١	An Optimized Approach for Methanol Production from CO ₂ by a Novel
۲	Magnetic MIL-101(Fe)-NH2-GO Photocatalyst via Response Surface
٣	Methodology
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٥	Mohammad Shahryari Mazraeh Shahi ¹ , Leila Vafajoo ^{1, 2*} , Mohammad Kazemeini ^{3*}
٦	¹ Chemical and Polymer Engineering Department, ST. C., Islamic Azad University, Tehran, Iran
٧	² Nanotechnology Research Center, ST. C., Islamic Azad University, Tehran, Iran
٨	³ Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box b11365-
٩	94655, Tehran, Iran
۱.	*: Corresponding Authors emails: vafajoo@iau.ac.ir and kazemini@sharif.edu
۱۱	Abstract
۱۲	Global warming, fueled by rising greenhouse gas concentrations in the atmosphere, stands
۱۳	as a significant environmental challenge in the 21st century. The mounting concerns have
١٤	sparked a surge in research efforts aimed at harnessing CO2 conversion into valuable
10	compounds. This investigation delves into the synthesis and characterization MI-101(Fe)-
١٦	NH2-GO-Fe3O4 photocatalyst, particularly focusing on the impact of NH2 surface
١٧	modification on MIL-101(Fe) in methanol production enhancement. The results notably
١٨	indicate an enhancement in the performance of the photocatalyst following the surface
۱۹	modification of MIL-101(Fe). Notably, MIL-101(Fe)-NH2-GO with 10% Fe3O4
۲.	photocatalyst exhibits the narrowest band gap at 1.68 eV, indicating superiority in catalytic
۲۱	activity. The study further establishes a p-n heterojunction in MIL-101(Fe)-NH2-GO with
22	10% Fe ₃ O ₄ photocatalyst, signifying advanced catalytic properties. An experimental
۲۳	framework utilizing design of experiment was implemented to investigate the influence of

various factors, including time, catalyst dosage, weight percentage of Fe₃O₄, and pH, on
operational parameters, with the aim of optimizing these variables. The study achieved
methanol production of 2978.25 mg/L under optimal conditions, using 0.46 g of MIL101(Fe)-NH₂-GO with 7.82% Fe₃O₄ photocatalyst in 107 min at pH 5. Further examination
of the process through GC-MS identified methanol, formamide, and formaldehyde as the
main products.

Keywords: CO₂ capture; MIL-101(Fe)-NH₂-GO; Optimization; Methanol; Fuel

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^{γγ} **1. Introduction**

٣٣ The 21st century is the era of severe concern of the world community about the excessive ٣٤ emission of CO₂ gas [1, 2]. The development and progress of the global industry has led to a ۳0 greater demand for energy and the subsequent use of fossil fuels as a source of energy supply; 37 Therefore, in addition to the environmental challenges, the lack of energy should also be ٣٧ considered. Achieving a comprehensive solution is a controversial point in many researches. ۳۸ One of the relatively comprehensive solutions that has the ability to supply fuel and reduce ۳٩ CO_2 at the same time is to use solar energy to convert [3-5]. Therefore, simultaneously ٤٠ removing CO₂ and turning it into a value-added product is a very ideal point. Currently, due ٤١ to the lack of a fully efficient catalyst, few CO₂ adsorption and conversion processes are used ٤٢ on a large industrial scale; Therefore, researchers are trying to invent suitable heterogeneous ٤٣ catalysts [6]. Metal-organic frameworks (MOFs) have garnered significant attention from ٤٤ researchers in recent years due to their wide range of modifiable structures and high porosity, 20 positioning them as a relatively novel category of catalysts. This research primarily focuses ٤٦ on exploring the properties and applications of MOFs in catalysis [7-12]. MOFs have found ٤٧ extensive application in various catalytic processes, including the degradation of pollutants, ٤٨ the production of hydrogen, and the reduction of CO2. As such, their photocatalytic activity ٤٩ can be increased by modifying ligands, using sensitizers, and connecting with 0. semiconductors [13, 14]. MOFs represent a fascinating category of porous crystalline hybrid structures characterized by their infinite regular frameworks comprising metal ions or 01 ٥٢ clusters at the core and organic binders serving as bridges. The diversity within these ٥٣ structures is evident in the variations observed in the links and branches, which can differ in 02 terms of size, shape, composition, geometry, and branching patterns [15]. The unique 00 properties of MOFs facilitate the development of a wide range of crystalline porous materials, ٥٦ highlighting their adaptability and potential utility across diverse applications [16].

٥٧ A group of MOFs utilized for the absorption of CO₂ gas falls under the category of Materials ٥٨ of Institute Lavoisier (MIL) [17, 18]. This particular class of MOFs was designed using ٥٩ trivalent metals as the central metal ions and carboxylic acid linkers. MILs have garnered ٦. significant attention for their exceptional gas absorption and separation capabilities, ٦١ stemming from their remarkable porosity, expansive cross-sectional area, and amenability to ٦٢ functionalization [19]. MIL-101 (Fe) stands out as a well-researched iron-based metal-٦٣ organic framework, featuring a core composed of iron ions and terephthalic acid ligands [20]. ٦٤ MIL-101 (Fe) is characterized by several remarkable features, including an exceptionally ٦٥ high specific surface area, substantial pore dimensions, and outstanding stability under both ٦٦ chemical and thermal conditions. The framework also exhibits unsaturated Lewis acid sites ٦٧ within its structure, imparting favorable characteristics for interactions with water ٦٨ molecules[21]. Owing to its distinct physicochemical properties and structural features, MIL-٦٩ 101 (Fe) finds wide-ranging applications in aqueous-phase absorption, storage, gas ٧. separation, and catalysis processes [22, 23]. Consequently, it finds utility across various ٧١ domains such as electrocatalysis [24], photocatalysis [21], adsorption [25], membranes [25], ۲۷ sensor technology [26], drug delivery systems [27], and other crucial fields of study. Through ٧٣ a comprehensive examination of these compounds, their utilization can be extended to ٧٤ catalytic reactions, gas separation processes, and CO₂ absorption mechanisms. It is ٧0 imperative to note that the polyamine chains within these frameworks should be kept ٧٦ relatively short, with the predominant basic groups being Lewis amines, responsible for the ٧٧ heightened absorption efficiency facilitated by the presence of these sites and nano-sized ٧٨ channels [27]. By amination MILs, they can be used in photocatalytic processes, gas ٧٩ separation and CO₂ adsorption. Of course, due to the narrow cavities of these structures, the ٨٠ polyamine chain should be short. Studies have shown that the absorption sites are the basic ۸١ groups of Lewis amines and high absorption is due to these sites and nano-sized channels ۸۲ [27-29].

