THERMOCATALYTIC CONVERSION OF CO_2 USING COBALT OXIDE CATALYST

A M.Sc. Dissertation report by:

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By

Ms. Adiksha Vishwas Devidas

To the

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Goa University

Goa 403206

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CERTIFICATE

This is to certify that the dissertation entitled **“Thermocatalytic Conversion Of CO_2 Using Cobalt Oxide Catalyst”** is bonafide work carried out by Ms. Adiksha Vishwas Devidas under my supervision in partial fulfillment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Dr. Pranay Morajkar	**Prof. Dr. Vidhyadatta Verenkar**
Guiding Teacher	Dean
School of Chemical Sciences	School of Chemical Sciences
Goa University	Goa University

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, **“Thermocatalytic Conversion of CO_2 Using Cobalt Oxide Catalyst”** is based on results of investigation carried out by me in the School of Chemical Sciences, Goa University, Goa under the supervision of Dr. Pranay Morajkar and the same has not been submitted elsewhere for the award of a degree or diploma.

Adiksha Vishwas Devidas

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Thermocatalytic conversion of CO_2 using cobalt based catalyst

1. **Introduction:** Various anthropogenic activities such as over-consumption of fossil fuel resources, deforestation and rapid industrialization over the last few decades has led to huge emissions of greenhouse gas such as CO_2 in the earth’s atmosphere, which has severely impacted the earth’s climate. Rising levels of CO_2 is the main culprit behind serious environmental problems such as global warming which is followed by excessive rainfall, melting of ice caps, rising sea levels, ocean acidification, extreme weather patterns. CO_2 emitted from anthropogenic sources has horribly disturbed the earth’s Carbon cycle and has accelerated environmental deterioration and resource depletion (Tabish et al. 2020).

   At global level, most countries have come forward and signed the Paris Agreement, which aims to abate the net atmospheric CO_2 levels by 2050. Along with afforestation various other measures are being adopted for sequestration of carbon dioxide. Carbon dioxide capture and storage technology (CCS), shifting to alternative sources of energy and chemical conversion to various value added chemicals are some of the recently developed technologies which are in forefront of CO_2 sequestration. Among the above measures, conversion of CO_2 to other chemical compounds such as methanol, methanal, etc. is of significant interest as it helps to reduce CO_2 by converting it into commercially viable products. CO_2 stored in terms of fuel based chemical compounds is simultaneously solving both the problems of energy crisis and environmental degradation. Thus, it also contributes to sustainable energy in order to meet the rising energy demand (Tabish et al., 2020; Xu et al., 2020).

   In order to yield chemicals and fuels, the chemistry and thermodynamics of CO_2 should be well known, CO_2 is one of the most stable molecules in which carbon is in its highest valence state. It is difficult to have an electrophilic reaction because of its poor electron affinity. Hence conversion of CO_2 is thermodynamically unfavorable due to the fact that the bond energy of C=O is 750 KJ/mol, making it difficult to break down. To complete such a reaction and to facilitate the cleavage of C=O bonds high temperature, high pressures, environment or highly efficient catalysts are typically required to provide the necessary energy. Till now, different strategies including catalytic approaches, namely, photochemical, electrochemical and thermochemical reactions are mainly being investigated to conduct reduction of CO_2 in which light, heat, or electricity were used to supply essential energy for the reaction (Tabish et al., 2020; Xu et al., 2020).

This literature survey discusses the recent performance of various cobalt (Co) electrocatalysts, including Co-single atom, Co-multi metals, Co-complexes, Co-based metal–organic frameworks (MOFs), Co-based covalent organic frameworks (COFs), Co-nitrides, and Co-oxides. These materials are reviewed with respect to their stability of facilitating CO_2 conversion to valuable products, and a summary of the current literature is highlighted, along with future perspectives for the development of efficient CO_2RR.

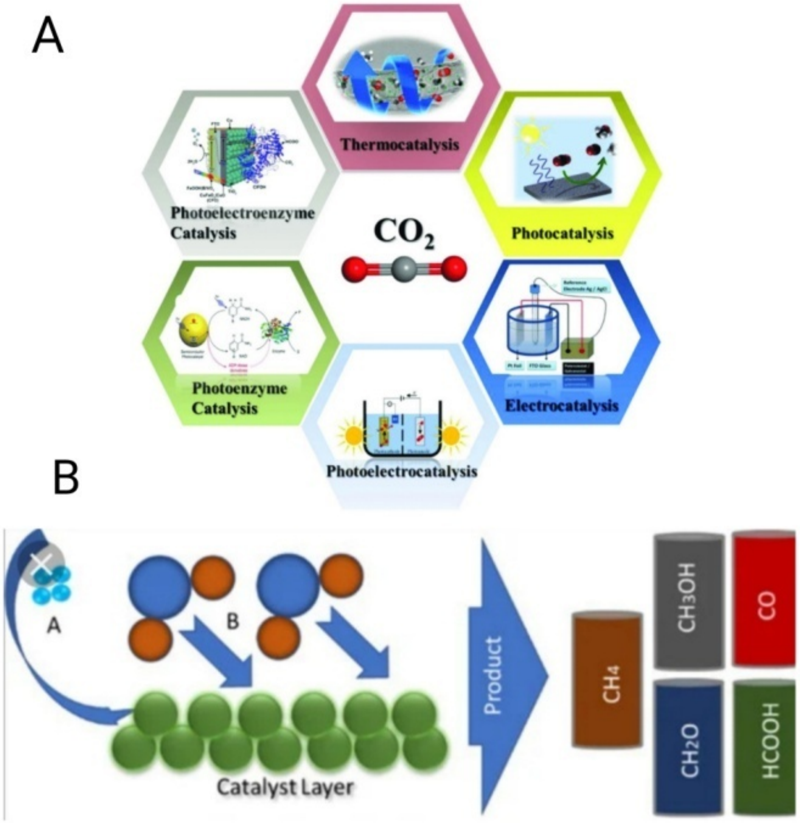

Figure 1:A) Schematic showing the strategies that are usually used in CO_2 conversion (Tabish et al. 2020). **B)**Various products of CO_2 conversion according to different catalyst (Saeidi et al. 2021).

