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CO_2 Reduction Reactions Using Monometallic and Bimetallic Nanomaterials in a Photochemical Reactor

Vaishali N. Patil[1]*, Kiran Kokate[2], Sivanagi Reddy Emani[3], Monika Taware[1], Suvarna Pawar[4], Shobha Waghmode[5], Rahul Shivaji Yadav[6] and Swanand Pasalkar[7]

[1]Department of Engineering Science and Humanities, Marathwada Mitramandal's College of Engineering Pune - 411052, Maharashtra, India; vaishalipatil@mmcoe.edu.in

[2]Dr. Vishwanath Karad, MIT World Peace University, Kothrud, Pune - 411038, Maharashtra, India

[3]Department of Physics Anurag Engineering College, Ananthagiri, Suryapet - 508206, Telangana, India

[4]Department of Computer Engineering, Trinity Academy of Engineering, Pune - 411048, Maharashtra, India

[5]Department of Chemistry MES Abasaheb Garware College, Pune - 411004, Maharashtra, India

[6]Department of Mechanical Engineering, Marathwada Mitramandal's College of Engineering, Karvenagar - 411052, Maharashtra, India

[7]Department of Electronics and Telecommunication Engineering, Marathwada Mitramandal's College of Engineering, Karvenagar - 411052, Maharashtra, India

Abstract

CO_2 is a renewable carbon source and an eco-friendly chemical reagent. CO_2 from greenhouses leads to global warming and is also used to convert valuable chemicals. Reduction of CO_2 to useful fuels and organics leads to an area of interest over a few decades. CO_2 is mainly used to convert into a useful fuel, which may become an alternative to unsustainable fuels. For this, there are several methods available, including thermochemical, sonochemical, electrochemical, photocatalytic, and hydrothermal. Among these, the most prominent research focuses on photosynthesis or solar energy to facilitate this conversion.

***Major Findings:** This study demonstrates effective CO_2 reduction using mono- and bimetallic nanoparticles in a photoreactor with polyamines, producing ethanol, methanol, and formic acid, as confirmed by ^1H NMR and GC analysis.*

Keywords: *CO_2 Reduction, Green Chemistry, Photocatalysis*

1.0 Introduction

Visible Light Photo Chemical (VLPC) is a clean, cheap, renewable driving force in the field of energy as well as organic synthesis[1]. Due to global environmental concerns regarding rising energy demand, depletion of fossil fuel and environmental pollution, solar energy is entering scientists' horizons and has shown great advantages in the organic synthesis field. Solar spectrum explains three main components of the spectrum, and these are ultraviolet, visible light and infrared (wavelength 200nm to >800nm). Approximately, UV contribute 5%, visible light contributes 43% and IR contributes 52% respectively. Many organic molecules absorb in the presence of UV radiation, but in the solar spectrum, the amount of this radiation is vcontributesso it is important to consider the visible or IR spectrum of solar radiation. To meet the activation energy demands of organic reactions, it is difficult to carry out reactions in low-energy IR wavelengths; hence, the option of the visible region is open to all chemists to work with

**Author for correspondence*

organic transformations. Visible light cannot be directly absorbed by reactants, though it is abundant in nature, so photo catalysts work as media to transfer energy from visible light to the substrate.

1.1 VLPC Mechanism

In VLPC, the reactions are carried out with catalysts in the presence of visible light, i.e. Light will be absorbed by the substrate, which can create electron-hole pairs, and further these will generate free radicals. In organic reactions, these free radicals undergo secondary reactions in the presence of catalysts. During this process, catalysts must have a band gap, i.e. semiconducting material, then a photon with equal or more energy than the material's band gap is absorbed by the semiconducting material. Then an electron is excited from the VB to the CB, which generates positive holes in the VB. If an electron and a hole recombine, then heat will be produced, and there will be no more VLPC reaction. So, during VLPC reaction between the excited electrons react with the oxidising material to produce a reduced product, and a reaction between the holes with the reducing agent produces an oxidised product. Thus, redox reactions take place on the surface of semiconductors.

1.2 Photocatalysts

Broadly, these photocatalysts can be classified into five categories.

- Homogeneous PCs- metal complexes of Ru, Ir, Re, Fe, mostly transition metal complexes.
- Heterogeneous PCs- semiconductors.
- Organic dyes as PCs- all coloured pigments.
- Plasmonic metal nanoparticles as PCs- The metal nanoparticles which have SPR (surface plasmonic resonance) in visible light.
- Novel photoelectric materials as a PC - CdS nanocomposite fabrication by photo deposition process.

In the visible light photo catalysis, the catalytic species is activated by the action of light, the photo catalytic material is mostly a semi-conducting material, which in turn is capable of activating even the small molecules[1-2]. When the catalytic material is irradiated with light, it undergoes the absorption of a photon, and the electron (e^-) is excited from the valence band to the conduction band; consequently, a positive electron hole is generated in the semiconductor material (H^+), and this process is termed photoexcitation. The excited electron then comes to ground state through the mechanisms such as recombination and dissipate utilizing non-radiative mechanism, in a sense, following the photoexcitation process, the catalytic material excited transfers the energy to the molecules in its proximity through an orthodox redox mechanism in a pure chemistry sense and Single Electron Transfer occurs (SET). For brevity, the mechanism is provided briefly. Overall, the light source excites the catalytic material and transfers the energy to other molecules close by, and the chemical reaction occurs. This new discipline opened a new science of photo physics and photochemistry of transition metal coordination compounds. In this paper, a discussion of the visual light photo catalysis of aldehyde compounds is presented. The discussion revolves around the recent developments in the chemistry of aldehydes in the domain of VLPC. The growing global demand for energy, largely driven by the consumption of fossil fuels, has contributed to rising atmospheric CO_2 levels and the escalation of global warming. To address this issue, it is crucial to both reduce fossil fuel use and implement strategies to remove CO_2 from industrial emissions or directly from the atmosphere, a process known as carbon capture. One commonly suggested solution is Carbon Capture and Sequestration (CCS), where captured CO_2 is stored to prevent its release. However, an alternative and potentially more sustainable strategy is Carbon Capture and Recycling (CCR), which involves converting CO_2 into useful fuels and materials, thereby closing the carbon loop.

