

Article

Synthesis and Characterization of Iron-Based Catalysts for Carbon Dioxide Valorization

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Abstract: The extensive release of carbon dioxide (CO₂) into the atmosphere is associated with the detrimental impacts of the global environmental crisis. Consequently, the valorization of CO₂ from industrial processes holds great significance. Transforming CO₂ into high added-value products (e.g., CH₄, C₁–C₃ deoxygenated products) has attracted considerable attention. This is feasible through the reverse water–gas shift (RWGS) and Fischer–Tropsch synthesis (FTS) reactions; CO is initially formed and then hydrogenated, resulting in the production of hydrocarbons. Iron-based materials have a remarkable ability to catalyze both RWGS and FTS reactions, enhancing the olefinic nature of the resulting products. Within this context, iron-based nanoparticles, unsupported and supported on zeolite, were synthesized and physico-chemically evaluated, applying multiple techniques (e.g., BET, XRD, FT-IR, Raman, SEM/TEM, DLS, NH₃-TPD, CO₂-TPD). Preliminary experiments show the potential for the production of C₂₊ deoxygenated products. Among the tested samples, supported Fe₃O₄ and Na-Fe₃O₄ (A) nanoparticles on HZSM-5 are the most promising for promoting CO₂ valorization into products with more than two carbon atoms. Results demonstrate that product distribution is highly affected by the presence of acid sites, as low-medium acid sites and medium acidity values enable the formation of C₂₊ hydrocarbons.

Keywords: iron-based materials; nanoparticles; heterogeneous catalysis; zeolites; carbon dioxide valorization



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1. Introduction

Over the last decades, the accumulation of greenhouse gases, such as carbon dioxide (CO₂), in the atmosphere has triggered substantial concerns. In 2022, a 1.0% increase in total energy-related greenhouse gas emissions was recorded, reaching a record high of 41.3% Gt CO₂-eq [1]. The significant amount of carbon dioxide emissions, as a result of the incessant use of fossil-derived fuels in various key sectors, such as transportation, power generation, and industry, is linked with severe financial and environmental concerns. The majority of modeled scenarios suggest that the atmospheric CO₂ levels will continue to increase in the short-to-mid-term future (i.e., 2021–2040), reaching unprecedented limits and highly contributing to global surface temperature rise [2]. As any level of global warming is expected to cause critical consequences, some applicable changes can mitigate the effect, but those require immediate action [3].

The imposition of net-zero targets and higher taxes to citizens and/or industries, the replacement of current energy sources with renewable ones, and the adoption of carbon capture, storage, and utilization technologies have the potential to inhibit the continuous growth of CO₂ emissions [3–5]. Despite these efforts, the fossil fuel demand is not yet sufficiently decreased, thus carbon capture utilization (CCU) technologies may offer a wide range of applications that enable CO₂ capture and utilization into numerous products [6,7].

Currently, only 230 Mt of CO₂ are used in CCU each year, but various utilization pathways are attracting significant interest because they effectively enable the transformation of carbon dioxide, from a harmful greenhouse gas to a wide range of added-value chemicals and/or energy carriers [8–10]. By 2030, 10 Mt of CO₂ are expected to be captured, out of which 7 Mt will be employed for the production of synthetic fuels [10]. Nevertheless, it is evident that further development of innovative processes for efficient CO₂ transformation of substantially higher amounts cf. current ones still lies ahead.

CO₂ constitutes a non-toxic, abundant, inexpensive building block that can be converted into products such as urea, formic acid, methanol, methane, dimethyl-ether, alcohols, and a wide range of hydrocarbons [11]. However, the selective CO₂ transformation requires efficient catalytic processes due to its high thermodynamic stability. CO₂ can be directly converted into added-value products through catalytic processes (e.g., electrocatalytic, photocatalytic, thermocatalytic) resulting in the formation of platform chemicals or C₂₊ hydrocarbons [12,13]. In fact, the application of tandem thermochemical processes employing inexpensive multifunctional catalytic materials can tune desired product selectivity; the combination of metal-based oxides with zeolites can promote selectivity towards olefins and aromatics via heterogeneous catalytic hydrogenation of CO₂, utilizing hydrogen from renewable resources [13–15].

Conventional CO₂ hydrogenation can proceed via two distinct reaction pathways; via the RWGS/FTS or the methanol-mediated route, whereas in both cases product distribution is highly affected by the selected catalytic system and/or the reaction conditions [16,17]. The first route involves the conversion of CO₂ into carbon monoxide (CO) through the reverse water–gas shift (RWGS) reaction, followed by Fischer–Tropsch synthesis (FTS) to generate C₁₊ hydrocarbons. The second route, methanol to hydrocarbons (MTH), involves an initial CO₂ transformation into methanol, which is subsequently converted into C₁₊ hydrocarbons. Direct RWGS/FTS CO₂ hydrogenation that can take place in a single reactor process is preferable with respect to economic aspects. Nonetheless, this approach mainly results in the production of CO and light paraffins, due to low CO hydrogenation and extensive olefin hydrogenation activity [18]. Conversion of CO₂ into C₁₊ hydrocarbons requires the presence of active catalytic phases so that CO₂ is adsorbed and activated, thereby forming carboxylate species [16]. The latter, due to hydrogen presence, form –HOCO intermediates that break down to –OH and –CO, which are hydrogenated into –H₂O, CO, and –HCO/–CH_x, producing paraffins or olefins via subsequent hydrogenation/dissociation/dehydration steps [19]. Thus, catalyst selection must focus on bifunctional activity on both reactions, under the same conditions, that can be enhanced by the addition of promoters or supports [15]. Iron and cobalt-based catalysts, using other metals or oxides as promoters (e.g., ZrO, Ce₂O₃, Zn), are typically used for the production of hydrocarbons through the RWGS/FTS route, even though precious metals, such as Pt and Pd, are also preferred because they effectively catalyze carbon dioxide activation [20]. The MTH route usually employs copper- and zinc-based catalysts, along with other metals, forming mixed metal oxides (e.g., In, Zr, Al, Ga, Zn) [21]. In both routes, hydrocarbon formation requires the combination of metal oxides with a suitable support in order for the tandem reactions to proceed under 300–400 °C and 0.5–5.0 MPa [21,22].

Iron-based materials (e.g., iron oxides and carbides) can be active as catalysts in both RWGS and FTS reactions, promoting olefin formation [15,23]. The addition of secondary metals, such as zinc (Zn), has been reported to enhance catalytic performance, acting as a structural promoter [24]. Alkali metal ions (e.g., K, Na) can be added to further improve catalytic behavior; potassium (K) addition suppresses methane formation and improves selectivity towards C₂₊ products [25], while sodium (Na) addition improves the basicity and the carburization of the surface of the magnetite nanoparticles [26], which are considered critical factors affecting hydrogenation of CO₂ to C₂₊ products [27]. Supported iron species can also affect reaction product distribution [28,29]; supports with high surface area, such as zeolites, carbon, or oxides, provide stabilization of the active sites during the reaction in the presence of water, even at high temperature and/or pres-

