Catalytic Hydrogenation of Carbon Dioxide over Magnetic Nanoparticles: Modification in Fixed-Bed Reactor

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Abstract: A specific finger-projected fixed-bed reactor (FPFBR) was designed to efficiently utilize magnetic nanoparticles (MnFe$_2$O$_4$/Bi-MnFe$_2$O$_4$) for a model reaction (hydrogenation of a greenhouse gas, CO$_2$, to valuable products: VPs). Coprecipitation method, with desired modification was used for the preparation of magnetic nanoparticles (MNs) with controlled shape and size. Eighteen fingers in a single chamber were designed in the fixed-bed reactor’s skeleton; each finger worked as an independent reaction core. Controlled flow of hydrogen and CO$_2$ was continuously provided to preheated reaction cores (catalyst beds) from saturator. One of the major products methanol (%: Conv, 22/Sel 61) among VPs was identified and quantified by GC. The efficiency of self-designed reactor was 74% for the direct catalytic hydrogenation of CO$_2$ to valuable organic products.

Keywords: fixed-bed reactor; nanoparticles; carbon dioxide; methanol

1. Introduction

Global efforts are required to mitigate the increased concentration of atmospheric CO$_2$, a greenhouse gas [1]. Accumulation of CO$_2$ in the atmosphere due to fossil fuel combustion contributes a foremost part to the global warming. Approximately 1.3 × 10$^9$ million tons of carbon dioxide are added to the atmosphere per year [2]. Capturing CO$_2$ from its sources of emission and then utilizing it as a precursor for VPs not only controls the aforementioned problems but also appears to be an economically viable process [3–9]. Methanol is one of the valuable products for which CO$_2$ can be used as a precursor [10]. For mitigation of greenhouse gas emissions, CO$_2$ reduction to valuable fuels and valuable chemical products has been suggested by many researchers [1–9].

In order to extend the catalyst’s life, achieve reliable quality, production rate, and control process conditions, reactor design is an elementary task in the process of CO$_2$ reduction [11]. Similarly, the choice of a proper reactor is one of the vital factors to improve the process of VPs production from CO$_2$ hydrogenation [12]. In this scenario, heterogeneous fixed-bed reactors have played efficient role in the process intensification [13] and, therefore, a variety of methodological approaches and fixed-bed reactors have been used for the process of CO$_2$ hydrogenation. Limitations of these conventionally used fixed-bed reactors such as less consideration of the catalyst durability and recyclability motivate us to investigate extensive modification in the skeleton of reactor [13–17].
Similarly, CO$_2$ is an inert species and requires an active catalyst in order to split into VPs [18]. The designing of highly stable, low cost and efficient catalysts is the key requirement of industry for VPs production from carbon dioxide [12]. Extensive research has been carried out for the production of VPs from carbon dioxide in the presence of simple and/or modified catalysts such as silica [19], alumina [20,21] and zirconia supported [22,23] active metal catalysts. However, due to their hydrophilic nature and low thermal stability, these catalysts are less favorable for hydrogenation of CO$_2$ to MeOH due to water generation. Therefore, magnetic nanoparticles (MNPs) have been screened for the production of VPs from greenhouse gas due to hydrophobic nature and extended life span. In addition, MNPs can be recycled from the reactor several times by a simple and easy method.

Herein, we modified the skeleton of a fixed-bed reactor specifically for MNPs. Internal erected fingers were designed for holding MNPs (MnFe$_2$O$_4$ or Bi-MnFe$_2$O$_4$). Each of them works as an independent reaction core for direct hydrogenation of CO$_2$ to VPs. The reactor shows excellent efficiency with mild operating conditions such as 413 K temperature and atmospheric pressure. In addition, the easy recyclability and extended life span of catalysts make the process industrially favorable.

2. Materials and Methods

Quartz glass was used for reactor design and building. Analytical grade chemicals were used throughout the experimental work without further purification. Iron (III) chloride hexahydrate (FeCl$_3$.6H$_2$O), iron (II) sulphate (FeSO$_4$), manganese (II) chloride dihydrate (MnCl$_2$.2H$_2$O), bismuth (III) chloride (BiCl$_3$) and sodium hydroxide (NaOH) were purchased from Scharlau. Both CO$_2$ and H$_2$ gases were supplied by British Oxygen Company (BOC) Pakistan Ltd. (Texila, Pakistan) in 48 cft cylinders with pressure-control analogue gauges. These gases were passed through filters and saturated in the saturator from where the gases were fed to the reactor through T-valves and needle valves.

