

Nanoreactor Engineering Can Unlock New Possibilities for CO₂ Tandem Catalytic Conversion to C–C Coupled Products

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Climate change is becoming increasingly more pronounced every day while the amount of greenhouse gases in the atmosphere continues to rise. CO₂ reduction to valuable chemicals is an approach that has gathered substantial attention as a means to recycle these gases. Herein, some of the tandem catalysis approaches that can be used to achieve the transformation of CO₂ to C–C coupled products are explored, focusing especially on tandem catalytic schemes where there is a big opportunity to improve performance by designing effective catalytic nanoreactors. Recent reviews have highlighted the technical challenges and opportunities for advancing tandem catalysis, especially highlighting the need for elucidating structure-activity relationships and mechanisms of reaction through theoretical and in situ/operando characterization techniques. In this review, the focus is on nanoreactor synthesis strategies as a critical research direction, and discusses these in the context of two main tandem pathways (CO-mediated pathway and Methanol-mediated pathway) to C–C coupled products.

sources and atmospheric air can be used as an alternative carbon source and can be coupled to green hydrogen and renewable energy to implement sustainable chemical production and minimize environmental impacts.^[4–6] Such processes are needed urgently and at great scales to lower CO₂ emissions associated with chemical production and establish a circular economy where carbon is recycled.^[7]

CO₂ capture and utilization (CCU) which involves the chemical conversion of captured CO₂ is a potential pathway to a low-emission industry.^[8] CCU is also appealing as a means to essentially recycle carbon in a circular economy. CO₂ could be an alternative feedstock for producing carbon-containing products and raw materials, many of which rely on

fossil hydrocarbons for their production at present. CO₂ is an abundant and geographically distributed carbon source that can be captured from industrial emission sources (such as cement manufacturing, and fossil-based power stations) or adsorbed from the air via direct air capture to produce chemicals with high added value.^[2,9,10] CCU can both offer revenue to incentivize lowering CO₂ emissions and provide a net-zero emission solution to replace fossil carbon which is used at present for the synthesis of the world's chemical products.^[11]


Many different CO₂ conversion technologies are under development, including thermochemical, biological, electrochemical, and photoelectrochemical methods.^[12] Among these approaches, thermochemical catalytic hydrogenation of CO₂ stands out as a mature technology with rapid kinetics and the potential for immediate deployment (if coupled with renewable energy-driven production of green hydrogen).^[7] Electrochemical, photochemical, and biochemical approaches are also highly promising emerging pathways for converting CO₂. Biological approaches such as algae growth have high operating costs but present the ability to produce long-chain (C₂–C₆) hydrocarbons with high selectivity.^[13] Other microorganisms such as *Scenedesmus obliquus*, *Chlorella vulgaris*, *Synechococcus elongates*, and *Synechocystis sp.* produce valuable carbon products (ethanol, biodiesel, isoprene, ethylene, etc.) using CO₂.^[14] Electrochemical approaches such as artificial photosynthesis and CO₂ electrolysis offer the advantage of directly using renewable electricity to drive reactions.^[15] However, there are substantial process development requirements that need to be considered in CO₂ utilization at scale, such as the reactor design for large-scale photochemical systems, improving the lifetime of electrochemical

1. Introduction

While the use of fossil fuels continues to dominate energy production, the atmospheric carbon dioxide (CO₂) concentration has exceeded 400 ppm, posing a great threat to our environment through climate change and ocean acidification.^[1,2] There is a constant increase in the concentration of CO₂ in the atmosphere and this is associated with negative and irreversible effects on the world's climate. The chemical industry uses fossil resources as sources of carbon and hydrogen and to supply energy to drive reactions, releasing large amounts of greenhouse gases (CO₂) in the process.^[3] As seen in **Figure 1**, CO₂ captured from industrial

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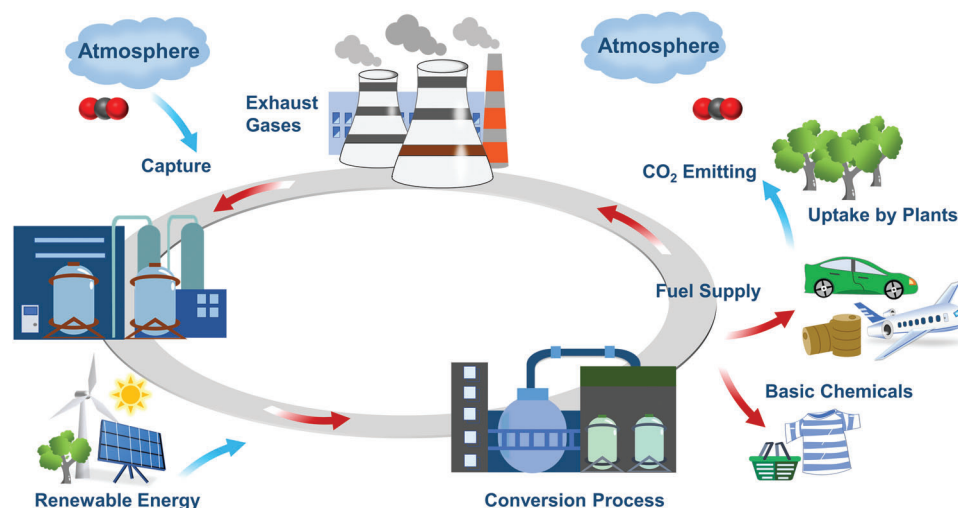


Figure 1. CO₂ Recycling circular economy.

catalysts, and controlling environmental conditions for biochemical systems.^[16] For example, changes on the catalyst surface in electrochemical reactions affect the stability of the system over time. These changes include contamination by metal impurities, surface poisoning by carbon species, and morphological changes of catalysts (dissolution, agglomeration, and coalescence of catalysts).^[17]

In this review, we focus on thermal catalysts for CCU applications and highlight nanoreactor design as an approach that can achieve high selectivity, conversion rate, and stability. Nanoreactors are tiny reaction vessels that can be used to catalyze and control chemical reactions at the nanoscale level. The nanoreactor approach can enable the development of tandem catalytic systems where CO₂ is converted into useful products such as fuels, chemicals, and other materials through multiple subsequent chemical transformations. In particular, nanoreactors can be envisioned as compartmentalized catalysts where CO₂ is first reduced to CO or methanol, and then, the product of this reduction (CO/methanol) then diffuses into a different compartment of the nanoreactor with a different catalytic site for subsequent transformation (e.g., to C–C coupled products). Nanostructuring to create a “nanoreactor” allows to control the access of specific molecules to specific catalytic sites, thus also enabling control over the local reaction environment. This is a powerful synthetic tool to improve activity and selectivity in tandem catalytic systems, due to the greater degree of flexibility offered in terms of controlling local environment of distinct catalytic sites working in tandem.