٨٣ Natural graphene is a quasi-metal or a semiconductor with zero energy gap and also has very ٨ź high electron mobility at room temperature [18]. On the contrary, the broad dimension of the Λ٥ graphene oxide (GO) strip serves as a substantial electron acceptor species, thereby ۸٦ enhancing the efficiency of charge transfer processes within the material [30]. This ۸٧ phenomenon leads to a decrease in the recombination rate of electrons and holes, and as a $\lambda\lambda$ result, the overall efficiency of the photocatalytic system increases [31]. The physical and ٨٩ chemical properties of magnetic nanoparticles make them highly efficient tools in chemical ٩. and industrial fields. These unique properties stem from their nanoscale dimensions, which ۹١ imbue them with enhanced reactivity and responsiveness to external stimuli [32]. ٩٢ Furthermore, magnetic nanoparticles can be effectively dispersed in aqueous solutions or

٩٣ organic solvents through the utilization of surfactants, thereby facilitating the creation of ٩٤ magnetic liquids with diverse functionalities and potential uses in various fields [33]. 90 Magnetite Fe₃O₄ garners significant interest because of its distinctive and uncommon ٩٦ characteristics, along with its inherent utility in diverse fields [34]. Magnetite Fe₃O₄ exhibits a black color and demonstrates ferromagnetic characteristics at a macroscopic scale. The ٩٧ ٩٨ magnetic properties of magnetite nanoparticles have garnered significant interest, leading to 99 a wide array of applications including imaging, soft magnetic materials, photocatalysts, 1.. among others [35-37].

The main objective of this research is to conduct a comprehensive analysis of how the amination of MIL influences the photocatalytic conversion of CO_2 into fuel. This research will delve into the intricate details of how amination alters the catalytic properties of MIL, shedding light on its potential for enhancing the efficiency and selectivity of the CO_2 conversion process. Furthermore, the investigation will involve meticulous scrutiny and finetuning of the operational parameters using the RSM to achieve optimal conditions for the photocatalytic reaction.

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2. Experimental details

2.1 Materials

Iron (II) chloride (FeCl₂), Iron (III) chloride (FeCl₃), N,N-Dimethylformamide (DMF) (C₃H₇NO 99.8%), 2-Aminoterephthalic acid (NH₂-H₂ bdc) (C₈H₇NO₄), graphite, sodium nitrate (NaNO₃), Potassium permanganate (KMnO₄ 99%), H₂O₂ and sulfuric acid (H₂SO₄)

112 98%) were acquired from Merck.

2.2. Method

2.2.1 Synthesis of MIL-101(Fe)-NH₂

114 The preparation of MIL-101(Fe)-NH₂ initially commenced with the utilization of a 119 hydrothermal approach. Initially, 1.24 mmol of NH2-H2 bdc was combined with 7.5 mL of 17. DMF and placed on a magnetic stirrer for 30 minutes to produce a uniform solution referred 171 to as solution 1. Following this, 2.5 mmol of FeCl₃.6H₂O was mixed with 7.5 mL of DMF ١٢٢ and stirred for 30 minutes to yield solution 2. Subsequently, solution 1 was gradually added ۱۲۳ to solution 2 in a dropwise manner and agitated for a period of one hour to guarantee thorough 175 integration. The resultant mixture was subsequently transferred to an autoclave system and 170 exposed to an oven setting maintained at 110°C for a duration of 24 hours to facilitate the 177 formation of the desired product. The resulting orange-hued precipitate obtained was ۱۲۷ meticulously washed four times with DMF solvent at a temperature of 70 °C to remove any ۱۲۸ impurities or unreacted reagents. The washed precipitate was dried at 80°C for 2 hours.

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۲۰۰ 2.2.2 Synthesis of GO-Fe₃O₄

A total of 0.05, 0.1, and 0.2 g of Fe₃O₄ were amalgamated with 1 g of GO in a volume of 25 mL of deionized water, subjected to agitation for a duration of 6 h utilizing a mechanical shaker, subsequently followed by magnetic separation through centrifugation and the thermal drying of the resultant composite particles at a temperature of 80 °C in a controlled oven environment.

ידי 2.2.3 Synthesis of MIL-101(Fe)-NH₂-GO-Fe₃O₄

1 γ 0.1, 0.125, and 0.2 g of Go-Fe₃O₄ along with 1 g of MIL-101 (Fe)-NH₂ were combined in a

17A 20 mL aqueous solution and agitated using a shaker for a duration of 4 hours. Subsequently,

the resultant particles were isolated by means of a centrifugation process, followed by subjecting them to a final drying stage conducted within an oven maintained at a temperature of 60 °C. The utilization of such methodological steps ensures the successful synthesis and preparation of the desired composite materials with tailored properties for specific applications in various fields.