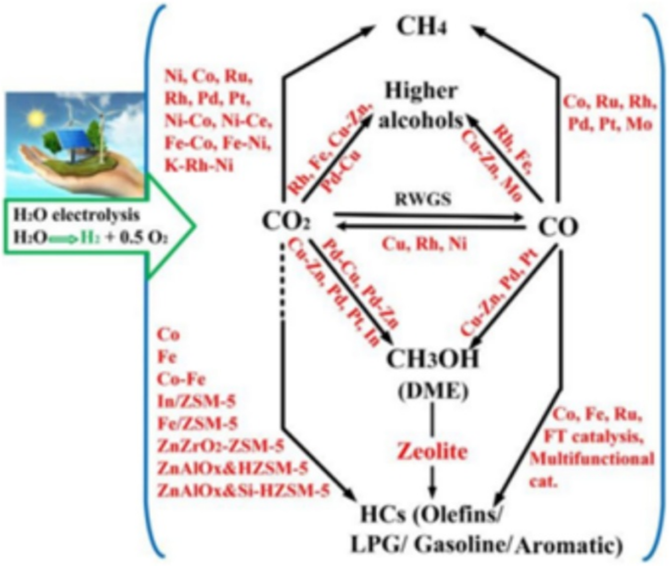

Figure 2: Conversion of CO_2 to value-added products by metal oxides (Khdary et al. 2022).

2. Themocatalytic CO_2 conversion using cobalt oxide catalyst

Most of the themocatalytic CO_2 conversion processes involves the hydrogenation reaction at relatively low temperatures (≤523K) to produce useful chemicals and feedstock materials such as CO, methane and methanol. Since CO_2 molecule is thermodynamically and chemically stable, large amounts of energy is required if CO_2 is used as a single reactant. The introduction of other substances with higher Gibbs free energy (such as H_2) as the co-reactant will make the thermodynamic process easier (Xu et al., 2020).

Thermochemical conversion of CO_2 using cobalt oxide catalyst are very important due to their extensive applications in many industrial processes, such as Fisher-Tropsch synthesis and CO_2 conversion. Co-based materials have many advantages over other because as a popular metal, Co belongs to the group of VIII-B of the periodic table having unique features like high electrical conductivity, thermal stability, unique electronic feature, chemical stability and high catalytic performance, which makes Co-based catalysts as promising materials for CO_2RR applications (Usman et al. 2021).

Cobalt as an earth-abundant transition metal is a splendid alternative to noble metals such as Pt, Ir, Ru, etc. For CO_2RR, Co has been used as a prominent source as noble metal-free electro/photocatalysts due to fascinating properties such as loosely held d-electrons and therefore readily available multiple oxidation states (Co(0), Co(I), Co(II), Co(III), Co(IV)). Moreover, it is found that a transition from Co(II) to Co(I) is involved at the intermediate state for CO_2 reduction achieving high activity, outstanding stability and product selectivity through Co-based catalyst. Cobalt is more reactive than other earth-abundant metals due to the possession of modest CO_2 adsorptions and d-bend closeness to the Fermi level (Usman et al. 2021).

Co is found to be an important stabilizers for major intermediates in CO_2 reduction. Co-based materials have applications in various other fields such as energy storage, catalysis and thermo power. Co-based materials (i.e.$NaXCoO_2$) play a critical role in cathode and anode materials for Na-ion batteries. Cobalt oxide and cobalt chalcogenides exhibit a high theoretical capacity for sodium storage. Thus, Cobalt has been reported as an important center for CO_2 reduction (Usman et al. 2021).

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Catalyst	**Year**	**Synthesis**	**Thermocatalytic/ Photothermocatalytic Condition**	**Products formed**	**Activity yield (%)**
Co-Pt-Al_2O_3	2002	Fisher-Tropsch synthesis (Zhang et al. 2002)	330-350°C	Methane	70
Co-doped Al_2O_3 catalyst	2007	Catalytic cracking	800°C	Hydrogen	15-22
Co/Al_2O_3	2012	Wet impregnation method	400°C	Methane	47
Co/TiO_2	2012	Fischer-Tropsch synthesis	180°C	Olefin and paraffin	5-13
CoO/TiO_2 CoO/SiO_2	2014	Colloidal method	250°C and 5 atm	Methane	100
Ni-Co/ZSM5	2015	Wet impregnation method	820°C	Hydrogen and Syngas	60
Co-Na-Mo based catalyst	2016	Direct hydrogenation method	1000°C	Hydrocarbons	90
Co@CoO NCS catalyst Co NCS catalyst Co@CoO-N Catalyst	2017	Facile direct current arc-discharge method	523K	CO	14.1 5.9 19.2
Single-site cobalt catalyst(SSC)	2017	Strong electrostatic adsorption	800°C	CO and Methane	95 5
Co/SiO_2	2017	Reverse water gas shift method	600°C	CO	95
Ni/Lanthanum strontium cobalt ferrite(LSCF)	2018	Wet-impregnation method	850°C, 1 atm	CH_4 H_2 CO	87.56 70.34 49.54
MnO_x-CO_3O_4	2019	Sol-gel inverse micelle method	250°C, 10 bar	Methanol	49.1
Co-CeO_2	2017	Co-precipitation method	440°C	CO and methane	6
CoAlOX	2018	Co-precipitation	140°C	Ethanol	92.1
NiOx/CO_3O_4	2018	A MOF-Template method	350°C	Toluene	95
CO_3O_4/TI_2AlC	2020	Impregnation	450°C	CO H_2	35
CuO/CO_3O_4	2020	A-MOF template method	229°C	Toluene	90
Alpha-Alumina supported cobalt catalyst	2020	CH_4 associative adsorption	923-1023K 5-50 KPa	Hydrogen rich syngas	89.5
Pt/m—Co_3O_4	2021	Polyol method	1 atm pressure	Methanol	80.53
Pt/c-Co_3O_4	2021	Hard template method	At ambient pressure , 473K-673K	Methanol	74.83

Table 1:List of Cobalt oxide catalyst and their CO_2 conversion efficiencies under thermocatalytic conditions.

