# **Catalytic Hydrogenation of Carbon Dioxide**

#### Subjects: Nanoscience & Nanotechnology

Contributor: Wan Nor Roslam Wan Isahak , Lina Mohammed Shaker , Ahmed Al-Amiery

Once fundamental difficulties such as active sites and selectivity are fully resolved, metal-free catalysts such as 3D graphene or carbon nanotubes (CNT) are very cost-effective substitutes for the expensive noble metals used for catalyzing  $CO_2$ . A viable method for converting environmental wastes into useful energy storage or industrial wealth, and one which also addresses the environmental and energy problems brought on by emissions of  $CO_2$ , is  $CO_2$  hydrogenation into hydrocarbon compounds. The creation of catalytic compounds and knowledge about the reaction mechanisms have received considerable attention. Numerous variables affect the catalytic process, including metal–support interaction, metal particle sizes, and promoters.  $CO_2$  hydrogenation into different hydrocarbon compounds like lower olefins, alcoholic composites, long-chain hydrocarbon composites, and fuels, in addition to other categories.

3D nanomaterial

carbon nanotube

graphene

catalyst

## **1. Introduction**

A common "Janus" type of molecule is carbon dioxide (CO<sub>2</sub>). Several issues, including the cost of the ligand and/or the base, remain unresolved when using ecologically desirable metals to reduce CO<sub>2</sub>. Hydrocarbons with oxygenated functional groups <sup>[1]</sup>, such as carbonylic (-CO-) <sup>[2]</sup> and alcoholic (-OH) groups, are known as oxygenated hydrocarbons (Oxy-HCs). Oxy-HCR has the potential to be a cleaner, more sustainable substitute for current fossil fuels. Steam reforming of mixtures of Oxy-HCs (Oxy-HCSR) is not thought to cause a net increase in atmospheric CO<sub>2</sub> because Oxy-HCs derived from biological/renewable resources are thought to be CO<sub>2</sub> neutral. In the semiconductor, precision machining, alcohol distillery, and biodiesel industries, oxy-HCs are typically obtained as waste byproducts [3]. Hydrocarbons are the principal constituents of petroleum and natural gas. They serve as fuels and lubricants as well as raw materials for the production of plastics, fibers, rubbers, solvents, explosives, and industrial chemicals. CO<sub>2</sub> is a stable compound and reactions with CO<sub>2</sub> are thus challenging. Nevertheless, there are various reaction pathways for CO<sub>2</sub> hydrogenation that are dependent on the nature of the catalyst, and a number of useful products can be obtained. Global climate change brought on by greenhouse gases has become a serious issue due to the continued use of fossil fuels, which has increased the amount of CO<sub>2</sub> in the atmosphere. Due to the continued increase in atmospheric CO<sub>2</sub> concentration (which exceeded 400 ppm in 2016), and its detrimental and potentially irreversible impact on the climate system, mitigation of CO<sub>2</sub> concentrations in the atmosphere is urgently needed [4]. Globally, there are plans and goals for this; the European Commission's goal is to achieve a reduction of 80–95% in greenhouse gas emissions by 2050 (compared to those of 1990) in order to achieve scientists' recommended reduction of at least 50% in global greenhouse gas emissions by 2050 [5]. China,

Brazil, and Korea, among other important international partners of Europe, are tackling these problems by advancing the "low carbon economy" <sup>[6]</sup>.

Currently, there are three approaches to minimize CO<sub>2</sub> emissions: by controlling CO<sub>2</sub> emissions, by capturing and storing CO<sub>2</sub>, and by chemically converting and utilizing CO<sub>2</sub> <sup>[Z]</sup>. Carbon storage is crucial for quickly reducing CO<sub>2</sub> emissions; however, it has the drawback of possible  $CO_2$  leakage <sup>[8]</sup>. As a substitute for other carbon sources,  $CO_2$ can be used to create feedstocks and value-added products that include carbon. In addition to providing a clean carbon supply for hydrogenation, using the CO<sub>2</sub> acquired through capture also helps to solve the leaking issue associated with CO<sub>2</sub> storage. The Sabatier reaction (CO<sub>2</sub> methanation) was therefore considered by the National Aeronautics and Space Administration (NASA) as a stage in recovering oxygen in closed-cycle life support systems [9]. It is possible to use even the CO<sub>2</sub> found in industrial exhaust gases directly as a feed for hydrogenation [10]. Therefore, it is essential and advantageous to make efficient use of renewable carbon resources in order to preserve the long-term and sustainable development of our civilization. Since CO<sub>2</sub> conversion needs energy input, pairing it with renewable energy would increase the sustainability and environmental friendliness of this technique. Electrocatalysis can be used to catalyze the reduction of  $CO_2$  <sup>[11]</sup>, as can photocatalysis <sup>[12]</sup> and thermal catalysis. Thermal catalysis stands out among these due to its quick kinetics and adaptable mixing of active ingredients. Being a very stable molecule, CO<sub>2</sub> requires energy just to be activated and then converted. The thermodynamics of the CO<sub>2</sub> conversion will be improved by the addition of a second material with a comparatively higher Gibbs energy. However, the fatal weakness of electrocatalysis and photocatalysis is low energy efficiency. To date, different types of metal-based electrocatalysts such as Au<sup>[13]</sup>, Cu<sup>[14]</sup>, Pd<sup>[15]</sup>, Ag<sup>[16]</sup>, Bi<sup>[17]</sup>, Sn<sup>[18]</sup>, and Co<sup>[19]</sup> have been intensively investigated in connection with electrochemical CO<sub>2</sub> reduction. Very recently, Chen et al. reported on the great importance of developing Au-based electrocatalysts with cost-effectiveness and high performance in order to commercialize  $CO_2$  reduction technology <sup>[20]</sup>. Among the materials examined by Brouzgou et al. in 2016, reduced graphene oxide-based hybrid electrocatalysts exhibit both excellent activity and long-term stability <sup>[21]</sup>. They concluded that the development of the electrocatalyst by using materials with three-dimensional structures facilitates the electron and mass transfer process.

 $CO_2$  is usually captured from high-concentration sources such as thermal power or chemical plants, steel mills, and cement factories. However, direct air capture (DAC) from the ambient air requires a separation unit to generate a concentrated  $CO_2$  stream <sup>[22]</sup>. Consequently,  $CO_2$  is hydrogenated with  $H_2$  created using sustainable energy sources <sup>[23]</sup>, and this is an exciting area of research that could yield chemicals and fuels as shown in **Figure 1** <sup>[24]</sup>.  $CO_2$  reacts over a catalyst with  $H_2$  produced from water using renewable energy <sup>[25]</sup> to produce formic acid <sup>[26]</sup>, lower olefins <sup>[27]</sup>, methanol <sup>[28]</sup>, and the higher alcohols <sup>[29]</sup>, etc. In certain studies, the presence of  $H_2$  was not detected, as reported by Sorcar et al. In 2019, in a study where researchers relied on natural sources, sunlight was used for a period of 6 h continuously (sustainable Joules) to recycle  $CO_2$  into Joules-hydrocarbon fuel with a photoconversion efficiency of 1% and an efficiency of quantity estimated at 86%. The researchers reported on the use of Cu-Pt nanoparticles (Cu-Pt NPs) for the photoreduction of  $CO_2$ . From this process, methane and ethane resulted in the proportions of 3 mmol g<sup>-1</sup> and 0.15 mmol g<sup>-1</sup>, respectively <sup>[30]</sup>. The former problem has received considerable attention, and researchers have already made significant strides in water electrolysis to produce  $H_2$  using electricity produced by solar, wind, or other renewable energy sources, as well as in water splitting using