sure (i.e., $>200\text{ }^{\circ}\text{C}$ and $>3\text{ MPa}$) [30]. Zeolite-like materials or aluminosilicates, such as SAPO-34 or HZSM-5, are used as substrates in CO_2 valorization as they enable surface modification and acidity tuning, as well as catalyze oligomerization, isomerization, and aromatization reactions [13,31–33]. The production of hydrocarbons is highly affected by the pore architecture and the acid strength/density, as these catalytic sites enable the conversion of CO_2 activation intermediates that were formed on the metal sites [14]. In fact, the proximity of the iron oxides and the substrate is also important because it is linked with the reaction product selectivity [22]. Dang et al. have reported the production of lower olefins via the modified FT synthesis, employing bifunctional catalysts of $\text{In}_2\text{O}_3\text{-ZnZrO}_x$ oxides supported on SAPO-34 zeolites, reaching 17% CO_2 conversion with 84% selectivity to $\text{C}_2\text{-C}_4$ olefins [34]. Potassium-modified HY zeolites coupled with iron species have exhibited improved selectivity to C_{5+} products (i.e., 18%), compared to the non-modified HY zeolite (i.e., 10%); adding cerium as a promoter further increased the selectivity to 32% [35]. Employing Fe-Zn-Zr species supported on HZSM-5, Hbeta and HY; among the samples tested, Fe-Zn-Zr/HZSM-5 catalysts showed the best performance with 21.0% CO_2 conversion and 50% selectivity to C_{5+} hydrocarbons (including CO), at 5.0 MPa, $340\text{ }^{\circ}\text{C}$, $3000\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$, and $\text{H}_2/\text{CO}_2:3$ [36]. Another group has used a sodium-modified Fe_3O_4 catalyst combining SAPO-11 and ZSM-5 supports, at $\text{H}_2/\text{CO}_2 = 3$, $320\text{ }^{\circ}\text{C}$, 3.0 MPa, $0.5\text{ g}_{\text{cat}}$, to achieve 31% CO_2 conversion to gasoline hydrocarbon fraction (72% selectivity) and isoparaffins (38%) [37]. Wei et al. have prepared a multifunctional Na- Fe_3O_4 /HZSM-5 catalyst, observing 22.0% CO_2 conversion towards gasoline-range hydrocarbons— $\text{C}_5\text{-C}_{11}$ (78% selectivity) and methane (4% selectivity) under the following reaction conditions: $\text{H}_2/\text{CO}_2 = 3$, $320\text{ }^{\circ}\text{C}$, 3.0 MPa, $4000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, in a dual-bed reactor [17]. Unsupported Na- Fe_3O_4 converted 34% CO_2 towards $\text{C}_5\text{-C}_{11}$ (38% selectivity), CO (14% selectivity), and methane (4% selectivity) under the same experimental conditions [17]. The same group has employed Na-promoted Fe_3O_4 nanoparticles supported on HZSM-5 in order to convert CO_2 (25.6% conversion) mainly into C_{4+} products, including isoparaffins (78% selectivity), under the following reaction conditions: $\text{H}_2/\text{CO}_2 = 2$, $320\text{ }^{\circ}\text{C}$, 3.0 MPa, $4000\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$ [38]. In a similar study, Cui et al. synthesized an Na-modified ZnFeO_x /HZSM-5 that converts CO_2 into aromatics with 41.2% conversion and 75.6% selectivity under the following reaction conditions: $\text{H}_2/\text{CO}_2/\text{N}_2: 73/24/3$, $320\text{ }^{\circ}\text{C}$, 3.0 MPa, $4000\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$ [39]. Another study employed multifunctional catalysts combining K-Fe/C and ZSM-5, to reduce the acidity of the aluminosilicate, resulting in 35% CO_2 conversion into C_{5+} hydrocarbons (70% selectivity) at $\text{H}_2/\text{CO}_2 = 2.5$, $320\text{ }^{\circ}\text{C}$, 2.0 MPa, $1200\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$ [40].

In this work, multi-functional iron-based catalysts, employing promoters such as alkalis (i.e., Na, K) or zinc (Zn) and dispersed on HZSM-5, have been synthesized in order to upgrade the CO_2 into C_{2+} hydrocarbons. The aim is to study potassium- and sodium-doped state-of-the art catalysts one step further in two different amounts. The respective catalysts have been successfully synthesized as proved by the diffraction diagrams of the TEM, importing the alkali ions in the Fe_3O_4 lattice. Synthesized samples have been physico-chemically characterized, and their performance has been evaluated through preliminary experimental CO_2 hydrogenation tests in order to correlate physicochemical properties with product distribution. The association of the obtained experimental data with the detected differences in TPD- NH_3 measurements, concerning the strength of the acid sites, shows that product distribution is highly affected by the presence of acid sites; Na addition suppresses formation of CO while the addition of K generates stronger acid sites that hinder the formation of C_{2+} hydrocarbons, promoting C_1 product formation.

2. Materials and Methods

Magnetite nanoparticles (Fe_3O_4) were synthesized through the co-precipitation method, using ammonia (NH_3) as the precipitating agent. Iron precursors, 2.58 g $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ and 7.03 g $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (molar ratio = 1:2), were dissolved in 100 mL of deionized water under nitrogen gas flow, remaining under mechanical stirring at room temperature. Then, 15 mL of 25% NH_3 (w/w) were added to the solution, and subsequently a black precipitate was

observed. The suspension was kept under stirring for 30 min. Sonication (15 min) to break through any aggregates was performed to the resulting suspension, employing a Branson 3510 ultrasonic cleaner. For the sonicator bath, deionized water was used. Finally, the suspension was washed with deionized water to remove the chloride ions until pH = 7 was obtained.

The addition of alkalis such as Na and K to magnetite nanoparticles with a molar ratio (Fe:Na or K) 1:1 (A) and 1:2 (B) was performed by adding NaCl (0.97 g for A and 0.48 g for B) and KCl (0.76 g for A and 0.38 g for B) to the precursors' mixture. Then, the procedure mentioned above was followed. The addition of Zn was successful using the following precursors: 1.29 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 7.03 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 1.93 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (molar ratio = 0.5:0.5:2).

All the synthesized nanoparticles were dispersed on HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$), which was commercially available (Zeolyst International, Conshohocken, PA, USA). The zeolite was initially calcined at 500 °C, under air flow, for 4 h, and 1 g of it was mixed with 2 mL of Fe_3O_4 suspension, resulting in 5 wt% oxide loading. The mixture was left to dry in air (120 °C) for almost an hour, in a Venticell drying oven. The same procedure was followed for all synthesized nanoparticles.

Table 1 summarizes all synthesized materials, both supported and unsupported.

Table 1. Synthesized materials.

Unsupported Materials	Supported Materials
Fe_3O_4	$\text{Fe}_3\text{O}_4/\text{HZSM-5}$
Na- Fe_3O_4 (A)	Na- Fe_3O_4 (A)/HZSM-5
K- Fe_3O_4 (A)	K- Fe_3O_4 (A)/HZSM-5
Na- Fe_3O_4 (B)	Na- Fe_3O_4 (B)/HZSM-5
K- Fe_3O_4 (B)	K- Fe_3O_4 (B)/HZSM-5
ZnFe_2O_4	$\text{ZnFe}_2\text{O}_4/\text{HZSM-5}$

BET surface areas, pore volumes, and average pore diameters were determined by N_2 physisorption at −196 °C, using an Autosorb-1 Quantachrome flow apparatus. Prior to measurements, samples were dried under vacuum overnight at 250 °C. The total pore volume was defined as the single point pore volume at a relative pressure of $p/p_0 = 0.95$.

XRD patterns of the catalyst were obtained using a Bruker D8 ADVANCE diffractometer (Bruker Corporation, Billerica, MA, USA) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a scan rate of $0.02^\circ/\text{sec}$ (2θ), from 5.0 – 80.0° .

FT-IR measurements were performed with FT-IR 6700 spectrometer (JASCO International Co. Ltd., Tokyo, Japan). All the samples were dried before the measurement as humidity affects the resulting spectra.

Raman spectra were recorded in the 100 – 3200 cm^{-1} region using a micro-Raman (Renishaw Qontor in-Via) Spectrometer (Renishaw plc, Gloucestershire, UK), equipped with a 532 nm (delivering $\sim 7.5 \text{ mW}$) laser that was used as an excitation source.

The particle size distribution (PSD) of the produced iron nanoparticles was determined by Dynamic Light Scattering (DLS, Cordouan Technologies SAS, Pessac, France), while that of HZSM-5 was determined by a laser ensemble diffraction method (Malvern Mastersizer, Worcestershire, UK). SEM images were obtained employing a JEOL JSM-IT500 Microscope (JEOL, Peabody, MA, USA), equipped with an OXFORD INCA x-act EDS (Oxford Instruments, Oxfordshire, UK), in the Secondary Electron mode at an accelerating voltage of 20 kV under high vacuum. The nanoparticles were also characterized for their morphology by transmission electron microscopy (TEM, JEOL JEM-2011) (JEOL, Peabody, MA, USA), dispersed on a holey carbon grid, and analyzed at 200 keV.

NH_3 -TPD measurements were conducted in a non-commercial custom-built gas flow system, using a quartz reactor. The materials (0.1 g) were first reduced under H_2 flow ($200 \text{ cm}^3 \text{ min}^{-1}$) for 4.0 h at 350 °C and then cooled to 100 °C. At 100 °C, samples were saturated with NH_3 for 1 h and subsequently purged with N_2 for 2 h. Finally, ammonia des-

orption was monitored by heating the sample up to 800 °C, at a heating rate of 10 °C/min, under N₂ flow. The concentration of ammonia was measured by a FTIR GASMET™ CR-SERIES Fourier Transform Infrared (FT-IR) (Gaset Technologies, Vantaa, Finland) gas analyzer.

