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Review

Engineering heterogenous catalysts for chemical CO₂ utilization: Lessons from thermal catalysis and advantages of yolk@shell structured nanoreactors

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ABSTRACT

The development of catalytic materials for the recycling CO₂ through a myriad of available processes is an attractive field, especially given the current climate change. While there is increasing publication in this field, the reported catalysts rarely deviate from the traditionally supported metal nanoparticle morphology, with the most simplistic method of enhancement being the addition of more metals to an already complex composition. Encapsulated catalysts, especially yolk@shell catalysts with hollow voids, offer answers to the most prominent issues faced by this field, coking and sintering, and further potential for more advanced phenomena, for example, the confinement effect, to promote selectivity or offer greater protection against coking and sintering. This work serves to demonstrate the current position of catalyst development in the fields of thermal CO₂ reforming and hydrogenation, summarizing the most recent work available and most common metals used for these reactions, and how yolk@shell catalysts can offer superior performance and survivability in thermal CO₂ reforming

and hydrogenation to the more traditional structure. Furthermore, this work will briefly demonstrate the bespoke nature and highly variable yolk@shell structure. Moreover, this review aims to illuminate the spatial confinement effect and how it enhances yolk@shell structured nanoreactors is presented.

Keywords: Yolk@shell; CO₂ utilization; Reforming; Hydrogenation; Confinement effect

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Jian Liu received his PhD degree in physical chemistry from the Dalian Institute of Chemical Physics, Chinese Academy of Science, China, in 2008, and worked at the Australian Institute for Bioengineering and Nanotechnology (AIBN), University of Queensland (UQ) as a research fellow. After working at Curtin University as a senior lecturer, he then joined DICP as a full professor and group leader of micro–nanoreactor and reaction engineering. He also held an adjunct Reader position in the Department of Chemical and Process Engineering, University of Surrey, UK, he is the executive director of DICP-Surrey Joint Centre for Future Materials. His research focuses on the design of micro–nanoreactors, energy materials, CO₂ utilization, anisotropic particles with patchy, multicompartment, and Janus architectures.

1. Introduction

The world today is increasingly aware of environmental pollution present in several forms, for instance: atmospheric, oceanic, urban and rural pollution. Of these, we are especially aware of our emissions to the atmosphere as our personal or national “carbon footprint” are well-known topics within the general population. These

“footprint” values are a partial driving force for the desire for solutions to our pollution problems, with the scientific community developing numerous processes or pieces of technology as solutions. Currently, pollutive emissions can be controlled in three ways: Controlled and limited emission, Carbon Capture and Storage (CCS) or Carbon Capture and Utilisation (CCU).

CCS is focussed predominantly on sequestering CO₂ into underground caverns, or more useful things like biodegradable polymers [1] or rock, through a rapid process of carbonate mineral formation as piloted in Iceland [2]. This method offers a rapid short-term solution to the problem, but there is potential for the captured gas to leak from containment.

The CCU approach takes advantage of this captured CO₂ by utilising it as a feedstock for fuels and chemicals usable in existing infrastructure, providing an elegant solution to both global pollution and energy concerns. The reformation of carbon dioxide directly forms a considerable part of CCU advancement, as the reactions concerned produce value-added chemicals from CO₂. However, due to the stability of the CO₂ molecule, a significant amount of energy is required for activation. This makes catalysts essential in these processes to reduce energy demand.

The field of catalysis predominantly revolves around supported metallic nanoparticles (SMNs) materials. SMNs are attractive catalysts because of their facile production methods that are scalable to industrial usage, high surface area and performance in terms of reactant conversion and product selectivity. When considering CO₂ reactions, noble metals offer highly sought levels of conversion, product selectivity and deactivation resistances; these metals are usually too expensive for anything other than laboratory scale usage or very low doping levels in a cheaper catalyst formulation. Base transition metals (*d*-block elements) are an obvious second

choice. These elements are considerably more abundant than the noble metals and are capable of comparable levels of conversion and product selectivity; the most effective metals for CO₂ reaction being Fe [3–6], Co [7–10], Ni [11–17] and Cu [18–20]. In particular, Ni and Co are extremely effective catalysts for CO₂ thermal reforming reactions, but these metals suffer from deactivation mechanisms, i.e. sintering and coking. Fe and Cu are capable of highly effective Fischer-Tropsch (FT) and the forward and reverse water gas shift reactions (WGS and RWGS, respectively).

This review aims to present the current situation of catalyst development in the field of thermal CO₂ utilization and deactivation resistance, demonstrating that the SMN catalysts are still the most widely applied morphology despite becoming increasingly complex to solve the problems of deactivation and reactive longevity; there are much simpler answers to these questions, such as material encapsulation. Catalyst development in this way has been reviewed previously [21–24], though these are either focussed entirely or heavily on documenting the synthetic pathways, in addition to the final application. The encapsulated morphologies are largely summarised in two varieties: core@shell and yolk@shell, the former is the encapsulation of a core particle by an outer layer (such as SiO₂ or Al₂O₃), while the latter follows the same structure but possesses a void space between the core and the shell, giving rise to a fascinating set of properties that are widely known as the confinement effect, which is covered later. A review by Li *et al.* [25] did investigate the potential of core@shell and yolk@shell catalysts within syngas production and Fischer-tropsch synthesis, though this review mainly focussed on core@shell materials. Yolk@shell catalysts, despite offering an array of extremely attractive properties, are perhaps not as favored as their simpler morphological siblings due to more complex synthetic methodology. It is the intent of this review, therefore, to highlight the application of yolk@shell catalysts and their

properties within the field of thermal CO₂ utilization.

1.1. Coking

Catalyst deactivation via coking, ranges in severity depending on the nature of the catalyst; the carbon can be either “soft” (amorphous) or graphitic (crystalline), with these two classifications being the beginning and end of the severity scale, respectively. Coking in the Dry Reforming of Methane (DRM) is a complex process that forms numerous types of carbon: C_α, C_β, C_γ, C_v and C_C, which are defined in Table 1 [26].

These carbonaceous deposits form sequentially, for example, C_α deposits form common side reactions, discussed later, which then react together to form C_β that then react together again to produce C_γ and so on. Particularly detrimental carbon deposits are the C_β and C_C, which encapsulate the active sites at temperatures <300-400°C and >650 °C, respectively [26,27].

Table 1. Description of different forms of carbon as defined in [26].

<i>Designation</i>	<i>Carbon Structure</i>
C _α	Adsorbed surface carbon – High levels of defects
C _β	Polymeric, amorphous films
C _γ	Metallic carbides
C _v	Filamentous carbon structures – carbon nanotubes
C _C	Graphitic platelet films – Crystalline

These carbon deposits can develop on a catalyst in numerous ways, such as Chemisorbing with the surface as a monolayer or adsorb to each other in multiple layers, blocking access to the active sites; Carbon could also fill the pores of the catalyst, preventing reactant molecules from reaching the active sites contained within; total encapsulation of the metal particle, causing complete deactivation; or in some cases, carbon filaments can build up within the support material pores to such a point that they cause the catalyst to fragment [27,28]. A diagram of these forms of carbon can be found

in Fig. 1. It is worth noting that this form of deactivation can occur even at low levels of carbon presence, but is fully reversible through oxidising the carbon [28].

1.2. Sintering

When very high temperatures are reached ($>500^{\circ}\text{C}$), most metals will have far surpassed their Hüttig [29] and Tammann [29,30] temperatures (T_H and T_T ,

Fig. 1. Diagram of supported metal nanoparticles being deactivated via (a) carbon layers chemisorbed on metal particles. (b) Encapsulation of metal particles by carbon deposits. (c) Growth of carbon nanofilaments that push metal particles off the support and (d) pore blockage by carbon deposits

respectively), making certain that the catalysts are also effected by sintering [31]. These two temperatures are crucial properties of a material that are based around its melting point (T_m); T_H is $0.3T_m$ and T_T is $0.5T_m$, T_H represents the point at which surface atoms at defect sites become mobile (atomic migration), while T_T is the point at which the bulk displays mobility (crystallite migration) and the T_m is when more liquid properties are displayed by the material [29]. These two temperatures represent the expected points that the sintering of the active phase begins and then when it becomes increasingly observable. Fig. 2 demonstrates the possible methods of sintering that can occur within a catalyst as a result of high temperature and Table 2 contains the T_H , T_T and T_m of Ni, Co, Fe and Cu, demonstrating the expectance of sintering above 500°C .

The high temperature can also cause the metallic active phase to interact with the support material to form spinel structures [32].

Fig. 2. Diagram of active phase sintering occurring over a support material: Blue ring - atomic migration to form larger crystallites; Red ring - the coalescence of crystallites

Table 2. Summary of the Hüttig, Tammann and melting point temperatures for Ni, Co, Fe, Cu.

Metal	$T_H (^{\circ}\text{C})$	$T_T (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$
Ni	435.9	726.5	1453
Co	448.5	747.5	1495
Fe	461.4	769	1538
Cu	325.5	542.5	1085

Sintering negatively affects the catalytic performance due to many reasons: the overall catalytically active surface area is reduced, loss of support material surface area due to its collapse causing a subsequent catalytic surface area loss and finally, chemical alteration of the catalytically active phases to non-active phases [27,30]. Ni particle size has been well-linked to the formation of carbon with increasing size, making smaller Ni particles crucial to coping prevention and performance [33–36]. As this form of deactivation involves the coalescence of larger particles from smaller, it is at best extremely difficult to reverse. Sintering, therefore, is easier to prevent through careful design.