photocatalytic, photo-electrochemical, or other photochemical processes. Density Functional Theory (DFT) calculations and experimental studies of the  $CO_2$  conversion mechanism and hydrocarbon chain formation have, however, received relatively little attention in reviews to date. Recent advances in catalytic performance and the conversion mechanism for  $CO_2$  hydrogenation into hydrocarbons that have been made both through experiments and DFT simulations are also discussed. The development of 3D nanomaterials and metal catalysts supported on 3D nanomaterials is important for  $CO_2$  conversion because of their stability and the ability to continuously support reverse transformation and Fischer–Tropsch catalysis (FT), in addition to the ability to reduce  $CO_2$  directly and hydrogenate it into oxygenated hydrocarbons.



Figure 1. CO<sub>2</sub> to be hydrogenated to produce chemical compounds and fuels.

### **2.** Characteristics and Applications of Carbon Nanotubesbased Catalyst

A variety of carbon bonds work to construct a new different structure of unique features. A layered structure with a weak out-of-plane van der Waals bond can be built by sp<sup>2</sup> hybridized carbon. The strong in-plane bonds play a major role in this purpose. A few to a few tens of concentric cylinders with regular periodic interlayer spacing locate around ordinary central hollow and made MWCNTs. The real-space analysis of multiwall nanotube images has shown a range of interlayer spacing (0.34 to 0.39 nm) <sup>[31]</sup>. It was discovered that CNTs had superior thermal transfer properties. For instance, it was discovered that CNTs had extraordinarily high axial thermal conductivities, around 2000 W/mK or more than 3000 W/mK for MWCNTs, and much higher for SWCNTs <sup>[32]</sup>, and it was found that CNT-in-polymer and CNT-in-oil suspensions had massively enhanced thermal conductivity. Even the short CNTs agglomeration, randomly entangled with one another, have been employed in earlier studies <sup>[33]</sup>. Then, on ceramic spheres, large-scale CNT arrays with millimeter vertical alignment have been constructed <sup>[34]</sup>. High-speed

shearing can easily spread them into fluffy CNTs. CNTs also demonstrated incredible catalytic uses [35]. Long CNTs (over 500 m) intercrossed Cu/Zn/Al/Zr catalyst (CD703) were produced in 2010 by dispersing CNT arrays of vertical alignment in Na<sub>2</sub>CO<sub>3</sub> fluid and co-precipitating with metal nitrite. When comparing Cu/Zn/Al/Zr catalytic compound without CNTs, the space time yield (STY) of methanol on CD703 rose by 7 and 8%, respectively, to 0.94 and 0.28 g/(g<sub>cat</sub> h) for CO and CO<sub>2</sub> hydrogenation. Additionally, dimethyl ether (DME) has been formed by one step CO and CO<sub>2</sub> hydrogenation with a STY of 0.90 and 0.077 g/(g<sub>cat</sub> h) at 270 °C when paired with y-Al<sub>2</sub>O<sub>3</sub> catalyst and HZSM-5. A CD703 catalyst exhibited great action with production of methanol as a result of phase separation, ions dopant, valence compensating, hydrogen reversibly adsorbent and storage on CNTs promoting hydrogen spillover. Since CNTs have higher thermal conductivity, CD703 has better stability. It was thus revealed that using Cu/Zn/Al/Zr catalytic compounds for the synthesis of methanol and DME from CO/CO<sub>2</sub> hydrogenation was wellpromoted by long CNTs [36]. Typically, bulk linked CNT constructions are used in the aerospace, automotive, robust electronics, and biomedical industries and have interesting properties [37]. It is still difficult to join CNTs at interconnects to form effective 3D constructions with a desired strength [38]. Spark plasma sintering (SPS) has been used under a range of pressure and temperature settings to synthesize bulk CNT linked structures. The interconnected 3D structures and the impact of processing conditions on structural damage to CNTs were examined with considerable detail using spectroscopic and microscopic techniques. Double-walled CNTs (DWCNTs) were produced in bulk by Guiderdoni et al., adopting SPS at 1100 °C and 100 MPa pressure <sup>[39]</sup>. According to reporting requirements, DWCNTs remained intact under those conditions. Extensive molecular dynamic simulations have been used to better study welding of CNTs that resulted in interconnected constructions. The Ozden team previously investigated how density and CNT structure are affected mechanically, electrically, and in terms of hydrophilicity (Figure 2) <sup>[40]</sup>. Al-Hakami et al. in 2013 investigated an approach to remove Escherichia coli (E. coli) bacteria from water using both naturally occurring CNTs and modified/functionalized CNTs containing 1-octadecanol groups (C18). As per their findings, E. coli was removed by CNT alone by 3-5%; however when paired with microwave radiation, unmodified CNT was able to remove up to 98% of bacteria. When CNT-C18 was employed in similar conditions, the bacteria had been removed by 100% [41]. Most textile wastewater is harmful and non-biodegradable. Semiconductor catalysts can be utilized to treat the environmental contamination.  $TiO_2$  is a significant photocatalyst; unfortunately, TiO<sub>2</sub> has a limited spectrum of light sensitivity and poor efficiency. However, TiO<sub>2</sub> and CNT together can boost photocatalytic activity <sup>[42]</sup>. Using MWCNT and Ti as source materials, Ming-liang et al. synthesized a CNT-TiO<sub>2</sub> composite in 2009 to accelerate the photocatalytic oxidation of water contaminants <sup>[43]</sup>. The composite's photoactivity was assessed through the conversion of methylene blue in liquid phase under UV radiation. Researchers came to the conclusion that the CNT-TiO<sub>2</sub> composite's ability to remove methylene blue is facilitating the transfer of electrons between MWCNT and TiO<sub>2</sub>, as well as MWCNT adsorption and TiO<sub>2</sub> photodegradation.



**Figure 2.** (a) Two CNTs are first arranged with their axes aligned at  $180^{\circ}$ . The atoms in red are heated from outside and are located at the contact tips of both tubes. (**b**–**e**). The tubes' final configuration following heating with heat fluxes of 1.0, 4.1, 4.3, and 5.4 kcal mol<sup>-1</sup> fs<sup>-1</sup>, respectively. Reprinted with permission from Ref. <sup>[40]</sup>. Copyright © 2016, John Wiley and Sons.