CO₂-TPD measurements were performed, loading 0.1 g of the sample in the same reactor employed for NH₃-TPD measurements. Following a similar procedure as described above, reduced samples were saturated with CO₂ at 50 °C and purged with N₂ flow for 2 h. Desorption of carbon dioxide was carried out under N₂ flow from 50 to 700 °C. The concentration of carbon dioxide was measured by a HORIBA VA-5111 CO₂ gas analyzer (HORIBA, Kyoto, Japan).

Catalytic performance tests were conducted in a stainless-steel continuous flow reactor equipped with thermocouples on top and bottom, heated line, pressure gage, condensate vessel, as well as gas inlet and outlet lines (Figure S1). Gas products of the outlet stream were analyzed online using a Shimadzu Nexis GC-2030 gas chromatographer (Shimadzu Corporation, Kyoto, Japan), equipped with a Barrier Ionization Discharge (BID) detector and a ShinCarbon ST 80/100 column (length: 30 m, diameter: 0.18 mm). Prior to the reaction, the catalytic materials were reduced at 350 °C for 4 h under pure H₂ flow, at atmospheric pressure. The typical reaction conditions were: 320 °C temperature, 3.0 MPa pressure, 40 mg of catalyst, and feedstock stream H₂/CO₂ at a ratio 3:1 (total inlet flow measured with mass flow controllers: 200 mL min⁻¹). The main gas-phase products detected under the typical experimental conditions were methane and carbon monoxide, while ethane, propylene, and propane were also detected. In all cases, water was not present in the outlet stream as any produced amount was condensed prior to the stream entering the GC for analysis. Fog presence in the condensation vessel showed that some liquid products were formed; however, their amount was not sufficient for collection and analysis. Thus, in selectivity calculations (Equation (2)), liquid products were assumed to be zero. The overall flow rate in the outlet stream of the reactor was considered equal to the inlet flow, allowing approximate approaches for all calculations, as variation of the molar flow rate is considered negligible due to low conversion levels. The carbon balance of the experiments was 97 ± 2%.

According to the above, approximated conversion and selectivity values were calculated using the equations described below:

$$\text{CO}_2 \text{ conversion}(\%) = \frac{\text{moles of CO}_{2\text{in}} - \text{moles of CO}_{2\text{out}}}{\text{moles of CO}_{2\text{in}}} \times 100 \quad (1)$$

$$\text{Selectivity to product } i(\%) = \frac{\text{Carbon moles of product } i}{\text{Total Carbon moles of identified Gas and Liquid Products}} \times 100 \quad (2)$$

Selectivity to each product was calculated, employing the total carbon moles of all identified gas products of the reaction (i.e., methane, carbon monoxide, ethane, propylene, and propane).

3. Results

3.1. Catalyst Characterization

Following material synthesis, characterization of supported and unsupported iron-based nanoparticles was performed employing selected methods (i.e., BET, XRD, FT-IR, Raman, DLS, SEM/TEM, NH₃-TPD, CO₂-TPD).

Table 2 summarizes BET surface area and porous characteristics of supported and unsupported materials, whereas letters (A) and (B) signify the addition of alkalis to magnetite nanoparticles with a molar ratio of 1:1 (A) and 1:2 (B). HZSM-5 exhibits the highest BET surface area and pore volume, equal to 409.4 m²/g and 0.243 cm³/g, respectively, while surface areas and porous characteristics of the supported samples slightly decrease, probably due to the metal oxide loading on the support [41]. BET surface areas of all unsupported nanoparticles are similar. The addition of zinc slightly improves the surface area as a result

of the synthesis procedure. As expected, the BET values of the supported materials are close to that of the support due to the low metal oxide loading. The addition of alkalis has no significant impact on the surface area of the catalyst and its porous characteristics. On the other hand, the pore volume and size of the ZnFe_2O_4 /HZSM-5 material, supported on zeolite, are slightly decreased.

Table 2. BET surface area and porous characteristics.

Materials	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	Crystallite Size (nm) *
Fe_3O_4	145.6	-	-	11.52
Na- Fe_3O_4 (A)	145.1	-	-	10.61
K- Fe_3O_4 (A)	148.3	-	-	10.34
Na- Fe_3O_4 (B)	136.1	-	-	10.90
K- Fe_3O_4 (B)	151.3	-	-	11.21
ZnFe_2O_4	178.3	-	-	9.16
Fe_3O_4 /HZSM-5	398.2	0.210	7.3	-
Na- Fe_3O_4 (A)/HZSM-5	401.1	0.194	6.6	-
K- Fe_3O_4 (A)/HZSM-5	395.8	0.194	6.7	-
Na- Fe_3O_4 (B)/HZSM-5	387.8	0.173	6.2	-
K- Fe_3O_4 (B)/HZSM-5	388.4	0.182	6.8	-
ZnFe_2O_4 /HZSM-5	389.5	0.148	4.5	-
HZSM-5	409.4	0.243	8.6	-

* Results of the XRD analysis, using the Scherrer equation.

Figure 1 shows the X-ray diffractograms of all unsupported samples. The main peaks identified for the reference sample (i.e., Fe_3O_4) are attributed to magnetite (JDPDS Card No. 01-071-6336), while the presence of a group of considerably weaker peaks can be assigned to the β - FeOOH (JDPDS Card No. 00-034-1266) phase (akaganeite). The observed 2θ peaks correspond to (220), (311), (400), (422), (511), and (440) crystal planes of the Fe_3O_4 cubic structure [42–44] (Figure 2). The presence of additional XRD peaks could be indicative of other iron structures, such as maghemite or non-cubic magnetite [45].

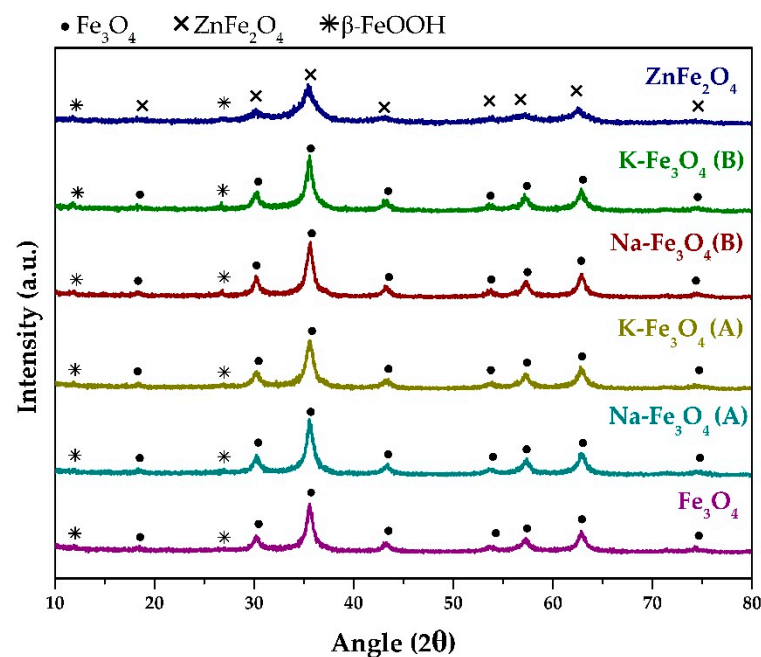


Figure 1. XRD diffractograms of unsupported samples.

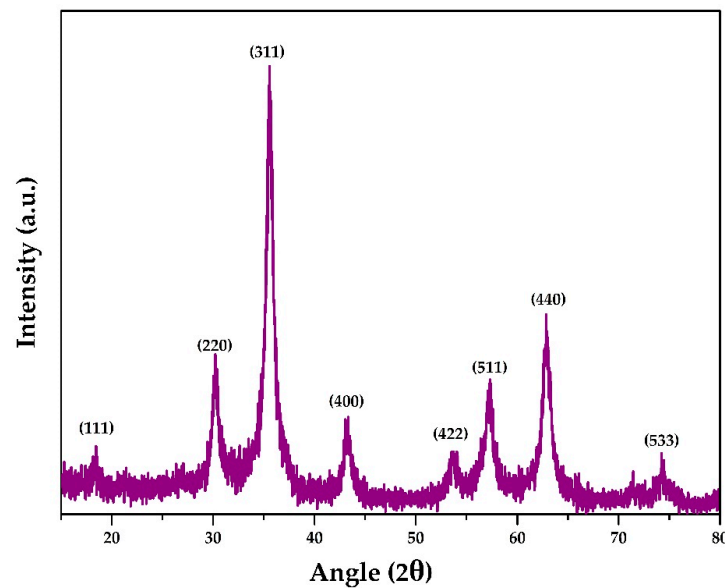


Figure 2. XRD patterns of unsupported Fe_3O_4 nanoparticles.