2.1. Finger-Projected Fixed-Bed Reactor and Reaction Setup

The reactor (FPFBR) consists of an elongated chamber of 80 cm length of quartz glass (diameter: 20 mm) with quick-fit sockets (19 mm) on both sides. A three-way quartz saturator (1000 cm$^3$) connected through a quartz adopter to a reactor consists of (a) an inlet for the gas supply (b) a narrow outlet for gas stabilization and (c) an outlet to the reactor as shown in Figure 1. The reactor has 18 finger projections toward the inside with a groove outside (length: 7 mm, outer diameter: 4.5 mm, inner diameter: 3.5 mm) in which magnetic beads are fixed externally, holding the MNPs (catalyst) to the inner side of the finger projections as shown in Figure 1. One end of this chamber is connected to the saturator while the other end is equipped with a six-port valve. All the connections (reactors) in the experimental setup were made through adopters of 19 mm quick-fit quartz cones. The temperature of the reactors was maintained by heating tapes, connected to a temperature controller with k-type thermocouple. A flow-sheet diagram for overall experimental setup involved in this process is presented in Figure S1.
2.2. Synthesis of Magnetic Nanoparticles

Manganese ferrites (MnFe$_2$O$_4$) and bismuth-doped MnFe$_2$O$_4$ (Bi-MnFe$_2$O$_4$) were prepared by a modified coprecipitation method. Salts of Fe$^{2+}$ (FeSO$_4$) and Mn$^{2+}$ (MnCl$_2$) were taken in molar ratio 2:1 respectively. Thus, 0.2 M solution (100 mL) of Fe$^{2+}$ and 0.1 M solution (100 mL) of Mn$^{2+}$ was prepared and mixed with surfactant (dopamine hydrochloride: 2% w/v). The mixture was sonicated for 10 min at 303 K and then dropped slowly into a 3 M solution (100 mL) of NaOH at a preheated temperature of 368 ± 5 K under vigorous stirring. The solution was aged for 4 h at the same temperature. The precipitates were filtered, washed three times with 1 N HCl/distilled water, dried at 373 K for overnight and calcined at 513 K (0.5 K/min) for 4 h in muffle furnace under N$_2$ atmosphere. The sample was reduced at 553 K for 2 h under hydrogen and nitrogen mixture (1:3) flow in U-shaped quartz reactor.

2.3. Synthesis of Bismuth-Doped MnFe$_2$O$_4$ (Bi-MnFe$_2$O$_4$)

Bi-MnFe$_2$O$_4$ was prepared by a coprecipitation method. Solutions of Fe$^{2+}$ (FeSO$_4$) 0.2 M/100 mL, Mn$^{2+}$ (MnCl$_2$) 0.1 M/100 mL and Bi$^{3+}$ (BiCl$_3$) 0.01 M/100 mL were mixed with surfactant (dopamine hydrochloride: 2% w/v). The mixture was sonicated for 10 min at 303 K and then dropped slowly into a 3 M solution (300 mL) of NaOH at a preheated temperature of 368 ± 5 K under vigorous stirring. The solution was aged for 4 h at the same temperature. The solution was filtered, washed three times with 1 N HCl/distilled water, dried at 373 K for 12 h and calcined at 513 K (0.5 K/min) for 4 h in muffle furnace under N$_2$ atmosphere. As Bi-doping reduces the magnetic properties of NPs [24], the catalyst was further calcined at high temperature of 753 K (0.5 K/Min) for 6 h to increase the magnetic character of nanoparticles [25]. Furthermore, the sample was reduced at 553 K for 2 h under a hydrogen and nitrogen mixture (1:3) flow in a U-shaped quartz reactor.

2.4. Characterization

MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ were characterized through scanning electron microscopy (SEM, JSM 5910, JEOL, Tokyo, Japan) and energy-dispersive x-ray (EDX, JSM 5910, JEOL, Japan). XRD spectra of the catalysts were obtained by an X-ray diffractometer (XRD, JDX-3532, with a CuK$\alpha$ radiation source, manufacturer: JEOL, Japan, 1.5406 Å, 2 theta-range 0–80°). Surface area and pore size were measured with (Quanta Chrome NOVA 1200e, Surface Area & Pore Size Analyzer, Boynton Beach, FL, USA) by a multipoint N$_2$ adsorption
method. FTIR spectra were recorded by (IR Prestige 21, Shimadzu, Japan). The particle size was calculated by Scherrer equation and average grain size intercept method (AGI).

2.5. Hydrogenation of CO$_2$

Continuous flow of CO$_2$ and H$_2$ in 1:3 was allowed into the reactor through saturator at a preheated temperature of 413 $\pm$ 5 K. The number of moles of reactants were calculated by using the formula ($n = \frac{PV_f}{RT}$) where $V_f$ = volume of flow rate. MNPs were taken in the reactor as mentioned earlier, held by externally fitted magnetic beads. The mixture of gases was allowed to pass through the reactor chamber. The temperature of the reactor (413–513 K) was maintained through heating taps as shown in Figure S1. Both ends of the reactor were blocked with glass wool to protect the gas line from sweeping the catalyst. Outflow was passed directly to the GC (Perkin Elmer Clarus 580) through six-port valve for analysis. There are two main reaction involved in the process of methanol synthesis.

i. CO$_2$ + 3H$_2$ $\rightarrow$ CH$_3$OH + H$_2$O

ii. CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O

i. Methanol synthesis for CO$_2$ hydrogenation with $\Delta H_{493 K} = -57.5$ kJ mol$^{-1}$ and ii. CO production form reverse water gas shift (RWGS) reaction with $\Delta H_{493 K} = 38.8$ kJ mol$^{-1}$ which further converts to methanol. The CO$_2$ conversion was calculated by using the following formula;

$$\% \text{Conv} = \frac{M_{\text{inflow}} - M_{\text{outflow}}}{M_{\text{inflow}}}$$

where, $M_{\text{inflow}}$ and $M_{\text{outflow}}$ are the moles of reactant and product, respectively.

