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Machine Learning-Based CO_2 Hydrogenation to High-Value Green Fuels: A Comprehensive Review for Computational Assessment

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ABSTRACT

The biggest candidate for climate change is the emission of CO_2 during the burning of fossil fuels and researchers are trying to capture this CO_2 efficiently and utilization effectively. This review highlights the parametric effects on conversion, utilization, and selectivity in CO_2 hydrogenation via the Fischer-Tropsch method using various catalysts. Collecting the data from reported studies as datasets for quantum mechanical-based simulation software such as DFT and Monte Carlo were employed to probe the characteristics of catalysts, the discovery of novel catalysts, theoretical models for utilization of catalysts and parameters for CO_2 hydrogenation such as operational, catalyst information, and mass transfer. Two syntheses such as methanol and methane were studied extensively via machine learning techniques. How artificial intelligence can help experimentalists for finding new catalysts has been discussed and how one can understand the catalytic features in a better way. Furthermore, the key challenges in CO_2 hydrogenation technology and future directions based on artificial intelligence have been discussed thoroughly.

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1. INTRODUCTION

In recent decades, humans have faced serious environmental problems i.e. sea-level rise, ocean acidification, species extinction, and global warming due to the emission of CO_2 in massive quantity (Asif *et al.*, 2023). The exponential trend of emission of CO_2 gas and subsequent temperature values have turned to 35 billion tons annually worldwide while its global concentration has reached up to 410 ppm, as shown in **Figures 1** and **2** (see https://ourworldindata.org/co2-and-greenhouse-gas-emissions; Zhong *et al.*, 2020). Now, the world is taking these tasks such as energy conservation, emission, and conversion seriously (Khan *et al.*, 2024a; Khan *et al.*, 2024b; Ahmed *et al.*, 2024). Scientists are working on new techniques and strategies for the reduction of excess CO_2 to tackle these issues (He *et al.*, 2022). Due to improvements in this field, researchers have a huge interest in this field. Here, the purpose of this study was to review current studies in the machine learning-based CO_2 hydrogenation to high-value green fuels. We made a comprehensive review for computational assessment.

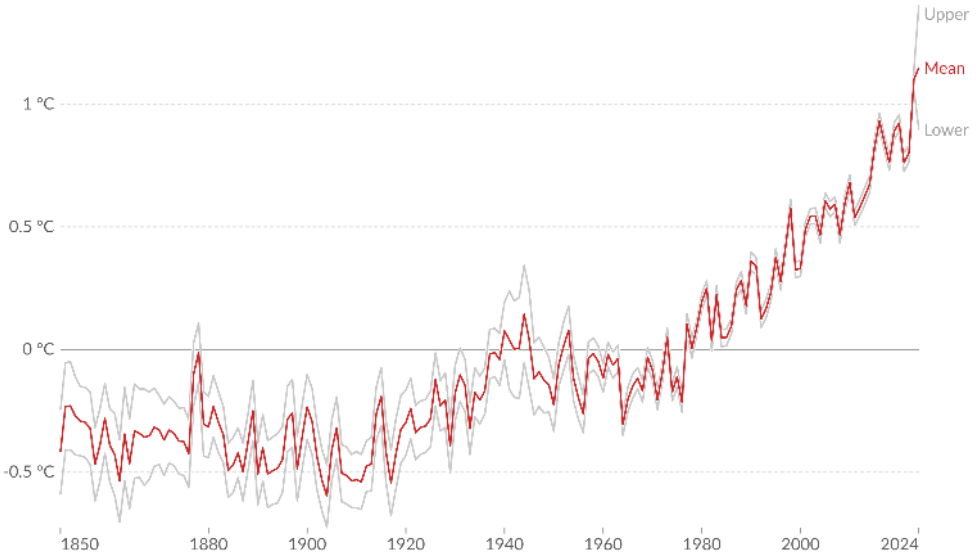

Figure 1. Globally average temperature anomaly (Liu *et al.*, 2022).

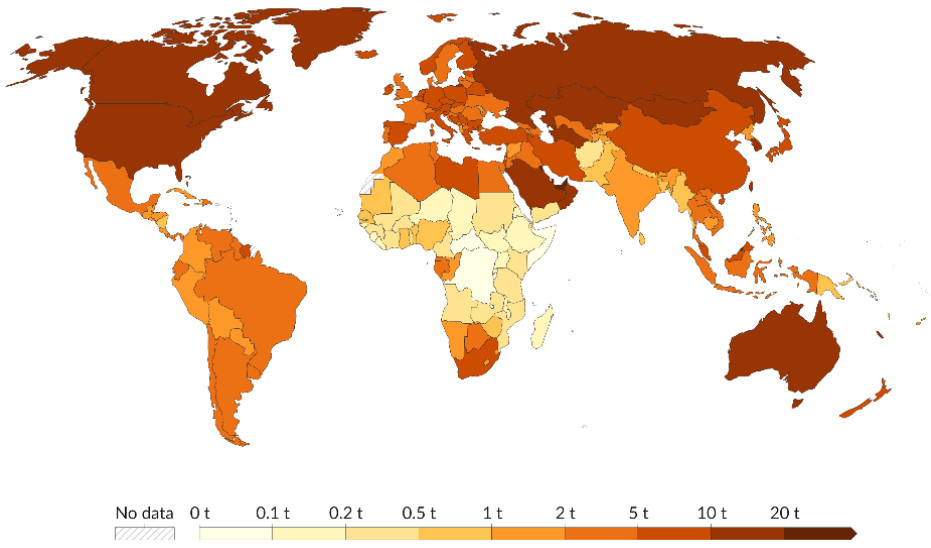

Figure 2. Globally per capita CO_2 emissions (Zhong *et al.*, 2020).

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2. METHOD

This review paper was made from data taken from internet literature. Specifically, we took data from articles published in international journals. Data was then collected to get information and concluded to make this review paper.