Thermochemical catalytic hydrogenation processes can convert CO₂ into single-carbon (C₁), or C–C coupled (C₂₊) products and they can be subject to lower barriers to increasing their technology readiness levels (TRL) compared to electrochemical and biological methods.^[12,18,19] Hydrogenation of CO₂ with H₂ from renewable energy sources not only offers a sustainable path to low or zero-emission chemicals production but a means to store variable renewable energy in the form of chemical bonds, in an approach termed “power-to-X” (where X is the chemical produced).^[7,20] There can be a lot of variations of this type of technology depending on what chemical (“X”) is targeted.^[21,22] The conversion of CO₂ to valuable products at an industrial scale

requires selective catalysts with stable long-term activity, and improved reactor and process technology.^[16,23] While hydrogen is currently produced by steam reforming of methane which is a CO₂ emitting method,^[24] projections indicate that green hydrogen produced by renewable energy-driven water electrolysis will become cost-competitive with fossil-derived hydrogen in the coming decades.^[25]

CO₂ hydrogenation has been explored for the production of lower olefins, higher hydrocarbons, formic acid, methanol, and higher alcohols.^[26–32] Today, only 4% of total CO₂ emissions are converted to chemicals (urea, methanol, salicylic acid, and organic carbonate).^[33,34] The conversion of CO₂ into liquid fuels such as methanol, gasoline, diesel, heating oil, or kerosene, can have a significant impact, as these products are responsible for 9Gt of CO₂ equivalent emissions, or 30% of the total CO₂ emitted today.^[35] Although there are many studies on the hydrogenation of CO₂ to chemicals, few of these developed technologies have been designed and implemented commercially. The largest facility in operation today is the facility in Reykjavik, Iceland, owned by Carbon Recycling International (CRI), which produces 4000 t/year of methanol from 5500 t/year of CO₂ conversion using heterogeneous catalysis and geothermal energy.^[36] The same group has also implemented a new commercial-scale project in Anyang city, Henan Province, China. Here, methanol production is planned with a capacity of 110 000 tons/year from CO₂ obtained from steel manufacturing.^[37] Finally, a methanol production facility was established in Niederaussem, Cologne, under the name of the pan-European MefCO₂ project (MefCO₂, 2020) producing 365 tons of methanol and capturing more than 550 tons of CO₂ annually.^[38]

The most mature CCU technologies are the synthesis of urea, methane, and methanol. Urea synthesis is the main source of CO₂ utilization and has been practiced for a long time. **Table 1** shows the location and operational parameters of some of the plants from around the world that produce urea from CO₂. Methanol synthesis using captured CO₂ and renewable H₂ is scaled up in the George Olah plant in Iceland and methanation of captured CO₂ is being practiced in Germany at a large scale for the synthesis of e-gas to power gas vehicles.^[39–42]

Table 1. Commercialized CCU plants for urea production, Reprinted with permission.^[39] Mitsubishi Heavy Industries.^[43,44]

Location	CO ₂ recovery capacity [metric ton/day]	Start of operation	Flue gas source
Kedah Darul Aman, Malaysia	160 (Max. 200)	October 1999	Natural gas-fired steam reformer flue gas
Fukuoka, Japan	283 (Max. 330)	October 2005	Natural gas and heavy oil-fired boiler flue gas
Aonla, India	450	December 2006	Natural gas-fired steam reformer flue gas
Phulpur, India	450	December 2006	Natural gas-fired steam reformer flue gas
Vijaipur, India	450	June 2012	Natural gas-fired steam reformer flue gas
Kakinada, India	450	March 2009	Natural gas-fired steam reformer flue gas
Bahrain	450	December 2009	Natural gas-fired steam reformer flue gas
District Ghotoki, Pakistan	340	2011	Natural gas-fired steam reformer flue gas
Phu My, Vietnam	240	2010	Natural gas-fired steam reformer flue gas
Perm, Russia	1200	2021 (Under Construction)	Natural gas-fired steam reformer flue gas
Polash, Narsingdi, Bangladesh	240	2023 (Under Construction)	Natural gas-fired steam reformer flue gas

Methanol is also very important in the chemical industry and is considered a solvent, raw material, and energy source of the future.^[45] Mixed metal oxides (Cu–ZnO–Al₂O₃), which are used to synthesize methanol industrially from mixed synthesis gas (CO/CO₂/H₂), show low yields and poor activity for CO₂/H₂ feeds due to the generation of significant quantities of water in the reaction.^[46] CO₂ methanation is also a mature process, and catalysis is carried out by using transition metals such as Co, Ni, Ru, Rh, and Pd. Co and Ni-based catalysts are preferred more than noble metals (Ru, Rh, Pd) due to their low cost.^[47,48] Ni-based catalysts are the most widely used industrially because they have high activity, high CH₄ selectivity, and earth abundance.^[49,50] In addition to these technologies, the production of synthesis gas (syngas), a mixture of carbon monoxide (CO), and H₂, from CO₂ is possible via the reverse water gas shift reaction (RWGS). Syngas is of interest as a product of CCU because commercial pathways^[51] from syngas exist for the production of a host of hydrocarbon products through the Fischer-Tropsch process.^[52–54]

Direct conversion of CO₂ to C–C coupled products in a single reactor is appealing due to the opportunity that offers in decarbonizing the broader chemical industry. It is very difficult to find active, selective, and stable catalysts in the production of olefins by the CO₂ hydrogenation reaction. This can be explained as follows: there are 3 ways to produce olefins from CO₂. These include 1) direct production with promoted catalysts; 2) methanol production followed by olefin synthesis (MeOH-mediated route); 3) CO production with RWGS followed by olefin synthesis with Fischer-Tropsch synthesis (FTS).

FTO, MeOH synthesis, and CO₂ methanation are exothermic while RWGS is an endothermic process. Accordingly, it is understood that lower temperatures favor FTO, MeOH synthesis, and methanation, but higher temperatures can achieve fast reaction rates. Tandem catalysis is recently being explored as a way of achieving higher selectivity at a lower cost through the efficient combination of reactions.^[1] The hydrogenation of CO₂ to C₂₊ hydrocarbons is very important because long-chain hydrocarbons have higher energy density and can be used as fuel or chemicals in different fields.^[55–57] In **Figure 2**, some preferred catalysts and reactions in fuel production from CO₂ are explained. There are two ways to hydrogenate CO₂ to hydrocarbons; these are direct

and indirect ways.^[58] One approach that has gathered much attention is the development of tandem catalysis schemes to diversify the processes for CO₂ utilization; these schemes combine catalysts with different functions to achieve a multistep conversion of CO₂ in the same reactor to products like olefins and alcohols. For the tandem approach to be selective, we need careful control of the microenvironment, selective access of certain molecules to specific active sites, and tunable placement and properties of active sites. Nanoreactors are materials that are structured to offer such controlled properties and catalytic behavior, which is the subject of this review, with a focus on their development for tandem catalytic conversion of CO₂ to chemicals. Tandem CO₂ conversion refers to the process of converting CO₂ into useful products in multiple steps or stages, where the products of one reaction are used as the reactants for subsequent reactions.^[59,60] Tandem reactions have the potential to achieve higher conversion rates and selectivities compared to single-step reactions, as well as to generate more valuable products.^[61] Tandem CO₂ conversion processes have been demonstrated in thermochemical as well as electrochemical approaches. One example of a thermochemical tandem catalytic CCU process is where CO₂ is first converted to CO via hydrogenation (RWGS), and then the CO further reacts on a separate catalytic site with hydrogen to produce hydrocarbons or other chemicals.^[62,63] In electrochemical approaches CO₂ reduction to CO can be achieved directly, without hydrogen feed.^[64–67] The resulting CO can be electrochemically converted into useful chemicals such as alcohols or olefins on a different active site of the catalyst.^[68,69]

Overall, tandem CO₂ conversion is a promising strategy for converting CO₂ into useful products and mitigating the negative effects of greenhouse gas emissions on the environment.