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150 2.2.4 Photocatalytic conversion of CO₂ into fuel

127 In this research, a discontinuous photocatalytic reactor made of quartz was designed and ١٤٧ built, and the performance of the synthesized catalysts with the highest specific level of ١٤٨ selectivity and photocatalytic conversion of CO₂ to methanol in the mentioned reactor was 129 investigated. Also, the effect of Fe₃O₄ weight percentage, photocatalyst mass, pH, time and 10. modification of MIL-101(Fe) surface by NH₂ in fuel production was studied and investigated. 101 In this manner, the photocatalysts that were synthesized, in conjunction with 50 mL of 101 distilled water, were subjected to UVA light emanating from a source with a power of 15 100 watts for varying durations. The objective was to validate the generation of methanol through 105 an examination of the samples utilizing Gas Chromatography with Flame Ionization 100 Detection (GC-FID) and Gas Chromatography-Mass Spectrometry (GC-MS) subsequent to 107 the completion of the photocatalytic procedure. The column used in this study was non-polar 101 and HP1. This experimental approach was crucial in determining the efficacy of the 101 photocatalysts in facilitating the conversion of methanol under the influence of UVA light.

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2.2.5 Design of Experiment

171 Response surface methodology (RSM) encompasses a suite of statistical techniques that are ١٦٢ adeptly utilized in the optimization of processes where the desired results are concurrently 177 affected by numerous variables [38, 39]. By employing this sophisticated statistical approach, 175 the necessity for conducting numerous experiments is mitigated significantly, leading to a 170 more efficient and cost-effective experimental design. Furthermore, RSM enables the 177 estimation of all coefficients within the quadratic regression model and facilitates the 177 assessment of the interplay between various factors, thereby providing valuable insights for ۱٦٨ process optimization and improvement [40, 41]. In the present study, the RSM based on BBD 179 was used. Additionally, this approach facilitated the optimization of combinations through ۱۷. the use of Design Expert 11 software. The effects of multiple variables, such as duration, 111 photocatalyst mass, percentage of Fe₃O₄ by weight, and pH levels, were thoroughly analyzed ۱۷۲ across three separate tiers to gain a holistic understanding of their impact on the aggregate ۱۷۳ results (Table 1). By employing this methodological framework, the researchers sought to ١٧٤ gain valuable insights into the intricate interplay between the specified variables and the 140 responses generated, thereby facilitating the optimization of the experimental conditions for ۱۷٦ enhanced efficacy and performance. The general response surface equation is a mathematical 177 representation that encapsulates the relationship between multiple input variables and an ۱۷۸ output response in a comprehensive manner, allowing for the exploration and analysis of 119 complex systems through a structured and systematic approach.

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_i \sum_{
(1)$$

Y denotes the expected outcome (Methanol synthesis (mg/L)), wherein Xi and Xj represent independent variables expressed in coded formats, $\beta 0$ indicates the constant term, and βi , $\beta j j$, and β_{ij} refer to the coefficients associated with linear, quadratic, and interaction effects, respectively, with k denoting the number of variables and ei symbolizing the error in the model.

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3 Results and discussion

3.1 Characterization

19. The XRD pattern identified for MIL-101(Fe)-NH₂ at 2 Θ angles of 9.35, 11.9, 18.65, 21.95, 191 24.24, 25.95, 33.35, and 36.0 aligns with the established reference standard, thereby 198 furnishing compelling evidence for the effective synthesis of MIL-101(Fe)-NH₂ with an 197 exceptionally high degree of purity. XRD patterns of MIL-101(Fe)-NH₂-GO-Fe₃O₄ 5%, 192 MIL-101(Fe)-NH₂-GO-Fe₃O₄ 10%, MIL-101(Fe)-NH₂-GO-Fe₃O₄ 20% at 2Θ 9.35, 11.9, 190 18.65, 21.95, related to MIL-101(Fe)-NH₂ and at 2 Θ 30.0, 35.5, 43.1, 53.6, 57.2, 62.5° ۱۹٦ corresponding to Miller plates (220), (311), (400), (422), (511) respectively and (440) ۱۹۷ correspond to Fe₃O₄ (Figure 1). Also, All diffraction peaks exhibit a strong correspondence ۱۹۸ with the typical characteristic diffractions associated with the Fe₃O₄ nanoparticles inverse 199 spinel configuration (JCPDS card no. 89-0691).

The results of FTIR for MIL-101 (Fe)-NH₂ are illustrated in Figure 2. The peak detected at approximately 3400 cm⁻¹ is attributed to the NH₂ functional group. Concurrently, the vibrational bands observed around 2900 cm-1 are associated with the methylene groups within the NH₂-H₂BDC benzene ring. The spectral peaks observed within the interval of 1300-1700 cm⁻¹ are associated with C-O vibrational modes. Furthermore, the stretching frequency corresponding to Fe-O is identified within the range of 541 cm⁻¹. All these results indicated that the coordination bond with NH₂-H₂BDC molecular Fe²⁺ ions is with the ۲۰۷ carbonyl group (C=O), not the amine group (NH₂). FTIR spectra for MIL101-(Fe) NH₂-GO-۲۰۸ Fe₃O₄ 5%, MIL-101 (Fe)-NH₂-GO-Fe₃O₄ 10%, MIL-101 (Fe) -NH₂-GO-Fe₃O₄ 20% ۲.9 catalysts are shown in Figure 2. The elastic band observable at 550 cm⁻¹ is associated with ۲١. the Fe-O stretching vibration found in Fe₃O₄, a significant compound in materials science. 117 This particular vibrational mode offers significant understanding regarding the bonding 717 attributes and structural characteristics of the Fe₃O₄ material. Furthermore, the stretching band located at 750 cm⁻¹ is specifically attributed to the out-of-plane C-H bending vibration ۲۱۳ 212 occurring in the H₂BDC benzene ring within the framework of MIL-101(Fe), a metal-organic 210 framework known for its diverse applications in catalysis and gas storage. The bands observed in the range of 1500-1600 cm⁻¹ are directly associated with the asymmetric 212 717 stretching vibrations of the carboxyl groups found in the H₂BDC ligand that is incorporated ۲۱۸ into the MIL-101(Fe) framework. In contrast, the vibrational band located within the range 219 of 1300-1400 cm⁻¹ is correlated with the symmetrical stretching of carboxyl moieties present ۲۲. within the identical ligand and framework assemblage. Furthermore, the absorption band 177 observed around 1600 cm⁻¹ can be ascribed to the vibrational dynamics linked to the C = C222 bonds inherent in GO, a multifaceted substance extensively investigated for its distinctive ۲۲۳ characteristics and prospective utilizations. Lastly, the peak detected at approximately 3400 ۲۲٤ cm⁻¹ is directly linked to the O-H stretching vibrations originating from water molecules that 220 are adsorbed onto the surface of GO, indicating the presence of surface functional groups and 222 interactions with the surrounding environment. This comprehensive analysis of various ۲۲۷ vibrational bands provides valuable information for characterizing and understanding the ۲۲۸ molecular structure and bonding interactions in these diverse materials.