3. RESULTS AND DISCUSSION

3.1. Brief Overview of CO_2 Hydrogenation

The CO_2 conversion is done commonly three ways electrocatalytic, photocatalytic, and thermos-catalytic (Huang *et al*., 2024; Han *et al*., 2022; Min *et al*., 2024; Jian *et al*., 2024; Yang *et al*., 2023; Vos & Koper, 2024; Verma & Fu, 2024; Wang *et al*., 2023; Zhu *et al*., 2022; Wang *et al*., 2021l Kattel *et al*., 2017). In all routes, thermos-catalytic is considered best because of its industrial applications and high efficiency. The raw material for the hydrogenation reaction is hydrogen and the water photo/electrolysis mechanism are used to produce the green hydrogen. Using green-based hydrogen for greenhouse-gas hydrogenation from the thermos-catalysis method is counted as an efficient way to resolve the above-mentioned issues. This CO_2 hydrogenation field has caught much attention as green hydrogen and CO_2 capture technologies have been developed (Nakamura *et al*., 2017).

This emergent CO_2 hydrogenation technology isn't reducing CO_2 concentration only but helps to synthesize beneficial fuels or chemicals like olefins, gasoline, alcohol, aromatics, etc. There are two pathways mainly for the reaction mechanism of CO_2 hydrogenation such as CO_2-based Fischer-Tropsch method (FTM) and methanol (MeOH)-assisted technique (Tang *et al*., 2024; Asif *et al*., 2022; Hassan *et al*., 2023). In the first technique, CO_2 is used to generate CO with the help of a reverse water-gas shift reaction (RWGS).

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (1)$$

Hydrocarbons are produced from FTM after the RWGS reaction which helps to convert huge quantities of CO_2. More conversions can be done via the Anderson-Schulz-Flory (ASF) method. The selectivity of diesel, C_2-C_4 hydrocarbons, jet fuel (C_8-C_{16}), and gasoline (C_5-C_{11}) are limited to 40, 58, 41, and 48%, respectively (Carrasco-Garcia *et al*., 2024). In the methanol-assisted technique, CO_2 hydrogenation is used to produce MeOH first and then chemically reacts via coupling reactions and dehydration to produce hydrocarbons. That's why, various MeOH-based methods have been established such as MeOH-to-gasoline (MTG), MeOH-to-olefins (MTO), and MeOH-to-aromatic (MTA) approaches. This route results in high yield selectivity with slow kinetics during the reaction time. The MeOH route demands dual-active sites for the generation and conversion of MeOH while the second step involves a temperature of about 300-500°C which is quite high for its synthesis. Therefore, each route and every step (MeOH or CO_2-FTS) have pros and cons.

3.2. Importance of CO_2 Utilization and Hydrogenation

The technology of CO_2 hydrogenation via the thermos-catalytic method has been dependent upon modern designs of catalysts as well as novel reaction routes. This also relies on the carbon-capture (CC) and green-hydrogen (GH) technologies. The CC technology discloses many doors for CO_2 utilizations like via chemical valorization of CO_2 route with GH (Mahnaz *et al*., 2024; Zhou *et al*., 2024; Dostagis *et al*., 2024). Due to this technology, the fuels are economically and practically converted into various stuff such as e-gas or e-gas via the FTM approach which helps to produce various types of chemical building blocks. Despite many industrial advantages, there are still some challenges because of the internal complexity

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involved during the reaction and it demands stunning research and developmental efforts (Baddour *et al*., 2020). A better understanding of this system, the top-down rules, simulations, and models are selected commonly, but still, some complexities make this challenging.

3.3. Introduction of Artificial intelligence (AI) and Its Potential in Catalysis

Nowadays artificial intelligence (AI) is been considered the best and potential candidates will compete in this race. AI works based on the availability of experimental and statistical data and offers a different path to solve problems up to maximum precision and accuracy. It collects the data first and then uses algorithms to solve with a scientific approach, understanding, mathematical equations, patterns, and rules. Many scholars have done pioneering work to utilize AI in a better way. A data-information-knowledge hierarchy module was proposed by Andrew et al., utilizing the previously published data which keeps a vast type of catalysts for various types of heterogeneous reactions (Medford *et al*., 2018). Some researchers studied the catalytic procedure in light of catalytic data and design via data science and established new ways of correlation (Takahashi *et al*., 2019). The in-situ carbon-assisted CO activation process based on the machine learning (ML) technique in the FTM approach was studied by Liu *et al*., (2021). Similarly, the ML technique was used by Motaev et al., to fabricate a model to link property and objective parameters using cobalt catalyst in the FTM approach (Motaev *et al*., 2023). Due to the internal complexities of the FTM approach, modern and deep efforts are needed to correlate features from the catalyst with other valuable parameters like temperature, pressure, gas hour space velocity (GHSV), unitless numbers, etc. So, based on ML technology, one can make useful and meaningful predictions.

3.4. Fundamentals of CO_2 Hydrogenation

Favorably, two major steps either RWGS and FTM techniques are followed for CO_2 hydrogenation, whereas the direct reaction is considered marginal (Krausser *et al*., 2024). The RWGS reaction contains two major reaction mechanisms such as redox and associative mechanisms. The redox is suitable for reaction over metal oxides while associative is suitable for iron-based catalysts (by introducing the production of formate). In both these techniques (RWGS and FTM), RWGS helps in the conversion of CO_2 with fast kinetics, specifically for iron-assisted catalysts, forming the FTM technique as a fundamentally rate-determining step (RDS) of whole reactions.