Recently, many researchers/research groups are discussing various aspects of tandem CO₂ conversion, including the design^[70] and optimization of catalysts,^[71] the identification of new reaction pathways and products, and the challenges associated with scaling up the processes.^[72,73] They also highlight the potential of tandem CO₂ conversion to contribute to the development of sustainable and low-carbon technologies.^[74,75]

Nanoreactor catalysts can offer superior performance and extended life over conventional catalysts for thermal CO₂ hydrogenation. Nanoreactor engineering refers to the design and

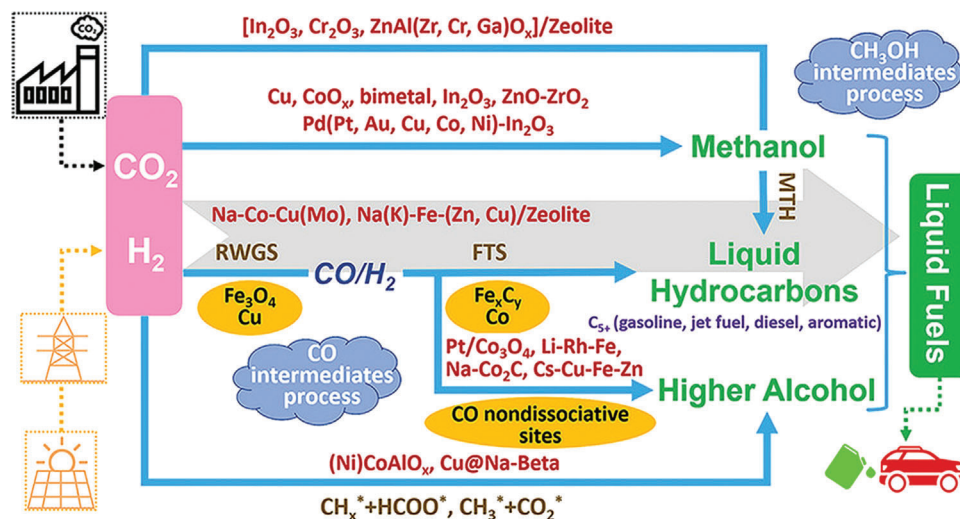


Figure 2. Summary schematic representation for the methods and catalysts used in the production of fuel from CO₂, Reproduced with permission.^[36] Copyright 2020, ACS Publications.

construction of nano-sized reactors that can be used for various chemical reactions, including CO₂ conversion.^[76] CO₂ conversion achieves the recycling of carbon dioxide into useful chemical products, such as fuels, chemicals, or materials.^[77,78] Nanoreactors can be used to enhance the efficiency and selectivity of CO₂ conversion reactions by providing a highly controlled environment for the reaction to take place.^[79]

Nanoreactors typically consist of a nano-sized container or cavity, which can be filled with a catalyst and/or reactant.^[80] The size and shape of the nanoreactor can be tailored to optimize the reaction conditions, such as temperature, pressure, and reactant concentration.^[81,82] In addition, the nanoreactor can be designed to enhance the interaction between the catalyst and reactants, improving the reaction efficiency and selectivity.^[83]

One approach to nanoreactor engineering for CO₂ conversion is the use of metal-organic frameworks (MOFs), which are porous materials made of metal ions and organic ligands.^[84,85] MOFs can be designed with specific pore sizes and structures, allowing for the precise control of reactant diffusion and reaction kinetics.^[86] They can also be functionalized with specific catalytic sites to enhance the reaction efficiency and selectivity.^[87] Another approach is the use of nanoparticles as catalytic sites within the nanoreactor. Nanoparticles can provide a high surface area for reactant adsorption and catalytic activity, and can be engineered with specific shapes and compositions to optimize the reaction conditions.^[88]

Overall, nanoreactor engineering offers a promising approach to CO₂ conversion, as it allows for the precise control of reaction conditions and catalytic activity, leading to improved efficiency and selectivity.^[89] Recent review articles highlight the uses of nanoreactor engineering for CO₂ conversion, focusing specifically on carbon-based systems, porphyrins, and yolk-shell structures, discussing recent advances and future prospects relevant to these syntheses.^[90–95] Herein we focus on applications relevant to tandem catalysis.

There are many advantages of using nanoreactors in CO₂ conversion, some of which can be explained as follows: 1) Increased catalytic efficiency: Nanoreactors can increase the catalytic effi-

ciency of CO₂ conversion by providing a high surface area for the catalyst to interact with CO₂. This can lead to higher reaction rates and improved product selectivity.^[94,96] 2) Precise control over reaction conditions: Nanoreactors can provide precise control over the reaction conditions, such as temperature, pressure, and pH, which can optimize the conversion process and improve product yield.^[97] 3) Reduction in energy requirements: Nanoreactors can reduce the energy requirements for CO₂ conversion by providing a confined reaction environment that can facilitate the reaction at lower temperatures and pressures.^[98] 4) Selective product formation: Nanoreactors can be designed to selectively convert CO₂ into specific products, such as methanol or other value-added chemicals, which can increase the economic viability of the process.^[99] 5) Versatility: Nanoreactors can be used for a variety of CO₂ conversion processes, including thermochemical, electrochemical, and photocatalytic reactions, allowing for a range of options for CO₂ conversion.^[100,101]

This review is aimed at presenting the current status of the development of nanoreactor catalysts for hydrocarbon production by thermal CO₂ hydrogenation. We begin by highlighting some promising CO₂ hydrogenation schemes and proceed to motivate the development of nanoreactor architectures that can achieve selective tandem catalytic conversion by employing some of these pathways.

2. High-Value Production Methods from CO₂ Conversion

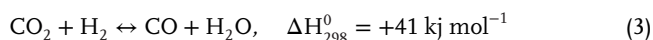
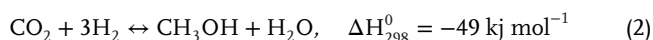
2.1. Two Step CO₂ Hydrogenation with RWGS + FTS

With thermochemical hydrogenation methods, CO₂ can be converted to one-carbon (C1) products such as methane (Equation (1)), methanol (Equation (2)), and carbon monoxide (Equation (3)) in a single-step process.^[102] It is possible to use the RWGS reaction (Equation (2)) as an initial step for conversion of CO₂ to C–C coupled products, by performing the FTS reaction

Table 2. Performance of selected catalysts for the RWGS reaction.

