CATALYTICAL CONVERSION OF CARBON DIOXIDE INTO VALUE ADDED PRODUCTS USING g-C_3N_4 AND Zn BASED CATALYST

A MSc Dissertation report by:

AASHNA M. GOLTEKAR

Roll No: 20P0490035

DEPARTMENT OF CHEMISTRY

GOA UNIVERSITY

GOA 403206

May 2022

CATALYTICAL CONVERSION OF CARBON DIOXIDE INTO VALUE ADDED PRODUCTS USING g-C_3N_4 AND ZINC (Zn) BASED CATALYST

A DESSERTATION REPORT

Submitted in Partial Fulfillment

Of

The Degree Of M. Sc. (Inorganic Chemistry)

By

Ms. Aashna M. Goltekar

To the

Department of Chemistry

Goa University

Goa 403206

MAY 2022

CERTIFICATE

This is to certify that the dissertation entitled catalytical conversion of carbon dioxide into value added products using g-C_3N_4 and Zn based catalyst is bonafied work carried out by MS. AASHNA M. GOLTEKAR under my supervision in partial fulfilment of the requirement for the award of the Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. Dr. Rohan Kunkalekar

Guiding Teacher

Dean of School Of Chemical Sciences

Goa University

Aashna M. Goltekar

(M Sc. Student)

ACKNOWLEDGEMENT

With deepest gratitude and appreciation, I humbly give thanks to the people who, with all they can, helped me in making my project successful.

First and foremost, I express my profound gratitude to my guide Dr. Rohan Kunkalekar, Professor in Inorganic Chemistry for giving me an opportunity to work under his guidance. I am grateful for his elevating inspiration and motivation in making the project a success.

I am very much grateful to Prof. Dr. Vidyadatta Verenkar (Dean of School Of Chemical Sciences) for his valuable guidance and support.

I also express sincere gratitude towards family and friends for their support and encouragement.

INDEX

INTRODUCTION

What is **carbon dioxide (CO_2)**?

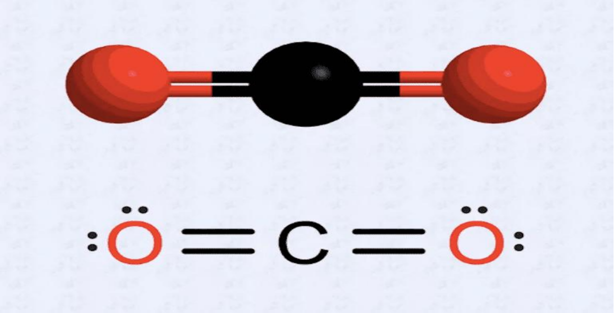
Carbon dioxide (CO_2) is a chemical compound occurring as an acidic colourless gas with a density about 53% higher than that of dry air. Carbon dioxide molecules consist of a carbon atom covalently double bonded to two oxygen atoms. It occurs naturally in Earth's atmosphere as a trace gas.

Carbon dioxide (CO_2) is one of the main greenhouse gases contributing to global climate change. According to the Natural Oceanic and Atmospheric Administration (United States), the global mean CO_2 level reached 410ppm in 2019[1].

CO_2 is thermodynamically stable molecule with the standard formation enthalpy of -393.5 kJ mol^{-1}[2].

STRUCTURE OF CO_2 MOLECULE:

In a CO_2 molecule, two σ bonds are formed through an sp hybrid carbon with two oxygen atoms. There are two delocalized π bonds with three centres and four electrons from un-hybridized p orbitals of the carbon atom with p orbitals of the oxygen atom in overlapping fashion[3]. As a result, the C=O bond length of CO_2 found to be 1.16Å, within the bond length of normal C=O(1.22Å) and C≡O (1.10Å). As the carbon atom in CO_2 is at the highest Valence state and high first ionization energy (13.97 eV), appropriate catalyst are required for CO_2 activation, leading to further conversion. On the other hand, CO_2 possesse un-occupied orbitals bearing low energy level and high electronic affinity (3.8 eV). Additionally CO_2,has a centre of symmetry and the asymmetric stretching is about 2340 cm^{-1}. Furthermore, the bond angle of CO_2 can be changed upon interaction with a metal complex[2].



The general properties of CO_2 molecule associated with its reactivity:

1) Bending of CO_2: For the uncharged state, bending of the molecule from its linear equilibrium geometry induces changes in the shape and energy level of the molecular orbitals. Changing the OCO bond angle from 180^o to 157^o, the proportion of the LUMO on the carbon is increased from 61% to 78%, while the distance between carbon and oxygen (<0.001Å) and the energy (ΔE<0.5 eV) remain almost constant. Importantly, this lowering of the in plane $2\pi_u$ orbital (LUMO) energy bending makes the carbon atom electrophilic.
2) Repartition of charges: When isolated, appositive charge can be founf on the carbon atom and negative charges on the two oxygen atoms (with population of -0.184) e). A polarised medium like water can increase the charge on the carbon to =0.407 e. This environmental effect together with the first point of LUMO lowering can make the carbon atom of CO_2 more reactive.

3) Electron transfer to CO_2 When an electron transfer to CO_2, it becomes a radical anion. The electron transfer is facilitated when CO_2 Is bent as the LUMO level is lower. Its equilibrium geometry is highly bent (ca. 135^o) with singly occupied molecular orbital at a very high energy level(i.e. nucleophilic), very close to the LUMO of the neutral CO_2 at 135^o OCO angle with almost the same orbital character. The bond angle elongated by ca. 0.008Å compared to the neutral linear state, indicating the weakening of the C-O bond[2].

CO_2 is a well known stable molecule that posses energy like H_2O (ΔG^o_f =-396 kJ/mol). Hence, CO_2 conversion into valuable products requires high energy depending on the downward steps for 4+ oxidation state of carbon. This reveals that energy required for CO_2 conversion, where O/C ratio >2 and H/C ratio equals to zero (i.e. reduction of CO_2). CO_2 is one of the main green house gas that contribute to global warming and is usually emitted due to anthropogenic activities. Although methane is also a significant green house gas attributing to associated environmental problems, CO_2 has the highest potential, thus attracting significant attention. It is well known that CO_2 has the highest probability of being trapped in the atmosphere for a long time[4].

Scientific research shows that the emitted CO_2 may last 100-160,000 years. The latest findings indicate that atmospheric CO_2 emissions increased by approximately 40% between 1750 and 2011, and more than 400 ppm was released in 2013 alone. The research findings also show that about 50% of CO_2 emissions into the atmosphere occurred in the past 45 years[4].

In carbon capture and storage, the elementary perception of is to capture CO_2 emission that prevent its release into the atmosphere. CCS includes sequestration and storage. CCS is the process of trapping and compressing in large amounts of CO_2. CCS requires CO_2 to be compressed from its source into high density CO_2 making it suitable for transport, storage and monitoring[5].

