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Advanced catalytic strategies for CO_2 to methanol conversion: noble metal-based heterogeneous and electrochemical approaches

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The next generation is threatened by climate change, the significant impacts of global warming, and an energy crisis. Atmospheric CO_2 levels have surpassed the critical 400 ppm threshold due to significant reliance on fossil fuels to satisfy the increasing energy demands of our fast-progressing society. An overabundance of manufactured carbon dioxide (CO_2) emissions severely disrupts the ecology. The synthesis of methanol by the selective hydrogenation of CO_2 is a viable approach for generating clean energy and sustainably safeguarding our biosphere. Methanol is a versatile molecule with several uses in the chemical industry as an alternative to fossil fuels. The methanol economy is recognized as a pivotal development in the pursuit of a net zero-emission fuel, representing a crucial stride toward a more sustainable planet. The developing green methanol industry, or renewable methanol initiative, primarily relies on CO_2 adsorption and usage. This novel technique is essential for mitigating global warming. This review focuses on the synthesis of methanol utilizing noble metal-based catalysts and electrochemical reduction methods, examining the associated thermodynamic challenges and outlining future directions for research. It emphasizes the role of noble metals, including palladium, gold, silver, and rhodium, in enhancing catalytic activity and selectivity during the CO_2 to methanol conversion process. The incorporation of these sophisticated catalytic processes improves methanol production efficiency and facilitates novel methods for carbon capture and usage, therefore advancing a more sustainable energy framework.

Sustainability spotlight

A perspective on noble metal-based catalytic conversion of CO_2 to methanol through heterogeneous and electrochemical approaches presents a promising solution to address the increasing concerns regarding climate change. The current situation is critical: CO_2 emissions from industrial activities constitute a significant contributor to global warming, and elucidating efficient methods for converting CO_2 into valuable products is crucial for achieving sustainable development. Noble metal catalysts play a pivotal role in enhancing the selectivity, efficiency, and stability of CO_2 reduction reactions. The sustainable advancement of this research lies in optimizing these catalysts to facilitate CO_2 conversion at reduced energy inputs, thereby rendering the process more cost-effective and scalable for industrial applications. This research aligns with SDG 7 (Affordable and Clean Energy) by enabling the production of methanol as a clean fuel, SDG 9 (Industry, Innovation, and Infrastructure) through the development of advanced catalytic technologies, and SDG 13 (Climate Action) by addressing the reduction of CO_2 emissions and advancing climate solutions.

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1. Introduction

The use of fossil fuels has ushered in an era of extraordinary wealth and improved living standards for humanity.[1,2] However, excessive fossil fuel burning for energy generation elevates the emission of anthropogenic greenhouse gases (GHGs), mostly in the form of pollutant CO_2. According to the International Energy Agency (IEA), Global Energy & CO_2 Status Report, in 2022 the worldwide CO_2 emissions will have peaked at about 36.8 Gt a new all-time high, and the current concentration of atmospheric CO_2 is approximately 421 ppm, which has increased by 50% since the beginning of the industrial age.[3] The massive release of CO_2 to the environment disrupts the Earth's natural

carbon cycle and global ecology, leading to substantial and feasibly irreversible changes in the world's climate such as global warming, ocean acidification, and sea level rise, which have a direct consequence on human health.[4–7] Green carbon science is the study and optimization of effective carbon resource processing, utilization, and recycling for lowering CO_2 emissions, lessening the greenhouse effect, reducing reliance on fossil fuels, and lowering the global carbon footprint.[8–13] Therefore, the creation of clean energy technology is the only option for the next generation.[14–20] In that sense, one of the main research focuses in energy engineering is the regulation and utilization of CO_2.[21–29] In fact, recent years have seen the development of carbon capture and storage (CCS) technologies, which separate CO_2 from combustion byproducts or chemical processes for subsequent recycling or storage.[30–35] Direct capture of CO_2 from the atmosphere has garnered scientific and practical attention in recent times.[36–46] Despite reducing CO_2 emissions to a certain degree, CCS is not a viable long-term solution due to its exorbitant expense and the possibility of leakage.[47–53] Internationally, there are currently 20 active large-scale carbon capture and storage (CCS) facilities that annually separate around 40 million metric tons of carbon dioxide (CO_2) and store it underground[54–60] (The Global Status of CCS; (Global CCS Institute: 2020). However, this amount represents only 0.1% of the total global carbon emissions. However, the majority of these CCS projects fall under the category of enhanced oil recovery (EOR), which involves injecting CO_2 underground to assist in extracting fossil fuels with the aim of creating a financially viable business model.[61–63] The price for CO_2 sequestration from a power plant ranges from $60 to $100 per metric ton of CO_2, excluding storage and transportation expenses.[64–68] Therefore, the implementation of EOR is essential to ensure the economic feasibility of CCS, which in turn leads to the introduction of more fossil fuels into the carbon cycle.[69–73] For CCS to have a significant influence on climate change, it must be commercialized through the development of cost-effective and energy-efficient systems.[74–82] Systems must ensure that the cost of producing CO_2, regulated by authorities, exceeds the cost of capturing and storing it. This will help create an artificial carbon cycle. Additionally, we need to turn CO_2 into chemicals and fuels that are in high demand (Fig. 1).[83,84] This will serve to effectively utilize a significant portion of the surplus global CO_2. Currently, around 230 million tons (Mt) of carbon dioxide (CO_2) are utilized annually, as reported by the IEA in 2019.[85,86] However, CO_2 usage represents less than 1% of overall CO_2 emissions.[87,88] Currently, the market size limits the conversion of CO_2 into chemicals. Thus, the catalytic hydrogenation of CO_2 into value-added products is a key method for CO_2 utilization, leading to the production of carbon-based substances such as methanol, dimethyl ether, formaldehyde, urea and various hydrocarbons.[89–95] Among the products stated above, methanol (CH_3OH) is a significant chemical feedstock that can be utilized as an alternative chemical for fossil fuels in internal combustion engines, fuel cells, and the production of formaldehyde, methyl-*tert*-butyl ether (MTBE), acetic acid, alkyl halides, *etc.*[96–98] According to the well-accepted hypothesis of Olah in a book titled "Beyond Oil and Gas: The Methanol Economy," methanol may be indispensable in the near future, and CO_2 hydrogenation is one of the most promising and regenerative routes for methanol synthesis.[99] The elevated

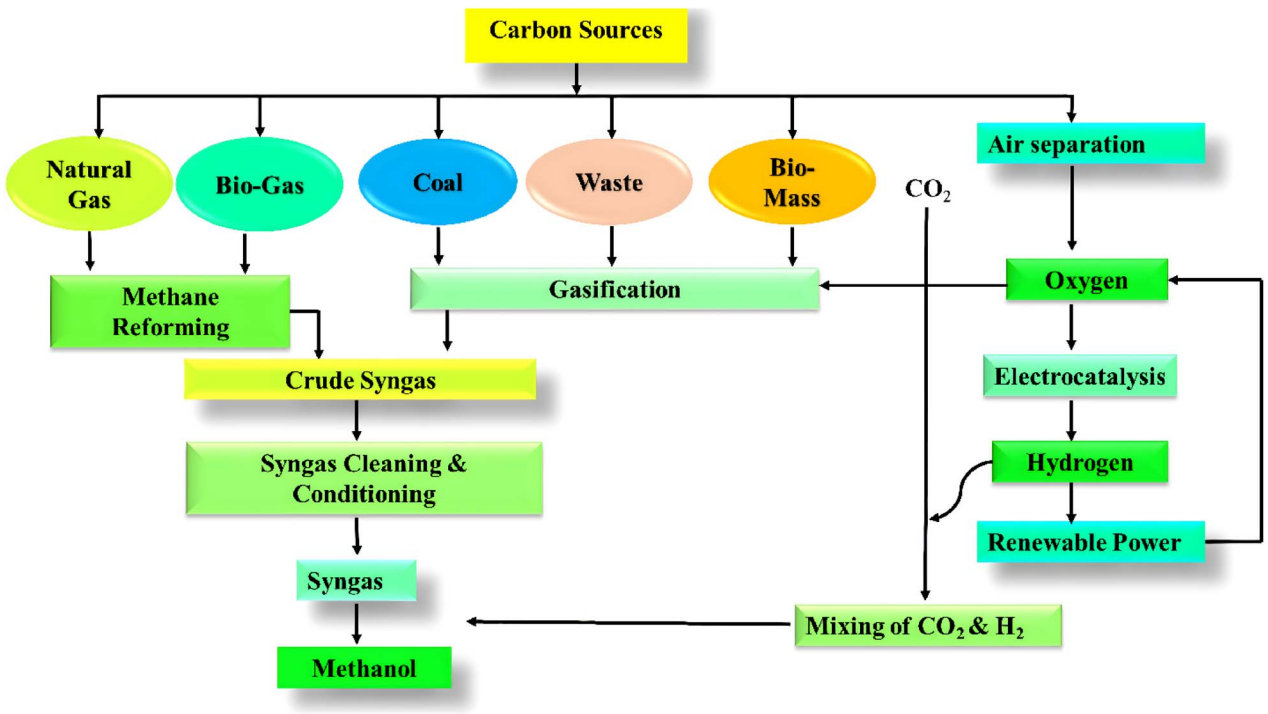

Fig. 1 Overview of key methanol synthesis methods using diverse carbon sources.

volumetric energy density of methanol renders it a feasible substitute for gasoline in internal combustion engines (ICEs), enhancing the octane rating. Moreover, in comparison to traditional gasoline internal combustion engines, methanol internal combustion engines produce markedly lower emissions of contaminants. The Indian government has been actively encouraging the adoption of clean transportation and the use of fuel-cell vehicles.[100] In 2012, the Dor Group initiated pilot testing following the decision by the Israeli government to explore alternative methods of reducing dependence on traditional fuels. One of the most promising approaches identified was the utilization of methanol as a substitute for petrol or as a component in petrol blends for internal combustion engines (Dor Group, 2019). China is also rapidly advancing the development of the methanol fuel market.

It is crucial to note that the hydrogen generated *via* water electrolysis can function as a long-term storage solution and be directly transferred to required locations for usage as a transportation fuel or in industrial applications. Moreover, hydrogen can be converted into electrofuels following the power-to-X concept, thereby storing renewable electrical energy within the chemical bonds of gaseous or liquid fuels.[101,102] Methanol can function as a carbon-neutral electrofuel when synthesized from hydrogen *via* electrolysis and carbon dioxide sourced from atmospheric capture, biomass, or industrial emissions[103,104] (Fig. 2). Methanol is a prominent and extensively traded chemical commodity, with the global methanol market projected to expand at a compound annual growth rate (CAGR) of 4.50% from 2022 to 2028.[105,106] In the chemical industry, methanol is used as both a feedstock and an energy carrier. Its applications range from organic transformations to sustainable energy solutions, highlighting its importance in both traditional and emerging chemical processes. Methanol can function as a C1 source to facilitate various C–C and C–N bond formations and dehydrogenative coupling reactions, which are significant in the realms of natural product synthesis and drug development.[107,108] For instance, methanol is crucial for the production of formaldehyde, methylamine, methyl halides, methyl ethers, methyl esters, dimethyl ether, and acetic acid. It is additionally used in the manufacture of pharmaceuticals, biomolecules, agrochemicals, and polymers. Methanol may be transformed into olefins such as ethylene and propylene, which serve as essential building blocks for the petrochemical industry.[109,110] Furthermore, methanol serves as a versatile compound with applications as a solvent and/or additive in diverse industries, including paint removal, windshield washing fluids, and as a fermentation substrate in microbial production processes.[111]

In this context, it is noteworthy to mention that homogeneous (organometallic catalysts, metal-free catalysts, and N-heterocyclic carbenes) and heterogeneous catalyst systems have recently been successfully developed, and they are excellent candidates for hydrogenation of CO_2 to produce methanol.[112–123] Another highly appealing strategy extensively studied by the scientific community is the direct electrocatalytic carbon dioxide reduction reaction (ECO_2RR).[124–126] In this instance, the term "direct ECO_2RR" denotes the complete conversion of CO_2 to a specific product, methanol, at a single electrode.[127–129] In electrocatalytic technology, customized catalysts can improve electrode interface reaction kinetics.[130,131] It lowers activation energy and helps electrolyte reactants move electrons.[132,133] Electrocatalysts accelerate electron transit from

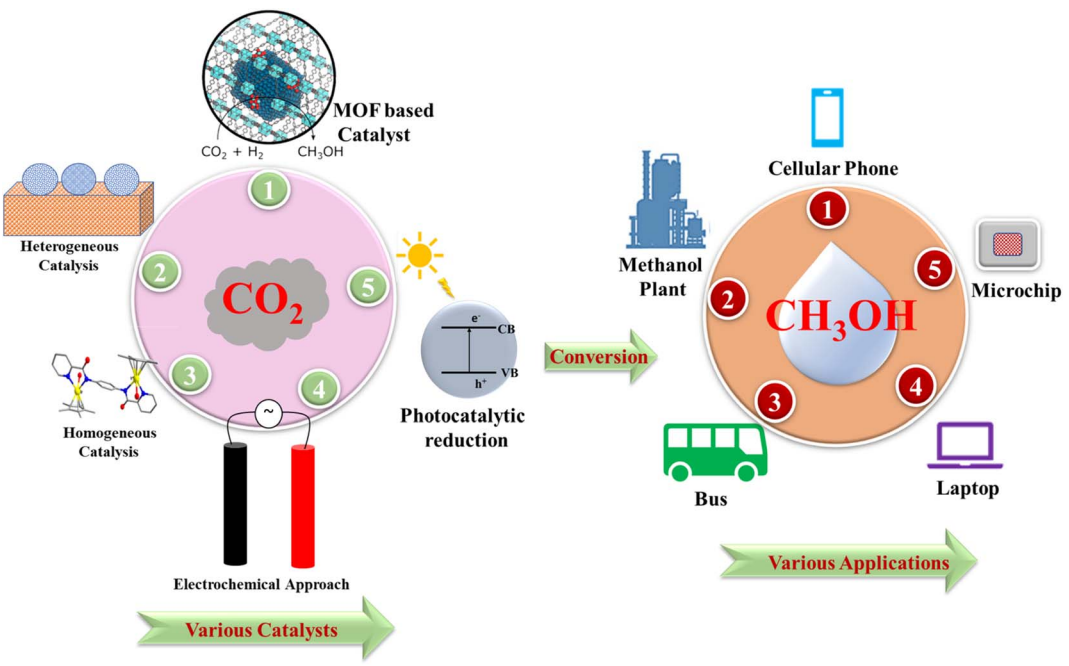

Fig. 2 Various approaches for converting CO_2 to CH_3OH.

noble metals to other materials by lowering voltage.[134–138] To improve performance, researchers strive to augment the number of active sites and elevate the intrinsic activity of these sites. This involves fine-tuning the electronic and structural properties of the active sites to improve their catalytic efficiency.[139] Recent methodologies exploit local electrostatic fields to enhance the adhesion of electrode surfaces for intermediates, facilitating proton transfer to electron-rich active species and enabling the electrochemical reduction of CO_2 to produce methane.[140] In another study, Zhou *et al.* reported the O-philic adsorption strategy to facilitate the electrosynthesis of urea.[141] This study enhances our comprehension of how to control the properties of reactant adsorption–desorption dynamics for targeted conversion pathways within a comprehensive reactive multistep process pertinent to diverse electrocatalytic applications.

