CATALYTIC INSIGHTS INTO CONVERSION OF CO_2INTO METHANOL: A COMPREHENSIVE REVIEW

Project Report submitted in fulfillment of major project of

BACHELORS OF TECHNOLOGY IN BIOTECHNOLOGY

by

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DECLARATION

I hereby declare that the major project work entitled *"Catalytic Insights into Conversion of CO_2 Into Methanol: A Comprehensive Review"* has been solely submitted to the Department of Biotechnology and Bioinformatics, Jaypee University of Information Technology, Waknaghat in due of the literature review and research work we have done under the major project in guidance of our supervisor **DR. ASHOK NADDA.**

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SUPERVISOR'S CERTIFICATE

This is to certify that the minor project work titled *"Catalytic Insights into Conversion of CO_2Into Methanol: A Comprehensive Review*" submitted by**Reva Bhardwaj**during their 8th semester in June 2020 in fulfilment for the major project in Biotechnology of Jaypee University of Information Technology, Solan has been carried out under my supervision. This work has not been submitted partially or wholly to any other University or Institute for the award of any degree or appreciation.

(Signature of Supervisor)

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At this juncture, with proud privilege and profound sense of gratitude we feel honored in expressing our deepest appreciation to **Dr. Ashok Nadda,** for being a lot more than just a supervisor and going beyond the call of duty in our guidance, support, advice, and motivation throughout. He has been the source of inspiration of come what may, these issues cannot bring you down. Sincere thanks for his insightful advice, motivating suggestions, invaluable guidance, help and support in successful completion of this major project and also for his constant encouragement and advice throughout our minor project work.

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In gratitude,

Reva Bhardwaj (171809)

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ABSTRACT

A consistent expansion in the quantity of ozone depleting substances is making genuine dangers the climate and life on earth. In this unique circumstance, CO2 is one of the significant competitors among them. Decreasing the abundance CO2 by changing over it into mechanical items is valuable for the climate and to help modern development. Transformation of CO2into methanol is extremely gainful as it is less expensive to create, less inflammable, can be delivered from biomass, and is favorable in numerous ventures. Methanol is acquiring prevalence as an option in contrast to oil based powers and is valuable for a more secure and cleaner climate. Bio-energy with carbon catch and capacity (BECCS) can be utilized to extricate bioenergy from biomass which can be utilized to catch and store the CO2 in this way, diminishing its environmental level. This biomass can be utilized to infer biofuels like methanol which can be utilized straightforwardly. Inexhaustible gaseous petrol called biomethane can likewise be delivered utilizing biomass which can additionally be utilized in cooking, and for different applications. It will in this manner lessen the utilization of non-renewable energy sources. To lessen the reliance on plastic, manufactured polymers, and expanding utilization of sustainable assets, bio-filaments, for example, cellulosic strands that are being utilized in the development and car industry. Bioproducts like rice husk, agrarian waste, kitchen squander like products of the soil strips, and so on that are gotten as biowaste can be utilized to create biofuels like methanol, ethanol, and other potential powers which can supplant the inordinate use of non-renewable energy sources. This article portrays the change of CO2 into methanol utilizing biocatalysts like microorganisms, compounds, natural solvents, polymers, nanostructures, and other substance draws near.

Keywords: *Bioenergy; biofuels; biofibres; bioproducts; biowastes, biomethane*.

INTRODUCTION

Expanding ozone harming substance outflows has become a danger to the earth and its animals. preferably, to lessen it we ought not utilize sources that discharge or delivery the CO2 or convert the created CO2 before its delivery into the environment. Different cycle strengthening methodologies have been created or are being scrutinized to accomplish these objectives. Simultaneously, an enormous measure of CO2 is being delivered into the climate from human exercises, businesses, autos, and power plants. This discharged CO2 is one of the significant supporters of the nursery impact causing unwanted environmental change and obliteration to the planet, yet it's anything but a fundamental segment for supporting life on earth (Zheng et al., 2017). Normal fauna on the earth and seas confer significantly to lessen the CO2 adjacent to these in a confined metropolitan region, city structures or businesses greener sources, algal pinnacle, material embedded boards, CO2-phillic solvents can be utilized to eliminate the delivered CO2. The significant test is the maintainability of the cycle as they need bigger extra room and after the response of the synergist interaction what will be the destiny of items and results stays unanswered. Thus, we need to track down an effective way that utilizes the CO2 present in the air and converts it into significant items. Environmentally friendly power energy or bioenergy based items are sought after to replace petroleum products. In this manner methanol incorporated by the change of CO2 can be one of the monetarily significant items that discharge a lower measure of CO2 after its burning. Grounded that methanol has high volumetric and gravimetric energy thickness and is a vital fuel that is supplanting the utilization of petroleum derivatives (Gutterød et al., 2020). Its great benefit is to lessen the outflow of GHGs from vehicles. It has the most noteworthy hydrogen to carbon proportion in contrast with any fluid fuel and can be promptly corrupted in both high-impact and anaerobic conditions. Out of the all out energy utilization of the world, 49% of it is met by powers like fuel, diesel, jetoils, and so on (Lewis and Nocera, 2006) When contrasted with regular powers, it is more worthwhile when contrasted with fuel and diesel. Methanol can possibly diminish fossil fuel byproducts by 65%-95%. The Gibbs free energy of methanol is - 166kJ/mol and the warmth of development is - 239 kJ/mol(Alper and Orhan, 2017). Methanol is an incredible fuel that can be utilized in the inside burning motors (ICE), direct oxidation methanol power devices (DMFC) and as a beginning material for the creation of light olefins (Olah et al., 2009). It is exceptionally flexible in making every day need items, it is productively burnable, handily dispersed, and generally accessible, making it moderate to utilize (Hengne et al., 2019). It can likewise be utilized in wastewater treatment, power creation, and as a significant forerunner for different modern responses (Leonzio, 2018) Many natural based techniques, enzymatic transformation strategies, chemo-enzymatic strategies, film adsorption, and so forth are being utilized to change CO2 over to methanol remembering, the way that no additional waste or destructive gases ought to be delivered and standards of green science ought to be followed. Food and agribusiness squander, metropolitan strong waste, and ranger service deposits are a portion of the huge destinations which give feedstock that can be utilized to deliver methanol utilizing measures like aging, gasification, Kraft measure, and so forth This will build methanol creation utilizing waste which would somehow or another have spoiled or metropolitan waste which would have just constructed tension on landfills. Obert and Dave accomplished a response for change of CO2 to methanol by switching the natural metabolic pathways. They made a blend of catalysts like FDH, FaldDH, and ADH for consecutive decrease of CO2 to methanol.In this enzymatic response, NADH was utilized as the terminal electron benefactor. (Baskaya et al., 2010) Another methodology was utilized by Wang et al., where they made a multi-protein course framework utilizing catechol and gelatin which were consecutively immobilized in the ultrathin, cross breed microcapsules. This method when contrasted with the one detailed by Obert and Dave showed slight improvement in the methanol yield for example 52.6%. (Wang et al., 2014)