3. Results and Discussions

3.1. Finger-Projected Fixed-Bed Reactor

Fixed-bed reactors have a great applicability in the direct hydrogenation of CO$_2$ to VPs [13]. Several fixed-bed reactors have been investigated for CO$_2$ hydrogenation to VPs over a variety of metals and supported metals catalysts (Cu/ZnO/Al$_2$O$_3$, CuO-Fe$_2$O$_3$-CeO$_2$/HZSM-5) under a range of working conditions [12,14–27]. However, reported investigations have many drawbacks such as elevated temperature, high pressure, less durability and short life span of catalysts. To overcome these drawbacks, we have modified a fixed-bed reactor for magnetic nanoparticles to enhance functionality and efficiency particularly in this model reaction. Here, we modified a fixed-bed reactor designed with numerous inner side-projected beds like fingers with a groove to the outside. Finger projections were designed in a zigzag manner counter to the flow of reactant gases in order to maximize collision chances of reactants with catalyst particles. A unique character of this reactor was the ease of recyclability of catalysts due to the use of external magnets for holding magnetic nanoparticles. To increase the production of VPs, additional chambers (up to five) were added. The reactors were connected through adopters of 19 mm quick-fit quartz cones as shown in Figure S1. To control the flow of reactant gases, precise valves were connected to the reactor assembly. The gases H$_2$ and CO$_2$ were saturated in the saturator from where the mixture of these gases was fed to a reactor. The efficiency of the reactor was calculated as 74% through modified equations, as given below.

$$\Pi = \frac{C_{\text{out}}}{C_{\text{in}}} \times 100$$

In Equation (1), $\Pi$ represents a dimensionless parameter for the efficiency of the reactor, $C_{\text{in}}$ is the reactants concentration entering the reactor and $C_{\text{out}}$ is the product concentration leaving the reactor. The friction factor is calculated in terms of the reactor’s
void fraction and as a function of the modified Reynolds number. These calculations were based on the following modified form of the Ergun equation:

$$f_p = \frac{150}{Gr_p} + 1.75$$

(2)

In Equation (2) $f_p$ is the reactor’s friction factor while $Gr_p$ represents modified Reynolds number of the reactant which is calculated with the following relation:

$$Gr_p = \frac{\rho V_s D}{(1-\varepsilon)\mu}$$

(3)

where $\rho$ is the density of inlet mixture gas, $V_s$ represents superficial velocity of the gaseous mixture at the reactor inlet, $D$ is the diameter of the reactor inlet, $\mu$ is the viscosity of the mixture gas while $\varepsilon$ represents the void fraction of the fixed-bed reactor. Hence, for the FPFBR, the gas flow along the wall of the chamber cannot be neglected because the value of $D$ is lesser than 10 $d_p$ ($D < 10 d_p$, where $D$ is the reactor diameter, while $d_p$ is the diameter of the finger (catalyst bed). Therefore $\varepsilon \neq 0$ for the designed reactor. The value of $\varepsilon$ is calculated by the equation:

$$\varepsilon = \frac{\rho_c - \rho_b}{\rho_c}$$

(4)

where $\rho_c$ is the density of the catalyst (lb/ft$^3$) and $\rho_b$ is the density of packed bed (lb/ft$^3$). The value of $\varepsilon$ calculated from repeated experimental procedure was 0.32 lb/ft$^3$.

3.2. Catalyst Characterization

Morphology of the catalysts was investigated by SEM at various magnifications. SEM images show the spinel geometry of MnFe$_2$O$_4$ while hexagonal rod shape was observed for the Bi-doped sample. The average grain size of the samples was calculated by AGI from SEM as MnFe$_2$O$_4$: 67 nm/Bi-MnFe$_2$O$_4$: 84.5 nm, as shown in Figure 2a,b,e,f. SEM analysis of the catalysts also show characteristic features of both the samples about their surface morphology. A typical SEM micrograph of MnFe$_2$O$_4$ presented in Figure 2a,b shows the presence of small grains of uniform size [28]. In Figure 2e,f, the appearance of needlelike fine filaments over the spherical granules of MnFe$_2$O$_4$ provides good confirmation for Bi-doping [24]. The surface of both catalysts has good porous nature and has edges, corners, step edges, step corners and defects due to bismuth doping, which act as active sites in catalytic bed for gaseous reactants. Surface area of the nanoparticles was determined by a BET surface area analyzer. BET surface area of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ was 32 m$^2$g$^{-1}$ and 29 m$^2$g$^{-1}$, respectively. The decrease in surface area of Bi-MnFe$_2$O$_4$ reveals that Bi-doping blocks the surface pores of MnFe$_2$O$_4$ as shown in Table 1. Figure 2c,d,g,h shows the EDX spectra and elemental analysis of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ respectively. The results confirmed the presence of constituent elements Fe, Mn and O along with the presence of Bi content in case of doping.