The first commercial methanol production unit was established in Anyang, Henan Province, China. Here methanol was synthesized using the waste carbon dioxide and hydrogen gases.[142] This process used the Emissions-to-Liquids (ETL) technology which was initiated by Carbon Recycling International (CRI) and the first pilot plant was established in Iceland.[143] Another emerging technology in the methanol economy is the CAMRE process, jointly developed by the Korea Institute of Science and Technology and POSCO.[144] Carbon Recycling International developed a pilot plant for the commercial synthesis of methanol from CO_2. In this, the source of CO_2 is the Orka geothermal power plant and hydrogen is generated from the electrolysis of water from the Icelandic power grid and the methanol production capacity is 4000 tons per year. Blue Fuel Energy (BFE) is Canadian Methanol Corporation's conventional methanol production unit which produces methanol and gasoline based on the MTG process. Emerging techniques for producing methanol from CO_2 include photocatalytic conversion, electrochemical reduction, photoelectrochemical reduction, chemical conversion and plasma reactor technologies.[145–154]

A large number of metal-based catalysts have been employed for methanol synthesis, but the most popular catalyst in CO_2-derived methanol synthesis is $Cu/ZnO/Al_2O_3$.[23,155–161] The major drawback of Cu based catalysts is their pyrophoric properties and low stability arising from sintering and agglomeration enhanced by the generation of water and mobility of ZnO.[156,162–165] This review focuses on the synthesis of CH_3OH from the hydrogenation of CO_2 by employing noble metal based heterogeneous catalysts. The main advantages of noble metal-based catalysts are their excellent stability and resistance to the sintering effect, making them alternatives to Cu-based catalysts.[166–170] An efficient heterogeneous catalyst possesses moderate binding strength with the reactant and intermediate.[171–174] The success of catalytic reactions depends on the identification of the active site, accompanied by an understanding of structure–activity relationships that derive catalytic descriptors to explain the catalysis.[175–179] Current research emphasizes that noble metal-based catalysts are superior for the conversion of CO_2 to CO *via* the so-called reverse water gas-shift (RWGS) reaction with high reaction rates and high selectivity.[180–184] Noble metal catalysts are excellent for CO_2 hydrogenation due to their unique electronic and structural properties, specifically their unique tunable d-band centers.[185–190] The d-band center mainly represents the energy level of the d-electrons relative to the Fermi level, strongly influencing the adsorption and activation of reactants such as CO_2 and H_2.[191–193] The alignment of the d band center with the Fermi level enhanced the catalytic activity by optimizing the binding strength of intermediates.[194,195] Pd exhibits an intermediate d band center, effectively balancing CO_2 activation and methanol desorption.[158,196] In contrast, Au with a lower d band center reduces the strong binding of intermediates, which enhances selectivity. Experimental evidence suggests that Pd based catalysts show high turnover frequencies (TOFs) and methanol selectivity compared to non-noble metals owing to their superior activation energies and adsorption energies.[197–199] So, the manipulation of d band centers enhances the catalytic performance by tailoring the adsorption energies.[200–202] It has been a widely accepted strategy to manipulate the[203] d-band center of noble metals integrated with other metal compounds such as metal oxides/hydroxides and carbides by the electronic effect, which influenced the interface of atomic rearrangement with the geometric effect and strain effect.[204] The catalytic reaction mainly occurs at the interface such as the metal–metal interface, metal–porous material interface or metal–metal oxides/hydroxides/carbides interface which leads to enhanced the catalytic activity of hydrogenation of CO_2.[205,206] The synthesis strategy of noble metal based heterogeneous catalysts with a proper understanding of structure–property relationships such as the active site of the catalyst, morphology, composition, strain, metal support interaction, crystallinity, defects *etc.* is one of the great achievements of the energy engineering sector.[185,207,208] A promising strategy should be adopted for utilizing noble metal-based catalysts. In this respect, the strategy of incorporating bulk metals into nanostructure supported catalysts boosts the cost-effective industrial production of methanol.

Recently, several excellent reviews have been published and paved the way to catalytic CO_2 conversion to value-added chemicals.[209–214] However, the main aim of this comprehensive review is the hydrogenation of CO_2 to CH_3OH using heterogeneous noble metal-based catalysts with an electrochemical approach. This review first focuses on the physical and chemical properties of CO_2 with thermodynamic considerations. Then we have briefly addressed various approaches to the catalytic conversion of CO_2 to CH_3OH such as the homogeneous approach, heterogeneous approach, photocatalytic approach, and electrochemical conversion approach, summarizing the catalytic journey of CO_2 to CH_3OH. The mechanism of the conversion of CO_2 to CH_3OH is one of the interesting sides of this article. Then the progress of noble metal-based heterogeneous catalysts is deeply discussed with structure–property relationships. We also provide an overview of the electrochemical reduction approach for the conversion of CO_2 to CH_3OH. The challenges and possibilities of CO_2 reduction for industrial applications are also included. Finally, we have included the future scope and perspectives of methanol synthesized from CO_2.

2. Physicochemical nature and activation of CO_2

A CO_2 molecule in its neutral state belongs to the $D_{\infty h}$ point group and has a linear structure, with a bond length between carbon and oxygen of 1.17 Å. Because of the electronegativity differences, the net electronic structure of the molecule can be represented as $O^{-\delta}$–$C^{+2\delta}$–$O^{-\delta}$.[215] In light of this, bifunctional catalytic sites are required to activate the C–O bond in an efficient manner, as the C atom is electrophilic and the O atoms are nucleophilic.[216] The highest occupied molecular orbital (HOMO) of CO_2 is located on the more electronegative oxygen atoms, whereas the lowest unoccupied molecular orbital (LUMO) is composed of the hybrid orbitals. The reduction of carbon dioxide (CO_2) introduces an electron into its LUMO. This results in the molecule undergoing a conformational shift to accommodate the energy differences between each orbital, thereby enhancing its ability to interact with nucleophiles. Simultaneously, the localized electron density of oxygen lone pairs allows the HOMO to interact with electrophiles. As a result, a meta-stable radical adduct ($CO_2^{\bullet-}$) is generated in a bent shape that is kinetically stable (an activation energy barrier of ~0.4 eV) with an average lifetime of 60–90 μs. The common metal center (metal oxide), which is usually used for CO_2 reduction, where CO_2 is physisorbed, exhibits several coordination modes, such as monodentate, bidentate, or even tridentate, depending on the surface atomic arrangement.[217]

3. Conversion of CO_2 to methanol: thermodynamic aspects

In the present era, syngas (CO and H_2 mixture) is one of the main resources for the commercial production of methanol. In methanol synthesis, the H/C ratio is crucial, so to balance this ratio, a small amount of CO_2, *i.e.* 2–8% is added to the CO/H_2 mixture to enhance the reaction rate.[218]

$$CO + 2H_2 = CH_3OH\ \Delta H_{298K} = -90.6\ \text{kJ mol}^{-1} \quad (1)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O\ \Delta H_{298K} = -49.5\ \text{kJ mol}^{-1} \quad (2)$$

Reverse water gas shift (RWGS) reaction:

$$CO_2 + H_2 = CO + H_2O\ \Delta H_{298K} = 41.2\ \text{kJ mol}^{-1} \quad (3)$$

The processes of making methanol from CO_2 hydrogenation and the RWGS reaction are limited by thermodynamics. As the reaction temperature increases, the CO_2 conversion rate drops. It is important to note that the synthesis of methanol from CO_2 is an exothermic process that competes with the RWGS reaction, an endothermic reaction. According to Le Chatelier's principle, high pressure and low temperature thermodynamically favor CO_2 conversion to methanol. But considering the chemical inertness of CO_2, a higher temperature makes CO_2 activation easier for methanol production, but it can also lead to increased selectivity towards the undesirable RWGS reaction thermodynamically to produce CO and H_2O. In this way, the RWGS process not only consumes hydrogen but also lowers the CO_2 equilibrium conversion rate, hence reducing the generation of methanol.[70] It was observed that less than 40% methanol was obtained from CO_2 at 200 °C but at the aforesaid temperature, more than 80% yield was obtained from the syngas process. Therefore, high pressure and lower temperature are required to control the RWGS process[219] (Fig. 3). According to the reaction (eqn (1)), as compared to the syngas strategy, methanol synthesis from CO_2 hydrogenation requires an additional quantity of hydrogen for the removal of one oxygen atom from CO_2, yielding water as a by-product (eqn (2)).[220] It is important to note that water, a byproduct of both processes, enhances catalyst sintering. This phenomenon deactivates the catalyst and reduces the efficiency of subsequent steps in methanol production.[221] Therefore, the foregoing explanation implies that thermodynamic equilibrium limits the maximum methanol yield; nevertheless, the equilibrium constraint on methanol yield may be bypassed by optimizing reaction conditions, activating the catalyst, using promoters, developing new reactor designs, *etc.*[222,223]

However, if we take into account the CO_2 thermodynamic potential, the following reduction reactions occur:

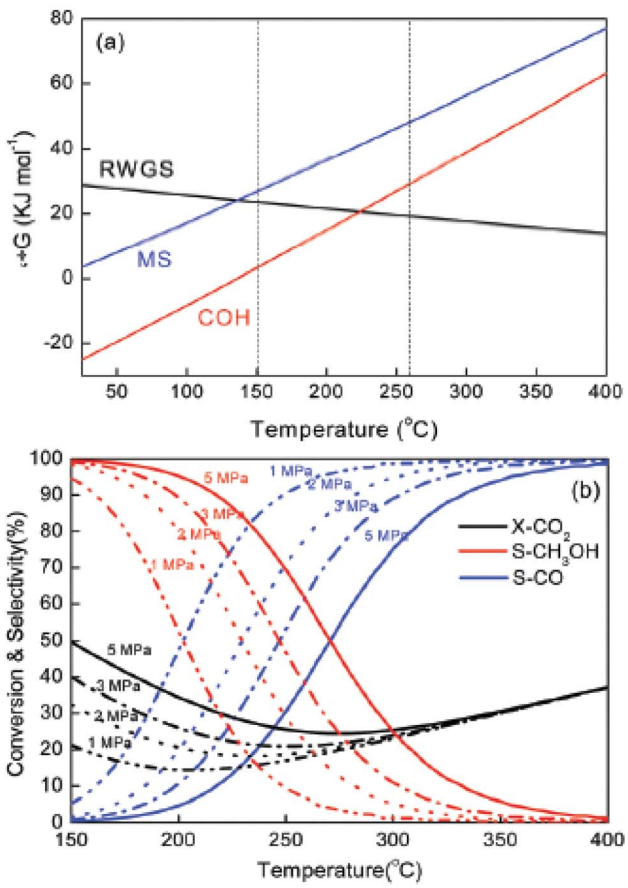

Fig. 3 (a) Free energy of methanol synthesis (MS) from CO_2, RWGS and syngas hydrogenation (COH). (b) Equilibrium conversion-selectivity values of the CO_2-hydrogenation reaction at various pressures Reprinted with permission from ref. 156. Copyright 2020 Royal Society of Chemistry.

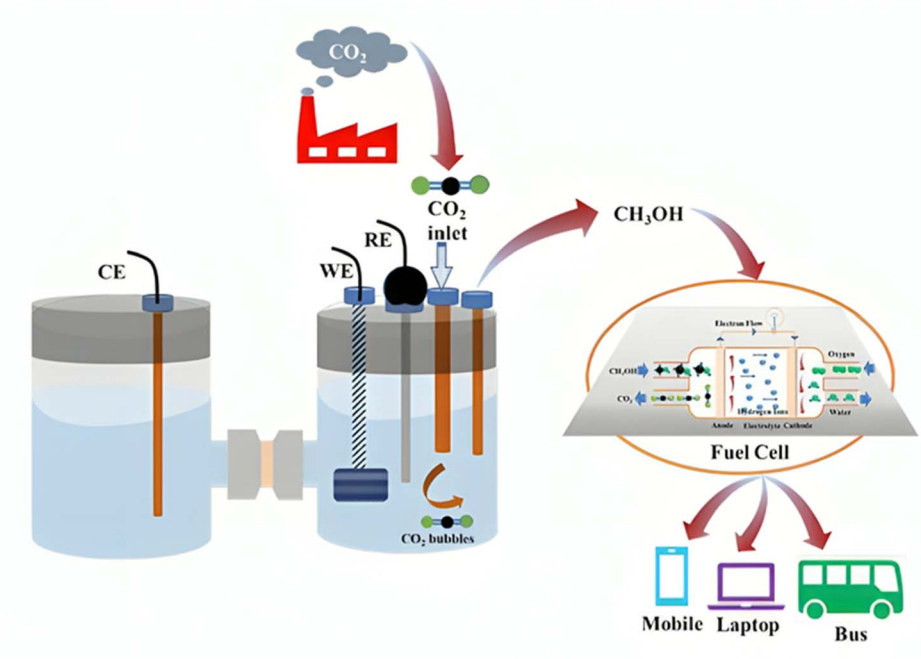

Fig. 4 Schematic representation of ECO_2R to CH_3OH.[138]

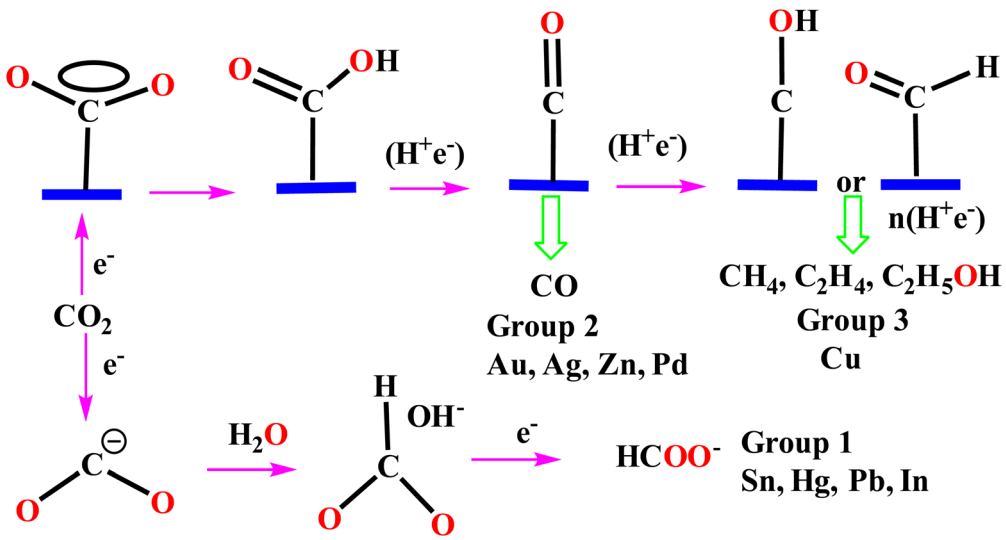

Fig. 5 Reaction mechanism of the electrochemical CO_2RR on metal electrodes in aqueous solutions.[224]

$$CO_2 + e^- \rightarrow CO_2^{\bullet -};\ E^0 = -1.9\ V \quad (4)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O;\ E^0 = -0.52\ V \quad (5)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH;\ E^0 = -0.61\ V \quad (6)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O;\ E^0 = -0.51\ V \quad (7)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O;\ E^0 = -0.24\ V \quad (8)$$

$$CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O;\ E^0 = -0.34\ V \quad (9)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O;\ E^0 = -0.38\ V \quad (10)$$

$$2H^+ + 2e^- \rightarrow H_2\ E^0 = -0.42\ V \quad (11)$$

From the above reaction sequences, it can be observed that the overpotential of CO_2 is high (eqn (4)) and it's a multi-electron process. The CO_2 reduction is challenging as it generates the hydrogen evolution reaction (HER) if we compare it with the last two reactions. Again, for the CO_2 reduction reaction, the following processes are involved in the cathode (reduction) and anode (oxidation):

Cathode: $CO_2 + 6H^+ + 6e^- \rightleftharpoons CO_2{+}H_2O,\ E^0 = 0.02$ *vs.* SHE

Anode: $3H_2O \rightleftharpoons 1.5O_2 + 6H^+ + 6e^-$, $E^0 = 1.23$ *vs.* SHE

Overall: $CO_2 + 2H_2O \rightleftharpoons CH_3OH + 1.5O_2$, $E^0 = 1.21$ *vs.* SHE

If we look at water splitting at 1.23 V *vs.* SHE and the overall CO_2 reduction reaction, then a positive difference of only 20 mV exists. Therefore, a catalyst with a high hydrogen overpotential is preferred as it allows the carbon dioxide reduction reaction to achieve high selectivity and excellent rates before water reduction occurs, which is a process bottleneck (Fig. 4).