In 2016, Jauris et al. reported a relationship between SWCNTs and two artificial dyes (methylene blue and acridine orange) <sup>[44]</sup>. Because of  $\pi$ - $\pi$  interactions' prevalence between each dye and the nanotubes, the researchers reached a conclusion that long-term configuration stability was where the dye is generally plano-parallel to the nanotube. SWCNT is a prospective adsorbent for dye degradation and could be employed commercially for treating wastewater. By increasing the nanotube's radius, the dye-nanotube binding energy increases. In order to prepare Au-TiO<sub>2</sub>@CNT composite photocatalysts for photocatalytic gaseous styrene removal, Zhang W. et al. used a simple micro/nano-bubble approach <sup>[45]</sup>. High ternary-structure stability can be formed by reacting Au, and TiO<sub>2</sub> NPs coated onto CNTs can be efficiently facilitated by the micro/nano-bubbles. The response surface central composite design approach has been applied to examine Au-TiO<sub>2</sub>@CNTs' photoactivity. Rapid development of a compact structure increased the photocatalytic degradation and mineralization of styrene over Au-TiO<sub>2</sub>@CNTs was further disclosed through the examination of EPR, UV-vis DRS, electrochemical characteristics, and TPD-O<sub>2</sub>.

The further identification of free radicals revealed that oxidative radicals like hydroxyls and superoxides were closely related to the photocatalytic degradation and mineralization of styrene, which was primarily because of CNT and Au NP synergistic influence for increased activity through the photocatalysis process.

# 3. CO<sub>2</sub> Hydrogenation into Hydrocarbons and Oxygenated Hydrocarbons

Under certain conditions, it is thought that CO<sub>2</sub> catalytic hydrogenation with renewable hydrogen is an appropriate method for the chemical recycling of this hazardous and chemical resistance molecule into energy-carrying agents and chemical compounds. With a precise hydrogenation product, CO<sub>2</sub> can be hydrogenated into C<sub>1</sub> compounds like methane and methanol. It is more difficult to produce high  $(C_{2+})$  hydrocarbons and oxygenates on a selective basis. Due to its higher volumetric energy density within a specific volume and compatibility with the current fuel infrastructure than C<sub>1</sub> compounds, such produced materials are desirable as entry platform chemicals and energy vectors [46]. The main challenge is integrating catalytic functions as effectively as possible for both the reductive and chain-growth stages  $\frac{[47]}{2}$ . The transformation of renewable energy also makes use of CO<sub>2</sub> as an energy carrier. Because renewable energy sources are intermittent by nature, there is presently a need for scalable storage <sup>[48]</sup>. Consequently, a much more practical and easier method for storing significant volumes of intermittent energy generated from renewable sources for longer durations is the generation of synthetic natural gas or liquid fuels. The power to gas (PtG) concept has received considerable attention, as seen in Figure 3 [49]. An alternate source of natural gas is produced when CO<sub>2</sub> combines with H<sub>2</sub>, which is created by water electrolysis using renewable wind or solar energy. In Copenhagen, especially in 2016, a commercial-scale PtG project with 1.0 MW of capacity had been operating and successfully exploiting the transition to a sustainable energy system [50]. In the period 2003–2009, with capacities ranging from 25–6300 kW, there were five initiatives in Germany utilizing CO<sub>2</sub> methanation at pilot-plant or commercial scale <sup>[51]</sup>. The French chemist Paul Sabatier published his first study on CO<sub>2</sub> methanation in 1902 <sup>[52]</sup>. This age-old craft has gained fresh traction as a result of the growing need to combat global climate change and store excess renewable energy. The Sabatier reaction is an excellent method for converting CO<sub>2</sub> into chemical feedstocks and fuels, storing renewable energy sources like wind and solar energy, and efficiently converting biogas to biomethane <sup>[53]</sup>. CO<sub>2</sub> methanation is an endothermic reaction with higher equilibrium conversion between 25 and 400 °C [54]. By using the right catalysts, CO<sub>2</sub> methanation can achieve 99% CH<sub>4</sub> selectivity, avoid further product separation, and get around the challenges of dispersed product distribution. As a result, such a thermodynamic characteristic increases the importance of CO<sub>2</sub> methanation in terms of energy effectiveness and commercial viability.



**Figure 3.** Chemical compounds and fuels produced sustainably using  $CO_2$ . At various temperatures, the equilibrium conversion of  $CO_2$  to methane is plotted from the previous literature data.

In order to synthesize  $C_{2^+}$  hydrocarbons, Fujiwara et al. (2015) investigated CO<sub>2</sub> hydrogenation over composite catalytic compounds made of Cu-Zn-Al oxide catalyst and HB zeolite via combining the production of methanol over Cu-Zn-Al oxide and the simultaneous conversion of methanol over HB zeolite <sup>[55]</sup>. The yield of C<sub>2+</sub> hydrocarbons was low (0.5 C-mol%) and lower than that of oxygenated compounds when a non-modified zeolite was employed for the composite catalyst (methanol and dimethyl ether). For the conversion of dimethyl ether to C<sub>2+</sub> hydrocarbons, the strong acid sites of zeolite were severely inactivated. The catalytic activity of the associated composite catalysts was significantly enhanced by the use of zeolites treated with 1,4-bis(hydroxydimethylsilyl) benzene to create C<sub>2+</sub> hydrocarbons in yields of more than 7C-mol%. Under a pressure of 0.98 MPa, the best C<sub>2+</sub> hydrocarbon production selectivity was approximately 12.6 C-mol%. Hydrophobic zeolites with water contact angles more than 130° were created by the disilane modifications. The disilane molecule was converted into a few condensed aromatics during CO<sub>2</sub> hydrogenation at 300 °C, although the hydrophobicity was maintained even after the reaction. The hydrophobic surface of the HB zeolite inhibits the deactivation of the strong acid sites, increasing catalytic activity. Even under low pressure situations, this enhanced composite catalyst will support the synthesis of C<sub>2+</sub> hydrocarbons from CO<sub>2</sub>.

In 2017, Zhang et al. suggested a procedure to create ethanol from paraformaldehyde, CO<sub>2</sub>, and H<sub>2</sub> <sup>[56]</sup>. Under benign conditions, a ruthenium–cobalt (Ru-Co) bimetallic catalyst using LiI as the promoter in 1,3-dimethyl-2-imidazolidinone (DMI) may effectively speed up the process. Overall products had a selectivity of 50.9 C-mol% for ethanol, which was obviously higher than that of the disclosed methods. Additionally, the TOF for ethanol based on Ru metal reached a maximum of 17.9  $h^{-1}$  as seen in **Figure 4**.



**Figure 4.** Synergy between the processes used to fabricate ethanol from paraformaldehyde,  $CO_2$ , and  $H_2$ . The active species of Ru and Co are represented, respectively, by Ru\* and Co\*. Reprinted with permission from Ref. [56]. Copyright © 2017, Royal Society of Chemistry.