XRD patterns of both samples are given in Figure S2a. Diffraction peaks appear at (111), (220), (311), (400), (422), (511) and (440) for MnFe$_2$O$_4$ in Figure S2a pattern (a), which shows the spinel structure of MnFe$_2$O$_4$ [28] while the comparable additional peaks (200), (211), (420), (421), (332), (521) and (541) in Figure S2a pattern (b) show the formation of secondary phases for Bi-MnFe$_2$O$_4$ [24]. The observed peaks indicate the preparation of single-phase spinel MnFe$_2$O$_4$ by the coprecipitation method, whereas for Bi-doped samples the additional reflection arises indicating the formation of secondary phases as shown in Table 1. The particle size of MNPs was calculated by Scherrer’s equation. The average particle size calculated for MnFe$_2$O$_4$ was 66.5 nm while for BiMnFe$_2$O$_4$ was 83.4 nm. Figure S2b, (curve a and b) shows the FTIR spectra of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ samples respectively. It is clear from the spectra that there is no large difference in the infrared spectra of the two samples. Absorption peaks below 1000 cm$^{-1}$ in both samples indicate the presence of ferrites. The absorption peaks between 400 and 700 cm$^{-1}$ in Figure S2b, (curve
a) are due to the stretching vibrations of (Fe-O) which indicate the formation of ferrites with spinel structure [29]. The absorption band at 557 cm$^{-1}$ in Figure S2b, (curve b) shows the presence of Bi-O (stretching) [30] which indicates the doping of Bi over MnFe$_2$O$_4$.

Figure 2. (a,b): SEM images of MnFe$_2$O$_4$ at different magnifications; (c,d): EDX spectra and elemental analysis of MnFe$_2$O$_4$; (e,f): SEM images of Bi doped MnFe$_2$O$_4$ at different magnifications; (g,h): EDX spectra and elemental analysis of Bi-MnFe$_2$O$_4$.

Table 1. Morphology, particle size and surface area of catalysts.

| Entry | Catalysts      | Morphology        | Size (nm) * | BET (m$^2$/g) |
|-------|----------------|-------------------|-------------|---------------|
| 1     | MnFe$_2$O$_4$  | Spinel            | 64.1        | 32            |
| 2     | BiMnFe$_2$O$_4$| Hexagonal/spinel  | 79.3        | 29            |

* Particle size calculated from XRD has good agreement with particle size calculated by AGI method.
3.3. Catalytic Activity

In the recent study hydrogenation of carbon dioxide to VPs over magnetic nanoparticles was carried out in FPFBR under desired reaction parameters (pressure: 1 atm, temp: 413–563K, GHSV: 22,000 h\(^{-1}\), run time: 120 min, feed ratio 3/1: H\(_2\)/CO\(_2\)). The distribution of VPs was dependent on temperature, pressure, feed ratio of H\(_2\)/CO\(_2\) and gas hourly space velocity (GHSV)\([31,32]\). Toyir et al. [33] obtained different VPs (CO, C\(_2\)H\(_4\), C\(_3\)H\(_6\)O\(_2\), CH\(_4\) and CH\(_3\)OH) with Cu-Ga/ZnO catalyst under reaction parameters (0.5 g), (3/1: H\(_2\)/CO\(_2\)), (543 K), (19.7 atm) and (150 mL/min). Here, we detected different VPs in the model reaction as given in the Table 2. However, further study focused only on the optimization of parameters for methanol synthesis from direct hydrogenation of carbon dioxide.

Table 2. Comparative study for valuable organic products under different reaction parameters.

| VPs Conditions: Cat, \(^{1}\) FR, \(^{2}\) T, \(^{3}\) P, \(^{4}\) GFR | Conv\(^{b}\) | Sel | Ref |
|---|---|---|---|
| H\(_2\)COCH\(_3\), CH\(_3\)OH | CuO-ZnO-Al\(_2\)O\(_3\)-ZrO\(_2\)+HZSM-5 (1), 3/1, 473, 49.3, 100 | 15.8/74 | [31] |
| CO | 20CuZnO-350-200 (0.8), 9/1, 498, 1,100 | 14/77.3 | [32] |
| CH\(_3\)OH | 5\%Pd/ZnO (0.5), 3/1, 523, 19.7, 30 | 10.7/39 | [34] |
| CH\(_3\)OH | Cu/ZnO/Al\(_2\)O\(_3\) (1), 7/2, 473, 29.6, 150 | 4/68 | [14] |
| CO | Cu/Al\(_2\)O\(_3\) (0.17), 3.8/1, 553, 355, 0.011 | 29/91.7 | [31] |
| H\(_2\)COCH\(_3\) | Cu/Al\(_2\)O\(_3\) (0.17), 3/1, 553, 98.7, 0,011 | 21/8.5 | [16] |
| C\(_2\)H\(_4\)O\(_2\) | Cu/Al\(_2\)O\(_3\) (0.17), 3.8/1, 443, 355, 0.011 | 3/3.1 | |
| CH\(_3\)OH | Cu/Al\(_2\)O\(_3\) (0.17), 3/1, 473, 355, 0.011 | 8/48 | |
| CH\(_3\)OH | Bi-MnFe\(_2\)O\(_4\) (2/chamber), 3/1, 493, 1, 40 | 22/61 | |
| C\(_2\)H\(_4\)O | Bi-MnFe\(_2\)O\(_4\) (2/chamber), 3/1, 563, 1, 40 | 6/33 | |
| H\(_2\)COCH\(_3\) | Bi-MnFe\(_2\)O\(_4\) (2/chamber), 3/1, 543, 1, 40 | 4/19 | Present work |