In order to be effective in CO_2 reduction, noble-metal-based catalysts must be able to reduce the overpotential by which their activity is enhanced and able to show remarkable selectivity and stability. The below figure depicts the groupwise metal activity on CO_2 reduction and the overall idea (Fig. 5).

4. Mechanism of CO_2 conversion to CH_3OH

The CO_2 hydrogenation mechanism depends on various factors such as stability, activity and selectivity of the catalyst.[157,225] According to the prevailing theory, the first step deals with the CO_2 conversion to CO, which acts as a scavenger to eliminate the H_2O and the function of derived oxygen species is to inhibit active metal sites.[226–228] The use of isotope tracer tests has further supported the notion that CO_2 serves as the elementary carbon source for the production of methanol from syngas or CO_2 (ref. 229) (Fig. 6).

The theoretical and computational tools provide the validation of this reaction mechanism with experimental results. In this respect, DFT analysis, microkinetic modeling, and Monte Carlo simulation offer novel methods for developing CO_2 hydrogenation catalysts.[230–235]

4.1 The HCOO mechanism

Researchers have followed the formate mechanistic path where CO_2 interacts with formate (HCOO) *via* the Eley–Rideal (ER) or Langmuir–Hinshelwood (LH) mechanism, and the reaction proceeds through H_2COO*, H_2CO*, and CH_3OH.[236–242] The RWGS approach generates unstable HCO* species which further dissociate into CO and H. Investigations using XPS, TPD, and IRAS techniques demonstrate that bidentate formate compounds play a crucial role in modifying the surface under

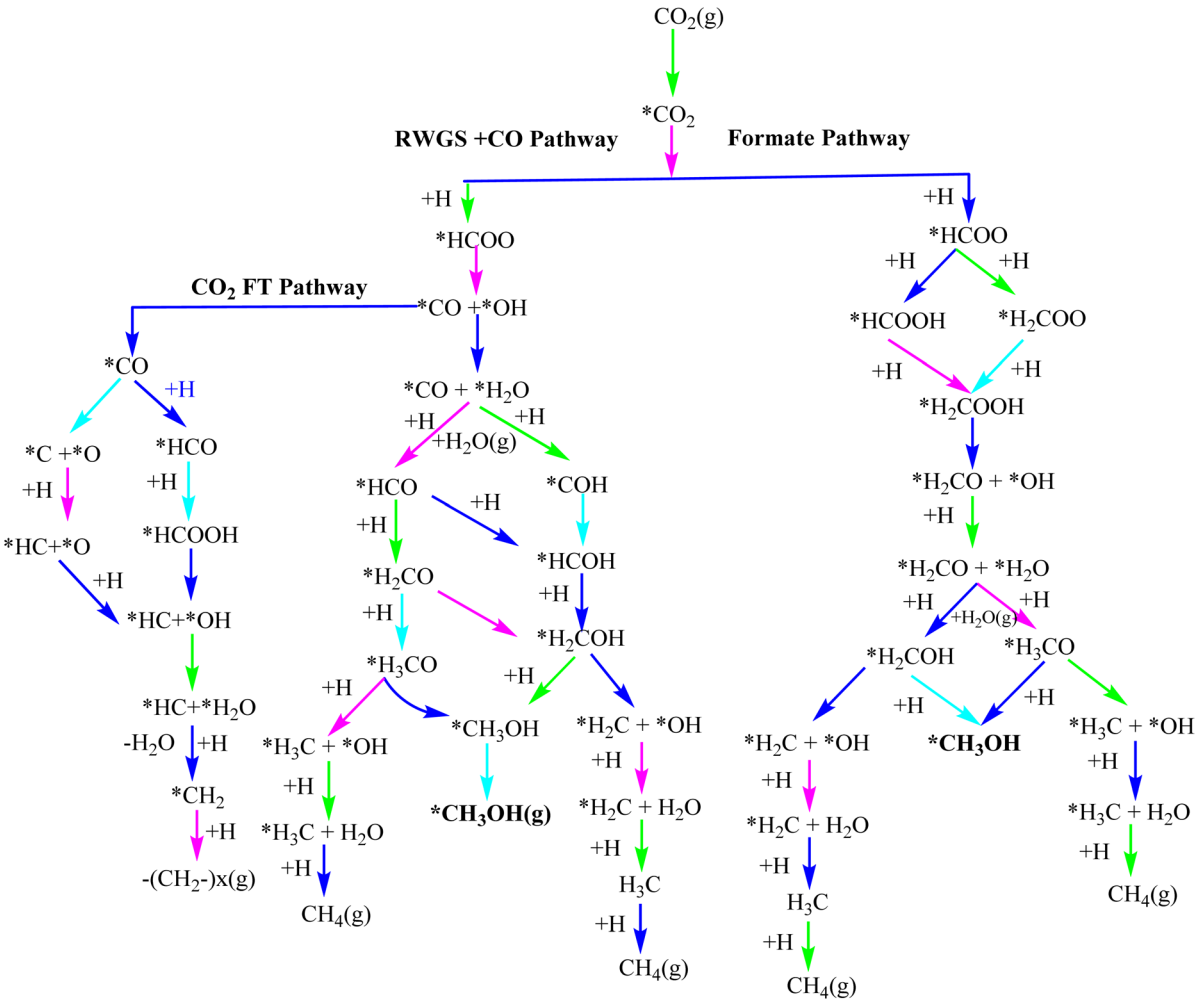

Fig. 6 Reaction mechanism of CH_3OH synthesis from CO_2.[157]

reaction conditions and serve as stable intermediates during the production of CH_3OH.[243,244] The methanol synthesis proceeds through the formate mechanistic pathway over Pd based catalysts Pd/β-Ga_2O_3, Pd@Zn core shell catalyst, and Pd_4/In_2O_3.[231,245,246]

In this mechanism, the C–O bond gets dissociated by the hydrogenation of HCOO*/H_2COO* and is the rate determining step of the reaction.[247–249] According to the microkinetic model, the rate determining step is the hydrogenation of HCOO to H_2COO on Pd–Ga_2O_3/silica.[250,251]

4.2 The revised HCOO mechanism

According to studies on a revised formate pathway, HCOO* is hydrogenated to form HCOOH*, which is then hydrogenated to form H_2COOH* and dissociates to form H_2CO* and OH. H_2CO* is then hydrogenated *via* intermediate CH_3O* formation to form methanol.[252,253] A similar r-HCOO mechanism was proposed by Behrens *et al.* The DFT calculation studies revealed that compared to $PsCu_3$(111), the surface of PdCu (111) with an unsaturated Pd atom is more active for the adsorption and activation of CO_2 and H_2.[253]

4.3 The RWGS + CO-hydro mechanism

In this mechanism, CO_2 is transformed to CO *via* a COOH* intermediate, then CO is hydrogenated to produce methanol using intermediates HC, H_2CO, and H_3CO and CO is the byproduct.[254–256] While HCO, H_2CO, and H_3CO intermediates directly contribute to the hydrogenation of methanol, CO can still be generated by dissociating CO_2 without an intermediate. This mechanism has been suggested for Au-based systems such as Au/CeO_x/TiO_2.[257]

4.4 The *trans*-COOH mechanism

Hydrocarboxyl COOH* is the first hydrogenated species in this molecular route. COOH is generated when CO_2 and the H atom of H_2O react.[226,258–260] Methanol is formed when COOH* is further hydrogenated to COHOH*, which is then dissociated to COH* *via* intermediates such as HCOH and H_2COH. This mechanism was proposed over the surface of Au/Cu–ZnO–Al_2O_3 and Ga_3Ni_5.[261,262]

One of the major challenges in methanol synthesis from CO_2 over heterogeneous catalysts is severe operating conditions including high pressure and temperature. Additionally, the thermodynamics and the continuous separation of methanol from CO_2 and byproducts in the recirculating process constrain CO_2 thermocatalytic hydrogenation. Various methods for CO_2 reduction to methanol have been developed in recent years, including homogeneous catalysis, photocatalysis, and electrocatalysis. The benefits of the new technologies encompass lower temperatures compared to heterogeneous catalysis, the utilization of alternate energy sources (light or electricity), and the potential for enhanced methanol selectivity.

4.5 Electrocatalytic mechanism

Electrocatalysis is a process in which the catalyst plays a pivotal role by decreasing the activation energy of the reaction *i.e.* accelerating the reaction with faster electron transfer and it remains unchanged at the end. Typically, these electrocatalysts are heterogeneous catalysts as the reactions take place on the surface of the electrocatalyst. The process involves three major steps: (a) reactants adsorb onto the catalyst surface, (b) the chemical reaction takes place on the surface, and (c) the products desorb from the catalyst surface. To evaluate the catalytic activity of different electrode materials, researchers commonly compare the current density at a fixed overpotential or determine the overpotential required to achieve a specific current density. An efficient electrocatalyst demonstrates high current density at low overpotential, indicating both high activity and energy efficiency.[263]

Electrocatalytic processes generally occur in cathodes and anodes of fuel cells and also in electrolysis devices. In the anode, fuel gets oxidized and at the cathode, the oxygen reduction reaction occurs, producing electrical energy. In the anode, various fuels can be used for oxidation purposes, such as methane, ammonia, alcohols, hydrogen and sugars. For the cathode, another alternative can be H_2O_2 as an oxidant. A single atom catalyst (SAC) represents the ultimate small size limit of metal particles, which is generally used as a catalyst with the help of a support such as metal oxides, metal surfaces or graphene. The SAC contains isolated atoms singly dispersed on a support. With well-defined dispersion on the support surface, it exhibits maximum efficiency and selectivity. Furthermore, the most efficient way to maximize the utilization of every metal atom in supported metal catalysts is to reduce the metal nanostructures to well-defined, atomically dispersed active centers, known as single-atom catalysts (SACs) (Fig. 7). This represents the ultimate achievement in fine dispersion. For example, Zhang *et al.* developed a practical platinum single-

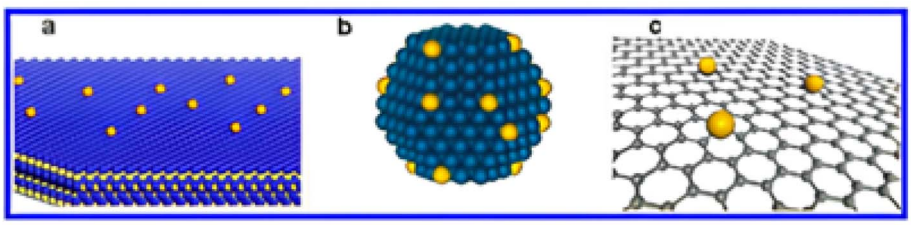

Fig. 7 Schematic diagrams illustrating different types of SACs. Reprinted with permission from ref. 264. Copyright permission from 2013 American Chemical Society.

atom catalyst supported on iron oxide designated as Pt_1/FeO_x.[264] Moreover, the preparation of SACs is very challenging as single atoms tend to get agglomerated. The SACs can be applied in different electrochemical applications, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), nitrogen reduction reaction, and carbon dioxide reaction. The mechanisms of these reactions are discussed in detail in ref. 265.

P. Sharma *et al.* reported a straightforward synthesis strategy for a single-atom ruthenium (Ru) catalyst integrated into a photoactive mesoporous C_3N_4 (mC_3N_4) support. Using the RuSA-mC_3N_4 catalyst under ambient conditions and visible light, efficient photocatalytic conversion of CO_2 into methanol was achieved. The process yielded an impressive 1500 μmol g^{-1} of methanol within 6 hours, utilizing a low ruthenium loading of just 0.4 wt%.[266] The image depicts the possible photocatalytic mechanism of the RuSA-mC_3N_4 catalyst under visible light irradiation during the conversion of CO_2 to methanol. They have narrowed the band gap compared to other prepared materials which helps to generate more electrons upon visible light irradiation. The incorporated Ru single atom on the C_3N_4 network traps electrons from C_3N_4 which helps to sustain the photogenerated electron–hole pair for a longer time. As a result, easy electron transfer occurs to reduce CO_2 which adsorbs on its surface and transforms into methanol (Fig. 8).

Here's an explanation of the process:

1. Photoexcitation (light absorption):

(a) When visible light is irradiated on the catalyst, the electrons present in the valence band of the mC_3N_4 photoactive support get excited.

(b) These excited electrons are promoted to the conduction band (CB), leaving behind holes (h^+) in the VB of the same metal.

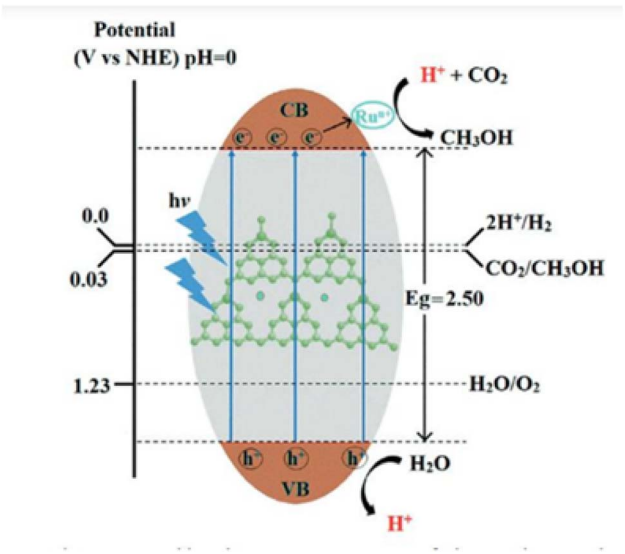

Fig. 8 A plausible schematic illustration of the photocatalysis pathway under visible light irradiation. Reprinted with permission from ref. 266. Copyright permission from 2021 Wiley-VCH GmbH.