1.3. Poisoning

Further to coking and sintering, another prevalent method of deactivation that affects catalysts is poisoning: The act of catalytic poisoning occurs when a substance chemisorbs to an active site, usually irreversibly, blocking the site (geometric effect), alters the absorptivity of other species (electronic effect) or poison can modify the chemistry of the active site through forming a new compound (reconstruction) [37,38]. Poisoning is also highly specific; a poison in one reaction is not necessarily a poison in another. For example, CO is a poison to the Pt anodes of polymer electrolyte fuel cells, while it is a fuel for Ni anodes in solid oxide fuel cells [38]. CO₂ utilization catalysts, such as Ni, Cu or noble metal-based materials, are predominantly affected by contaminants such as S or NO_x within the feed stream that chemisorb and block the active sites through the formation of metal sulphide species. Sulphur poisoning on Ni catalysts has been found to occur in all three of the poisoning routes described earlier, making it a very potent poison for Ni-based CO₂ utilization catalysts [39].

Sulphur poisoning is resistible with the addition of certain components; CeO₂ has been found to help prevent sulphur poisoning through the exploitation of the oxygen mobility that this material is known for. The mobile oxygen is then able to interact with the S present on the catalyst sites to form sulphur oxides that are more easily removed at the high temperatures used for reforming reactions [40–42]. Another method to prevent S poisoning is using alkaline materials as sacrificial components to adsorb the S before it can reach the catalyst active sites [39,43].

Other methods used to prevent poisoning include synergistic catalyst design to benefit from the sulphur resistances of several components [44–46] and varying the catalyst structure towards alloys, perovskites [47–52] or core@shell materials [53–56]. The

core@shell materials achieved this resistance through physical separation of the H₂S from the smaller reactants (i.e. H₂, CO₂, CO) or through the adaptation of the inert shell to include other materials that would bind to the S contaminant [53,56].

While all these forms of deactivation require understanding and consideration to take meaningful steps towards preventing, most studies focus on the use of ideal or purified feed streams, making materials that are capable of high conversion and desired selectivity, while also demonstrating sintering and coking resistance larger considerations for this review [32,57–61], over poisoning mechanisms. With this being said, more studies should be undertaken that account for the inclusion of contaminant materials to better emulate the direct use of exhaust gases as feed streams for these processes.

2. CO₂ reforming

To subsidize the existing fossil oil-based production of chemicals and fuels, while reducing the overall greenhouse gas (GHG) emission from their usage, methods of combining CCU and natural gas reserves are attractive options. Methane, found usually as natural gas or produced from biomatter decomposition as biogas (approx. 50% methane, 50% CO₂) [62], represents a substantial source of high-value products, for instance, syngas. Syngas is a mixture of carbon monoxide and hydrogen that is used to produce many valuable materials (i.e. dimethyl ether, alcohols or hydrocarbon fuels and waxes); some of the most effective reactions that facilitate the production of syngas are known as reforming reactions. The reforming reactions are attractive methods of syngas production as they commonly involve the use of CO₂ as an oxidant. Syngas can

also be separated into its constituents as a source of hydrogen or assist in the hydroformylation process to produce aldehydes and alkenes (Fig. 3).

Fig. 3. Illustration of the stream of processes that can be achieved using waste gases

Eqs. (1)–(4) demonstrate the oxy-reforming of methane (ORM or autothermal reforming), steam reforming of methane (SRM), bi-reforming of methane (BRM) and dry reforming of methane (DRM), respectively. These reactions produce differing ratios in the final syngas, allowing for an appropriate quality of syngas to be obtained, depending on the intended higher value product.

The BRM and DRM reactions offer much more usable syngas ratios compared to the other reactions, though these are also the most endothermic of the presented routes. These two reactions also garner attention for another reason; they utilize two GHGs, rather than one. This allows for the overall production to have a meaningful impact on the collective emission of these GHGs, provided that the required heat can be supplied from non-fossil fuel sources [32,63].

While the syngas ratio produced by the DRM (Eq. 4) is comparatively low to those achieved by the SRM and BRM reactions, achieving a ratio closer to 1, this is highly beneficial for the selective generation of long-chain hydrocarbon materials through the Fischer-Tropsch process [32,64–68] as well as an ideal H_2/CO ratio for hydroformylations [69,70].

At the temperatures required for optimum DRM performance, there is a multitude of competing reactions that take place that negatively affect the catalyst and the product ratio. These reactions are the reverse water gas shift (RWGS) reaction that consumes hydrogen and produces CO (Eq. 5), reducing the syngas ratio; the decomposition of methane that reduces methane to form C (Eq. 6); and finally the Boudouard reaction that sees CO disproportionate at the catalyst surface to form C and CO_2 (Eq. 7).

Fig. 4(a and b) details the thermodynamic equilibrium for conversion (Fig. 4a) and the whole system (Fig. 4b) of the DRM reaction at 1 atm and as a function of temperature. The equilibrium data details $\text{H}_2:\text{CO}$ ratios higher than 1, due to the lower levels of CO as a result of the Boudouard reaction; Above 900 °C, this shifts back to the expected ratio unity, as C formation becomes less favorable. When designing a catalyst for the DRM, its performance is governed by the nature of the metal and the support, surface area, metal particle size and the degree of synergy between the metal and its support [32,71].

Fig. 4. (a) Equilibrium conversion of CO_2 and CH_4 , (b) all equilibrium products for the DRM, considering C formation. The data for these figures was produced using ChemStations' ChemCad software, using the SRK equation of state in a Gibbs reactor, $\text{CH}_4:\text{CO}_2 = 1$

2.1. Supported metal nanoparticles

It is well-founded that noble metals (i.e. Pt, Rh, Ru) are extremely resistant to coke formation and sintering, compared to base metals [72–79]. However, their expense makes them unattractive for large quantity usage [80,81], thus doping/promoting is the only method these metals are viable in catalytic formulations. It has been found that using noble metals in this way allows the base metal catalyst to develop significantly improved deactivation resistances.

The industrial standard catalyst for these reactions is Ni or Co supported on Al_2O_3 ,

due to being capable of comparable performance with noble metals [57,82–90]. However, these catalysts are extremely vulnerable to coking mechanisms [32,57,91,92].

A notable work concerning noble metal doped Ni catalysts in the DRM reaction found just how effective noble metals are at resisting deactivation while preserving activity. The study investigated two base metal catalysts (10 wt% Ni and Co) in addition to a series of noble metal catalysts (5wt% Rh, Ru, Ir, Pt and Pd), all of which were supported on Al_2O_3 [74]. Testing of each catalyst was undertaken at 800°C, 60,000 mL $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ and was assessed on their conversion and coke formation. The authors found that none of the noble metal catalysts, excepting Pd, developed any coke, while both the Ni and Co catalysts developed significant amounts of coke. However, the Ni and Co catalysts displayed highly comparable levels of CO_2 and CH_4 conversions to those reported for the noble metal catalysts, perfectly demonstrating the viability of these base metals for DRM catalysis [74].

To prevent the rapid onset of deactivation for these catalysts, the use of another metal as a promoter, or to produce an alloy, with an initial metal is very common. When two metals are combined, depending on the synthetic method, several different structures can be obtained (Fig. 5). The act of noble/base metal promotion or alloying is thought to be an effective means of preventing coke formation or sintering, by influencing the overall metal particle size, towards smaller particles, and improving the dispersion [57,80,93–97] (Table 3).

The reason that bimetallic catalysts display altered properties and performance is thought to be the interaction between the two metals, producing geometric and/or electronic effects [28,98]. The geometric effect can be considered as the reduction in the surface presence of one metal by its dilution into another, reducing the size of the overall collective. This drastically affects the performance of the catalyst, as it is often

these bimetallic sites that are most active for the reaction. The electronic effect is produced by a difference in the electronic affinity between the metals. This variance then produces fluctuations in the electron density of the main metal; high electron density if the secondary metal has lower electron affinity and lower electron density if the secondary metal has higher electron affinity. These modifications in the electronic density alter the processes of adsorption or desorption of the reactive species during the reaction, affecting activity, residence time and selectivity [98].

Fig. 5. Potential structures of bimetallic systems: (a) Core-shell, (b) heterostructure, (c) nanoalloy, (d) segregation, and (e) ensembles – reproduced with permission from [98].

A recent work investigated a series of catalysts, both Ni and Ni-Ru, supported on SiO_2 , Al_2O_3 , MgAl_2O_4 and ZrO_2 . The monometallic Ni catalyst series found that Ni on the MgAl_2O_4 and Al_2O_3 supports exhibited the highest conversions of CO_2 and CH_4 , while the Ni/ SiO_2 demonstrated the lowest. This trend carried over to the Ni-Ru catalysts, finding the same trend with the MgAl_2O_4 and Al_2O_3 supports, though the Ni-Ru/ MgAl_2O_4 catalyst showed a 10% drop in CO_2 conversion throughout the reaction. Due to the more stable performance exhibited by the Ni-Ru/ Al_2O_3 catalyst during the initial testing, its stability was monitored for 6 hours. Following this, no loss in activity was observed and very minimal carbon formation was determined to have taken place, explained by favorable dopant-metal and metal-support interactions [99]. Similar to this, another study investigated the effect of Ru loading on a monometallic Ni/ $\text{MgO-Al}_2\text{O}_3$.

The study found that the addition of Ru detrimentally affected the performance of the catalyst, with the original, undoped Ni/MgOAl₂O₃ catalyst performing significantly better. This was attributed to the Ru altering the electronic structure of the Ni and also masking the step-edge sites of the Ni that effected the sensitivity of the Ni sites towards methane activation [100]. Another expansive investigation into the effect of metal promotion on Ni/SiO₂ catalysts involved the use of La, Mg (limited to only 10 wt%) and Rh (0.1 wt%, 0.225 wt% and 0.5 wt%). The study found that the Rh promoted catalyst was the most effective for low-temperature DRM (500 °C), with the highest loading demonstrating the highest activity. The trend found from the results of the other catalysts was that the Ni particle size was the key factor in improved DRM performance, except when Rh was used [101].