Catalyst	Temperature [°C]	Pressure [MPa]	CO ₂ conversion [%]	CO selectivity [%]	WHSV [mL _{g_{cat}} ⁻¹ h ⁻¹]	Reference
2% Pt/CeO ₂	225	N/A	13.7	99	N/A	[119]
Ru-Cu/ZnO/Al ₂ O ₃	500		47	100	100 000	[120]
K/Mn/Fe/ Al ₂ O ₃	300 °C	1.83	44.7	47.3	N/A	[121]
K-Mo ₂ C/γ-Al ₂ O ₃	450 °C	2.1	44	98	6120	[51]
Cu/β-Mo ₂ C	600 °C	0.1	44.7	99.2	300 000	[122]
1% Cu/β-Mo ₂ C	350 °C	0.1	11	40	300 000	[123]
Mo ₂ C/γ-Al ₂ O ₃	300 °C	2.1	5.9	87.8	N/A	[124]
%5 Ru/CeO ₂	350 °C	0.1	16	31	120 000	[125]
RuNi/CeZr	350 °C	0.1	53	93	24 000	[126]
FeNi/CeZr	350 °C	0.1	13	60	24 000	[126]
1 wt.% K-Mo ₂ C/γ-Al ₂ O ₃	300 °C	2.1	24.3	73.5	3060	[127]
%5 Ru/Sm-CeO ₂	350 °C	0.1	16	69	120 000	[125]
3.2% PtCo/CeO ₂	300 °C	0.1	9.1	92.3	N/A	[128]
Ni ₂ P/SiO ₂	650 °C	0.1	58	84	12 000	[129]
Mo-P-SiO ₂	750 °C	0.1	69.1	85.1	12 000	[130]
3.2% PtCo/TiO ₂	300 °C	0.1	8.2	98.8	N/A	[128]
2D(δ)-MnO ₂	850 °C	0.1	50	100	40 000	[131]

(Equation (4)) in tandem.^[58]



It is possible to perform CO₂ hydrogenation to CO followed by FTS in two reactors, where the first reactor would operate at high temperatures (200–600 °C) and intermediate pressure (0–20 bar) conditions^[103,104] for RWGS and the second (FTS) reactor is operated at a temperature of 200 to 300 °C and a pressure of 10 to 40 bar.^[105] Because RWGS is an endothermic reaction, high temperatures are required for high conversions.^[106,107] Tandem catalysis schemes seek to perform both RWGS and FTS reactions in a single reactor by coupling an RWGS catalyst with an FTS catalyst and operating at a range of conditions that compromise between the two reactions.^[104] A tandem catalyst required to produce C₂₊ products (light olefin, liquid fuel, or higher alcohol products) from CO₂ must be active for both RWGS and FTS under the same conditions to be effective.^[55,108] It is proposed that consumption of the product of RWGS (CO) by the FTS reaction can lead to additional synergies in operation.

2.2. Catalysts for the RWGS Reaction

Various catalytic materials have been used in research to carry out the RWGS reaction and several reviews have covered the development of these catalysts in recent years.^[109–112] Regarding the

noble metal-based catalysts, the most widely used are the supported Pt catalysts,^[113,114] which exhibit significant activity and selectivity for the hydrogenation of CO₂ to CO.^[110,115–118] **Table 2** contains details on CO₂ conversion and CO selectivity of some RWGS catalysts under certain reaction conditions.

Transition metal-based non-precious catalysts are desirable due to their abundance as raw materials, and low cost. Copper-based catalysts were found to be selective in the production of CO by RWGS reaction.^[132–139] Mo-based catalysts are also common for RWGS. In particular, Mo₂C is widely studied^[51,122,140,141] in many studies because they are active and selective in RWGS reactions.^[124] Potassium-promoted molybdenum carbide catalyst supported on γ-Al₂O₃ (K-Mo₂C/γ-Al₂O₃) was recently shown to achieve 40.5% CO₂ conversion and 98.2% CO selectivity at 2.1 MPa and 450 °C. The results of this study show that it is a low-cost, stable, and highly selective catalyst for RWGS reactions.^[127] It has also been shown that molybdenum phosphide is a suitable catalyst for the RWGS reaction, and preserves its chemical structure in hydrogen up to 950 °C, important for its stability.^[130] In addition, phosphite-containing catalysts showed high catalytic performance in studies such as dry reforming of methane (DRM), hydrodeoxygenation of guaiacol, and conversion of CO₂ by RWGS reaction.^[142–144] In a different study, Mo₂C also differentiated itself from other catalysts for CO₂ conversion, with its dual functionality for H₂ dissociation and C=O bond scission, and properties similar to reducible oxides.^[145]

2.3. Catalysts for FTS

The syngas is catalytically converted to higher hydrocarbons by FTS, which is then converted into clean fuels, oils, or chemicals. Ru,^[146] Ni,^[147] Fe,^[148] and Co^[149] catalysts are the most preferred active metals in FTS. However, active metals Fe and Co are used as commercial FTS catalysts.^[150] Co-based catalysts can be said to

Table 3. Catalysts for converting syngas into hydrocarbons via FTS.

Catalyst	Temperature	Pressure	Conversion			Selectivity			Reference
			CO	H ₂	CO ₂	CH ₄	C ₂ –C ₄	C ₅₊	
Co/ γ -Al ₂ O ₃	230 °C	20 Bar	52.4	58.3	13.1	15.2	8.7	76.1	[154]
CeCo/ γ -Al ₂ O ₃	230 °C	20 Bar	54.0	64.3	20.3	10.5	5.3	84.3	[154]
LaCo/ γ -Al ₂ O ₃	230 °C	20 Bar	61.5	66.7	21.9	9.7	5.5	84.8	[154]
CeLaCo/ γ -Al ₂ O ₃	230 °C	20 Bar	62.9	67.9	22.1	9.6	5.4	85.0	[154]
CoRu/ γ -Al ₂ O ₃	200 °C	20 Bar	20	-	-	10.6	-	74.3	[155]
Fe	350 °C	2MPa	90.04	-	-	24.46	8.04	20.56	[156]
FeAl	350 °C	2MPa	97.16	-	-	25.96	10.30	19.94	[156]
Fe–Cu–Mn/AC	300 °C	2MPa	98	-	-	24	30		[157]
Co/PGNS	220 °C	1.8 MPa	70.6	-	-	12.3		86.8	[158]

Table 4. Performance of some tandem catalysts for methanol-mediated CO₂ conversion to hydrocarbons.

Catalysts	Temperature [°C]	Pressure [MPa]	CO ₂ Conversion [%]	Selectivity [%]	Targeted Product	Reference
CuZnZr@(Zn)-SAPO-34	400	2	20	72	C ₂ –C ₄	[166]
ZnO/ZrO ₂ -ZSM-5	340	3	9	40	C ₂ –C ₄	[167]
ZnZrO/ZSM-5	320	4	14	73	Aromatics	[168]
ZnO–ZrO ₂ /H-ZSM-5	340	4	16	76	Aromatics	[169]
ZnCrOx-ZnZSM-5	320	5	19.9	81.1	Aromatics	[170]
Cr ₂ O ₃ /H-ZSM-5	350	3	34.5	75.9	Aromatics	[171]
Cr ₂ O ₃ /Zn-ZSM-5@SiO ₂	350	3	22.1	70.1	Aromatics	[172]

be the most suitable catalyst in gas-to-liquid conversion technologies due to their high efficiency and selectivity, low prices, as well as low WGS activities for syngas with a high H₂/CO ratio.^[151] However, Fe-based catalysts are preferred for low H₂/CO ratio syngas because these catalysts have high intrinsic selectivity for the WGS reaction.^[152] The reaction temperature has great importance in the selection of the catalyst. FTS catalysts are operated using cobalt-based or iron-based catalysts at low temperatures (220–260 °C) and using iron-based catalysts at medium temperatures (260–300 °C) or high temperatures (320–350 °C).^[153]

Table 3 contains some recent studies on iron, cobalt, lanthanum, copper, and manganese catalysts used for FTS, including catalyst type, reactant conversion, and product selectivity. Also, this table summarizes the reaction conditions, CO conversion, and CH₄, C₂–C₄, and C₅₊ fraction selectivity, as these reactants are important products from FT synthesis.