(c) In this particular case *i.e.* the RuSA-mC_3N_4 catalyst has a band gap (energy difference between the CB and VB) of approx. 2.50 eV, enabling the absorption of photons from visible light.

(2) Electron transfer and catalysis:

(a) After excitation of the electrons to the CB, the electrons are transferred to the Ru single atoms (Ru^+) embedded in the mC_3N_4 matrix, also reducing the photocarrier transfer barrier. These Ru atoms act as active sites for catalytic reactions.

(b) The electrons reduce CO_2, leading to the formation of methanol (CH_3OH) and side products identified as CO and CH_4 gases.

3. Hole utilization:

(a) The holes (h^+) in the VB participate in the oxidation of water (H_2O), producing oxygen (O_2) and releasing additional protons (H^+).

(b) This step regenerates protons necessary for the reduction process.

4. Reduction and oxidation reactions:

(a) On the CB side, the reduction reactions include: first, CO_2 gets adsorbed on the surface of the catalyst, reduced to a COOH* intermediate, and then further reduced to CO. Later CO transformed into methanol after 6 steps, as given below:[265]

$$1e^- + 1H^+ + CO_2 \rightarrow *COOH$$

$$1e^- + 1H^+ + *COOH \rightarrow H_2O + *CO$$

$$*CO + 1e^- + H^+ \rightarrow *C\text{–}OH$$

$$*C\text{–}OH + 1e^- + H^+ \rightarrow *CH\text{–}OH$$

$$*CH\text{–}OH + 1e^- + H+ \rightarrow *CH_2\text{–}OH$$

$$*CH_2\text{–}OH + 1e^- + H+ \rightarrow *OH\text{–}CH_3$$

$$*O\text{–}CH_3 + 1e^- + H^+ \rightarrow *OH\text{–}CH_3$$

$$*OH\text{–}CH_3 \rightarrow CH_3\text{–}OH + *$$

(b) On the VB side, oxidation reactions occur:

$$^{\cdot}H_2O \rightarrow O_2 + H^+ + e^-$$

5. The catalytic journey of the CO_2 hydrogenation reaction

The review provides a strategic action plan to address the negative impacts of CO_2 emissions on Earth's ecosystems. The strategy places an emphasis on reducing the use of fossil fuels and implementing catalytic technologies for CO_2 conversion. Specifically, it focuses on the mixed and electrocatalytic transformation of carbon dioxide to methanol using noble metals. It goes into great detail about thermodynamics, problems, and techniques used in CO_2 hydrogenation. We present a study of the historical development of catalysts and their industrial

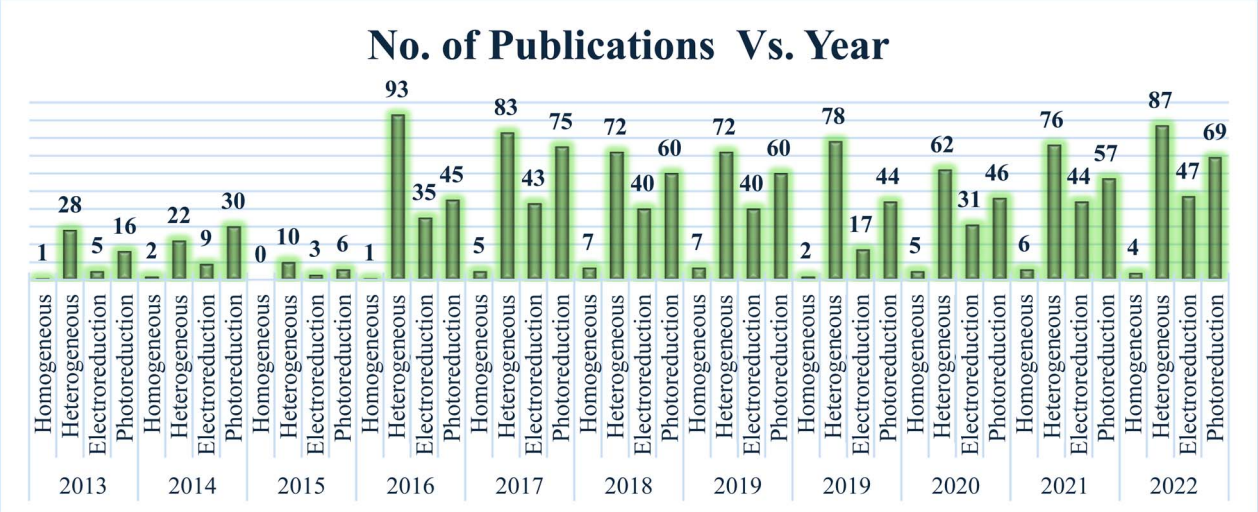

Fig. 9 The number of publications per year during the period of 2013 to 2022.

applications, emphasizing the novel approach towards achieving carbon neutrality. The transformation of carbon dioxide (CO_2) into methanol is a subject of ongoing research and development in the field of catalytic science (Fig. 9). Over time, the discovery of numerous catalysts and the increasing understanding of their behavior and effectiveness have led to significant progress towards a sustainable future. The recognition of the BASF-ZnO-Cr_2O_3 compound as a catalyst for the reduction of carbon dioxide to methanol in 1920 marked a significant achievement in this area.[267] The discovery of ICI–Cu–ZnO–Al_2O_3 as an effective catalyst for the same process in 1960 significantly expanded the potential of this conversion.[267] The discovery that Frost made in 1988 on the "Junction Effect Interaction" of catalysts opened up new doors for the creation of catalysts that were more effective.[268] The Nobel Prize for the "Methanol Economy" in 1994 highlighted the importance of converting carbon dioxide into methanol as a means of promoting sustainability. The year 1994 further solidified this concept. Significant progress in the conversion of carbon dioxide to methanol was made possible by the development of catalysts that were supported on nanocrystals of copper in 2002. Subsequently, researchers conducted an investigation into the correlation between oxygen vacancies and reactive flaws in ceria surfaces, leading to the development of even more effective catalysts.[269] The publication of the book "Beyond Oil and Gas: The Methanol Economy" in 2006 heightened awareness of methanol's potential as an environmentally friendly alternative to fossil fuels.[270]

In 2011, the idea of an "Anthropogenic Chemical Carbon Cycle for a Sustainable Future" was presented, with the primary focus being placed on the necessity of converting carbon dioxide into methanol in order to reduce greenhouse gas emissions.[83] The creation of copper-ceria/copper-ceria-titania catalysts in 2014 was a significant step forward, as these catalysts demonstrated increased efficiency in the process of converting carbon dioxide to methanol.[274] In 2017, active sites on Cu/ZnO catalysts were investigated, yielding significant knowledge on the mechanism of CO_2 reduction to methanol.[275] The catalyst support primarily scatters the active phase to prevent metal particles from sintering, while also ensuring thermal stability. Numerous experiments have demonstrated that the catalyst support influences the activity and selectivity of the methanol reaction. There are several types of carbon nanofibers (CNFs), including zirconia, silica, alumina, and carbon nanotubes (CNTs).[276–285] In certain instances, a promoter may not yield the desired effect. Furthermore, it has the potential to influence the catalyst's efficiency by either promoting the intended reaction or minimizing the incidence of undesirable reactions. As a result, incorporating promoters has the potential to improve both the product's selectivity and the catalyst's activity. There are several researchers who have documented the utilization of promoters for CH_3OH synthesis catalysts. Some examples of these promoters are gallium oxide (Ga_2O_3), zinc oxide (ZnO), niobium oxide (Nb_2O_5), and others.[286–290] The year 2019 saw the discovery of ternary interactions in Cu–ZnO–ZrO_2 catalysts, which extended the possibilities for catalyst development that are even more effective.[291] The year 2020 saw the discovery of the one-of-a-kind interaction that occurs between copper and zinc in the Cu/ZnO system. This discovery opened up new possibilities for the creation of catalysts that are even more efficient.[292] The most recent breakthrough in this area is the creation of a new black indium oxide catalyst in 2022. This catalyst facilitates the effective conversion of carbon dioxide into methanol, which serves as a source of energy and a chemical feedstock, and represents a significant step towards a more sustainable future.[293] The constant process of transforming carbon dioxide into methanol through the application of catalytic technology, defined by countless discoveries and breakthroughs, has been a journey. These achievements are critical milestones in developing a sustainable future and highlight the potential of catalytic science in making the world a better place (Fig. 10).

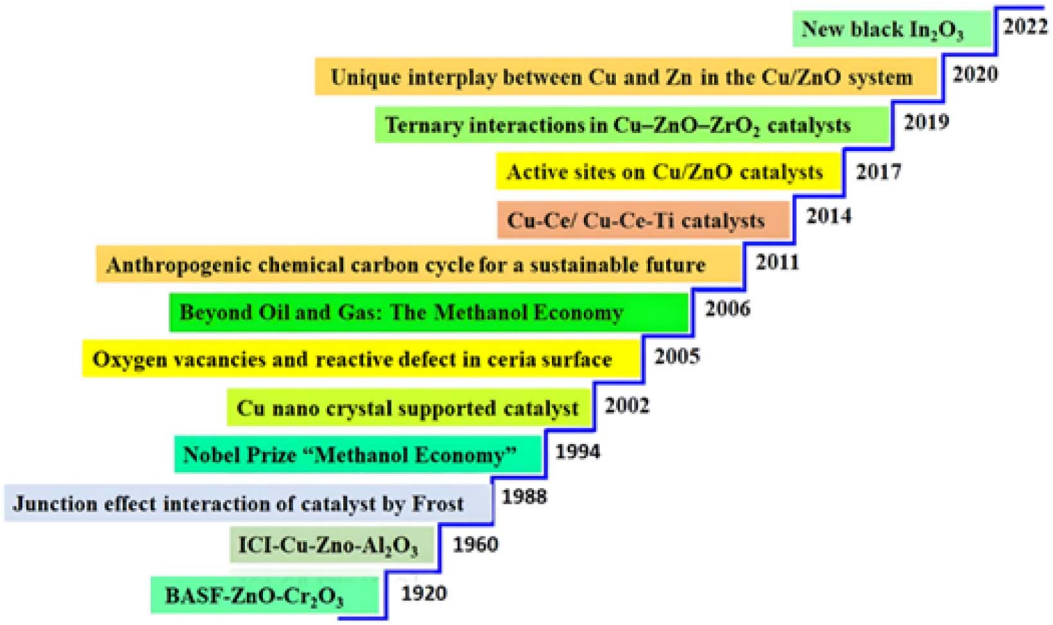

Fig. 10 Some remarkable journeys of hydrogenation of CO_2 to CH_3OH using heterogeneous catalysts.[83,225,268–273]

5.1 Noble metal-based heterogeneous catalysts

In the mid-19th century, heterogeneous catalysts were utilized for the production of CH_3OH from syngas, employing a Cu–ZnO based heterogeneous catalyst in this exothermic process.[294,295] The Cu–ZnO catalyst exhibited significant deactivation and diminished activity with standard syngas, which improved in the late 1990s, followed by the introduction of noble metal-based heterogeneous catalysts that enhanced the hydrogenation conversion of CO_2 to CH_3OH. Compared with transition metal-based catalysts, noble metal-based catalysts generally have higher activity in the CO_2 hydrogenation process. For successful CO_2 hydrogenation, both CO_2 and H_2 should be activated simultaneously, and the noble metal nanoparticles are usually more active for H_2 activation with the enhanced hydrogen spillover phenomenon than transition metal nanoparticles, hence noble metal-based catalysts usually outperform transition metal-based catalysts in CO_2 hydrogenation. Furthermore, noble metal nanoparticles are more endurable than transition metal nanoparticles in terms of coke formation, which allows noble metal-based catalysts to have a longer catalytic lifetime. The details about the noble metal-based heterogeneous catalysts for CO_2 to methanol conversion are discussed as follows.

5.1.1 Pd based catalysts. CH_3OH production from CO_2 is catalyzed using two main catalytic systems: Cu and Pd catalysts, which have good catalytic activity and selectivity.[155,242,296–299] One of the main difficulties in producing methanol from CO_2 is catalyst deactivation.[300–302] Pd serves as a promoter for the Cu–ZnO catalyst in the hydrogenation of syn-gas to methanol.[303,304] The electronic state of the catalyst affects the interaction between Pd and Cu, with Pd promoting hydrogen spillover and enhancing the stability of the Cu active site against CO_2 oxidation.[305,306] The alloy phase diagram has shown that Pd-based metal alloy catalysts such as Pd–Zn, Pd–Cu, Pd–Ga, and Pd–In alloys can be employed for CO_2 hydrogenation.[307–313] The new active site with high activity is created by changing the chemical properties of the metal surface by employing alloys and ultimately increasing the catalytic activity. The alloy composition depends on the metal composition and reduction conditions to tune the atomic ratio of the two components. Different Pd supported catalysts, including mesoporous MCM-41, SBA-15, and carbon based materials such as CNFs, CNTs, *etc.*, increased catalytic activities and led to the development of various synthetic routes, including CVI (chemical vapour impregnation), citrate decomposition, incipient wetness impregnation, atomic layer deposition *etc.*[314–317] These methods are crucial for CH_3OH synthesis activity and the development of highly active catalysts at low temperatures.