Table 3. Noble metal catalysts used in the DRM from recent literature.

Catalyst	Temperature (°C)	WHSV (mL/g _{cat} h)	CH ₄ Conversion (%)	CO ₂ Conversion (%)	Catalyst stability (hours)	Ref.
Ni-Re/MgAl ₂ O ₄	800	-	100	75	6	[99]
10 wt% Ni/Al ₂ O ₃	800	60,000	67.4	73.7	2	[74]
5 wt% Rh/Al ₂ O ₃	800	60,000	56.9	63.8	2	[74]
10Ni1Ru/La ₂ O ₃ -ZrO ₂	800	12,000	93	97	20	[102]
6Ni0.5Pd/Al ₂ O ₃	750	22,400	82	86	100	[103]
NiPt(0.71)/Al ₂ O ₃	700	120,000	10.2	-	20	[104]
5Ni0.1Pt/MgO	700	15,000	80	83	50	[105]
4.5Ni0.3Rh/CeO ₂ -ZrO ₂	650	12,000	16	37	24	[106]
RhNi/Ce(3%)Al ₂ O ₃	650	200,000	88	-	20	[94]
0.3Pt-10Ni/Al ₂ O ₃	650	15,600	72	-	14	[95]
Ni/Mg-Al ₂ O ₃	650	150,000	55	65	-	[100]
Ni-Ru/Mg-Al ₂ O ₃	650	150,000	30	40	-	[100]
3%Ru@Ni-MC-41	600	36,000	35	43	4	[107]
Ni ₁₀ Rh _{0.5} /SiO ₂	500	88,000	63	67	12	[101]

An alternative to combining Ni with noble metals is the use of base metals (Table 4); Cobalt is another effective metal for the DRM reaction that suffers from similar deactivation issues and is not as active as Ni. A study that thoroughly investigated monometallic Co catalysts over a multitude of support materials (MgO, SrO, CaO, BaO,

Al_2O_3 and SiO_2) found only two formulations to be effective for the DRM; Co/MgO and $\text{Co/Al}_2\text{O}_3$. The activity of these two materials was attributed to the formation of solid solutions between the Co and support [108,109].

However, Co does possess better coking resistance compared to Ni; when a series of bimetallic Ni-Co/ Al_2O_3 catalysts were compared to monometallic Ni and Co on Al_2O_3 , a synergy between the two metals was noted to improve the methane conversion of the catalyst through combining the activity of Ni with the C oxidation properties of Co [110], which is in turn related to the oxygen affinity demonstrated by Co [111–116]. These results were supported by several other works concerning similar NiCo catalysts within the DRM [117,118,127–132,119–126]. The performance of the NiCo bimetallic catalysts has been linked to the ratio of Ni:Co, as well as the selected support material [133]. Co has also been shown to influence the support material, where the Co produced a new $\text{La}_2\text{O}_2\text{CO}_3$ phase following the collapse of the perovskite structure, which better oxidised C deposits [134]. Building on the performance of Co solid solution catalysts, NiCo/Mg- Al_2O_3 is known to be one of the most effective DRM catalysts because of its solid solution characteristics that promoted metal-support interaction and dispersion [135].

In addition to Co, Fe and Cu are other well-documented base metals that are capable of enhancing the performance of a Ni catalyst in this reaction [136–140] and usually take the form of perovskite or spinel structure, rather than SMN [133]. Fe, while not active itself towards DRM, is thought to improve a Ni DRM catalyst in many ways, for example: improving the reducibility of the Ni species [141], the formation of a surface enriched Fe alloy [142], the formation of FeO with a Ni-rich alloy [4,136] or perhaps the Fe activated gasification of steam [143]. However, Fe has been known to migrate to the catalyst surface during the reaction [139]. A prominent example of the

advantageous addition of Fe to a Ni bimetallic catalyst was reported by Theofanidis *et al.* [4], discovering that the repeated formation-separation of a Ni-Fe alloy drastically improved the catalyst lifetime. When the alloy separated, it produced a mixture of Ni and FeO_x; This iron oxide species was found to be crucial in the removal of Ni-C species. Theofanidis *et al.* went on to investigate carbon gasification over spent Ni-Fe DRM catalysts, finding that Fe alters the reaction mechanism of the DRM [144], a conclusion that was later corroborated [136].

Like Fe, Cu is another effective base metal promoter for Ni catalysts, which enhances the performance of the catalyst. One paper suggests that the inclusion of Cu dramatically impacts the kinetics of both methane decomposition and the Boudouard reaction within the DRM [19]. The authors postulated that the inclusion of Cu (up to a threshold limit) in a Ni catalyst caused the decomposition of methane reaction to be less favorable, such that coke deposited on the surface is easily managed by removal mechanisms and thus prevents a build-up of carbonaceous deposits [19]. This was corroborated by another work that also found that Cu inclusion made the Ni species more reducible and sintering resistant [20]. Other studies of Ni-Cu bimetallic catalysts over numerous supports concluded that Cu not only improved the DRM activity of the catalyst but also prevented coke formation on the active sites [145–150]. One of these works notes the increase in metal-support interaction when synthesising the catalyst using a phyllosilicate, which produced well dispersed, small Ni-Cu nanoparticles [150]. As noted with Co addition, this work found the inclusion of Cu has a limit before the performance of the catalyst is affected, that limit being Cu/Ni 1:3.

Table 4. Collection of base metal catalysts used in the DRM from literature.

Catalyst	Temperature (°C)	WHSV (mL/g _{cat} h)	CH ₄ Conversion (%)	CO ₂ Conversion (%)	Catalyst stability (hour)	Ref.
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12 wt% CoMgO	900	60,000	95.7	97.4	50	[108]
NiCu/Al ₂ O ₃ -ZrO ₂	850	24,000	90	95	24	[148]
NiCo/Al ₂ O ₃ -ZrO ₂	850	24,000	95	95	24	[148]
NiCu/Al ₂ O ₃	850	24,000	60	60	24	[146]
NiCo ₂ (4.6)/ MgAl ₂ O ₄	800	120,000	85	-	225	[120]
3Ni0.15Ce0.05Ca/Al ₂ O ₃	800	2640	87	87	100	[93]
³ 50Ni50Co/CaO-ZrO ₂	750	32,000	88	90	50	[129]
Ni _{0.5} Co _{0.5} /Al ₂ O ₃	600	144,000	34	-	23	[110]
Ni _{0.75} Co _{0.25} /Al ₂ O ₃	600	-	16	18	3	[117]
Ni _{0.5} Fe _{0.5} /Al ₂ O ₃	600	-	12	16	3	[117]
5Ni10Co/Al ₂ O ₃	600	36,000	67	71	4	[118]

Other investigated promoters of DRM catalysts are a number of the lanthanide series, for example, La and Ce oxides [151–156]. These promoters are effective when combined with active phase or with the support, in the form of mixed metal oxides like CeO₂-Al₂O₃. Both La₂O₃ and CeO₂ are known to benefit the catalyst activity and carbon resistance, though CeO₂ acts best as a promoter of the catalyst, rather than the sole support due to very strong metal-support interactions that ultimately degrades the catalyst activity [152].

As some of these studies have identified, the addition of other metals is not the only method of preventing deactivation in reforming reactions; careful selection of the support media also imbue deactivation resistances and enhance conversion performance. This is due to potential synergistic properties of the support material, i.e. the redox properties of CeO₂, or due to specific metal-support interaction. The use of CeO₂ as a support itself or as part of a mixed metal oxide (i.e. CeO₂-Al₂O₃) is well documented and is known to provide very beneficial properties to a material in the form

of altered electronic and chemical properties [157–161].

2.2. Structural variants

In advancement to the SMN structure, perovskites (ABO_3) have been extensively researched as stable and resistant catalysts for the DRM reaction [32]. These structures are favored for the DRM as they are extremely resistant to coke formation and sintering due to a reversible redox process that cycles between metal particles on the surface and within the bulk structure [162,163]. This has led to perovskites being thought of as “self-regenerating” and become a very popular choice for DRM catalysts.

Several Ni-Fe perovskites have been reported for the DRM reaction, with a common finding that the exchange of Ni for Fe reduces overall reactive activity, but extends the catalysts’ lifetime [164–166]. Another study found that when investigating different ratios of Ni:Fe within a Ni-Fe perovskite catalyst, that the lowest Fe incorporation demonstrated the most favorable performance, even compared to the Ni perovskite. The authors noted that there were many factors involved with making a Ni-Fe perovskite effective for the DRM: effective synthesis, catalyst calcination temperature and considered selection of support [167]. It is likely that this “characteristic exchange” has made Ni-Fe perovskites, and SMN catalysts, unpopular as stability and deactivation resistance can be imbued using other metals that also promote catalytic activity. Another such study concerned Ni and Re loaded onto a LaFeO_3 perovskite [168]. The alloy particles between the Ni and Re were deemed responsible for the improved activity, as well as Ni-Re-Fe alloys resulting from the exsolution of Fe from the

perovskite structure; a known mechanism with this structure of material.