2.0 Ways to Utilise CO_2 into Valuable Products

CO_2 is converted into methanol by using similar copper heterogeneous catalysts. Besides heterogeneous catalysts, CH_3OH can be synthesised from CO_2 at a mild temperature with metal-based homogeneous catalysts prepared by rational catalyst design. In this context, one pot CO_2 capture and subsequent conversion to fuels (CCR) has started to attract considerable interest. Recent studies have demonstrated that a ruthenium-based PNP pincer complex can effectively catalyze the

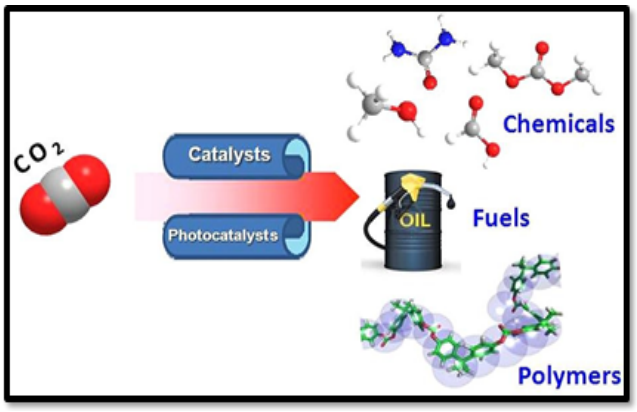


Figure 1. Ways to utilise CO_2 into valuable products.

hydrogenation of carbon dioxide into valuable products such as methanol (CH_3OH), dimethyl formamide (DMF), and dimethyl ammonium format, particularly in the presence of dimethylamine (Me_2NH) and potassium phosphate (K_3PO_4)[3]. Several reports also highlight the use of relatively mild reaction temperatures (125–165 °C) when employing pentaethylene hexamine (PEHA) alongside the Ru-PNP catalyst. Following the reduction of CO_2, methanol can be easily separated from the reaction mixture by distillation, allowing the remaining system to be reused for further methanol production. This concept aligns with the "methanol economy" approach, which envisions methanol as a key energy

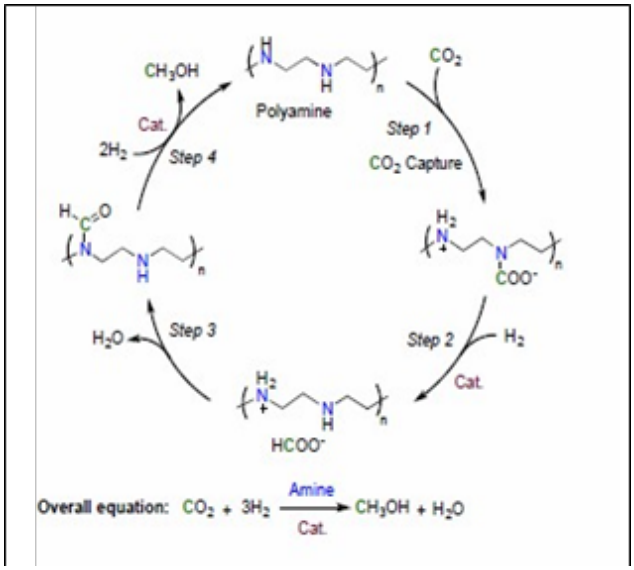


Figure 2. Ways to utilise CO_2 into valuable products.

carrier and chemical feedstock. A practical example of this technology is found in the George Olah Renewable Methanol Plant in Reykjavik, Iceland, where CO_2 is converted into methanol using heterogeneous catalysts and geothermal energy[4]. Like solar panels, nanomaterials can be used as panels to capture CO_2 from the air directly and further converted into fuel molecules.

In this research proposal simple approach is used to capture CO_2 using amines/ polyamines, as these have very high basicity, high amine content (N-H moieties), i.e. high nitrogen content, good stability due to high boiling and promising reducing ability for CO_2. So selectively it achieves an appreciable CO_2 absorption[5]. Thus, hydrogenation of CO_2 using polyamines with base and catalyst (BMNMs) is the best approach to reach fuel at the end or methanol economy, and sometimes it ends to formic acid. For this purpose, plant extracts will be employed, as they effectively accommodate two metal centres and exhibit redox behaviour, which contributes to improving the Turnover Number (TON) of the catalyst[6-12].

Similarly, MMNMs are used as catalysts for the reaction. In earlier reports, most of the time Ru, Rh, Pd and Pt metals are used, but due to the USA endangered list and first time, going to use Fe and Cr, as both are capable of redox behaviour. For CO_2 work, concentrated CO_2 (cylinder) as well as synthetic air were used and finally CO_2 panels for atmospheric absorption[13-17].