5.1.2 Pd–ZnO based catalysts. The Pd–Zn alloy is one of the notable bimetallic catalysts employed for the synthesis of CH_3OH. In 2004, Iwasa *et al.* reported a Pd/ZnO catalyst for CH_3OH synthesis from CO_2.[318] The catalytic performance of Pd/ZnO/Al_2O_3 was investigated by Geng and coworkers.[319] Pd–Zn alloys can influence the deactivation of the catalyst for methanol synthesis and stabilize formate intermediates during CH_3OH synthesis, as reported by Bahruji and coworkers. The particle size and oxidation state have a significant impact on the catalytic performance of Pd, as shown by Bahruji and coworkers.[320,321] Liao and co-workers developed the low-pressure methanol synthesis method by utilizing a Zn enriched Pd–Zn core–shell catalyst from sodium selenite, cadmium nitrate, and 5% Pd with ZnO supported (Pd/CdSe–ZnO) precursors. The uniqueness of this catalyst is that it suppresses the CO production by the RWGS reaction.[322] Zaman and co-workers were the first to report Ca doped Pd–Zn on the CeO_2 catalyst for methanol synthesis from CO_2 hydrogenation. It was observed that CeO_2-supported PdZn showed high

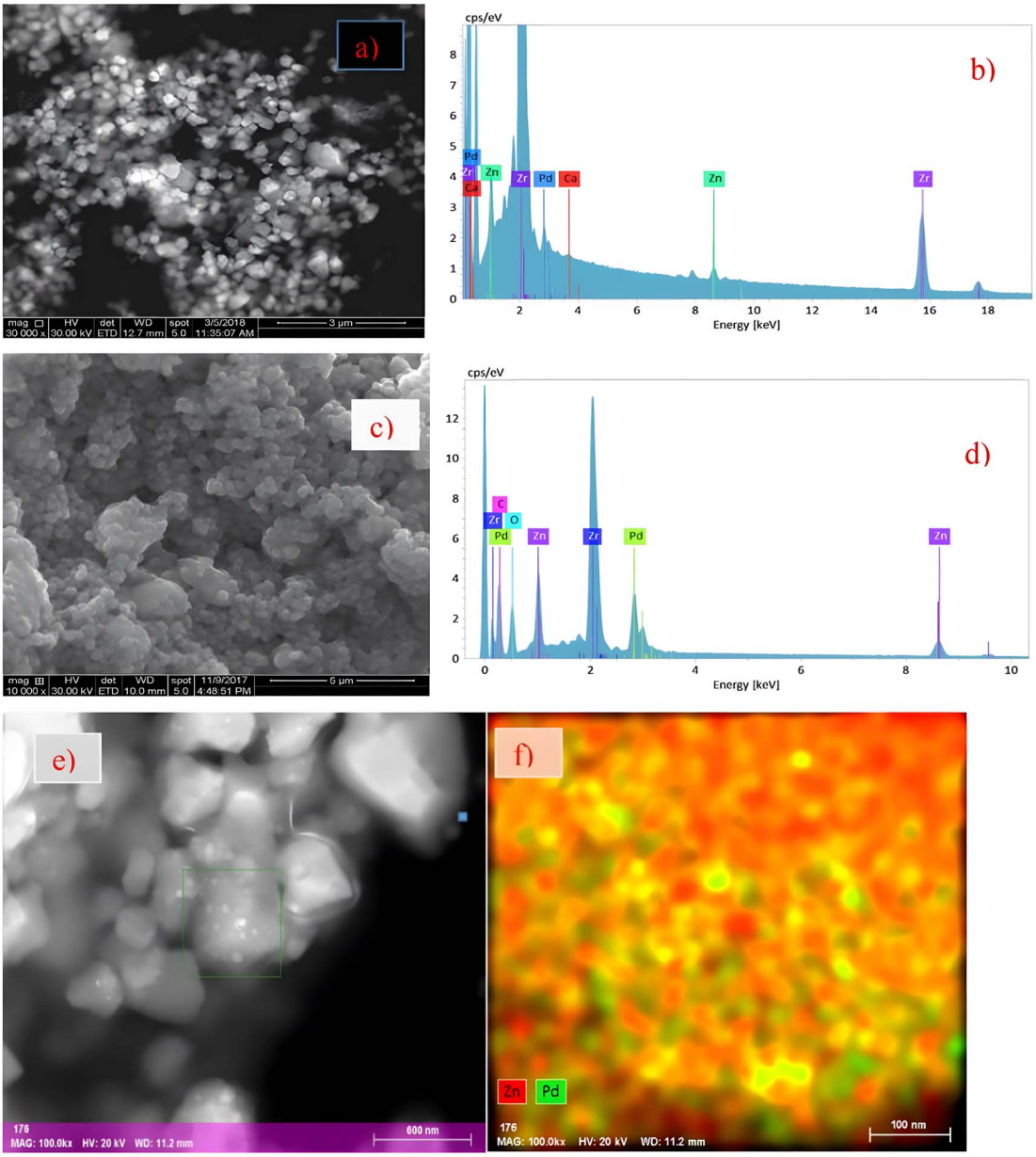

Fig. 11 Electron microscopy and spectroscopy of spent catalyst 0.5Ca5P5ZZr-IMP. SEM image (a) and corresponding energy dispersive spectrum (EDS) (b) of 0.5Ca5P5ZZr-IMP, SEM image (c) and EDS (d) of 5P5ZZr-IMP. Surface mapping (e) and PdZn distribution (f) in 5P5ZZr-IMP.[323] Copyright 2019 Elsevier.

selectivity in catalytic activity and Ca-doped $PdZn/CeO_2$ showed 100% methanol selectivity at low temperatures[323] (Fig. 11). Diez-Ramirez and coworkers reported a carbon nanofiber-based PdZn catalyst for methanol synthesis from CO_2 at atmospheric pressure, with the performance of the catalyst dependent on the particle size.[324] In recent years, Yerga *et al.* synthesized PdZn–ZnO catalysts on TiO_2 with Zn/Pd molar ratios of 2.5, 5, and 7.5 using metal organic precursors. The experimental studies reveal that the catalyst with the highest ZnO content achieved the best methanol yield (78.9 $mmol_{MeOH}\ min^{-1}\ mol_{Pd}{}^{-1}$) due to enhanced CO_2 adsorption, greater ZnO particle stability, and intermediate hydrogenation.[325] Tian and coworkers synthesized a Pd/ZnO single atom catalyst for methanol steam reforming. The experimental studies showed that the TOF of $2PdZn/Al_2O_3$ NP is 1.4 times that of 0.2PdZn SAC.[326]

5.1.3 Pd–Cu based catalysts. There has been a surge in research utilizing bimetallic Pd–Cu catalysts for the synthesis of methanol from CO_2. Jiang *et al.* examined the utilization of SiO_2-supported Pd–Cu catalysts in the process and determined that the partial pressure has a significant impact on CO_2 hydrogenation. The use of bimetallic catalysts was found to enhance the activity and reduce the selectivity of methanol. A kinetic study showed that the synthesis of CH_3OH was dependent on the H_2/CO_2 ratio and that the Pd–Cu bimetallic catalyst played an active role.[327]

This group reported another study that elaborated on the connection between the size effect, surface alloy composition and catalytic efficiency. This work mainly focused on the manufacture of a Pd–Cu bimetallic catalyst; the ratio of Pd/(Pd + Cu) lies within 0.25–0.34 and is used for the hydrogenation of CO_2 to produce CH_3OH. The main observation is that Pd–Cu(2.4)/SiO_2, which has a lower metal loading than a commercial catalyst, produces 2 times as much CH_3OH at 523 K and 4.1 MPa concerning metal-based space-time yield (STY).[328] Lin *et al.* conducted an investigation into the use of various supports, including TiO_2, ZrO_3, CeO_3, Al_2O_3, and SiO_2, for the Pd–Cu catalyst. The results indicated that TiO_2 and ZrO_2 showed the highest activity for methanol synthesis. The adsorption capacity for methanol synthesis is attributed to the influence of metal support interaction on the process, with the Pd–Cu catalysts facilitating the bonding between H_2 and CO_2 on the surface.[329] The changes in metal–support interactions were primarily attributed to enhancing moderate interactions between the metal and support, which aimed to boost adsorption capacity and promote methanol synthesis. This study supported the idea that Pd–Cu catalysts play a significant role in shifting adsorption toward bonding between H_2 and CO_2 on the alloy surface.

5.1.4 Pd–Ga catalysts. Several research studies have been conducted to explore the use of Pd–Ga_2O_3 catalysts for methanol synthesis from CO_2. Fujitani *et al.* reported that the Pd–Ga_2O_3 catalyst showed higher catalytic activity compared to the commonly used Cu/ZnO catalyst.[330] In 2002 Collins *et al.* reported that dissociated atomic hydrogen spillover from metallic Pd to Ga_2O_3 causes Pd NPs to accelerate the hydrogenation rate of carbonaceous species chemisorbed over the surface of b-Ga_2O.[331] Behrens *et al.* synthesized a series of Pd–Ga catalysts consisting of intermetallic compounds, and found that gamma Ga_2O_3 played a significant role in the selective hydrogenation of methanol.[332] Damsgaard and co-workers synthesized a non-dispersed intermetallic $GaPd_2/SiO_2$ catalyst for the synthesis of methanol from CO_2. This intermetallic catalyst showed higher catalytic activity than Cu/Zn/Al_2O_3 which was the most used catalyst. *Ex situ* and *in situ* characterization techniques, reveal that different aspects of the catalytic structure show a good correlation between the results at various pressures. The TEM study introduced a deeper evaluation of the dynamic catalytic activity during methanol synthesis at atmospheric pressure.[333] Tsang and co-workers reported that the interaction of Pd and Ga_2O_3 nanocrystals with a predominant 002 surface on metal supports resulted in enhanced catalytic activity for the synthesis of methanol from CO_2 hydrogenation. This work emphasizes electron transfer from Ga_2O_3 to Pd NPs (nano particles) thereby enhancing the reduction process of Ga^{3+} and directly enriching the conversion process from CO_2 to methanol.[334] Williams and co-workers synthesized a colloidal Pd_2Ga-based catalyst by thermal decomposition of Pd(II) acetate in the presence of the Ga(III) state. Various characterization techniques, such as HR-TEM, STEM, XPS, and XRD support the formation of Pd_2Ga nanoparticles with an average diameter of 5–6 nm. This work is considered the benchmark of methanol synthesis and the Pd/Ga colloidal catalyst shows promising stability and higher catalytic activity than the Cu–ZnO–Al_2O_3 catalyst for the conversion of CO_2 to methanol.[335] Michael Bowker and his colleagues conducted another intriguing study. This study examines the Pd deposition on Ga_2O_3 and In_2O_3 for CO_2 hydrogenation to methanol. The interesting finding in this work is that Ga_2O_3 is active alone, but In_2O_3 achieves high conversion and 89% methanol selectivity.[336]

Morgan and coworkers[336] synthesized a nanodispersed intermetallic $GaPd_2/SiO_2$ catalyst; industrially relevant high-surface-area SiO_2 is impregnated with Pd and Ga nitrates, then dried, calcined, and reduced in hydrogen (Fig. 12). The

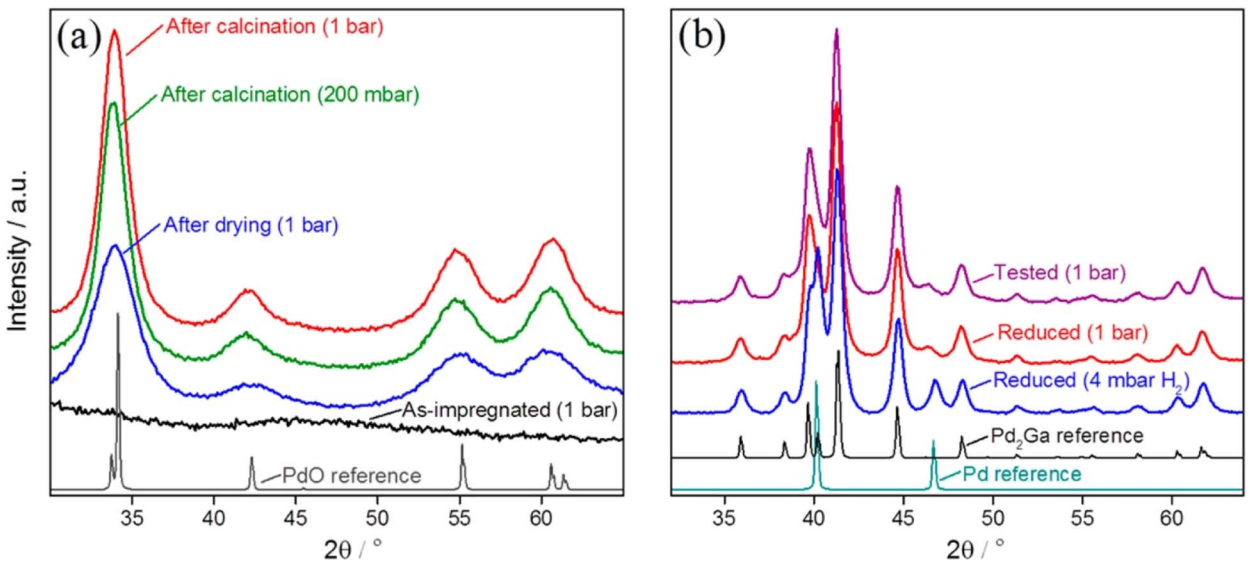

Fig. 12 (a) XRD patterns obtained from the impregnated, dried, and calcined catalyst precursor at room temperature and atmospheric pressure, and (b) from the reduced and tested $GaPd_2/SiO_2$ catalyst for CO_2 hydrogenation. Reprinted with permission from ref. 333. Copyright 2015 American Chemical Society.

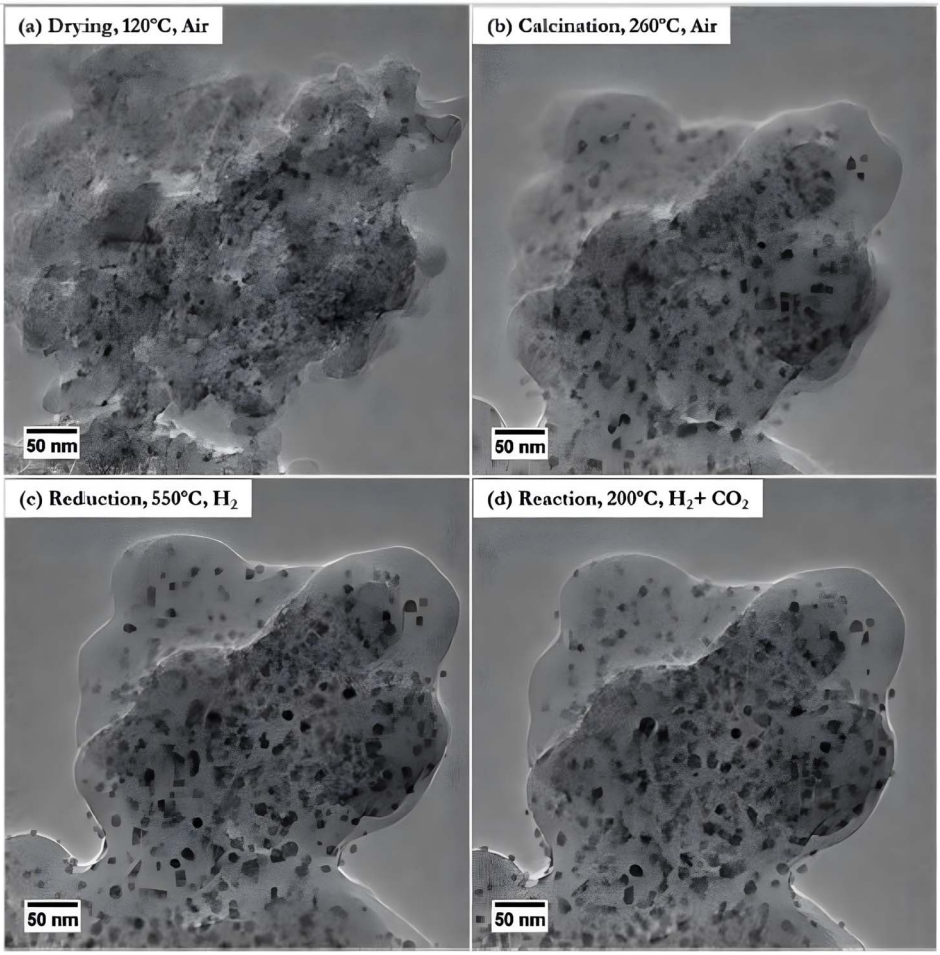

Fig. 13 IL-TEM images of the $GaPd_2/SiO_2$ catalyst acquired after drying (a), calcination (b), reduction (c), and methanol synthesis (d).[333] Copyright 2015 American Chemical Society.

$GaPd_2/SiO_2$ catalyst outperforms the traditional $Cu/ZnO/Al_2O_3$ catalyst for CO_2 hydrogenation to methanol at ambient pressure. Additionally, it produces less unwanted CO. The $GaPd_2/SiO_2$ catalyst is investigated using both *in situ* and *ex situ* approaches (Fig. 13).