2.4. Two-Step CO₂ Hydrogenation with Methanol Synthesis (MS) + Methanol to Olefins (MTO)

In the methanol-based (CH₃OH) two-step conversion of CO₂, the hydrogenation of CO₂ to methanol is followed by a methanol-to-olefins (MTO) transformation. In the tandem catalytic process, first, CO₂ and H₂ are converted to CH₃OH (Equation (2)) on a partially reduced oxide surface (e.g., Cu, In, and Zn) or over noble metals.^[159]

When the studies carried out in recent years are examined, it is reported that direct conversion of CO₂ to hydrocarbons can be achieved in one reactor with a CH₃OH-mediated method

(**Table 4**). In₂O₃/HZSM-5 composite catalyst was shown in a study to perform much better for CO₂ hydrogenation with higher activity and higher selectivity towards hydrocarbons while comparing other metal oxides combined with HZSM-5 such as Ga₂O₃, Fe₂O₃, ZnO–Cr₂O₃, and ZnO–ZrO₂.^[160] According to these studies, H-ZSM-5 is active for hydrocarbon oligomerization, isomerization, and aromatization, and adjusting the acidity of H-ZSM-5, promotes the production of gasoline and aromatics. In the studies carried out, the selective production of gasoline has been made from zeolites such as H-ZSM-5, H-Y, H-beta, and H-MCM-22, while aromatics have been predominantly produced from H-ZSM-5 zeolites. As explained in the studies, the stronger Brønsted acidity of H-ZSM-5 supports the aromatization reaction, while the weaker acidity of H-beta or H-MCM-22 supports the isomerization reaction.^[161,162] The content of the final product can be adjusted by adjusting the acid strength and pore size of the zeolites. Oxygen cavities on the surface of In₂O₃ are proposed to activate CO₂ and hydrogen, resulting in the formation of methanol. Afterward, C–C coupling takes place in the zeolite pores, producing gasoline-grade high-octane hydrocarbons. The combination of these two components plays an important role in slowing down the unwanted RWGS reaction and providing a high selectivity for high-carbon fuels.^[160]

Lower reaction temperatures and higher reaction pressures positively affect the synthesis of CH₃OH. At the same time, these stated conditions have in some cases increased the formation of by-products such as formic acid, methane, and formaldehyde, and therefore a selective catalyst is required that is also stable under such conditions.^[163]

Hydrogenation of CO₂ based on the methanol (CH₃OH) reaction can be performed by combining two sequential reactions on a tandem catalyst.^[36] As mentioned earlier, CO₂ and H₂ are first converted to CH₃OH via a CO or formate pathway, either on the partially reduced oxide surface (e.g., Cu/ZnO/Al₂O₃, In₂O₃/ZrO₂) or noble metals.^[111] It is then dehydrated or combined with zeolites or alumina. Therefore, tandem catalysts are formed that can convert CO₂ into high-value C₂+ compounds, such as DME, light olefins, and gasoline. An effective catalyst to be used for these reactions must be active for both CH₃OH synthesis and dehydration/C–C coupling. In the C₂+ hydrogenation reactions of CO₂, the reactions of CO₂ to CH₃OH and CH₃OH to C₂+ compounds take place on bifunctional catalysts at 200–300 and 400 °C, respectively. Accordingly, it is necessary to investigate the reaction conditions, catalyst properties, and catalytic performance of the products CO₂ to CH₃OH and CH₃OH to C₂+

Considering the catalysts used for the synthesis of CH₃OH from the synthesis gas used on an industrial scale, Cu/ZnO/Al₂O₃ catalysts were widely studied.^[163] For the methanol-to-olefins step, medium porous zeolite/microporous materials are preferred to produce C₅–C₁₁ hydrocarbons, while small porous molecular sieves are preferred to produce C₂–C₄ hydrocarbons. ZSM-5 is commonly used for converting methanol to gasoline (MTG) and SAPO-34 molecular sieves for methanol to olefins (MTO).^[164,165] SAPO-34 molecular sieves are particularly preferred to achieve high selectivity in the production of light olefins.^[111]

2.5. Catalysts for Methanol Synthesis from CO₂

Recently, there have been significant developments involving copper (Cu)- and indium (In)-based catalysts for methanol synthesis.^[173,174] Cu catalysts (Cu/ZnO/Al₂O₃) are industrially used for the synthesis of methanol from CO₂/H₂ or syngas (CO/CO₂/H₂) under the operating conditions of 220–300 °C and 50–100 bar temperature and pressure, respectively.^[175,176] Also, Pt and Pd are effective, especially in the low-temperature and pressure synthesis of methanol from CO₂.^[132,133]

The Cu catalyst is one of the preferred catalysts of choice to produce methanol from CO₂. Because methanation is partially prevented by the reaction, the standard Cu/ZnO/Al₂O₃ catalyst is preferred in industrial methanol production. In a study using CuO/ZnO catalysts, filament-like ZnO and rod-like ZnO synthesized by the hydrothermal method were used as components. These newly developed catalysts were tested in the hydrogenation of CO₂ to methanol and compared with the CuO/ZnO catalyst prepared by the conventional method. The activities of these catalysts were found to be strongly dependent on the ZnO morphology. The catalyst prepared with filament-like ZnO exhibited the best activity with 78.2% methanol selectivity at H₂/CO₂ = 3, 240 °C, 3.0 Mpa.^[177]

Cu–ZnO–Ga₂O₃/SiO₂ and LaCr_{0.5}Cu_{0.5}O₃ have also been shown to demonstrate higher catalytic performance towards methanol with selectivity of 99.1% and 90.8% and conversion of 2.0% and 10.4% at 250 and 270 °C, respectively.^[178,179] However, these mixed oxides did not maintain a stable structure for long reaction cycles^[180] that In₂O₃, which is used as a catalyst in the

conversion of CO₂ to methanol, has good catalytic activity and can be further promoted with Pd, Ni, etc.^[181–186]

There are several recent papers about methanol production that Cu–ZnO composites with less than 30% CO₂ conversion and CH₃OH selectivity ranging between 30% and 70%. The reaction conditions of temperature, pressure, and H₂/CO₂ ratio were 220–300 °C, <5 MPa and 3, respectively have been considered.^[187,188] If the pressure and the H₂/CO₂ molar ratio are increased to 36 MPa and 10, respectively, on a Cu–ZnO–Al₂O₃ catalyst; 95.3% CO₂ conversion and 98.2% methanol selectivity are obtained.^[189]

In a study to produce methanol from CO₂, Fluorinated Cu/Zn/Al/Zr hydrotalcite was synthesized using (AlF₆)³⁻. In this study, it was stated that the amount and strength of adsorption applied to CO₂ has an effect on methanol production and is a guide for the development of efficient catalysts.^[190] Rungtaweeworani et al. developed a catalyst where Cu nanocrystal (NC) is encapsulated in a Zr(IV)-based MOF, designated as CuCuUiO-66; UiO-66 [Zr₆O₄(OH)₄(BDC)₆, BDC = 1,4-benzenedicarboxylate] for hydrogenation of CO₂ to methanol. They found that CuCu UiO-66 created an eightfold increased catalytic activity compared to the Cu/ZnO/Al₂O₃ catalyst while maintaining 100% selectivity towards methanol.^[191]