The Earth's atmosphere is surrounded by gases like 78% Nitrogen, 21% Oxygen, 0.9 % Argon and 0.1% trace gases like Helium, Ozone, Nitrous oxide, Neon and 0.04 % CO_2, etc. These gases help to maintain our environmental balance. These gases help in various living and non-living things for respiration, photosynthesis, industries, etc. Over the last few decades increase in the percentage of these gases has caused an increase in temperature of earth which causes global warming, depletion of the ozone layer, sea level rise, adverse effects on biodiversity, and climate change, which affects living things. Till 2014, because of fossil fuel combustion and some industrial processes, CO_2 emissions in India were 7%, China 30%, the United States 15%, Russia 5% and other countries around 30%[18-20]. CO_2 is mainly used to convert into a useful fuel, which may become an alternative to unsustainable fuels.

CO_2 can also convert formaldehyde, formic acid, methane, methanol, ethanol, gasoline (C-2, C-4), which helps to reduce the environmental crisis. Trapping/capturing or converting to valuable products as a source or to store energy like fuel cells, since there are many techniques found to utilize and convert CO_2 to methanol divides into mainly, i) mitigation of CO_2, ii) create renewable and sustainable source from CO_2, iii) to store as energy source. For this, there are a number of methods available, like thermochemical, sonochemical, electrochemical, photo catalytic, hydrothermal, etc. Among these, the topmost research takes place by photosynthesis/solar energy.

Approach: Dr. Suryaprakash, who 1st published the paper on CO_2 to methanol[20]. Chemical industries currently produce more than 70 million tons of methanol, but the challenge is to find a good catalyst to increase the rate of reaction, and the problem is that these reactions require a temperature of 150°C, which may cause decomposition of the catalyst.

The storage of the non-polar CO_2 molecule in a solid proved difficult, yet progress is being made using a range of high surface area macro and microporous materials, such as inorganic materials (e.g. alumina, silicas and zeolites), organic materials (e.g. activated carbons), etc.[21] Metal oxides are frequently used as supports for the dispersion of metals and their ability to bind and activate CO_2 largely depends on their basicity and reducibility Reduced oxides have a strong tendency to react with CO_2.

A wide range of recent studies have focused on enhancing industrial performance, heat transfer, fuel efficiency, and sustainability. Human-robot collaboration is identified as a key strategy for improving safety and manufacturing efficiency[22]. Investigations into trapezoidal ducts with delta wing vortex generators reveal significant improvements in thermal performance and heat transfer[23,24].

Photochemical machining has been explored for precision metal sheet processing[25]. Heat dissipation in electronics was improved using phase change materials, and biodiesel blends were shown to enhance diesel engine performance sustainably. Oxygenated additives have demonstrated emission reduction potential in gasoline vehicles[26-28]. Studies also compare various heat exchanger coil geometries, assess corrosion resistance using coconut shell ash, and simulate battery cooling in EVs[29-31].

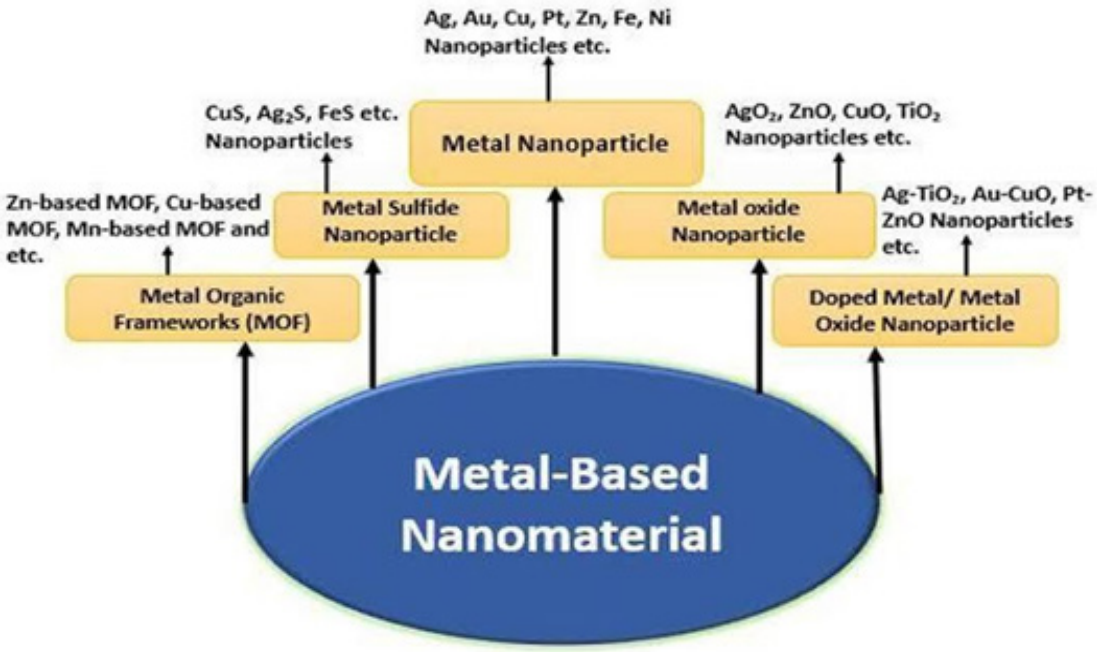


Figure 3. Metal-based nanomaterials.

Additional works present sustainable fuel production from plastic waste, innovative vehicle bumper designs for impact safety, and enhanced heat transfer using nanofluids. Automation in HVACR duct design has been advanced using programming-based approaches. Mechanical properties of curved steel plates under varying thickness and welding parameters have also been evaluated[32-37].