Significant information about the involvement of oxygen in the electrochemical reduction of CO<sub>2</sub> on Cu electrodes was presented in 2017 by Le Duff and colleagues. They also regulated the surface structure and composition of Cu single crystal electrodes over time <sup>[57]</sup>. Since the pulse sequence may be controlled to ensure consistent beginning conditions for the reaction at every fraction of time and at a certain frequency, this was accomplished using pulsed voltammetry. Compared to the selective CO<sub>2</sub> reduction achieved using cyclic voltammetry <sup>[58]</sup>, and chronoamperometric techniques <sup>[59]</sup>, under alternating voltage, a wide range of oxygenated hydrocarbons was discovered. The coverage of oxygen species, which is reliant on surface structure and potential, was linked to product selectivity towards the synthesis of oxygenated hydrocarbon. A nanowire-like WSe<sub>2</sub>-graphene catalyst was created by Ali and Oh in 2017 and examined for its ability to photocatalytically convert CO<sub>2</sub> into CH<sub>3</sub>OH when exposed to UV-visible light. XRD, SEM, TEM, Raman, and XPS were used to further characterize the produced nanocomposite. Using gas chromatography (GCMS-QP2010SE), the photocurrent analysis was further evaluated for its photocatalytic reduction of CO2. The sacrificial agent (Na2S-Na2SO3) was added to WSe2-graphene nanocomposite to further increase the photocatalytic effectiveness, and it was discovered that this improved the photocatalytic efficiency, with the methanol output reaching 5.0278 mol  $g^{-1} h^{-1}$  [60]. In a different study, Biswas et al. (2018) reported using ultrasonic techniques to create a WSe<sub>2</sub>-Graphene-TiO<sub>2</sub> ternary nanocomposite  $\frac{61}{2}$ . According to estimates, the WSe<sub>2</sub>-Graphene-TiO<sub>2</sub> band-gap is 1.62 eV, which is adequate for the photocatalytic degradation when exposed to UV-visible light. For the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH, the photocatalytic capability of nanocomposites was examined. After 48 h, WSe2-G-TiO2 with an optimal graphene loading of 8 wt% shown high photoactivity, yielding a total CH<sub>3</sub>OH yield of 6.3262 mol  $g^{-1}$  h<sup>-1</sup>. The gradual synergistic relationship between the

WSe<sub>2</sub>-TiO<sub>2</sub> and graphene components in the heterogeneous system is what causes this exceptional photoreduction activity. Ethylene could be produced from CO<sub>2</sub> electroreduction; however, present systems are constrained by low conversion efficiency, slow production rates, and unstable catalysts. In contrast to a reversible hydrogen electrode (RHE), Dinh et al. (2018) found that a copper electrocatalyst at an abrupt reaction interface in an alkaline electrolyte converts CO<sub>2</sub> to ethylene with a 70% faradaic efficiency (FE) at a potential of -0.55 volts  $\frac{62}{2}$ . The activation energy barriers for CO<sub>2</sub> reduction and carbon monoxide (CO)-CO coupling are lowered by hydroxyl ions on or near the copper surface, and as a result, ethylene evolution begins at -0.165 volts versus an RHE in 10 molar potassium hydroxide virtually concurrently with CO generation. By sandwiching the reaction interface between different hydrophobic and conductive supports, a polymer-based gas diffusion layer was introduced to increase operational stability while maintaining continuous ethylene selectivity over the first 150 operating hours. In 2019, Ma and Porosoff proposed reaction mechanisms by combining in situ characterization techniques with DFT calculations, identifying structure-property relationships for the zeolite support, strategizing methods to increase catalyst lifetime, and developing advanced synthesis techniques for depositing a metal-based active phase within a zeolite for highly active, selective, and stable tandem catalysts <sup>[63]</sup>. The critical research topics of reaction mechanism elucidation by combining in situ characterization methods with density functional theory calculations, identifying structure-property relationships for the zeolite support, developing advanced synthesis techniques for depositing a metal-based active phase within a zeolite for highly active, selective, and stable tandem cations, and strategizing methods to extend catalyst lifetime, are suggested as future research directions. An appealing method for storing such a renewable energy source in the form of chemical energy is the conversion of CO<sub>2</sub> into hydrocarbons using solar energy. A system that couples a photovoltaic (PV) cell to an electrochemical cell (EC) for CO<sub>2</sub> reduction can do this. Such a system should have minimum energy losses related to the catalysts at the anode and cathode, as well as the electrolyzer device, in order to be advantageous and usable. It should also use inexpensive and easily processed solar cells. All of these factors were taken into account by Huan et al. in 2019 when setting up a reference PV-EC system for  $CO_2$  reduction to hydrocarbons <sup>[64]</sup>. Combined with a fairly priced, state-of-the-art perovskite photovoltaic minimodule, this system sets a standard for a low-cost, all-earth-abundant PV-EC system with a solar-to-hydrocarbon efficiency of 2.3%. In 2019, Wu et al. demonstrated cobalt phthalocyanine (CoPc) catalysis for the six-electron reduction of CO<sub>2</sub> to methanol with considerable activity and selectivity when immobilized on CNTs  $\frac{65}{2}$ . They discovered that the conversion produces methanol with FE > 40% and a partial current density exceeding 10 mm/cm<sup>2</sup> at -0.94 volts with respect to the reversible hydrogen electrode in a near-neutral electrolyte. CO serves as an intermediary in a special domino mechanism that moves the conversion along. By adding amino substituents that donate electrons to the phthalocyanine ring, it is possible to prevent the harmful reduction of the phthalocyanine ligand from having a negative effect on the catalytic activity. With significant activity, selectivity, and stable performance for at least 12 h, the enhanced molecule-based electrocatalyst converts CO<sub>2</sub> to methanol.

A novel multifunctional catalyst made of  $Fe_2O_3$  encapsulated in  $K_2CO_3$  was introduced by Ramirez et al. in 2019 and has the ability to use a tandem process to convert  $CO_2$  into olefins <sup>[66]</sup>. The authors established that, unlike the conventional systems in FT processes, very large K loadings are essential to activate  $CO_2$  via the well-known "potassium carbonate mechanism." While utilizing  $CO_2$  as a feedstock, the suggested catalytic process proved to

be just as productive as currently used commercial synthesis gas-based techniques. By employing Cu-doped MgAl<sub>2</sub>O<sub>4</sub> (Mg<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>) and a straightforward deposition–reduction process, Tada et al. in 2020 investigated the synthesis of Cu NPs. The following three Cu<sup>2+</sup> species were present in Mg<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> <sup>[67]</sup>: short O-Cu octahedrally coordinated [CuO<sub>6</sub>]<sub>s</sub>, elongated O-Cu octahedrally coordinated [CuO<sub>6</sub>]<sub>el</sub>, and tetrahedrally coordinated [CuO<sub>4</sub>]<sub>t</sub>. The first two were discovered in Mg<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> of the normal-spinel type. In addition, they made it clear that their percentage is related to Cu loading by concentrating on the variation in the reducibility of the Cu<sup>2+</sup> species. Mg<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> predominantly comprised the [CuO<sub>6</sub>]<sub>s</sub> species at low Cu loading (x < 0.3). In contrast, the fraction of the [CuO<sub>6</sub>]<sub>el</sub> and [CuO<sub>4</sub>]<sub>t</sub> species rose with high Cu loading (x ≥ 0.3). Notably, the H<sub>2</sub>-reduced Mg<sub>0.8</sub>Cu<sub>0.2</sub>Al<sub>2</sub>O<sub>4</sub> (x = 0.2) catalyst showed the best photocatalytic activity among the synthesized catalysts because it had the most exposed metallic Cu sites. Therefore, the formation of metallic Cu NPs on metal oxides depends on the H<sub>2</sub> reduction of [CuO<sub>6</sub>]<sub>s</sub>.