3. Review of Literature

Several studies have been reported on thermocatalytic CO_2 conversion using Co-based catalysts. The first was given by Zhag et al in the year 2002 reported Co-Pt-Al_2O_3 catalyst which showed the activity of CO_2 conversion to 70% resulting in methane production (Zhang et al. 2002).

Similarly, Nuernberyet al in the year 2007 reported Co-doped Al_2O_3 catalyst which showed the activity of CO_2 conversion to 15-22% to produce hydrogen as the product (Nuernberg et al. 2008).

Furthermore, Bekar et al in the year 2012 reported Alumina supported cobalt oxide based catalyst (Co/Al_2O_3) which showed 47% activity of CO_2 conversion and selectivity of 67.80% for the methane product. Moreover,Yao et al in the year 2012 reported Co/TiO_2 catalyst which showed 5-13% activity of CO_2 conversion resulting in olefin and paraffin production. And, Gerome Melaet et al in the year 2014 reported CoO/SiO_2 and Co/SiO catalyst for CO_2 conversion and thus represented a challenge for achieving 100% selectivity for a desired product (i.e. methane) (Bekar et al. 2012).

Also, Estephane et al in the year 2015 reported ZSM5 cobalt monometallic and bimetallic catalyst for CO_2 conversion which showed activity of 60% resulting in the formation of hydrogen and syngas. Also reported that cobalt based catalyst exhibit stability due to reduced carbon deposition (Estephane et al. 2015).

Besides, Owen et al in the year 2016 reported Co-Na-Mo based catalysts which showed the activity of >90% for CO_2 conversion and relatively high methane selectivity (58%) resulting in the formation of hydrocarbons. Further, Le et al in the year 2017 reported Co-CeO_2 catalyst which showed activity of 6% for CO_2 conversion. Also reported that cobalt can be selected as the most active metal for methanation reaction to produce C_2 and C_3 hydrocarbons to increase the value of synthetic natural gas (Owen et al. 2016).

Next, Yin et al in the year 2017 reported Cobalt-Cobalt oxide core-shell catalyst (Co@CoONCS ,Co NCS Catalyst and Co@CoO-N Catalyst) for CO_2 conversion which showed activity of 14.1, 5.9 and 19.2% respectively for the desired product (CO). Also reported that the route of conversion CO_2 to CO by reverse water –gas shift (RWGS) reaction, showing great potential due to the product can be directly used as a feedstock in the significant industrial processes e.g the well known Fischer-Tropsch synthesis. Recent successful investigation of cobalt-modified Molybdenum Carbide (Co-MO_2C) was reported to decompose CO_2 gas with a conversion of 9.5% and CO selectivity of 98% at 573K. Then, Juan Jimenez et al in the year 2017 reported Single-Site cobalt catalyst (SSC) which showed activity for CO and CH_4 of 95% and 5% respectively for CO_2 conversion (Yin et al. 2018).

Ayodele et al too in the year 2018 reported Nickel supported lanthanum strontium cobalt ferrite (Ni/LSCF) for CO_2 conversion which showed the activity in steam methane reforming at 750°C, 800°C and 850°C for CH_4, H_2 and CO of 73.46%, 78.67% and 87.56% selectivity respectively. Also reported that the stability test conducted at 480 min time in stream (TOS) revealed that the commercial Ni-αAl_2O_3 was more stable in the steam methane reforming then the NI/LSCF catalyst (Alsaffar et al. 2021).

Furthermore, Wang et al in the year 2018 reported CoAlOX catalyst for CO_2 conversion which showed the activity of 92.1% at 140°C with the ethanol yield at 0.444 $mmolg^{-1}h^{-1}$. Similarly, Chen et al in the year 2018 reported NiOx/CO_3O_4 catalyst for CO_2 conversion which showed the activity of 95% with ethanol yield (Wang et al. 2018).

Similarly, Stengeland et al in the year 2019 reported mesoporous manganese-cobalt oxide spinel catalyst (MnOX-CO_3O_4)for CO_2 conversion which showed the activity of 49.1% and the highest methanol selectivity of 29.8% (reaction conditions, 250°C, 10 bar, 44-400 h^{-1}) with 20% wt % manganese in a methanol formation rate of 2280mg/(gcath) (Stangeland et al. 2019).

Then Lloret et al in the year 2020 reported cobalt oxide supported on MAX phase catalyst (CO_3O_4/Ti_2AlC) for CO_2 conversion which showed the activity for CO and H_2 as 64% and 35% respectively. Dry reforming catalysis usually suffer from deactivation through sintering of active site and cooking (Ronda-Lloret et al. 2020).

Moreover, Alsaffar et al in the year 2020 reported alpha-alumina supported cobalt catalyst for CO_2 conversion which showed the activity of 89.5% with the hydrogen and syngas yield. Xu et al too in the year 2020 reported bimetal oxide CuO/Co_3O_4 catalyst for CO_2 conversion which showed the activity of 90% with the toluene as the product (Alsaffar et al. 2021).

Further, Anastasiia et al in the year 2021 reported Pt/m-CO_3O_4 and Pt/C-CO_3O_4 catalyst for CO_2 conversion in the CO_2 methanation which showed the activity of 80.53% and 74.83% respectively with the methanol yield (Efremova et al. 2022).