5.1.5 Pd–In based catalysts. Pd–In-based catalysts have emerged as a promising option for the production of methanol from CO_2 due to the presence of oxygen vacancies, which allow for the adsorption of carbon dioxide. The catalytic activity of these catalysts can be improved through catalytic activation. García-Trento *et al.* proposed a bimetallic PdIn nanoparticle synthesized by the thermal decomposition of $Pd(acetate)_2$ and $In(acac)_3$. This Pd/In (5–10 nm) nanoparticle catalyst showed improved > 80% methanol selectivity at 270 °C compared to the reference $Cu/ZnO/Al_2O_3$ catalyst.[337] Snider *et al.* synthesized Pd–In-based catalysts with different In/Pd ratios (1 : 0, 2 : 1, 1 : 1, 1 : 2, and 0 : 1) and enhanced the methanol synthesis process from CO_2/H_2 at 40 bar and 300 °C. The highest methanol selectivity of 61% was achieved using the In : Pd (2 : 1)/SiO_2 catalyst. *In situ* XAS characterization technique revealed that the synergistic effect of the intermetallic compound indium–palladium enhances the selectivity and activity of methanol synthesis.[338] Liu *et al.* synthesized Pd/In_2O_3 catalysts by thermal treatment of In_2O_3 powder with a Pd/peptide composite. The Pd/In_2O_3 catalyst showed higher activity of methanol synthesis from CO_2 conversion *i.e.* >20% and methanol selectivity of 70%.[339] Jeschke and coworkers developed the catalyst Pd–In_2O_3–ZrO_2 by flame spray pyrolysis methods for the conversion of CO_2 to methanol. Its high and persistent methanol productivity can be explained by the improved formation of oxygen vacancies revealed by this particular catalyst architecture, according to a ground-breaking procedure designed to quantify them using *in situ* electron paramagnetic resonance spectroscopy.[340] Recently, Cai *et al.* have reported that hollow In_2O_3 supported Pd based catalysts are suitable for CO_2 hydrogenation to methanol. The main finding of this work is that the hollow morphology of In_2O_3 supported Pd based catalysts led to higher catalytic performance (10.5% CO_2 conversion, a methanol selectivity of 72.4% and a methanol space time of 0.53 $g_{MeOH}\ h^{-1}\ g_{cat}^{-1}$ over 100 h on stream at 3 MPa and 295 °C) compared to In_2O_3 nanotube or nanorod morphology.[341] Jiang and coworkers reported the use of an In_2O_3/SBA-15-supported Pd-based catalyst and observed a CO_2 conversion rate of 12.6% with 83.9% methanol selectivity.[342] Hua and coworkers developed the Pd/In_2O_3

nanocatalyst by employing innovative electrostatic self-assembly methods. This catalyst exhibited an increase in the concentration of oxygen vacancies which enhanced the methanol production. This catalyst led to a space time yield (STY) of 0.54 $g_{MeOH}\ h^{-1}\ g_{cat}{}^{-1}$ (300 °C, 3.5 MPa, 21 000 mL $g_{cat}{}^{-1}\ h^{-1}$).[343]

5.1.6 Mesoporous molecular sieves supported Pd-based catalysts. Song and co-workers reported a nanostructured Pd-based catalyst by the incorporation of mesoporous MCM-41 and SBA-15 and created a nano-sized pore channel using alkali/alkaline earth metal additives, where they observed the addition of an alkali/alkaline earth metal as a promoter enhanced the catalytic activity of methanol synthesis from CO_2.[344–346]

The CNT-supported Pd-based catalyst shows high catalytic activity for methanol synthesis. Zhang and coworkers synthesized Pd–ZnO supported multi-walled carbon nanotube-based catalysts showing a high rate of catalytic conversion of methanol from CO_2. A large amount of hydrogen is reversibly adsorbed using CNT-supported Pd–ZnO catalysts, which boosts the concentration of active H-species at the surface of the working catalyst and accelerates the kinetics of the hydrogenation reaction.[347] Kong and co-workers developed a MWCNT supported Pd–Ga catalyst for the synthesis of methanol by hydrogenation. This catalyst improved the molar percentage of catalytic activity of Pd^0 species and also increased the catalytic activity of adsorbing/activating H_2.[348] Li *et al.* investigated the Pd nanoparticle supported inside and outside CNT-based catalysts. Higher catalytic activity and methanol selectivity are displayed inside the Pd/CNTs than outside. The turnover frequency of Pd/CNTs (inside) is 3.7 times higher than that of outside-supported CNTs. The selectivity difference between inside and outside CNT-based catalysts is due to the relative concentration of Pd^+ species.[349]

Pd metal actively influences the chemical and electronic properties of the catalyst surface. Furthermore, it is impossible to overstate the importance of Pd's role in converting H_2 into H-add species and permitting them to overflow onto support surfaces because this is still an essential step in the synthesis of methanol, without which hydrogenation cannot proceed properly. The Pd precursor employed for the synthesis of the catalyst will also affect its overall performance.

5.1.7 Effect of Pd as a promoter. In chemistry, catalyst promoters play an important role by improving the catalytic activity and selectivity. In this section, we have discussed the role of Pd as a promoter and its direct influence on the physiochemical properties of the CO_2 hydrogenation reaction and enhancing the surface area and mechanical strength of the catalyst.

The promoters on a Pd surface enhance the CO_2 adsorption capacity by generating an electrostatic field. Cabrera *et al.* observed that Pd itself acts as a promoter which increases the catalytic activity of Cu + ZnO (Al_2O_3) and improves the rate of hydrogenation of CO_2 due to the hydrogen dissociated on the surface of Pd particles and spillover on the surface of the Cu + ZnO catalyst. In another remarkable study established by Lee and co-workers, the catalytic activity of Cu/CeO_2 was increased by the addition of a small amount of Pd. A small amount of Pd is added to the Cu/CeO_2 catalyst to facilitate the reactivity of Cu sites, which in turn increases methanol productivity. The interaction with highly dispersed Pd increases the surface and dispersion concentration of Cu. The transfer of electrons from palladium to copper leads to a reduction in copper sites, while the addition of palladium as a promoter diminishes the surface area of cerium dioxide. So, it can be concluded that the rate of hydrogenation of CO_2 and methanol productivity can be increased with the addition of a small amount of Pd to the Ce/CeO_2 catalyst.[350] Hu *et al.* reported Pd promoted Cu–ZnO catalysts for the synthesis of a series of Pd doped Cu–ZnO catalysts with a constant Cu/Zn ratio (1 : 1) and varied Pd molar ratios from 0.01 to 0.04 mol%. It was observed that the 1% Pd doped Cu–ZnO catalyst promotes the methanol space-time yield by 2.5 times and turnover frequency (TOF) by 3.5 times at 543 K as compared to the undoped Cu–ZnO catalyst. Tsang *et al.* investigated the effect of the promoter Pd on the $Pd/ZnO/Al_2O_3$ catalyst. The result indicated that methanol selectivity depends on the ratio of Pd^0/PdZn and the EXAFS study showed that the Pd-modified ZnOx possesses an active site for methanol synthesis.[305] Koizumi *et al.* investigated the incorporation of Pd nanoparticles into mesoporous supports such as MCM-41, and SBA-15 with promotion using alkali/alkaline earth metals synthesized by incipient wetness impregnation. It was observed that without impregnation of any promoters, Pd-supported mesoporous silica showed weak activities towards methanol synthesis, but the addition of alkali or alkaline earth metals such as K, Mg, and Ca increased the catalytic activities of K(Ca) promoted Pd-supported mesoporous SBA-15 producing two times higher methanol yield than that of Pd-supported mesoporous silica. Song and co-workers synthesized Pd supported catalysts by the impregnation method with $Pd(NO_3)_2$. CaO promoted the CO_2 hydrogenation activity with the highest selectivity for methanol over Pd/MCM-41.[344] Yin and co-workers reported a metal–organic framework-based PdZnO catalyst from the Pd@zeolitic imidazolate framework (ZIF-8) for hydrogenation of CO_2. The formation of small-sized PdZn alloy particles after H_2 reduction and the abundance of surface oxygen defects on ZnO are crucial for such a high methanol production. The SMSI between PdZn and ZnO also ensures the long-term stability of the PdZn catalysts. Lastly, it can be proposed that the active site strongly associated with methanol formation is the PdZn alloy rather than metallic Pd.[351]

(i) Au based catalysts

Researchers have discovered that gold nanoparticles act as highly active catalysts for CO_2 hydrogenation. Vourros *et al.* successfully investigated the activity of Au nanoparticles supported on various oxides (M_xO_Y – Al_2O_3, TiO_2, Fe_2O_3, CeO_2, and ZnO) to catalyze the synthesis of methanol from the hydrogenation of CO_2. Au nanoparticles based on Au/CeO_2 (82%) and Au/ZnO (90%) show high selectivity towards CH_3OH synthesis at temperature below 250 °C.[352] Behm and co-workers synthesized metal oxide-supported Au catalysts (Au/Al_2O_3, Au/TiO_2/Au/ZnO, and Au/ZrO_2) for the synthesis of 'green methanol' from CO_2. The Au/ZnO catalyst is one of the potential candidates for green methanol technology. With an increase in the diameter of Au nanoparticles in the Au/ZnO catalyst, the rate of methanol

Table 1 The summary of noble-metal based catalysts for the hydrogenation of CO_2 to methanol

Catalyst	CO_2/H_2 ratio	Temp./K	MPa	Space velocity	Conv.	Selectivity	STY	Ref.
Pd/ZnO	1 : 3	523 K	2	3600(W)	10.7	60	77.4	320
PdZn-400	1 : 3	543 K	4.5	21 600(W)	15.1	56.2	650	365
Pd/Ga_2O_3	1 : 3	523 K	5	—	19.6	51.5	*c.a* 20.8	334
Pd–In_2O_3 (Co-precipitation)	1 : 4	553 K	5	24 000		75	0.061	366
Pd(0.25–Cu/SiO_2	1 : 3	250 °C	41	3600	6.7	30	0.03	367
Pd/SiO_2	1 : 3	523 K	2	—	0.33	31.6	0.013	349
Pd/Cu–P25	1 : 3	523 K	4.1	—	16.4	25.7	1.80	368
Pd/In_2O_3	1 : 4	300 °C	50	21 000	20	72	0.89	369
Pd–Pt/In_2O_3	1 : 4	300 °C	5	21 000	17.7	68.3	0.725	370
PdZn/ZnO-3.93Al	1 : 3	523 K	3.0		14.2	51.6	*c.a* 4.51	371
Pd/Zn SiO_2	1 : 3	260 °C	3		2.6	11.2	0.03	372
2Pd/CeO_2−R	1 : 3	240	3	2000	6.2	29	0.012	373
5% Pd/ZnO, IM	1 : 3	523 K	2.0	—	8.7	1	0.055	320
$0.5Ca_5Pd_5ZnZr$	1 : 3	523 K	3.0	2400	14.2	51.6	*c.a* 4.51	374
Pd–Cu/SBA-15	1 : 3	250 °C	4.1	3600(W)	6.5	23	23	375
Pd/Zn/CNTs	1 : 3	250 °C	3	1800(W)	6.3	99.6	37.1	376
Pd Cu/CeO_2	1 : 3	523 K	4.1	—	9.9	28.4	1.37	368
Pd/TiO_2	1 : 3	523 K	5	—	15.5	3.9	*c.a.* 1.21	377
Pd–P/In_2O_3	1 : 4	498 K	5		Ca 3	Ca 95	6.01	339
Pd/In_2O_3/SBA-15	1 : 4	533 K	5		12.6	83.9	11	314
Pd–$ZnZrO_x$	1 : 4	320 °C	5	24 000	16	58	0.63	378
Pt/In_2O_3	1 : 4	300 °C	5	21 000	17.6	54	0.542	379
Pt/In_2O_3	1 : 3	300 °C	4	24 000	8.8	71.5	0.480	380
Rh/In_2O_3–ZrO_2	1 : 4	300	5	21 000	18.1	66.5	0.684	381
UiO-67-Pt		170	0.8	6000	1.5	19.0	0.0024	382
Au/ZnO	1 : 3	240 °C	0.5	4800(G)	0.3	82	N/A	383
Ag/ZrO_2	1 : 3	240	80	3600		55		359
Ag/In_2O_3	1 : 4	300 °C	5	21 000	13.6	58.2	0.450	384
Au/In_2O_3–ZrO_2	1 : 3	250	50	21 000(G)	5.0	90	0.59	385
Au/Al_2O_3	1 : 3	220	5	24 000(W)	2.0	3.8		383
Au/CeO_2	1 : 3	240	5	9000	1–2	40	0.412	386
Au/In_2O_3	1 : 4	300	5	21 000	11.7	67.8	0.47	387

formation reduces and the selectivity of methanol increases from 56% to approximately 82%.[353] This group also reported better catalytic behaviour of the Au/ZnO-based catalyst for the synthesis of methanol than the conventional Cu–Zn–Al catalyst. From the kinetic and IR spectrophotometer studies, it is revealed that the conversion of CO_2 to methanol proceeds through the formation of formate and methoxy intermediates initiated using the proposed Au/ZnO catalyst.[354] Han *et al.* reported an Au-supported ZrO_2 catalyst for methanol synthesis with a selectivity rate of 73% at 180 °C.[355] The electrical polarization at the metal oxide CeO_x/TiO_2 anchored with Au nanoparticle-based substrates, as proposed by Chen *et al.*, actively promoted CO_2 adsorption under low pressure conditions and led to greater selectivity of methanol production. According to the AP-XPS study, Au possesses a partial negative charge and CeO_x shows a Ce^{3+} state. The DFT calculation studies supported the substantial charge redistribution occurring at $Au_3/CeO_x/TiO_2(110)$, with Au atoms becoming negatively charged, and negatively charged Au and the positively charged Ce^{3+} site bind to the positively charged C atom and the negatively charged O atom of CO_2, respectively.[356] Rodriguez and coworkers investigated the catalytic properties of In/Au(111) alloys and InO_x/Au(111) inverse systems for CO_2 hydrogenation by employing AP-XPS studies and batch reactors. The experimental evidence shows that InO_x/Au(111) demonstrates significant potential for CO_2 hydrogenation combining high activity and selectivity for methanol production.[357]

(ii) Ag-based catalysts

Ag-based catalysts received less attention than Pd and Au-supported catalysts for the hydrogenation of CO_2.[358] Grabowski *et al.* investigated the catalytic activity of Ag/ZrO_2 and Ag/ZrO_2/ZnO catalysts. The XPS and Auger spectroscopic techniques confirmed the electronic state of silver and the contents of the zirconia polymorphic phases (tetragonal and monoclinic). The presence of oxygen vacancies in ZrO_2 directly influenced the thermodynamically unstable t-ZrO_2 and Ag^+ species connected with oxygen vacancies thereby accelerating the active phase for methanol synthesis.[359]