Another study into perovskite structured catalysts for DRM investigated several different perovskites that followed the general structure of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ni}_{0.8}\text{M}_{0.2}\text{O}_3$, where $\text{M} = \text{Bi}, \text{Cr}, \text{Co}, \text{Cu}$ or Fe . Of these, the Co and Cr initially performed well, but then deactivated via extreme coke formation. The Fe and Cu substituted perovskites were found to be much improved, though these materials excelled in different areas: the Cu variant demonstrated the best catalytic activity in the DRM, while the Fe variant demonstrated better stability. This apparent specialization of the two materials was linked to the Fe variant possessing a stronger metal-support interaction and abundance of lattice oxygen species, promoting surface carbon deposit oxidation, over C-H bond activation [145]. A comparison between Co perovskite and a Co-Cu perovskite found that the addition of Cu in the structure greatly enhanced the catalysts ability to resist sintering and coking, while also improving the metal-support interaction; the Co-Cu perovskite required an almost 1:1 ratio of $\text{Cu}:\text{Co}$ to achieve this effect [169].

3. CO₂ hydrogenation

As previously stated, the conversion of CO₂ is achieved using a multitude of reactions, some of which were presented in Section 2.1. Further to those reactions, the field of CO₂ hydrogenation includes the RWGS (Eq. 5), Sabatier (also known as CO₂ methanation, Eq. 8), CO₂-to-Methanol (Eq. 9), CO₂-to-Dimethyl Ether (DME) (Eq. 10).

The RWGS reaction (Eq. 5), is one of the reactions becoming more popular owing to its applicability towards CO₂ recycling and production of 1:1 syngas. The RWGS reaction is seen as a key intermediate step in CO₂ hydrogenation as it effectively produces CO from CO₂; CO is a much more reactive feedstock for C1 chemistry [170]. That it occurs at lower temperatures is another factor that makes the reaction significantly more attractive.

Several well-known hydrogenation reactions can be fed with CO₂: The Sabatier reaction to produce methane as a source of synthetic natural gas as fuel (Fig. 6), the CAMERE process (Fig. 7a) [171] that produces methanol from CO₂ via the RWGS and

the Fischer-Tropsch (FT) process that requires syngas, produced by methods similar to those discussed in Section 2.1 [172–174]. CO_2 -to-DME (Eq. 10) is another attractive reaction, that proceeds from CO_2 to DME via the formation of methanol followed by its dehydration into dimethyl ether. This reaction is seeing a resurgence in interest given that DME is a viable alternative to petrochemical hydrocarbons as a fuel or as a precursor for other complex compounds [175–178]. Furthermore, the formation of olefins, aromatics and gasoline can be formed from methanol that is ultimately synthesized from CO_2 hydrogenation [176].

Fig. 6 Illustration of importance of the Sabatier reaction for energy generation –adapted from [171]

The CAMERE and FT processes have reported enhanced efficiencies (approximately 20%) when CO generated from RWGS reaction was used as raw material [172]. However, the Sabatier reaction exists as a major competing reaction and occurs at low temperature ($<500\text{ }^{\circ}\text{C}$) (Fig. 7b); A highly unwanted material where F-T or CAMERE processes are concerned. As an additional drawback, the Sabatier reaction consumes 4 moles of hydrogen per mol of CO_2 , thus imposing extra process cost. In this regard, there should be an emphasis on producing a selective and efficient reverse water gas

shift catalyst, to control the cost and purity of the final product.

Fig. 7. (a) A diagram of the CAMERE process and how the RWGS takes part - taken from [171]. (b) Equilibrium compositional plot for the hydrogenation of CO₂ – reproduced from [170].

3.1. Noble metal catalysts

Towards this end, a variety of catalytic materials has been investigated for RWGS reaction; An early work by Wambach *et al.* investigated a number of metals supported on ZrO_2 to assess their CO_2 hydrogenation ability [179]. This study found that Cu and Ag were highly effective for methanol formation; Ni and Ru mainly produced CH_4 ; finally, Au, Pd, Pt and Rh were shown to produce a mixture of methanol, CO and CH_4 [179]. Noble metals, such as Au, Pt, Pd, Rh and Ru, exhibit high activity, stability and selectivity for CO_2 reduction to CO [179,180]. Research has since progressed in this

field, detailing that it is the unfilled D-orbital of the noble metals that facilitate the relatively strong reactant adsorption, further allowing for the formation of the reactive intermediate species [170]. A series of studies by Kim *et al.* and Chen *et al.* focus on the use of Pt/TiO₂ as RWGS catalysts [181–183]. These studies found the reducibility of the TiO₂ support to be extremely valuable to the reaction, as the creation of oxygen defect sites in the support structure allowed for facile CO₂ activation, producing Pt-O_v-Ti³⁺ interfaces. However, these catalysts are prone to CH₄ production at lower temperatures ($\geq 10\%$ at ca. 500 °C), though this was shown to increase proportionally with Pt wt% [181]. Pt and Pd were loaded onto La-ZrO₂ and Y-ZrO₂ and compared to Ni, Fe and Cu over the same supports within the RWGS reaction, with the assistance of an electric field to aid in the reduction of the reaction temperature [184]. The study found that while the noble metals converted more CO₂, Pt > Pd / 10 wt% La-ZrO₂, their CO selectivity reached ca. 99% (Pt) and ca. 98.5% (Pd). These values were improved when the electrical field assistance was increased from 3 mA to 7mA, though this only served to bring the Pd CO selectivity in line with the Pt CO selectivity. This same increase in electrical field assistance produced a 10% increase in CO₂ conversion for the blank support and the noble metal catalysts. Interestingly, increasing the metal loading from 1 wt% to 2.5 wt% only elicited a decrease in the Pt and Pd catalysts performance.

Alternatively to Pt, Büchel *et al.* investigated an Rh/Al₂O₃ catalyst with Ba and K promotion [185]. The promotion was affected using a two-nozzle spray pyrolysis method that allowed for the Rh to be selectively deposited on the Al or the promoter. This selective deposition demonstrated profound effects on the catalyst activity; the Al-Ba/Rh catalyst demonstrated superior CO₂ conversion to the Rh/Al-Ba catalyst, meaning that Rh benefited more from being deposited on Al, rather than Ba. Meanwhile,

the reverse was true for the K promoted material, with the Al-K/Rh catalyst displaying minorly improved CO₂ conversion to the Rh/Al-K catalyst. Regardless of which promoter was used, the performance was markedly less than the Rh/Al₂O₃ catalyst below 500°C. The K promotion was found to exhibit greater CO₂ conversion and demonstrated 100% CO selectivity across the entire temperature window, where Ba promotion favored methanation. Interestingly, both Ba and K promotion caused the catalyst to store CO₂ as carbonates of the respective metals, though this did not influence the overall performance [185]. Another study found that a bimetallic Pt-Co catalyst on CeO₂ was fully selective towards the RWGS reaction, with negligible production of methane [182]. Compared to the Pt-Ni catalyst also tested in the study, the Pt-Co material did not convert as much CO₂; the Ni containing catalyst was noted to produce significantly more methane as Ni is known to promote methanation reactions [186].

Pt and Pd, in particular, are effective for methanol synthesis [176,187–189]. Several studies were published on noble metal catalysts for low temperature and pressure synthesis of methanol from CO₂: Fiordaliso *et al.* produced a Ga-Pd/SiO₂ catalyst that demonstrated significantly improved performance compared to the standard Cu/ZnO/Al₂O₃ [190]. However, the catalyst still demonstrated CO selectivity, as did the Cu/ZnO/Al₂O₃ catalyst, but to a greater extent. Another bimetallic catalyst, Pt-MoO_x/TiO₂, demonstrated high methanol yields with increasing Pt and MoO_x loading, up to 3 wt% and 30 wt% respectively [191]. The authors noted that the key to the success of this catalyst was the inclusion of MoO_x, which promoted the hydrogenation of CO₂ at low temperature, especially towards methanol production. As discussed in Section 2.2.1, the redox properties of CeO₂ are well known to aid catalytic processes; Yang *et al.* compared Cu/CeO₂/TiO₂ and Au/CeO₂/TiO₂ for the production of CO and

methanol [192]. Intriguingly, the Au catalyst preferentially produced more methanol than the Cu catalyst. The authors attributed this behaviour to the effect of CeO_2 producing an abundance of Au- CeO_x interface sites, as well as the CeO_2 taking an active role in the activation of CO_2 .

The activity of noble metals has been extensively investigated within the Sabatier reaction, displaying both high CO_2 conversion and CH_4 selectivity [193–198]. Many works in this area focus on Ru as the active phase [199–204]. Most investigate bimetallic formulations, using baser metals to promote the Ru active phase: one particularly interesting work investigated the use of Li, Na and K against a pure Ru/ Al_2O_3 catalyst [202]. Of these, only the addition of Li produced a superior catalyst to Ru/ Al_2O_3 ; the addition of Li was found to drastically improve the CO_2 conversion of the catalyst across the entire investigate temperature window (200–450 °C), though the selectivity was unaffected, having already reached the equilibrium production of CH_4 . The activation energy required for CO_2 increased when using the alkali metals, to a maximum of 87 kJ/mol for the Li-Ru/ Al_2O_3 catalyst (compared to 73.3 kJ/mol for Ru/ Al_2O_3), however, the reaction rate was increased almost 5 fold compared to the Ru catalyst. Another work investigated two complex Ca oxide supports on the performance of Ru catalysts, one reduced and the other, not [203]. The non-reduced Ca oxide supported Ru catalysts were found to exhibit considerably higher levels of CO_2 conversion compared to the reference Ru/ Al_2O_3 catalyst, reporting TOFs 26 times greater.