* Valuable organic products detected in the hydrogenation of CO\(_2\) under different reaction parameters: \(^{1}\) catalyst (g), \(^{2}\) feed ratio (H\(_2\)/CO\(_2\)), \(^{3}\) temperature (K), \(^{4}\) pressure (atm), \(^{5}\) gas flow rate (mL/min), \(^{6}\) conversion (%), \(^{b}\) selectivity (%).

Reaction parameters for efficient catalytic activity and selectivity of the catalysts were comprehensively studied. Hasliza et al. [35] have reported an optimum selectivity of methanol formation (70%) per hour from direct CO\(_2\) hydrogenation over Pd/ZnO catalysts at 523 K and 20 bar in a fixed-bed flow reactor. Similarly, in the current study, the effect of reaction duration on the production rate of methanol was explored under the same set of reaction conditions. It was found that the production rate of MeOH attained steady state after 90 min, so this was used as the optimal time for collection of further data. While selectivity to methanol decreases up to 60%, which is due to the appearance of other products like C\(_2\)H\(_4\)O and H\(_2\)COCH\(_3\), a very small amount of carbon monoxide was detected at TCD at our temperature zone.

Generally, increase in catalyst loading increases the rate of MeOH production [32]. The effect of catalyst loading was studied for the hydrogenation of CO\(_2\) to MeOH using 0.75 mol/h flow of H\(_2\) and 0.25 mol/h flow of CO\(_2\) at 493 K and data was collected after 90 min (for each individual study) under atmospheric pressure, as shown in Figure S3. The rate of MeOH production increased with the increase of catalyst loading up to some extent. The maximum product was observed at a dose of 2 g per reactor chamber (0.11 g per finger projected fixed-bed). Therefore, 2 g/chamber of catalyst was utilized for all experiments otherwise specified. The justification for this loading limit is that the finger-projected fixed beds are covered by the catalyst with a maximum quantity of 2 g/chamber and best ratio of reactant molecule to catalyst particles. It was found that the doped nanoparticle (Bi-MnFe\(_2\)O\(_4\)) shows better catalytic properties and selectivity for the reaction throughout the study as shown in Figure S4. The maximum selectivity of MeOH from CO\(_2\) under atmospheric pressure and 3/1 feed ratio of H\(_2\)/CO\(_2\) was reported at low temperature.
hydrogenation. Ramirez et al. [32] reported the effect of temperature on selectivity for MeOH production at atmospheric pressure. They noticed decrease in selectivity up to elevated temperature, because high temperature favors the production of some other compounds during CO$_2$ hydrogenation [14]. The reaction of CO$_2$ hydrogenation for the purpose of MeOH production is usually favorable at lower temperatures because the product appears with a negative enthalpy ($\Delta H = -94.4 \text{ kJ mol}^{-1}$). In this study, the temperature was gradually increased in equal intervals from 413 to 563 K, MeOH formation first increased with the increase in temperature and then showed a gradual decline due to the appearance of C$_2$H$_4$O$_2$, H$_3$COCH$_3$ and CO, as shown in Figure 4.

**Figure 3.** Time profile study of CO$_2$ conversion to MeOH by MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ catalysts. Reaction conditions: pressure: 1 bar, temp: 493 K, GHSV: 22,000 h$^{-1}$, feed ratio 3/1: H$_2$/CO$_2$.