۲۲۹ Raman spectroscopy played a crucial role in validating the structural phase of the catalysts ۲۳. under investigation. The analysis of the resulting peak derived from MIL-101 (Fe)-NH₂ ۲۳۱ revealed significant vibrational features, with the prominent vibrational band observed at 660 cm⁻¹ being attributed to NH₂ vibrations. Furthermore, additional vibrational bands at 1618, ۲۳۲ 1461, 1149, and 873 cm⁻¹ were detected, providing strong evidence for the presence of ۲۳۳ aromatic and dicarboxylate groups within the H2BDC framework. Upon further examination 272 170 of MIL-101 (Fe)-NH₂-GO-Fe₃O₄ photocatalysts with varying compositions (5%, 10%, and ۲۳٦ 20%), it was observed that the vibrational bands associated with MIL-101 (Fe)-NH₂ remained ۲۳۷ consistent, indicating the presence of NH₂ vibrations, aromatic groups, and dicarboxylate moieties from H₂BDC. Additionally, a distinct vibrational band at 1350 cm⁻¹ corresponding ۲۳۸ ٢٣٩ to GO and Fe₃O₄ was identified, as illustrated in Figure 3 of the study.

۲٤٠ A SEM was utilized to analyze the surface structure of the photocatalyst particles, revealing 251 that the iron oxide particles exhibit a spherical morphology. Furthermore, these particles are ٢٤٢ found to be within the nanoscale range and have been successfully integrated onto GO, MIL-٢٤٣ 101(Fe), and MIL-101-(Fe) NH₂. Moreover, the research findings have established that the 755 average dimensions of the GO and Fe₂O₃ sheets are approximately 30 and 25 nm, ٢٤0 respectively, as illustrated in Figure 4. This detailed examination sheds light on the precise 252 characteristics of the photocatalyst particles and their interactions with different materials, ۲٤٧ contributing significantly to the understanding of their behavior in various applications.

The Tauc curve, a commonly utilized approach for determining band gap, utilizes the reflectance spectrum in order to calculate this parameter. Tauc, Davies, and Matt proposed the relationship $(\alpha hv)1/n=A(hv-E_g)$ to clarify this phenomenon, where h symbolizes Planck's constant, v indicates the vibrational frequency, α represents the absorption coefficient, E_g 101 denotes the band gap, and A is the proportionality constant. In the particular scope of this 100 investigation, where direct transmission was deemed a suitable mechanism, the value of n 702 for the samples under scrutiny was established as 1/2. Subsequent to the collection of 100 reflectance spectrum data, it is converted into the Kobelka-Munk function. The F ($R\infty$) on 207 the vertical axis of this function is directly linked to the absorption coefficient. Following 201 this, the initial α in the Touch equation is substituted with F (R ∞) to derive the revised expression: $(F(R\infty)hv)^2 = A(hv-E_g)$. This transformation facilitates a more detailed analysis ۲٥٨ 209 of the band gap and absorption characteristics within the material.

The Kubelka-Munk equation is as follows:

(2)
$$F(R\infty) = (1-R^2)/2R$$

It is stated that R represents the reflectance spectrum in percentage. Then $(F(R\infty)hv)^2$ will be 222 ۲٦٣ drawn in terms of hv and the value of $(hv-(hv F(R\infty))^2)$ which is the tangent line at the bend 225 point of the curve will be drawn and using the tangent line Drawn from the previous step, the 220 energy value of the band gap is obtained from the point of intersection of the tangent line to 222 the curve and the horizontal axis. The DRS spectrum is obtained by shining light on the ۲٦۷ surface of a solid material and measuring the amount of diffuse reflection or absorption of ۲٦٨ the sample in terms of wavelength and comparing it with a standard sample. Diffuse 229 reflectance measurement is particularly suitable for evaluating the optical properties of ۲٧. powder materials. In this particular investigation, the determination of the band gap energy ۲۷۱ was carried out by analyzing the reflective spectrum that penetrates based on the Touch 777 equation. The outcomes of these calculations have been meticulously presented in both Table ۲۷۳ 2 and Figure 5 for comprehensive examination and reference. A relevant and noteworthy ۲۷٤ study conducted by Lin and colleagues in the year 2020 delved into the band gap 200 characteristics of MIL-101 (Fe), establishing it at a value of 2.41 eV initially [42]. 277 Interestingly, as the concentration of GO increased to 10 wt%, there was noted a reduction ۲۷۷ in the band gap, down to 2.17 eV. Upon careful analysis of the findings derived from the 211 present research endeavor, it is discerned that the MIL-NH₂-GO-Fe-10% catalyst exhibited ۲۷۹ the narrowest band gap, quantified at 1.68 eV. Conversely, the MIL-GO-Fe-20% ۲٨٠ photocatalyst was observed to possess the widest band gap, also measured at 1.76 eV. These ۲۸۱ comparative results shed light on the intriguing variations in band gap energies across ۲۸۲ different catalyst compositions, offering valuable insights for further exploration in this ۲۸۳ domain.