Further to bimetallic catalysts, a recent trimetallic catalyst, Ru-Fe-Ce/ Al_2O_3 , was also investigated [200]. The catalyst was reported to possess considerable CO_2 conversion over 40 hours (ca. 95%) with almost total methane selectivity, owed to the presence of

Fe within the active phase. A similar Pd-Fe bimetallic system was investigated by Luo *et al.* [205], which purported the intermetallic bonding, between the two metals to be a key factor in its performance through the maintenance of surface Fe crystallites. This formulation was so effective, there was essentially no activity loss after 60 hours of continuous operation.

As with CO₂ reforming, noble metal-based catalysts **within CO₂ hydrogenation** are ill-suited to industrial application due to their cost and scarcity, making it desirable to **supplement** these materials by introducing more economically appealing catalysts.

3.2 Base metal catalysts

As with the DRM, the literature standard for catalysts in CO₂ hydrogenation is SMNs. This structure has borne considerable fruit, with the development of synergistic support media that prevents deactivation processes or aids in tuning the reactive selectivity, with recent research finding many promising catalysts developed using clays [206], ceria-alumina supports [207] and MoO₃/FAU zeolites [208], among many others [170,180,209] (Table 5). Transition metal-based catalysts represent an economically interesting alternative to noble metals, as they present comparable activity and selectivity [210] at a much more attractive cost, despite their drawbacks. For instance, copper-based catalysts were found to be more selective for CO production via the RWGS reaction [211–215]. Cu is one of the main choices for RWGS and methanol production from CO₂ due in part to its methanation suppression [206,216–218] properties, with the industrial standard for methanol production being Cu/ZnO/Al₂O₃

[219]. This formulation is favored as the ZnO imbues several key benefits to the Cu catalyst: improved dispersion and stabilisation, lattice oxygen vacancies and the ZnO possess a lone electron pair that is active for methanol synthesis [220]. An investigation was done into the effect of Cu:Zn ratio alteration and the effects had on performance; the authors determined that a Cu rich catalyst ($\text{Cu:Zn} > 3$) over alumina produced the best activity, revealing the linear relationship of catalytic activity and Cu surface area [220].

Iron and Cobalt are other potential candidates, though these two metals are extremely selective towards hydrogenation reactions that produce C_{2+} products [170,176,221,222]. Despite this selectivity preference, these metals have displayed RWGS activity [223]. Fe has shown promise as a promoter of or combined with, other metals [224–227]. In particular, Fe catalysts promoted with Mn or K produced a range of hydrocarbon material, from CO to $\text{C}_1\text{-C}_{5+}$ [226] at low temperatures ($<400^\circ\text{C}$). This was found to rely on a combination of Fe_3O_4 and Fe_5C_2 that is formed during the reaction; this latter phase was found to be responsible for the formation of the more developed carbon material, while the former phase is responsible for the RWGS performance. Once the temperature increased, the catalyst was much more selective towards the RWGS. When combined with Cu, Fe was found to prevent sintering and coke deposition, greatly improving the performance of the Cu catalyst. The Fe acted as an oxygen sink, binding to O atoms that spilled over from Cu, allowing the Cu active phase to remain reduced [224]. When combined with either Mo [225] or K [228], the Fe catalysts were found to be extremely effective high-temperature RWGS catalysts. The addition of the promotor

metals facilitated the stabilisation of reactive intermediates but also promoted the dispersion of Fe. Interestingly the Fe-Mo catalyst was found to form $\text{Fe}_2(\text{MoO}_4)_3$ that prevented the reduction of other Fe oxides that would otherwise have reduced the catalytic activity [225]. Although CO_2 conversion can be effectively achieved over Ni, which performs exceedingly well towards hydrogenation reactions like the Sabatier reaction, rather than the RWGS [229]. Therefore Ni catalysts require modification to achieve better selectivity and stability for RWGS reaction [230,231].

Table 5. Collection of base metal catalysts used in the RWGS reaction from literature.

Catalyst	Temperature (°C)	H ₂ :CO ₂ Ratio	CO ₂ Conversion (%)	CO Selectivity (%)	WHSV (mL/g _{cat} h)	Ref.
NiCu/Sap	700	4	73	93	15,000	[206]
FeCu/CeAl	700	4	70	100	30,000	[207]
RuNi/CeZr	700	4	72	91	24,000	[217]
FeNi/CeZr	700	4	71	91	24,000	[217]
Vanadium Carbide-2*	600	3	45	100	20,000	[232]
Vanadium Carbide-1*	600	3	35	100	20,000	[232]
FeMo/Al ₂ O ₃	600	1	N/R	32	30,000	[225]
Cu/CeO ₂ -hs	600	3	50	N/R	300,000	[233]
Mo(1)/FAU	500	1	14	99	7500	[234]
Ni(1)/FAU	500	1	17	45	7500	[234]
Mo ₂ C/N-C(100)	400	3	30	88	24,000	[235]
Mo ₂ C/N-C(10)	400	3	18	100	24,000	[235]
Pt-Pd@UiO-67**	400	3	18	81	24,000	[236]
80 wt% Cu/CeO ₂ rod*	400	4	45	90	60,000	[237]
FeK/m-C***	300	3	50.6	8	2000	[238]

* This catalyst was tested under these conditions at 0.1 MPa; **This catalyst was tested under these conditions at 2 MPa; ***Catalyst tested at 25 bar and produced numerous C₂+ hydrocarbons

Recent advances in catalyst design for the hydrogenation of CO₂ focus on the use of transition metal carbides (TMCs) over noble metals, owing to their ability to maintain

high levels of H_2 dissociation and $\text{C}=\text{O}$ bond scission [170]. A recent work detailed extremely high levels of activity for CO_2 hydrogenation [180] with the use of Ni, Au, and Cu particles deposited on TiC. The authors noted that the main product of the reaction over these materials was CO. This was attributed to the presence of small 2D particles or clusters close to the TiC. They went on to detail that further hydrogenation of CO over the Au and Cu materials produced methanol.

Further to TiC, Mo carbides (α -, β - Mo_2C and δ -MoC) have been demonstrated so effective at H_2 dissociation and $\text{C}=\text{O}$ scission drastically outperforms Pt- or Pd-M/ CeO_2 (M = Ni or Co) in the RWGS reaction [239,240]. The activity of the (001) faces of both β - Mo_2C and δ -MoC were investigated using DFT calculations, where it was determined that Mo terminated edges of the (001) face of Mo_2C is extremely effective at adsorbing and decomposing the CO_2 molecule and producing methanol and CO. This performance was linked to the ratio of C:Mo, showing that the higher ratio present in Mo terminated Mo_2C presented vast improvements over MoC [241]. Mo_2C was compared to many other TMC materials (TiC, ZrC, NbC, TaC and WC) where it displayed substantially superior performance in the low-temperature RWGS [242]. This study linked high RWGS performance to Mo_2C possessing the lowest oxygen binding energy of the examined carbide catalysts. Furthermore, Mo carbides are further improved when loaded with metals like Cu [243,244]. This was further developed by Zhang *et al.* [243] where they synthesised a Cu/ β - Mo_2C catalyst that completely outclassed its comparative catalysts, two of which were noble metal catalysts. This catalyst demonstrated impressive stability, only decreasing 15% over 40 hours. The

performance was attributed to strong metal-support interaction between the Cu and the hexagonal structure of the carbide, which was found to both increase dispersion and prevent sintering.

Another prominent TMC is Vanadium carbide (Fig. 8); the activity of this material was linked to C vacancies, as VC has an extremely low affinity for oxygen [245,246], which conventional understanding of the RWGS reaction suggests should make VC a poorly performing catalyst. DFT calculations found that V *d* and C *p* orbitals also produce hydrogen binding energies slightly lower than those present in Mo₂C and WC [247–249]. The presence of C vacancies was confirmed experimentally and theoretically via DFT calculations to increase the adsorption energies of H₂ and CO₂ and thus, reducing

Fig. 8. (a) Potential energy reaction profiles (PBE-D3 including the ZPE term) for the RWGS on the VC (001) surface (grey) and on the VC-vac (001) surface model (green). (b) Equivalent Gibbs free energy reaction profiles at $T=873$ K, $p_{\text{CO}_2}=20.26$ kPa, $p_{\text{H}_2}=60.79$ kPa, and $p_{\text{CO}}=p_{\text{HO}_2}=0.20$ kPa – reproduced with permission from [232].

the activation barrier for their dissociation [232]. This was most clearly demonstrated in the plots of potential and Gibbs free energy presented in Fig. 8.

The use of TMCs is not the only method of incorporating oxygen storage properties

into a material; CeO₂ was investigated in a 2017 work, using this material as the support for Ni, Co, Fe, Mn and Cu catalysts. Interestingly, the Fe, Mn and Cu-CeO₂ catalysts reported the lowest conversions of CO₂, but also the highest subsequent CO selectivity of all the materials tested [250]. The most active catalyst found in this paper in terms of CO₂ conversion was the Ni-CeO₂, followed by Co-CeO₂ > Cu-CeO₂ > Fe-CeO₂ > Mn-CeO₂ > CeO₂. While the Ni and Co variants reported the highest CO₂ conversion, these two catalysts also were the only materials to report CH₄ production. The Cu-CeO₂ variant was found to maintain 100% CO selectivity throughout, but with substantially improved CO₂ conversion when compared to the Fe- and Mn-CeO₂ catalysts (31% vs 8.6% and 8.1% CO₂ conversion, respectively). The results of this paper raise the potential for a bimetallic formulation involving Ni and Cu with CeO₂ to benefit from both high CO₂ conversion and CO selectivity. Cu is particularly interesting as it is capable of the direct conversion of CO₂ to methanol. Cu is most efficiently applied to synthesize methanol from CO₂ when coupled with ZnO, which provides Cu dispersion and stabilization but also an electron pair and contains lattice oxygen vacancies that are both active towards methanol synthesis [251].