Microporous natural polymers (MOPs) are additionally utilized for CO2 catch and transformation credited to the processability, high selectivity, moderate actual maturing, high gas penetrability, the high dissolvability of gases, and high surface space of these films. The utilization of these layers with CO2-philic materials gives a similarly less expensive and energy-productive technique for CO2 catch and change into methanol and different synthetic compounds and fluid energizes like formic corrosive, methane, and carbonate. (Ashley et al., 2012)

The at first CO2 being discharged from enormous assembling enterprises, concrete plants, and geothermal cycles in higher focus appeared to be possible to catch and change over. However, profoundly productive detecting gadgets and crossover CCS innovations made it conceivable to distinguish the CO2 at 400 ppm level and catch it. (Campbell, 1997) Several procedures including thermochemical, photochemical, electrochemical, and natural have been utilized to change over CO2 into valuable items. Direct electrochemical decrease of CO2 produces methane, methanol, just as ethanol-dependent on response conditions. (Zarandi et al., 2019). CO2 can be valorized through hydrogenation, focussing on Reverse water-gas shift response (RWGS), methanation, and methanol creation (Gutterød et al., 2020). The methanol combination from CO2 hydrogenation and RWGS is a thermodynamically restricted response and harmony change of CO2 diminishes with expanding response temperature, in this way it's anything but a reactant framework (Dang et al., 2019). Methanol is likewise set up by the hydrogenation of CO2 by the RWGS response. The impetus Ni/Al12O19 can be utilized at the modern scale(Samimi et al., 2019). As of late, it has been seen that indium oxide is a profoundly specific impetus in the warm hydrogenation of CO2 to methanol Recently, the hydrogenation of CO2 to methanol was completed utilizing heterogeneous CuZnO upheld on Al2O3 (Chun and Song, 2020). Methanol integrated by CO2 hydrogenation is productive for putting away energy as solid O-H securities and has an unbiased carbon impression with a perfect wellspring of energy.

The expanding cost of raw petroleum and decrease in its accessibility has expanded the interest for its substitutes. Methanol can likewise be gotten from warm synergist change of syngas. It can straightforwardly be utilized by energy units and ignition motors, as a substitute to fuel and diesel-controlled motors and can be utilized by implication as a structure square of significant worth added synthetic compounds. Methanol delivered from syngas by joining H2 to CO or CO2 is advantageous to lessen the measure of CO2 from the environment (Hengne et al., 2019). Any carbonaceous feedstock can be changed over to a scope of hydrocarbons and H2O by means of methanol with colossal modern significance. Like methanol to olefins (MTO), methanol to propene (MTP), Mobil's olefin-to-fuel, and distillate measure (MOGD) and Topsoe's improved gas combination (TIGAS), and so forth (Dang et al., 2019). The three principle pathways for CO2 transformation into important items are mineral carbonation, compound change, and natural change (Burkart et al., 2019). Aspen HYSYS business programming stage has been utilized for the advancement of three CO2 to methanol change methods and for playing out the demonstrating tasks (Abdelaziz et al., 2017).

Different parts of transformation of CO2 to methanol have been talked about in this survey article focussing on materials and composites, natural solvents, substance obsession of CO2, and change utilizing organisms and other natural microorganisms.

Material and composites- for CO_2 conversion to methanol

CO_2 can be converted into methanol using a variety of methods. A good catalyst suitable for CO_2 conversion into methanol is the one which is active in reducing in CO_2, it should be stable and should not get poisoned by the released gases or by-products and should have a high faradaic efficiency towards the production of methanol. Some of the efficient methods used for the conversion of CO_2 to methanol are the electrocatalytic reduction of CO_2 to methanol using homogeneous or heterogeneous catalysts to speed up the rate of reaction, heterogeneous catalysts being a better choice. Porphyrins are very robust materials with unique properties and colorful structure which are widely being used these days for the conversion of CO_2 to methanol.