To further rationalize the effect of the amine functionalization of the undertaken material, Figure 6 is provided. It displays the UV-Vis absorption behaviors for the following samples: a) MIL101 (Fe)-GO-Fe₃O₄ 10% and b) MIL101 (Fe)-NH₂-GO-Fe₃O₄ 10%. Based upon the presented results, it is a foregone conclusion that, the MIL101 (Fe)-NH₂-GO-Fe₃O₄ 10% species has a higher absorption in the range of 300-450 nm compared to its nonfunctionalized counterpart. This means that, the former material indeed may become highly active under the UVA light irradiation which make it more desirable to use.

Based on the BET/BJH results, these isotherms are placed in the type (IV) isotherm group for mesoporous materials with hysteresis loops in the range of 0.6 (p/po(1 according to the IUPAC contract. The nitrogen adsorption-desorption technique is a crucial method utilized for analyzing the physical characteristics of particulate materials. This methodology is commonly employed to determine the surface area, volume, and pore sizes of nanostructured materials. The International Union of Pure and Applied Chemistry (IUPAC) has established specific criteria for categorizing pore sizes and adsorption isotherms, delineating six distinct

۲۹۸ classifications. The Type I isotherm is characteristic of microspores, whereas Types IV and 299 V are associated with mesoporous materials. In contrast, Types II, III, and VI denote various ۳.. other nanoporous structures. The current study performed nitrogen adsorption measurements 3.1 on degassed samples at a temperature of 77 K. The results from the BET and BJH analyses ۳.۲ are presented in Table 3. The findings indicate that the synthetic catalysts exhibit type IV ۳.۳ isotherms. Furthermore, the study indicates that the integration of GO and Fe₃O₄ into MIL-3.5 101(Fe) and MIL-101(Fe)-NH₂ leads to a reduction in surface area, pore volume, and average 7.0 pore diameter (see Figure 7 and Table 3).

۳.٦ TGA was employed to assess the thermal characteristics of the synthesized specimens within ۳.۷ a temperature interval of 25-800 °C at a rate of 10 min⁻¹. The TGA graph corresponding to ۳.۸ the produced samples is depicted in Figure 8. In short, the TGA analysis provides information ۳.٩ upon thermal stability, composition, decomposition stages, and residues, all of which are influenced by the material's chemical structure (bond strength, additives), physical structure 31. 311 (crystalline vs. amorphous), composition (fillers, impurities), and undergoing test conditions. 311 This ultimately helps to understand how do materials behave under heat, which is indeed 317 crucial for applications that require thermal resistance. According to the findings, the 312 observed 20% reduction in weight of GO within the temperature spectrum of 150-20 °C is 310 ascribed to the desorption of both surface and interlayer moisture. The thermal ranges of 200-317 300 °C are indicative of the degradation of epoxy functionalities within GO. In addition, a 311 34% weight loss is observed in the temperature range of 50-400 $^{\circ}$ C for the Go-Fe₃O₄ catalyst. 311 In the scenario involving MIL-101(Fe)-NH2-Go-Fe3O4 catalysts with loadings of 5%, 10%, 319 and 20%, the recorded weight reductions are 29.15%, 55.8%, and 60.98%, respectively. This ۳۲. increase in mass loss is clearly related to the added weight of Fe₃O₄.

۳۲۱ In the realm of semiconductor physics, the Matt-Schottky curve serves as a crucial tool for ۳۲۲ distinguishing between positive and negative type semiconductors based on the direction of ۳۲۳ the slope [14]. Specifically, a negative slope within this curve signifies a positive type ٣٢٤ semiconductor, while a positive slope indicates a negative type semiconductor, reflecting the 370 underlying electrical characteristics of the material under study. Furthermore, by analyzing 377 the potential of the flat strip in relation to the intersection of the linear portion of the Matt-322 Schottky curve, one can discern the nature of the semiconductor material, with a negative 377 slope once again pointing towards a positive type semiconductor, thereby providing valuable 379 insights into its behavior and properties. In Figures 9 a) and, b), it can be observed that the ۳۳. slopes associated with the Schottky matte data pertaining to GO and MIL-101-NH₂ exhibit 371 distinct characteristics: a positive slope for GO and a negative slope for MIL-101-NH₂. These ۳۳۲ opposing slopes serve as indicators of the respective types of conductivity, with the positive ۳۳۳ slope indicative of p-type conductivity and the negative slope suggestive of n-type ٣٣٤ conductivity. The outcomes of the study reveal that the MIL-101-(Fe) NH₂-GO-Fe₃O₄ 10% 370 photocatalyst displays both negative and positive slopes, suggesting the presence of a p-n 377 heterogeneous junction, as illustrated in Figure 9. This intricate heterojunction structure is a 327 key factor in determining the efficiency and effectiveness of the photocatalytic process in ۳۳۸ transforming CO₂ into methanol (Figure 9 c).

The figure illustrating the oscillating magnetometer graph of the nanocomposite MIL-101 (Fe)-NH₂-GO-Fe₃O₄ 10% is presented in Figure 10. Upon analysis of the oscillating magnetometer curve pertaining to the nanocomposite MIL-101 (Fe)-NH₂-GO-Fe₃O₄ 10%, it can be deduced that the curve exhibits characteristics such as a hysteresis loop, hysteresis, and anti-hysteresis field. These features are indicative of the fact that these materials 325 necessitate a magnetic field for magnetization and demonstrate a tendency to retain their 320 magnetic properties, thereby classifying them as materials possessing magnetic 321 characteristics. The particles within this nanocomposite exhibit properties of ٣٤٧ ferromagnetism, highlighting their magnetic nature. It is noteworthy that this compound ٣٤٨ displays a saturation magnetization value of 8.59 emu/g, underscoring its magnetic behavior 329 and further emphasizing its suitability for various applications involving magnetic properties. ۳0. In the pursuit of examining the influence of catalyst type on the process, a series of 501 experiments were meticulously carried out, leading to the revelation that among the tested 302 catalysts, the photocatalyst MIL-101 (Fe)-NH2-GO-Fe3O4 10% emerged as the most efficient 808 performer in the realm of methanol production, as visually depicted in Figure 11. 302 Accordingly, the BET/BJH results provided earlier revealed that, through modifying the 000 photocatalyst surface with the NH₂ group, the surface area was enhanced while the UV-Vis 307 analysis displayed that, the adsorption band gap was reduced. Both these findings confirmed 7°V that, an increase in the photocatalytic efficiency should be expected.