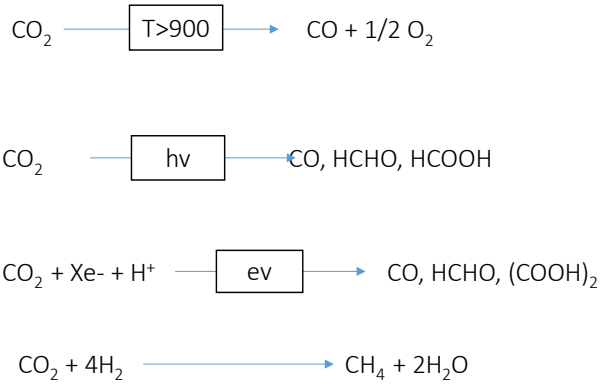
Thermal analysis in electronic substrates and temperature management in vehicles using I-Cool materials offer additional engineering insights. Comparative studies on mono-composite and metal leaf springs and grinding performance using Al_2O_3 nanofluids under MQL conditions underline material and manufacturing innovations[38-44].

With the rising industrial demand for methanol, significant research is being directed toward the conversion of CO_2 into methanol. Copper-based catalysts, often combined with ZnO and/or Al_2O_3, have been employed commercially for over five decades for this purpose. Although these catalysts are well-established, their ability to fully activate CO_2, particularly under low-temperature conditions (below approximately 500 K), remains limited, and they exhibit relatively low efficiency in CO_2 hydrogenation. While higher temperatures improve CO_2 activation, they also promote side reactions such as the Reverse Water-Gas Shift (RWGS), leading to the unwanted formation of carbon monoxide and water. From an energetic standpoint, converting one mole of CO_2 to methanol requires approximately 228 kJ of energy and involves the transfer of six electrons to reduce the carbon atom from an oxidation state of +4 in CO_2 to +2 in methanol.

2.0 Various Ways to Reduce CO_2

CO_2 can be reduced by various methods as below:

1. Radiochemical
2. Chemical Reduction
3. Thermochemical
4. Photochemical
5. Electrochemical



6. Biochemical
7. Bio photochemical
8. Photo electrochemical

3.0 Methods to Synthesise Methanol

The first developed method of methanol synthesis was the synthesis of syngas in the 1920s. A gas mixture of hydrogen and carbon monoxide is called syngas. Currently, three methods are commonly used to produce the precursor synthesis gas from the methane component in natural gas. The methods are steam-methane, partial oxidation with molecular oxygen, and a combination of the two, autothermal reforming.

Catalysts such as copper oxide are capable of operating at lower temperatures and are used to efficiently produce modern methanol. Metal ion binds to organic chains at a very low density, with voids of 10-20. Binding energy is very weak in a large, complex unit cell. H_2 binding is dominated by van der Waals forces. Air exposure is the main concern while dealing with MOFs.

The present catalyst most commonly used is Cu/ZnO/Al_2O_3, porous materials like zeolite have been used for a long time in industrial applications as a catalyst in the petroleum industry in H_2O purification, gas separation or drying agent. It is mainly based on Si/Al_2O_3, also additional cations, i.e. Na^+, K^+, Mg^+, Ca_2^+, etc., to modify pores. Due to the large channel, it depends on the low density of SiO_2 (2.65g/cm^3), Al_2O_3 (4.00g/cm^3), and CaO (3.34g/cm^3). Zeolite have advantages over conventional catalyst due

to great acid strength and adaptability and high thermal stability, but the limitation are 1) when reaction carried out in liquid phase some diffusion limitations and gets out of pore system, 2) Si/Al ratio the stability affected by ratio, poor crystalline if there is high concentration of Al, 3) high cost, 4) Lack of definite understanding of active sites, 5) Instability of catalyst at relatively high concentration of CO_2 conversion, 6) There is problem whether Cu or ZnO act as structural modifier, hydrogen reservoir or direct promoter for bond activation, 7) Cu/ZnO/Al_2O_3 catalyst most cases prevent one from obtaining conclusive information regarding active sites under reaction difficult to recognized enhancement of catalytic performance.

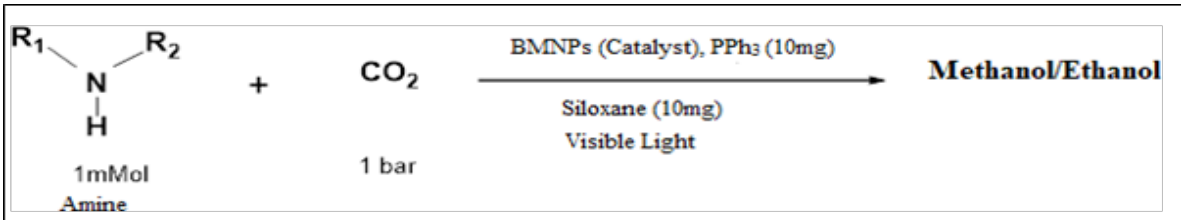
e.g. catalyst ZnO-ZrO_2 having methanol selectivity around 86-91 %, remains stable after 500hrs on stream, which is used in separation for large-scale production. ZnO-ZrO_2 has a greater percentage of conversion on Cu/ZnO/Al_2O_3.

4.0 CO_2 Reduction Reactions by Using Monometallic and Bimetallic Nanomaterials

Visible Light Photo-Catalysed Reaction

Scheme 3 (Visible Light Photocatalyzed CO_2 reduction Reactions)

Procedure - In a photoreactor flask, amine (1mM) like dicyclohexyl amine (DCHA)/penta ethyl hexamine (PEHA)/Triethylamine/methylamine, etc., is taken, to which 10mg each of triphenylphosphine and siloxane is added along with 150ml distilled water. Then bimetallic nanoparticles such as iron-copper/iron-nickel/iron-zinc/iron-cerium are added, and CO_2 gas is passed for a 30-minute to 1-hour duration. After that, visible light in ice-cold conditions was allowed to pass CO_2 gas with continuous stirring of the reaction mixture. Later, the