Indium-based catalysis has been accepted among the alternatives for the conversion of CO₂ to methanol. It was found that a pure In₂O₃ catalyst at 330 °C and 5 MPa could convert approximately 7% of CO₂ to CH₃OH with selectivity above 39%.^[181] In another study with In-based catalysts, a Pd/In₂O₃ catalyst at 300 °C and 5 Mpa reaction conditions with many interfacial regions and oxygen vacancies (to increase CO₂ adsorption) achieved more than 20% CO₂ conversions and over 70% methanol.^[174] In another study, O. Martin et al. prepared a stable In₂O₃/ZrO₂ composite catalyst for methanol synthesis, and this catalyst showed 1000 recycling capabilities.^[192] In₂O₃ nanoparticles overcome the RWGS reaction and offer 100% selectivity to methanol at all temperatures, while Cu–ZnO–Al₂O₃ provides 47% methanol yield due to the formation of the RWGS reaction.^[193]

Ni–Ga and MoP are also among the recently developed catalysts targeting hydrogenation of CO₂ to methanol. For example, at 10 bar and 200–270 °C using Ni–Ga, Au–Ni–Ga, Co–Ni–Ga, and Cu–Ni–Ga catalysts, methanol can be synthesized with CO₂ conversion of 0.35–1.2, 0.2–0.8, 0.3–1, and 0.4–1.6 and selectivity of 55–45, 70–50, 65–55, and 65–55, respectively. Also, Au is seen to improve turnover frequency through a promotion effect.^[194] Ni₅Ga₃ catalysts were synthesized for the hydrogenation of CO₂ to methanol and the effects of surface oxidation/reductions on Ga catalytic performance by ex situ and in situ characterization techniques were investigated. At the end of the study, it was found that the presence of amorphous Ga₂O₃ on the surface of metallic nanoparticles was involved in methanol synthesis and promoted CO₂ activation rather than preventing CO₂ reduction.^[195] Molybdenum phosphide (MoP) catalysts have been recently developed, showing a stable performance for methanol synthesis catalysts that are not affected by the ratio of CO and CO₂ in the feed. The formate binding strength over MoP catalysts was found to be a determining factor in controlling feed-agnostic activity for methanol synthesis.^[196] When zirconia (ZrO₂) was used as a support for MoP nanoparticles, methanol selectivity, and conversion

rate were found to be improved greatly over other metal oxide supports.^[197]

A Ga-Pd/SiO₂ catalyst with higher performance compared to standard Cu/ZnO/Al₂O₃ was developed, they stated in their study that the CH₃OH selectivity of the GaPd₂/SiO₂ catalyst is two times higher than that of the conventional copper catalyst.^[135] One study implied that Pd-Cu bimetallic catalysts exert a strong synergistic effect on the selective incentive for the formation of CH₃OH in CO₂ hydrogenation in the ratio Pd/(Pd+Cu): 0.25–0.34 and reaction conditions of 523K, 4.1 MPa.^[136] Noble metal-based catalysts such as Ga–Pd, Au–CeO_x/TiO₂, and Pt–MoO_x/Co-TiO₂ have been developed and used to produce CH₃OH from CO₂ at low pressure or low temperature.^[135,137,138] Similarly, the synthesis of methanol was obtained at 255 °C and 0.1 MPa with the catalyst series containing In₂O₃ such as Ni–In–Al/SiO₂ and La–Ni–In–Al/SiO₂.^[198,199]

3. Nanoreactors

Nanoreactors are an important and innovative means to mimic processes occurring in nature.^[76,200] Nanoreactors first appeared in the 1990s and have become increasingly more significant in catalytic applications.^[201] Nanoreactors refer to compartmentalized nanostructures to perform catalytic functions under controlled local environments, analogous to cellular organelles in a living organism, with the aim of increasing reaction rates and production efficiency. Nanoreactors have some advantages over conventional catalysts. These include performing parallel chemical reactions, producing less undesirable products, and increasing the catalytic performance due to large surface-to-volume ratios.^[200]

The size, shape, particle composition, and microenvironment of the structure contained within a nanoreactor play a significant role in chemical reactions and can provide renewed stability and selectivity.^[202] In the most general sense, nanoreactors are divided into two groups: they are natural and synthetic nanoreactors. Natural nano-reactors contain protein-based bacterial microcompartments, protein cages, and viruses. Synthetic nanoreactors, on the other hand, have more types and include molecules, macromolecules, nanostructures, and porous solids. A molecular nanoreactor is formed by the accumulation of several molecules together and forming a cavity for a chemical reaction. For macromolecular nanoreactors, polymers are preferred in the form of large single molecules that are hollow or in self-assembled structures with one or more cavities. In core-shell nanostructures, variable-core structures embedded in a hollow shell have been greatly enhanced. If the outer shell of the nanostructure is permeable to the reactants, these structures become nanoreactors with variable catalytic cores. The commonly preferred compounds in the porous solids group are the porous structures of silicate and zeolite. Zeolites are composed of aluminosilicate and are porous compounds. The sizes of cavities in silicates and zeolites range from a few angstroms to a few nanometers.^[81,203]

3.1. Encapsulated Materials

The creation of a core-shell nanostructure can protect the active site of a catalyst from deactivation through agglomeration, as

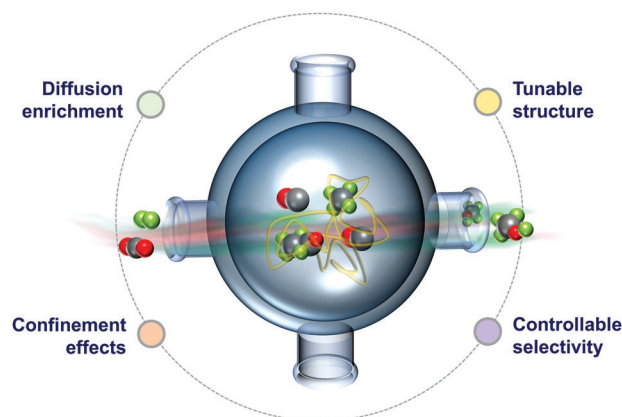


Figure 3. A schematic representation of some unique features of YolkShell.^[213]

is often observed for metallic nanoparticle catalysts or surface-coating hybrids.^[204,205] A majority of tandem catalysis schemes use supported metal nanoparticles (SMN), sometimes in combination with zeolites. However, these innovative encapsulated materials are more useful than SMN in the protection of the metallic core, where the catalytic reaction takes place, by the porous shell. This shell protects the metallic core from agglomeration or coking that occurs in traditional SMN formulations.