Electrocatalytic reduction of CO2 in methanol medium

Electrocatalytic decrease of carbon dioxide is the cycle of decrease of carbon dioxide into important mixtures and powers like methanol utilizing power for decrease. Decreased compound species are acquired after the electrocatalytic CO2 decrease response. Electrochemical decrease of CO2 can be utilized to create synthetics or different energizes and feedstocks like methanol, formic corrosive, methane, carbon monoxide, and so on The electrolytes utilized in these responses influence the decrease of CO2. Solvents utilized additionally assume a vital part in looking after pH, conductivity, and harmfulness.

The decrease response during the time spent change of carbon dioxide which is a steady particle, to methanol includes 6 electrons which makes it a dynamically more slow response. (Albo et al., 2015) This change requires the utilization of proficient and exceptionally specific impetuses for its transformation into energizes and other important products(Lashgari et al., 2017).

Utilizing heterogeneous impetuses for transformation of CO2 to methanol is broadly utilized for mechanical purposes. Multifunctional Cu/Zn impetuses and their oxides are utilized on different supporting material as an impetus for modern cycles because of their high selectivity and change rate. Impetuses dependent on metals like Pd, Ni, Ag, Au, In among others like Pt nanoparticles are utilized in heterogeneous catalysis for CO2conversion to methanol. (Wang et al., 2017a) Heterogeneous reactant hydrogenation of vaporous CO2 into methanol utilizing electrical energy is additionally seen to be advantageous for the change of CO2 into biofuels, adding to sustainable power and green science. Most existing impetuses are not proficient because of side response of hydrogen creation, helpless selectivity, long haul security is low and the harming of respectable metals may happen. The action of a heterogeneous impetus can be improved by appropriate help. Thus, a decent impetus with appropriate help ought to be given to heighten the exhibition. Carbonaceous materials like initiated carbon and carbon nanotubes can be utilized as extraordinary impetus upholds. They enjoy numerous benefits like less expensive assembling, great warm conductivity, huge pore volume, and explicit high surface area(Wang et al., 2019). For instance, in an investigation by Han et al. distributed in the Chem, polymeric cobalt phthalocyanine upheld on carbon nanotube is accounted for to be a profoundly productive impetus utilized in carbon dioxide decrease. (Han et al., 2017)

Notwithstanding heterogeneous synergist hydrogenation responses, some homogeneous impetuses are additionally being utilized for the transformation of CO2. These impetuses are accessible in various structures like natural solvents, ionic solvents, and metal complexes(Zarandi et al., 2019). As of late, it is seen that essential heterocyclic natural mixtures like pyrimidine increment the decrease response of CO2 transformation when contrasted with other homogeneous impetuses. (Albo et al., 2015).

Alteration is done in electrocatalysts to expand the decrease effectiveness and increment the faradaic productivity. As of late, the impetuses are being changed and intended to control the elements of nano-particles showing a mono-dispersive configuration(Zarandi et al., 2019). The accompanying table gives data about the impetuses utilized for CO2 transformation to methanol and the response conditions needed for something very similar.

Table: Heterogeneous catalysts and the reaction conditions (pressure, temperature) for the conversion of carbon dioxide to methanol, %age of CO_2 conversion, and methanol yield.

CATALYST	**PRESSURE (MPa)**	**TEMP. (K)**	**CO_2 CONVERSION (%)**	**METHANOL YIELD**	**H_2/CO_2**	**REFERENCES**
Cu/Al_2O_3	10	473	2.4	1.05 mol kg-cat^{-1} h^{-1}	3.8/1	(Bansode et al., 2013)
$Cu\text{-}Ba/Al_2O_3$	10	473	3.6	0.14 mol kg-cat^{-1} h^{-1}	3.8/1	(Bansode et al., 2013)
$Cu\text{-}K/Al_2O_3$	10	473	2.8	1.62 mol kg-cat^{-1} h^{-1}	3.8/1	(Bansode et al., 2013)
12Cu10Zr/ɣ -Al_2O_3	3	513	14.30	-	3/1	(Zhang et al., 2006)
Cu–V/ɣ-Al_2O_3	3	513	14.10	-	3/1	(Zhang et al., 2006)
$Cu/ZnO(Al_2O_3)$	5	443	25.90	-	3/1	(Liu et al., 2007b)
$Cu/ZnO/Al_2O_3$	-	493	-	-	1/1	(Wang et al., 2010)
$Cu/ZnO/Al_2O_3$	3	513	12	212 g L^{-1}cat h^{-1}	3/1	(Wang et al., 2011)