The diffractograms of all unsupported samples doped with Na or K show that the above-mentioned phases are also present (Figure 1). The calculated crystallite size of samples doped with Na or K is lower compared to the reference material, while among the doped materials, crystallite size does not differ noticeably (Table 2). However, small shifts of the main Fe_3O_4 diffraction peak for the doped samples have been detected, suggesting that the dopant ions have possibly been incorporated into the crystal lattice [46]. Peaks attributed primarily to ZnFe_2O_4 (JDPDS Card No. 00-001-1108) have been identified on the ZnFe_2O_4 sample, along with smaller peaks of $\beta\text{-FeOOH}$.

The diffractograms of all supported samples are presented in Figure 3. Due to the low iron oxide loading, for all samples, the dominant peaks are those of the HZSM-5 support. All the peaks of the HZSM-5 diffractogram are attributed to the aluminum silicate phase of the zeolite (JDPDS Card No. 00-044-0003). Nonetheless, there are minor peaks assigned to Fe_3O_4 and ZnFe_2O_4 oxides for the corresponding samples.

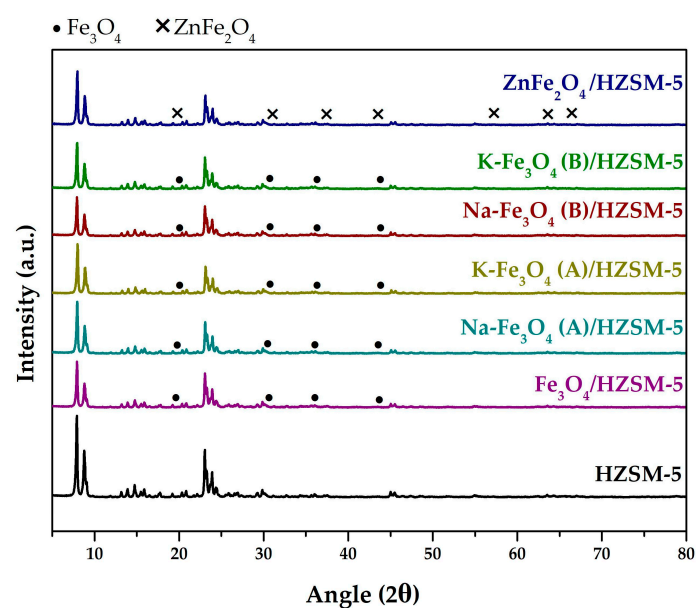


Figure 3. XRD diffractograms of supported samples.

Figure 4 presents FTIR spectra for all unsupported samples. As the FTIR measurements are affected by humidity and atmospheric carbon dioxide, peaks detected within the region of $3100\text{--}3800\text{ cm}^{-1}$ and $1600\text{--}1700\text{ cm}^{-1}$ can be assigned to the O–H stretching and bending vibrations of the surface –OH groups [47,48]. Additionally, the peaks at the band $1650\text{--}1830\text{ cm}^{-1}$ correspond to the C=O bond stretching of the CO_2 molecule [48]. The effect of the promoters can be observed on the respective spectra. The broad band between 400 and 600 cm^{-1} can be attributed to the Fe–O bond of magnetite [49,50]. Specifically, the two intense peaks observed on the Fe_3O_4 spectrum can be attributed to the Fe–O stretching vibration mode of the octahedral and tetrahedral sites, respectively [51]. The absorption band at 629 cm^{-1} , as well as the broad band at $640\text{--}730\text{ cm}^{-1}$, can be linked with slight oxidation of the nanoparticles' surface (maghemite formation) [52]. The peak at 418 cm^{-1} can also be associated with maghemite presence (Fe–O octahedral symmetric stretching) [53]. However, peaks at $\sim 420\text{ cm}^{-1}$ and between 640 and 700 cm^{-1} could also be attributed to akaganeite [54]. Peaks around 800 and 890 cm^{-1} can be assigned to the γ -OH and δ -OH stretching vibrations of goethite, respectively [55]. The peak at $\sim 1200\text{ cm}^{-1}$ can be due to the –OH in plane deformation of the Fe–OH bond [56]. Spectra of Na- and K-doped samples present no significant variations, indicating that all the above species are possibly formed along with Fe_3O_4 . Nonetheless, the absorption bands of the ZnFe_2O_4 spectrum are different; the substitution of Zn^{2+} ions for Fe^{2+} results in significant changes in the intensity of the peaks around 432 , 623 and 693 cm^{-1} due to disordering of the cation vacancies within the octahedral sites of the lattice, as ordering in these sites is highly affected by the foreign cation [57,58]. Additionally, as zinc ions replace iron ions of the tetrahedral sites of the Fe_3O_4 lattice, Fe–O vibration bands shift to lower frequency [59].

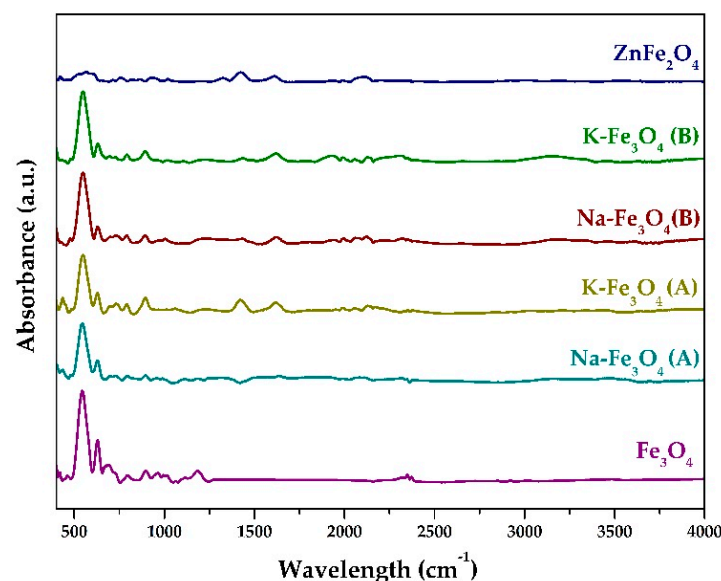


Figure 4. FTIR spectra of the unsupported samples.

The Raman spectrum of the Fe_3O_4 sample has four distinct peaks at 367 , 508 , 677 , and 719 cm^{-1} (Figure 5); $367\text{ (T}_{2g}\text{)}$, $508\text{ (E}_g\text{)}$, and $719\text{ (A}_{1g}\text{)}\text{ cm}^{-1}$ are characteristic of maghemite, while the additional peak at 677 cm^{-1} can be attributed to magnetite [60]. The latter is the main peak (A_{1g}), characteristic of magnetite. Peak deconvolution of the Fe_3O_4 sample spectrum (Figure 6) supports identified phases of maghemite and magnetite. Also, the 3T_{2g} active modes (~ 530 , $440\text{--}480$, and 190 cm^{-1}), and E_g ($290\text{--}300\text{ cm}^{-1}$) of magnetite cannot be excluded as they are probably hidden within the observed broad bands [61]. The spectra of the doped samples present similar Raman bands (Figure 5). The Raman spectrum of cubic ZnFe_2O_4 shows three characteristic peaks at $\sim 356\text{ (F}_{2g}(2)\text{)}$, $492\text{ (F}_{2g}(3)\text{)}$, and $665\text{ (A}_{1g}\text{)}\text{ cm}^{-1}$ [62,63]. The mode at 665 cm^{-1} is related with the stretching of the Zn–O bonds in tetrahedrons [63]. The F_{2g} modes are assigned to iron ($\text{F}_{2g}(2)$) and zinc ($\text{F}_{2g}(3)$) cation

vibrations in octahedral sites [64]. Peaks at 176 and 310 cm^{-1} are indicative of the presence of akaganeite [65]; nevertheless, the observed peak at $\sim 176 \text{ cm}^{-1}$ can also be attributed to the $F_{2g}(1)$ mode of zinc ferrite [66]. Finally, the 728 cm^{-1} corresponds to maghemite [67]. For all samples, the broad Raman peaks are linked to nano-particle size [62].