CO_2 conversion to hydrocarbon fuels involves a high energy process, where the C oxidation state is 2+ or lower for possible production of compound such as HCCOH, H_2CO, CH_3OH, CH_4 and other HC. The conversion of CO_2 can lead to several different chemical/ fuel products depending on the material/ catalyst and/or methods employed, including carbon monoxide(CO), formic acid(HCOOH), methane(CH_4), methanol(CH_3OH), ethylene(C_2H_4), ethane(C_2H_6), propane(C_3H_8), ethanol(C_2H_5OH), acetic acid(CH_3COOH), acetone, n-propanol, acetaldehyde, allyl alcohol, dimethyl ether, glycolaldehyde, hydroxyacetone, ethyl glycol, propionaldehyde and glycerol[1].

Catalytical conversion of CO_2 can occur in gas phase, liquid phase, or electrochemical cells. Because the solubility of CO_2 is quite low in aqueous solution, the CO_2 conversion in liquid phase typically have low output. Various metal oxides, metal oxides, metal carbides, and doped carbon materials have been used as catalyst.

Recent studies shows that the mechanism of MeOH to HC conversion proceeds via two steps:

1. Short induction period.
2. Auto catalytic dual- cycle.

The direct configuration of C-C bond takes place in the induction period for the coupling of two MeOH molecules through surface methoxy species while, the dual cycle involves the methylation and cracking of olefin, methylation and de-alkylation of aromatics, H_2 transfer and cyclization that takes over the catalyst and selectivity of the product[4].

❖ Graphite-Carbon Nitrite (g-C_3N_4)

The nitrogen containing carbon materials, such as carbon nitrides are unique class of materials which can be prepared economical nitrogen and carbon containing precursors. Since, this material has a large number of nitrogen contents, it can be used for the CO_2 activation and adsorption. Among the porous materials, carbon materials have a high surface area, tunable porosity, hydrophilicity for CO_2 adsorption under-hydrated condition, high thermal and chemical stability, and functional ability. The adsorption capability improves if the nitrogen-doped or nitrogen-containing carbon materials are considered. Nitrogen –containing carbon materials induce the interactive forces between CO_2 and nitrogen groups present in the material. CO_2 is a weak Lewis acidic molecule because carbon atom in the CO_2 is electron deficient. Nitrogen doped carbon atoms are negatively charged and nitrogen sites act as electron donor and behave like Lewis base, therefore nitrogen containing carbon materials have acid-base interaction through which CO_2 molecules are chemisorbed. Strong dipolar C=O bond generates an electric quadrupole moment in the CO_2 molecule whereas nitrogen doping induces local polarisation in the porous carbon matrix. N_2 has lower electric dipole moment than CO_2. Hence, the interaction between the CO_2 molecular quadrupole and high electrostatic potential of N-doped carbons enhances the CO_2 adsorption energy, leading to selective and higher CO_2 adsorption from the flue gases[6].

The graphite carbon framework provides high thermal stability and conductivity which would be good for photocatalysis and electrocatalysis. Based on this characteristic features, a unique carbonaceous material known as graphite carbon nitride can best serve this purpose[6].It has been also reported to be an excellent substrate for supporting catalyst. Using g-C_3N_4 as a substrate to support noble-metal catalysts for CO_2 hydrogenation offers a number of inherent advantages, including maintaining the noble-metal atoms in their neutral state,directly providing hydrogen source and possessing excellent solar light absorption[7].

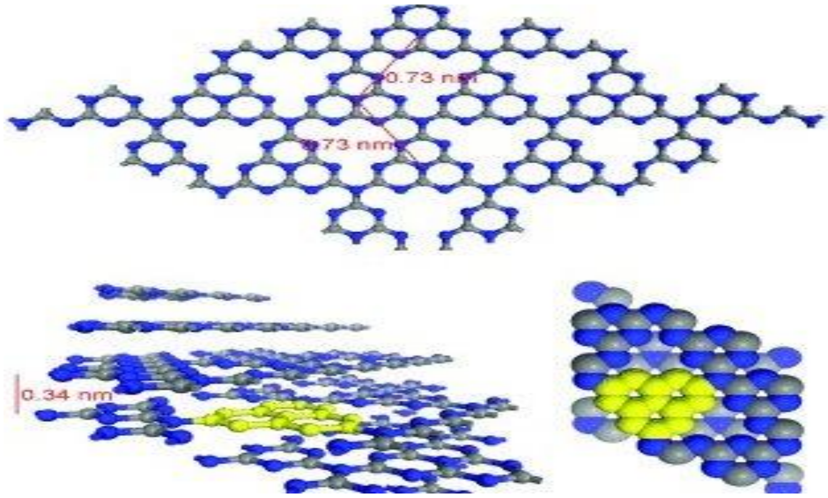
In 1834, Berzelius, a simple nitrogen-rich organic compound (such as cyanamide, dicyandiamide, etc.) was thermally-polymerised in the temperature range of 500-700 ^{o}C, it produced carbon nitride. However its potential as a catalyst was realized in 2006[6]. Theoretical g-C_3N_4 should have an ideal C/N ratio of 0.75 and should not possess any H and O atoms, however, XPS and elemental analysis suggest that it has H and O atoms in small quantities in addition to C and N[6].

g-C_3N_4 has strong resistance to oxygen and electron-rich properties (surface basic sites), being a suitable catalyst for ‘NO’ decomposition. In addition, the polar C−N−C groups of gC_3N_4 can also provide ideal adsorption sites for ‘NO’ (that is a polar molecule). In order to verify the applicability of g-C_3N_4 to ‘NO’ decomposition, theoretical simulations based on density functional theory (DFT) calculations were attempted, showing that the N−O bond length can be elongated from 1.163 to 1.381 Å when ‘NO’ is parallelly adsorbed on g-C_3N_4, conforming that g-C_3N_4 is a suitable catalyst for ‘NO’ dissociation[8].

