DIFFERENT METHODS OF CONVERSION OF CO_2 BY COBALT CATALYST

A MSc Dissertation report by:

Komal Rajendra Gawade

Roll No: 20P0490030

To,

Department of Chemistry

Goa University

Goa 403206

May 2022

CERTIFICATE

This is to certify that the dissertation entitled **"Different Methods of Conversion of CO_2 by Cobalt Catalyst"** is a Bonafide work carried out by Ms. Komal Rajendra Gawade under my supervision in partial fulfillment of the requirement for the award of the degree of Masters of Science in Chemistry at the School of Chemical Sciences, Goa University.

Dr. Rohan Kunkalekar	
Guiding Teacher	
School of Chemical Sciences	Komal Gawade
Goa University	(M.Sc Student)

INDEX

INTRODUCTION

Carbon dioxide (CO_2) is the most abundant renewable carbon source in nature. Chemical fixation of CO_2 is therefore one of the most important subjects in organic synthesis, and much effort has been devoted to this particular subject. Various methods for CO_2 fixation have been developed despite the low reactivity and narrow synthetic scope of CO_2. Although the Kolbe–Schmitt reaction and carboxylation reactions using Grignard reagents are well-known chemical fixations of CO_2, these non-catalytic reactions have some limitations. On the other hand, catalytic reactions are considered to be essential for widening and deepening the synthetic utility of CO_2. Both reactions and catalysts need to be developed for this purpose. A large number of inorganic, organic, and metal catalysts have been developed for various chemical conversions of CO_2. The synthesis of cyclic carbonates or polycarbonates from CO_2 and epoxides, carboxylation reactions with CO_2, reduction of CO_2, and other fascinating reactions have been developed and studied extensively and intensively [1].

Due to the high emissions of CO_2 and the related environmental impact, the chemical transformation of CO_2 to useful industrially relevant products or their precursor is of significant interest. Recycling CO_2 as a building block for the synthesis of chemicals may not only reduce further emission by at least replacing oil-derived feedstocks, but also provide the advantages of CO_2 as an inexpensive, non-toxic and easily available substrate. The catalytic conversion of CO_2 into small, useful molecules such as carbonates, methyl amines, methanol, formic acid, etc. by molecular catalysts is an interesting topic that has strongly developed in recent years.

The challenge climate change poses to mankind has never been more actual than today as perceived from the media. There is wide scientific consensus that the increase of the concentration of green- house gases in the atmosphere is a main driver for the current climate change. According to the EPA (United States Environmental Protection Agency) the largest contribution to greenhouse gases in the world comes from carbon dioxide emissions (81% in 2016). Transportation

(28%), industry (22%) and electricity generation (28%) were identified as the main sources of emissions. The rise of CO_2 concentration in the atmosphere (currently over 2 ppm per year) can be monitored as such or by the rising global average temperature over the last few decades, warmer and more acidic sea water and increasing sea levels (up to 3.2 mm per year between 1993 and 2010). As an effect, sudden changes in weather, droughts and extreme climatic events have been noted.[2]

As an earth-abundant transition metal, cobalt is regarded as one of the most promising ideal substituents for noble metals, like platinum (Pt), iridium (Ir) or ruthenium (Ru), in the design of CO_2 reduction catalysts, especially due to their outstanding catalytic activity, product selectivity and catalytic stability.[3] Cobalt is a group VIIIB element, which is very easily accessible oxidation states, including Co0, CoI, CoII, CoIII and CoIV. The CO_2 reduction reaction mediated by cobalt catalysts usually involve the transition of CoII to a CoI intermediate state. There were already some reviews on earth-abundant- metal catalysts for CO_2 reduction; however, there is no specific review on cobalt-based catalysts. One of the crucial points in achieving an efficient conversion of CO_2 from the economic and environmental standpoints is its efficient activation by catalytic systems that, despite the high thermodynamic stability of CO_2, might allow for accessible reaction barriers. Transition metal complexes and coordination compounds, in particular, can exploit the weak Lewis acidity of the central carbon or the Lewis basicity of the terminal oxygen atoms to form “activated” CO_2 adducts as the initial stage of carbon dioxide conversion.[2] CO_2 photoreduction proceeds under light irradiation and CO_2 electroreduction needs applied potential at room temperatures immersed in electrolyte. Investigations of photocatalysis mainly focus on visible light driven because about half of solar light being situated in the visible range with average intensity of ~136.6 mW·cm-2.34 The selection of suitable metal cations significantly influences the electron transfer efficiency from light-harvesting centres to catalytic active sites, adsorption capacity of CO_2 molecules and supply electrons to reactants. For electrocatalysis, the employed electrocatalysts and applied electrode potential are significant for their final products. In this perspective, Co-based catalysts were chosen due to their outstanding activity and selectivity for CO_2 reduction.[3]

During the past decades, heterogeneous electrochemical CO_2 reduction has been explicitly investigated, and various catalysts have been investigated to generate products such as carbon monoxide, formic acid, methane, and methanol[4] . The activity of metal catalysts obtained by the reduction of metal oxides is usually higher than that in other methods. Investigated cobalt, associated with loosely bonded d electrons and high electrical conductivity, as a promising catalyst for the conversion. They synthesized two- dimensional cobalt/cobalt oxide hybrid by using a solvothermal method with high electrocatalytic activity for the conversion, and the main product was formate. An ideal way for the conversion of CO_2 is the catalytic hydrogenation of CO_2 to methanol, which usually contains three cascade catalytic cycles, the hydrogenation of CO_2 to formic acid, the hydrogenation of formic acid to formaldehyde with the formation of water, and the hydrogenation of formaldehyde to methanol. In addition to its potential application in hydrogen storage, formic acid is also widely used in synthetic chemistry and industrial processes. In 1970, Haynes et al. reported the first catalytic hydrogenation of CO_2 reaction. Since then, steady progresses have been achieved in homogeneously catalytic hydrogenation of CO_2 using noble transition metals, such as rhodium, ruthenium, platinum, and iridium. [5]