Flowchart for CO_2 reduction in photoreactor

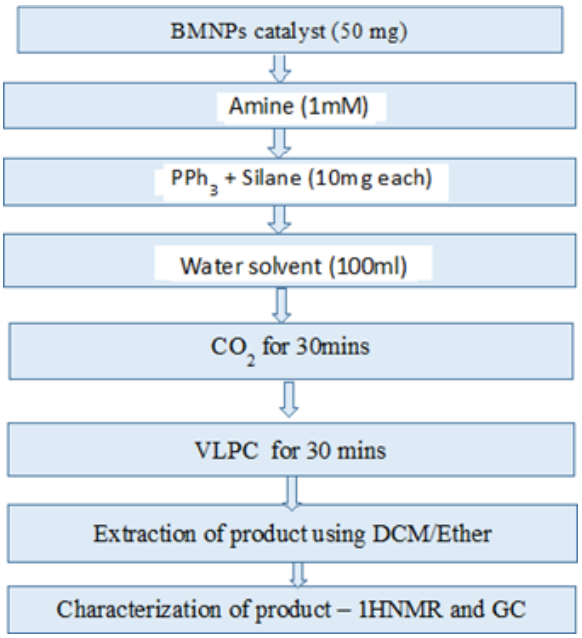




Figure 4. A photochemical reactor used for VLPC reaction.

Table 1. Reactions of CO_2 reduction by using bimetallic catalysts

Sr. No.	Reagent	Catalyst	CO_2	Solvent	VLPC	Extraction
1	Mono Ethanolamine	Fe-Ce	30min	Water	30min	Diethyl Ether
2	Diethanolamine	Fe-Ce	30min	Water	30min	Ether
3	N, N – Dimethyl Aniline	Fe-Ce	30min	Water	30min	Ether
4	DCHA	Fe-Ce	30min	Water	30min	Ether
5	PEHA	Fe-Ce	30min	Water	30min	Ether
6	Triethylamine	Fe-Ce	30min	Water	30min	Ether
7	3 – Picolamine	Fe-Ce	30min	Water	30min	Ether
8	Methyl amine	Fe-Ce	30min	Water	30min	Ether
9	Ethylene Diamine	Fe-Ce	30min	Water	30min	Ether
10	Propyl Amine	Fe-Ce	30min	Water	30min	Ether
11	Diethanolamine	Fe-Cu	30min	Water	30min	Ether
12	DCHA	Fe-Cu	30min	Water	30min	Ether
13	PEHA	Fe-Cu	30min	Water	30min	Ether
14	Triethylamine	Fe-Cu	30min	Water	30min	Ether
15	3 - Picolylamine	Fe-Cu	30min	Water	30min	Ether
16	Methyl amine	Fe-Cu	30min	Water	30min	Ether
17	Propyl Amine	Fe-Cu	30min	Water	30min	Ether
18	Diethanolamine	Fe-Ti	30min	Water	30min	Ether
19	DCHA	Fe-Ti	30min	Water	30min	Ether
20	PEHA	Fe-Ti	30min	Water	30min	Ether
21	Triethylamine	Fe-Ti	30min	Water	30min	Ether
22	3 - Picolylamine	Fe-Ti	30min	Water	30min	Ether

23	Propyl Amine	Fe-Ti	30min	Water	30min	Ether
24	Mono Ethanolamine	Fe-Y	30min	Water	30min	Ether
25	Diethanolamine	Fe-Y	30min	Water	30min	Ether
26	DCHA	Fe-Y	30min	Water	30min	Ether
27	PEHA	Fe-Y	30min	Water	30min	Ether
28	Triethylamine	Fe-Y	30min	Water	30min	Ether
29	3 - Picolylamine	Fe-Y	30min	Water	30min	Ether
30	Methyl amine	Fe-Y	30min	Water	30min	Ether
31	Propyl Amine	Fe-Y	30min	Water	30min	Ether
32	PEHA	Fe-Zn	30min	Water	30min	Ether
33	Methyl amine	Fe-Zn	30min	Water	30min	Ether
34	Propyl Amine	Fe-Zn	30min	Water	30min	Ether
35	DCHA	Fe-Ce	60min	Water	60min	Ether
36	PEHA	Fe-Ce	60min	Water	60min	Ether
37	DCHA	Fe-Cu	60min	Water	60min	Ether
38	PEHA	Fe-Cu	60min	Water	60min	Ether

Table 2. ^{1}HNMR Data of CO_2 reduction reactions using bimetallic nanomaterial

Sr. No.	Reagent	Catalyst	^{1}H NMR DATA			
1	PEHA	Fe-Ti	1.2		2.4	3.48
2	PEHA	Fe-Y	1.2		2.4	3.48
3	PEHA	Fe-Zn	1.2	1.6		3.48
4	PEHA	Fe-Ce	1.2	1.59		3.48
5	PEHA	Fe-Cu	1.2	1.6		3.48

reaction product was extracted using diethyl ether and characterised using ^{1}H NMR (Proton nuclear magnetic resonance spectroscopy) and GC (gas chromatography) to observe the formation of methanol or ethanol as a product.