From the above reviews of literature it has been concluded that CoO/TiO_2 and CoO/SiO_2 catalyst shows the highest activity of 100% for CO_2 conversion under thermocatalytic/photocatalytic conditions of 250°C and 5 atm pressure (Bekar et al. 2012).

4. Synthesis of cobalt-based catalyst for CO_2 conversion

Most of the catalysts discussed above were synthesized by Catalytic cracking method, Wet impregnation method, Fisher-Tropsch synthesis, Colloidal method, Direct hydrogenation method, Facile direct current arc-discharge method, Strong electrostatic adsorption, Reverse water gas shift method, Sol-gel, inverse micelle method, Co-precipitation method, A MOF-Template method, CH_4 associative adsorption, Polyol method and Hard template method.

Out of these, catalytic cracking, wet-impregnation method were seen to be best as catalytic cracking has the major advantage the possibility of obtaining a H_2-rich gas effluent, free from CO and CO_2, eliminating the necessity for the separation of hydrogen from the other gaseous products. And the application of the wet impregnation method for preparing supported metal catalyst has the advantage of improving the dispersion of the active species on the support.

Zhag et al synthesized Co-Pt-Al_2O_3 catalyst using cobalt nitrate solution added dropwise to alumina via impregnation at 80°C in a rotary evaporator. Following cobalt addition, tetramine platinum nitrate solution was added by an incipient wetness impregnation method to give a platinum loading of 0.5%. The catalyst was then dried in a rotary evaporator at 80°C and calcined at 400°C for 4 h (Zhang et al. 2002).

Nuernbery et al synthesized Co-doped Al_2O_3 catalyst using catalytic cracking method where 3.0g of chitosan $(C_6H_{11}O_4N)n$ were dissolved in 100 mL of acetic acid solution (5% v/v) and 9.20g of $Al(NO_3)_3.H_2O$ were dissolved in 40 mL of distilled water. The Al aqueous solution were then added with stirring to the polymer solution. The CO/Al_2O_3 samples were obtained by annealing the dried samples at 600°C in air flow for 90 min with a heating rate of 5°Cmin^{-1} $^{\text{(Nuernberg et al. 2008)}}$.

Bekar et al synthesized Cao/Al_2O_3 catalyst using wet impregnation method where Cobalt (II) nitrate, tetraamineplatinum (II) nitrate and ruthenium (III) chloride hydrate were dissolved separately using a minimum amount of distilled water. The clear solutions formed were then mixed with the dopant according to the fixed atomic ratio, dopant to based metal oxide or co-dopant in a beaker and stirred continuously for 10 min at room temperature to homogenize the mixture. Alumina beads were then immersed into the mixture for 10 min. In order to modulate the morphology and structure and to eliminate the solvent the coated alumina beads were aged in an oven at 80°C for 24 h. To remove all the anionic precursors and excess water it was then calcined in the furnace at 400, 600, 700, 800, 900 and 1000°C for 5 h (Bakar et al. 2012).

Yao et al synthesized Co/TiO_2 catalyst using Fischer-Tropsch synthesis method by impregnating TiO_2 with a cobalt nitrate solution. TiO_2 was mixed with distilled water in a mass ratio of 1:1, and dried in air at 120˚C for 1 h. The support was calcined in air at 400˚**C** for 16 h. After calcination the support was crushed and sieved, and the particles with diameters between 0.5 and 1 mm were chosen for use. The support was then impregnated with a sufficient quantity of cobalt nitrate $(Co(NO_3)_2 6H_2O)$ solution to give a cobalt metal loading of 10% by mass. Thereafter the support was dried in air at 120˚C for 16 h, and then calcined in air at 400˚C for 6 h to allow it to decompose and transform from cobalt nitrate to cobalt oxide (Yao et al. 2012).

Melaet et al synthesized CoO/TiO_2 and CoO/SiO_2 catalyst using colloidal method by capturing CO_2 and green GreenH_2 (Melaet et al. 2014).

Estephane et al synthesized Ni-Co/ZSM5 catalyst using wet impregnation method where 1g of the support was impregnated with aqueous solutions prepared by dissolving appropriate amounts of cobalt $(Co(NO_3)_2{\bullet}6H_2O)$, in 10 mL of distilled water. The resulting slurry was then stirred for 3h at room temperature and then dried at 60˚C for 12h before calcinations for 5h in a muffle furnace at 450˚C (Estephane et al. 2015).

Owen synthesized Co-Na-Mo based catalyst using direct hydrogenation method where $Co(NO_3)_2{\bullet}6H_2O$, NaOAc and $(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$ as metal precursors. A variety of supports were used including SiO_2, CeO_2 , ZrO_2, ϒ-Al_2O_3, TiO_2, ZSM-5(NH_4^+) and MgO. During synthesis, the support was suspended in the minimum amount of methanol. 20mL of methanol containing 20 wt% of cobalt was added drop wise under stirring. Followed by 1 wt% of sodium disssolved in methanol and $(NH_4)_6Mo_7O_{24}{\bullet}H_2O$ dissolved in in deionised water were added slowly into the solution. The resulting mixture was stirred for 10 min before using sonicated for 60 min. The solvent was removed under vacuum while being heated through the use of a rotary evaporator until a powder of constant mass was obtained. The obtained powder then calcined in air for 16h at 873K (Owen et al. 2016).

Yin et al synthesized Co@CoO NCS catalyst, Co NCS catalyst and Co@CoO-N Catalyst using facile direct current arc discharge method where 8 mm cobalt rod was used as the anode and pure graphitic rod as cathode Co NCS catalyst and Co@CoO-N Catalyst were obtained in He/H_2 and He/CO_2, respectively. The CO_2 was chosen as a mild oxygen source because the inert CO_2 can provide a mild oxidizing environment. N-doped Co@CoO monochains (Co@CoO NCS) were produced when NH_3 gas were introduced during arc discharging (Yin et al. 2018).