Catalysts are essential and reusable materials for lowering the activation energy (Ea) in CO_2 reduction reactions because CO_2 molecules structural stable and inert. For example, the Ea will be decreased when CO_2 and Co catalysts are combined due to avoiding high energy CO_2 radical intermediates. So far, the catalysts of CO_2 reduction have suffered from many challenges including (i) the low product selectivity from the competing hydrogen evolution reaction (ii) the unsatisfactory catalytic stability, (iii) poor conversion efficiency, (iv) high overpotential in electrocatalysis, (v) rapid recombination of electron holes in photocatalysis, (vi) high-cost and low- content compositions etc. The low efficiency and selectivity, due to the multiple reaction pathways and various byproducts, severely limit large-scale application of CO_2 reduction. Generally, catalysts are categorized into homogeneous catalysts and heterogeneous catalysts. The former demonstrates an outstanding product selectivity and catalytic activity due to precisely manipulate the spatial arrangement of catalytic centers, but they are expensive and complicated to be separated in later stage, hindering their large -scale industrial applications. In contrast, the latter can bypass the process of catalytic diffusion and possess high reusability. In addition, catalytic materials which are combined by the homogeneous molecular catalysts and heterogeneous catalysts can even possess a better selectivity and stability. For example, Wang et al. found that high catalytic selectivity of 100% and current density of 9.3 mA•cm^{-2} at the low overpotential of 0.34 V for at least 4.5 h could be achieved when associating a Co-based molecular catalyst to a heterogeneous material.[3]

Besides metal-based systems, other molecular catalysts are able to activate CO_2. In particular, organic nucleophiles such as amines, heterocyclic N-nucleophiles and N-heterocyclic carbenes can form reactive adduct with CO_2 that can subsequently undergo further transformation. Given the relevance and current public interest in the topic, several reviews dealing with the conversion of CO_2 have been published in recent years under different perspectives and covering topics such as CO_2 hydrogenation, sustainable CO_2 conversion, electro- and photochemical CO_2 conversion, carboxylation, alkylation of amines with CO_2, conversion of CO_2 to cyclic carbonates, industrial scale CO_2 conversion, and energy-related CO_2 conversion. However, there has been a lack of reviews providing a comprehensive overview of the key advances in the catalytic activation of CO_2 by molecular catalyst. Therefore, this review initially presents a selection of relevant examples of CO_2 conversion by metal-based catalysts that have appeared in recent years. However, to avoid potential overlap with excellent reviews focused on electro- and photoelectrocatalysis and on the synthesis of MeOH from CO_2.[6]

The activity of catalysts mainly depends on the quantities of total surface active sites and corresponding intrinsic activity. Obviously, the nanostructured catalysts usually own a larger surface area, i.e. more surface active sites than that of bulk ones. Noble metals possess high intrinsic activity but they are expensive with low content. The low-cost transition metals show similar catalytic activity which is more economic. Wanvnakao et al. studied three kinds of metals as catalytic active sites with strong, moderate and weak binding strength. They found that Co metals exhibited highest catalytic activity for CO_2. In addition, the Co active sites possess a loose bond of d electrons for high electrical conductivity. Co center also possesses a modest adsorption intensity of CO_2 molecule, polyvalency, high coordination, unsaturated d-orbitals of electrons, and alloying, all of which contributes to excellent catalytic performance. Cobalt species show an excellent electron-mediating function spatially when they transfer electrons. Compared to Fe complexes, Co complexes possess lower overpotential and are more stable for CO_2 reduction. Wang et al. found that among four kinds of polyoxometalate-metalloporphyrin organic frameworks (M- PMOFs) where M means Co, Ni, Fe and Zn, the Co-PMOF showed smallest charge transfer resistance of 9.83 Ω, indicating faster electron transfer in the reaction process. Towards this effort, cobalt-based catalysts manifest high catalytic performances towards CO_2 capture and reduction with much lower applied potential. Therefore, Cobalt-based catalysts are considered high-efficient and robust catalysts for CO_2 reduction with high yield of CO or/and HCOOH. This review introduces the catalytic reduction mechanism based on Co-based catalysts and corresponding synthetic methods. Then, analyze the factors influencing the catalytic properties of Co-based catalysts for CO_2 photo/electroreduction such as CO_2 adsorption, CO_2 activation, CO_2 conversion, product selectivity and catalyst stability. Finally, this review concludes with some perspectives and strategies on how to enhance the catalytic performance of Co-containing catalysts.[3]

LITERATURE REVIEW

Li, Caihong[3] studied Photocatalysis systems, inspired by the photosynthesis of plants, generally are composed of photosensitizers (PS), photocatalysts and sacrificial electron donor. A PS is used to capture photons from light irradiation and supply energy (hv) for the photocatalysis reactions and a sacrificial electron donor aims to afford electrons on photo-induced command by PS. The photo-induced electrons then will be transferred to catalysts to reduce CO_2 in photocatalytic reduction. The excited state of PS, i.e. PS*, may be quenched through a reductive quenching process to be PS- via a sacrificial electron donor. Another quenching mode is oxidative quenching where PS* tends to give an electron to the acceptor forming PS+ firstly and then returns to the original state PS with the action of a sacrificial electron donor. For instance, He et al. Have investigated the multifaceted Si NWs_4 serving as robust PS with a molecular Co catalyst in photoelectrochemical CO_2 reduction. It exhibited stronger light harvesting capacity and less negative applied potentials compared to planar Si, Ru-based, or Ir-based complexes are frequently-used PSs with high sensitized ability. Nevertheless, these two noble-metal-based PSs should be replaced by earth-abundant metal complexes or organic compounds for economic consideration.