3.4.1. Chemical reactions involved

There are the following possible main products that can be produced in CO_2 hydrogenation. The Equations 2-5 identify the CO production via the RWGS mechanism while FTM synthesis refers to the generation of 1-alkenes, n-alkanes, and alcohols. Besides traditional polymerization reactions, during FTM synthesis, the reactants (CO & H_2) need to be converted into monomers first and initiators on the active catalytic sites, and after this further happens to the polymerization process for FTM synthesis.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (2)$$

$$CO + 2H_2 \rightarrow \frac{1}{n} C_nH_{2n} + H_2O \quad (3)$$

$$CO + \frac{2n+1}{n} H_2 \rightarrow \frac{1}{n} C_nH_{2n+2} + H_2O \quad (4)$$

$$CO + 2H_2 \rightarrow \frac{1}{n} C_nH_{2n+1}OH + \frac{n-1}{n} H_2O \quad (5)$$

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3.4.2. Catalytic mechanisms

Generally, there are two types of mechanisms namely one-path monomer & initiator and two-paths for initiation & propagation. Here, one path includes CO insertion, carbide, alkenyl, and enol, while two paths are associated with H-based dissociation and CO insertion-carbide, etc. A brief detailed investigation is summarized in **Table 1**.

Table 1. A detailed comprehensive summary of different mechanism.

Mechanism	Monomer	Initiator	Supporting evidence	Reference
Carbide	S-CH_2	-	Generation of Carbide on various metals	Tavasoli *et al*. (2008)
Enol	S-CH-OH	CHOH	Initiator by alcohol & aldehyde	Davis (2009)
Formate	CO	S-OH	Co-MgO catalyst & chain lengthening	Schulz (2013)
CO insertion	S-CO	S-CH_3	Transients/back-transients of gaseous species	Schweicher *et al*. (2012)
Alkyl	S-CH_2	S-CH_3	C_2 is mainly ethylene in noble gas	Maitlis (2004)
Alkenyl	S-CH_2	S-CH_2=CH_2	Same PD with 1-alkene	Overett *et al*. (2000)
AHM	S-CH+S-H	S=CH-CH_2-S	CH+H as a monomer by D trace analysis	Ciobîcă *et al*. (2002)
H-based CO dissociation	S-CO+S-H	-	DFT & isotropic studies	Loveless *et al*. (2013)
CO insertion-carbide	S-CH_2+S-CO	S-CH_3	Alcohol probes co-feeding & dual ASF superposition	Chai *et al*. (2023)
CO insertion-CLD model	S-CO	S-CH_3	Exponential descending O/P ratio	Kuipers *et al*. (1995)
Carbide-non-CLD model	S-CH_2	-	O/P independent to C-number on alloy catalyst	Sun *et al*. (2021)

The deep advantages of adopting top-down simulations, rules, and models are clear and if this yields better regression fitting against experimental and statistical databases, then the above-mentioned mechanisms could be logically and effectively applied in explaining experimental outcomes. Moreover, there are some other complex and accurate mechanisms like two-pathway mechanisms can be disclosed by researchers visualizing the internal complexities of CO_2 hydrogenation via the FTM technique. This two-pathway procedure adds a few simultaneous independent pathways-initiations, propagation, and then termination using an iron-assisted catalyst to prove the development in experimental analytical instruments and theoretical tools. Schulz and Visconti contributed to get better understanding of reaction mechanisms (Schulz, 2020). There are three independent active site mechanisms have been accepted for iron-assisted catalysts, from which RWGS is run by Fe_3O_4, the chain propagation helps to form the main hydrocarbons by carbide/Fe, and Fe metal is considered a key factor behind olefin re-adsorption & secondary hydrogenation (Han *et al*., 2020; Nie *et al*., 2016; Asif *et al*., 2023). Both the metal Fe and carbide/Fe are essential for the production of main products, which are critical for the FTM pathway. For all growing products, using constant chain growth probability α, the renowned Anderson-Schulz-Flory (ASF) distribution is found as:

$$Xn = (1+ \alpha)\ \alpha^{n-1} \quad (6)$$

where Xn denotes the molar fraction of species and n is the carbon number. Based on the mechanistic hypothesis, the two most common top-down models are being followed, which are the Langmuir-Hinshelwood-Hougen-Watson (LHHW) models and power law models. The

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information related to individual product generation rate is accessed by LHHW models, its internal complexities like Byzantine assumptions for active intermediates. Till now, limited work has been done on this model because it limits its practical-based direct applications in directly shorting the reactor (Teng *et al*., 2006; Mousavi *et al*., 2015). While on the opposite side, power-law models are much more practical because of their internal simplicity for designing the reactor (Elbashir *et al*., 2020). Other than the kinetics of power law expression, the generation of monomers during CO_2 hydrogenation is a crucial step, which is approximately associated with RWGS so far. That's why, when studying the conversion of CO_2 and its selectivity i.e. CO and CH_4 would be helpful to understand the chain initiation mechanism. The hydrogenation of CO_2 is done via different catalytic techniques, as shown in **Figure 3**.

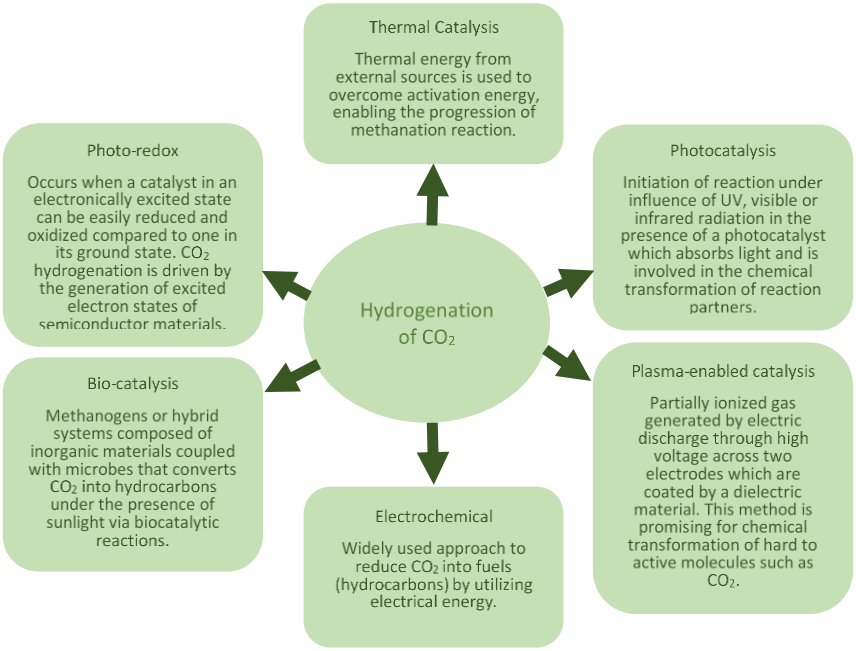

Figure 3. Different catalytic techniques for CO_2 hydrogenation.