Synthesis strategies adopted for the preparation of carbon nitrides for improved CO_2conversion

1) **Template free synthesis for improved catalysis:** Nitrogen-rich organic compound such as cyanamide and dicyanamide was heated in semi-closed systems in oxygen-lean conditions to form g-C_3N_4. g-C_3N_4 was formed by the various condensation steps in which the first melamine was formed at lower temperatures (<350^oC) followed by removal of NH_3 leading to tris-s-triazine at a temperature around 400^oC. The polymerisation of tris-s-triazine takes place at around 500^oC to form g-C_3N_4. During the polymerisation process, the amines groups of tris-s-triazine does not condense completely which results in the formation of uncondensed amine group-containing g-C_3N_4 with about 2% of H content with C/N ratio less than 0.75. Such structural defect are is important for the adsorption of the reacting molecule which is good for catalytic reaction. High temperature polymerisation leads to crystalline form ofg-C_3N_4 which is better for charge carrier separation and a high degree of π conjugation. With increase in the pyrolysis temperature aggregated bulk g-C_3N_4 changes to nano-sheets and nanoflakes like morphology with improved surface area[6].
2) **Template-mediated synthesis strategy to produce g-C_3N_4 with high surface area and porosity for improved CO_2 adsorption:** The various templte-mediated synthetic utilize silica based mesoporous materials (SBA-15, SBA-16, KIT-6, MCM-41, MCM-48) as the template. Nitrogen-containing organic precursor of carbon and nitrogen precursor are infiltrated into the porous architecture of silica materials via incipient wet impregnation or wet impregnation method followed by pyrolysis which results in the formation of g-C_3N_4 / silica hybrid materials. Then the silica template is removed chemical etching using various etching agents, for example NaOH, HF, NH_4HF_2. The final product has the same architecture like that of the original silica material. In general, the pore diameter of the resulted material is smaller than porous silica material due to volume shrinkage of g-C_3N_4 filled inside the pore during the condensation. The surface area and porosity significantly depend on Si/ precursor, hard template and an etching agent. The surface area can be further improved if the original silica material is treated with acid to enhance the surface reactivity that allows large number of organic precursor to in-filter that improves the surface area of the resultant material. This synthetic strategy produce a low yield of g-C_3N_4 and therefore difficult for the application in the large scale synthesis of mesoporous g-C_3N_4. To overcome this problem, $CaCO_3$ has been used as a hard template in which the template is removed with dilute HCl after polymerisation leading to the formation of high surface area of g-C_3N_4 with improved catalytic activity. Large scale synthesis of mesoporous g-C_3N_4 can be achieved using the soft template method. Since the soft template is a carbon –based compound, therefore , g-C_3N_4 with higher C/N is formed with diverse functionality. Among the soft template, only a few templates such as triton-100 and ionic liquids have produced g-C_3N_4 with large surface area and porosity. Ionic liquids act as soft modifiers for the thermal polymerization leading to tunable textural properties, morphology and reactivity. Template mediated synthesis strategies can provide materials with high surface area and porosity but it is difficult to tune N content[6].
3) **Strategies to functionalize and dope elements to improve catalytic activities and light absorption properties:** Template-mediated synthetic strategies can improve the surface area and porosity. However, for tuning the catalytic activities relating to the efficient adsorption of reactants and light adsorption; suitable doping and functionalizations are required. By H_2O_2 treatment, O doped g-C_3N_4 with high surface area is obtained that exhibits efficient charge carrier separation, and red –shift in the absortion spectra. Oxygen group

containing melamine precursor alsoproduces O doped g-C_3N_4. Organic surfactant mediated synthesis produces C doped g-C_3N_4. Diammonium hydrogen phosphate ,hexachloro-cyclotriphosphazene, 2-aminoethylphosphonicacid, etc. have been used as P source to dope P into the g-C_3N_4 framework. H_2S treatment and thiourea and tri-thiocyanic acid precursor are known to dope S in the g-C_3N_4[6].



Reaction mechanism:

CO_2 reduction occurs sequentially involving multiple electrons and protons. Also, it requires splitting of highly stable C=O bonds and the creation of C-H bonds. The complete reduction occurs via the formation of several radical intermediates, which also tend to recombine at different stages during the course of a reaction. The most important parameters influencing these reactions include band edge potentials and band gap, reaction conditions, medium and catalyst[6]. During CO_2 reduction, the individual metal atoms function as the active sites, while g-C_3N_4 provides the source of hydrogen (H*). Graphite carbon nitrite is a promising stable, active, metal-free photocatalyst capable of efficiently splitting water into hydrogen.

Synthesis of methanol using c3 n4:

The CO_2 reduction pathways to HCOOH and CH_3OH on the Pd/ g-C_3N_4 catalyst. The overall reaction of CO_2 reduction to form CH_3OH on the Pd/g-C_3N_4 catalyst in the presence of hydrogen is expressed as follows:

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$

Her the Pd acts as the active site for the formation of carbon intermediates while g-C_3N_4 provides the hydrogen source from the evolution reaction ($H^+ + e^- \rightarrow H^*$) for the hydrogenation of CO_2 during reduction. The reaction includes 6 steps: The initial step of CO_2 reduction is the formation of HCOO*, which is followed by the hydrogenation of HCOO* to give HCOOH*. The approach of the third hydrogen induces the dissociation of HCOOH into HCO* and H_2O*. The HCO* is further hydrogenated to form CH_2O*, CH_2OH* and the final product , CH_3OH*. All the intermediate and product are adsorbed on the Pd atom, reacting with the hydrogen.that is bonded to g- C_3N_4. The rate determining step is the hydrogenation of CH_2OH with a barrier of 1.46 e V[7].

LITERATURE REVIEW

In 2017, Shi et al. produced g-C_3N_4 nanosheets modified by Cu particles via calcination and subsequent microwave hydrothermal route. In this work, compared with the unmodified g-C_3N_4 , the Cu doped g-C_3N_4 composites displayed higher absorption efficiencies in visible-light region, with a significant red shift, signifying better light harvesting. In another similar work, Cu-promoted g-C_3N_4 nanorods synthesized via sonication-assisted impregnation method. According to their results, in CO_2 -methane system, H_2/CO which could be applied in the liquid fuels production, produced. While CH_4 was the main product of CO_2-water system. The total yield of the products in the CO_2-CH_4 system(220µmolg-catal.$^{-1}$ h^{-1}) was higher than that of CO_2-H_2O system (131µmol g-catal.$^{-1}$ h^{-1}). Hence, Cu-promoted g-C3N4 is introduced as highly efficient photo-catalyst for CO_2 conversion into cleaner fuels suchasCH_4 using solar energy. The total yield of all the products produced in the presence of CO_2-water system is 131 mol g-catal.$^{-1}$h^{-1}, while the amounts of products in the presence of CO_2-methane system reaches to 220 mol g-catal.$^{-1}$h^{-1} [9].

Huang et al. reported H_2SO_4 treated, protonated acidic functionalities containing carbon nitride, which has been investigated for the solvent-free cycloaddition of CO_2 with epichlorohydrin for the synthesis of corresponding carbonate. This protonation process has altered the electronic, textural properties, and surface chemistry which results in the incorporation of hydroxyl groups and amine groups to the bulk urea derived carbon nitride that provides 17 folds higher catalytic activity. Surface hydroxyl groups (-OH) and amine groups (-NH_2) are responsible for this improved reactivity[6].