It has been confirmed that MNPs can be used as effective catalysts for CO$_2$ conversion to MeOH. Dependence of rate of reaction on temperature was calculated from Arrhenius equation. The apparent activation energy ($E_a$) was calculated as 115.2 kJ mol$^{-1}$ and 100 kJ mol$^{-1}$ for MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ respectively. Yang et al. [36] have reported an amount of 133 kJ mol$^{-1}$ activation energy ($E_a$) for the catalytic hydrogenation of CO$_2$ to MeOH at low temperature (403–453 K) and a total pressure of 6 bar over copper catalysts which is in good agreement with recent study as shown in Table S1, entry 1. MnFe$_2$O$_4$ has shown efficient catalytic activity in a number of gas phase chemical reactions [37]. Subsequent studies have shown that doping of various other metals over MnFe$_2$O$_4$ considerably increases the catalytic properties of such nanoparticles [38], due to their synergistic effect. In this study we found that doping of Bi in smaller concentration increased the catalytic properties of MnFe$_2$O$_4$. The interaction of metal and metal oxide proves phase modification for the good catalytic activity of Bi-MnFe$_2$O$_4$. Throughout the study Bi-MnFe$_2$O$_4$ shown better catalytic performance but with reduction in magnetic properties. Figure S4 shows
comparison of the catalytic activity of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ at different time intervals and temperature values.

![Figure 4](image)

**Figure 4.** Effect of temperature on the rate of MeOH production and selectivity. Reaction conditions: pressure: 1 bar, GHSV: 22,000 h$^{-1}$, data collected after 90 min, feed ratio: 3/1 H$_2$/CO$_2$.

### 3.4. Stability of Catalysts

As discussed earlier, MnFe$_2$O$_4$ can be reused several times for the model reaction due to its hydrophobic nature. A series of experiments was carried out under the optimal set of parameters in order to check the stability and recyclability of the catalysts. Both catalysts showed stable catalytic activity after being used for extended time (72 h) and recycling for five consecutive cycles. MNPs were recovered by removing the external magnets from the grooves of the fingers after the completion of reaction. Doped MNPs showed their enhanced catalytic activity under the described set of parameters. Figure 5 shows the life span of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ for CO$_2$ conversion to MeOH.

![Figure 5](image)

**Figure 5.** Life span/reusability of MnFe$_2$O$_4$ and Bi-MnFe$_2$O$_4$ for CO$_2$ conversion to MeOH. Reaction conditions: pressure: 1 bar, temp: 493 K, extended time: 4320 min, GHSV: 22,000 h$^{-1}$, feed ratio: 3/1 H$_2$/CO$_2$, (a) no. of runs: 5 (data collected after 90 min).
3.5. Comparative Study of Different Reactors

Several types of reactors have been used for catalytic hydrogenation of CO\textsubscript{2} to MeOH so far. The higher efficiency of recently used FPFBR shows that fixed-bed reactors can be modified in many ways for the utilization of CO\textsubscript{2} to various valuable organic products. The greater advantage of recently used FPFBR over the conventional fixed-bed reactors is due to the fact that the gas molecules pass over 18 fixed beds in a single reactor chamber (90 beds in five chambers) in comparison to a single or few beds of the conventional fixed-bed reactors. This means that the reactant molecules have greater chance to collide with catalyst particles over 18 beds/chamber and hence maximum reaction rate is expected. Moreover, mild operational conditions like atmospheric pressure and low temperature dominate the reactor over the conventionally used fixed-bed reactors. Marina and coworkers [Table S1, entry 4] have used a heterogeneous model of fixed-bed reactor in which they performed direct catalytic hydrogenation of CO\textsubscript{2} to MeOH over Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst under pressure up to 100 bar and temperature of 473–533 K. They achieved maximum yield with an activation energy value of 44 kJ mol\textsuperscript{-1}. Similarly, fixed-bed reactors have been used for the catalytic hydrogenation of CO\textsubscript{2} to MeOH over Cu/ZnO catalyst at 525–575 K and 5 bar. They observed maximum yield at activation energy 116.7 kJ mol\textsuperscript{-1} is presented in Table S1, entry 6. Elsewhere a fixed-bed reactor was used for CO\textsubscript{2} over Pd-CuZnO at 503–543 K and 45 bar. The observed activation energy value was 31 kJ mol\textsuperscript{-1} in their study, as presented in Table S1, entry 10. The reported literature tabulated in the Table S1 is a stimulus for modification in fixed-bed reactor for magnetic nanoparticles with excellent performance trials.