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3.2 Design of Experiment

In the present investigation, the impacts of various variables such as time in minutes, mass of catalyst in grams, Fe₃O₄ weight percentage in wt%, and pH were examined across three different levels. Following the completion of the experimental procedures, it was observed that the maximum rate of methanol production reached 2896 mg/L. The visual representation portrayed in Figure 12 a) offers a graphical depiction of the assumption related to the normal distribution of the data, suggesting a closeness to a Gaussian distribution. Moreover, the results indicate a conformity of the residuals to a The Gaussian distribution pattern reveals a 321 significant association between the outcomes derived from the experimental approach and 377 the values anticipated through statistical methodologies. This alignment between the 379 empirical data and statistically forecasted values signifies a high degree of agreement and ۳٧. dependability in the analysis that was carried out. These findings emphasize the robustness 371 of the relationship between the variables studied and the outcomes generated, enhancing the 3777 credibility and validity of the research findings. The thorough evaluation of the experimental ۳۷۳ variables at different levels has contributed to a deeper understanding of the factors ٣٧٤ influencing the production rate of methanol, shedding light on the intricacies of the catalytic 340 process involved in the study. Overall, the outcomes of this study underscore the importance 377 of integrating empirical observations with statistical analyses to achieve a comprehensive 777 and insightful understanding of the phenomena under investigation. In Table 4, the selected ۳۷۸ model, which is of the second degree of significance, proves to be suitable for the data. T and 379 P are interconnected, displaying similarities in statistical results. Larger T-Value absolute ۳٨. values correspond to smaller P-values, decreasing the likelihood of accepting the null 371 hypothesis. Empirical research is conventionally performed at a confidence threshold of ۳۸۲ 95%, where a P-value lower than 0.05 results in the dismissal of the null hypothesis. ۳۸۳ Regression seeks to minimize the disparity between actual and estimated values, with the ۳٨٤ objective of decreasing the total sum of squared residuals. R-Squared measures data 300 proximity to the regression line, with Adj R-Squared differing by considering only actual 377 independent variable effects on the dependent variable. The results of the ANOVA analysis ۳۸۷ indicated R-Squared and Adjusted R-Squared values of 0.9446 and 0.8529, respectively, ۳۸۸ which demonstrate the accuracy of the model. The significance of the factors pH, weight

percentage of Fe₃O₄, mass of the catalyst, and duration was assessed and ranked accordingly
(Figure 12 b).

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*****9**Y 3.3 Effect factors in photocatalytic conversion**

393 The effect of varying the dosage of the photocatalyst on the photocatalytic conversion of CO₂ 395 to methanol was examined by modifying the quantity of photocatalyst used, ranging from 890 0.1 to 1 g, under UVA irradiation. Upon 2 hours of UVA light exposure, Figure 13 illustrates 397 the progression of methanol production through photocatalysis. The production of methanol 391 exhibited a steady rise as the amount of catalyst increased from 0.1 to 0.5 g. An elevation in 391 the concentration of the photocatalyst in the solution is associated with a rise in the overall 399 quantity of active sites present on the surface of the photocatalyst, as demonstrated in Figure ٤.. 14. As a result, the effectiveness of the photocatalyst is improved owing to the increased ٤.١ availability of active sites for the conversion process. Figure 13 shows the amount of CO₂ ٤.٢ oxidative removal in a period of 2 h. The results of this investigation show that at the ٤٠٣ beginning of the reaction, it started with a relatively fast rate; until it reaches its highest level ٤.٤ after 2 h from the start of the reaction. The obtained results showed that the conversion rate ٤.0 is high in the initial times, which can be caused by the high catalytic level and the volume of ٤.٦ holes at the beginning of the work. With the passage of time and the transformation of the ٤٠٧ pollutant on the catalyst, the holes of the catalyst are gradually filled and the production ٤٠٨ efficiency decreases.

The reaction of reducing CO_2 to fuel at different initial pH is shown in Figure 13. Changing the pH has an obvious effect on the efficiency of those compounds. Higher yields were obtained when tests were performed in acidic solutions than in alkaline solutions (Figure 13). ٤١٢ Low pH enhances proton concentration, potentially lowering the theoretical reduction ٤١٣ potential of CO_2 by facilitating electron transfer via protonation, while carbonate and ٤١٤ bicarbonate species present greater reduction challenges and may act as hole scavengers, 210 rendering their effect negligible in acidic solutions, thereby favoring reductions at pH 5. In ٤١٦ order to examine the impact of varying weight percentages of Fe₃O₄, several different ratios ٤١٧ such as 5%, 10%, and 20% were introduced into the experimental reaction setup. The ٤١٨ findings revealed that elevating the weight percentage of iron oxide from 5% to 10% resulted 219 in a reduction in the band gap, alongside an enhancement in electron and hole transfer ٤٢٠ processes within the photocatalytic activity. Conversely, a subsequent increase in the weight ٤٢١ percentage of iron oxide from 10% to 20% led to an expansion in the band gap, coupled with ٤٢٢ a decline in both electron and hole transfer efficiencies (Figure 13). This experimental data ٤٢٣ highlights the critical role played by the weight percentage of Fe₃O₄ in influencing the ٤٢٤ photochemical properties of the reaction system.