In 2021, Tada et al. suggested bifunctional tandem  $ZnZrO_x$  catalysts for the hydrogenation of  $CO_2$  to methanol along with a number of solid acid catalysts (for subsequent methanol conversion to light olefins) <sup>[68]</sup>. Researchers used zeolites and silicoaluminophosphates with a variety of topologies, including MOR, FER, MFI, BEA, CHA, and ERI, as solid acid catalysts. A study using ammonia adsorption revealed that they likewise displayed the equivalent acid characteristics. Lower olefins were being synthesized in one step using the tandem catalysts, whereas with  $ZnZrO_x$  alone, no hydrocarbons could be produced. There appears to be no relationship between product yields and acid strength, at least according to the reaction test and ammonia adsorption. The product selectivity is influenced by the pore sizes and the channel dimensionality of the zeolites; zeolites with small pores, like MOR, SAPO-34, and ERI, are promising, whereas zeolites with bigger pores, like MFI, generate heavier hydrocarbons. The outcomes offer fresh perspective on the creation of creative catalysts for CO<sub>2</sub> usage. A low-temperature atmospheric surface dielectric barrier discharge reactor that converts biogas into liquid chemicals was introduced by Rahmani et al. in 2021 <sup>[69]</sup>. The effect of steam on the conversion of methane and  $CO_2$  was investigated, as well as the distribution of products in relation to a given energy input based on the operational circumstances. The authors reported conversion rates of 44% for  $CH_4$  and 22% for  $CO_2$ . When steam was introduced at the in-feed, the lowest energy cost of 26 eV/molecule was attained. For liquid hydrocarbons, a selectivity of 3% was attained. The transformation of biogas (CH<sub>4</sub> + CO<sub>2</sub>) resulted in the production of more than 12 compounds. At ambient temperature, the most prevalent oxygenated hydrocarbon liquids were acetone, methanol, ethanol, and isopropanol.  $H_2$ , CO,  $C_2H_4$ , and  $C_2H_6$  were the major gases produced.

In order to explain an alternative approach for the chemical  $CO_2$  reduction reaction, Islam et al. in 2021 subjected up to 3%  $CO_2$ -saturated pure water, NaCl, and artificial seawater solutions to high-power ultrasound (488 kHz ultrasonic plate transducer) <sup>[70]</sup>. The converted  $CO_2$  products under ultrasonic settings were discovered to be mostly  $CH_4$ ,  $C_2H_4$ , and  $C_2H_6$ , as well as a significant amount of CO that was later converted into  $CH_4$ . The analysis revealed that adding molecular  $H_2$  to the  $CO_2$  conversion process is essential, and that raising the hydrogen concentration boosted hydrocarbon yields. However, it was found that the overall conversion decreased at higher hydrogen concentrations because hydrogen, a diatomic gas, is known to reduce cavitation activity in liquids. Additionally, it was discovered that the maximum hydrocarbon yields (nearly 5%) were achieved with 1.0 M NaCl solutions saturated with 2%  $CO_2$  + 98%  $H_2$ , and that increasing salt concentrations further decreased the yield of hydrocarbons due to the combined physical and chemical effects of ultrasound. By diluting the flue gas with hydrogen, it was demonstrated that the CO<sub>2</sub> present in a synthetic industrial flue gas (86.74% N<sub>2</sub>, 13.5% CO<sub>2</sub>, 0.2% O<sub>2</sub>, and 600 ppm of CO) could be transformed into hydrocarbons. Additionally, it has been demonstrated that the conversion process can be carried out in ambient circumstances, i.e., at room temperature and pressure, without the use of catalysts, when low-frequency, high-power ultrasound is used. Tian et al. in 2022 newly manufactured In<sub>2</sub>O<sub>3</sub>, MnO-In<sub>2</sub>O<sub>3</sub>, and MgO-In<sub>2</sub>O<sub>3</sub> catalysts using the co-precipitation method, and they looked into the hydrogenation of  $CO_2$  to methanol [71]. The ability of  $In_2O_3$  to absorb  $CO_2$  was significantly improved by the addition of Mn and Mg oxides. The CO<sub>2</sub> adsorption capacity and the changing trend of methanol selectivity were consistent. As opposed to In<sub>2</sub>O<sub>3</sub>, the methanol selectivity of MnO-In<sub>2</sub>O<sub>3</sub> and MgO-In<sub>2</sub>O<sub>3</sub> catalysts is higher. ODP, or oxidative dehydrogenation of propane with  $CO_2$ , is a promising solution for efficient  $CO_2$  usage. In a new study published in 2022, Chernyak et al. included various C-materials for the first time as supports for Cr-based catalysts of CO<sub>2</sub>-assisted ODP <sup>[72]</sup>. A commercially available activated carbon was evaluated alongside CNTs, jellyfish-like graphene nanoflakes, and their oxidized and N-doped derivatives. The oxidized CNT- and pure GNF-supported catalysts showed the highest activity and a propylene yield of up to 25%. Raman spectroscopy was used to confirm that these two catalysts were stable throughout tests against disintegration and particle sintering. The oxidized CNT- and pristine graphene nanoflakes-supported catalysts' high activity and durability were explained by their macro- and mesoporosity, which improve reagent and product diffusion, as well as by the highest surface graphitization degree, which was validated by XPS. These catalysts performed significantly better than the catalyst supported by activated carbon. As a result, CNTs and graphene nanoflakes are suitable supports for CO<sub>2</sub>-ODP catalytic compounds. Several main catalysts used in the hydrogenation of CO<sub>2</sub> to hydrocarbon were summarized in Table 1.

Catalysts	Metal/Metal- free	Preparation Method	Process Type	Conversion	Selectivity
Cu-Zn-Al oxide and HB zeolite	Metal	Co-precipitation method	The production of $C_{2+}$ hydrocarbons by $CO_2$ hydrogenation.	2.8%	12.6 C- mol%
Ru-Co	Metal	-	The production of ethanol from paraformaldehyde, CO <sub>2</sub> , and H <sub>2</sub>	-	50.9 C- mol%
WSe <sub>2</sub> -graphene	Metal	Ultra-sonication method	Photocatalytic reduction of CO <sub>2</sub> into CH <sub>3</sub> OH	5.0278 µmol g <sup>-1</sup> h <sup>-1</sup> .	-
WSe <sub>2</sub> -graphene- TiO <sub>2</sub>	Hybrid	Ultra-sonication method	CO <sub>2</sub> reduction to CH <sub>3</sub> OH	6.3262 µmol g <sup>-1</sup> h <sup>-1</sup>	-
hydroxide- mediated Cu	Metal	Hydroxide- mediated abrupt reaction interface	CO <sub>2</sub> conversion to ethylene	70%	65%

Table 1. Some of the main catalysts used in the hydrogenation of CO<sub>2</sub> to hydrocarbon products.