3.5. Role of Artificial Intelligence (AI) in CO_2 Hydrogenation

The concurrent study of CO_2 hydrogenation from catalyst design to reaction variables analysis has gained much attention in the recent two decades. So, its study based on conventional literature or based on meta-analysis is no more helpful in this field, so, researchers are turning towards tools and concepts of machine learning (ML).

3.5.1. Machine learning (ML) for catalyst design

ML can be helpful a lot to coming up with constructive and valuable knowledge after setting up the database for one time only (Zavyalova *et al*., 2011; Toyao *et al*., 2020). This creative knowledge can be extended via either descriptive/statistical analysis of data. Predictive analytics helps to extract the performance and efficiency of the catalytic process under various input conditions and parameters, and it leads to identifying the most accurate and relevant descriptors that affect the catalytic process (Li *et al*., 2021; Smith *et al*., 2020). However, only a few updates or efforts were reported about the inclusion of ML in catalysis (Li *et al*., 2021; Smith *et al*., 2020; Nguyen *et al*., 2019; Şener *et al*., 2018). These works have their pros and cons due to the limited availability of models and less interpretability as well as experimental validation limits the outcomes. To introduce data science in catalysis, the ML

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models are considered to be explainable and they should rationalize the predictions of the model, which would help for deep analysis to experimental experts for experiment validation and guiding thoroughly.

Two major categories have been defined for interpretable ML methods such as grey-box ML methods and glass-box ML methods. In these, grey-box ML methods are considered a combination of black-box algorithms which includes neural networks, tree-assisted and ensemble algorithms, followed by posterior feature-based analysis, while glass-box methods are fundamentally interpretable ML algorithms which include generalized additive, linear, or symbolic models (Esterhuizen *et al*., 2022). Both these models have their own merits and demerits but the grey-box ML methodology is widely accepted for catalytic purposes (Suzuki *et al*., 2019). This may be due to the outperformance of black-box models in glass-box algorithms for computational precision for complex and large datasets, whereas feature-based analysis helps to interpret the patterns and relations gained by black-box models via local or global explanations (Kumar & Singh, 2021; Ahmed *et al*., 2023; Zeb *et al*., 2023). Based on these deep insights, the practitioners become enable to quantify the relative importance of various descriptors and help to attain the highest predictive efficiency and performance. For supervised learning, the inherently interpretable ML algorithms produce math free-form formulas as input features and these formulas and equations don't imply causality but lead to translation of their critical and analytical statements for practical-based applications. Furthermore, they help to guide the experiments or transfer learning where the focus is set on scientific development at a high level of accuracy (Asadzadeh *et al*., 2021).

3.5.2. Computational simulations

Commonly, there are two methods for simulations prominent in the research community such as grand canonical Monte Carlo (GCMC) and density functional theory (DFT). Several points are the following:

(i) **Quantum mechanism-based modeling.** Monte Carlo runs randomly to sample a statistical mechanical ensemble for the computation of average equilibrium quantities. Here, researchers are interested in DFT-based simulations which is a quantum mechanical (QM) tool used for computational analysis of electronic structures and energies of many particle systems. This is based on the Schrodinger wave equation for the N-electron system, although many terms are functions of electron density instead of functions of positions of all the existing electrons (Hohenberg & Kohn, 1964; Kohn & Sham, 1965; Tariq *et al*., 2023). A significant contribution is made by electronic energies in the internal energies of systems, therefore DFT can provide a better insight to probe these energies with the QM approach. Additionally, DFT is appreciated in quantifying the chemical bonding and its calculations are more realistic and reliable than physical or chemical-based results.

(ii) **High-throughput screening techniques.** For in-depth characterization of individual catalysts, researchers need more advanced and smart resources. In this respect, DFT helped to boost the activity of discovering new materials through discovering structure and activity relationships (Goldsmith *et al*., 2018). For the discovery of new catalysts with the help of QM methods in screening processes, the biggest challenge is the high computational cost so far (Nørskov *et al*., 2009). The conventional type of simulation guidelines contains a systematic exploration and explanation of reaction mechanisms, which can be somehow hectic because they need highly experienced modelers' careful interventions which makes them quite challenging for high-throughput screening purposes. One of the widely accepted mechanisms allows for predicting the critical rate-

DOI:
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limiting steps, however, researchers are trying to replace the quest for highly expensive with a high-throughput simulation-friendly, and data-driven protocol. These protocols should contain simulated and chemically corresponding intermediate adsorption energies of reactions on desired surface-active sites. The combination of relevant experimental parameters and generic descriptors is further coupled with targeted response parameters to probe the rules and regulations of design with critical key parameters (Pablo-Garcia *et al*., 2022; Saadun *et al*., 2020). Then these rules and regulations keep the responsibility of lowering the number of configurations that are needed, which ultimately tends to reduce the computational cost and in return increases the speed of prediction.