4. Conclusions

The calculated efficiency of the reactor (74%) shows the usefulness of the self-architecture reactor (finger-projected fixed-bed reactor) for the catalytic hydrogenation of carbon dioxide (CO\textsubscript{2}) to VPs using magnetic nanoparticles (MnFe\textsubscript{2}O\textsubscript{4}/Bi-MnFe\textsubscript{2}O\textsubscript{4}) as catalysts. The fixed-bed reactor was modified for magnetic nanoparticles with multifocused points, such as (i) availability of many reaction cores, (ii) enhancing collision probability of reactant/catalysts molecules, (iii) easy handling and mild conditions of operation, (iv) easy recovery of catalysts, and (v) performance trial efficiency. Furthermore, high activity and selectivity were obtained at 493 K, when MnFe\textsubscript{2}O\textsubscript{4} was calcined at 513 K (0.5 °C/min) for 4 h and reduced at 553 K for 2 h, while in the case of Bi-MnFe\textsubscript{2}O\textsubscript{4}, calcination was performed at 753 K (0.5 °C/min) for 6 h and reduced at 553 K for 2 h. Further reduction modified mix phases of metal/metal oxide system which indeed enhanced the catalytic activity. Bismuth doping no doubt increases the catalytic activity but decreases the magnetic properties of the MnFe\textsubscript{2}O\textsubscript{4}. The magnetic properties were retrieved by high temperature treatment for extended time (6 h). In short, a finger-projected fixed-bed reactor in combination with magnetic nanoparticles will be an excellent alternative for industrial conversion of CO\textsubscript{2} to MeOH to boost the world economy and mitigate greenhouse gases.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11050592/s1, Figure S1: Schematic diagram of reaction setup and finger-projected fixed-bed reactor (FPFBR) used for hydrogenation of CO\textsubscript{2} to methanol; Figure S2: a, XRD pattern of MnFe\textsubscript{2}O\textsubscript{4} (pattern a), Bi-MnFe\textsubscript{2}O\textsubscript{4} (pattern b), b, FTIR spectra of MnFe\textsubscript{2}O\textsubscript{4} (curve a), Bi-MnFe\textsubscript{2}O\textsubscript{4} (curve b); Figure S3: Effect of catalyst loading per chamber on the rate of CO\textsubscript{2} hydrogenation to MeOH; Figure S4: Comparison of the catalytic activity of MnFe\textsubscript{2}O\textsubscript{4} and Bi-MnFe\textsubscript{2}O\textsubscript{4} for CO\textsubscript{2} conversion to MeOH; Table S1: Different types of reactors used for hydrogenation of CO\textsubscript{2} to MeOH under various reaction conditions.

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Catalysts

11. Rahimpour, M. A two-stage catalyst bed concept for conversion of carbon dioxide into methanol. Fuel Process. Technol. 2019, 38, 98–111. [CrossRef]

12. Liu, X.-M.; Lu, G.Q.; Yan, Z.-F.; Beltramiini, J. Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO₂. Ind. Eng. Chem. Res. 2003, 42, 6518–6530. [CrossRef]

13. Din, I.U.; Usman, M.; Khan, S.; Helal, A.; Alotaibi, M.A.; Alharthi, A.I.; Centi, G. Prospects for a green methanol thermo-catalytic process from CO₂ and recent strategies for alternative fuels through photocatalytic reduction with titania-based materials. J. Environ. Chem. Eng. 2017, 5, 102813. [CrossRef]

14. Bukhtiyarova, M.; Lunkenbein, T.; Kähler, K.; Schlögl, R. Methanol Synthesis from Industrial CO₂ Utilization by Environmental-merit-order curves. Environ. Sci. Technol. 2016, 50, 1093–1101. [CrossRef]

15. Tursunov, O.; Kustov, L.; Kustov, A. A Brief Review of Carbon Dioxide Hydrogenation to Methanol Over Copper and Iron Based Catalysts. Oil & Gas Sci. Technol. Rev. d’IFP Energ. Nov. 2017, 72, 30. [CrossRef]

16. Bansode, A.; Tidona, B.; von Rohr, P.R.; Urakawa, A. Impact of K and Ba promoters on CO₂ hydrogenation over Cu/Al₂O₃ catalysts at high pressure. Catal. Sci. Technol. 2013, 3, 767–778. [CrossRef]

17. Arab, S.; Commenge, J.-M.; Portha, J.-F.; Elkamel, A.; Lohi§, A. Dynamic Optimization Strategies of a Heterogeneous Reactor for CO₂ Utilization by Environmental-merit-order curves. Environ. Sci. Technol. 2016, 50, 1093–1101. [CrossRef]

18. Zhang, J.; Wang, H.; Dalai, A.K. Effects of metal content on activity and stability of Ni-Co bimetallic catalysts for CO₂ reforming of CH₄. Appl. Catal. A Gen. 2008, 339, 121–129. [CrossRef]

19. Sugawa, S.; Sayama, K.; Okabe, K.; Arakawa, H. Methanol synthesis from CO₂ and H₂ over silver catalyst. Energy Convers. Manag. 1995, 36, 665–668. [CrossRef]

20. Hong, Z.S.; Cao, Y.; Deng, J.F.; Fan, K.N. CO₂ hydrogenation to methanol over Cu/ZnO/Al₂O₃ catalysts prepared by a novel gel-network-co-precipitation method. Catal. Lett. 2002, 82, 37–44. [CrossRef]

21. Chary, K.V.; Kumar, C.P.; Rao, P.V.R.; Rao, V.V. Dispersion and reactivity of V₂O₅ catalysts supported on Al₂O₃–ZrO₂. Catal. Commun. 2004, 5, 479–484. [CrossRef]

22. Dominguez, J.; Hernandez, J.; Sandoval, G. Surface and catalytic properties of Al₂O₃–ZrO₂ solid solutions prepared by sol–gel methods. Appl. Catal. A Gen. 2000, 197, 119–130. [CrossRef]

23. Yoon, T.-J.; Lee, W.; Oh, Y.-S.; Lee, J.-K. Magnetic nanoparticles as a catalyst vehicle for simple and easy recycling. New J. Chem. 2003, 27, 227–229. [CrossRef]