Catalysts	Metal/Metal- free	Preparation Method	Process Type	Conversion	Selectivity
CoPc/CNT	Hybrid	CO <sub>2</sub> reduction to methanol	Dispersion process	40%	-
Fe <sub>2</sub> O <sub>3</sub> @K <sub>2</sub> CO <sub>3</sub>	Metal	CO <sub>2</sub> conversion to olefins	Mortar mixing	40%	60%

benign, nevertheless, because of the increased stability and inertness of  $CO_2$ , this reaction is thermodynamically constrained. The reaction below reveals the process of methanol production.

$$\mathrm{CO}_2 + 3\mathrm{H}_2 \leftrightarrow \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O} \;, \; \Delta \mathrm{H}_{25\ ^\circ\mathrm{C}} = -49.5 \; \mathrm{kJ} \cdot \mathrm{mol}^{-1}$$
(1)

The reaction is thermodynamically advantageous at low temperatures and high pressure, according to the Le Chatelier's principle. The enhanced thermal stability and chemical inertness of  $CO_2$  means that this method of methanol synthesis requires a high temperature to proceed. Indeed, at elevated reaction temperatures (for example, higher than 240 °C),  $CO_2$  activation and subsequent methanol production are facilitated. However, the higher temperature procedure strongly conflicts with the reaction's thermodynamics. Furthermore, when the reaction is conducted at a higher temperature, undesired byproducts including higher alcohols and hydrocarbons are formed. Similar to this, because the  $CO_2$  hydrogenation process produces methanol, which is a molecular reducing reaction, it is thermodynamically more advantageous at high pressure. By employing various catalysts, various reaction pressure sizes have been suggested for the best  $CO_2$  conversion <sup>[46]</sup>.

#### References

- 1. Ma, R.; Xu, B.; Zhang, X. Catalytic partial oxidation (CPOX) of natural gas and renewable hydrocarbons/oxygenated hydrocarbons—A review. Catal. Today 2019, 338, 18–30.
- Hasan, S.Z.; Ahmad, K.N.; Isahak, W.N.R.W.; Pudukudy, M.; Masdar, M.S.; Jahim, J.M. Synthesis, Characterisation and Catalytic Activity of NiO supported Al2O3 for CO2 Hydrogenation to Carboxylic Acids: Influence of Catalyst Structure. IOP Conf. Ser. Earth Environ. Sci. 2019, 268, 012079.
- 3. Palmeri, N.; Chiodo, V.; Freni, S.; Frusteri, F.; Bart, J.; Cavallaro, S. Hydrogen from oxygenated solvents by steam reforming on Ni/Al2O3 catalyst. Int. J. Hydrogen Energy 2008, 33, 6627–6634.
- 4. Kahn, B. Earth's CO2 Passes the 400 PPM Threshold—Maybe Permanently. Sci. Am. 2016. Available online: https://www.scientificamerican.com/article/earth-s-co2-passes-the-400-ppm-threshold-maybe-permanently/ (accessed on 1 November 2022).

- 5. Capros, P.; Tasios, N.; De Vita, A.; Mantzos, L.; Paroussos, L. Model-based analysis of decarbonising the EU economy in the time horizon to 2050. Energy Strat. Rev. 2012, 1, 76–84.
- 6. European Commission. A Roadmap for Moving to a Competitive Low Carbon Economy in 2050. COM(2011) 112 Final; European Commission: Brussels, Belgium, 2011; Volume 34, pp. 1–34.
- Dimitriou, I.; García-Gutiérrez, P.; Elder, R.H.; Cuéllar-Franca, R.M.; Azapagic, A.; Allen, R.W.K. Carbon dioxide utilisation for production of transport fuels: Process and economic analysis. Energy Environ. Sci. 2015, 8, 1775–1789.
- 8. Ma, X.; Wang, X.; Song, C. "Molecular Basket" Sorbents for Separation of CO2 and H2S from Various Gas Streams. J. Am. Chem. Soc. 2009, 131, 5777–5783.
- 9. Du, G.; Lim, S.; Yang, Y.; Wang, C.; Pfefferle, L.; Haller, G.L. Methanation of carbon dioxide on Niincorporated MCM-41 catalysts: The influence of catalyst pretreatment and study of steady-state reaction. J. Catal. 2007, 249, 370–379.
- 10. Duyar, M.S.; Treviño, M.A.A.; Farrauto, R.J. Dual function materials for CO2 capture and conversion using renewable H2. Appl. Catal. B Environ. 2015, 168–169, 370–376.
- 11. Lee, C.-Y.; Zhao, Y.; Wang, C.; Mitchell, D.R.G.; Wallace, G.G. Rapid formation of self-organised Ag nanosheets with high efficiency and selectivity in CO2 electroreduction to CO. Sustain. Energy Fuels 2017, 1, 1023–1027.
- 12. Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous Photocatalytic CO2 Conversion to Solar Fuels. ACS Catal. 2016, 6, 7485–7527.
- Welch, A.J.; DuChene, J.S.; Tagliabue, G.; Davoyan, A.R.; Cheng, W.-H.; Atwater, H.A. Nanoporous Gold as a Highly Selective and Active Carbon Dioxide Reduction Catalyst. ACS Appl. Energy Mater. 2019, 2, 164–170.
- 14. Xie, H.; Wang, T.; Liang, J.; Li, Q.; Sun, S. Cu-based nanocatalysts for electrochemical reduction of CO2. Nano Today 2018, 21, 41–54.
- Huang, H.; Jia, H.; Liu, Z.; Gao, P.; Zhao, J.; Luo, Z.; Yang, J.; Zeng, J. Understanding of Strain Effects in the Electrochemical Reduction of CO2: Using Pd Nanostructures as an Ideal Platform. Angew. Chem. Int. Ed. 2017, 56, 3594–3598.
- Ma, M.; Trześniewski, B.J.; Xie, J.; Smith, W.A. Selective and Efficient Reduction of Carbon Dioxide to Carbon Monoxide on Oxide-Derived Nanostructured Silver Electrocatalysts. Angew. Chem. Int. Ed. 2016, 55, 9748–9752.
- 17. Su, P.; Xu, W.; Qiu, Y.; Zhang, T.; Li, X.; Zhang, H. Ultrathin Bismuth Nanosheets as a Highly Efficient CO2 Reduction Electrocatalyst. Chemsuschem 2018, 11, 848–853.
- 18. Li, Q.; Fu, J.; Zhu, W.; Chen, Z.; Shen, B.; Wu, L.; Xi, Z.; Wang, T.; Lu, G.; Zhu, J.-J.; et al. Tuning Sn-Catalysis for Electrochemical Reduction of CO2 to CO via the Core/Shell Cu/SnO2 Structure.