5%Au–20% Cu/Cr_2O_3 . $3Al_2O3$	4	533	-	66 g Kg^{-1}cat h^{-1}	3/1	(Mierczynski et al., 2011)
2wt%SiO_2–TiO_2/ CuO–ZnO–Al_2O_3	2.6	533	40.70	16.8%	3/1	(Zhang et al., 2012)
$Cu/ZnO/Al_2O_3$	36	533	65.80	7.7 g g^{-1}cat h^{-1}	10/1	(Bansode and Urakawa, 2014)
$Cu/ZnO/Al_2O_3/Y_2O_3$	9	503	29.90	0.57 g g^{-1}cat h^{-1}	73/24	(Gao et al., 2015b)
Cu–ZnO–ZrO_2–MgO/Al_2O_3	2	523	12.12	31 g Kg^{-1}cat h^{-1}	3/1	(Ren et al., 2015)
$Cu/ZnO/Al_2O_3$	3	523	-	-	-	(Kunkes et al., 2015)
$Cu.ZnO/Al_2O_3$	5	543	9	-	3/1	(da Silva et al., 2016)
$Cu/ZnO/Al_2O_3$	44.2	553	65.30	15.3 g g^{-1}cat h^{-1}	3/1	(Gaikwad et al., 2016)
CuZnZr	3	503	19.6	2.3 mol kg-cat^{-1}	3/1	(Bansode and

				h^{-1}		Urakawa, 2014)
CuZnZr	3	513	17	1.65 mol kg-cat^{-1} h^{-1}	3/1	(Xiao et al., 2015)
CuZnZr	5	513	22.4	14.13 mol kg-cat^{-1} h^{-1}	3/1	(Arena et al., 2013a)
CuZnZr	5	513	9.7	37.05 mol kg-cat^{-1} h^{-1}	3/1	(Arena et al., 2013a)
CuZnTi	3	513	16.4	1.51 mol kg-cat^{-1} h^{-1}	3/1	(Xiao et al., 2015)
CuZn	3	513	16.1	1.39 mol kg-cat^{-1} h^{-1}	3/1	(Xiao et al., 2015)
CuZnTi-Zr	3	513	17.4	1.79 mol kg-cat^{-1} h^{-1}	3/1	(Xiao et al., 2015)
CuZnZrLa	3	503	20.5	2.7 mol kg-cat^{-1} h^{-1}	3/1	(Bansode and Urakawa, 2014)
CuZnZrCe	3	503	22.8	3.2 mol kg-cat^{-1} h^{-1}	3/1	(Bansode and Urakawa, 2014)
ZrO_2 doped	5	523	26.41	0.22 g mL^{-1}	3/1	(Yang et al.,

CuZnO				h^{-1}		2006)
$Cu/ZnO/ZrO_2$	3	523	19.40	-	3/1	(Raudaskoski et al., 2007)
Cu/Zn/Al/Zr	4	513	20.51	0.435 g mL^{-1} h^{-1}	3/1	(An et al., 2007)
$Cu–ZnO/ZrO_2$	3	513	17.50	-	3/1	(Arena et al., 2007)
$Cu–ZnO/ZrO_2$	1	473	3.20	-	3/1	(Arena et al., 2008)
$CuO/ZnO/ZrO_2$ (CZZ)	3	513	17	9.6%	3/1	(Guo et al., 2009)
$CuO/ZnO/ZrO_2$ (CZZ)	3	493	12	8.5%	3/1	(Guo et al., 2010)
Cu/ZrO_2	2	523	13.60	1.76 mmol $g^{-1}h^{-1}$	3/1	(Zhuang et al., 2010)
$Cu/ZnAl_2O_4$	4	533	-	233 g g^{-1}cat h^{-1}	3/1	(Maniecki et al., 2010)
$Cu/ZnO/ZrO_2$	3	513	15.70	9.1%	3/1	(Guo et al., 2011a)
$La-Cu/ZrO_2$	3	493	6.20	4.3%	3/1	(Guo et al., 2011b)

ZnOCu/CeZrO_2	3	513	16.90	-	3/1	(Bonura et al., 2011)
Cu/ZnO	0.7	413-433	-	-	9/1	(Karelovic et al., 2012)
Cu/Zn/Al/Y	5	523	26.90	0.52 g g^{-1}cat h^{-1}	3/1	(Gao et al., 2013)
Cu–ZnO/ZrO_2	5	513	22.40	14.3%	3/1	(Arena et al., 2013b)
Cu–ZnO–ZrO_2	7	523	22	22 mol kg-cat^{-1} h^{-1}	3/1	(Ladera et al., 2013)
Cu-ZrO2/CNF	3	443	-	4.28 g Kg^{1}cat h^{-1}	3/1	(Din et al., 2014)
Cu/CrCuO_4 and Cu/ Mo_2C	4	408	-	-	3/1 (V:V)	(Chen et al., 2015)
CuO/ZnO-filament	3	513	16.50	0.55 g g^{-1}cat h^{-1}	3/1	(Lei et al., 2015)
CuO–ZnO	3	513	17.40	7.6%	3/1	(Xiao et al., 2015)
Cu/Hal	3	553	15	-	3/1	(Witoon et al., 2016)
CuO–ZnO–	3	513	12.10	6.5%	3/1	(Li et al., 2015)