Tong, Xin [3] studied CO_2 electroreduction an appealing process because it can not only work under ambient conditions in aqueous media but also couple with renewable energy sources such as solar energy and wind energy. However, electrocatalytic CO_2 reduction still encounter poor performance including high overpotential and low faradaic efficiencies (FE). FE means the percentage of electrons used to form a given product, which is directly associated with product selectivity. CO_2 electroreduction requires an applied potential due to the presence of reaction energy barrier in the process of CO_2 activation. CO_2 reduction conducts through CO• — 2 radical intermediates adsorbed on the catalytic metal sites in charged catalysts. The following is the proposed mechanism of electrocatalytic CO_2 reduction with Co catalysts. Firstly, the catalytically active CoI species are generated after two electron transfer and reduced to CoII-hydride species（only for HCOOH pathway） via proton-coupled electron transfer (PCET) process. In PCET, the proton and the electron start from different orbitals and are transferred to different orbitals. For CO pathway, CoI species activate CO_2 molecule by nucleophilic attack. Then these species react with CO_2 molecules to form Co-COOH or Co-OCHO species by PCET reduction. Finally, CO or HCOOH is released through desorption from Co centre.

Qing Guo[7] studied the use of Co2C as a novel catalyst for cycloaddition of CO_2 with epoxides by using solar energy to replace external thermal energy input for following reasons: (i) the high specific surface area and tuneable chemical composition provide abundant surface active sites to activate CO_2 and/or epoxides; (ii) the effective CO_2 adsorption ability on TMC favours the very first step of CO_2 conversion; (iii) the giant heat released from the excellent photo-to-thermal conversion process would promote the endothermic reaction (high C=O bond energy of 750 kJ/mol); and (iv) the feasible separation and reusability of the heterogeneous catalysts is beneficial for large-scale application. The flower-like Co_2C was synthesized through a modified method of solution pyrolysis at high temperature. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) clearly showed the flower-like morphology of the synthesized material. TEM characterization indicated that the average diameter of the nanoflowers was determined as ~500 nm. Moreover, the selective area electron diffraction (SAED) pattern confirmed the polycrystalline nature of the synthesized materials. In addition, elemental mapping analysis indicated the coexistence of Co, C and O elements which matched well with the X-ray photoelectron spectroscopy (XPS) results.

Etienne Boutin,[8] studied electroreduction CO_2 into CH_3OH in aqueous media through a CO intermediate using cobalt phthalocyanine (CoPc) as a catalyst. CoPc, a well-studied catalyst in electrochemistry, belongs to the phthalocyanine family that is used as a dye at a large scale in the painting industry. This catalyst is particularly appealing due to its low cost. Upon mixing the cobalt complex with multi-wall carbon nanotubes (MWCNT) and Nafion resin in a mixture of ethanol and ethylene glycol, a colloidal, stable ink was obtained. After ink deposition onto porous carbon paper, the material was dried at 100°C resulting in the porous catalytic film observed from SEM. The typical CoPc concentration in the film was about 15.7-0.7 $nmolcm^{-2}$. Electrolyses were then conducted in aqueous solutions under a series of various pH conditions and CO_2 or CO atmosphere. Both the liquid and the gas phases were analyzed following electrolysis by 1 H NMR and gas chromatography (GC), respectively. After 3 h of electrolysis in a CO_2 -saturated 0.5m $KHCO_3$ solution (pH 7.2) at an applied potential of 0.68 V vs. RHE, no traces of CH_3OH were detected. However, when decreasing the potential to 0.88 V vs. RHE, we detected a small amount of CH_3OH from the 1H NMR spectra of the electrolyte solution. This corresponds to a Faradaic efficiency (FE) of 0.3% and to a partial current density (jCH_3OH) of 30 $mAcm^{-2}$.

CoPc can first efficiently catalyze the electrochemical CO_2-to-CO conversion with a high FE (95%) in a flow cell with current densities up to 150 $mAcm^{-2}$. The catalyst is the same for each step, while the pH and the electrode potential are adjusted to maximize each partial reduction process. From the total number of transferred electrons, a global Faradaic efficiency of 19.5% is calculated and the chemical selectivity is about 7.5%.

Guilin Zhou[9] studied Mesoporous Co/KIT-6 and Co/meso-SiO_2 catalysts were prepared via hydrogen reduction and were subsequently used in CO_2 catalytic hydrogenation to produce methane. The properties of these catalysts were investigated via low-angle X-ray diffraction (XRD), Bru- nauereEmmetteTeller (BET) analysis, and transmission electron microscopy (TEM). The results indicate that the synthesized Co/KIT-6 and Co/meso-SiO_2 catalysts have mesoporous structures with well-dispersed Co species, as well as high CO2 catalytic hydrogennation activities. The Co/KIT-6 catalyst has a large specific surface area (368.9 m^2 g^{-1}) and a highly ordered bicontinuous mesoporous structure. This catalyst exhibits excellent CO_2 catalytic hydrogenation activity and methane product selectivity, which are both higher than those of the Co/meso-SiO_2 catalyst at high reaction temperatures. The CO_2 conversion and methane selectivity of the Co/KIT-6 catalyst at 280°C are 48.9% and 100%, respectively. The high dispersion of the Co species and the large specific surface area of the prepared Co- based catalysts contribute to the high catalytic activities. In addition, the highly ordered, bicontinuous, mesoporous structure of the Co/KIT-6 catalyst improves the selectivity for the methane product.