Samanta et al. have synthesized urea and thiourea derived carbon nitride CN-(UTU) which exhibits moderate catalytic activity better than the counter analogs urea/thiourea under the solvent-free cyclic carbonate synthesis from epichlorohydrin without any co-catalyst.Further, to improve the catalytic activity, the resultant materials have been chemically exfoliated with H_2SO_4 which results in the simultaneous incorporation of –SO_3H and –NH_2 groups into the melem framework[6].

Microstructure dependent CO_2 reduction activity has been reported by Mao et al. The authors have observed that the urea derived mesoporous, flake-like, g-C_3 N_4 has produced a mixture of oxygenated hydrocarbons (C_2H_5OH and CH_3OH) while melamine derived, non-porous flaky C3_3N_4, has produced CO and CH_4 as products. The varied product selectivity is correlated to the reaction medium $NaHCO_3$ and CO_2 gas, where CO_2 is available in the activated form (HCO^{3-}) that can be more accessible to the catalyst. In this process, O_2 is obtained as a side product and it is established that the holes and electrons are consumed in a close -ratio of ~ 1 during the reaction with the apparent quantum efficiency of 0.18% at 420 nm[6].

J. Qin et al. investigated the co-polymerization effect of monomer burbutyric acid with urea to synthesize g-C_3N_4 that eventually, extends the pi-conjugated network, engineers the molecular hetero-interface and tailors the optical, surface area and nanostructural properties of g-C_3N_4 semiconductors for the CO_2 reduction with the involvement of $Co(bpy)_3^{2+}$ as a co-catalyst and acetonitrile containing triethanolamine solution as a sacrificial electron donor, and CO_2 gas. In this, 56.3 micro mol selective CO gas production was obtained in 4 h. ^{13}C isotope tracing measurement has confirmed that the CO_2 gas is the sole source of carbon, and in fact, the control experiment has proved that all the components are essential for triggering the CO_2 photo-reduction K [6].

Wang et al. reported the S-doped g-C_3N_4 (TCN) which has been prepared via a simple heat combustion method and the first-principle calculation suggests that some of the bi-dentate N atoms of the tris-triazine of melem framework are replaced by sulfur during this process having a narrow and gap energy (Eg =2.63 eV) as compared to the melamine derived bulk g-C_3N_4 (2.7 eV). The CO_2 photoreduction result demonstrates the selective production of methanol with a yield of 1.25 micro mol g^{-1} in 3 h from the ($NaHCO_3$+HCl) induced (CO_2+H_2O) vapour medium and Pt co-catalyst[6].

Fu et al. reported O-doped C_3N_4 nanotube from control thermal oxidation etching which exhibits selective CH_3OH production with a yield of 2.6 micro mol in 3 h from ($NaHCO_3$+H_2SO_4) mixture as CO_2 and protons sources, respectively. The oxygen doping caused a lowering in the conduction band by 0.16 eV by substituting the nitrogen atom of the melem unit, as evidenced by theoretical calculation, which is the prime reason for this selectivity control. Moreover, the higher CO_2 affinity and CO_2 uptake are also supported by the CO_2-TPD and CO_2 adsorption analysis. The mechanism of the methanol formation was confirmed by the in-situ FTIR and GC analysis[6].

B. Liu et al. synthesized phosphorus-doped g-C_3N_4 nanotubes through a one-step thermal condensation between melamine and sodium hypophosphite monohydrate which simultaneously dopes P and introduces surface amino groups. These modifications have attributed the higher CO_2 uptake and favorable CO_2 adsorption that have been experimentally confirmed by CO_2 uptake and zeta potential measurements. The resultant material has converted CO_2 to 9.48 micro mol CO and 7.24 µmol CH_4 in 3 h[6].

D. Vidyasagar et al. synthesized a phenyl grafted g-C_3 N_4 scaffold by reacting phenyl urea, melamine, and urea with the enhanced π-π stacking which lowers the bandgap and provides favorable band edge potential for CO_2 photoconversion from (DMF+TEOA+H_2O+CO_2 gas) to produce CH_4, CH_3OH, and HCOOH with the yield of 0.907 micro mol CH_4, 450 µmol CH_3OH, and 5 µmol HCOOH, respectively, in 24 h using 20 W LED bulb. The achieved apparent quantum yield is calculated to be 0.96%[6].

S. Samanta et al. synthesized C, O co-doped C3N4 through a thermal poly-condensation of urea, thiourea, and 2-methyl imidazole as starting materials in an air atmosphere. The co-doping has increased the CO_2 uptake, porous cotton-like morphology, lowers the conductance band edge potentials, and also red-shifts the light-harvesting domain. The material converts CO_2 gas saturated (TEOA+H_2O) solution to methanol with the yield of 4.18 mmol.g-1 in 6 h under the visible light illumination[6].

A. Roy et al. a synthesized cobalt phthalocyanine (CoPPC) grafted polymeric graphitic carbon nitride photocatalyst in which the favourable CO_2 electro-reduction credibility, as well as light sensitization properties of cobalt phthalocyanine, has been emphasized. The combining characteristic features of C_3N_4 and CoPPc enable the material to reduce CO_2 to CO in organic solvents (ACN+TEOA) under UV/Vis light (AM 1.5G, 100 mW.cm^{2-} λ=300nm) with a cobalt-based turnover number of 90 for CO after 60 h. More interestingly, in the complete aqueous phase reaction conditions, the catalyst exhibits 60 µmol CO corresponding to the TON of 5.1 per CO[6].

J. Zhang et al. synthesized grain boundary controlled carbon nitride using 5-amino tetrazole as high nitrogen-containing organic compound and NaCl/KCl. The synthesized catalyst (CN-ATZ-NaK) exhibits 14 µmol.g^{-1}.h^{-1} CO, 1.2 µmol.g^{-1}.h^{-1} CH4, and <1 µmol.g^{-1}.h^{-1} CH3OH production rates from activated CO_2 source ($NaHCO_3$) and H_2SO_4 as a proton donor. The grain boundary tailoring is the main reason for this impressive catalytic activity. Another carbon and oxygen co-doped g-C_3N_4 has been achieved by aqueous dispersion of glucose with melamine followed by thermal treatment. The resultant optimized material has produced 55.2 µmol CO g^{-1} with nominal amount of CH_4 and CH_3OH under visible light from CO_2 dissolved (TEOA+ACN+TEOA) reaction mixture in 12 h. Simultaneous co-doing has improved the visible light absorption and fast electron extraction which are responsible for this activity enhancement[6].