ZrO_2						
$(CuZnGa)_{MW}$	3	543	15.90	4241 mmol kg-cat^{-1} h^{-1}	3/1	(Cai et al., 2015)
$Cu_2Zn_1Al_{1.2}Zr_{0.1}$	9	523	36.50	0.45 g g^{-1}cat h^{-1}	73/24	(Gao et al., 2015a)
Cu–ZnO	3	523	-	-	3/1	(Tisseraud et al., 2015)
core–shellCu/ZnO@m-SiO_2	5	543	11.90	153.9 g kg^{1}cat h^{-1}	73/24	(Yang et al., 2016)
Cu/β -Mo_2C	2	573	28	-	5/1	(Posada-Pérez et al., 2016)
Cu-ZrO_2	3	523	-	-	3/1	(Ro et al., 2016)
Cu/Zn/Al/Zr fibrous	5	523	25.50	-	3/1	(Kiss et al., 2016)
Cu/ZnO/ZrO_2	5	543	23	0.21 g mL^{-1} h^{-1}	3/1	(Dong et al., 2016)
CuZn/rGO	1.5	523	26	424 mg g_{cat}^{-1} h^{-1}	3/1	(Deerattrakul et al., 2016)
CuO–ZnO–ZrO_2	2	513	13.20	219.7 g kg^{1}cat h^{-1}	3/1	(Witoon et al., 2016)

Cu–ZnO	3	523	-	-	3/1	(Tisseraud et al., 2016)
$ZnO\text{-}ZrO_2$	2	573	3.4	7.75 mol kg-cat^{-1} h^{-1}	3/1	(Wang et al., 2017a)
	5	593	10	23.04 mol kg-cat^{-1} h^{-1}	3/1	(Wang et al., 2017a)
$Pd\text{-}Cu/SiO_2$	4.1	523	6.6	1.12 mol kg-cat^{-1} h^{-1}	3/1	(Jiang et al., 2015)
Pd-Cu/P25	4.1	523	16.4	1.80 mol kg-cat^{-1} h^{-1}	3/1	(Lin et al., 2019)
$Pd\text{-}Cu/CeO_2$	4.1	523	9.9	1.37 mol kg-cat^{-1} h^{-1}	3/1	(Lin et al., 2019)
$Pd\text{-}Cu/ZrO_2$	4.1	523	15.8	1.87 mol kg-cat^{-1} h^{-1}	3/1	(Lin et al., 2019)
$Pd\text{-}Cu/Al_2O_3$	4.1	523	12.4	1.69 mol kg-cat^{-1} h^{-1}	3/1	(Lin et al., 2019)
$Pd\text{-}Cu/Ti_{0.1}Zr_{0.9}O_2$	4.1	493	6.4	1.80 mol kg-cat^{-1} h^{-1}	3/1	-
Pd/Mo_2C	4	473	97	-	3/1	(Chen et al., 2016)
Pd-	4.1	523	10.1	2.23 mol kg-	3/1	-

$Cu/Ti_{0.1}Zr_{0.9}O_2$				cat^{-1} h^{-1}		
Pd-P/In_2O_3	5	573	20	27.81 mol kg-cat^{-1} h^{-1}	4/1	(Rui et al., 2017)
Pd-I/In_2O_3	5	573	18	25 mol kg-cat^{-1} h^{-1}	4/1	(Rui et al., 2017)
Pd-In_2O_3CP	5	553	-	31.56 mol kg-cat^{-1} h^{-1}	4/1	(González-Garay et al., 2019)
Pd-In_2O_3CP	5	553	-	19.06 mol kg-cat^{-1} h^{-1}	4/1	(González-Garay et al., 2019)
Pd–ZnO	3	523	6.3	37.1 mg g^{1}cat h^{-1}	3/1	(Liang et al., 2009)
Pd@Zn	4.5	543	-	12 g g^{1}cat h^{-1}	-	(Liao et al., 2016)
Pd/ZnO	0.1	423-573	4	-	9/1	(Díez-Ramírez et al., 2016)
Pd–Cu/SiO_2	4.1	523	6.6	0.31 µmol g^{1}cat h^{-1}	3/1	(Jiang et al., 2015)
Pd/β–Ga_2O_3	1.7	543	12	-	7.5/1	(Oyola-Rivera et al., 2015)

Pd-ZnO	5	543	7	343 mg g^{1}cat h^{-1}	3/1	(Liang et al., 2015)
Pd-Ga_2O_3	5	523	9.8	555 mg g^{1}cat h^{-1}	3/1	(Kong et al., 2011)
Au/Al_2O_3	0.5	493	2	0.02 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2015)
Au/ZnO	0.5	493	0.2	0.08 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2015)
Au/ZnO	5	513	1	4.23 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2016)
	0.5	513	0.4	1.19 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2016)
Au/ZnO	0.1	498	1	0.09 mol kg-cat^{-1} h^{-1}	9/1	(Vourros et al., 2017)
Au/ZrO_2	0.5	493	5.3	0.18 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2015)
Au/TiO_2	0.5	493	9.4	0.04 mol kg-cat^{-1} h^{-1}	3/1	(Hartadi et al., 2015)
Au/CeO_2	0.1	498	1	0.15 mol kg-cat^{-1} h^{-1}	9/1	(Vourros et al., 2017)
Au-CuO/SBA-	3	523	24.2	-	3/1	(Li et al., 2017)

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Materials for CO_2 conversion

Nanomaterials

Studies are being done to decrease CO2 and convert it into significant items, one of them being methanol. Among numerous methodologies used to diminish CO2 and combine methanol, utilizing nanomaterials as an impetus has stood out because of their different properties. High surface region, low planned locales, and enormous edge parcel are the properties that give these metallic nanoparticles an interesting synergist execution when contrasted with the other mass materials.(Yang et al., 2018) Direct hydrogenation of methanol from CO2 is a harmless to the ecosystem response when it is performed utilizing efficient impetuses. Bi-metallic Pd-In nanoparticles were created for this response and they showed great synergist movement. These intermetallic nanomaterials were seen to be generally effective as they showed 70% higher methanol rates during fluid stage methanol combination tests, they likewise displayed >80% improved methanol selectivity at 270˚C when contrasted with the recently utilized heterogeneous impetus, Cu/ZnO/Al2O3 which showed just 45% methanol selectivity. Cu/ZnO/Al2O3 shows low methanol selectivity, solidness, and normal synergist movement. Creating impetuses dependent on In2O3 (Martin et al., 2016), PdGa2O3 (Fiordaliso et al., 2015), AuZnO (Hartadi et al., 2016), PdZnO (Bahruji et al., 2016), and CuCeO2 (Johnston-Peck et al., 2013) are totally demonstrated to be viable nanomaterials.