The ordered mesoporous Co/KIT-6 and Co/meso-SiO_2 catalysts were prepared via the excess impregnation method. $Co(NO_3)_2.6H_2O$ (Tianjin Kermel Chemical Reagent Co., Ltd., China) was used as the metal oxide precursor, whereas the synthesized KIT-6 and commercial meso-SiO_2 (mesoporous SiO_2, Qingdao Ocean Chemical Reagent Co., Ltd., China) were used as the supports for the Co/KIT-6 and Co/meso-SiO_2 catalysts, respectively. The prepared KIT-6 and meso-SiO_2

were each appended in an aqueous cobaltous nitrate solution, which was prepared by dissolving a specified amount of cobaltous nitrate in deionized water. The mixtures were then evaporated at a fixed temperature, dried at 383 K for 24 h, and calcinated in air at 773 K for 3 h. The catalyst precursors were then subjected to hydrogen reduction to produce the Co/KIT-6 and Co/meso-SiO_2 catalysts. These catalysts were then used for CO_2 catalytic hydrogenation to produce methane.

The low-angle XRD, BET, and TEM results indicate that the prepared Co/KIT-6 catalyst has a large specific surface area, highly dispersed Co species, wide pore diameter, narrow pore size distribution, and highly ordered mesoporous structure. The large specific surface area promotes the adsorption and activation of the reactant molecules (CO_2 and hydrogen), resulting in the improvement of the CO_2 catalytic hydrogenation.

Pawan Kumar[10] studied the New graphene oxide (GO)-tethered–CoII phthalocyanine complex [CoPc–GO] was synthesized by a stepwise procedure and demonstrated to be an efficient, cost-effective and recyclable photocatalyst for the reduction of carbon dioxide to produce methanol as the main product. The developed GO-immobilized CoPc was characterized by X-ray diffraction (XRD), FTIR, XPS, Raman, diffusion reflection, UV/ Vis spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). FTIR, XPS, Raman, UV/Vis and ICP-AES along with elemental analysis data showed that CoII–Pc complex was successfully grafted on GO. The prepared catalyst was used for the photocatalytic reduction of carbon dioxide by using water as a solvent and triethylamine as the sacrificial donor. Methanol was obtained as the major reaction product along with the formation of minor amount of CO (0.82 %). It was found that GO-grafted CoPc exhibited higher photocatalytic activity than homogeneous CoPc, as well as GO, and showed good recoverability without significant leaching during the reaction. Quantitative determination of methanol was done by GC flame-ionization detector (FID), and verification of product was done by NMR spectroscopy. The yield of methanol after 48 h of reaction by using GO–CoPc catalyst in the presence of sacrificial donor triethylamine was found to be

3781.8881 m molg^{-1} and the conversion rate was found to be 78.7893 m molg^{-1}. After the photoreduction experiment, the catalyst was easily recovered by filtration and reused for the subsequent recycling experiment without significant change in the catalytic efficiency.

GO was obtained from the oxidation of graphite with $KMnO_4$ and H_2SO_4 following the literature procedure. High specific surface area of GO along with easily accessible ample oxygen functionalities decorated on both side of GO nanosheets provide great potential as a support material for various catalysts. Prior to the immobilization, the GO was treated with chloroacetic acid to convert the epoxy groups into carboxy (COOH) groups, which were subsequently used for the grafting of CoPc to the GO surface. The morphology and structure of as-prepared GO and GO–CoPc catalyst was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image of GO–CoPc shows twisted and crumpled nanosheets in an agglomerated phase with lot of wrinkled features of GO–CoPc catalyst. The TEM images also reveal the nanoscopic features with layered structure of GO–CoPc. The TEM image of carboxylic group (COOH) containing GOES before immobilization of CoPc. The dark spots in the TEM image are probably due to the COOH functionalities located on the surface of GO. Selected area electron diffraction pattern of GO– CoPc shows that material was amorphous in nature.

Toshiyasu Sakakura[11] studied Transformation of Carbon Dioxide. CO_2 is so thermodynamically and kinetically stable that it is rarely used to its fullest potential. However, due to the electron deficiency of the carbonyl carbons, CO_2 has a strong affinity toward nucleophiles and electron-donating reagents. In other words, CO_2 is an “anhydrous carbonic acid”, which rapidly reacts with basic compounds. For example, organometallic reagents such as Grignard reagents readily react with CO_2 even at a low temperature. Water, alkoxides, and amines also add to CO_2 in similar manners to produce compounds with a carboxyl or carboxylate group. These reactions conveniently produce carbonic and carbamic acids. Further reactions of these species with electrophiles lead to the formation of organic carbonates and carbamates. On the other hand, reactions of low valent metal complexes (mainly nickel (0) and palladium (0)) with CO_2 and unsaturated compounds lead to the formation of five-membered metallalactones. Because the valence of the metal increases by two, this type ofreaction is called an “oxidative cycloaddition”. Hence, reactions involving CO_2 can be categorized into two patterns: (1) formation of a carboxyl group through nucleophilic attack and (2) generation of a five-membered ring through oxidative cycloaddition.

Organic carbonates are roughly categorized into cyclic and linear carbonates. Because both compounds have three oxygens in each molecule, they are relatively suitable from a thermodynamic point of view as synthetic targets starting from CO_2. Four industrially important organic carbonates are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diphenyl carbonate (DPC). EC, DMC, and DPC are useful intermediates for manufacturing polycarbonates through a non-phosgene process. In addition, EC, PC, and DMC are employed as electrolytes in lithium ion batteries and are widely used as aprotic polar solvents. Furthermore, the excellent properties of DMC as a fuel additive have attracted much attention. Moreover, linear carbonates are important alkylating agents, as are alkyl halides or dialkyl sulfates, and carbonylating agents, as is phosgene or carbon monoxide. This section illustrates synthetic methods of linear carbonates, especially dimethyl carbonate (DMC), starting from CO_2. It should be noted that cyclic carbonates can be easily synthesized by reacting CO_2 and epoxides.