Where thermal CO₂ methanation is concerned, the most popular topical catalysts are Ni, Co and Fe, which have been demonstrated extensively to be effective [198,252,261,262,253–260] towards this reaction (Table 6). While the Sabatier reaction is usually performed between 250-300°C, some very recent and promising works have found a way combining the combustion of H₂ with methanation, allowing the reaction

to be undertaken at room temperature [263,264]. The authors coined this combination to be “auto-methanation”; the reactant gas including 1%–7% O₂ to facilitate the combustion; The investigated Ni/CeO₂ catalyst was not affected by active site oxidation. The same group investigated Ni/X and Ru/X (X = SiO₂, ZrO₂, Y₂O₃, MgO, Al₂O₃ and TiO₂) to determine if this auto-methanation character was specific to Ni/CeO₂ [265]. The results of this work found that these materials are capable of the auto-methanation character (operating at 25 °C) with impressive CO₂ conversions (*ca.* 70% for Ni/CeO₂) with complete selectivity towards methane at an extremely high space velocity (80,000 mL/g_{cat}/h). This displayed character was shown empirically to deteriorate with increasing temperature, but only mildly. Remarkably, the inclusion of oxygen into the reaction mixture was not found to cause the combustion of methane, a phenomenon which the authors attributed to the minimum ignition energy of methane and oxygen is much higher than hydrogen and oxygen. Huynh *et al.* presented a Ni-Fe bimetallic catalyst, aimed at large scale methane production [266]. The choice of this catalyst was made around further reducing the cost of Ni-based catalysts, with Ni-Fe alloys being even cheaper than pure Ni. In this work, the authors investigated a 20 wt% Ni- 2 wt% Fe catalyst derived from hydrotalcites to exploit the resultant strong metal-support interactions and high levels of active phase dispersion. When tested, the catalyst demonstrated high levels of methane selectivity in the higher temperatures (>250 °C) and was found to perform consistently over 65 hours of continuous reaction at 300 °C, reporting 70% CO₂ conversion and 95% CH₄ selectivity.

In a variation from incorporating other transition metals with Ni to enhance methane

selectivity and carbon dioxide conversion, Vogt *et al.* have explored the use of an alkali metal, K, as dopants for Ni catalyst to produce methane in electrocatalytic cascade reaction that produces the required hydrogen [267]. The method of K promotion is intriguing; the K component is added *in-situ* as a result of a poisoning mechanism due to the use of KOH and water to produce hydrogen. Promotion in this way caused the Ni/SiO₂ catalyst to achieve significantly higher TOFs compared to unpromoted and *ex-situ* K promoted Ni/SiO₂.

Table 6. Collection of base metal catalysts used in the methanation reaction from literature.

*Tested with 0% O₂; **Tested at 5% O₂; ***calculated using 60mg catalyst + 600mg SiC; + calculated using 200mg catalyst + 800mg SiC

Catalyst	Temperature (°C)	H ₂ :CO ₂ Ratio	CO ₂ Conversion (%)	CH ₄ Selectivity (%)	WHSV (mL/g _{cath})	Ref.
Ni-MgAl (hydrotalcite)	400	4	80	100	5017h ⁻¹	[268]
Ni/CeO ₂ *	350	4	80	100	80,000	[264]
NiFe-1M	350	4	80	95	9000 (100,000***)	[266]
Co/CeO ₂ nanorod	350	4	50	85	30,000	[269]
Ni/CeO ₂ nanorod	350	4	ca. 90	100	30,000	[269]
Ni/ZrO ₂	350	4	80	ca. 99	20,000	[270]
Ni/CaZrO ₂	350	4	ca. 75	100	4800 (24,000+)	[271]
Ni/CeO ₂ *	250	4	0	0	80,000	[263]
Ni/CeO ₂ **	250	4	65	100	80,000	[263]

4. Encapsulated materials

Having validated the use of Fe, Co, Ni and Cu as effective CO₂ recycling materials in a variety of formulations and applications, the focus now shifts to the topic of this review, the developing field of morphological variation, specifically encapsulation.

Further to the well-established SMN materials, there exists a family of catalysts that use an engineered structure: yolk@shell (YS) materials. This structure, a derivation of the more common core@shell (CS), encapsulates the active phase within a protective, porous shell material to prevent the more usual forms of deactivation (sintering and coking) while maintaining a void between the active phase and the shell (Fig. 9).

Fig. 9. Graphic representation of synthetic routes for core shell and yolk shell morphologies – reproduced from [24].

Catalysts that use this morphology are still emerging as the structures' benefits are better explored and understood [24,272–277]; a key benefit offered is that of the confinement effect. This phenomenon is often under-discussed for these materials as it is still not fully understood, but is divided into two types: quantum and spatial, with the difference between the two explored in more detail elsewhere [278–280]. The confinement effects can be summarised as both a considerable protective and performance-enhancing boon, that serve to prevent the build-up of carbon deposits and sintering, while providing a homogeneous reaction environment that allows for the enrichment of reactants [281–286], in addition to potentially increasing internal pressure to facilitate more complex reactions [278]. It has been postulated that the confinement of the active sites to avoid sintering, has the knock-on effect of also

preventing sintering: the relationship between Ni particle size and carbon formation being well established. Depending on the composition of the shell or intensity of interaction between metal and shell, it is also possible that if the surface of the shell becomes rapidly functionalised with -OH groups due to CO₂ dissociation, which are highly effective at preventing coke build up [287]. Another explanation of the coking resistance is that confinement prevents the linear adsorption of carbonaceous molecules that would otherwise become a carbon deposit [288]. The reasoning behind why the prevention of the linear adsorption of these carbonaceous molecules could be explained by another recent work; a 2D model of graphene/Pt(111) was proposed to best describe the confinement effect phenomena, owing to the relatively well-defined structure of the overall model as well as ease of its modelling [278]. This study demonstrated how different forms of graphene-based “covers” (hexagonal boron nitride (h-BN), graphene, graphane and ZnO/Pt) altered the activity of Pt(111) in the oxygen reduction reactions (ORR); finding that a graphane “cover” offered the best improvement for this reaction over plain Pt(111). The structure of the carbon “covers” varies by hydrogen content: Graphene is an entirely C-C, 1-atom thick honeycomb sheet, graphane is a half hydrogenated variant of graphene and graphane is a fully hydrogenated variant of graphene. It was seen to produce the best activity with favorable surface binding energies (ΔE_O) for O atoms, demonstrated on a Volcano Plot as being close to the apex.

Fig. 10. Volcano plot displaying the activity against binding energies of the various Pt catalysts. The peak illustrated by the dashed line shows the ideal binding energy and activity for the oxygen reduction reaction. Fig. reproduced with permission from [278].

This can be interpreted as a “Goldilocks Zone” of activity where conditions are “just right” (Fig. 10). The study found a significant weakening of adsorption in atoms in the void between Pt(111) and graphene.

Encapsulated materials have been seen in literature in the 1990s with works detailing silica-coated gold colloids [289], followed by silica-coated gold nanoparticles [290] being prominent. These nanoreactors are capable of simultaneous reactions, have higher product selectivity than traditional catalytic material, and display an overall enhanced performance due to the higher active surface area. All these factors make them highly capable catalytic materials with a varied range of applications that researchers have devoted significant resources into exploring [291–296].

The terms “nanoreactors” and “nanorattles” are two of the more common terms associated with YS materials that generally follow “core@void@shell” structure. This

structure is directly responsible for the high surface area to volume ratios that partly make this morphology so attractive. Another defining feature is the porous shell, which allows for the diffusion of reactants and products in and out of the shell while protecting the core. Generally, these particles consist of a metal or metal oxide core within an inorganic or polymeric shell; common choices for which are silica or carbon as these are highly stable, abundant and inert [297–299]. There are also limited reports of the use of Ceria [300] and Iron [301] as shell media. The performance of this morphology is highly dependent on factors such as overall particle size, the thickness of the shell and sample uniformity, all of which can be carefully tuned through the synthetic method. Synthetic techniques for YS particles include selective etching [294] and soft [302,303] or hard templating [304]. These methods provide a high degree of control required to properly tailor these particles towards catalytic purposes.

With the high degree of interest in YS catalysts, the development of more advanced and complex YS structures that further enhance the performance benefits offered by this structure was undertaken (Fig. 11). These more complex structures vary from the “basic” single encapsulated core (Figs. 9 and 11a), to multiple encapsulated cores, so-called “raspberry cores” [305], and even a single core with multiple shells [306]. Generally, these more advanced variations are derived from the single encapsulated core and offer increased performance benefits due to the structural variant, e.g. multiple cores display higher active surface area [305]. Although each variant has its specific benefits, no one variant can be defined as superior, as each chemical process has different demands better suited to one version or another, making reaction tailored YS particles necessary.

Fig. 11. Schematic illustration of several YS variations: (a) Standard single core yolk shell, (b) multi-core yolk shell, (c) single core yolk shell with cores embedded in the shell and (d) single core yolk shell with multiple shells

Another factor that makes these materials more attractive than SMNs is that the metallic core, responsible for the catalytic reaction, is protected by the porous shell [292,294,307,308] from the conditions that would cause agglomeration or severe coking in traditional SMN formulations.

There are several reviews concerning YS materials and their varied catalytic applications and synthetic methods [274,291,309,310]. However, for this work, we will specifically focus on the use of YS materials towards CO₂ valorisation. As the use of YS materials is under-reported, this review has included several CS catalyst studies to demonstrate the effectiveness of simply encapsulating the active phase, to promote the investigation of the potential benefits of applying the YS morphology in these same areas.