270 Under optimal conditions, the synthesis of methanol was enhanced by the application of 0.46 577 g of MIL-101(Fe)-NH₂-GO-Fe₃O₄ (7.82%) as a photocatalyst over a time span of 107 ٤٢٧ minutes at a pH of 5, yielding a methanol concentration of 2978.25 mg/L (Figure 14). Under ٤٢٨ ideal experimental conditions, the photocatalytic conversion assessment was executed, and ٤٢٩ the findings revealed the generation of methanol quantified at 2965.06 mg/L, which is ٤٣٠ significantly aligned with the optimal parameters established by the computational software. ٤٣١ Also, Under ideal circumstances, the conversion efficiency and selectivity were assessed, ٤٣٢ revealing that the conversion efficiency of CO_2 to methanol attained a remarkable 91%, with ٤٣٣ a selectivity of 83%.

 $\mathfrak{L}^{\mathfrak{r}\mathfrak{l}}$ After performing the photocatalytic process in optimal conditions, the resulting sample was detected in the GC-MS machine. Based on the results, the sample contains methanol, formamide and formaldehyde (Figure 15).

٤٣٧

۲۸ **3.4 Mechanism of conversion**

٤٣٩ It is essential to comprehensively assess the photocatalytic reduction mechanism of CO₂ to ٤٤. methanol within aqueous systems, and to meticulously examine the potential reactions that 221 could transpire following the absorption of photons possessing specific energy levels. The ٤٤٢ magnitude of the band gap inherent to the employed photocatalyst is pivotal in the ٤٤٣ aforementioned process. In this investigation, the absorption of light photons, possessing 222 energy levels that are equivalent to or exceed the band gap energy of the 10% MIL-101(Fe)-220 NH₂-GO-Fe₃O₄ photocatalyst, triggers the excitation of electrons 227 (e) and the formation of hole pairs (h⁺), which are subsequently elevated to the unoccupied ٤٤٧ conduction band (CB) and the available valence band (VB), correspondingly, thereby ٤٤٨ enhancing the generation of energetic charge carriers that are integral to ensuing chemical 559 transformations. The highly energetic charge carriers, upon their generation, serve as 20. catalysts for a sequence of intricate redox reactions that ultimately culminate in the synthesis 201 of the target final products. In this framework, equations (3) and (4) delineate the specific 202 activation reactions pertinent to the 10% MIL-101(Fe)-NH2-GO-Fe3O4 semiconductor, 208 thereby enhancing the comprehension of the fundamental mechanisms operating within this 202 photocatalyst.

$\mathfrak{sov} \quad h^+e^- \longrightarrow h^+ VB + e^- CB$

501 Charge carriers produced via the photocatalytic mechanism may take several distinct 209 pathways, each characterized by specific mechanisms and interactions that ultimately ٤٦. increase the overall efficiency of photocatalytic processes. After a comprehensive review of 571 previous experimental research, it has been found that the products resulting from CO₂ 277 conversion often have significant similarities with traditional reactions, which are, however, ٤٦٣ limited to CO, HCOOH, HCHO, CH₃OH, CH₄ and C2H5OH, as a result of the potential of 272 these compounds. They emphasize to act as efficient reducing agents in a variety of chemical 270 reactions. The process of photocatalytic oxidation of water occurs as a result of the direct 277 exposure of light to the surface of the magnetic semiconductor MIL-101 (Fe)-NH₂-GO-Fe₃O₄ ٤٦٧ at a concentration of 10%. This mechanism leads to the generation of highly reactive ٤٦٨ hydroxyl radicals, while simultaneously promoting the production of hydrogen ions (H⁺) by 579 harnessing electrons obtained from the conduction of hydrogen bonds. Consequently, this ٤٧٠ mechanism enhances the overall photochemical efficiency of the system.

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٤٧٢ **4.** Conclusion

^{$\xi \vee \gamma$} The study focused on the photocatalytic conversion of CO₂ into fuel utilizing synthetic ^{$\xi \vee \xi$} catalysts. The analysis explored the effects of surface modification of MIL-101 (Fe) with ^{$\xi \vee \circ$} amine groups on methanol synthesis. The study focused on the photocatalytic conversion of ^{$\xi \vee \gamma$} CO2 into fuel utilizing synthetic catalysts. A thorough examination of the data revealed that ^{$\xi \vee \gamma$} the MIL-101(Fe)-NH₂-GO-Fe₃O₄ 10% photocatalyst establishes a p-n heterojunction. In ^{$\xi \vee \gamma$} optimal circumstances, methanol synthesis was accomplished utilizing 0.46 grams of MIL-^{$\xi \vee \gamma$} 101(Fe)-NH₂-GO-Fe₃O₄ (7.82%) as a photocatalyst over a duration of 107 minutes at a pH 5^{A} of 5, yielding a concentration of 2978.25 mg/L. Subsequent to the photocatalytic process conducted under optimal conditions, the product was identified through GC-MS. The examination indicated the detection of methanol, formamide, and formaldehyde within the specimen. In summary, it can be deduced from the findings that the transformation of CO₂ into methanol utilizing the MIL-101-(Fe) GO-Fe₃O₄ 7.82% catalyst constitutes a mild, efficient, and economically viable methodology.

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EAV Conflict of Interests

- ξ_{AA} On behalf of all contributors, the corresponding authors affirm that there are no conflicts of
- $\epsilon_{\Lambda 9}$ interest to disclose.
- ٤٩٠
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Figure 2.



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Figure 3.













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Vo. Vol Vol



V0T V0E



(a)



Figure 9.

VOV VOA VO9 V7.













Figure 13.





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Retention time (min)



Table 1. STD RUN Methanol production Time Mass of catalyst pН Fe₃O₄ (min) (g) (wt.%) (mg/L)0.3 0.3 0.3 12.5 0.3 12.5 0.3 0.1 0.5 12.5 12.5 0.3 0.1 12.5 0.3 0.3 0.3 0.3 12.5 0.3 12.5 0.1 12.5 0.5 12.5 0.1 12.5 0.5 0.1 12.5 0.3 12.5 0.3 12.5 0.5 0.5 12.5 0.1 12.5 0.5 0.3

Tables

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Table 2.