Ruwen Wang,[12] studied Conversion of CO_2 into valuable compounds, including fuels, with renewable energy sources and sustainable compounds was a challenge addressed by artificial photosynthesis research. In particular, the application of solar assisted electrochemical (EC) processes, in which electrons are furnished by a photovoltaic (PV) cell. A PV-EC system is described, consisting of a CIGS (copper indium gallium selenide) PV unit linked to a carbon electrode loaded with cobalt phthalocyanine as molecular catalyst, able to achieve the CO_2 reduction to CO and then to methanol in aqueous media with limited bias voltage. Using CO as starting material, a partial current density of 0.6 $mAcm^{-2}$ for methanol is obtained at a bias voltage, corresponding to a low 240 mV overpotential. Remarkably, the liquid fuel production can be sustained for at least 7 h. Under ideal conditions, the CO_2-to-CH_3OH reaction shows a global Faradaic efficiency of 28%.

In this purpose, employed CIGS (copper indium gallium selenide) materials which possess a strong absorption in the visible range and tunable band gaps by adjusting the In/Ga ratio. Moreover, CIGS-based PV cells recently reached high conversion efficiencies (above 24%).Following this strategy, report about the use of a carbon paper porous electrode loaded with a CoPc catalyst and powered by a CIGS PV cell enabling to achieve the CO_2 to methanol conversion. Experiments were conducted at ambient pressure and temperature and in aqueous solutions. As previously reported, a catalytic ink was first prepared by mixing CoPc with multi-walled carbon nanotubes (MWCNT) and Nafion resin in a mixture of ethanol and ethylene glycol, to obtain a stable colloidal solution. Ink deposition onto porous carbon paper was made by drop casting, and the operational catalytic film was obtained after a drying at 100 °C.

Since the same catalyst can be used for reducing first CO_2 to CO, and then CO to methanol, pH and electrode potential could be adjusted to maximize each partial reduction process. The first CO_2 -to-CO pure electrochemical step can be achieved with typical 95% faradaic efficiency in neutral pH conditions as already shown while the second step may be achieved with a PV-EC cell as described in this study. From the total number of transferred electrons, a global Faradaic efficiency of 28% is calculated and the chemical selectivity is equal to ca. 11.6% .

For Electrode Characterisation the composition of the CoPc loaded porous carbon electrode was determined by X-ray photoelectron spectroscopy (XPS) recorded on an ESCALAB 250 spectrometer (Thermo Sci.) accompanied by a microfocalized X-ray source and a double monochromator. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted with an iCAP 6300 ICP-OES CID spectrometer (Thermo Sci.). A test was performed with a RACHID detector including a diode array, a peristaltic pump, and argon plasma (analyzes present at 50 rpm, 1150 W). The CoPc MWCNTs carbon paper electrode was immersed in 2 mL 69% nitride acid for 20 h and then diluted to 20 mL solution to get the sample for ICP measurement.

Charles M. Lieber and Nathan S. Lewis[13] studied electrocatalytic reduction of aqueous solutions of $CO_2(g)$ to CO(g). The reaction occurs on carbon electrodes modified by adsorption of cobalt phthalocyanine, Co (Pc). The CO_2 be achieved within 300 mV of the thermodynamic CO_2/CO redox potential, and essentially the only carbon-containing product is CO(g). In contrast, Co (Pc) dissolved in homogeneous solution yields poor stability and low catalytic efficiency for CO_2 activation. Thus, in addition to an energy- efficient activation of CO_2 (g), this system demonstrates the effectiveness of chemical modification of electrodes in suppressing deleterious decomposition pathways during electrocatalysis. Primary focussed upon utilizing transition-metal complexes to promote reduction of CO_2 to CO via following reaction

$$CO_2\,(g) + 2e^- + 2H^+(aq) \longrightarrow CO(g) + H_2O(l)$$

CO (Pc)[4] was deposited onto pyrolytic graphite or carbon cloth surfaces either by adsorption from THF/Co(Pc) solutions or by droplet evaporation of THF/Co(Pc) solutions. Controlled potential electrolysis of such modified carbon cloth electrodes at -1.0 V vs. SSCE in aqueous solution (pH 5.0, 0.05 M citrate buffer, $E_o'(CO_2/CO) = -0.65$ V vs. SCE) under 1 atm of CO_2 (g) produced CO(g) as the major carbon-containing species. The catalytic nature of the reaction has been confirmed by formation of over 105 molar equiv of CO per molar equiv of electroactive catalyst.

The pH dependence of the Co (Pc)[4] reduction implies an initial protonation step in the reaction sequence, which is followed subsequently by further reduction of the complex and attack by CO_2. Precedent for the reaction steps involved in such catalysis can be found in proposed mechanisms for catalysis of the water-gas shift reaction. A similar reaction sequence has been invoked previously by Eisenberg to explain redox catalysis in the CO_2 /CO transformation by homogeneous Co and Ni macrocyclic complexes, where a one-electron reduction to a metal hydride species is implicated. The product distribution is similar to that obtained with these macrocyclic ligands, but an important difference in the system is that the "hydride" (either ligand or metal centered) is not reactive enough to reduce $C0_2$ and must itself be reduced further (by two electrons in this case) to yield the observed catalysis. The ease of reduction of the Co (Pc) complex allows the $C0_2$ transformation to proceed at a much lower overpotential, yet with faster rates, than in previous catalytic systems for CO production. A comparison of the current density to the amount of electroactive catalyst on Co (Pc)/C electrodes indicates that turnover numbers for $C0_2$ reduction can exceed 100 s^{-1}, which are over 3 orders of magnitude greater than the values of 2-7 turnovers/h reported for catalysis in homogeneous systems.

Yuan Zhu, Shiran Zhang[14] studied Catalytic conversion of CO_2 to CH_4 on cobalt oxide and Ru-doped cobalt oxide nanorods with in-house ambient pressure X-ray photoelectron spectroscopy (AP−XPS) using monochromated Al Kα. A correlation between catalytic performances of the two catalysts and their surface chemistry under reaction conditions was built. Active phases of the two catalysts are metallic cobalt and bimetallic Co−Ru, respectively. Light-off temperature of Co−Ru catalyst is lower than that of a cobalt catalyst. Selectivity to production of CH_4 and activity on the Ru-doped cobalt oxide are obviously enhanced by formation of bimetallic Co−Ru ultrathin film in its surface region in contrast to that of cobalt catalyst in the temperature range of 200−340 °C.