Porphyrins

Porphyrins are broadening their approval towards catching CO2 and its transformation into some significant items like methanol. Effective porphyrin-based materials are being created like porphyrin-based nanoreactors, porphyrin-based translucent materials, porphyrin-based dendrimers, covalent natural structures, metal-natural systems, and permeable natural polymers for CO2 catch and porphyrin and metalloporphyrin-based impetuses have been utilized for its transformation into esteem added items like methanol. (Kumar et al., 2015)Methanol, as a final result after CO2 change, relies upon the focal particle of the porphyrin ring. Metals, for example, Cu, Ag, Au, Ni, and Pd as focal metal iotas in the porphyrin ring produce methanol. (Tripkovicet al., 2013) Photoelectrocatalysis method (PEC) was applied interestingly to change over CO2 into methanol utilizing porphyrin, Ti/TiO2 nanotubes were covered with a complex of copper (II) porphyrin ([Cu(T4H3MPP)]), giving (Ti/TiO2NT-CuP), this framework was upheld by Na2SO4 electrolyte and ¬optimized under encompassing conditions giving a methanol yield of 0.033mmol/L. (Brito et al., 2020) Photosensitized-TiO2 nanotube adjusted by Zn (II) porphyrins and Ru (II) polypyridyl/edifices was utilized as a porphyrin-based impetus for CO2 decrease and transformation into methanol with an item centralization of 746 µmol/L/gcat-1 (Wang et al., 2012) Liu et al., utilized Cu¬¬¬2+ in a porphyrin-based MOF, (5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin TCPP) based MOF for CO2 catch and change into methanol, mirroring the cycle of photosynthesis.

In the wake of checking on writing identified with CO2 change into methanol, it tends to be summed up that doping porphyrin moieties into different impetuses can build the fluid stage age of methanol altogether.

Table: Reduction of CO_2 to methanol using a photocatalyst doped with porphyrins, the medium of reaction, and yield of methanol produced.

Porphyrin-doped photocatalyst	**Reaction medium**	**Temperature (˚C)**	**Product(s)**	**Methanol yield**	**Reference**
Ti-MCM-48(25)CuTPP	0.1M ($NaOH/Na_2SO_3$)	25	Methanol	297.06 µmol.g^{-1}	(Nadeem et al., 2018)
Ti-MCM-48(25)	0.1M ($NaOH/Na_2SO_3$)	25	Methanol	85.23 µmol.g^{-1}	(Nadeem et al., 2018)
Cu complex/GO	DMF/H_2O (9:1)	-	Methanol	1600 µmol.g^{-1}	(Kumar et al., 2015)
CuPpMOF	H_2O/ Triethyl	5	Methanol	262.6 µmol.g^{-1}.h^{-1}	(Liu et al., 2013)
TiO_2NTs/Cu porphyrin-Ru complexes	0.05M ($NaOH/Na_2SO_3$)	50	Methanol	733 µmol.g^{-1}	(Wang et al., 2012)
Cophthalocyanine/ TiO_2	$NaOH/Na_2NO_3$	-	Methanol, Methane, Hydrogen, CHO, Formic acid	2.1 µmol.g^{-1}	(Liu et al., 2007a)
Ti-Si thin film	CO_2, H_2O Vapours	-	Methanol, Methane	Approx. 16 µmol.g^{-1}	(Ikeue et al., 2002)
Ti-β(F)/Ti-β(OH) Zeolites	CO_2, H_2O Vapours	-	Methanol, Methane	>0.5 µmol.g^{-1}	(Ikeue et al., 2001)
Ti-MCM-41/ Ti-MCM-48	CO_2, H_2O Vapours	-	Methanol, Methane	1.5 µmol.g^{-1}	(Anpo et al., 1998)

Metal Organic Frameworks (MOFs)

Table: MOF-based catalysts for the conversion of CO_2 to methanol using heterogeneous catalysis method for conversion and their catalytic performance under ambient conditions.