Jimenez et al synthesized Single-site cobalt catalyst (SSC) using strong electrostatic adsorption where hexamine (II) chloride were taken as the precursor and supporting it on silica gel (300 $m^2/g^)$ at an initial pH of 11. For CO_2 hydrogenation, the gel feed was mixture gas with stoichiometric ratio of 4:1 H_2/CO_2 with a 10% Ar internal standard at a pressure of 10 bar, products were analysed in-line with a GC equipped with a TCD and KID detector (Jimenez 2016).

Ayodele et al synthesized Ni/LSCF using wet impregnation method where the queous solution of the active metal precursor ($Ni(NO_3)_2{\bullet}6H_2O$ required to obtain the equivalent amount of the Ni loading was calculated in order to obtain the right composition of the Ni loading in the final catalyst. Subsequently the aqueous solution of the the $Ni(NO_3)_2{\bullet}6H_2O$ was impregnated into the LSCF powder. The resulting mixture of the catalyst and the support were stirred continuously at room temperature for 3h using a magnetic stirrer. Later, the catalyst slurry formed was dried in the oven overnight at 105˚C and successively air calcined in a furnace at 900˚C at a heating rate of 10˚C/min. The as-synthesized fresh calcined Ni/LSCF catalyst was cooled and sieved to particle size range of 140-250μm (Ayodele et al. 2019).

Stangeland et al synthesized MnO_x-CO_3O_4 using sol-gel inverse micelle method where cobalt (II) nitrates hexahydrate and manganese (II) nitrate hydrate was dissolved in a solution containing 1-butanol, HNO_3 in a 200 mL beaker at room temperature (RT) under magnetic stirring. The obtained clear gel was placed in an oven at 100˚C for 6h. The resulting powder was crushed, washed several times with ethanol and centrifuged. Finally the powder was dried in an oven at 100˚C overnight. The dried powders were calcined under flowing synthetic air at 150˚C for 12h, 250˚C for 4h and 350˚C for 2h with a heating rate of 2˚C/min to the desicated temperature (Stangeland et al. 2019).

Le et al synthesized Co-CeO_2 using co-precipitation method where at room temperature $Co(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were first dissolved in deionized water to make solutions with different mole fractions of Co. Then, aqueous Na_2CO_3 solution was added dropwise under vigorous stirring to reach a final pH 9 and the slurry was aged for 3h without stirring at room temperature. The suspension was filtered and washed with deionized water and dried at 110°C and calcined in air at 500°C for 5h. For comparison, Co_3O_4 was synthesized by precipitation method from an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ and Na_2CO_3. It was calcined in air at 500°C for 5h and the catalysts were reduced in hydrogen at 500°C before reaction (Le et al. 2017).

Wang et al synthesized CoAlOX catalyst using co-precipitation method assisted with urea, followed by calcination to CoAl mixed oxides. After reduction in hydrogen at different temperatures from 300 to 650°C, the alumina supported cobalt catalysts were obtained, which are denoted as CoAlOx-T (T is the reduction temperature) (Wang et al. 2019).

Chen et al synthesized NiOx/CO_3O_4 catalyst using a MOF-template method where a series of NiOx/Co3O4 composites derived from ZIF-67 template, as described in two steps: (1) $Ni(NO_3)_2$ was first pre-absorbed on the ZIF-67 to form $Ni(NO_3)_2$/ZIF-67 precursor; (2) and then the as-obtained precursor was pyrolyzed in air at 350ºC to obtain hollow NiOx/Co_3O_4 composite by burning off the organic ligands of ZIF-67 (Chen et al. 2018).

Lloret et al synthesized Co_3O_4/TI_2AlC using impregnation method using Co $(NO_3)_2 \cdot 6H_2O$ as the cobalt precursor. The Ti_2AlC support was prepared by mixing Ti, Al, and TiC powders at 1350°C and high pressure. Ti_2AlC, TiO_2, TiC, ϒ-Al_2O_3 and α-Al_2O_3 as supports. 0.53 g of Co $(NO_3)_2 \cdot 6H_2O$ dissolved in 10 mL of water was poured into a slurry containing 2 g of support and 10 mL of water. The resulting slurry was stirred under heating at 65°C for 24 h, until the water was completely evaporated. After impregnation, the catalysts were dried under air at 120°C for 2h and then calcined under air at 450°C for 4h (Ronda-Lloret et al. 2020).

Xu et al synthesized CuO/CO_3O_4 using a MOF-template method by dispersing 600 mg of ZIF-67 in 80 mL of ethanol solution containing 35 mM copper nitrate and soaking for 0.5 h under stirring. After that, the particles were collected by filtration and dried at 80˚C for 6 h. Finally, the as-obtained particles were annealed at 500˚C for 2 h with a temperature ramp rate of 1˚C/min in air flow. For comparison, the physical mixture of Co_3O_4 and CuO with the same Co/Cu molar ratio was obtained by grinding the as-obtained Co_3O_4 and CuO in an agate mortar for 0.5 h, named as Mix-CuO/Co_3O_4 (Xu et al. 2021).

Alsaffar et al synthesized Alpha-alumina supported cobalt catalyst using CH_4 associative adsorption method by impregnating cobalt (II) nitrate hexahydrate into alpha-alumina support to give an equivalent Co-loading of 20%. Prior to the catalyst preparation, the alpha-alumina support was heat-treated at 1073 K for 6 h to remove moisture and impurities. Afterward, the mixture was continuously stirred at room temperature and there after dried at 393 K overnight. The dried catalyst slurry was calcined in the air environment for 6 h at 1073 K and subsequently crushed and sieved. The catalyst was reduced in situ in a stream of 60 ml/min H_2/N_2 at a ratio of 1:5 for 1 h at 973 K using a heating rate of 5 K/min. The reduced catalyst was purged for 20 min in a stream of 50 ml/min of N_2 and subsequently employed for the kinetic studies of thermo-catalytic conversion of methane and carbon dioxide hydrogen-rich syngas in a stainless-steel fixed bed reactor (Alsaffar et al. 2021).