Co_3O_4 nanorods were synthesized with a modified wet chemistry protocol reported in literature. A doped oxide, $(Co_{0.95} Ru_{0.05})_3O_4$ nanorod was synthesized by using a protocol similar to the synthesis of Co_3O_4. Both cobalt (II) acetate and ruthenium (III) chloride with a molar ratio of Co to Ru at 19:1 are used as starting materials. The synthesized Co_3O_4 and $(Co_{0.95} Ru_{0.05})_3O_4$ nanorods are precursors of cobalt and Ru- doped cobalt catalysts active for CO_2 conversion. Size and shape of the synthesized nanorods were identified with Titan TEM (FEI Titan 80−300, 300 kV FEG TEM with point resolution 0.2 Å). Then 100 mg of catalysts were loaded into a fixed-bed microreactor. Catalytic performance was measured with a gas chromatography (GC) in the temperature range of 100−420 °C with a flow rate of 10 mL min−1 for CO2 and 40 mL min−1for H2, which gave an approximate gas hourly space velocity of 5.9 s^{-1}. The pressure in the microreactor is about 1 bar. The ratio of CO_2 to H_2 in the mixture reactant is 1:4.

In terms of the sample for AP−XPS studies, Co_3O_4 or Ru-doped Co_3O_4 nanorods were dispersed on gold foil or graphite surfaces. This in-house AP−XPS has a reaction cell which is integrated with a monochromatic Al Kα and differential pumping system aligned with an energy analyzer. The sample located in the reaction cell is placed at the cross point of X-ray beam and coaxial direction of focal points between prelens and lens 1 and that between lenses 1 and 2 in the differential pumping stages. Then 0.1 Torr CO_2 and 0.4 Torr H_2 were introduced into the reaction cell of AP−XPS system. Gas pressure of reactants in the reaction cell is regulated with leak valves which can seal UHV and precisely tune leak rate at a middle level. Monochromatic Al Kα irradiates the sample surface through a Si_3N_4 window. Catalysts in a reaction cell filled with reactant gases were heated through thermal conduction of a metal foil which was heated in UHV environment with an e-beam. Surface composition and oxidation states of catalyst surfaces at different reaction conditions are examined in a reaction cell where reactant gases flow through. Flat Au foil (99.995%) with a thickness of 0.5 mm was used as a substrate to load catalysts. Binding energies of all peaks were calibrated to Au 4f measured at same experimental conditions.

Pengju Yanga, Ruirui Wang[15] studied unique cobalt nitride/nitrogen-rich carbons (Co_4 N/NCs), which can work as noble-metal-free catalysts for CO_2-to-CO con- version. The mass activity of Co_4 N/NCs is two orders of magnitude higher than those of previously reported CO_2 photoreduction catalysts. The quantum yield for CO production at 450 nm reaches 7.2% with a turnover frequency per Co atom of 0.97 s^{-1}. The electronic structure and coordinated environment of catalysts are analyzed by X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy. The reaction processes are investigated by in-situ diffuse reflectance infrared fourier transform spectroscopy and density functional theory calculations. Results suggest that the synergetic effects between the Co_4 N and the NCs can consolidate the adsorption and activation of CO_2 and accelerate the interfacial electron-transfer kinetics between the Co_4 N/NCs catalysts and light-harvesting antenna, thereby resulting in the outstanding activity for synthesizing CO from CO_2 . This work offers the possibility to design Co-based host-guest topology for highly-efficient CO_2 reduction.

Construction of a unique Co_4 N/nitrogen-rich carbons (Co_4 N/NCs) catalyst by a photochemical assembly approach for the first time. The Co_4 N/NCs exhibited excellent activity for CO_2-to-CO conversion along with a photosensitizer under visible light. The QE for CO production at 450 nm was calculated to be as high as 7.2%. The highest turnover frequency (TOF) per Co atom within Co_4N/NCs reached 6.7 s^{-1}. Result suggested that the remarkable activity of Co_4N/NCs was mainly originated from the unique hybrid structure and the synergistic effects between the Co_4N and the NCs.

Firstly, ammonium hydroxide (1 mL, 25-28 %) was added into deionized water (125 mL) and stir well. Then, adenine (1 g) and Co $(NO_3)_2 \cdot 6H_2O$ (25 mg) were dissolved in the above solution. Finally, the above solution was irradiated with a 125 W high pressure Hg lamp at 20 ℃. After 24 h irradiation, black Co_4N/NCs p was obtained. The obtained Co_4N/NCs was washed with ethanol and then dried at 60 ℃ for 12 h to get the final catalysts. The Co_4N sample was prepared according to previous study.

Transmission electron microscopy (TEM) images and element mapping test of the obtained Co_4N/NCs. Results suggest that the Co_4N nanoparticles were uniformly dispersed on the nitrogen-rich carbon matrix with an average size of approximately 1.7 nm. The high-resolution TEM (HRTEM) image of Co_4N nanoparticles displayed a distinct lattice fringe of 0.207 nm, which corresponds to the (1 1 1) plane of Co_4N. The obtained sample was further investigated by X-ray diffraction (XRD). The diffraction peak at 26.8° corresponded to graphite-like carbon, agreeing with the Raman result. The diffraction peaks at 43.8° and 51.03° were ascribed to Co_4N (JCPDS 41-0943), supporting the HR TEM observation. The XRD broadening may relate to the small size and the low crystallinity of the Co_4N/NCs.