Antonietti and co-workers in 2006 who used mpg-C_3N_4 as a base catalyst to activate the CO_2 molecules for the generation of CO and O_2 gas in the conversion process of benzene to phenol. Later, Azofra et al. theoretically demonstrated the mechanistic aspects of photocatalytic CO_2 reduction on planar and corrugated conformations of the 2D-C_3N_4 material by using well-resolved density functional theory. According to their investigation, the planar structure of C_3N_4 is stabilized into corrugated conformation because of its enhanced stability and also diminish the electronic repulsions caused by the lone pair of electrons present on the N atoms positioned in the framework. Corrugated structural configuration of C_3N_4 not only enhances its stabilization but also increases the depth of the p-holes linked with the π -conjugated framework, representing the improvement in the active sites for the catalytic transformation of CO_2 into CO/CH_3OH selectively[10].

Zhu et al. thoroughly studied the CO_2 adsorption ability of g-C_3N_4 from the first principle calculation by consideration of all kinds of possible adsorption sites, including adsorption conformations, separation distances and rotation angles .These results demonstrated that CO_2 molecules are more favourable to adsorb onto the nitrogen atom with double coordination and adsorption energy of −0.4181 eV contributed to both of the conduction and valence band (VB) edges. In addition, g-C_3N_4 single layers exhibit more favorable CO_2 adsorption than bulk g-C_3N_4 having a larger thickness[10].

Wu et al. have systematically investigated the photo-reduction of CO_2 to CO in all micro processes, such as the generation of protons, the adsorption of CO_2, and the formation of carbamate, involved in the whole reaction on the nitrogen atom at the edge of g-C_3N_4 using first-principles density functional theory calculations. The calculated results demonstrated that two adjacent bare nitrogen atoms at the edge of g-C_3N_4 could be the activation sites for the proton and CO_2 molecule respectively, which are crucial to the formation of carbamate[10].

Mao et al. have prepared mesoporous flakes like C_3N_4 (u-g-C_3N_4) with a BET surface area of 35.4 m^2 g^{-1} through the direct heat treatment of urea. Asprepared u-g-C_3N_4 has been used for photocatalytic CO_2 reduction in an aqueous suspension comprising CO_2–NaOH solution under visible-light irradiation and the efficiency compared with that of the melamine-derived nonporous graphitic m-g-C_3N_4. The u-g-C_3N_4 demonstrated a higher photoreduction capability toward CO_2 conversion for the production of CH_3OH and C_2H_5OH with an apparent quantum efficiency (AQE) of 0.18%, whereas, m-g-C_3N_4 leads to the production of C_2H_5OH exclusively with an AQE of 0.08%. The difference in selectivity of the products and catalytic activity for the CO_2 photoreduction over u-g-C_3N_4 and m-g-C_3N_4 is attributed to the differences in the crystallinity, bandgap, mesoporous features, and microstructure[10].

ZnO is another typical example of wide-bandgap semiconductor and has emerged as the leading candidate for photocatalysis. Yu et al. reported the preparation of a binary g-C_3N_4/ ZnO photocatalytic system via an in situ process by annealing a mixture of $Zn(NO_3)_2$ and urea mixture and further used as a photocatalyst for CO_2 reduction. The resulting g-C_3N_4/ ZnO hetero-structure demonstrated excellent photocatalytic activity for the reduction of CO_2 and produced 0.6 μmol g^{-1} h^{-1} yield of CH_3OH, which is 2.3 times and 1.5 times higher when compared with pure g-C_3N_4 and commercial ZnO sample. The Z-scheme mechanism was found to be accountable for the overall photoactivity increment in the g-C_3N_4/ZnO[10].

Su et al. also stressed the importance of the existence of edge defects of g-C_3N_4 as active sites, demonstrating the superior catalytic activity of partially condensed g-C_3N_4 for CO_2 conversion to cyclic carbonates[10].

In another study, a facile calcination process was used by Zhou et al. to synthesize g-C_3N_4/N-TiO_2 nanocomposites by doping nitrogen with TiO_2, and using urea and $Ti(OH)_4$ as precursors. The studied mass ratios of urea to $Ti(OH)_4$ were 50:50 (Ct-50), 60:40 (CT-60), and 80:20 (CT-80). The HRTEM images of the photocatalysts revealed that the particle sizes of TiO_2 was decreased in the CT-60 nanocomposite compared with the CT-80 nanocomposite. This demonstrated that the employed urea content during the catalyst synthesis significantly affected the dispersion of TiO_2 nanoparticles on the surface of g-C_3N_4. The fabricated g-C_3N_4/N-TiO_2 photocatalysts exhibited improved photocatalytic performance and stability for photoreduction of CO_2 using water vapour as electron donor. The CT-50 sample was found as the optimal sample with highest CO and CH_4 evolution amounts of 5.71 and 3.94 μmol within 12 h of the light irradiation[9] .

CO_2 conversion using Zn- based catalyst:

Zinc oxide were obtained by thermal decomposition of zinc salts (acetate and nitrate) and by precipitation (chloride and nitrate). XRD showed that ZnO crystals exhibited similar morphologies, while the crystal size and the particles morphology, availed by SEM, are dependent on the preparation method and the precursor salt utilized. The catalytic properties of ZnO surface are strongly dependent on crystal size, atmosphere of reaction and zinc salts precursor. Catalytic reactions on semiconductors would involve, mainly, a combination of acid–base chemistry and oxidation–reduction. Zinc oxide is an n-type semiconductor and its properties originate from defects on the surface and by the solid degree of non-stoichiometry. The literature data show that these characteristics could be altered by pre-treatment of the sample. There is no available data regarding ZnO catalytic activity in different gas atmospheres in reaction (oxidant and reducing)[11].

Wang et al. prepared a CuO–ZnO–ZrO2–MxOy (CZZM, M = Cr, Mo, and W) catalyst with a molar ratio of 5/2/2.5/0.5 to verify the synergistic effect between ZrO2 and the Cu catalyst, which enhances the catalytic performance in the hydrogenation of CO_2 to form methanol. The activity tests were performed at 240^oC, 3MPa, and 2400mL/$g_{catalyst}$.h. The main products were carbon monoxide, methanol, and water. Upon comparing CZZM to the CZZ catalyst in terms of the CO2 conversion, methanol selectivity, and yield, MoO_3 and WO_3 exhibited better catalytic performances than CZZ, while for Cr_2O_3 the opposite was true. CZZW showed the highest selectivity and yield, which was 15 and 22 % higher than that observed for the CZZ catalyst. The XRD peaks showed that Mo and W suppressed the crystallization of Cu and reduced the size of the Cu crystallites, while Cr promoted the crystallization of Cu and increased the crystallite size. As a result, the surface areas of CZZMo and CZZW were larger than CZZ, while the surface area of CZZCr was lowered. Not only the XRD data, but also the H_2-TPR and XPS results indicate that W and Mo improve the properties of the Cu/ZnO catalyst. Therefore, CZZW and CZZM exhibit raise methanol yields. The methanol selectivity was determined using the Zn/Cu ratio on the surface of the catalyst and the number of strongly basic sites[5].