Zhu et al synthesized Pt/m—Co_3O_4 and Pt/c-Co_3O_4 using Polyol method and hard template method where Co_3O_4 nanorods were synthesized with a modified wet chemistry protocol. A doped oxide, $(Co0.95Ru0.05)_3O_4$ 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 $(Co0.95Ru0.05)_3O_4$ nanorods are precursors of cobalt and Ru doped cobalt catalysts active for CO_2 conversion (Zhu et al. 2012).

5. Characterization of cobalt-based catalyst for CO_2 conversion

Most of the catalysts discussed above were characterized by X-Ray Photoelectron Spectroscopy (XPS), In-Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), X-Ray Absorption Fine Structure Spectroscopy (XAFS), High Resolution Transmission Electron Microscopy (HR-TEM), High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray powder diffraction (XRD), Transmission electron microscope (TEM), Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX), N_2-physisorption analysis and H_2-Temperature programmed reduction (H_2-TPR).

Zhag et al characterized Co-Pt-Al_2O_3 catalyst using Transmission electron microscope (TEM) image of pure Co_3O_4. The as-synthesized nanorods have a diameter of about 6−8 nm and length of of 100 nm. The high-resolution image clearly showed the crystallization. The preferentially exposed surface is (110) (Zhang et al. 2002).

Nuernbery et al characterized Co-doped Al_2O_3 catalyst using N_2 adsorption/desorption isotherms obtained at the temperature of liquid nitrogen. Specific surface areas were calculated according to the Brunauer–Emmett– Teller (BET) method and the pore size distributions were obtained. The crystalline phases of freshly prepared catalysts were characterized by X-ray diffraction (XRD), with graphite monochromated Cu K α irradiation. The sample morphologies were observed on scanning electron micrographs, operating at an accelerating voltage of 20 kV. The chemical analysis, BET specific surface area and pore size distribution values of all the Co/Al_2O_3 showed the highest BET surface area, 336 m^2g^{-1}.The X-ray diffraction analysis of the catalysts showed the diffraction peaks at 2h = 32°, 37°, 45°, 60° and 66° can be attributed both to the Co_3O_4 of the spinel structure and the $CoAl_2O_4$ (cobalt aluminate) (Nuernberg et al. 2008).