3.6. Applications and Case Studies

3.6.1. Methanol synthesis

Here, we present a workflow, which is a combination of experimentation and high-throughput computation that involves of ML algorithm as shown in **Figure 4**. Using this workflow, one can identify the rules and descriptors, which hold the desired power of prediction for the potential development of new catalytic species. Here one thing must be noted no prerequisite knowledge about curated reaction steps is required by this protocol, but one can proceed by having general knowledge of possible intermediates. Therefore, this protocol is much worthy for novel catalyst compositions where one lacks experimental proof of reaction mechanisms, so data-driven identification can help for insight study on hypothesized mechanism very quickly. For simplicity, we keep methanol as the desired target species here, which is the best substitute for clean and green fuel and can help produce new chemical commodities (Sharma *et al*., 2021; Martin *et al*., 2016). For CO_2 hydrogenation, In_2O_3/ZrO_2 is set as the benchmark system of catalysts because its stability is much appreciable under CO_2-rich conditions as compared to Cu-based catalysts (Khatamirad *et al*., 2023; Dang *et al*., 2020).

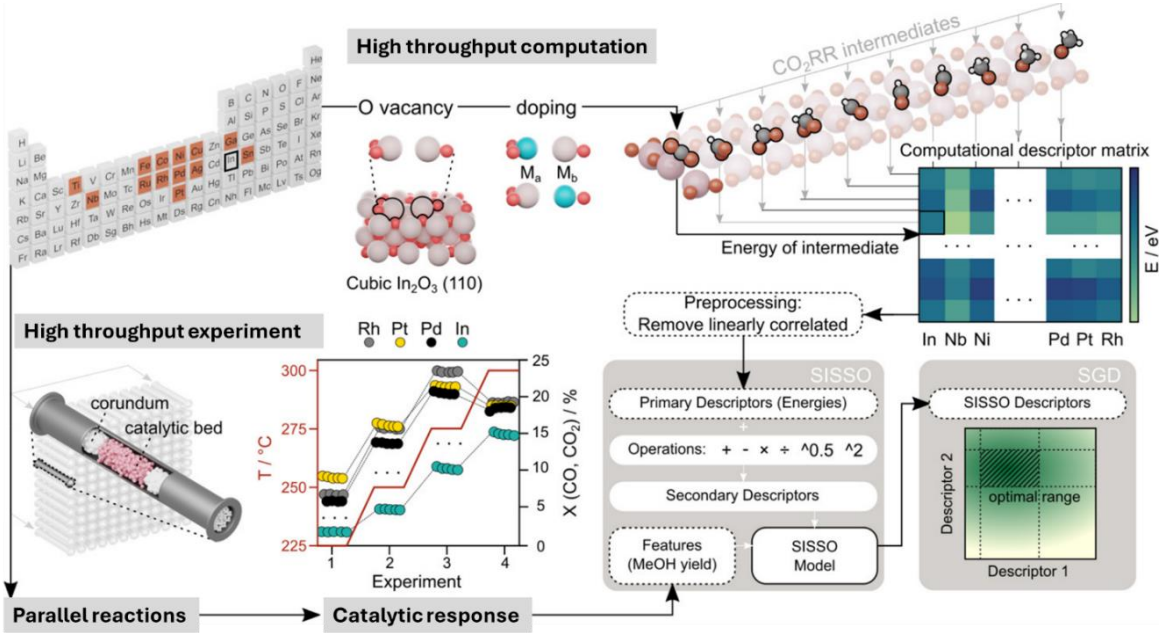

Figure 4. Schematic illustration of the workflow of work (Khatamirad *et al*., 2023).

DOI:
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Here we discuss a case study in which a simple promotion strategy was adopted having 13 different types of promoters varying from transition to post-transition metals for the synthesis of In-modified catalysts from the co-impregnation method (Trunschke, 2022). For the production of catalysts, the molar ratio of promoter: In = 1:3 was utilized, and ZrO_2 was firstly ground and then sieved to achieve a targeted fraction of 250-315 μm. For con-impregnation of 13 co-promoter as well as impregnation of In, the already ground and sieved ZrO_2 product was mixed with a hydrated nitrate solution having In and respective co-promoter.

After this, evaporation of the solvent was done, and calcination at 300°C was done. For the catalytic test, a 16-fold parallel reactor in the gas phase in Germany was used, first, it was filled with 0.5 ml of a pre-calcined catalytic product having pre-/post-bed of corundum. In each reactor, the product was reduced under these ratios $H_2 : N_2 : Ar = 30 : 60 : 10$, and then checked for CO_2 hydrogenation to methanol formation. For this reaction, different parameters such as pressure were 80 bar, three different values of temperature (225, 250, and 275 ^oC), total flow = 48 Lh^{-1}, and $CO : CO_2 : H_2 = 1.9 : 17.1 : 76$. Using in-line TCD-GS, the yields were calculated and data out of thermodynamic equilibrium was followed, while above 275 ^oC temperature was ignored in this screening. For catalytic efficiency and performance, one can establish a descriptive model considering the behavior of active catalyst under-lined reaction conditions.

Here, the classical approach may demand extensive operation characterization as well as multi-level theoretical concepts (Trunschke, 2022; Weckhuysen & Yu, 2015; Urakawa, 2016). Therefore, DFT is very valuable here, and to develop the model, an oxygen vacancy was constructed on (110) site of cubic In_2O_3 and then chemical impact promoters were introduced by shifting one in atom at oxygen vacancy by promoter. All of the intermediates probed this site as well as two competing routes for methanol and CO formation. On the DFT level, a total of 1350 intermediate relaxations were tested and adsorption and formation energies were calculated for each 14 catalysts one by one. Finally, a correlation was done among CO formation, methanol formation routes, and energies of each possible intermediate in the form of a bivariate correlation matrix to identify pairs of descriptors (Siddiqi *et al*., 2022; Ahmed *et al*., 2021). Here, the Pearson coefficient was found close to 0.9 and 27 DFT out of 92 descriptors were not correlated.

There are still other descriptors that have a strong effect on the catalytic performance and these correlations might be linear but not in all cases. Thus, for non-linear correlations to develop a predictive model for methanol synthesis, a sure independence screening and sparsifying operator (SISSO) algorithm was used (Ghiringhelli *et al*., 2017). This algorithm gives the mathematical form of a targeted feature which is further a function of non-linear variables related to input (Ghiringhelli *et al*., 2015; Aonishi *et al*., 2022; Jung & Hu, 2015).