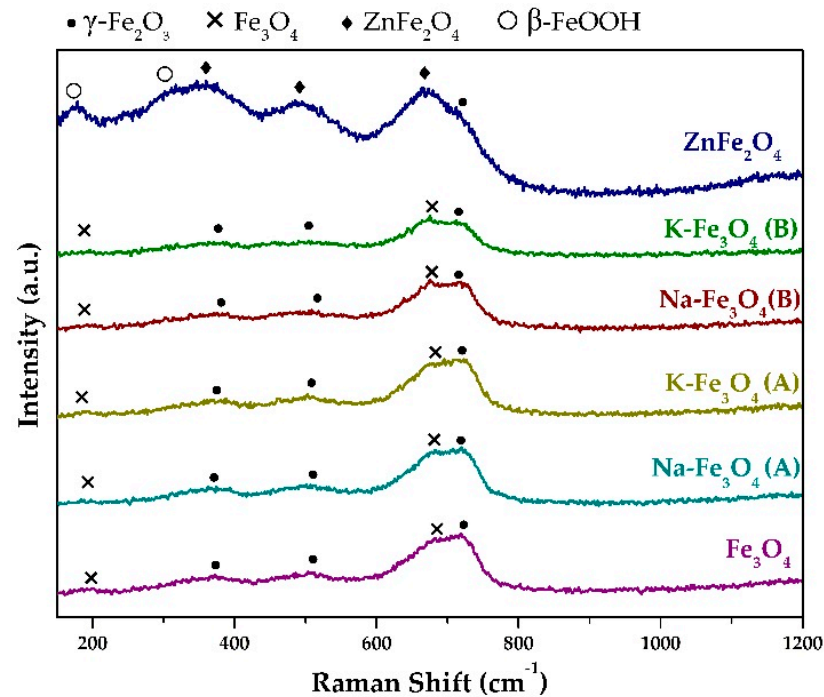


Figure 5. Raman spectra of the unsupported samples.

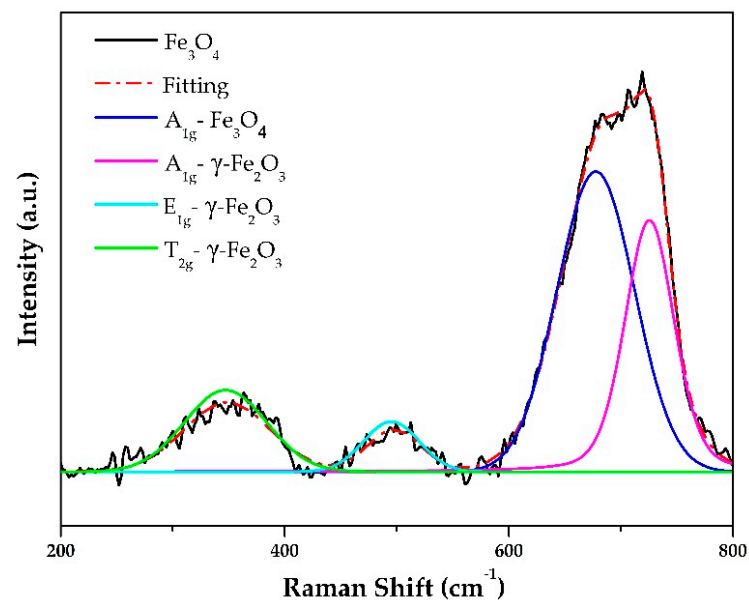


Figure 6. Raman deconvolution of unsupported Fe_3O_4 .

Catalyst acidity is considered a key property, especially for the hydrocarbon formation step of the reaction. In order to qualitatively and quantitatively determine the acidic sites on the catalytic surface, temperature-programmed desorption of ammonia (NH_3 -TPD) has been employed for all supported samples upon reduction. Acid sites that present desorption peaks at 150–250, 250–350, 350–500, and >500 $^\circ\text{C}$ are defined as weak, medium, strong, and very strong, respectively [68,69]. Figure 7 presents the ammonia desorption

peaks for all samples, including those of the HZSM-5 for reference. All desorption profiles follow the pattern of the support, which shows two desorption peaks at 200–250 °C and 400–500 °C that correspond to weak/medium and strong acid sites [70]. The addition of Fe_3O_4 on the HZSM-5 does not significantly affect the temperature of the desorption peaks. The total acidity of the sample $\text{Fe}_3\text{O}_4/\text{HZSM-5}$, as calculated by the desorbed ammonia of the TPD profile, is slightly lower than that of the support (Table 3). Comparing the alkali-doped samples with the $\text{Fe}_3\text{O}_4/\text{HZSM-5}$ sample, the addition of K ($\text{K-Fe}_3\text{O}_4$ (B)) results in small shifts on both temperature peaks towards lower values, while the addition of Na ($\text{Na-Fe}_3\text{O}_4$ (A)) also causes a slighter shift. Despite the above, the acid site strength, as well as the total acidity, of all samples is similar.

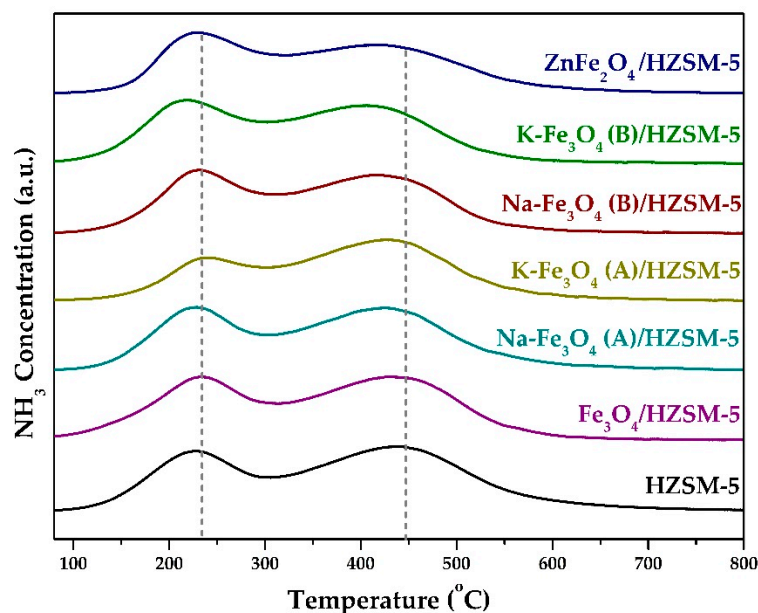


Figure 7. NH_3 -TPD profiles of supported samples.

Table 3. Desorbed ammonia (NH_3 -TPD).

Materials	Desorbed Ammonia (mmol $\text{NH}_3/\text{g}_{\text{cat}}$)
$\text{Fe}_3\text{O}_4/\text{HZSM-5}$	0.637
$\text{Na-Fe}_3\text{O}_4$ (A)/HZSM-5	0.684
$\text{K-Fe}_3\text{O}_4$ (A)/HZSM-5	0.573
$\text{Na-Fe}_3\text{O}_4$ (B)/HZSM-5	0.637
$\text{K-Fe}_3\text{O}_4$ (B)/HZSM-5	0.633
$\text{ZnFe}_2\text{O}_4/\text{HZSM-5}$	0.595
HZSM-5	0.718

NH_3 -TPD measurements have also been performed for unsupported samples, showing relative acidity (Figure S2). Ammonia desorption peaks can be attributed to weak/medium acid sites, while the desorbed ammonia is not affected by the addition of alkalis (Table S1).

Temperature-programmed desorption of carbon dioxide (CO_2 -TPD) has been employed for all supported and unsupported samples, in order to determine their basicity. Figure S3 presents the CO_2 desorption patterns for all supported samples, including that of the support. Desorption profiles do not show any significant peaks, indicating that the catalytic surfaces do not contain any basic sites. On the other hand, CO_2 desorption peaks of unsupported samples confirm the presence of basic sites (weak and medium basicity) on the catalyst surface (Figure S4). Desorbed amounts of CO_2 show that the employed dopants do not affect total basicity, but slightly modify the relative strength of the basic sites (Table S2).