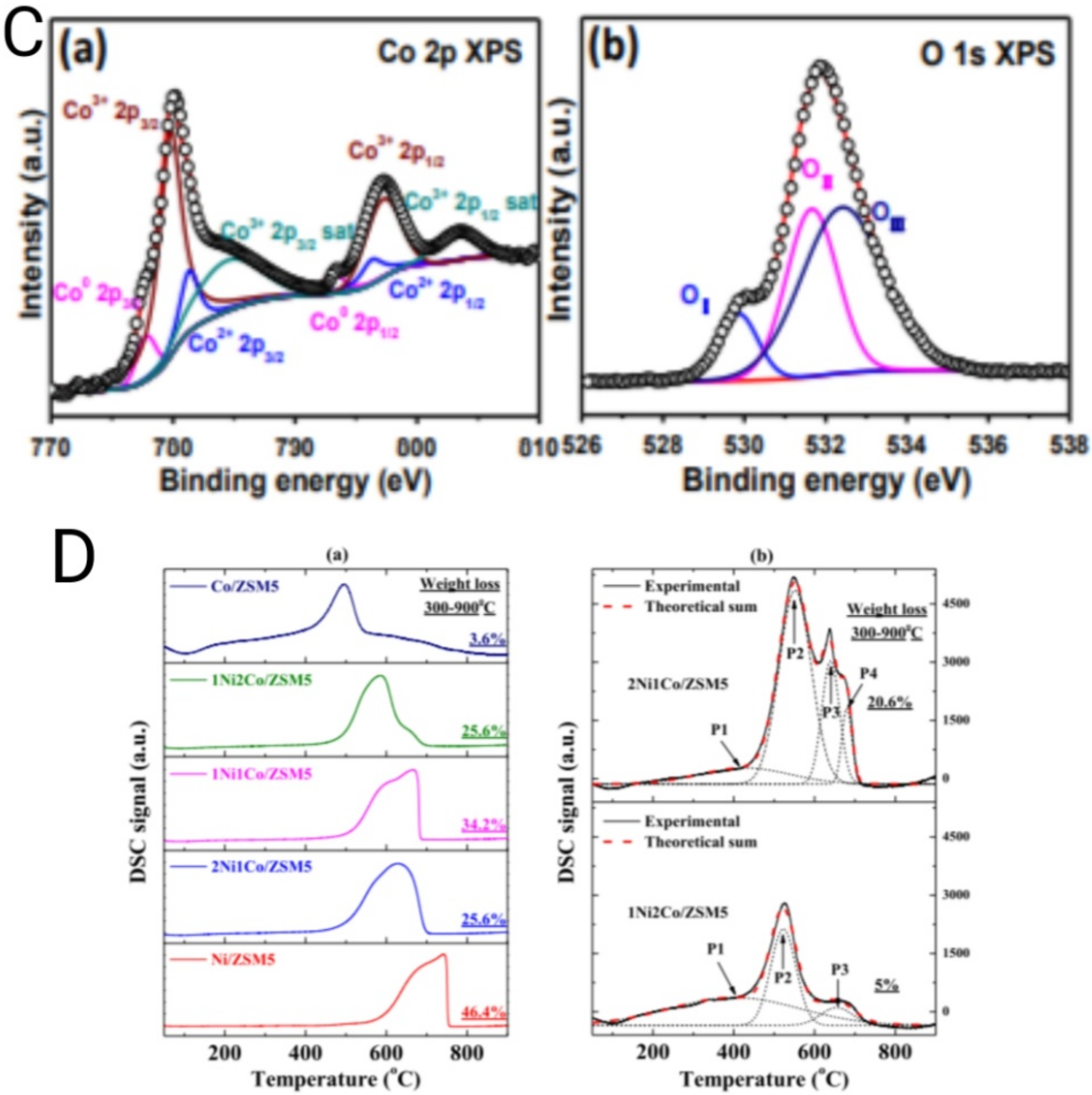

Figure 3 C):XPS Co 2p and O 1s of Co@CoO$_X$-N NCS (Yin et al. 2018), **D):**DSC signals and weight loss values obtained for the different solids after DRM reaction and DSC signals, peak deconvulation and weight loss for 2Ni1CoZSM5 and 1NiCo/ZSM5 after 12 h on steam (Estephane et al. 2015).

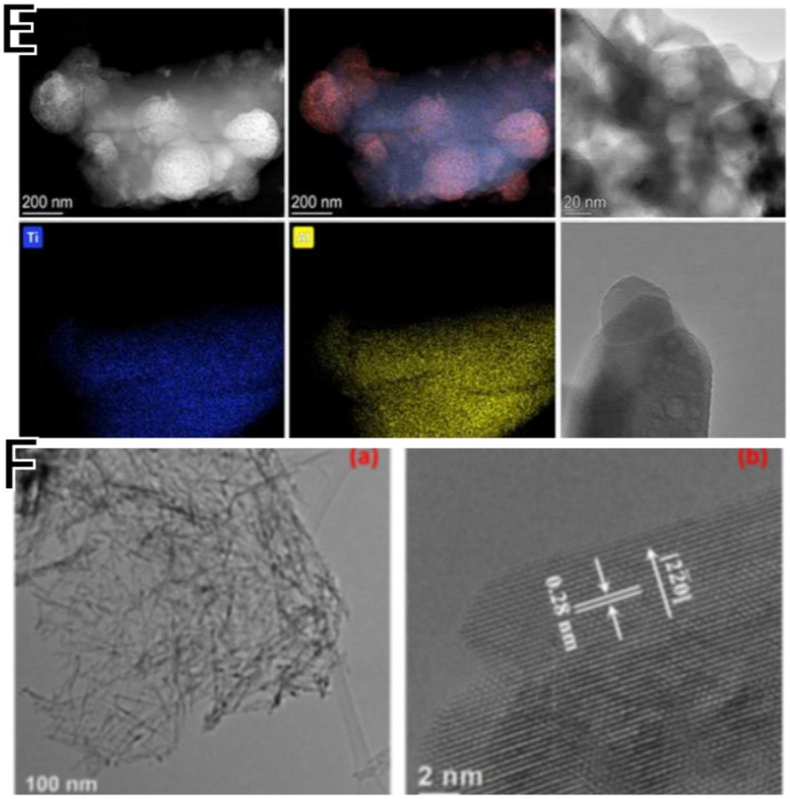

Figure 4 E):HAADF-STEM images of Co_3O_4/TiAlC catalyst (Ronda-Lloret et al. 2020), **F):**TEM images of synthesized Co_3O_4 nanorods (Khdary et al. 2022).

Bekar et al characterized Cao/Al_2O_3 catalyst using X-Ray Diffraction (XRD) with Cu target (CuK= 0.154 nm) radiation. Data was collected over the range of 2° from 10° to 80°. Field Emission Scanning Electron Microscope-Energy Dispersive X-Rays Analysis (FESEM-EDX) was carried with energy of 15.0 kV analyzer and bombarded using electron gun with tungsten filament under 25 kV resolutions to get the required magnification image. The properties of catalyst surface were evaluated by Nitrogen Adsorption Analysis (NA). Functional group on the surface catalyst can be determined by FT-IR technique. Thermal stability of desired catalyst was monitored by Thermogravimetry Analysis-Differential Thermal Analysis (TGA-DTA). EDX analysis shows that the composition of Co on the fresh Pt/Co(10:90)/Al_2O_3 catalyst was higher than Pt (Bekar et al. 2012).

Melaet et al characterized CoO/TiO_2 and CoO/SiO_2 catalyst using TEM, HR-TEM, and STEM/EDS spectral maps at Co and Ti K lines of the Co/TiOx spent catalyst cycled at elevated temperatures (up to 450°C) and reactive gas pressures (up to 5 bar) indicate no particle agglomeration (Melaet et al. 2014).

Estephane et al characterized Ni-Co/ZSM5 catalyst usingX-ray diffractograms using Cu Ka radiation (l ¼ 0.15406 nm) over a 2q range of 4e80° using a step size of 0.02°. The specific surface areas of the calcined support and the different calcined catalysts were measured using the BET technique. The ZSM5 zeolite support exhibited the highest surface area of 293m^{2}g^1 $^{(Estephane\ et\ al.\ 2015)}$.

Owen characterized Co-Na-Mo based catalyst using N_2 adsorption was carried out at 77K after degassing (at 120°C for 12 h under high vacuum). Temperature programme reduction (TPR) were reduced using 30 mL min$^-$1 of 5% H_2/Ar from room temperature up to 1000°C with a ramp rate of 10K min t^{-1} $^{(Owen\ et\ al.\ 2016)}$.

Yin et al characterized Co@CoO NCS catalyst, Co NCS catalyst and Co@CoO-N Catalyst usingthe transmission electron microscopy (TEM) images illustrate that all the samples contain uniform NCs consisting of small nanospheres. The NCs are in an average diameter of 30 ±10 nm and a length range up to several micrometers. As the high-resolution (HR) TEM data shown in, Co@CoO and Co@CoO-N exhibit an unique core-shell structure, and the thickness of the shells is 3~5 nm. The HRTEM image of the shell of Co@CoO-N in exhibits the lattice parameter (0.212 nm) of CoO(200), indicating the dominant presence of CoO in the shell.F rom the XRD data, the core of NCs is metallic Co while the shell is mainly CoO. Energy-dispersive X-ray (EDX) elemental mappings of Co@CoO-N demonstrate the uniform distribution of Co and O in the whole core-shell NCs structure and the successfully doped N atoms.X-ray photoelectron spectroscopy (XPS) is used to investigate the surface chemical bonding and element valence state of the NCs (Yin et al. 2018).