(iii) Pt/Rh based catalysts

In heterogeneous reactions, dispersed catalysts have a remarkable place due to the low coordination environment of the metal center, quantum size, and SMSI effect.[360] Zheng *et al.* prepared atomically dispersed Pt/MoS_2 catalysts with Pt amounts up to 7.5% and reported that the synergetic interaction between neighboring Pt monomers reduces the activation energy and enhances the catalytic activity relative to isolated Pt monomers in CO_2 hydrogenation. Unlike isolated Pt monomers, neighboring Pt monomers hydrogenate CO_2 sequentially into formic acid and methanol.[361] Song *et al.* investigated a PtCo alloy-based catalyst for methanol synthesis where zigzag Pt–Co

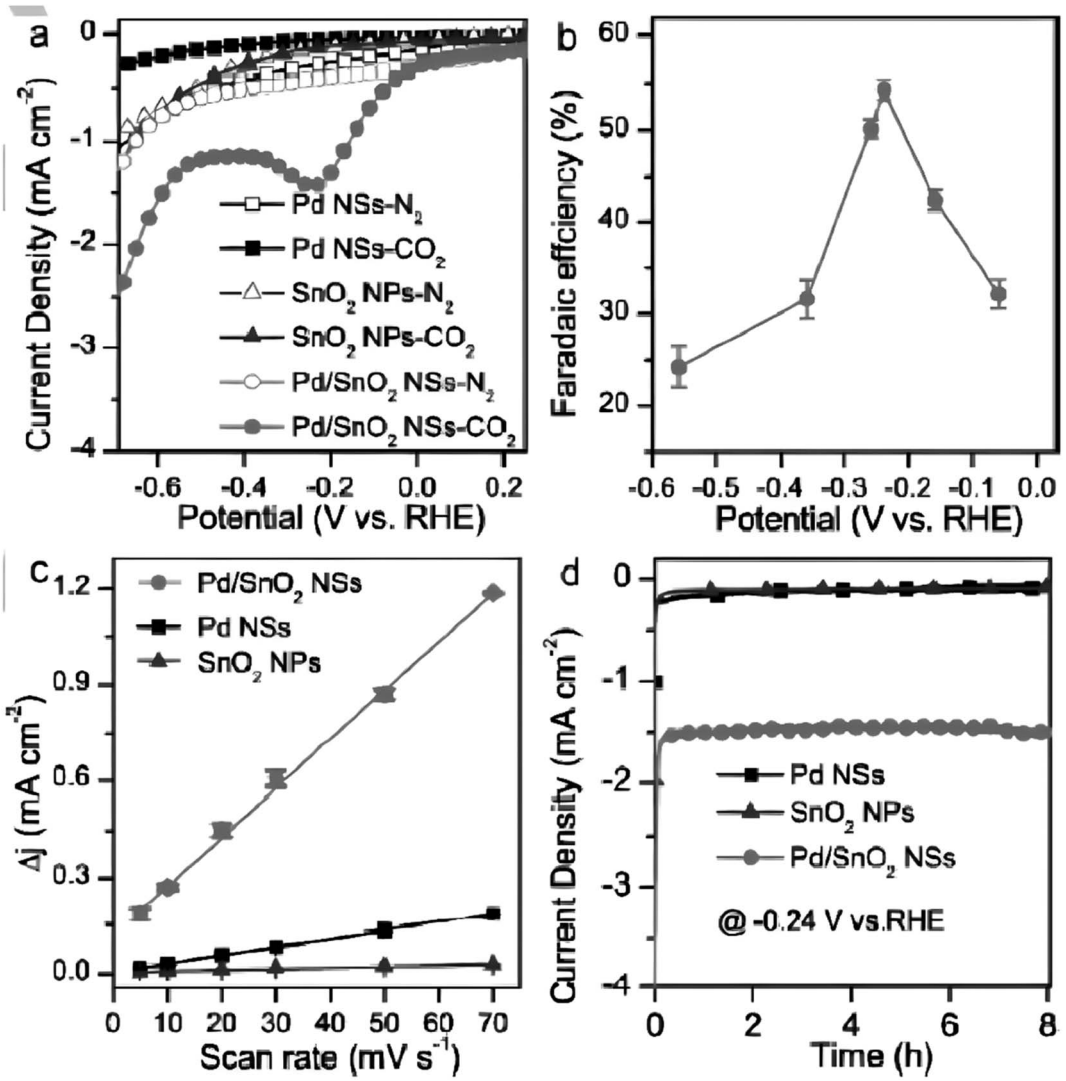

Fig. 14 Electrochemical characterization studies of Pd/SnO_2 NSs (Pd : Sn = 1 : 1) in comparison with Pd NSs and SnO_2 NPs. (a) LSV curves obtained in 0.1 M $NaHCO_3$ solution. (b) FE for CH_3OH at various applied potentials. (c) Charging current density differences plotted against scan rates. (d) Chronoamperometry studies of different catalysts. Reprinted with permission from ref. 390. Copyright permission from 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

nanowires with a Pt-rich surface and abundant step/edges (defects) were utilized to obtain high catalytic activity. Pt_4Co NWs/C showed the best performance among other PtCo alloys.[303] Analysis using Fourier transform infrared spectroscopy demonstrated that when Pt_4Co NWs/C was used as a catalyst, the process involved CO_2 adsorption and activation *via* a carboxylate intermediate, resulting in enhanced CH_3OH yield. Shimizu *et al.* investigated a Pt nanoparticle loaded $MoOx/TiO_2$ catalyst for the hydrogenation of CO_2 to produce CH_3OH in 73% yield under mild conditions. The X-ray absorption fine structure study suggested that reducing the MoO_x species promoted the hydrogenation reaction.[362] Han *et al.* investigated that the methanol selectivity of In_2O_3 increased (72.2% to 91.1%) by introducing a small amount of Pt.[363] Zeng and co-workers reported that the RhW alloy with a nanosheet structure acts as a catalyst for the synthesis of methanol by hydrogenation of CO_2. The 1D quantum confinement effect leads to a larger d band level in the RhW alloy-based nanosheet, while an electronic effect associated with the alloy mechanism results in a negatively charged Rh surface (Table 1).[364]

Electrochemical catalytic conversion of CO_2 to methanol using precious metal catalysts is another interesting approach to CO_2 reduction that can be made through the electrochemical pathway. In this regard, several electrocatalysts such as CuAu, CuPd, and AgZn were found to be excellent candidates for enhancing the CO, CH_4, and CH_3OH productions, respectively. In addition, palladium-based electrocatalysts have not received much attention despite Pd's exceptional ability to show low overpotentials for the electrochemical reduction of CO_2. In this case, when Pd is supported on carbon (Pd/C), the C added to metals improves their different properties by making them more active because carbon materials are porous. Additionally, we can use C materials with a high surface area and good electrical conductivity to stabilize high metal loadings and

enhance the electron transfer rate in both directions (from and to) of metal catalyst sites.

Similarly, Pd/C started producing formate at 0.00 V *vs.* RHE, with hydrogen being the only by-product (0.00 to −0.20 V *vs.* RHE).[388] So, the unwanted hydrogen evolution happens at the same time at Pd (supported on C) electrodes, along with the electrocatalytic reduction and hydrogenation of CO_2 to formate. However, the combination of Pd with Zn led to the formation of formate species that remain adsorbed on the PdZn alloy surface for long enough to be converted into CH_3OH. Another interesting study on Pd-based materials was reported by Han *et al.* Herein, the Pd combined with SnO_2, forming plentiful Pd–O–Sn interfaces, undergoes four-electron transfer mechanisms for selective CO_2 reduction to methanol.[389] This excellent design helped to achieve a faradaic efficiency (FE) of 54.8% ± 2% for CH_3OH at −0.24 V *vs.* RHE, and was able to deliver higher energy density as compared to sole Pd nanosheets (NSs) and SnO_2 nanoparticles. They also reported that the current densities of Pd/SnO_2 NSs didn't change much, and a high FE of 54% retains over 24 hours, indicating that it is more stable. This structure not only facilitated CO_2 adsorption on the SnO_2 surface, but also made it difficult for CO to remain on Pd due to the Pd–O–Sn interface weakening the binding strength of CO to Pd. In turn, enhancing Pd catalysts' CO_2RR performance is

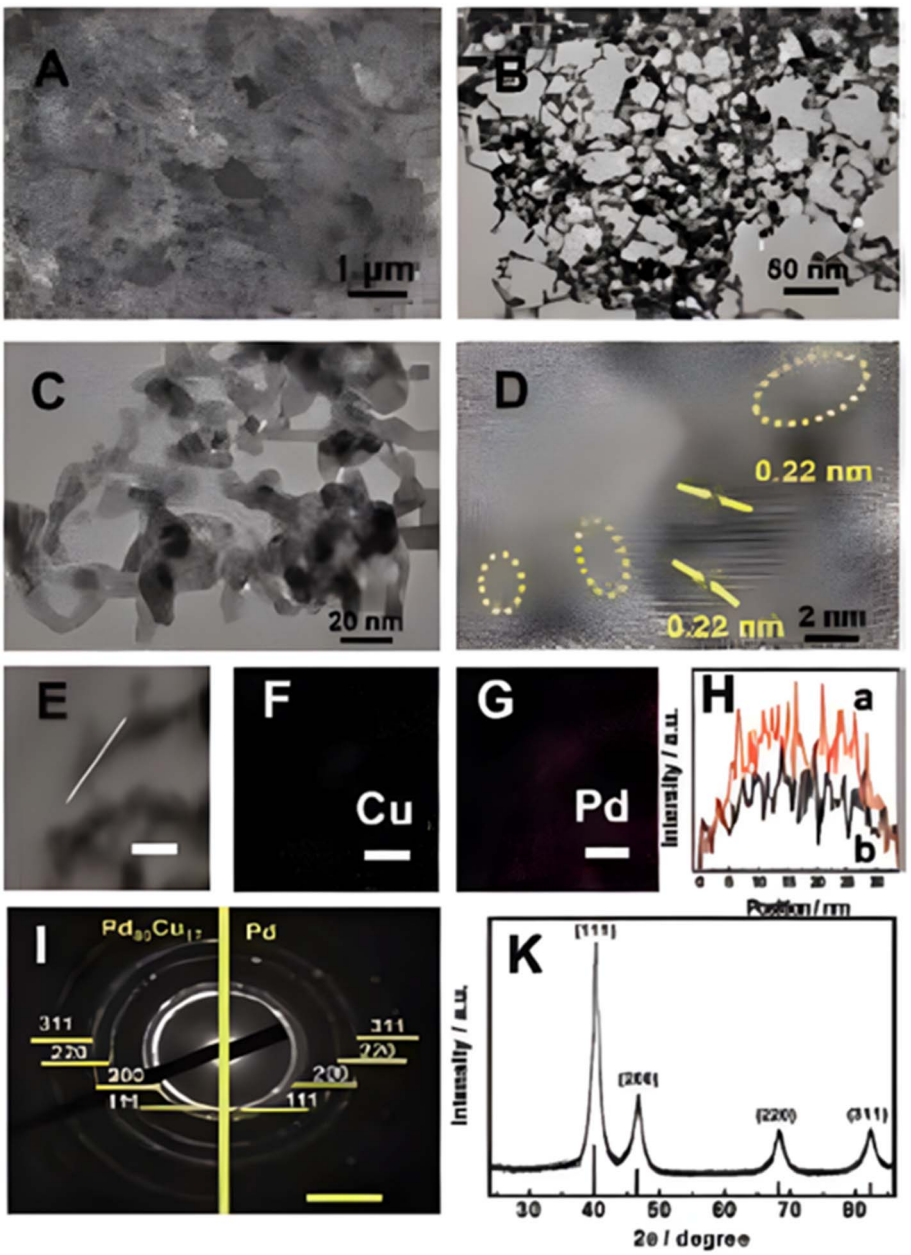

Fig. 15 (A) SEM, (B) and (C) TEM, (D) HR-TEM, and (E)–(G) EDX mapping images (scale bar: 20 nm). (H) Distribution of Pd (a) and Cu (b) in $Pd_{83}Cu_{17}$ by line-scan analysis. (I) SAED pattern of the $Pd_{83}Cu_{17}$ and pure Pd (scale bar: 10 1 nm@1). (K) XRD pattern of the $Pd_{83}Cu_{17}$ aerogel. Reprinted with permission from ref. 389 Copyright permission from 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

crucial in such a circumstance. Different types of electrochemical studies performed are given in Fig. 14.

Another excellent study was carried out by Buxing Han *et al.*;[389] they developed a Pd_xCu_y aerogel electrocatalyst and investigated it in a CO_2-saturated aqueous ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BmimBF_4) electrolyte containing 25 mol% [Bmim]BF_4 and 75 mol% water *via* a H-type cell. The characterization studies of that sample were carried out by SEM, TEM, HRTEM, SAED and XRD and the results are given in Fig. 15.

They achieved the highest Brunauer–Emmett–Teller (BET) surface area of 76.9 $m^2\ g^{-1}$ for $Pd_{67}Cu_{33}$ aerogels. This aerogel was capable of delivering FE efficiency for CH_3OH within the range of −1.9 V to −2.4 V (*vs.* Ag/Ag^+). It has been found that the proportion of Cu present in the aerogel also played a crucial role in the FE of CH_3OH. In a [Bmim]BF_4 aqueous solution with 25 mol% [Bmim]BF_4 and 75 mol% water, the FE for CH_3OH production for $Pd_{83}Cu_{17}$ is highest (80.0%) among others at −2.1 V (*vs.* Ag/Ag^+) after 5 hours of electrolysis. For this material, the results of the electrochemical characterization studies are given in Fig. 16.