5.0 Results and Discussion

The CO_2 reduction was done by using bimetallic nanomaterials, Fe-Cu, Fe-Ce, Fe-Zn, Fe-Y and Fe Ti with different amines such as Ethanolamine, Diethanolamine,

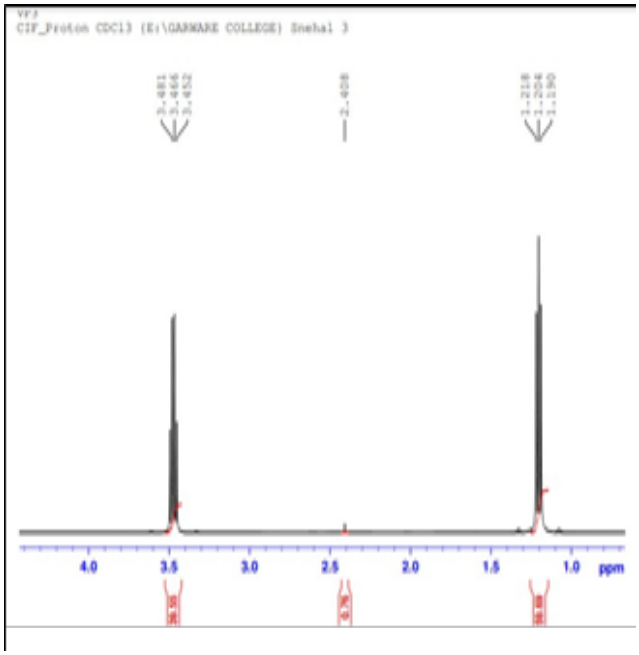


Figure 5. ^{1}H NMR Plot of Fe-Ti catalyst with PEHA.

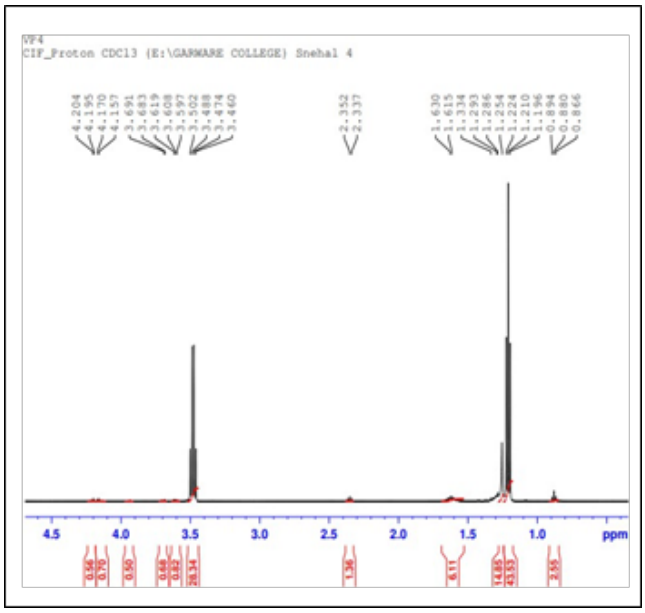


Figure 7. ^{1}H NMR Plot of Fe-Zn catalyst with PEHA.

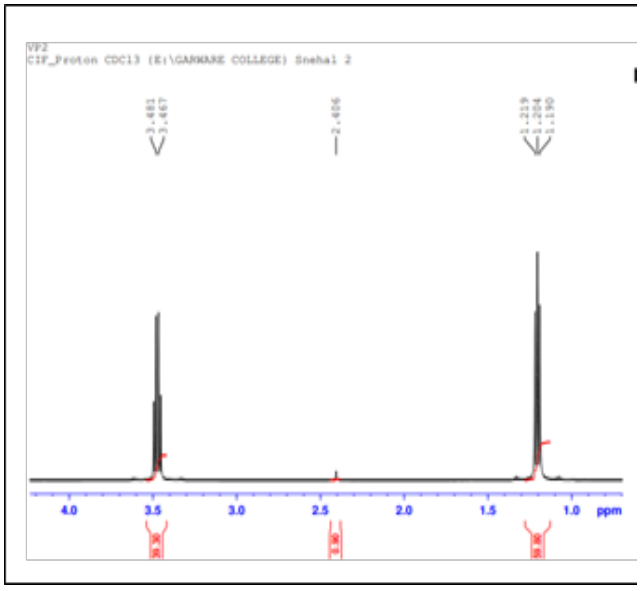


Figure 6. ^{1}H NMR Plot of Fe-Y catalyst with PEHA.

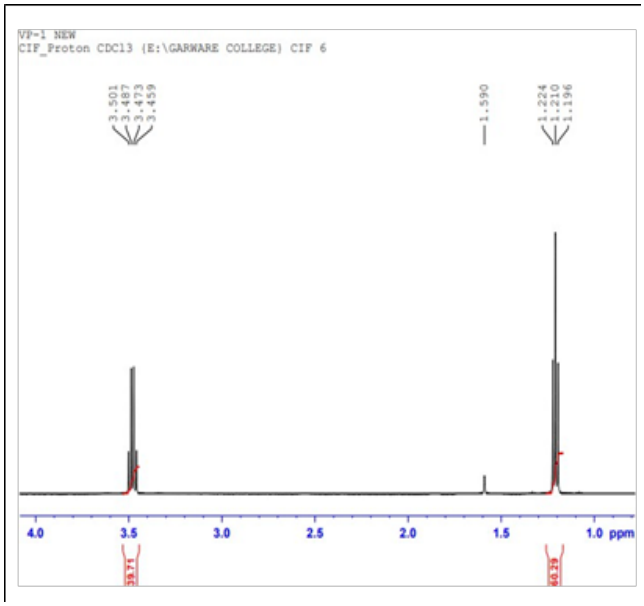


Figure 8. ^{1}H NMR Plot of Fe-Ce catalyst with PEHA.