Here, the inputs were reaction temperature T and 27 DFT-oriented descriptors and to represent non-linearity secondary descriptor term was used. Two parameters determine the complexities of the model such as some possible mathematical functions for the creation of secondary descriptors (O) and many non-zero coefficients or dimensions (D). Following the sensitivity of ML models for data scaling, first, the optimum model complexity and different pre-processing methods were performed to obtain the possible accuracy. Four different methods were reported to develop SISSO models having the reference complexity of 3D, and 3O, and to validate their output, root mean square error (RMSE) was used as mentioned in **Table 2**.

DOI:
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Table 2. RMSE data obtained for the SISSO model with 3D, 3O (Zeb *et al*., 2023).

Method employed	1	2	3	4
RMSE-train	2.17	2.23	2.35	2.23
RMSE-test	2.66	3.81	3.90	3.85

To get numerical stability, all of these methods employed a common treatment of shift of E_{min}-E_0 to whole computed values via DFT. Here, E_0 is taken as a small but positive value to ensure the presence of non-zero values in the dataset while E_{min} is the minimum calculated adsorption energy. To scale all of the primary features, these methods were processed simultaneously at a time such as, (i) for each primary feature the scale values ranging from 0 to 1, (ii) dividing each feature by the smallest one, (iii) replaced absolute *T* with *log(T)*, (iv) wiped out T from features and divided all of the DFT-assisted values by ratio of T/T_0, here T_0 = 225°C, a lowest reaction temperature. The lowest RMSE values were obtained via the pre-processing method for both train and test sets, therefore moving towards the SISSO model.

After scaling, optimum model complexity is necessary to note because it defines the accuracy of the model. It is prohibited to do the overfitting and to develop a trade-off between generalization ability and model accuracy, the leave-one-group-out cross-validation method was adopted (Jung & Hu, 2015). Using this validation procedure, 16-level model complexity was considered and each group was allotted from one of the 14 processed catalysts. It means each validation is trained by a model having data from 13 different catalysts and checked with unseen data from the 14th catalyst. Furthermore, the average regression coefficient R^2 was used to do the cross-validation performance across the trained models, and this method is globally accepted for the evaluation of ML models having smaller datasets.

$$Y_{methanol} = C_1 \times (T \times A) + C_2 \times (\frac{B}{C}) + C_3 \times (\frac{D}{E}) + C_4 \quad (7)$$

Here, A, B, C, D, and E are primary DFT features, T is reaction temperature, and C_1, C_2, C_3, and C_4 are fitting constants, and these obtained values are tabulated in **Table 3**. This Eq. (7) can show the performance of catalytic sites in DFT-derived and scaled descriptors. It further helps to notice impact performance and desired final product. For the establishment of design criteria to increase the catalytic performance, these primary and secondary features are utilized as potential descriptive parameters, and for this one needs a subgroup-discovery (SGD) algorithm. The results obtained from SGD ensure the reaction temperature and key features for developing the outstanding model and its performance as shown in **Figure 5**.

Table 3. Parameters along with their respective values (Zeb *et al*., 2023).

Parameter	Value
A	E_{ads} of linear CO_2
B	E_{ads} of linear CHO_2
C	E_{ads} of linear CO
D	E_{ads} of linear CO_2
E	E_{ads} of linear CO + OH
C_1	49.48
C_2	-29.04
C_3	7.06
C_4	-18.40

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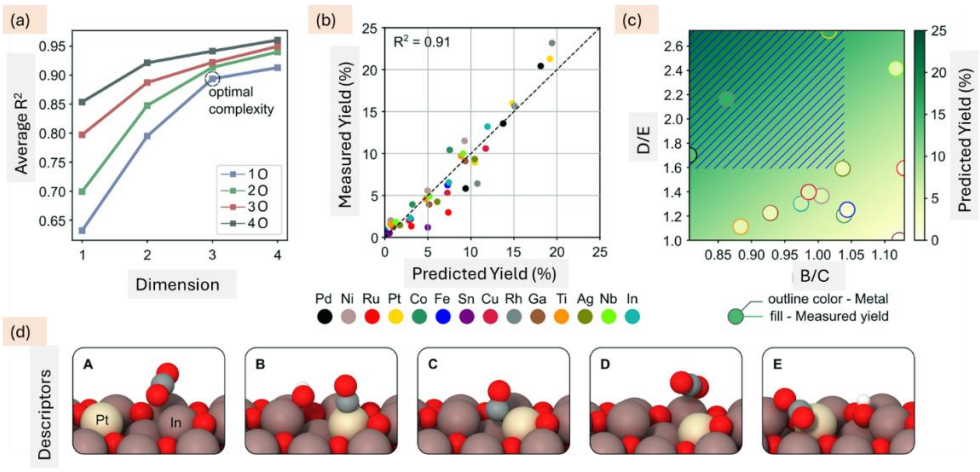

Figure 5. (a) Evaluation data after cross-validation of each model, (b) Model accuracy, (c) measured constraints on SIS-based descriptors for subgroups, (d) SISSO-based structures of intermediates (Zeb *et al*., 2023).

3.6.2. Methane synthesis

The hydrogenation of CO_2 leads to form methane, also called as Sabatier reaction, which converts a mixture of CO_2 and $4H_2$ into water and methane.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (8)$$

A great abundance of CO_2 in the earth's atmosphere is present due to industrial workouts or fossil fuel burning, so CS and GH technologies have been developed constantly (Zeb *et al*., 2021; Riaz *et al*., 2018). Hence, it is certain that CS technology is a bit costly and has long-lasting effects on environmental behavior. That's why, CO_2 methanation is obtaining the focus of scientists because it can use greenhouse gas and can produce green and clean fuel that will be enough to compete with energy demands for upcoming decades. It is obvious that H_2 gas is costly but it can be synthesized using various methods and one of them is the splitting of water using solar or wind energy. Additionally, CH_4 is easy to store and considered a high yield and energy density product that is fuel of efficient energy carrier. Thus, the conversion of CO_2 into methane is considered a hot area of research that may lead to the production of clean and green fuels in the future. The schematic illustration of CO_2 capturing and conversion into energy and fuels is shown in **Figure 6**.