0.3

Photocatalyst	Band gap (eV)
MIL-GO-Fe-5%	1.90
MIL-GO-Fe-10%	1.82
MIL-GO-Fe-20%	1.87
MIL-NH ₂ -GO-Fe-10%	1.68
MIL-NH ₂ -GO-Fe-20%	1.76

	Table 3.		
Photocatalyst	a _s , BET (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)
MIL-101 (Fe)	342.92	0.32	3.74
GO	27.91	0.12	18.11
GO-Fe ₃ O ₄	41.88	0.19	4.92
MIL-101 (Fe)-NH ₂ -GO-Fe ₃ O ₄ 5%	164.96	0.09	8.11
MIL-101 (Fe)-NH ₂ -GO-Fe ₃ O ₄ 10%	196.53	0.18	8.2
MIL-101 (Fe)-NH ₂ -GO-Fe ₃ O ₄ 20%	134.87	0.05	6.45

Table 4.

Source	Sum of	Degree of	Mean	F-	P-value	
	squares	14			FTUD >F	0' '0' '
Model	5.377E+06	14	3.841E+05	32.69	< 0.0001	Significant
A-Time	2.619E+06	1	2.619E+06	222.88	< 0.0001	
B-Mass of catalyst	3.881E+05	1	3.881E+05	33.03	< 0.0001	
C-pH	7.570E+05	1	7.570E+05	64.42	< 0.0001	
D-Fe ₃ O ₄	3.968E+05	1	3.968E+05	33.77	< 0.0001	
AB	13456.00	1	13456.00	1.15	0.3056	
AC	76176.00	1	76176.00	6.48	0.0256	
AD	14161.00	1	14161.00	1.21	0.2938	
BC	21609.00	1	21609.00	1.84	0.2000	
BD	9604.00	1	9604.00	0.8173	0.3838	
CD	87025.00	1	87025.00	7.41	0.0186	
A ²	3.254E+05	1	3.254E+05	27.69	0.0002	
B ²	22533.33	1	22533.33	1.92	0.1913	
C ²	5808.00	1	5808.00	0.4943	0.4954	
D2	4.913E+05	1	4.913E+05	41.81	< 0.0001	
Residual	1.410E+05	12	11750.39			
Lack of Fit	1.408E+05	10	14080.20	138.95	0.072	Not significant
Pure Error	202.67	2	101.33			-
Cor Total	5.518E+06	26				

Leila Vafajoo's Technical Information

Dr. Leila Vafajoo is an Associate Professor in the department of Chemical and Polymer
 Engineering at the Islamic Azad University, South Tehran Campus. Her academic journey
 includes the completion of her <u>B.Sc.</u> and <u>M.Sc.</u> Degrees at the Sharif University of
 Technology in 1994 and 1996, respectively. Subsequently, she earned her PhD from
 Av. Amirkabir University of Technology (Tehran Polytechnique) on 2001. Dr. Vafajoo's
 extensive research portfolio is dedicated to the development, characterization, and

hvv physiochemical evaluation of adsorbents and catalysts designed for CO₂ capturing, as well as the treatment of industrial wastewater. Moreover, her scholarly pursuits encompass the mathematical modeling of chemical and environmental processes, alongside the innovation of lab-on-chip pollutant detection systems. Her multidisciplinary work significantly contributes to addressing of pressing global challenges of environmental sustainability and process engineering.

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Mohammad Kazemeini's Technical Information

٨٨. Mohammad Kazemeini received his B.E. degree from the Univ. of Minnesota at Minneapolis ۸۸۱ USA on 1984. Then he graduated with an M.S. degree from the Univ. of Virginia at ۸۸۲ Charlottesville, USA on 1986. Finally, he received his PhD degree from the Univ. of Illinois ۸۸۳ at Chicago, USA on 1990. Currently, he is a faculty member at the Chemical and Petroleum $AA \Sigma$ Engineering Dept. at the Sharif University holding a distinguished Professor Rank. His current research interests include; preparation, characterization and physiochemical $\Lambda\Lambda\circ$ ٨٨٦ evaluations as well as; mathematical modelling of chemical and physical kinetics of regular, Core-Shell and Magnetic catalysts. Furthermore, investigating Alumina, carbons (CNTs, $\Lambda\Lambda V$ $\lambda\lambda\lambda$ Graphene Oxide and carbon Nano-Fibers), Zeolites and MOF supported catalysts and ٨٨٩ sorbents are being worked on. Moreover, designing and fabrication as well as investigating ٨٩٠ performance of microreactors and microfluidic systems applied to catalytic HDS and ODS 191 (i.e.; Hydro- and Oxidative- Desulfurization) as well as; photocatalytic and catalytic API ٨٩٢ (i.e.; activated pharmaceutical ingredients) and organic as well as pharmaceutical pollutants 198 removing materials are of close and recent interests.

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Mohammad Shahriari Mazraeh Shahi's Technical Information

٨٩٦ Mohammad Shahriari is progressing in Chemical Engineering. He earned his BSc degree from the Islamic Azad University (South Tehran Branch) in 2007 and a MSc degree from the ٨٩٧ Islamic Azad University (Shahrood Branch) in 2012. In 2016, he began his PhD studies at ٨٩٨ ٨٩٩ the Islamic Azad University (South Tehran Branch). His research focuses on developing ۹.. photocatalyst composites from Metal-Organic Frameworks and Graphene Oxide. He studies how these catalysts can capture CO2 and convert it into fuel, utilizing a photoreactor under 9.1 9.1 UVA conditions. This work demonstrates his commitment to addressing critical 9.5 environmental challenges and contributes to the advancement of sustainable energy solutions

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