Xiao et al. have synthesized a Cu–Zn–Al–Zr precursor ($Cu^{2+}/Zn^{2+}/Al^{3+}/Zr^{4+}$ = 2:1:1.2:0.1) to prepare a series of Cu/ZnO/Al_2O_3 /ZrO_2 catalysts using a co-precipitation method at pH values ranging from 6.0–11.0 to study the effect of the pH on the properties of the catalysts. The performance of the catalyst was investigated at 190^oC and 5MPa using a 3:1M ratio of H_2/CO_2. Only methanol and CO was formed as the only products of the reaction. The CO_2 conversion and methanol selectivity have a volcanic shape upon increasing the pH. The catalyst prepared at pH 6 has a much lower CO_2 conversion than the other catalyst because of the incomplete reduction and presence of Cu cations. The CO_2 conversion and methanol selectivity have a maximum value of 10.7 and 81.8 % when using the catalyst prepared at pH 9. The catalyst at pH 9 has the minimum copper particle size which makes the efficient interaction among Cu and ZnO. All catalysts, except for the catalyst prepared at pH 6, exhibit methanol selectivity >80 %. The low selectivity at pH 6 is because of the presence of Cu^+ species. It was found that the copper particle size has an important role during the hydrogenation of CO2 in the way that, if there is increase in the copper particle size it decreases the hydrogenation activity[5].

Dasireddy et al. prepared a series of Cu/Zn/Al catalysts using different methods to find the best preparation method to obtain high surface area catalysts. The methods used were: Co-precipitation, ultrasonic co-precipitation, sol-gel combustion, and solid-state synthesis. The catalysts were studied at the temperature range of 200–400 ^{0}C at 20 bar for 5 hours. In the blank situation, no CO_2 conversion was observed. All methods were evaluated in terms of the textural properties, CO_2 conversion, and methanol selectivity. The catalyst prepared using ultrasonic co-precipitation had the highest surface area and sol-gel combustion gave the lowest surface area. None of the catalysts showed alumina peaks, indicating that Al was in an amorphous or disordered state. The crystallite size of Cu was in the range of 9–16nm no matter how the catalyst was prepared. At lower temperatures, i.e. 200–250 ^{0}C, through the ultrasonic method the highest conversion were obtained, while all the catalysts showed similar CO_2 conversions (38 %) at higher temperature because they reached a thermodynamic equilibrium point. Methanol selectivity was good at 200–250 ^{0}C using the co-precipitation and ultrasonic co-precipitation methods[5].

Fujutani studied the effect of ZnO and other metal oxide supports for the methanol synthesis. Their experiments showed that ZnO/SiO_2 exhibits a synergistic effect with Cu/SiO_2 for methanol formation. When there was no ZnO in the catalyst, the activity observed in the reaction did not change as the reduction temperature increased, while the catalyst with ZnO showed a significant increase. A larger synergistic effect was observed when using a higher amount of ZnO in the reduction temperature range from 300 to 450 ^{0}C. However, the turnover frequency (TOF) for methanol synthesis was at its maximum at 0.19 of Zn and started to decrease above 0.20. Above 0.5, no methanol synthesis activity was observed. The activation energy of methanol synthesis was 83.7kJ/mol at 0.19 Zn. The TOF for CO started to decrease, especially at 0.15–0.2 Zn and became zero at 0.5 Zn. Other metal oxides such as A_2O_2, Ga_2O_2, ZrO_2, and Cr_2O_3 also showed synergistic effects with the Cu–ZnO catalyst. It was found that Al and Zr increased the surface area of Cu and Ga, and Cr increased the specific activity of Cu. These multi-component catalyst showed better activity and thermal stability than binary or ternary catalysts. When a small amount of silica was present, the catalyst showed improved long-term stability. This is because silica suppressed the crystallization of the metals in the catalyst. However, too much silica decreased the catalytic activity and the optimum amount of silica was determined to be 0.5–0.9wt.%[5].

Huang et al. used a ZnO plate to prepare a Cu/ZnO plate catalyst and evaluated its performance during the hydrogenation of CO2 using different reducing gases (5vol% Co–Ar, 2.5vol% H_2/2.5vol% Co–Ar, and 5vol% H_2 – Ar) at 300 ^{0}C for 6h. The main purpose of this study was to investigate the synergistic effect between the Cu nano-particles and migrated Zn on the activity of methanol synthesis. The reaction occurred at 220–300 ^{0}C and 3MPa, and the catalytic performance of catalyst was evaluated in terms of the conversion and selectivity under specific conditions varying the concentration of the reducing gas. 5vol% H_2 gave the highest performance and 5vol% Co showed the lowest performance at the same temperature. Similarly, the methanol selectivity was highest using 5vol% H_2 and 5vol% CO had the lowest selectivity with the same conversion. Using 5vol% H_2 showed a two-fold increase in the CO_2 conversion and methanol yield when compared to 5vol% CO_2. The catalyst with 5vol% H_2 has the smallest particle sizes. However, the particle size is not the unique factor for CO_2 hydrogenation. The catalyst with high performance has spherical shape while the low performance catalysts have irregular shape[5].

Allam et al. prepared catalyst through a polyol method using a Cu/Zn/Ce molar ratio of 1:1:2 and Cu/Zn/Al molar ratio of 1:1:2. To evaluate the hydrogenation of CO2 to form methanol, the influence of the metal dispersion and properties of binary and ternary catalysts were investigated. The catalysts were tested in the temperature range of 190–240 ^{o}C. The binary catalyst did not show any conversion, while the ternary catalysts showed similar conversions. The catalysts remained stable after 4h of reaction. The best result was obtained with the CuO–ZnO–CeO_2 catalyst with 20 % CO_2 conversion and 65 % methanol selectivity. This was attributed to the synergistic effect between Cu and Zn, and the basicity of Ce. The conversion showed a steep increase until 1h and then became stationary. When the reaction temperature was increased, the methane selectivity increased, while the methanol selectivity decreased, indicating that methanol was transformed into methane and water at high temperature in the presence of hydrogen[5].

Kattel et al. studied the Zn/Cu and ZnO/Cu catalysts used for the hydrogenation of CO_2. It was seen that Zn in the Zn/Cu catalyst was transformed to ZnO because Zn was unstable under the CO_2 hydrogenation reaction conditions. The catalytic activity increased after Zn was transformed into ZnO and decreased after the concentration of ZnO reached 0.2. Thus, exposure of both ZnO and Cu on the catalyst surface enhances the production of methanol and the optimal composition for methanol conversion was ZnO/Cu. The reduction of ZnO was not observed under H_2-rich conditions. Two methods for methanol production are present:

i) The RWGS reaction, which produces CO as an intermediate and

ii) The formate pathway, which produces HCOO as an intermediate. Based on density function theory (DFT) and kinetic Monte Carlo (kmc) simulations, only a small amount of CO was hydrogenated to methanol. Therefore, the second pathway was preferred for the conversion of CO_2 to form methanol[5].