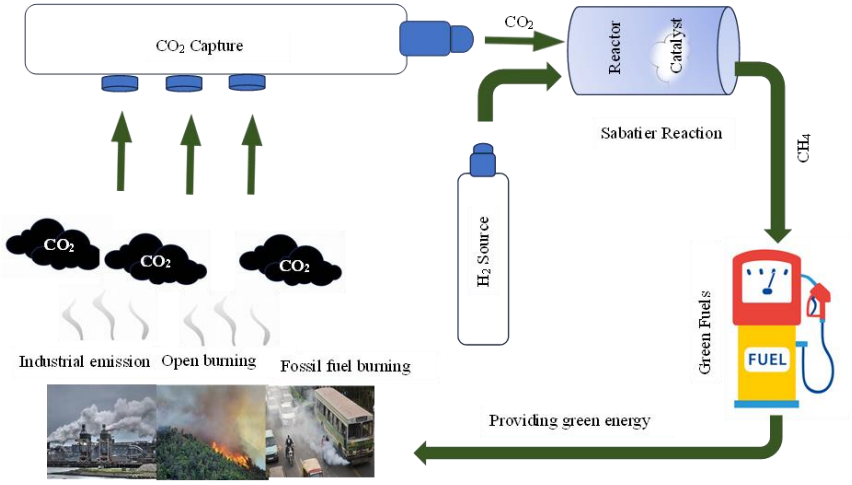

Figure 6. Schematic illustration of methane synthesis.

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Till now, researchers have tried many methods such as photo redox, plasma-assisted catalysis, photocatalysis, and electrochemical (Tahir & Tahir, 2020a; Tahir & Tahir 2020b; Gao *et al*., 2021; Azzolina-Jury, 2019; Manthiram *et al*., 2014; Alitalo *et al*., 2015; Ryu *et al*., 2017). Here are two possible mechanisms that have high yield, one is the formate technique and the second is the CO route. Formate technique is exothermic having -165.03 kJ/mol as standard enthalpy.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \rightarrow \Delta H_{298\,K} = -165.03\ kJ/mol \quad (9)$$

During the above reaction, there are many possible ways to produce methane like reverse dry reforming reaction and CO methanation reaction. These reactions are possible if RWGS reaction takes place which helps to split carbon dioxide into carbon monoxide for further hydrogenation. The reaction kinetics involved in RWGS, CO methanation, and dry reforming reactions are shown in Eqs. (10-12)**.** Respectively. Like the Formate technique, reverse dry reforming reaction and CO methanation both are exothermic while RWGS is endothermic (Rönsch *et al*., 2016l Vogt *et al*., 2019). Methanation of CO_2 can be proceeded in two different ways, first is direct hydrogenation to produce H_2O and methane, whereas second is the conversion of CO_2 into CO, where subsequently the emitted CO is hydrogenated to produce CH_4. At high temperatures, the RWGS is dominant which generates CO by-products as well as coke formation also happens. Thus, to elevate the yield of CH_4 and reduce the coking level, the methanation reaction is ordered to proceed at relatively low temperatures. Low-temperature hydrogenation enables the long-lasting of catalysts and saves them from degradation like agglomeration and sintering.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \rightarrow \Delta H_{298\,K} = 41.17\ kJ/mol \quad (10)$$

$$CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O \rightarrow \Delta H_{298\,K} = -206.19\ kJ/mol \quad (11)$$

$$CO_2 + 2H_2 \leftrightarrow CH_4 + CO_2 \rightarrow \Delta H_{298\,K} = -247.36\ kJ/mol \quad (12)$$

From history, it is noted that many mega projects were initiated for CO_2 methanation, and one of them is the Audi e-gas plant installed in Germany. This e-gas plant has a capacity of 6.3 MW power input that was commissioned in 2013. This plant capitalizes on hydrogen from alkaline electrolyzers based on wind energy and uses CO_2 which is produced from a nearby biogas plant via amine scrubbing (Vogt *et al*., 2019). Similarly, after 3 years, a new plant by Denmark was commissioned in 2016 having a capacity of 1 MW power input (Younas *et al*., 2016). Many other pilot projects have been started like the PtG plant in Stuttgart and PtG ALPHA in Germany (Ghiringhelli *et al*., 2017; Weckhuysen & Yu, 2015). Thus, it is concluded that for the production of green and clean energy and fuels, CO_2 methanation is the potential step to tackle the energy crisis of the increasing population as well this methanation process also helps to fabricate practical applications at lab and bulk scale.

3.7. Academic Research Advancement

3.7.1. Novel catalyst discovery

All performed millions of experiments are now stored as a databank for collective purposes and this cloud-based technique is highly appreciated for future research. Using this databank, researchers, scientists, and theoreticians determine and process the dimension of the datum matrix by using the ML algorithms that are available to both industrialists as well as academic experts. So, the involvement of AI in this technology will surely boost to identification of catalysts of novel characteristics. Not only computer experts, but dimensional data matrix experts would be able to probe exceptional properties. A well-known prototype study-based

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system, the DECADE is used for the identification, selection, and usage of catalysts [105, 106]. There are novel catalysts that have been discovered so far for CO_2 hydrogenation to liquid fuels such as [In_2O_3, Cr_2O_3, ZnAl(Zr, Cr, Ga) O_x]/Zeolite, Cu, CoO_x, bimetal, In_2O_3, ZnO-ZrO_2, Pd(Pt, Au, Cu, Co, Ni)-In_2O_3, Na-Co-Cu(Mo), Na(K)-Fe-(Zn, Cu)/Zeolite, Pt/Co_3O_4, Li-Rh-Fe, Na-Co_2C, Cs-Cu-Fe-Zn, (Ni)$CoAlO_x$, Cu@Na-Beta, and so on (Gao *et al*., 2020).