Unlike Pd, the intermediate cannot be stabilized long enough for the reverse water-gas shift (RWGS) reaction to proceed without the intermediate first being decomposed to give CO and H_2O.[320]

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Here, we need to discuss the RWGS process. In general, an exothermic reaction occurs during the generation of methanol from carbon dioxide using a catalytic hydrogenation process. Numerous pilot plants have used this technical method, which combines the normal methanol synthesis process with the RWGS process.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O,\ \Delta H_{298} = -49.5\ kJ\ mol^{-1};\ \Delta G_{298}=3.30\ kJ\ mol^{-1}$$

$$CO_2+H_2 \rightarrow CO + H_2O,\ \Delta H_{298} = 41.2\ kJ\ mol^{-1};\ \Delta G_{298} = 28.6\ kJ\ mol^{-1}$$

$$CO_2+2H_2 \rightarrow CH_3H_3,\ \Delta H_{298} = -91\ kJ\ mol^{-1};\ \Delta G_{298} = 25.34\ kJ\ mol^{-1}$$

The water formation at the 2nd step inhibits the methanol synthesis through a catalytic way. Hence, the design of materials is important in which the metal's tolerance towards the water is essential. Brisard *et al.*, using differential electrochemical mass spectrometry, studied the electroreduction of carbon dioxide at a Pt porous electrode.[391] With their findings, it was demonstrated that a Pt electrodeposited electrode could be

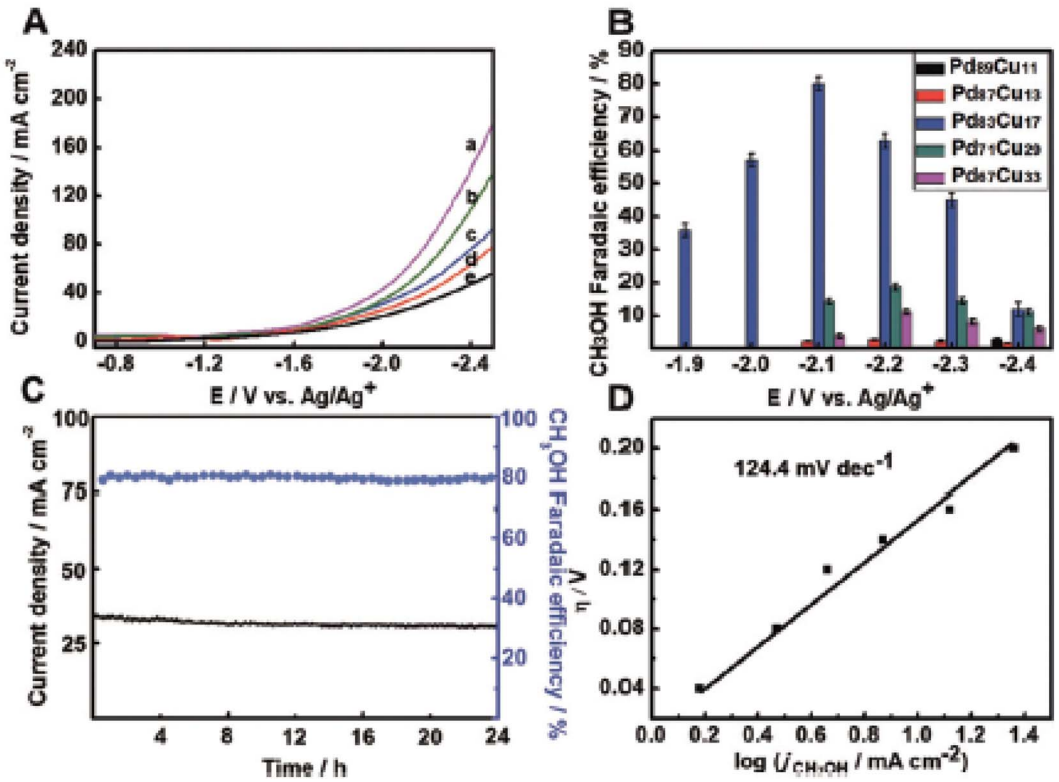

Fig. 16 The as performed CO_2 electroreduction reactions in ionic liquid [Bmim]BF_4 aqueous solution combined with 25 mol% [Bmim]BF_4 and 75 mol% water. (A) Different LSV curves for Pd_xCu_y aerogels are given such as: (a) $Pd_{67}Cu_{33}$, (b) $Pd_{71}Cu_{29}$, (c) $Pd_{83}Cu_{17}$, (d) $Pd_{87}Cu_{13}$, and (e) $Pd_{89}Cu_{11}$. (B) The FE for CH_3OH over Pd_xCu_y aerogels. (C) Current density and FE over $Pd_{83}Cu_{17}$ aerogel electrodes at @2.1 V *vs.* Ag/Ag^+. (D) Tafel plots for CH_3OH production over $Pd_{83}Cu_{17}$ aerogel electrodes. Reprinted with permission from ref. 389. Copyright permission from 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

used to produce CH_3OH in the presence of acidic media. These findings further indicated that CO was formed as an intermediate leading to the production of CH_3OH. As part of efforts to develop a reversible fuel cell based on CH_3OH, Shironita *et al.* recently studied the electroreduction of CO_2 on the carbon-supported Pt (Pt/C) and Pt–Ru (Pt–Ru/C) electrodes through a single cell. Faradaic efficiency estimates for the electroreduction of CO_2 range from 30–50%. They concluded that the reduction current decreases over time because of the accumulation of CH_3OH on the reaction active sites of the electrocatalyst (Pt/C). This is the reason the efficiency of yielding CH_3OH went from 0.03% at Pt/C compared to 7.5% in the case of Pt–Ru/C. Also, cyclic voltammetry measurements showed that the faradaic efficiencies of Pt/C and Pt–Ru/C were 35% and 75%, respectively. In addition to having a significant impact on the selectivity, reduction mechanisms, and efficiency of the CO_2 electroreduction process, the metal surface was also affected by a variety of other factors. In fact, it has been discovered that changing supporting electrolytes and operating circumstances has a significant impact on current density, product selectivity, and energy efficiency in CO_2 reduction even for the same metal electrode with the same purity.[392]

The binding energy of the reaction intermediates on the catalyst surface affects both the catalyst's reaction activity and selectivity. During the electrochemical reduction of CO_2, a complex reaction occurs that involves multi-electron transfers and a diverse array of intermediates and products, hence it is necessary to regulate the adsorption energy of the various intermediate species that are produced. In order to modify the binding energy of intermediates for desired end products, it is rational to create specialized surface structures.

6. Challenges and possibilities of CO_2 conversion

A diverse range of problems, along with intriguing prospects, exists for the conversion of CO_2 into frequently utilized formal products. Despite CO_2 being a plentiful and inexpensive source, its chemical inertness frequently makes conversion procedures energy-intensive and economically impractical at large scales. Recent advancements in catalysis, electrochemistry, and process engineering are generating new opportunities for effective CO_2 usage for methanol production (Fig. 17).

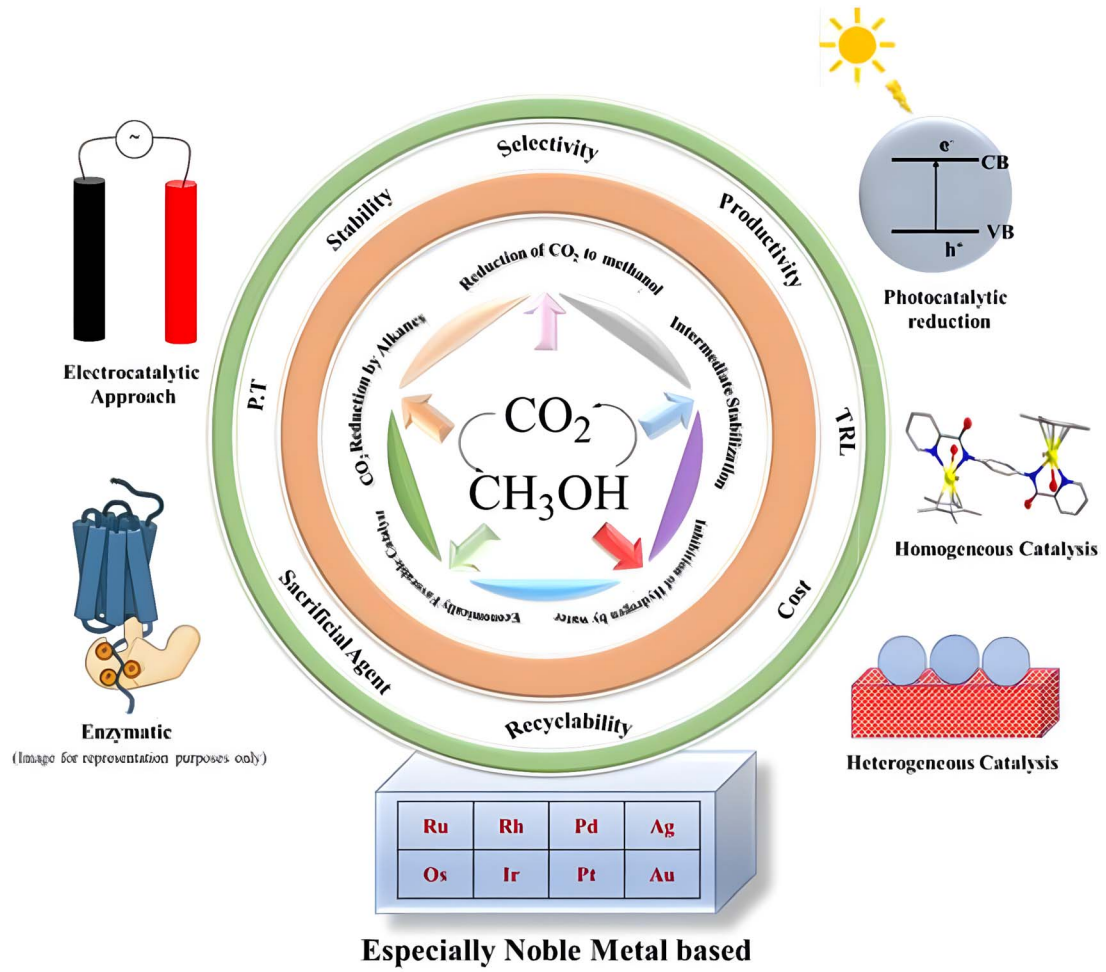

Fig. 17 Different Challenges and possibilities of CO_2 to methanol conversion (with various catalysts used).

(i) CO_2 is a linear, kinetically inert, nonpolar molecule with two opposite reactive sites, *i.e.*, carbonyl carbon has an electron-donating nature, and oxygen is an electron withdrawing species. Therefore, breaking the two double bonds present in the inert CO_2 molecule requires a higher energy, which poses the main challenge for the reduction of CO_2 to methanol.[257] The conversion of CO_2 to CO or other value-added products is facilitated using the metal surface catalysts.[258]

The methanol synthesis from CO_2 generates water as a byproduct, which directly influences the rapid sintering and deactivation of the Cu/ZnO catalyst. As a result, if the RWGS reaction occurs at a high temperature, it continues in an endothermic mode, and if it occurs at a lower temperature, it reduces the catalytic activity, which can be considered the main drawback of CO_2.[69,259,260]

(ii) Intermediate stabilization

In methanol synthesis from the hydrogenation of CO_2, controlling the intermediate stabilization is another critical challenge. CO is a crucial intermediate in the catalytic hydrogenation of methanol synthesis. From a thermodynamic perspective, the bonding between CO and the catalyst surface develops a stronger binding energy that increases the reaction rate of methanol or any other hydrocarbon synthesis process, while the bonding between the catalyst surface and CO initiates the RWGS reaction with weaker binding energy.[261] For methanol synthesis, controlling the stabilization of the intermediate, *i.e.*, CO, is crucial for increasing the yields.[123] DFT calculations and studies reveal that multiple factors influence catalytic properties. These include the key intermediate, oxygen adsorption energy, the relationship between catalyst structure and properties, and CO_2 adsorption phenomena. This understanding provides a novel approach for catalyst development.[393]

(iii) Inhibition of hydrogenation by water

The production of large amounts of water during the reduction of CO_2 by H_2 reduces the catalytic activity of the catalyst through the formation of hydroxyl. The main challenge of researchers is to develop a hydrothermal catalyst that resists catalyst poisoning. However, some research groups improved the catalytic activity of methanol production from CO_2 by using promising noble metals, primarily Pd, Pt-based microporous SiO_2-supported catalysts, and carbon shell-supported catalysts.[394,395]

(iv) Development of economically favorable catalysts

One of the challenges researchers face is developing a low-cost, economically advantageous catalyst with good recycling and reducible qualities that would produce large amounts of methanol from the CO_2 hydrogenation process.[396] Recently, some research groups developed a Mo_2C catalyst; however, this catalyst's main disadvantage is coke formation because, during the reaction, it binds firmly to intermediate hydrocarbons.[397]

(v) CO_2 reduction by alkanes

Researchers are trying to develop an alternative path for the reduction of CO_2. An alternate substance that can be used to reduce CO_2 might be light alkanes.[398] Although methane dry reforming can be employed as an alternative to hydrogen gas, researchers have observed that the catalyst rapidly loses effectiveness when exposed to elevated temperatures. But in the case of ethane, thermodynamically favorable conditions are available for CO_2 hydrogenation. In the near future, one of the hotspot research topics for energy engineering would be CO_2 reduction *via* light alkanes.[389]

7. Conclusion & future perspectives

This review emphasizes the use of noble metal-based catalysts for the hydrogenation of CO_2 to produce methanol. It is evident that several aspects of catalysts are important including promoters, support types, synthetic procedures, reaction circumstances, large surface area, and particle size, all of which must be taken into consideration to design catalysts to achieve higher performance.

The "Methanol Economy" offers a promising strategy for addressing global warming by utilizing CO_2 as a renewable energy resource. Methanol can serve as an energy storage medium, hydrocarbon feedstock, and alternative fuel. Various catalysts, including those based on noble metals, have been developed for the hydrogenation of methanol from CO_2. The conversion of CO_2 to methanol using heterogeneous and electrochemical catalysts holds industrial promise but faces significant challenges. Heterogeneous catalysts, such as noble metal-based systems, are advantageous due to ease of separation and recyclability but are hindered by mass transport and diffusion limitations. Electrochemical catalysts offer high selectivity and efficiency but require precise control of operating conditions and are sensitive to electrode materials and electrolytes. Nanostructured catalysts can enhance surface area and tunability, improving reaction rates and stability. However, scaling these technologies from lab to industry involves challenges in reactor design, mass transport, and heat management, essential for commercial viability. Addressing these issues is crucial for the success of CO_2 to methanol conversion technologies. The procedure's efficacy depends on understanding fundamental chemistry, catalyst characterization, and reactor characteristics. Researchers aim to develop dual-function promoters to improve CO_2 to CH_3OH conversion and reduce CO *via* the RWGS reaction. While noble metal-based catalysts show exceptional efficacy, their limited activity and high cost make them economically impractical. To commercialize CO_2-derived methanol synthesis, researchers need to integrate multiple elements into a single material or process. This may involve creating innovative materials that combine the catalytic abilities of noble metals with more abundant and cost-effective components, enhancing efficiency and reducing costs. Additionally, improving reactor designs to increase CO_2–catalyst interaction could further boost conversion rates and overall feasibility.

The hydrogenation of CO_2 to methanol, despite its limitations, offers promising pathways for sustainable fuel production. Although progress has been made in understanding reaction mechanisms and catalyst design, critical areas still require further research. This study establishes a foundation for sustainable fuel production methods, potentially reducing fossil fuel dependence. By identifying key areas for future research, it paves the way for advances in CO_2 utilization and catalyst design, which could significantly impact climate

change mitigation and the shift to sustainable energy. Priority areas include developing low-temperature reactive catalysts, optimizing reaction conditions and reactor designs, and employing guided rational catalyst design and synthesis. Future efforts may utilize advanced analytical techniques and computational methods to further elucidate reaction mechanisms. Bridging the gap between model catalysts and industrial-scale processing remains crucial for commercialization. The field shows promise through the development of novel materials, particularly noble metal-based catalysts, and the exploration of energy-efficient technologies. Ultimately, achieving sustainable methanol production from CO_2 hydrogenation will necessitate interdisciplinary collaboration and innovative strategies to overcome existing challenges, contributing significantly to global initiatives aimed at reducing atmospheric CO_2.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Soumalya Roy: conceptualization, investigation, data generation, and writing–original draft. Ezhava Manu Manohar: administration and data validation. Dr Sujoy Bandyopadhyay: administration and data validation. Dr Manik Chandra Singh: administration and data validation. Yeji Cha: administration and data validation. Dr Soumen Giri: writing and editing. Dr Sharad Lande: writing and editing. Dr Kyungsu Na: conceptualization, result validation, supervision, writing, editing, and methodology. Dr Junseong Lee: conceptualization, result validation, supervision, writing, editing, and methodology. Dr Sourav Das: conceptualization, result validation, supervision, writing, editing, and methodology.

Conflicts of interest

The authors declare no competing financial interest.

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