Dynamic light scattering (DLS) measurements of Fe_3O_4 , $\text{Na-Fe}_3\text{O}_4$ (A), and $\text{K-Fe}_3\text{O}_4$ (A) are presented in Figure 8, along with the measurement for HZSM-5 (by Mastersizer). Measured particle size of the unsupported samples, in comparison to the TEM images that follow, exhibits that nanoparticles are aggregated; $\text{Na-Fe}_3\text{O}_4$ aggregates have a size distribution around 100 nm, $\text{K-Fe}_3\text{O}_4$ aggregates were approximately 500 nm, and Fe_3O_4 aggregates were 900 nm. HRTEM images of the synthesized unsupported nanoparticles are presented in Figures 9 and S5. According to TEM micrographs, all samples consist of small aggregated monocrystalline nanoparticles of similar size with an average primary particle diameter of ~ 11 nm (Figures 10a and S6). The samples are composed of crystals with relatively uniform crystal planes. According to the selected area electron diffraction (SAED) pattern of the Fe_3O_4 sample (Figure S7) the detected rings can be linked with the reflections (220), (311), (440), (444), and (511) of magnetite, as well as of other iron oxide species, such as maghemite or $\text{Fe}_{2.96}\text{O}_4$, in agreement with the XRD results [71]. The calculated lattice constants (Table S3) show that there is a slight decrease for all doped samples compared to the Fe_3O_4 reference material, thus indicating the incorporation of the dopant ions in the crystal lattice.

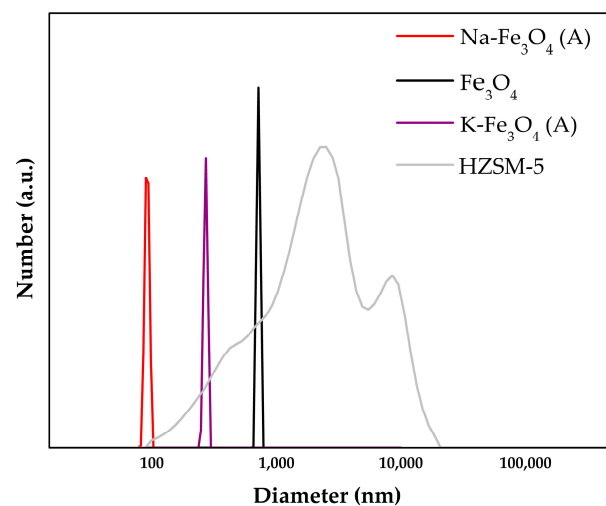


Figure 8. Particle size distribution measured by DLS for Fe_3O_4 , $\text{Na-Fe}_3\text{O}_4$ (A), $\text{K-Fe}_3\text{O}_4$ (A), and by Mastersizer for HZSM-5.

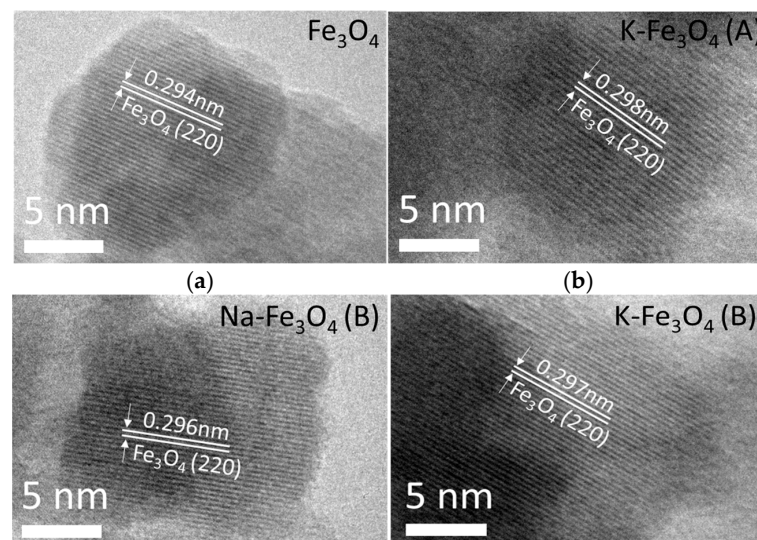


Figure 9. HRTEM micrographs of unsupported samples: (a) Fe_3O_4 ; (b) $\text{K-Fe}_3\text{O}_4$ (A); (c) $\text{Na-Fe}_3\text{O}_4$ (B); (d) $\text{K-Fe}_3\text{O}_4$ (B).

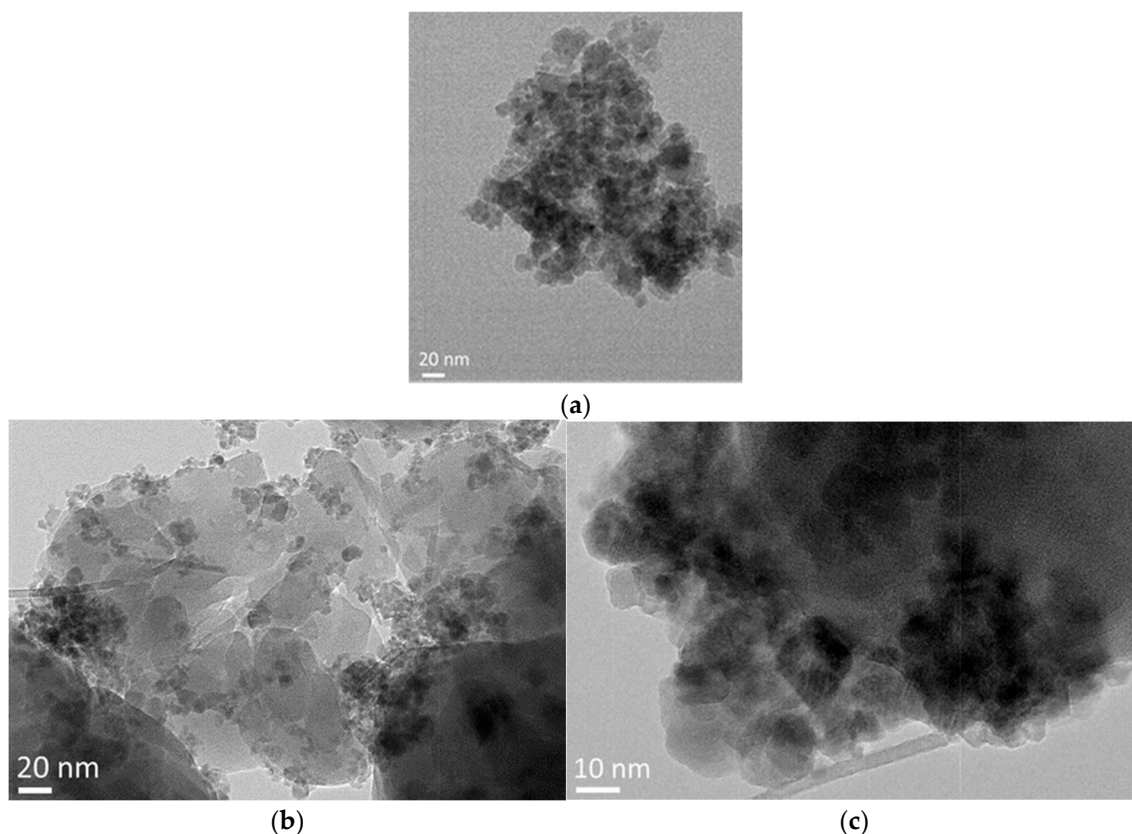


Figure 10. TEM micrographs of: (a) unsupported Fe_3O_4 ; (b,c) supported $\text{Fe}_3\text{O}_4/\text{HZSM-5}$.

Figure 10a presents the TEM image of the unsupported Fe_3O_4 , while Figure 10b,c show the images of the supported $\text{Fe}_3\text{O}_4/\text{HZSM-5}$. The latter confirm the dispersion of the iron nanoparticles on HZSM-5 surface.

Figure S8 shows representative SEM micrographs of unsupported Fe_3O_4 (Figure S8a), Fe_3O_4 supported on HZSM-5 (Figure S8b), and HZSM-5 (Figure S8c) to evaluate surface morphology. Unsupported Fe_3O_4 particles are agglomerated due to their small size and magnetic properties. SEM images of the supported $\text{Fe}_3\text{O}_4/\text{HZSM-5}$ sample and the corresponding iron distribution (Figure 11a,b) confirm the dispersion of iron species on the homogeneous surface of HZSM-5, as also supported by TEM.