3.7.2. AI guideline

AI has improved the efficiency of catalysts for CO_2 hydrogenation by discovering new and accelerated catalysts because it can identify new and powerful catalysts more quickly than conventional trial and error techniques. It predicts the performance based on their electronic characteristics and structural properties. Computational modeling, simulation, and ML techniques help to understand the working mechanisms of catalytic reactions and correlate the activity, selectivity with catalyst structure, and further guide to design models. AI can guide the optimum conditions for reactions like pressure, temperature, and molar ratio of reactants (H_2 : CO_2) to enhance the catalyst performance. By comparing the computational simulations with experimental data, one can refine the reaction conditions to attain higher productivity and efficiency via AI algorithms. It can help to optimize the durability and stability of catalysts under various operating conditions and to predict the sintering, surface oxidation, poisoning, etc. Knowing these parameters, one can guess about the long-term catalyst performance and lower the quest for frequent catalyst replacement and regeneration. To quickly screen huge libraries of catalytic materials and reactions, one can couple AI algorithms with high-throughput experimentation techniques and this coupling opens new doors for the discovery of novel catalysts.

3.8. Challenges and Future

To achieve the target of carbon neutrality, thermos-catalytic CO_2 hydrogenation technology is much appreciable (Shahbaz *et al*., 2019), however, there are some critical problems linked with this such as hydrogen supply and carbon dioxide capture.

3.8.1. H_2 price and abundance

For CO_2 hydrogenation, H_2 is an important raw material and its price is considered more than half of the production cost in the coming days. The conventional sources of H_2 are either fossil fuels or gasification, which produce CO_2 that leads to environmental pollution and other serious problems. Alternatively, green hydrogen is selected as the best candidate for CO_2 hydrogenation because its production doesn't produce CO_2 and it is produced by electrolysis of H_2O with the help of electricity which can be provided by wind, nuclear, solar, or other energy sources. But the cost of green hydrogen may be much greater than conventional type of hydrogen, so, we have to look for other green sources of hydrogen production to reduce its cost. More than 200 hydrogen energy power projects have been initiated worldwide, especially in Asia, Australia, and Europe. It is projected that by 2050, the cost of green hydrogen will be dropped to 1 $/kg according to the International Renewable Energy Agency and Hydrogen Council report (see https://hydrogencouncil.com/en/about-the-council/).

3.8.2. CO_2 capture

On the other hand, CO_2 capture is another big challenge for CO_2 hydrogenation. However, the abundance of CO_2 has increased up to 410 ppm, but there is still a problem with collecting direct CO_2 from the atmosphere for utilization. Now, worldwide efforts have been started to collect CO_2-rich waste gas and these efforts are promoting CO_2 capture and storage

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technologies. This capturing of CO_2 is an energy-intensive step so far, but different mechanisms and reactions such as CaO-based sorbents are much more helpful for CO_2 capture (Chen *et al*., 2020). There are some other adsorbents such as metal-organic framework, ionic liquids, and zeolites which are being considered for CO_2 capture (Eiaz *et al*., 2018; Zeb *et al*., 2017).

3.8.3. Future directions

No doubt CO_2 causes to greenhouse effect but on the other side, it is a precious feedstock also. There has been great development for catalysts for CO_2 hydrogenation but still many challenges are there such as unclear CO_2 hydrogenation mechanism, low target-product selectivity, and low CO_2 conversion, etc. For example, different paths in reactions require different conditions like a closer distance between acidic zeolite and reducible metal oxide facilitates mass transfer in the MeOH-based pathway, which further suppresses the by-products and entertains the formation of aromatics. In modified FTM analysis, a long distance between zeolite and iron-assisted catalyst is considered very crucial for the synthesis of aromatics. Thus, to develop the catalysis theory, there should be a strong relationship between catalyst structure and catalytic performance. Therefore, in-situ characterization techniques help out the development of efficient catalysts offer new pathways to probe the CO_2 hydrogenation mechanism further encourages the identification of reaction intermediates, and assure the existence of active sites on every possible catalytic component in the process of tandem catalysis. It is noted that at high temperatures, more CO by-products are produced. Thus, it is another key problem to suppress the by-product selectivity. Many doors are to be disclosed in the future, to break the ASF model one should develop continuously efficient catalysts for the CO_2 hydrogenation and should work on the improvement of target yield via a deep understanding of water behavior in reaction. One should utilize the advanced and in-situ characterization methods to sort out the catalytic mechanisms as well as one should find convenient and economical ways to understand green-hydrogen production and CO_2 capture. One should explore the key differences between CO_2 hydrogenation and syngas conversion, and these efforts will make new directions for the later industrialization of CO_2 hydrogenation technologies.

4. CONCLUSION

In this review work, we have discussed the hydrogenation of CO_2 extensively and its various possible mechanisms. Then a variety of catalysts and reaction parameters were studied. We have summarized the methods for CO_2 hydrogenation and possible target products such as ethanol and methane. We have studied the role of AI in the discovery of novel catalysts based on quantum mechanical study tools such as DFT and Monte Carlo. CO_2 emission is increasing day by day, which leads to the greenhouse effect. Thus, environment-friendly sources of CO_2 emission and H_2 emission were studied. How AI can assist in validating the reaction performance and tune the reaction parameters, we have explored. In this article, we have proposed future directions in the CO_2 hydrogenation industry by exposing new ideas to improve this industry. Data science experts, AI researchers, chemists, engineers, and experimentalists are highly encouraged to couple in this field to improve and explore new catalytic conditions as well as catalytic materials for high-throughput, instantly performance evaluation, 3D modeling, prototype simulated models, in-situ characterizations, and monitoring the rapidly discovered novel catalysts. For theoretical understanding and predictions, computational science experts and machine learning experts should couple for

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automated computational simulations and reaction modeling with high-throughput responses.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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