Chan Kwak, Tae-Jin Park[16] studied the performance of the platinum–cobalt catalysts in a carbon monoxide preferential oxidation (PROX) reactor was investigated for polymer electrolyte fuel cell systems. First, the PROX reaction was analyzed based on two major reactions involved in it, i.e., oxidation of carbon monoxide and the H2–O2 reaction. Both reactions were affected by the other reaction depending on the reaction temperature regions, but the extent of the influence is not so large. The platinum–cobalt catalysts were found to exhibit high performance in PROX of carbon monoxide in rich hydrogen as a result of catalytic synergy effect between platinum and cobalt. In order to improve such synergy effect, the catalysts were prepared by sol–gel method and subsequent supercritical drying. The platinum–cobalt catalysts prepared by the single step sol–gel procedure exhibited higher activity for PROX than the catalysts prepared by the conventional impregnation. Supercritical drying preserved the active species of platinum–cobalt phase, therefore, the platinum–cobalt composite aerogel catalyst exhibited excellent ability for the carbon monoxide removal.

Osarieme Uyi Osazuwa [17] studied the catalytic behaviour of samarium-cobalt-trioxides perovskite catalyst for the mitigation of greenhouse gas (carbon dioxide) to provide cleaner energy (hydrogen and carbon monoxide) and environment. X-ray photoelectron spectroscopy analysis of the as-synthesized catalyst showed peaks corresponding to complexes of cobalt (II), dual oxygen species, and samarium (III) ions. X-ray diffraction pattern showed a monophasic samarium-cobalt-trioxides perovskite structure, while post-reaction analysis showed modification of the perovskite. The temperature-programmed reduction analysis showed peaks corresponding to reduction of cobalt (II) to Co (0). The temperature-programmed desorption displayed peaks ascribed to medium strength basic and acidic sites. Performance test carried out on the catalyst via methane dry reforming, showed excellent reactants conversions of above 90% which was maintained for the duration (30 h) of the experiment. The catalyst remained active over the time of experiment, even though the temperature-programmed oxidation, scanning electron microscopy and energy dispersive X-ray spectroscopy analyses of the used catalyst showed evidence of carbon deposit.

The synthesis of $SmCoO_3$ perovskite catalyst was carried out using the sol-gel citrate method. Mixture of the transition metal; $Co(NO_3)_2.6H_2O$ (99.99% purity, Sigma Aldrich) and citric acid (anhydrous, Sigma Aldrich) was prepared at room temperature in a molar ratio of 1:2. The nitrate of the rare earth metal; $Sm(NO_3)_3.6H_2O$ (99.99% purity, Acros Organics), was added to the mixture in the ratio of 1:1 with the transition metal, and stirred at room temperature until a clear solution was attained. The resulting homogeneous solution was continuously stirred and heated at 353 K for 4 h to obtain a gel, before being dried to powder at 383 K. The powder was ground and annealed in a furnace (carbolite AAF 11/3) at 1123 K with a heating rate of 5 K min^{-1}. In addition, the oxides of the individual metals were prepared by mixing their nitrates in distilled water, and then drying at

383 K for 4 h. The dried powder was then annealed in a furnace with heating rate of 5 K min^{-1} at 1123 K.

CONCLUSION

CO_2 reduction can decrease the concentration of CO_2 in the atmosphere and produce carbonaceous valued-added fuel molecules and chemical feedstock based on cost-efficient and earth-abundant catalysts. Compared to precious metals like Au, Ag and Pt, non-precious transition metals, such as cobalt, are favored for CO_2 reduction in the long run. [3] The conversion of carbon dioxide remains a main focus for industry and multiple research groups all over the world. Due to its advantages as a cheap, non-toxic molecule, which can be applied in different physical states, it is – in principle – an interesting substrate for the synthesis of small molecules or functional groups. Though the activation energy is quite high due to the stability of carbon dioxide, several catalysts were discovered and developed to overcome this issue. Recent efforts are being focused on the development of environmentally friendly and economical catalysts, operating under mild reaction conditions such as low temperature and pressure.[2]

The element Co possesses modest CO_2 adsorption intensity, polyvalency, high coordination, unsaturated d-orbitals of electrons, alloying, etc. Cobalt-containing catalysts exhibit larger specific surface area and supply more active sites due to the optimized Co content, synthetic methods and morphology for CO_2 catalytic reduction. More importantly, Co nanoclusters showed size- dependent dissociative adsorption of CO2 molecules to CO and O ligands, more energetically contributing to the subsequent CO_2 activation.

A novel flower- like cobalt[4] was synthesized through a facile hydrothermal method with the aid of n- butylamine. The morphological features facilitate both the exposure of the active sites and the mass transfer of the active species, favoring the electrocatalysis of the carbon dioxide reduction reaction. The electrocatalytic activity of flower- like cobalt is found to be 3.5 and 4 times higher than that of the $Co(OH)_2$ and bulk Co metal, respectively. Electrochemical analysis reveals that the divalent oxide is essential to constitute the active sites for the CO_2 reduction reaction. In addition, this catalyst is highly active for the oxidation of reduced product, thus acting as a bifunctional catalyst. An efficient CO_2 cycloaddition reaction with epoxides [7]is achieved on low-priced photothermal catalyst of Co_2C nanoflowers. The yield of cyclic carbonates is up to ~95% with visible-light irradiation, owing to the excellent photothermal effects of Co_2C nanoflowers in converting light to heat. Besides, the high specific area as well as efficient CO_2 adsorption on the exposed Co atoms of the catalysts can simultaneously activate the adsorbed CO_2 and epoxides, thus promoting the reaction of CO_2 fixation. This work provides new insights into the utilization of TMCs in the field of advanced photothermal-driven catalysis.