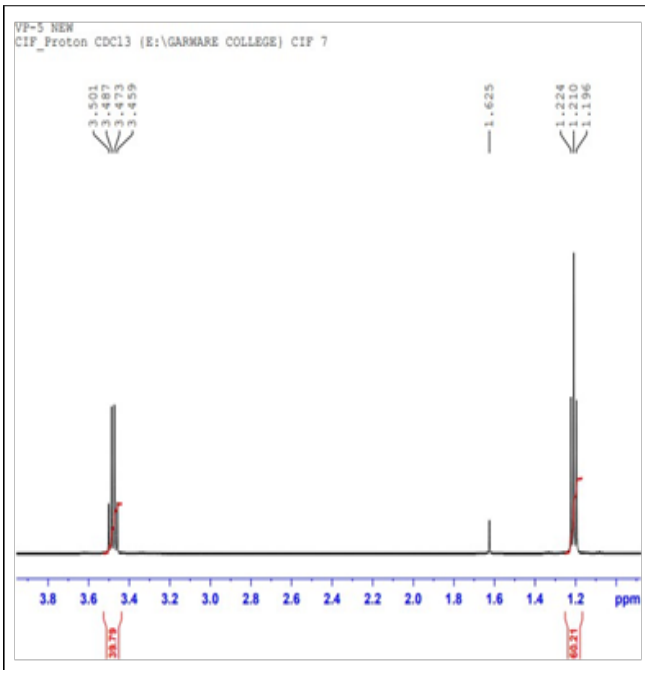


Figure 9. ^{1}H NMR Plot of Fe-Cu catalyst with PEHA.

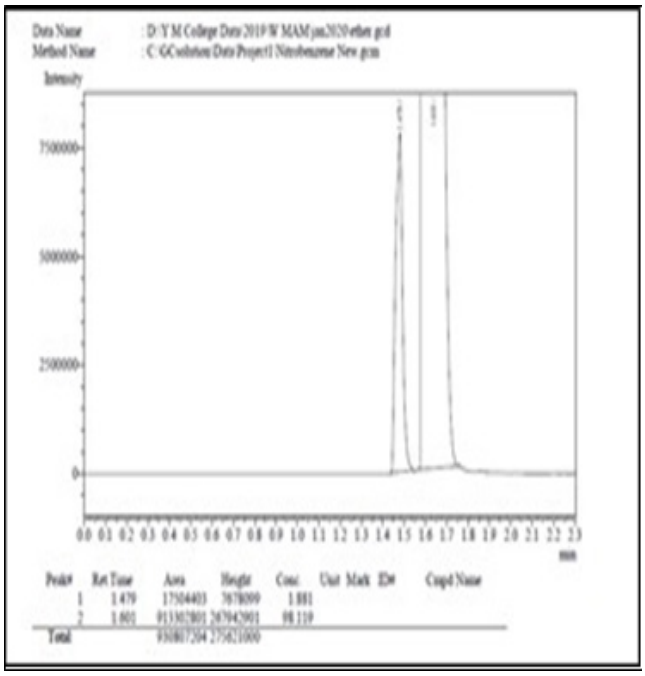


Figure 10. GC of std. Ether (solvent).

N, N – Dimethyl Aniline, Cyclohexylamine, PEHA (Penta ethylene hexamine), Triethylamine, 3 – Picolylamine, Methyl amine, Ethylene Diamine, Propyl Amine as per procedure explained above in photoreactor and out of this Fe- Cu, Fe-Ce, Fe-Zn with only PEHA (Penta ethylene hexamine) poly amine ends into product as a fuel molecule ethanol with ^{1}H NMR with peaks 1.2, 1.6 and 3.48 delta values which confirms formation of ethanol formation.

6.0 Gas Chromatograph Results

Fe-Cu and Fe-Ce show ethanol as a product in the gas chromatogram when CO_2 reduction occurs in the photoreactor with PEHA. Ethanolamine shows methanol as a product.

With monometallic, no reduction of CO_2 in the photoreactor. Similar results are obtained with ^{1}H NMR.

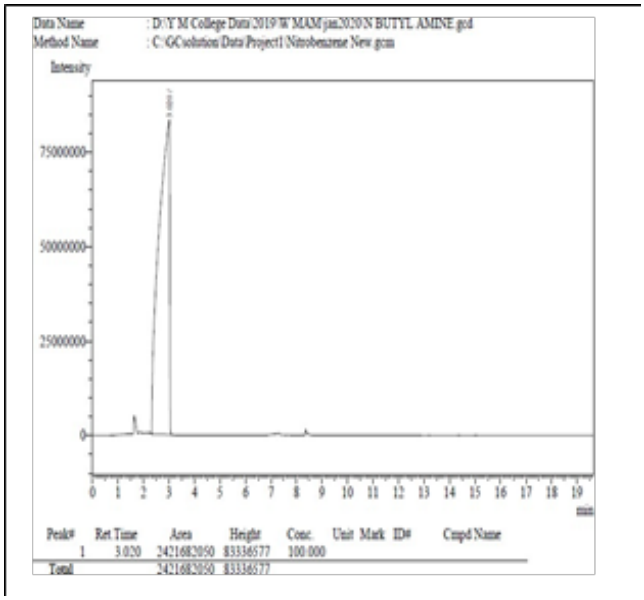


Figure 11. GC of std. Butyl amine (Reagent)E.

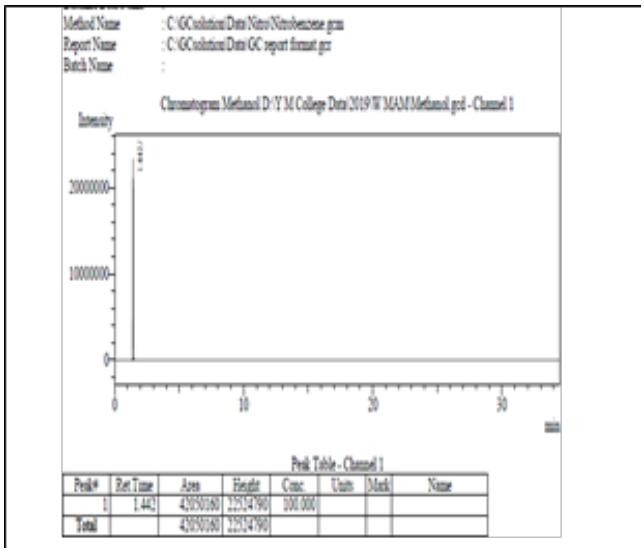


Figure 12. GC of std. Methanol (solvent).