M. Bahmani et al. studied the effect of the catalyst preparation method on the activity and stability of the catalyst. Four different mixed Cu, Zn, and Al nitrate solutions (CZ_AN, CZ_AN + AH, CZ_SA, and CZSA + NA) with varying the Al source was prepared. The molar ratio of Cu/Zn/Al was 60:30:10. The Cu/ZnO/Al_2O_3 catalysts were prepared via a co-precipitation method. The catalytic activity was investigated in a tubular fixed-bed reactor at 230 ^{o}C and 5MPa using a feed gas composition consisting of 80vol.% H_2, 12vol.% CO, and 8vol.% CO_2. Methanol, small amounts of methane, water, and other oxygenated byproducts with the unreacted gases were obtained as the products. There are three possible reactions occurring during the synthesis:

i) Methanol synthesis from CO_2,

ii) water gas shift reaction(WGS), and

iii) methanol synthesis from CO. Among the four different catalysts, the CZ_SA + NA catalyst showed the highest performance because the alumina hydrous oxide solution decreases the particle size and, as a result, more Cu is exposed to the reaction. The CZ_SA + NA catalyst retained 60 % of its activity after 120h, while the other catalysts lost >50 % of their initial activities. The results show that the aluminum hydrous oxide solution was a good source of Al and may form a more durable catalyst[5].

Wang et al. studied the hydrogenation of CO_2 using a $ZnO–ZrO_2$ catalyst to synthesize methanol. The catalytic performance was studied in terms of the selectivity, catalytic activity, and stability. The reaction was conducted in a tubular fixed-bed continuous-flow reactor combined with gas chromatography. The reactions were conducted at 180–400 ^oC and 1–5MPa. The stability of the 13% $ZnO–ZrO_2$ catalyst was investigated and a stable CO_2 conversion of 10 % was achieved for 500h without deactivation. The effect of temperature on the selectivity and conversion was reported. The CO_2 conversion to methanol increases with decrease in reaction temperature, whereas the selectivity increased[5].

In another study conducted by Phongamwong et al. , investigated a series of SiO_2-doped CuO–ZnO–ZrO_2 catalysts in terms of their catalytic effect toward the synthesis of methanol. A reverse co-precipitation method was applied to prepare the catalysts using different amounts of SiO_2. The CuO–ZnO–ZrO_2 catalyst prepared using 1.0wt.% silica achieved a 26 % increase in the conversion to methanol when compared to the catalyst prepared using less silica at 240 ^oC. It was also reported that the presence of silica as a promoter enhanced the stability from 17.34 % lost activity using the silica free catalyst to 12.33 % lost activity using the 1wt.% silica-doped catalyst after 96h of reaction. Increasing the amount of silica to >1.5wt.% resulted in the separation and formation of a heterogeneous microstructure catalyst, which reduced the amount of desorbed H_2. However, the reported conversion (5%) and methanol selectivity (65.44 %) using the proposed catalyst appeared to be very low for industrial application[5].

Over ZnO catalyst, methanol formation is low about two orders of magnitude compared with that over Cu catalyst. ZnO is just a promoter to Copper. Therefore, interfacial sites between Copper and ZnO is very important for effective methanol synthesis. Recently Fujitani et al. have found a good correlation between oxygen coverage of Copper surface of catalyst and specific activity for methanol production over various Cu based catalysts. The maximum specific activity was obtained at oxygen coverage=0. 17. Oxygen coverage was determined by in situ N20 titration of catalyst. This result shows that about 20% of metallic Copper surface was oxidized and, in other words, coexistence of metallic Copper and partially oxidized Copper is essential for effective production of methanol[12].

Lunkenbein et al. utilized a thermal stimulus using an electron beam to transform the industrial Cu/ZnO catalyst structure into Cu NPs surrounded by metastable “graphite like” ZnO after reductive activation. Defects could play a key role in the stability of the ZnO overlayer and lead to the presence of some ZnOx species acting as a co-catalyst in methanol synthesis , illustrating the migration of Zn to the Cu surface is closely related to the formation of a stable Cu-ZnO interface and Cu-ZnOx active sites in the process of reduction and evolution[13].

Ramaroson and Erdtlhelyi reported that when Pd was loaded on a basic support like as La_20_3, methanol was obtained with a considerable good selectivity, although the space-time yield (STY) of methanol was only 87 g/l.h[14].

Inoue et al. tried methanol synthesis from CO_2 and H_2 on the catalysts of support Pt and Rh; however, the yield of methanol was very little like as 0.3% and 0.1% respectively[14].

Gasser et al. studied methanol synthesis from CO_2 and H_2 using the amorphous Cu-$Zr0_2$ catalyst under 15 atm. and obtained methanol with a fairly high selectivity: however, even maximum STY of methanol was only 36 g/l'h[14].

The g-C_3N_4 highly dispersed in mesoporous silica channels were prepared by Huang et al. to maximize the exposure of active sites of the g-C_3N_4 for CO_2 activation and conversion. In this work, it was proved that water residue in the silica channel and HF treatment to remove the silica could deactivate the edge sites of g-C_3N_4. They also doped several metals (Zn^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Mn^{2+}) in the g-C_3N_4/silica to enhance the conversion efficiency and selectivity of the catalysts. Among them, Zn^{2+} and Fe^{3+} are the most effective dopants to increase the catalytic activity of the g-C_3N_4/SBA-15 for CO_2 conversion to epoxides and olefins, respectively[10].

Vourros et al. carried out a complete experimental study about the activity of Au nanoparticles supported on several oxides to catalyse the CO_2 hydrogenation to methanol at atmospheric pressure. Five different M_xO_y oxide-supports were studied: Al_2O_3, TiO_2, Fe_2O_3, CeO_2, and ZnO. The gold nanoparticles supported on ZnO and CeO_2 were highly selective towards methanol (nearly 90%, and 82% respectively at temperature below 250^{o}C)[15].

Hartadi et al. also carried out a systematic study with different supports for Au nanoparticles and also found the best behaviour for the synthesis of methanol when supported on ZnO. The behaviour of Au/ZnO based catalysts was compared with that of the conventional Cu-Zn-Al catalyst (at 0.5–5.0 MPa and 240 ^{o}C) and it was found that the Au/ZnO catalysts have similar methanol formation rate but higher selectivity towards methanol compared to conventional Cu/ZnO/Al_2O_3[15].