Nanoreactors can also be designed as yolk@shell materials.^[206] Compared to the core-shell architecture, the yolk-shell has a void between the “yolk” and the metallic core, associated with improved catalytic performance.^[200,205,207–211] Yue et al. have devised the synthesis of a new type of yolk-shell magnetic mesoporous silica microspheres. The resulting yolk-shell Fe₃O₄@SiO₂@hollow mSiO₂ microspheres have open and regular mesoporous channels (2.2 nm) and a controllable void space (320–430 nm). These large void space catalysts exhibited excellent catalytic performance with high conversion and selectivity.^[212] Yolk shell structures provide several advantages and three of them stand out.^[213,214] 1) the total exposure time of the active center can be adjusted to the desired values for some degree of catalytic efficiency and stability; 2) the volume of the void can expand for catalytic reaction and mass transfer to occur; 3) Modifications to the shell, yolk, void or a combination of these provide a flexible and dynamic nature of catalytic efficiency, stability, and recyclability. The design and development of YS achieve these goals, and many special features of YS are emerging, as briefly described in **Figure 3**. Many different synthesis strategies have been developed to prevent deactivation, including Atomic Layer Deposition (ALD), Strong Metal Support Interaction (SMSI), non-hydrolytic sol-gel, and core-shell methods.^[215] Also, encapsulating the active phase with a protective and porous shell material prevents normal deactivation states. The benefits of the structures of catalysts using this morphology are better understood by the studies. Its most important benefit is confinement effects. These confinement effects prevent carbon deposits from accumulating and sintering while providing a homogeneous reaction environment, both as a protective and performance-enhancing feature.^[216,217] At the same time, it is easier for more complex reactions to occur due to increased internal pressure. These nanoreactors

exhibit improved performance due to simultaneous reaction capability, higher product selectivity, and larger active surface area compared to conventional materials.^[206,218]

If we look at their general properties, these particles consist of a metal or metal oxide core within an inorganic or polymeric shell; Silica or carbon are commonly preferred choices, as they are extremely stable, abundant, and inert.^[219] The performance of this morphology depends on several factors. These factors are particle size, shell thickness, and sample homogeneity, which can be adjusted by synthetic methods.

With the increasing interest in YS catalysts, more advanced and complex YS structures have been developed.^[220–223] These complex structures range from “basic” single-encapsulated cores to structures with multiple encapsulated cores called “raspberry cores” and are even present in structures with a single multi-shelled core.^[221,224] In general, these more advanced variations derived from the single encapsulated core exhibit more advanced performance due to their structural diversity. For example, multiple cores offer higher active surface area.^[225] Although each generated variant has its advantages, no variant can be described as a superstructure because of the possible different needs for each chemical process. Therefore, YS particles tailored to the reaction are required.^[211,226,227]

3.2. Applications of Nanoreactors for CO₂ Hydrogenation

Based on the studies reported in the literature, the yolk@shellYS structure can be said to be very effective in producing alcohols from CO₂ with a Cu-encapsulated catalyst.^[191,228,229] In a study, ultra-small Cu/ZnO_x nanoparticles were produced in MOF cavities to perform CO₂ hydrogenation. These Cu/ZnO_x@MOF catalysts obtained showed very high activity with 100% selectivity to methanol and high stability over 100 h.^[230] The catalyst used in another study is synthesized by cobalt nanoparticles onto amorphous silica (Co@Si_x) to form Co–O–SiO_n that stabilizes methoxy (*CH₃O) species in CO₂ hydrogenation. By optimizing the cobalt-to-silica ratio, they achieve better performance than the noble metal catalysts as well as the supported copper catalysts used to convert CO₂ to methanol.^[231] They have obtained methanol selectivity of 70.5%, CO₂ conversion of 8.6% at 320 °C, 2 MPa, and methanol productivity of 3.0 mmol g_{cat}⁻¹ h⁻¹ for Co@Si_{0.95}. In a different study, core-shell catalysts with Cu and Cu/ZnO nanoparticles coated with mesoporous silica shells (Cu@m-SiO₂ and Cu/ZnO@m-SiO₂ nanocatalysts) were produced and used for the hydrogenation of CO₂ into methanol. After 168 h of reaction, the CO₂ conversion and CH₃OH selectivity decreased by 1.6% and 1.0%, respectively, compared to the initial values. They found that the core-shell Cu/ZnO@m-SiO₂ catalyst provided maximum CH₃OH yield (153.9 g kg cat⁻¹ h⁻¹) with high stability.^[228]

In another study, a new core-shell structured CuIn@SiO₂ catalyst was produced by the solvothermal method and used to catalyze the hydrogenation of CO₂ into methanol. This new catalyst has improved CO₂ adsorbing ability to provide more CO₂ for hydrogenation reaction and 9.8% CO₂ conversion and 78.1% CH₃OH selectivity are obtained. According to the authors, this newly prepared CuIn@SiO₂ catalyst offers high catalytic stability and catalytic performance due to core-shell formation.^[232] The

catalytic performance of the catalyst was 9.8% CO₂ conversion, 78.1% CH₃OH selectivity, and 13.7 mmol_{CH₃OH} h⁻¹ gcat⁻¹ space-time yield at 280 °C and 3 MPa.

Generally, catalysts are prepared by conventional methods of co-precipitation, impregnation, or physical mixing and may contain multiple components, including various supports. They can show significant uncertainties in the spatial arrangement of active areas. In a recent study, a well-defined CeO₂-Pt@mSiO₂-Co core-shell catalyst was prepared (Figure 4). Here, the synthesis of C₂-C₄ hydrocarbons from CO₂ conversion with a two-step tandem reaction is targeted. While the RWGS reaction produces CO on a CeO₂/Pt interface, the FTS process takes place at the Co/mSiO₂ interface to form C-C coupled products. According to the study, catalyst synthesis has four steps. The first step is the synthesis of well-dispersed and uniform CeO₂ nanoparticles, as seen from the TEM images (Figure 4b,c). The second step is to load Pt nanoparticles onto pre-prepared CeO₂ by the Pt overgrowth method (Figure 4d,e). In the third step, a sol-gel method is preferred to coat a mesoporous SiO₂ shell on the CeO₂-Pt core (Figure 4f,g). The cobalt-hexane solution was added to CeO₂-Pt@mSiO₂ powder by mixing slowly, thus a uniform cobalt nanoparticle distribution on the silica shell was obtained (Figure 4h,i). With this four-step synthesis, CeO₂-Pt@mSiO₂-Co tandem catalysts were obtained (Figure 4j). They tested the catalyst under 0.6 MPa pressure and 250 °C reaction conditions. They found out that the CO₂ conversion (%), CO selectivity (%), CH₄ selectivity (%), and C₂-C₄ (%) selectivity values as 2.0, 78.0, 60.0, and 40.0, respectively. In this catalyst, CO₂ and H₂ were converted to CO via the Pt/CeO₂ interface, and the other interface, Co/mSiO₂, produced C₂-C₄ hydrocarbons by a subsequent Fischer-Tropsch process.^[233]

Hollow spherical dual-layer Co@hsZSM5@Pt nanocatalysts were found to be highly effective in converting CO₂ with 46% hydrocarbon selectivity of C₂₊ by the Fischer-Tropsch reaction at 400 °C and 20 bar. According to the tandem hydrogenation mechanism, Pt on the outer surface also carries out the initial conversion of CO₂ to CO (RWGS), and the inner Co is known to convert CO to C₂₊ and methane (FTS).^[234]