J. Am. Chem. Soc. 2017, 139, 4290-4293.

- Hu, X.-M.; Rønne, M.H.; Pedersen, S.U.; Skrydstrup, T.; Daasbjerg, K. Enhanced Catalytic Activity of Cobalt Porphyrin in CO2 Electroreduction upon Immobilization on Carbon Materials. Angew. Chem. Int. Ed. 2017, 56, 6468–6472.
- 20. Chen, Q.; Tsiakaras, P.; Shen, P. Electrochemical Reduction of Carbon Dioxide: Recent Advances on Au-Based Nanocatalysts. Catalysts 2022, 12, 1348.
- Brouzgou, A.; Song, S.; Liang, Z.-X.; Tsiakaras, P. Non-Precious Electrocatalysts for Oxygen Reduction Reaction in Alkaline Media: Latest Achievements on Novel Carbon Materials. Catalysts 2016, 6, 159.
- 22. Alaba, P.A.; Abbas, A.; Daud, W.M.W. Insight into catalytic reduction of CO2: Catalysis and reactor design. J. Clean. Prod. 2017, 140, 1298–1312.
- 23. Centi, G.; Perathoner, S. CO2-based energy vectors for the storage of solar energy. Greenh. Gases Sci. Technol. 2011, 1, 21–35.
- 24. Porosoff, M.D.; Yan, B.; Chen, J.G. Catalytic reduction of CO2 by H2 for synthesis of CO, methanol and hydrocarbons: Challenges and opportunities. Energy Environ. Sci. 2016, 9, 62–73.
- 25. Gao, P.; Li, S.; Bu, X.; Dang, S.; Liu, Z.; Wang, H.; Zhong, L.; Qiu, M.; Yang, C.; Cai, J.; et al. Direct conversion of CO2 into liquid fuels with high selectivity over a bifunctional catalyst. Nat. Chem. 2017, 9, 1019–1024.
- 26. Song, H.; Zhang, N.; Zhong, C.; Liu, Z.; Xiao, M.; Gai, H. Hydrogenation of CO2 into formic acid using a palladium catalyst on chitin. New J. Chem. 2017, 41, 9170–9177.
- Visconti, C.G.; Martinelli, M.; Falbo, L.; Infantes-Molina, A.; Lietti, L.; Forzatti, P.; Iaquaniello, G.; Palo, E.; Picutti, B.; Brignoli, F. CO2 hydrogenation to lower olefins on a high surface area Kpromoted bulk Fe-catalyst. Appl. Catal. B Environ. 2017, 200, 530–542.
- Larmier, K.; Liao, W.-C.; Tada, S.; Lam, E.; Verel, R.; Bansode, A.; Urakawa, A.; Comas-Vives, A.; Copéret, C. CO2-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface. Angew. Chem. Int. Ed. 2017, 56, 2318–2323.
- 29. Bai, S.; Shao, Q.; Wang, P.; Dai, Q.; Wang, X.; Huang, X. Highly Active and Selective Hydrogenation of CO2 to Ethanol by Ordered Pd–Cu Nanoparticles. J. Am. Chem. Soc. 2017, 139, 6827–6830.
- Sorcar, S.; Hwang, Y.; Lee, J.; Kim, H.; Grimes, K.M.; Grimes, C.A.; Jung, J.-W.; Cho, C.-H.; Majima, T.; Hoffmann, M.R.; et al. CO2, water, and sunlight to hydrocarbon fuels: A sustained sunlight to fuel (Joule-to-Joule) photoconversion efficiency of 1%. Energy Environ. Sci. 2019, 12, 2685–2696.

- 31. Ajayan, P.M.; Ebbesen, T.W. Nanometre-size tubes of carbon. Rep. Prog. Phys. 1997, 60, 1025– 1062.
- Ruoff, R.S.; Lorents, D.C. Mechanical and thermal properties of carbon nanotubes. Carbon 1995, 33, 925–930.
- 33. Dong, X.; Zhang, H.-B.; Lin, G.-D.; Yuan, Y.-Z.; Tsai, K. Highly Active CNT-Promoted Cu–ZnO– Al2O3 Catalyst for Methanol Synthesis from H2/CO/CO2. Catal. Lett. 2003, 85, 237–246.
- 34. Huang, J.; Zhang, Q.; Zhao, M.; Wei, F. A review of the large-scale production of carbon nanotubes: The practice of nanoscale process engineering. Chin. Sci. Bull. 2012, 57, 157–166.
- 35. Schnorr, J.M.; Swager, T.M. Emerging Applications of Carbon Nanotubes. Chem. Mater. 2011, 23, 646–657.
- Zhang, Q.; Zuo, Y.-Z.; Han, M.-H.; Wang, J.-F.; Jin, Y.; Wei, F. Long carbon nanotubes intercrossed Cu/Zn/Al/Zr catalyst for CO/CO2 hydrogenation to methanol/dimethyl ether. Catal. Today 2010, 150, 55–60.
- Ozden, S.; Tiwary, C.S.; Hart, A.H.C.; Chipara, A.C.; Romero-Aburto, R.; Rodrigues, M.-T.F.; Taha-Tijerina, J.; Vajtai, R.; Ajayan, P.M. Density Variant Carbon Nanotube Interconnected Solids. Adv. Mater. 2015, 27, 1842–1850.
- 38. Ozden, S.; Narayanan, T.N.; Tiwary, C.S.; Dong, P.; Hart, A.H.C.; Vajtai, R.; Ajayan, P.M. 3D Macroporous Solids from Chemically Cross-linked Carbon Nanotubes. Small 2015, 11, 688–693.
- 39. Guiderdoni, C.; Estournes, C.; Peigney, A.; Weibel, A.; Turq, V.; Laurent, C. The preparation of double-walled carbon nanotube/Cu composites by spark plasma sintering, and their hardness and friction properties. Carbon 2011, 49, 4535–4543.
- 40. Ozden, S.; Brunetto, G.; Karthiselva, N.S.; Galvão, D.S.; Roy, A.; Bakshi, S.R.; Tiwary, C.S.; Ajayan, P.M. Controlled 3D Carbon Nanotube Structures by Plasma Welding. Adv. Mater. Interfaces 2016, 3, 1500755.
- Al-Hakami, S.M.; Khalil, A.B.; Laoui, T.; Atieh, M.A. Fast Disinfection of Escherichia coli Bacteria Using Carbon Nanotubes Interaction with Microwave Radiation. Bioinorg. Chem. Appl. 2013, 2013, 458943.
- 42. Khalid, N.; Majid, A.; Tahir, M.B.; Niaz, N.; Khalid, S. Carbonaceous-TiO2 nanomaterials for photocatalytic degradation of pollutants: A review. Ceram. Int. 2017, 43, 14552–14571.
- 43. Chen, M.-L.; Zhang, F.-J.; Oh, W.-C. Synthesis, characterization, and photocatalytic analysis of CNT/TiO2 composites derived from MWCNTs and titanium sources. New Carbon Mater. 2009, 24, 159–166.
- 44. Jauris, I.M.; Fagan, S.B.; Adebayo, M.A.; Machado, F.M. Adsorption of acridine orange and methylene blue synthetic dyes and anthracene on single wall carbon nanotubes: A first principle

approach. Comput. Theor. Chem. 2016, 1076, 42-50.