4.1. Application towards the dry reforming of methane

Within the context of YS materials applied to CO₂ recycling, yolk@shells are often applied to the DRM [311–314]. Owing to the high-temperature requirement of DRM, the yolk@shell morphology offers an answer to the common problems of sintering and coking that are exhibited by SMNs. Studies for this reaction focus almost exclusively on Ni, due to its well-documented activity towards this reaction, with the use of a variety of dopants or promoters as a widespread variation. The common finding of the studies that apply these YS materials to DRM, usually utilising Ni@SiO₂, is that there is almost a complete elimination of sintering and a significant reduction in coke formation. The lack of sintering is due to the confinement effect that the encapsulation provides. The reason for the resistance to coking, however, is more difficult to determine. The use of YS catalysts in CO₂ recycling reactions is an increasingly documented subject, though literature focuses on the application towards the DRM reaction. However, the literature concentrates largely on the use of Ni and SiO₂ with minimal variation from this combination. Several works concerning the use of Ni@SiO₂ YS materials for the DRM reaction have been reported in recent years [276,311,315–317], demonstrating a high level of effectiveness for this material combination. Notably, Lu *et al.* [311] detail a simple synthesis for a multicore YS material that displayed no sign of deactivation over 50 hours of continuous exposure to the DRM reaction, though their technique produced a wide distribution of particle sizes. In Li *et al.*'s 2014 work [276], they produced a Ni@Ni@SiO₂ material that involved not only a central Ni core but other Ni cores dispersed throughout the SiO₂ sphere. This material performed extremely effectively within the DRM, displaying high conversion

with negligible deactivation and carbon deposition, after over 80 hours of continuous reaction. This serves to demonstrate the longevity provided by the porous shell and its associated confinement effects. Our group has recently demonstrated the superior performance of Ni@SiO₂ catalysts in comparison to “state of the art” materials in DRM such as Ni/CeO₂ and Ni/Al₂O₃ (Fig. 12).

Fig. 12. (a) Schematic representation of DRM reaction over-engineered Ni@SiO₂ catalysts. (b) CH₄ conversion in a DRM test comparing Ni@SiO₂ vs state of the art catalysts at 850°C, WHSV = 30 L g_{cat}⁻¹ h⁻¹ and a reactant ratio CH₄:CO₂ = 1:1; (c) fresh Ni@SiO₂ sample pre-reaction; (d) post-reaction sample. Image (b) is from [317]. Images (c and d) from [316] – published by the Royal Society of Chemistry.

In this study, Ni core particles are protected by an SiO₂ outer layer of resulting in a

nanoreactor of *ca.* 500nm. As shown in Fig. 12(b), traditional catalysts collapsed after a few hours of reaction while the encapsulated materials remain stable. Our seminal works [316,317] serve as a proof of concept to showcase the efficiency of Ni@SiO₂ catalysts for gas-phase CO₂ recycling via DRM. Nevertheless, we observed the formation of well-defined carbon nanotubes (Fig. 12d) when the reaction is run for long

periods (140 h) resulting in some level of deactivation. This observation reveals a key aspect of yolk-shell catalysis: Full encapsulation of the active phase is very challenging but results essential to achieve long-term stability. Unencapsulated Ni particles are prone to sinter and large Ni cluster are easily coked.

Although both Ni and SiO₂ provide numerous reasons for their success in this field, for example, the thermal and chemical resistivity of SiO₂ and high activity of Ni towards CO₂ reduction, this shows clear room for diversification within the catalytic composition.

Careful selection of promoters or support media greatly improves the life span of a catalyst. For example, the utilisation of materials like CeO₂ provide redox properties [318,319] to increase the resistance to carbon formation, while materials like SiO₂ or Al₂O₃ provide thermal resistivity and high dispersion to prevent sintering. Whereas these inclusions are relatively simple for SMP catalysts, their inclusion in the YS morphology can be more complex, as the main active sites are contained within the shell. Core size is very much a constraining factor. There are many reports of YS materials ranging in size from 200–800 nm [274,316,320,321], while SMP materials often feature sizes in the range of microns. Therefore, the incorporation of synergistic materials can be achieved through the adaptation of the shell material. There are examples of metal@CeO₂ YS particles [300] that are particularly resistant to coking within the DRM while maintaining the high surface area. It can be inferred, therefore, that the support design considerations that SMP materials enjoy are analogous towards

the shell material of encapsulated catalysts.

Another study suggests that the inhibition of carbon formation could be related to the thickness of the SiO_2 shell, stating a shell thickness of >8.6 nm to be most effective at reducing carbon deposition [276]. Another paper suggests that the impetus for carbon diffusion in Ni crystallites might be weakened if the size of the Ni crystallite is maintained below 5 nm [35]. These conditions still allow for the formation of “soft” carbon. As this can be gasified on the Ni surface to CO or methane, the effect on performance can be considered negligible. The use of dopants such as MgO [322,323], ZrO_2 [324] or CeO_2 [325,326] has been found to improve the performance of Ni catalysts within the DRM. A study by Zhao *et al.* [314] put this finding into effect when they produced NiCe@SiO_2 yolk@shell materials, utilising the oxygen storage capacity of CeO_2 to assist in the removal of surface carbon [326]. Upon comparison against traditional SMPs, the NiCe@SiO_2 material displayed the most absorbed oxygen, thus demonstrating a better ability to combat coke formation. In terms of catalytic activity towards the DRM over 40 hours, the YS material had higher CH_4 and CO_2 conversion and only a 2.9% drop in activity, thus validating the use of Ce as a highly effective dopant for catalysts used in the DRM.

The use of dopants follows the extensive investigation of the use of Noble metals, i.e. Au [327–329], Pt [327,330], Pd [327]. Catalytic materials that incorporate these materials often display very impressive results in terms of conversion, in addition to improved stability and coke resistance [75,331]. However, these results come at a significant expense that limits their use to low wt% dopant loadings. It comes as a

surprise then, to find Au used liberally in an Au-Fe core@shell material developed by Sun *et al.* [332], not only incorporating Au into the core but also utilising it as the shell media. In addition to the cost being justified as being less than pure Au, the most admirable quality of this reported CS material lies in the small particle size and the considerable long-term activity (90 hours) towards electrochemical CO₂ reduction to CO, with faradaic efficiencies of 97.6%. This is a vast improvement over 30.5% displayed by pure gold nanoparticles.

Generally, however, the use of noble metals remains firmly in the aspect of doping. While it is also possible to dope with cheaper metals, another approach is to create bimetallic materials to benefit from similar effects that dopants offer, while in some cases using a specific quantity to form an alloy. A 2013 work investigated an alloy of Ni-Cu with CS morphology towards the DRM, achieving extremely small particle size with no measurable activity loss following 16 hours continued use [333]. These Ni-Cu alloy cores displayed no elemental separation and a crystallite size averaging 12 nm after XRD characterisation, confirming the formation of extremely small bimetallic alloy nanoparticles. HRTEM confirmed this further, displaying fringe spacing within the range for (111) pure Cu and Ni. A more recent work combined the benefits of noble metal doping and bimetallic alloys with a PtCu alloyed *yolk@shell* particle for electrochemical applications. The difference in shape positively altered the effectiveness of the material, owing to the presence of different crystal planes, displaying 2.5 times the activity of the commercial Pt/C electrocatalyst for methanol oxidation [334]. There are further examples of bimetallic YS materials used for a

variety of applications, for example, batteries [335], oxygen evolution [336] and even protein detection [337].

4.2. Application towards CO_2 hydrogenation

Fig. 13. Generalised application of yolk@shell catalysts towards CO_2 hydrogenation reactions, as well as the benefits of the morphology – Reproduced with permission from [24]

This structure with base metals is beginning to find increasing use within hydrogenation reactions [24] (Fig. 13); recent work has found $\text{Ni}@ \text{UiO-66}$ to be particularly effective for the Sabatier reaction. The combination of small Ni nanoparticles and extremely high surface area from the UiO-66 allowed for this catalyst to convert 57.6% CO_2 at 300 °C with 100% CH_4 selectivity for 100 hours.

The authors investigated $\text{Ni}@ \text{SiO}_2$ and $\text{Ni}@ \text{ZrO}_2$ as comparison materials and found these to perform worse than the UiO-66 encapsulated variant, though the $\text{Ni}@ \text{ZrO}_2$ was noted to achieve much better conversion than the SiO_2 [338]. Another recent study detailed the use of $\text{Ru}@ \text{RuC}$ CS particles for CO_2 methanation at very low temperatures (160 °C) [339]. This series of catalysts investigated several ways of generating the

carbide species, which was found to facilitate the direct and complete conversion of CO_2 to methane. These catalysts only displayed activity loss when the surface carbide species were removed during the reaction (Fig. 14b).

A very effective Sabatier reaction catalyst was reported in 2014, where the authors reported over 100 hrs of activity at 300 °C with 87% CO_2 conversion and 99% selectivity towards CH_4 using a Ni-MgO@SiO_2 catalyst [340]. The authors attributed

Fig. 14. (a) Diagram of the Ru@RuC core shell material. (b) Stability data of Ru@RuC catalyst containing 20 wt% Ru –Reprinted with permission from [339]. Copyright {2020} American Chemical Society

the high activity to the dispersion and stabilisation of Ni in the MgO solid solution, in addition to the protection provided from the SiO_2 shell. A year later, a Ni@MOF-5 catalyst was reported for the same reaction, under similar conditions, however, the reaction was conducted at 320 °C [341]. This latter material was reported lower CO_2 conversion (75%) than the Ni-MgO@SiO_2 catalyst, though the Ni@MOF-5 catalyst contained significantly less Ni. An extensive work reported the doping of $\text{Ni/Al@Al}_2\text{O}_3$ with a wide array of different metals (Mn, Ce, Zr, Mg, K, Zn and V) applied towards the Sabatier reaction [342]. Following reactive testing, only two variants (K and Zn) performed worse than the undoped $\text{Ni/Al@Al}_2\text{O}_3$, with the best material reaching 100%

CO₂ conversion at just below 300 °C (Ni-Mn/Al@Al₂O₃). This catalyst also presented CH₄ formation rates far superior to any of the comparison catalysts.