Another hollow ZSM-5 zeolite nanoparticle with Fe₃O₄@MnO₂ was used to convert syngas directly into aromatic-rich gasoline. Approximately 70.0% CO conversion and selectivity of 73.5% for gasoline-grade hydrocarbons at 320 °C and 4.0 MPa were obtained. The article mentioned that forming a hollow structure shortens the diffusion length and thus increases the stability of zeolite nanoparticles.^[235]

In a study, 24.1% CO₂ conversion and 86.3% selectivity of light olefins were obtained with the ZrO₂-ZnO-(CeO₂)₂/SAPO-34 catalyst at T = 350 °C, p = 2.6 MPa and GHSV = 6000 mL (gca h)⁻¹. Also, the catalyst with a strong CO₂ and H₂ adsorption capacity was obtained by incorporation of CeO₂ into Zr-Zn oxide which was greatly increased concentration of oxygen vacancies on the catalyst surface.^[236]

In a different study, methanol and dimethyl ether (DME) were produced at between 180–260 °C by 10Fe-10Cu/silica-aluminosilicate core-shell and 10Fe-10Cu/silica-aluminosilicate infiltrated catalysts from CO₂ with the assistance of a magnetic field.^[237] While the percentage of CO₂ conversion was found to be similar for both catalysts, the core@shell catalyst was more selective for methanol while the infiltrated catalyst was more

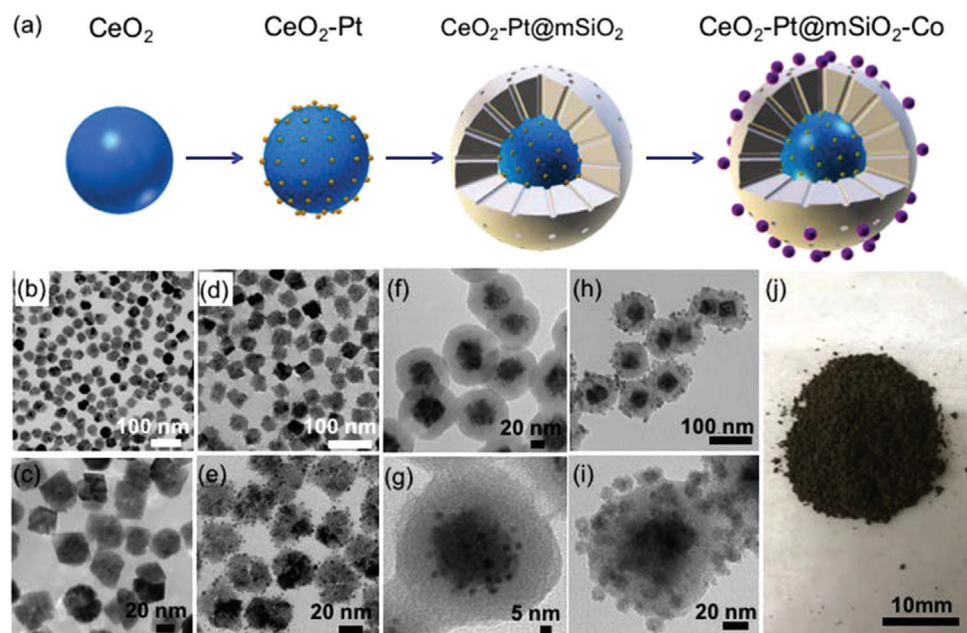


Figure 4. Synthesis and TEM images of the CeO₂-Pt@mSiO₂-Co tandem catalyst. a) Illustration of the synthetic process. TEM images of each step: b,c) CeO₂ nanoparticles, d,e) Loading of Pt nanoparticles on CeO₂, f,g) silica shell coating on CeO₂-Pt, h,i) settling of Co nanoparticles on CeO₂-Pt@mSiO₂, and j) CeO₂-Pt@mSiO₂-Co nanoparticles. Reproduced with permission.^[233] Copyright 2017, ACS Publications.

selective for DME. The researchers tested both catalysts at a temperature range of 180–260 °C and a total pressure of 10 bar. Both catalysts produced CO above 220 °C and even at 260 °C, the CO₂ conversions in both catalysts remained below 10%. Jiang et al. developed a fixed-bed process using a series of Pd/In₂O₃/SBA-15 catalysts to convert CO₂ to methanol. The 10% Pd/In₂O₃/SBA-15 catalyst exhibited excellent catalytic performance at 260 °C, 5 Mpa and 15 000 cm³ h⁻¹ g_{cat}⁻¹, with a methanol selectivity of 83.9%, a CO₂ conversion of 12.6%, and a catalyst yield of 1.1×10⁻² mol h⁻¹ g_{cat}⁻¹. According to the results obtained, the oxygen vacancies in In₂O₃ increased with the addition of Pd, and they reported that this process facilitated the activation of CO₂. With these, the H needed to hydrogenate CO₂ into methanol was provided, with which Pd could easily separate large amounts of H₂.^[238] In light of the data obtained from this study, the catalysts used can be evaluated in nanoreactor studies.

As described above, many valuable chemicals and fuels can be produced from CO₂ with tandem catalysts especially when nanoreactor configurations are employed. While producing some chemicals and fuels from CO₂ provides economic benefits, it also provides benefits for the environment by reducing the CO₂ level in the atmosphere. In recent studies, especially tandem and nanocatalyst technologies are combined, and the effective use of yolk-shell and core-shell structures in CO₂ conversion is described. Although many advances have been made academically and industrially, CO₂ conversion rates are not industrially sufficient. In order to overcome this deficiency, there is a need to develop tandem nano-catalysts with a higher conversion rate of core-shell or yolk-shell structure. To achieve this, the relationship between the design and performance of nanocatalysts must be understood. Studies in which characterization techniques are

applied to see the structural changes that occur during catalytic reactions should be emphasized.

4. Conclusions and Outlook

Nanoreactors offer a way to achieve precision in catalyst synthesis and some examples of the nanoreactor approach have been demonstrated for tandem catalytic conversion of CO₂ to C-C coupled products by synthesis of a core-shell or yolk-shell structure. Nanoreactors can be used to perform multiple reactions operating in tandem to achieve high selectivity and rates for desired products, such as in combined RWGS + FTS or MS + MTO pathways. Here, since the porosity of the outer shell can be customized to adjust the diffusion rate of the reactants, it provides the advantage of better controlling the reaction rate and catalytic performance. However, more studies are needed on these materials to reveal their true potential. In addition to studies on lifetime and deactivation, improvements can be made for effective and scalable catalyst production. In particular, the necessity of precision manufacturing makes the commercial production of nanoreactors a challenge that must be addressed for commercial implementation. First, the relationship between structure and performance needs to be understood for the design of nanocatalysts. To see the structural changes of nanocatalysts that occur during catalytic reactions, characterization techniques should be applied. Second, there are two very important steps to increase the efficiency of catalytic CO₂ conversion, these are to reduce the activation barrier of CO₂ and accelerate the formation of intermediates. The calculations of the inclusion of defects and vacancies in the structure of nanocatalysts are critical for the efficiency of catalytic CO₂ conversion and this issue is confirmed by some

theoretical calculations. An important method for accelerating CO₂ conversion is to incorporate single-atom centers into nanocatalysts that have high catalytic activities for CO₂ activation and conversion.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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