- 45. Zhang, W.; Li, G.; Liu, H.; Chen, J.; Ma, S.; An, T. Micro/nano-bubble assisted synthesis of Au/TiO2@CNTs composite photocatalyst for photocatalytic degradation of gaseous styrene and its enhanced catalytic mechanism. Environ. Sci. Nano 2019, 6, 948–958.
- 46. Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent advances in catalytic hydrogenation of carbon dioxide. Chem. Soc. Rev. 2011, 40, 3703–3727.
- 47. Wang, D.; Xie, Z.; Porosoff, M.D.; Chen, J.G. Recent advances in carbon dioxide hydrogenation to produce olefins and aromatics. Chem 2021, 7, 2277–2311.
- 48. Duyar, M.; Ramachandran, A.; Wang, C.; Farrauto, R.J. Kinetics of CO2 methanation over Ru/y-Al2O3 and implications for renewable energy storage applications. J. CO2 Util. 2015, 12, 27–33.
- 49. Mutz, B.; Carvalho, H.W.; Mangold, S.; Kleist, W.; Grunwaldt, J.-D. Methanation of CO2: Structural response of a Ni-based catalyst under fluctuating reaction conditions unraveled by operando spectroscopy. J. Catal. 2015, 327, 48–53.
- 50. Younas, M.; Kong, L.L.; Bashir, M.J.K.; Nadeem, H.; Shehzad, A.; Sethupathi, S. Recent Advancements, Fundamental Challenges, and Opportunities in Catalytic Methanation of CO2. Energy Fuels 2016, 30, 8815–8831.
- Rönsch, S.; Schneider, J.; Matthischke, S.; Schlüter, M.; Götz, M.; Lefebvre, J.; Prabhakaran, P.; Bajohr, S. Review on methanation—From fundamentals to current projects. Fuel 2016, 166, 276– 296.
- 52. Potocnik, P. Natural Gas; BoD–Books on Demand; IntechOpen: London, UK, 2010.
- 53. Thampi, K.R.; Kiwi, J.; Grätzel, M. Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure. Nature 1987, 327, 506–508.
- 54. Koschany, F.; Schlereth, D.; Hinrichsen, O. On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)x. Appl. Catal. B Environ. 2016, 181, 504–516.
- Fujiwara, M.; Satake, T.; Shiokawa, K.; Sakurai, H. CO2 hydrogenation for C2+ hydrocarbon synthesis over composite catalyst using surface modified HB zeolite. Appl. Catal. B Environ. 2015, 179, 37–43.
- 56. Zhang, J.; Qian, Q.; Cui, M.; Chen, C.; Liu, S.; Han, B. Synthesis of ethanol from paraformaldehyde, CO2 and H2. Green Chem. 2017, 19, 4396–4401.
- 57. Le Duff, C.S.; Lawrence, M.J.; Rodriguez, P. Role of the Adsorbed Oxygen Species in the Selective Electrochemical Reduction of CO2 to Alcohols and Carbonyls on Copper Electrodes. Angew. Chem. 2017, 129, 13099–13104.

- 58. Climent, V.; Feliu, J.M. Cyclic Voltammetry. In Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry; Elsevier: Amsterdam, The Netherlands, 2018; pp. 48–74.
- 59. Ezenarro, J.J.; Párraga-Niño, N.; Sabrià, M.; Del Campo, F.; Muñoz-Pascual, F.-X.; Mas, J.; Uria, N. Rapid Detection of Legionella pneumophila in Drinking Water, Based on Filter Immunoassay and Chronoamperometric Measurement. Biosensors 2020, 10, 102.
- 60. Ali, A.; Oh, W.-C. Preparation of Nanowire like WSe2-Graphene Nanocomposite for Photocatalytic Reduction of CO2 into CH3OH with the Presence of Sacrificial Agents. Sci. Rep. 2017, 7, 1867.
- Biswas, R.U.D.; Ali, A.; Cho, K.Y.; Oh, W.-C. Novel synthesis of WSe2-Graphene-TiO2 ternary nanocomposite via ultrasonic technics for high photocatalytic reduction of CO2 into CH3OH. Ultrason. Sonochem. 2018, 42, 738–746.
- Dinh, C.-T.; Burdyny, T.; Kibria, M.G.; Seifitokaldani, A.; Gabardo, C.M.; de Arquer, F.P.G.; Kiani, A.; Edwards, J.P.; De Luna, P.; Bushuyev, O.S.; et al. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 2018, 360, 783–787.
- 63. Ma, Z.; Porosoff, M.D. Development of Tandem Catalysts for CO2 Hydrogenation to Olefins. ACS Catal. 2019, 9, 2639–2656.
- Huan, T.N.; Corte, D.A.D.; Lamaison, S.; Karapinar, D.; Lutz, L.; Menguy, N.; Foldyna, M.; Turren-Cruz, S.-H.; Hagfeldt, A.; Bella, F.; et al. Low-cost high-efficiency system for solar-driven conversion of CO2 to hydrocarbons. Proc. Natl. Acad. Sci. USA 2019, 116, 9735–9740.
- 65. Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. Domino electroreduction of CO2 to methanol on a molecular catalyst. Nature 2019, 575, 639–642.
- Ramirez, A.; Ould-Chikh, S.; Gevers, L.; Chowdhury, A.D.; Abou-Hamad, E.; Aguilar-Tapia, A.; Hazemann, J.; Wehbe, N.; Al Abdulghani, A.J.; Kozlov, S.M.; et al. Tandem Conversion of CO2 to Valuable Hydrocarbons in Highly Concentrated Potassium Iron Catalysts. Chemcatchem 2019, 11, 2879–2886.
- 67. Tada, S.; Otsuka, F.; Fujiwara, K.; Moularas, C.; Deligiannakis, Y.; Kinoshita, Y.; Uchida, S.; Honma, T.; Nishijima, M.; Kikuchi, R. Development of CO2-to-Methanol Hydrogenation Catalyst by Focusing on the Coordination Structure of the Cu Species in Spinel-Type Oxide Mg1– xCuxAl2O4. ACS Catal. 2020, 10, 15186–15194.
- Tada, S.; Kinoshita, H.; Ochiai, N.; Chokkalingam, A.; Hu, P.; Yamauchi, N.; Kobayashi, Y.; Iyoki, K. Search for solid acid catalysts aiming at the development of bifunctional tandem catalysts for the one-pass synthesis of lower olefins via CO2 hydrogenation. Int. J. Hydrogen Energy 2021, 46, 36721–36730.
- 69. Rahmani, A.; Aubert, X.; Fagnon, N.; Nikravech, M. Liquid oxygenated hydrocarbons produced during reforming of CH4 and CO2 in a surface dielectric barrier discharge: Effects of steam on conversion and products distribution. J. Appl. Phys. 2021, 129, 193304.

- Islam, H.; Burheim, O.S.; Hihn, J.-Y.; Pollet, B. Sonochemical conversion of CO2 into hydrocarbons: The Sabatier reaction at ambient conditions. Ultrason. Sonochem. 2021, 73, 105474.
- 71. Tian, G.; Wu, Y.; Wu, S.; Huang, S.; Gao, J. Influence of Mn and Mg oxides on the performance of In2O3 catalysts for CO2 hydrogenation to methanol. Chem. Phys. Lett. 2022, 786, 139173.
- Chernyak, S.A.; Kustov, A.L.; Stolbov, D.N.; Tedeeva, M.A.; Isaikina, O.Y.; Maslakov, K.I.; Usol'Tseva, N.V.; Savilov, S.V. Chromium catalysts supported on carbon nanotubes and graphene nanoflakes for CO2-assisted oxidative dehydrogenation of propane. Appl. Surf. Sci. 2022, 578, 152099.

Retrieved from https://encyclopedia.pub/entry/history/show/90943