Different metal catalyst like Cu, Zn, Ag, Cr, and Pd was used for CO2 hydrogenation to methanol (Katteletal.,2017a;Dangetal.,2019b;Dinetal.,2019). Also, Cu-based catalysts exhibit a high catalytical activity and selectivity. Different promoters (such as ZnO, ZrO2, and LaOx, etc.) was used to improve the activity of Cu-based catalysts (Ham et al., 2018; Hu et al., 2018; Chen et al., 2019a; Mureddu et al., 2019; Noh et al., 2019)[16].

CONCLUSION:

CO_2 is one of the most abundant green house gases (GHG) generated from carbon feedstock, contributing tremendously to the global warming.

The rapid industrial development and excessive use of fossil fuels have produced a significantly large volume of CO_2 in the atmosphere. The efficient conversion of CO_2 to useful chemicals and fuels is an important step towards reducing the concentration of CO_2. To overcome the thermodynamic and kinetic barriers involving CO_2 activation and conversion, an effective heterogeneous catalyst and a suitable form of energy, such as thermal, photochemical, and electrochemical, are necessary.

Carbon capture, utilization, and sequestration (CCUS) technologies have recently received a great deal of attention for providing a pathway in dealing with global climate change.

In most cases, activity and durability of Cu-ZnO catalyst can be increased dramatically by incorporating promoters (such as Cu, zeolite, etc.).

Capturing CO_2 from flue gas and the atmosphere and its catalytical conversion to fuel and chemicals using H_2 from renewable energy can lead to sustainable future for humankind. Methanol can be used as fuel-substitute and raw material for hydrocarbon and chemicals with many industrial applications. The hydrogenation of CO_2 to methanol not only effectively alleviates the greenhouse effect, but also produces fuel and value added chemicals.

The development of new catalyst is toward the direction of lower energy consumption (e.g. low pressure hydrogenation process) and higher methanol yield (e.g. low temperature mmethanol synthesis). Highly efficient in –situ by product H_2O removal through water-conduction membrane has led to a drastic increase in ethanol yield in CO_2 hydrogenation to methanol.

REFERENCES :

[1] J. He and C. Janáky, “Recent Advances in Solar-Driven Carbon Dioxide Conversion: Expectations versus Reality,” *ACS Energy Lett.*, vol. 5, no. 6, pp. 1996–2014, 2020, doi: 10.1021/acsenergylett.0c00645.

[2] A. Álvarez *et al.*, “CO2 Activation over Catalytic Surfaces,” *ChemPhysChem*, vol. 18, no. 22, pp. 3135–3141, 2017, doi: 10.1002/cphc.201700782.

[3] Q. W. Song, Z. H. Zhou, and L. N. He, “Efficient, selective and sustainable catalysis of carbon dioxide,” *Green Chem.*, vol. 19, no. 16, pp. 3707–3728, 2017, doi: 10.1039/c7gc00199a.

[4] M. D. Garba *et al.*, “CO2towards fuels: A review of catalytic conversion of carbon dioxide to hydrocarbons,” *J. Environ. Chem. Eng.*, vol. 9, no. 2, p. 104756, 2021, doi: 10.1016/j.jece.2020.104756.

[5] T. A. Atsbha, T. Yoon, P. Seongho, and C. J. Lee, “A review on the catalytic conversion of CO2using H2for synthesis of CO, methanol, and hydrocarbons,” *J. CO2 Util.*, vol. 44, no. December 2020, p. 101413, 2021, doi: 10.1016/j.jcou.2020.101413.

[6] S. Samanta and R. Srivastava, “Catalytic conversion of CO2to chemicals and fuels: The collective thermocatalytic/photocatalytic/electrocatalytic approach with graphitic carbon nitride,” *Mater. Adv.*, vol. 1, no. 6, pp. 1506–1545, 2020, doi: 10.1039/d0ma00293c.

[7] G. Gao, Y. Jiao, E. R. Waclawik, and A. Du, “Single Atom (Pd/Pt) Supported on Graphitic Carbon Nitride as an Efficient Photocatalyst for Visible-Light Reduction of Carbon Dioxide,” *J. Am. Chem. Soc.*, vol. 138, no. 19, pp. 6292–6297, 2016, doi: 10.1021/jacs.6b02692.

[8] J. Zhu, P. Xiao, H. Li, and S. A. C. Carabineiro, “Graphitic carbon nitride: Synthesis, properties, and applications in catalysis,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 19, pp. 16449–16465, 2014, doi: 10.1021/am502925j.

[9] A. Akhundi, A. Habibi-Yangjeh, M. Abitorabi, and S. Rahim Pouran, “Review on photocatalytic conversion of carbon dioxide to value-added compounds and renewable fuels by graphitic carbon nitride-based photocatalysts,” *Catal. Rev. - Sci. Eng.*, vol. 61, no. 4, pp. 595–628, 2019, doi: 10.1080/01614940.2019.1654224.

[10] S. N. Talapaneni *et al.*, “Nanostructured Carbon Nitrides for CO2 Capture and Conversion,” *Adv. Mater.*, vol. 32, no. 18, pp. 1–21, 2020, doi: 10.1002/adma.201904635.

[11] O. W. Perez-Lopez, A. C. Farias, N. R. Marcilio, and J. M. C. Bueno, “The catalytic behavior of zinc oxide prepared from various precursors and by different methods,” *Mater. Res. Bull.*, vol. 40, no. 12, pp. 2089–2099, 2005, doi: 10.1016/j.materresbull.2005.07.001.

[12] Y. Wang *et al.*, “CO2 activation by ZnO through the formation of an unusual tridentate surface carbonate,” *Angew. Chemie - Int. Ed.*, vol. 46, no. 29, pp. 5624–5627, 2007, doi: 10.1002/anie.200700564.

[13] H. Yang *et al.*, “A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons,” *Catal. Sci. Technol.*, vol. 7, no. 20, pp. 4580–4598, 2017, doi: 10.1039/c7cy01403a.

[14] T. Inui and T. Takeguchi, “Effective conversion of carbon dioxide and hydrogen to hydrocarbons,” *Catal. Today*, vol. 10, no. 1, pp. 95–106, 1991, doi: 10.1016/0920-5861(91)80077-M.

[15] R. Guil-López *et al.*, “Methanol Synthesis from CO2: A Review of the Latest Developments in Heterogeneous Catalysis,” *Materials (Basel).*, vol. 12, no. 23, p. 3902, 2019, doi: 10.3390/ma12233902.

[16] X. Zhang, G. Zhang, C. Song, and X. Guo, “Catalytic Conversion of Carbon Dioxide to Methanol: Current Status and Future Perspective,” *Front. Energy Res.*, vol. 8, no. February, pp. 1–16, 2021, doi: 10.3389/fenrg.2020.621119.