Converting CO_2 to carbonaceous value-added molecules has a profound effect on the environment and energy in the future. The CO_2 photo/electroreduction can further be combined with an innovative method of big data and predictive analytics to boost the efficiency and reduce carbon release. This review uncovers the proposed catalytic mechanism for CO_2 photo/electroredution and shows some efficient synthetic methods for Co-based catalysts including metal, inorganic metal oxide and metal-organic compound catalysts. Some strategies that improve the catalytic performances and catalyst stability are presented based on cost-efficient and earth-abundant cobalt-containing catalysts for CO_2 reduction.[3]

BIBLIOGRAPHY

[1] S. C. Maeda, T. Ema, and C. Sci, “As featured in : Catalysis Science & Technology,” 2014, doi: 10.1039/c3cy00993a.

[2] N. A. Tappe, R. M. Reich, V. D. Elia, and F. E. Kühn, “Current advances in the catalytic conversion of carbon dioxide by molecular catalysts : an update,” pp. 26–30, 2018, doi: 10.1039/c8dt02346h.

[3] C. Li *et al.*, “Carbon dioxide photo/electroreduction with cobalt,” *Journal of Materials Chemistry A*, vol. 7, no. 28. Royal Society of Chemistry, pp. 16622–16642, 2019. doi: 10.1039/c9ta03892b.

[4] G. Yang, Z. Yu, J. Zhang, and Z. Liang, “A highly efficient flower-like cobalt catalyst for electroreduction of carbon dioxide,” *Cuihua Xuebao/Chinese J. Catal.*, vol. 39, no. 5, pp. 914–919, May 2018, doi: 10.1016/S1872-2067(18)63021-9.

[5] H. Ge, Y. Jing, and X. Yang, “Computational Design of Cobalt Catalysts for Hydrogenation of Carbon Dioxide and Dehydrogenation of Formic Acid,” pp. 2–7, 2016, doi: 10.1021/acs.inorgchem.6b01723.

[6] W. Walker, H. Miller, and K. Miller, “Catalytic Hydrogenation of Carbon Dioxide to Higher Hydrocarbons1,” pp. 2446–2454.

[7] A. Manuscript, “ChemComm,” 2020, doi: 10.1039/D0CC01091J.

[8] E. Boutin *et al.*, “Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine,” *Angew. Chemie*, vol. 131, no. 45, pp. 16318–16322, Nov. 2019, doi: 10.1002/ange.201909257.

[9] G. Zhou, T. Wu, H. Xie, and X. Zheng, “Effects of structure on the carbon dioxide methanation performance of Co-based catalysts,” *Int. J. Hydrogen Energy*, vol. 38, no. 24, pp. 10012–10018, Aug. 2013, doi: 10.1016/j.ijhydene.2013.05.130.

[10] P. Kumar, A. Kumar, B. Sreedhar, B. Sain, S. S. Ray, and S. L. Jain, “Cobalt phthalocyanine immobilized on graphene oxide: An efficient visible-active catalyst for the photoreduction of carbon dioxide,” *Chem. - A Eur. J.*, vol. 20, no. 20, pp. 6154–6161, May 2014, doi: 10.1002/chem.201304189.

[11] T. Sakakura, J. C. Choi, and H. Yasuda, “Transformation of carbon dioxide,” *Chemical Reviews*, vol. 107, no. 6. pp. 2365–2387, Jun. 2007. doi:

10.1021/cr068357u.

[12] R. Wang, E. Boutin, N. Barreau, F. Odobel, J. Bonin, and M. Robert, “Carbon Dioxide Reduction to Methanol with a Molecular Cobalt-Catalyst-Loaded Porous Carbon Electrode Assisted by a CIGS Photovoltaic Cell**,” *ChemPhotoChem*, vol. 5, no. 8, pp. 705–710, Aug. 2021, doi: 10.1002/cptc.202100035.

[13] D. J. Darensbourg, A. Rokicki, B. Fischer, and R. Eisenberg, “Intramolecular SN2 Bridge Formation Kinetics of Undecacarbonyl(7’-bis(dipheny1phosphino)methane)-triosmium,” 1984.

[14] Y. Zhu *et al.*, “Catalytic conversion of carbon dioxide to methane on ruthenium-cobalt bimetallic nanocatalysts and correlation between surface chemistry of catalysts under reaction conditions and catalytic performances,” *ACS Catal.*, vol. 2, no. 11, pp. 2403–2408, Nov. 2012, doi: 10.1021/cs3005242.

[15] P. Yang, R. Wang, H. Tao, Y. Zhang, M. M. Titirici, and X. Wang, “Cobalt Nitride Anchored on Nitrogen-Rich Carbons for Efficient Carbon Dioxide Reduction with Visible Light,” *Appl. Catal. B Environ.*, vol. 280, Jan. 2021, doi: 10.1016/j.apcatb.2020.119454.

[16] C. Kwak, T. J. Park, and D. J. Suh, “Preferential oxidation of carbon monoxide in hydrogen-rich gas over platinum-cobalt-alumina aerogel catalysts,” *Chem. Eng. Sci.*, vol. 60, no. 5, pp. 1211–1217, Mar. 2005, doi: 10.1016/j.ces.2004.07.126.

[17] O. U. Osazuwa and C. K. Cheng, “Catalytic conversion of methane and carbon dioxide (greenhouse gases) into syngas over samarium-cobalt-trioxides perovskite catalyst,” *J. Clean. Prod.*, vol. 148, pp. 202–211, 2017, doi: 10.1016/j.jclepro.2017.01.177.

ACKNOWLEDGEMENT

I would like to thank my Guide Dr. Rohan Kunkalekar who gave me this opportunity to work on this project. I got to learn a lot from this literature review on **"Different Methods of Conversion of CO_2 by Cobalt Catalyst"**. I would also like to thank our Dean of School of Chemical Sciences Dr. Vidyadatta Verenkar.

At last, I would like to extend my heartfelt thanks to my parents. And finally, I would like to thank my dear friends who also helped me complete my literature review.