24. Venkataraju, C.; Satishkumar, G.; Sivakumar, K. Effect of bismuth on the properties of Mn ferrite nanoparticles prepared by co-precipitation method. J. Mater. Sci. Mater. Electron. 2012, 23, 1163–1168. [CrossRef]
25. Prabhakaran, T.; Mangalaraja, R.; Denardin, J.C.; Jiménez, J.A. The effect of calcination temperature on the structural and magnetic properties of co-precipitated CoFe$_2$O$_4$ nanoparticles. J. Alloys Compd. 2017, 716, 171–183. [CrossRef]

26. Zhang, Y.; Fei, J.; Yu, Y.; Zheng, X. Study of CO$_2$ Hydrogenation to Methanol over Cu-V/γ-Al$_2$O$_3$ Catalyst. J. Nat. Gas Chem. 2007, 16, 12–15. [CrossRef]

27. Zhou, X.; Su, T.; Jiang, Y.; Qin, Z.; Ji, H.; Guo, Z. CuO-Fe$_2$O$_3$-CeO$_2$/HZSM-5 bifunctional catalyst hydrogenated CO$_2$ for enhanced dimethyl ether synthesis. Chem. Eng. Sci. 2016, 153, 10–20. [CrossRef]

28. Han, A.; Liao, J.; Ye, M.; Li, Y.; Peng, X. Preparation of nano-MnFe$_2$O$_4$ and its catalytic performance of thermal decomposition of ammonium perchlorate. Chin. J. Chem. Eng. 2011, 19, 1047–1051. [CrossRef]

29. Jacintha, A.M.; Umapathy, V.; Neeraja, P.; Rajkumar, S.R.J. Synthesis and comparative studies of MnFe$_2$O$_4$ nanoparticles with different natural polymers by sol–gel method: Structural, morphological, optical, magnetic, catalytic and biological activities. J. Nanostruct. Chem. 2017, 7, 375–387. [CrossRef]

30. Abraham, S.D.; David, S.T.; Bennie, R.B.; Joel, C.; Kumar, D.S. Eco-friendly and green synthesis of BiVO$_4$ nanoparticle using microwave irradiation as photocatalyst for the degradation of Alizarin Red S. J. Mol. Struct. 2016, 1113, 174–181. [CrossRef]

31. Yang, H.; Zhang, C.; Gao, P.; Wang, H.; Li, X.; Zhong, L.; Wei, W.; Sun, Y. A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. Catal. Sci. Technol. 2017, 7, 4580–4598. [CrossRef]

32. Díez-Ramírez, J.; Dorado, F.; De La Osa, A.R.; Valverde, J.L.; Sánchez, P. Hydrogenation of CO$_2$ to Methanol at Atmospheric Pressure over Cu/ZnO Catalysts: Influence of the Calcination, Reduction, and Metal Loading. Ind. Eng. Chem. Res. 2017, 56, 1979–1987. [CrossRef]

33. Toyir, J.; De La Piscina, P.R.; Llorca, J.; Fierro, J.-L.G.; Homs, N. Methanol synthesis from CO$_2$ and H$_2$ over gallium promoted copper-based supported catalysts. Effect of hydrocarbon impurities in the CO$_2$/H$_2$ source. Phys. Chem. Chem. Phys. 2001, 3, 4837–4842. [CrossRef]

34. Iwasa, N.; Masuda, S.; Ogawa, N.; Takezawa, N. Steam reforming of methanol over Pd/ZnO: Effect of the formation of PdZn alloys upon the reaction. Appl. Catal. A Gen. 1995, 125, 145–157. [CrossRef]

35. Wang, Y.; Kattel, S.; Gao, W.; Li, K.; Liu, P.; Chen, J.G.; Wang, H. Exploring the ternary interactions in Cu–ZnO–ZrO$_2$ catalysts for efficient CO$_2$ hydrogenation to methanol. Nat. Commun. 2019, 10, 1166. [CrossRef] [PubMed]

36. Yang, Y.; Mims, C.A.; Mei, D.; Peden, C.H.; Campbell, C.T. Mechanistic studies of methanol synthesis over Cu from CO/CO$_2$/H$_2$/H$_2$O mixtures: The source of C in methanol and the role of water. J. Catal. 2013, 298, 10–17. [CrossRef]

37. Yang, Y.; Liu, J.; Zhang, B.; Liu, F. Density functional theory study on the heterogeneous reaction between HgO and HCl over spinel-type MnFe$_2$O$_4$. Chem. Eng. J. 2017, 308, 897–903. [CrossRef]

38. Wang, Z.; Ma, H.; Zhang, C.; Feng, J.; Pu, S.; Ren, Y.; Wang, Y. Enhanced catalytic ozonation treatment of dibutyl phthalate enabled by porous magnetic Ag-doped ferrospinel MnFe$_2$O$_4$ materials: Performance and mechanism. Chem. Eng. J. 2018, 354, 42–52. [CrossRef]