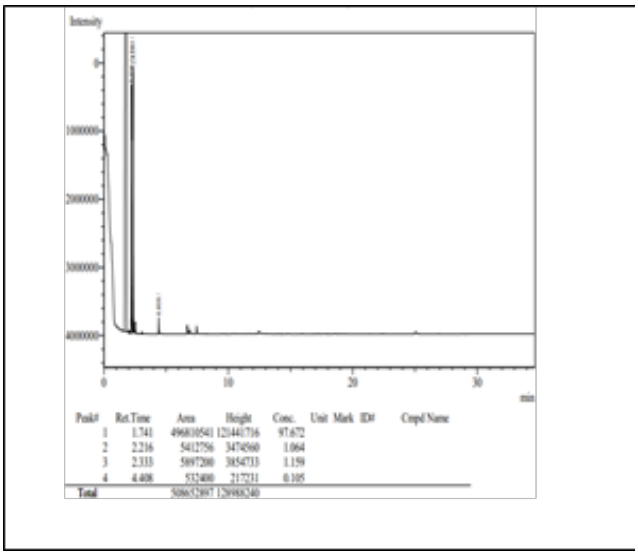


Figure 14. GC of Fe-Ce with PEHA.

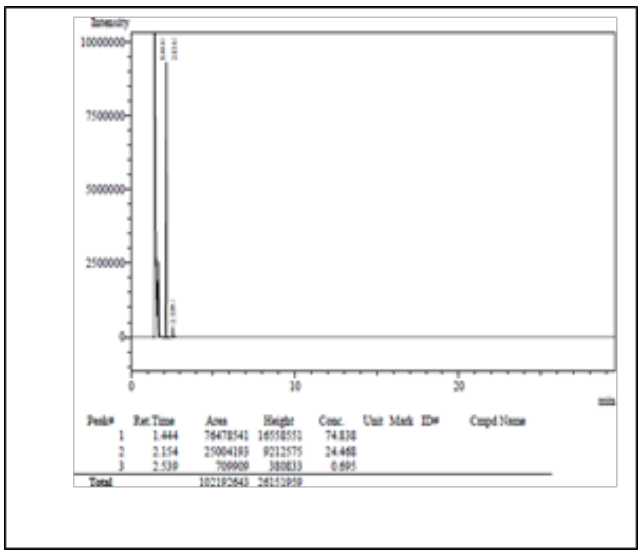


Figure 13. GC of Fe-Cu with PEHA.

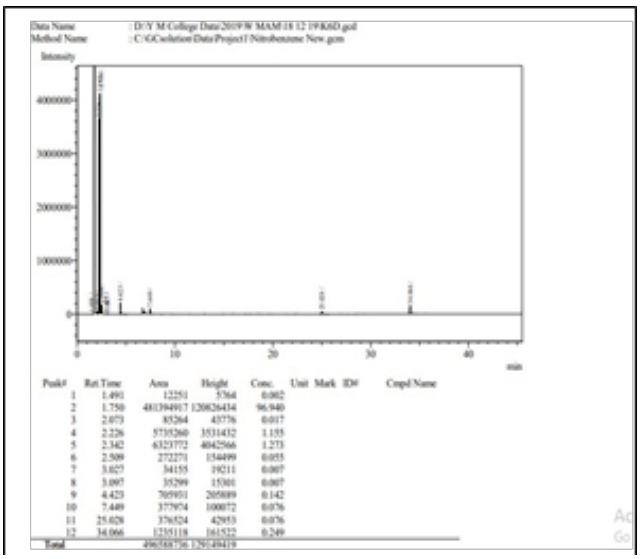


Figure 15. GC of Fe-Ce with ethanolamine.

Table 3. Gas chromatography analysis

Sr. No.	Name	Retention Time	Concentration
1	Std. Methanol	1.44	100
2	Std. Ether	1.60	100
3	Std. Ethanol	1.76	100

4	t. Butyl amine	3.020	100
5	Fe-Cu with Ethanolamine	1.75	26.7
6	Fe-Ce with ethanolamine	1.49	9.561
7	Fe-Ce with PEHA	1.74	97.67
8	Fe-Cu with PEHA	1.44	74.85

7.0 Conclusion

In this work, single nanoparticles as well as bimetallic nanomaterials are used for CO_2 reduction in the presence of a photoreactor and polyamines the good substrates for reduction. These reactions were characterised by using ^{1}H NMR, Gas Chromatography as a characterisation of products. Here, ethanol, methanol and formic acid are the products of reactions of CO_2 reduction. The study demonstrates that among the various bimetallic nanomaterials (Fe–Cu, Fe–Ce, Fe–Zn, Fe–Y, and Fe–Ti) tested with different amines, only the Fe–Cu, Fe–Ce, and Fe–Zn systems in combination with PEHA (Penta ethylene hexamine) effectively facilitated CO_2 reduction in the photoreactor to yield ethanol as a fuel molecule. The successful formation of ethanol was confirmed by ^{1}H NMR peaks at δ 1.2, 1.6, and 3.48, validating the selective catalytic role of these bimetallic-amine systems in converting CO_2 into value-added fuels.

8.0 References

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