MOF-based Electrocatalyst	Reaction time (h)	Faradaic efficiency of methanol	Remark	Reference
Cu/C derived from MOF	5	43.2%	Low yield	(Zhao et al., 2017)
HKUST-1	17	5.6%	Very low FE	(Albo et al., 2017)
Ru doped-HKUST-1	1	$FE_{methanol} + FE_{ethanol} = 47.2\%$	Catalytic activity unstable for longer reaction period	(Perfecto-Irigaray et al., 2018)
Co-Pc-PBBA	24	-	Not specific for methanol production	(Yao et al., 2018)
Ti/TiO_2-ZIF-8	50	-	Relatively low methanol yield	(Cardoso et al., 2018)

Biochar

Squander natural matter or biomass is a modest and economical carbon-rich matter, it's anything but an effective option to other petro-determined fills because of its pervasive and carbon-nonpartisan nature. (Li et al., 2014)

It is pyrolyzed or thermochemically changed over into a strong material in an oxygen-restricted climate. This strong result is known as biochar. Biochar can be gotten by biomass carbonization as the fundamental item and by biomass gasification and quick pyrolysis as a result. Various sorts of biochar are acquired dependent on the substance of lignin, cellulose, and hemicellulose (Xiong et al., 2017)

An increment in temperature while transformation of biomass to biochar diminishes its yield yet additionally expands the surface space of biochar which is useful for better adsorption. (Madhu et al., 2016)

The accompanying table shows a few instances of biomass crude material utilized in the development of biochar under a given temperature.

Table- Biochar yield from biomass raw material at a given temperature.

Biomass raw material	**Temperature (K)**	**Biochar yield (%)**	**References**
Corncob	673-973	34.2-20.2	(Zhang et al., 2009)
Corncob	723-1523	5.7-30.6	(Demirbas, 2004)
Olive husk	723-1523	19.4-44.5	(Demirbas, 2004)
Pine	573-723	26-58	(Shabangu et al., 2014)
Rice husk	673-873	25.5-33	(Williams and Nugranad, 2000)
Sewage sludge	623-1223	39-52	(Sánchez et al.,

2009)

In a study reported by Lobos et al., they researched for electro-oxidation of methanol using biochar supported Cu-Ru@Pt nanoparticles as a catalyst which exhibited a 3-9 times higher catalytic activity as compared to commercial Pt-Ru/C catalyst. (Lobos et al., 2016)The following table presents biochar-based catalysts used in the conversion of biomass to methanol under ambient conditions.

Table: Biodiesel production using biochar catalyst under ambient conditions (temperature and time)

Catalyst	**Biodiesel production**	**Ratio**	**Temperature (Celcius)**	**Time**	**Catalytic activity**	**References**
Waste eggshells supported on fly ash biochar	Soybean oil and methanol	1:6.9	70	5h	FAME yield of 96.97%	(Chakraborty et al., 2010)
Bovine bone waste biochar	Soybean oil and methanol	1:6	65	3h	FAME yield of 97%	(Smith et al., 2013)
Crab shell biochar	Karanja oil and methanol	1:8	65	120 min	Biodiesel yield of 94%	(Madhu et al., 2016)
Chicken manure biochar	Waste cooking oil and methanol	1:20 (V: V)	350	-	FAME yield of 95%	(Jung et al., 2018)
Pig meat and bone	Palm oil and methanol	1:7	65	150 min	Biodiesel yield of	(Wang et al., 2017b)

meal biochar					98.2%	
Coconut shell	Palm oil and methanol	1:30	60	6h	Biodiesel yield of 88.15%	(Endut et al., 2017)
Hardwood biochar	Methanol/oil	15:1	65	24h	85.1 gL^{-1} (FAME)	(Dehkhoda and Ellis, 2013)
Wood-mixture biochar	Methanol/oil	15:1	150	3h	44%	(Yu et al., 2011)
Peanut hull-biochar	Methanol/oil	20:1	60	6h	70%	(Kastner et al, 2011)
Commercial biochar	Methanol/oil	10:1	150	3h	48%	(Dehkhoda et al, 2013)
Rice husk biochar	Methanol/oil	20:1	110	15h	88%	(Li et al, 2014)
Palm kernel shell biochar	Methanol/ sunflower oil	9:1	60	6h	99%	(Bazargan et al., 2015)

Bio-inspired materials for CO_2 sequestration

Designing a catalyst is a challenging task. One of the ways of overcoming this challenge is by taking ideas from natural systems that have evolved over many years to efficiently perform redox reactions at lower energy costs. Like, the mineral greigite can reduce CO_2 to methanol at ambient conditions owing to its structural similarity to modern-day CO_2 converting enzymes. (Roldan et al., 2015)Naturally, there are six mechanisms to reduce carbon dioxide, i.e. reductive pentose phosphate cycle, reductive acetyl-CoA pathway, reductive citric acid cycle, dicarboxylate cycle, 4-

hydroxybutyrate cycle, and 3-hydroxypropionate bi-cycle. The designing of bio-inspired catalysts is a way to modify the living systems by adding certain characteristics to improve their performance. Bio-inspired materials have many advantages like biodegradability, low corrosion, ease of disposal, and easy configuration. (Carrera et al., 2017)One such study was reported by Apkle et al., where they designed a biocatalyst inspired by honeycomb. It was prepared by thermal condensation of Si-O_2 templates and dicyandiamide creating a honeycomb-like structure in HC-C_3N_4 accumulating $Ni(OH)_2$ nanoclusters as a replacement to platinum, on the surface of the catalyst to improve charge segregation efficiency. This biocatalyst showed an excellent reduction of CO_2 to methanol by generating 0.73µmol/h/g (Akple et al., 2020)Tsung and his co-workers prepared a synthetic catalyst for the conversion of CO_2 to methanol, that is the most active system reported till date, after getting inspired by the naturally occurring fuel-producing supramolecular protein assemblies. They used ruthenium-based catalysts, encapsulating one of them in MOF UiO-66 so that it could be used later. The catalytic activity could be modulated by changing the positions of the catalysts similar to the supramolecular protein assemblies in enzymes. The multi-catalytic system carried out the conversion process in three steps. First, converting CO_2 to formate, then esterification of formic acid to formate, and finally, the conversion of formate to methanol showing $2.23*10^{-7}$mmol catalytic activity in the final step. (Rayder et al., 2020)

