_inertial = 1.75 * rho_g * Utarget2/(eps_mf3 * dp);

%% Alternative verification: solution of the quadratic equation
A = 1.75 * rho_g/(eps_mf3 * dp);
B = 150 * (1 - eps_mf) * mu/(eps_mf3 * dp2);
C = -S;

U_check = (-B + sqrt(B2 - 4*A*C))/(2*A);

%% Results
fprintf('rho_bulk_cat = %.4f g/cm3\n', rho_bulk_cat_g);
fprintf('rho_p_app_cat = %.4f g/cm3\n', rho_p_g);
fprintf('rho_g = %.4f kg/m3\n', rho_g);
fprintf('mu = %.4e Pa s\n', mu);
fprintf('S = %.4f\n', S);
fprintf('C1 = %.4f\n', C1);
fprintf('C2 = %.4f\n', C2);
fprintf('eps_mf = %.5f\n', eps_mf);
fprintf('term_viscous = %.4f\n', term_viscous);
fprintf('term_inertial = %.4f\n', term_inertial);
fprintf('sum_terms = %.4f\n', term_viscous + term_inertial);
fprintf('left_side = %.4f\n', S);
fprintf('U_check = %.6f m/s = %.3f cm/s\n', U_check, U_check*100);

```

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