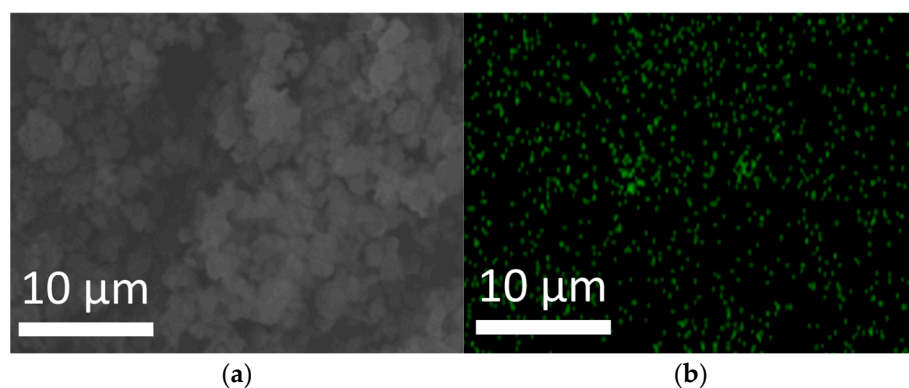


Figure 11. SEM micrographs of supported sample $\text{Fe}_3\text{O}_4/\text{HZSM-5}$ and EDS mapping: (a) original image; (b) iron distribution.

3.2. Catalyst Evaluation

Preliminary catalytic evaluation tests have been performed employing selected materials to study the effect of the promoters on the reaction product distribution. Prior to

the hydrogenation reaction, the catalytic materials were reduced at 350 °C for 4 h under pure H₂ flow. A blank (i.e., without any catalyst in the reactor) test was carried out at the same reaction conditions, exhibiting 0.6% CO₂ conversion and 100% selectivity to CO. Catalytic tests show relatively increased conversion levels, compared to the blank test; however, product distribution is highly influenced by the formulation used (Table 4). The low conversion levels allowed for the inlet total flow (i.e., 200 mL min^{−1}) to be considered as constant, so that it could be used as the basis for all calculations. Figure S9 includes original GC raw data for selected tests.

Table 4. Overview of preliminary reaction tests * carried out per catalytic material.

Materials	CO ₂ Conversion (%)	Product Selectivity (%)				
		CO	CH ₄	C ₂ H ₆ /C ₂ H ₄ C ₃ H ₆	C ₃ H ₈	
-	0.6	100	0.00	0.00/0.00	0.00	0.00
Fe ₃ O ₄	1.1	11.16	55.37	26.40/0.50	1.69	4.88
HZSM-5	3.4	89.02	10.98	0.00/0.00	0.00	0.00
Fe ₃ O ₄ /HZSM-5	3.0	11.76	62.02	17.25/0.00	0.20	8.77
Na-Fe ₃ O ₄ (A)/HZSM-5	2.7	6.97	76.01	10.10/0.00	0.00	6.92
K-Fe ₃ O ₄ (A)/HZSM-5	3.8	42.57	47.27	4.71/0.00	0.15	5.30
ZnFe ₂ O ₄ /HZSM-5	3.1	22.24	64.19	6.27/0.00	0.59	6.71

* Reaction conditions: 320 °C, 3.0 MPa, H₂/CO₂ (3:1).

Overall, CO₂ conversion for all tested samples is considerably low probably due to limitations of the employed testing unit, as only a small amount of catalyst could be loaded (0.04 g). However, those conversion values are noticeably higher compared to the blank test results. Among all samples evaluated, CO₂ conversion is the highest over the K-Fe₃O₄ (A)/HZSM-5 catalyst; nevertheless, there are no notable differences among all materials tested.

Undoubtedly, the presence of a catalyst affects product distribution, as methane (CH₄) is the main product formed, along with CO, ethane (C₂H₆), propane (C₃H₈), and propene (C₃H₆). Over Fe₃O₄/HZSM-5, methane is the main product formed (62.02% selectivity), along with ethane (17.25% selectivity) and CO (11.76% selectivity). Products with three carbon atoms have also been formed; 8.77% selectivity to propene and 0.20% to propane. The addition of Na in the Fe₃O₄/HZSM-5 promotes formation of CH₄ (76.01% selectivity) at the expense of CO, while a measurable negative effect on C₂-C₃ products is also identified. On the other hand, K addition seems to promote C₁ product formation (47.27% selectivity to CH₄ and 42.57% selectivity to CO), thus suppressing C₂₊ product formation compared to the reference sample. Substituting Fe₃O₄ by ZnFe₂O₄ is not effective as overall selectivity towards hydrocarbons formation is clearly lower and CO formation is nearly doubled; the main products formed are CH₄ (64.19% selectivity) and CO (22.24% selectivity), while ethane, propane, and propene are also detected. Despite the fact that the addition of Zn has been reported to enhance catalytic performance, the Fe-Zn interaction probably inhibits formation of longer chain hydrocarbons [72,73]. In conclusion, the performance of the Fe₃O₄ and Na-Fe₃O₄ (A) supported on HZSM-5 appears to be the most promising, favoring CO₂ conversion into C₂₊ products.

Additional tests have been performed employing separately either the unsupported Fe₃O₄ oxides or the HZSM-5 support (Table 4). Over Fe₃O₄, CO₂ conversion is rather limited (1.1%); methane, ethane, and carbon monoxide are the main products formed (55.4%, 26.4%, and 11.2% respectively). Comparing the catalytic performance of the reduced Fe₃O₄ with that of the supported Fe₃O₄/HZSM-5, methane formation is suppressed (55.4% selectivity) and the total C₂₊ production is enhanced (ethane 26.4%, propane 4.9%, propene 1.7%, and ethylene 0.5%). A reaction test carried out using HZSM-5 showed similar CO₂ conversion with the supported Fe₃O₄/HZSM-5. At the same time, product distribution

differed significantly as only C_1 products were formed (89.0% selectivity to CO and 11.0% to CH_4).

Fe_3O_4 presence is substantial in order for the reaction to proceed towards the formation of C_{2+} products. Adding the HZSM-5 support, CO_2 conversion increases but total selectivity to C_{2+} products is slightly reduced.

4. Discussion

In the current study, iron-based catalysts, supported on HZSM-5 zeolite, have been synthesized for carbon dioxide valorization (Table 1). In this context, synthesized nanoparticles were doped with sodium (Na) and potassium (K) in five distinct chemical compositions at ratios of 1:1 and 1:2, and additionally a Zn-doped sample was also employed. All samples were subjected to comprehensive physicochemical characterization. Our aim was to correlate physicochemical properties with product distribution.

Fe_3O_4 is the primary phase detected for the reference sample, as well as for the alkali-doped materials (Figure 1). Nonetheless, apart from magnetite (Fe_3O_4), maghemite ($\gamma-Fe_2O_3$), akageneite ($\beta-FeOOH$), and goethite ($\alpha-FeOOH$) are also detected (Figures 1, 4, and 5). The addition of alkalis, in different molar ratios, does not affect the formation of the above-mentioned phases, but slightly reduces the crystallite size and causes a small shift of the XRD peaks, as they have most likely been incorporated within the lattice. $ZnFe_2O_4$ is the main phase detected for the Zn-doped sample; akageneite and maghemite are also present (Figures 1, 4 and 5). The addition of Zn slightly reduces crystallite size (Table 2). Due to the low nanoparticle loading on the supported samples, the main phases detected in all cases are magnetite and HZSM-5 (Figure 3). The main phases detected on the supported zinc-promoted sample are zinc ferrite and HZSM-5 (Figure 3).