Biomaterials	**Temperature/ Pressure**	**Adsorption removal capacity for Carbon Capture and Storage**	**Reference**
KOH activated starch	298 K/ 1 Bar	15.2 wt%	(Cooper, 2015)
KOH activated cellulose	298K/ 1 Bar	15.2 wt%	(Cooper, 2015)
Celtuce derived porous carbon	298 K/ 1 Bar	19.2 wt%	(Cooper, 2015)
Sawdust derived carbon sorbents	298 K/ 1 Bar	21.2 wt%	(Cooper, 2015)
LC-1 700	273-298 K/ 0.01-1.00 Bar	0.29	(Cooper, 2015)
LC-2 600	273-298 K/ 0.01-1.00 Bar	0.27	(Cooper, 2015)
LC-2 700	273-298 K/ 0.01-1.00 Bar	0.30	(Cooper, 2015)
LC-2 700H	273-298 K/ 0.01-1.00 Bar	0.31	(Cooper, 2015)
LC-2 800	273-298 K/ 0.01-1.00 Bar	0.32	(Cooper, 2015)
LC-3 700	273-298 K/ 0.01-1.00 Bar	0.28	(Cooper, 2015)
Amine-Mg (DOBDC) MOF	298K/ 1 Bar	5.66 mmolg^{-1}	(He et al., 2018)
Mg-MOF-74	296K/ 1 Bar	8 mmolg^{-1}	(Shao et al., 2013)
D-PEO	308K/ 3.5 Bar	-	(Qian et al., 2015)
D-PEO-1	308K/ 3.5 Bar	49 Barrer	(Qian et al., 2015)
Am-PEO	308K/ 4.05 Bar	12 Barrer	(Hull et al., 2012)
XLPEGDA	308K/ 4.05 Bar	12 Barrer	(Hull et al., 2012)
LCM	-	17 Barrer	(Zhu et al., 2015)

Table: Enzymatic conversion of CO_2 into methanol using multi-enzymatic systems and the average rate of formation of methanol per hour.

Enzymes	**System**	**Methanol productivity (Mm/h)**	**Reference**
CIFDH+BmF$_{ald}$DH+YADH+PTDH	Free enzyme	0.55	(Singh et al., 2018)
CIFDH+BmF$_{ald}$DH+YADH+PTDH	Free enzyme	0.49	(Singh et al., 2018)
CIFDH+BmF$_{ald}$DH+YADH+PTDH+EMIM-Ac	Free enzyme	1.13	(Singh et al., 2018)
CIFDH+BmF$_{ald}$DH+YADH+PTDH+EMIM-Ac	Free enzyme	1.31	(Singh et al., 2018)
CbFDH+ PpF$_{ald}$DH+ YADH	Free enzyme	0.007	(Yadav et al., 2014)
CbFDH+ PpF$_{ald}$DH+ YADH+ PTDH	Free enzyme	0.014	(Cazelles et al., 2013)
CbFDH+ PpF$_{ald}$DH+ YADH+ GDH	Co-immobilized	0.040	(El-Zahab et al., 2008)
CbFDH+ PpF$_{ald}$DH+ YADH	Immobilized	0.002	(Jiang et al., 2009)

Chemo-enzymatic conversion of CO_2 into methanol

Biochemical techniques can be utilized for the decrease of CO2 and its transformation to lessen the contamination brought about by the results for example make the cycle eco-accommodating and increment the usage of CO2. Biochemical strategies are favorable as the necessary energy for carbon catch is less, usefulness can be improved by straightforwardly infusing CO2 and green growth can be used at lower costs when contrasted with different techniques. (Yaashikaa et al., 2019)Sulphuric corrosive or a strong base can be utilized as impetuses yet they have a few burdens like erosion of equipment.Microbialelectrosynthesis analyze showed that homoacetogens may deliver extracellular acetic acid derivation and 2-oxobutyrate utilizing carbon dioxide and electrons are provided through graphite electrode(Nevin et al., 2010). Microbial electrosyntheis (MES) is getting mainstream among researchers because of its properties like potential for sunlight based to item productive change of CO2 when contrasted with heterotrophic aging routes(Claassens et al., 2016). Electrochemical responses including biocatalysts don't deliver any harmful mixtures and are savvy. MES is more specific towards acetic acid derivation and methane from CO2 decrease. Electro-aging is likewise accomplished for the bioconversion of different sorts of natural matter.(Chu et al., 2020)The CO2 catch from the air is costly, henceforth the mechanical creation of powers and different items utilizing CO2 ought to be decentralized and high volume squander CO2 can be utilized as a crude material(Bui et al., 2018; Haas et al., 2018). Lipase can be utilized as an impetus for transesterification since it is productive and explicit. It actually has numerous disadvantages to be utilized as an impetus like longer response time, response conditions should be kept up stringently and the compound can't be reused (Xiang et al., 2019). Aminopyridine cobalt complex can be utilized for transformation of CO2 to CO, aminopyridine cobalt complex copies the impact of CO-dehydrogenase(Wang et al., 2019)

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