Jimenez et al characterized Single-site cobalt catalyst (SSC) using Raman spectroscopy shows the presence of Co-O vibrational modes at 700 and 480cm^{-1}, which are distinctly different from Co3O4 peaks at 680, 480, and 190cm^{-1}. UV-vis was used to discern the electronic structure of the single-site catalyst, which yielded the triplet peak at 530, 580, and 680 nm that is characteristic of Co2+ (Td). XPS data collected on the single-site catalyst yielding only the Co2p3/2 peak at 780.6 eV with the associated satellite peak at 785.3 eV at ambient conditions, where no Co3+ peak or its associated satellite peak were observed (Jimenez 2016).

Ayodele et al characterized Ni/LSCF using the N_2-physisorption analysis was employed for the measurement of the textural properties (the porosity and the specific surface area) of the catalyst. The quantification of the amount of carbon deposited on the used catalyst under TG-DTG experimental conditions was carried out over a temperature range of 50e900°C at a heating rate of 10°C/min in a flow of 50 ml/min of pure air (Ayodele et al. 2019).

Stangeland et al characterized MnO_x-CO_3O_4 usingthe XRD patterns were obtained at 2θ of 10-90° with a step interval of 2°/min. XPS was employed to analyze the surface composition of the bimetallic catalysts. The H_2-TPR study was carried out to investigate the effect of manganese on the reducibility of the catalysts (Stangeland et al. 2019).

Le et al characterized Co-CeO_2 usingthe N_2 physisorption after the sample was degassed under vacuum for 6 h at 200°C. H_2-TPR patterns were obtained for Co-CeO_2 catalysts calcined in air at 500°C to find out the reducibility of cobalt oxide species (Le et al. 2017).

Wang et al characterized CoAlOX catalyst using X-ray absorption near-edge structure (XANES) spectroscopy was carried out to investigate the coordination and the oxidation state of Co on the CoAlOx samples. Scanning electron microscopy (SEM) image of CoAlOx-600 the layered structure was destroyed by calcination, the plate-like morphology still remained. Transmission electron microscopy (TEM) provides a direct observation of the CoAlOx-600 sample, showing highly dispersed Co particles with a mean size of 4.6 nm on the amorphous Al_2O_3 support. The Co nanoparticles were well identified on Al_2O_3 support by using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), where the Co species display brighter contrast than Al_2O_3. The Co and Al distribution was further confirmed by using EDX elemental maps. To investigate the reaction intermediates, the operando FTIR was carried out to understand the interaction between CO_2 and hydrogen on the cobalt catalysts (Wang et al. 2019).

Chen et al characterized NiOx/CO_3O_4 catalyst to confirm the structure transformation of the oxides, Raman spectra of the samples have been investigated. The Co_3O_4-MOF sample shows five peaks (690, 479, 618, 519 and 194 cm^{-1}) of a typical Raman active phonon modes (A1g+Eg+3F2g) of an ideal spinel structure.35, 38 The most intense peak at A1g (690 cm^{-1}) can be ascribed to the vibration of CoO_6 sites of the spinel Co_3O_4, 39 which is more sensitive to lattice defect. The morphology and structure of the samples are investigated by SEM and TEM. ZIF-67 precursor shows the well-defined polyhedron structure with the size in the range of 500-

1500 nm. TEM of 35-NiOx/Co_3O_4 displays the hollow structure with the shells composed by homogenous Ni and Co elements (Chen et al. 2018).

Lloret et al characterized CO_3O_4/TI_2AlC during the calcination of the Co_3O_4/Ti_2AlC catalyst, the surface of the MAX phase changes. Co_3O_4/Al_2O_3 and Co_3O_4/TiO_2 catalysts are mesoporous materials with a Brunauer–Emmett-Teller (BET) surface area of 187 and 76 $m^2 \cdot g^{-1}$ (Ronda-Lloret et al. 2020).

Xu et al characterized CuO/CO_3O_4 usingthe morphologies of samples were characterized by SEM and TEM, the dodecahedral ZIF-67 was used as the precursor of Co_3O_4 and CuO/Co_3O_4 via the pyrolysis process. Nitrogen adsorption-desorption isotherms and pore size distribution of samples were investigated. The samples containing Co_3O_4 exhibit the typical III isotherms with H_3 hysteresis loop, which suggest the existence of irregular mesoporous structure. XPS was carried out to further study the elemental composition, valence state of metal element and oxygen species on the surface of samples. For Co_3O_4, Mix-CuO/Co_3O_4 and CuO/Co_3O_4, the asymmetrical Co 2p3/2 XPS peak can be fitted in two components with the binding energies at around 779.5 and 780.9 eV (Xu et al. 2021).

6. Conclusion

Thermal catalysis can effectively alleviate the greenhouse gas CO_2. The catalyst is the key component of different CO_2 reducing systems. A suitable catalyst can not only reduce energy consumption but also fascilitate generation and transfer of electrons. On one side, from the perspective of energy consumption, we wish to complete the conversion of CO_2 while consuming as little energy source as possible to save the energy and the environment. On the other side, the selectivity of products has challenged the development of CO_2 conversion. Specific product generation from CO_2 will greatly reduce the cost of the subsequent product separation and purification. In general, the conversion of CO_2 to valuable fuels or chemicals (Takalkar and Bhosale 2019) ; (Zhang et al. 2022).

7. References

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