Analysis of high-resolution transmission electron microscopy (TEM) images reveal a slight increase in lattice plane from 2.94 to 2.98 Å for the doped samples (Figure 9), along with a minor shift in the (220) X-ray diffraction (XRD) peak (Figure 1), suggesting the insertion of Na and K ions into the Fe_3O_4 crystal lattice. The nanoparticles exhibit monocrystalline structures with primary particle sizes ranging from 5 to 20 nm, aggregating into larger agglomerates. Dynamic light scattering (DLS) measurements indicate that Na- Fe_3O_4 (A) aggregates have a size distribution around 100 nm, while K- Fe_3O_4 (A) aggregates are approximately 500 nm, and Fe_3O_4 aggregates are to 900 nm (Figure 8). The addition of alkali ions in the Fe_3O_4 lattice affects the charge of the nanoparticles. The size distribution measurement (DLS) of the nanoparticles takes place on suspension form, thus the higher the charge of the nanoparticle, the lower the aggregation. The catalytic behavior is assessed on the supported samples, where the nanoparticles are all dispersed in solid form on the surface of the zeolite micro-particle, thus all are aggregated in their solid form. TEM/SEM imaging on the hybrid Fe_3O_4 /HZSM-5 catalyst confirms that these aggregates are dispersed on the HZSM-5 surface (Figures 10 and 11).

The support provides the material with weak and relatively strong acidic sites, promoting bi-functionality, as catalysts contain metal sites from the iron nanoparticles and acid sites from HZSM-5 [74,75]. The metal sites of the iron species are active in both RWGS and FTS reactions while the acid sites of the support promote oligomerization, isomerization, and aromatization reactions. NH_3 -TPD patterns of unsupported samples show that the unsupported iron-based oxides also contain acid sites, primarily of weak/medium and relatively strong acidity (Figure 7). As expected, basic sites are absent from the CO_2 -TPD patterns of all supported samples due to the low loading of nanoparticles on the acidic support (Figure S3). However, the unsupported samples present weak and medium basicity (Figure S4). In fact, the addition of K does not affect total measured basicity (Table S2) but causes shifts of the carbon dioxide desorption peaks towards higher temperatures, demonstrating the formation of stronger basic sites. K presence seems to cause the same effect on the acid sites, which is more observable for the unsupported samples.

Preliminary catalytic tests show relatively low conversion levels for all supported samples (Table 4) under the applied reaction conditions compared to the literature [38],

due to the limited catalyst loading allowed by the current experimental setup. Product distribution seems to differentiate over the selected catalysts (Table 4); the $\text{Fe}_3\text{O}_4/\text{HZSM-5}$ reference sample performed better by suppressing CO production while enhancing formation of CH_4 , C_2H_6 , C_3H_8 , and C_3H_6 (26.22% total selectivity towards C_{2+} products). The addition of Na further suppresses CO formation, but selectivity to C_{2+} products is not improved (17.02%). K presence, which provided stronger basic sites, increased selectivity towards CO and slightly reduced that of CH_4 ; measured selectivity towards C_{2+} products was the lowest (10.16%). The stronger acid sites of the $\text{K-Fe}_3\text{O}_4$ (A)/HZSM-5 do not favor the formation of products with more than two carbon atoms. Over the $\text{ZnFe}_2\text{O}_4/\text{HZSM-5}$ catalyst, despite the fact that CO production is relatively decreased compared to $\text{K-Fe}_3\text{O}_4$ (A)/HZSM-5, selectivity to CO is higher than the Fe_3O_4 (A)/HZSM-5 and $\text{K-Fe}_3\text{O}_4$ (A)/HZSM-5 samples. Product distribution resembles that of the reference material, but the total selectivity to C_{2+} products is 13.78%. Acidity seems to play an important role in C_{2+} product formation; unsupported Fe_3O_4 containing relatively lower acidity and acid sites within the low-medium temperature region (Table S1), compared to the supported samples (Table 3), exhibits an interesting product distribution favoring the formation of C_{2+} products, especially that of ethane. Among the supported samples, the addition of Na suppresses CO formation, while that of K generates stronger acid sites that suppress the formation of C_{2+} hydrocarbons (Figure S2). Overall, acidity is required to selectively convert CO_2 into higher hydrocarbons; however, our results point out that low-medium acid sites and medium acidity values favor the formation of C-C bonds. This conclusion is in line with recent studies of other research groups [17,24].

Previous studies [17,26] have demonstrated that the proximity of Fe_3O_4 -based catalysts to HZSM-5 particles influences reaction kinetics, resulting in increased selectivity towards methane (CH_4) and decreased selectivity towards carbon monoxide (CO) with closer proximity. Consistent with these findings, our catalysts exhibit similar trends (Table 4). As TEM micrographs (Figure 10b,c) show that the iron nanoparticles are well dispersed on the surface of the zeolite micro-particle, the respective morphology is considered of close proximity. Specifically, the catalyst with 100 nm $\text{Na-Fe}_3\text{O}_4$ (A)/HZSM-5 (76% CH_4 and 7% CO), which had closer proximity to the zeolite surface compared to $\text{Fe}_3\text{O}_4/\text{HZSM-5}$ (62% CH_4 and 12% CO), showed enhanced selectivity towards CH_4 . Furthermore, we anticipate that the yield to $\text{C}_5\text{-C}_{11}$ hydrocarbons will increase with appropriate proximity of the catalytic system, although direct measurement of C_{5+} hydrocarbons was not feasible due to limitations in our in situ gas measurement setup. Higher hydrocarbons would be analyzed ex situ by GC-MS spectroscopy; for current sampling, a collection/condensation bottle was in line to the reactor exit, exhibiting fog presence, which was not sufficient for collection and analysis. Fog presence suggests that additional unidentified products are formed, in line with the calculated carbon balance ($97 \pm 2\%$). In summary, our findings suggest that the proximity of the catalyst to the HZSM-5 surface plays a crucial role in determining the selectivity of the RWGS/FTS reaction, with implications for the production of desired hydrocarbon products.

5. Conclusions

This study employs iron-based catalysts, doped with alkalis (Na, K) and zinc, supported on zeolite for the conversion of CO_2 into C_{2+} hydrocarbons. Synthesized materials have been physico-chemically characterized, and their catalytic performance has been evaluated through preliminary tests.

The iron phases detected on the synthesized materials correspond primarily to magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). TEM results prove that alkali ions have been successfully incorporated within the Fe_3O_4 lattice. Both SEM and TEM micrographs show that iron nanoparticles are well dispersed on the HZSM-5 surface indicating close proximity, especially for the $\text{Na-Fe}_3\text{O}_4$ (A)/HZSM-5 catalyst, which presented enhanced selectivity to CH_4 and reduced selectivity to CO. Preliminary tests show that product distribution is highly affected by the presence of acid sites; low-medium acid sites and medium acidity

values of the above samples are correlated with the formation of C_{2+} hydrocarbons. In general, among the supported samples, $Fe_3O_4/HZSM-5$ and $Na-Fe_3O_4$ (A) /HZSM-5 are the most promising for promoting CO_2 conversion into C_{2+} products, as Na addition suppresses CO formation, even though it does not affect C_{2+} selectivity. On the other hand, K addition results in the formation of stronger acid sites that favor CO formation. Testing the catalyst under higher residence times in a larger experimental setup is anticipated to surpass the constraints of the current setup, thereby facilitating the production of higher hydrocarbons tailored for future sustainable fuels.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14114959/s1>, Figure S1: Lab testing unit flow chart; Figure S2: NH_3 -TPD profiles of unsupported samples; Figure S3: CO_2 -TPD profiles of supported samples; Figure S4: CO_2 -TPD profiles of unsupported samples; Figure S5: HRTEM micrograph of the $Na-Fe_3O_4$ (A) unsupported sample; Figure S6: TEM micrographs of unsupported samples: (a) $Na-Fe_3O_4$ (A); (b) $K-Fe_3O_4$ (A); (c) $Na-Fe_3O_4$ (B); (d) $K-Fe_3O_4$ (B); Figure S7: Selected area electron diffraction (SAED) pattern of Fe_3O_4 ; Figure S8: SEM micrographs of: (a) unsupported Fe_3O_4 ; (b) supported Fe_3O_4 on HZSM-5; (c) HZSM-5; Figure S9: GC raw data: (a) experiment without catalyst; (b) experiment over $Na-Fe_3O_4$ (A)/HZSM-5; (c) experiment over Fe_3O_4 (A)/HZSM-5 (retention time of identified gases (min): 0.585 (H_2), 1.393 (CO), 2.856 (CH_4), 4.375 (CO_2), 6.853 (C_2H_6), 10.099 (C_3H_6), 10.718 (C_3H_8)); Table S1: Desorbed NH_3 (NH_3 -TPD); Table S2: Desorbed CO_2 (CO_2 -TPD); Table S3: Lattice constants of alkali-doped nanoparticles.

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