Aside from MOFs or metal oxides, HZSM-5 has also been found to be an effective media to protect active metal nanoparticles [343,344]. When investigating the potential of a Ni@HZSM-5 catalyst compared to Ni/SiO₂, the encapsulated material far surpassed the SMN material at 400 °C, where the catalyst demonstrated over 40 hours of continued operation (66% CO₂ conversion, 99.8% methane selectivity). Furthermore, the encapsulated material successfully prevented leaching and sintering, which the comparison materials demonstrated considerable weakness. A carefully designed

hollow Co@HZSM-5@Pt catalyst was found to be highly effective for the conversion of CO₂ to C₂₊ within the Fischer-Tropsch reaction due to a tandem hydrogenation mechanism, where the outer Pt facilitated the initial conversion of CO₂ to CO (RWGS), and the inner Co converted this into C₂₊ and methane (Fischer-Tropsch) [345]. Only the hollow Co@HZSM-5@Pt catalysts were found to produce C₂₊ material in addition to methane, which increased with increasing Pt wt% up to 5%, before decreasing: 2.5 wt% Pt = 23% C₂₊, 5 wt% Pt = 46% C₂₊, 7.5 wt% Pt = 40% C₂₊ and 10 wt% Pt = 12%

C₂₊.

Similarly, CoSi@Pt and MnSi@Pt catalysts were prepared from ZIF-67 nanocubes, which went on to display impressive low-temperature RWGS (200 °C) and Sabatier performance [346]. Cascade reaction catalysts created in this manner benefit from the physical separation of the two metallic phases, maintaining the individuality of the two (or more) metals that facilitate different reactions to occur.

There is very little reported work regarding the hydrogenation of CO₂ to CO as the product and what work does exist, reports very low CO₂ conversions. A 2016 work, however, does note favorable selectivity towards CO at 370 °C [347] using a series of Fe₃O₄-Fe₅C₂@carbon catalysts. The best of the reported catalysts demonstrated a 20% CO₂ conversion with 78% CO selectivity, with the closing of the carbon balance including CH₄ and C₂-C₅ hydrocarbon materials.

Another recent work details several Rh@X catalysts (X = Silicate, KZSM and HZSM), displaying profoundly different selectivity between CO and CH₄ [348]. The most interesting results presented concern the Rh@SiO₂, which exhibits RWGS preference (*ca.* 90% CO selectivity) between 250-500°C; this activity was associated with the lack of acidic centres and subsequent spill-over mechanism present in the ZSM materials. However, the highest CO₂ conversion was found on the Ru@SiO₂-OH variant, *ca.* 80%, though almost completely selective towards CH₄ at 450-500 °C (Fig. 15).

Fig. 15. Reaction performances of the (a) Rh@HZSM-5, (b) Rh@S-1, (c) Rh@S-1-OH and (d) Rh@KZSM-5 – Reprinted with permission from [348]. Copyright {2020} American Chemical Society

Two other noble metal catalysts (Au@Pd@MOF-74 and Au@Pd@UIO-67/Pt@UIO-67) reported in the same year as the Rh@SiO₂ were reported to perform significantly worse than the Rh materials in terms of CO₂ conversion. However, the Au@Pd@MOF-74 catalyst did report almost 100% selectivity towards CO at 400 °C [349], which was attributed to the potential for steric hindrance of the CH₄ molecule to permeate the shell. Meanwhile, the Au@Pd@UIO-67/Pt@UIO-67 catalyst demonstrated *ca.* 35% CO₂ conversion with 80% CO selectivity at 400 °C [350]. In this case, it appears that the selectivity was governed by the UiO shell and the extra incorporation of the Pt aided in boosting conversion. A non-noble metal catalyst was also reported; Co@CoO-N was reported to be capable of almost 100% CO selectivity at 250°C and very high space velocity [351]. As with the noble metal catalysts, this material possesses very low CO₂ conversion, but considering the temperature that this catalyst was examined at, the

presented conversion could be due to the high space velocity. If this catalyst were to be tested at comparable conditions to the noble metals, it could be far superior.

The yolk@shell structure is most effective for the production of alcohol from CO₂, with several Cu encapsulated catalysts being reported in the literature [352–357]. Alcohols like methanol are important chemical feedstocks or fuels. The production of these alcohols from CO₂ is an extremely attractive method of valorising this greenhouse gas, as long as the hydrogen can be produced renewably. This area of CO₂ recycling is dominated by Cu/ZnO catalysts, owing to their high methanol selectivity at temperatures between 200–300 °C. Above these temperatures, the RWGS reaction is favored.

A very recent example detailed a CuIn@SiO₂ catalyst for the direct conversion of CO₂ to methanol using a soft template synthesis route. This catalyst was compared internally to Cu@SiO₂, In@SiO₂ and CuIn/SiO₂; the results found that the CuIn@SiO₂ material drastically outperformed the others in terms of CO₂ conversion, but demonstrated the third-highest methanol selectivity, finding that even under conditions that favored methanol production, CO was being produced (*ca.* 21.8% selectivity) [355]. Despite this, however, the effect of the morphology came to the fore during the stability test, where the CuIn@SiO₂ catalyst displayed 100 hours of consistent performance, with no sign of deactivation.

Two catalysts, 10Fe-10Cu/silica-aluminosilicate core-shell and infiltrated were prepared to produce methanol and dimethyl ether (DME) from CO₂ with the aid of a

magnetic field [358] between 180–260 °C. While the CO₂ conversion was found to be very similar between the two, the core@shell variant was more selective for methanol and the infiltrated variant was found to be more selective towards DME, with the highest selectivities reported with 4N-S and the reversed direction 4S-N magnetic field below 220 °C, exploiting the magnetic polarizability of the Fe component to affect the production of polar intermediates that form methanol and DME. Above 220 °C, both catalysts produced mainly CO; even at 260 °C, CO₂ conversions for both catalysts was below 10%.

5. Perspective and outlook

Following the inclusive review of the catalysts currently being used for the dry reforming of methane and CO₂ hydrogenation reactions, a number of things are clear: firstly, the pursuit of improved catalysts for the utilization of CO₂ remains a hot topic and that supported metallic nanoparticle catalysts are still the favored structure. The use of noble metals to improve selectivity and conversions continues to be investigated at laboratory scale, while Fe, Ni, Co and Cu have been established as very competitive and cost-effective alternatives. Furthermore, transition metal carbides, like TiC, MoC, Mo₂C, etc are notable, high-performance materials for the hydrogenation of CO₂.

However, the supported metallic nanoparticle structure, while tried and tested, is beginning to stagnate; to continue to develop these catalysts, the compositions are ever-

expanding as more and different metals are being combined in the active phase or the support phase to affect improvement. This is an issue as increasing the number of components drastically increases the complexity of the mechanisms occurring within the reaction, making understanding and control much harder to be certain of. In order to move away from these overly complex catalysts, morphological variation would enable a return to less convoluted compositions while providing the enhancements that are sought. As evidenced by the works in Section 4, encapsulation is a very effective morphological variation for catalytic development.

The use of encapsulated materials to affect enhanced catalytic lifetimes and deactivation resistance is highly effective and attractive. This review has included several instances of core@shell catalysts that demonstrate the effectiveness of confining an active phase for deactivation resistance; yolk@shell catalysts could present much more enhanced performance through the exploitation of the confinement effects in addition to the physical confinement offered by core@shell materials. The yolk@shell materials that are reported for CO₂ reforming and hydrogenation, demonstrate impressive levels of conversion and selectivity, in addition to compositional versatility to become cascade or multi-functional catalysts as nanoreactors. However, these materials require more research into their deactivation resistance and reaction performances, both of which are likely linked to the spatial and quantum confinement effects, in order to better understand these materials and unlock their true potential as high-performance catalysts.

Through investigating the current literature on **yolk@shell** materials, several gaps have been identified, which the following thesis material will attempt to address:

- (1) A reliable method of producing **yolk@shell** materials.
- (2) Non-Ni based **dry reforming of methane yolk@shell** catalysts.
- (3) Base-metal encapsulated catalysts (both core and **yolk@shell**) for the **reverse water gas shift** are drastically under-investigated or reported.
- (4) The use of reaction synergistic shell media that maintains deactivation resistance while assisting with the reaction mechanisms.
- (5) In terms of nanoreactors, research regarding the spatial and quantum confinement effects and their impact on reactive performance and deactivation resistances needs significantly more attention.

It is expected that these indicators of future directions that development can take will ensure the growth in the field of encapsulated catalysis, specifically **yolk@shell** materials, for the improvement and benefit to any reaction they are applied towards; **the access to “active” shell media in particular allows for the potential of creative formulations to produce cascade reaction catalysts or “cascade catalysts”, while the spatial confinement effect could hold the key to low(er) pressure alcohol/fuel production.** In particular, we foresee great potential for the implementation of these advanced catalytic materials to tackle CO₂ conversion reactions and contribute towards a low-carbon future.

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Description:

The topic of enhanced catalysts for CO₂ conversion is becoming more saturated with one method of advancement: increased complexity. Encapsulation brings a variety of advanced effects in order to maintain simplicity and effectiveness

Graphical Abstract:

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: