Redox and Nonredox CO_2 Utilization: Dry Reforming of Methane and Catalytic Cyclic Carbonate Formation

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ABSTRACT: CO_2 emissions are too large to tackle with a single process, but a combination of avoidance with chemical utilization may be able to slow global warming. In this Focus Review, we identify two large-scale CO_2 conversion processes based on their viability and opposite energy requirements. In the high-energy, stationary path, CO_2 reforming of methane could provide gigatons of CO_2 utilization through synthesis gas. The main problem is the lack of a durable, effective, low-cost dry reforming catalyst. The exothermic cyclic carbonate formation from CO_2 and organic epoxides offers a low-energy, mobile, nonredox route. The catalysts, however, must be metal-free and robust, have a high surface area, and be low-cost while being easily scalable. These two processes could potentially address at least a quarter of all current CO_2 emissions.
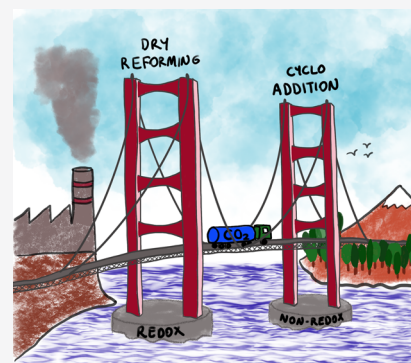
Climate change and energy sustainability are the leading global challenges in the twenty-first century. Climate change is primarily driven by the combustion of fossil fuels because carbon dioxide (CO_2) is commonly identified as the main greenhouse gas.[1] Indeed, CO_2 emissions increased from an average rate of 1.72% (1970−2000) to 2.75% (2010−2014) per year, and if the emissions proceed with business as usual, they will overshoot the six-degree scenario (6DS) of global warming by 2050.[2] It appears necessary to control CO_2 emissions by both averting them as much as possible and removing CO_2 from point sources and the atmosphere.[3] In fact, capture of CO_2 from dilute sources is identified as one of the seven challenging chemical separations to change the world.[4] The United Nations' (UN) Sustainable Development Goals (SDGs) include 4 out of 17 that are directly related to CO_2 emissions and uncontrolled use of fossil fuels: climate action (#13), affordable and clean energy (#7), responsible consumption and production (#12), and sustainable cities and communities (#11).[5]

CO_2 fixation into stable molecules (a.k.a., CO_2 utilization) coupled with switching energy sources to renewables or nuclear may be the best solution for tackling excess emissions and climate change. However, in the best scenario of current industrial reuse of CO_2, we would be taking out only up to 300 million tons/year (Mt/yr) CO_2 through fixation, although the amount is constantly increasing.[6−9] Considering the unwanted emissions are over 42 gigatons/year (Gt/yr),[10,11] the CO_2

market is not large enough to make a meaningful impact. In addition, there are only a few industries where direct reuse of CO_2 is profitable. For example, 6 Mt is currently used as process gas, around 11 Mt for food and beverage industries, and 25 Mt for enhanced oil/gas recovery (EOR and EGR).[12] As a more appealing strategy, conversion of CO_2 into useful commodities such as fuels, plastics, and fine chemicals could provide a much needed economic incentive for CO_2 fixation and increase the CO_2 market size substantially.[13] Carbon dioxide utilization (CDU) will enhance carbon cycling and "close to zero emissions" may, in principle, be possible by converting spent carbon to working carbon.[14]

CO_2 requires significant thermal input to be converted because its formation enthalpy is exceptionally high ($\Delta H_f^\circ = -394$ kJ/mol) and contains the highest oxidation state of carbon (+4), but there are a number of industrial chemical processes that require its utilization.[15] Urea synthesis is the most voluminous among those (150 Mt/y) (Table 1)[12] and already uses 112 Mt of exhaust CO_2 emissions that is generated in
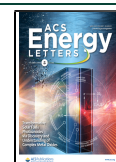
Table 1. Examples of Redox and Nonredox Processes for CO_2 Utilization

Process	Reaction		Production
Redox	CO_2 + $2H^+$ + $2e^-$ ------→ CO + H_2O		
	CO_2 + $4H^+$ + $4e^-$ ——→ HCHO + H_2O		9.7 Mt/y
	CO_2 + $6H^+$ + $6e^-$ ——→ CH_3OH + H_2O		100 Mt/y
	CO_2 + $8H^+$ + $8e^-$ ------→ CH_4 + $2H_2O$		
Non-redox	CO_2 + NH_3 ——→	H_2N⎯C(=O)⎯NH_2	150 Mt/y
	CO_2 + (epoxide, R) ——→	(cyclic carbonate, R)	0.8 Mt/y
	CO_2 + MeOH ——→	H_3CO⎯C(=O)⎯OCH_3	10 Mt/y
	CO_2 + (epoxide, R) ——→	(polycarbonate, R)$_n$	4 Mt/y

——→ Commercialized   ------→ Proposed

ammonia production.[16] Similarly, we should be finding new processes where waste CO_2 could be used. Methanol production (100 Mt/yr) and cyclic/poly carbonates (>10 Mt/yr) have great potential, although very little of the needed CO_2 comes from emissions.[15] It is imperative that nonredox CO_2 fixation should use reclaimed CO_2 rather than synthetic sources, thus making contributions to lowering CO_2 emissions. However, the redox processes that could use CO_2 (Table 1) conventionally prefer the synthesis gas (*syngas*), as the hydrogen for reduction would have to come from the hydrocarbon reforming processes anyway. Direct CO_2 hydrogenation is another promising route to reclaim CO_2 into valuable feedstocks. We refer readers to the extensive literature on the advantages and challenges of such a path for further reading.[17]

Reforming is, in fact, useful in curbing greenhouse gas (GHG) emissions by also removing gaseous hydrocarbons, primarily methane (also a 21-times more potent GHG), if applied downstream to the feeds like flare gas.[18] Industry prefers steam reforming of methane (SRM, CH_4 + H_2O ⇌ CO + $3H_2$, $\Delta H_{298}° = 206$ kJ·mol^{-1}) for syngas production, a reaction where water is heated with methane in the presence of catalysts.[19] The process is endothermic and produces hydrogen-rich syngas (H_2/CO = 3), which in turn makes the overall process energy intensive (requires 25.5% of the energy value of methane).[20] Catalytic dehydrogenation of hydrocarbons at high temperature leads to the deactivation of catalysts by coke formation, and the presence of steam brings corrosion issues; all of these considerations demand costly investment. Still, SRM is the common practice with a mature technology. An alternative is the dry reforming of methane (DRM, CH_4 + CO_2 ⇌ 2CO + $2H_2$, $\Delta H_{298}° = 247$ kJ·mol^{-1}), where CO_2 provides the oxygens for reforming the hydrocarbons. DRM produces syngas with an H_2/CO ratio (≤1) that could find direct use in chemical synthesis, at times with the addition of supplementary hydrogen (preferably from renewable sources), and would normally be more attractive considering the use of two greenhouse gases at once to produce commodities. However, it is energetically more demanding (20% more endothermic than SRM), and a coke- and sintering-resistant catalyst has yet to be developed. Apart from these challenges, the DRM process operates at lower cost[21] and produces higher-purity syngas than the other reforming reactions.[22,23]

In this Focus Review, we aim to explore the two most promising methods of CO_2 utilization: (1) dry reforming for redox CO_2 fixation and (2) cyclic carbonates for nonredox CO_2 use. Dry reforming could potentially remove several gigatons of CO_2 every year if hydrogen production was switched from steam reforming. If fuel production was from the syngas provided by dry reforming, then the gains would be far greater. For low-energy intensive utilization, cyclic carbonates are feasible in terms of high-volume conversions. Electrocatalytic conversions are also noteworthy, but they are reviewed in detail elsewhere.[24] In DRM, we highlight nickel-based non-noble inorganic catalysts for sustainability, whereas we focus on metal-free catalysts in cyclic carbonate formation. The two different paths
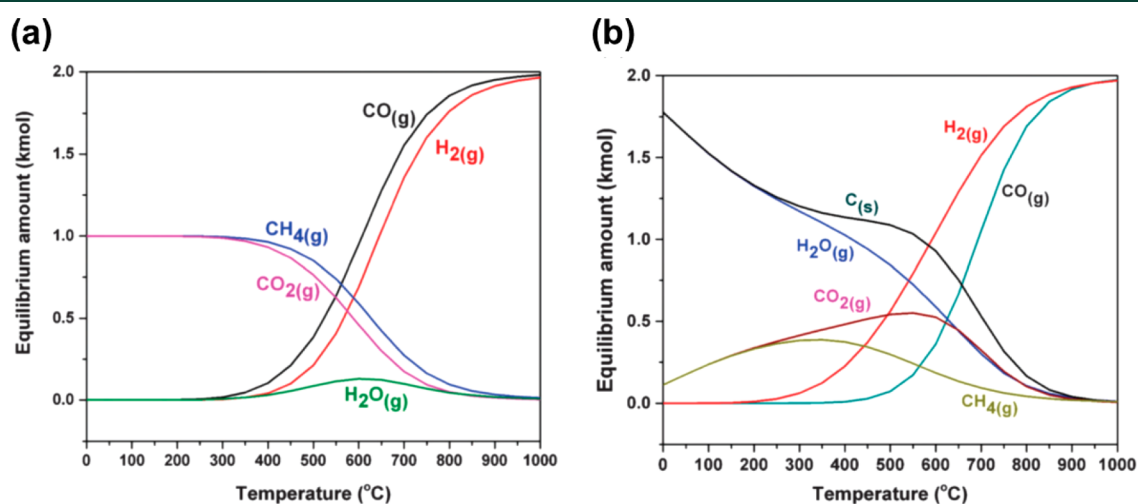
Figure 1. Dry reforming of methane (DRM) and associated reactions. Thermodynamic equilibrium plots for DRM (a) and assuming coke formation occurs (b).[23,25] High reaction temperatures are commonly employed to promote the endothermic conversion and also to avoid reverse water gas shift reaction. Reproduced with permission from ref 23. Copyright 2014 Royal Society of Chemistry.
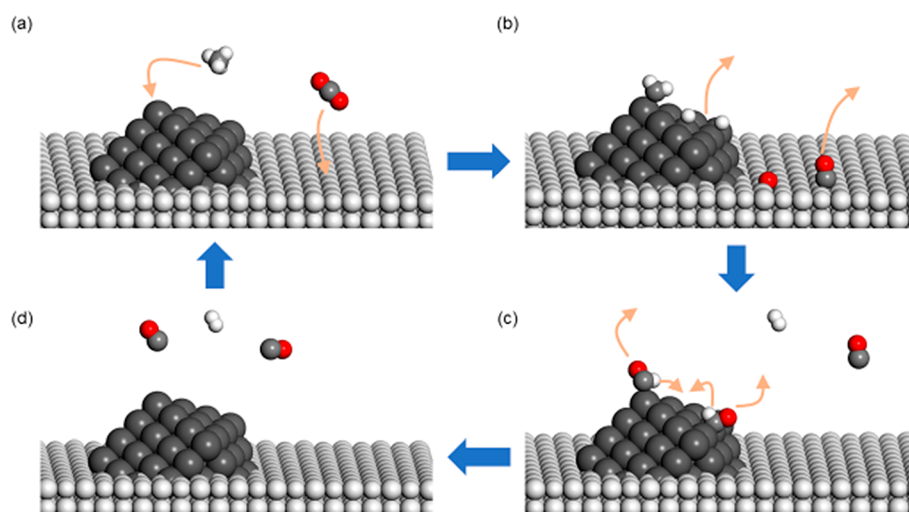
Figure 2. Commonly accepted mechanism for the dry reforming reaction between CH_4 and CO_2 using a bifunctional catalyst (adapted from Aramouni et al.[30]). Methane scission proceeds over the metal catalyst (a), and an H_2 molecule leaves while CO_2 disassociates into CO and oxygen atom (b). The reactive oxygen atom combines with the left-over carbon from CH_4 scission to produce CO (c), and the remaining hydrogen atoms recombine to make another molecule of H_2 (d).

Table 2. Activity of Ni/MgO Catalysts in Dry Reforming of Methane

active metal	other metals	support	other supports	conversion	temp (°C)	duration (hours)	deactivation	WHSV	H_2/CO ratio	ref
Ni		MgO	CeO_2	CH_4: 45% CO_2: n.a.	700	20	n.a.	CH_4:CO_2 = 2:1 12000 mL·g_{cat}^{-1} h^{-1}	n.a.	52
Ni		MgO		CH_4: 95% CO_2: 97%	750	200	CH_4: 94.8% → 94.4% CO_2: 97.0% → 96.1%	70000 mL·g_{cat}^{-1} h^{-1} CH_4:CO_2:He= 1:1:12	0.98	53
Ni	Pd	MgO		CH_4: 97% CO_2: 96%	750	200	CH_4: 96.8% → 96.7% CO_2: 96.2% → 95.8%	70000 mL·g_{cat}^{-1} h^{-1} CH_4:CO_2:He= 1:1:12	0.99	53
Ni	Co	MgO	Al_2O_3	CH_4: 79.2% CO_2: 84.8%	800	8	qualitative detection of carbon by TPO	12000 mL·g_{cat}^{-1} h^{-1}	0.90	54
Ni		MgO	ZrO	CH_4: 86% CO_2: 98%	900	50	1.5 wt % coke	15000 mL·g_{cat}^{-1} h^{-1}	1.25	55
Ni		MgO	Al_2O_3	CH_4: 75% CO_2: 80%	700	12	qualitative detection of carbon by TPO and SEM	18000 mL·g_{cat}^{-1} h^{-1}	0.92	56
Ni		MgO	Al_2O_3 FeCrAl-fiber	CH_4: 80% CO_2: 85%	800	270	0.52 mg$_{coke}$·g_{cat}^{-1} h^{-1}	5000 mL·g_{cat}^{-1} h^{-1}	0.85	57
Ni		MgO		CH_4: 63.7% CO_2: 70.2%	850	2.3	CH_4: 42.16% CO_2: 48.60% (in 2.3 h) 350 mg$_{coke}$·g_{cat}^{-1} h^{-1}	168000 mL·g_{cat}^{-1} h^{-1}	0.6	58
Ni		MgO	SiO_2	CH_4: 89% CO_2: 92%	700	50	21.1% coke in TGA; filamentous carbon on SEM	18000 mL·g_{cat}^{-1} h^{-1}	n.a.	59
Ni		MgO		CH_4: 55% CO_2: 70%	700	50	qualitative TPO; filamentous carbon on SEM	18000 mL·g_{cat}^{-1} h^{-1}	n.a.	60
Ni		MgO		CH_4: 70% CO_2: 85%	760	100	CH_4 and CO_2 conversion decreased by 15% and 25%, respectively 0.325 mg$_{coke}$·g_{cat}^{-1} h^{-1}	20000 mL·g_{cat}^{-1} h^{-1}	0.9	61
Ni	Co	MgO		CH_4: 75% CO_2: 90%	760	100	0.361 mg$_{coke}$·g_{cat}^{-1} h^{-1}	20000 mL·g_{cat}^{-1} h^{-1}	0.9	61
Ni	Mo	MgO		CH_4: 98% CO_2: 99%	800	850	no deactivation	60000 mL·g_{cat}^{-1} h^{-1} CH_4:CO_2:He= 1:1:8	1.0	62

converge in the promise of providing exceptional methods in reclaiming the CO_2 emitted from fossil fuel-powered industries while providing the breadth of chemical products one can realize.

High-Energy, Redox Process: Dry Reforming of Methane with CO_2. Dry reforming of methane (DRM) has been studied extensively, as early as 1928 by Fischer and Tropsch[26] using a combination of nickel and cobalt catalysts. In 1949, Reitmeier et

al.[27] quantified the deactivation problem by studying the relation between reactant composition and coke deposition. Since then, considerable interest has been devoted to developing a catalyst for the DRM reaction and addressing the deactivation issues. To achieve high yield of syngas and prevent reverse water gas shift reaction, DRM requires high temperatures such as 900 °C. At these temperatures, most of the metal catalysts are prone to deactivation due to sintering and coke deposition (Figure 1).[28] Thus, the main criteria for a catalyst to be efficient in the DRM reaction are thermal stability and deactivation resistance.[29] Overall, the choice of catalyst and reaction conditions primarily governs the formation of syngas and the underlying mechanism.[23] The performance of a heterogeneous catalyst is directly related to the combination of the active metal and support. In general, for any material to be a good catalyst for the DRM reaction, it should possess a bifunctional nature (Figure 2).

Active Metal Choice and Coke Formation. Generally, group VIII, IX, and X metals are active in DRM, and in particular Ru, Rh, and Pt are more resistant to coke formation than any other transition metals.[31−35] For noble metals, the virtues are being highly active and coke resistant, except Pd which usually leads to a carbon deposition of 4.9 mg$_{coke}$/g$_{cat}$·h.[30] The order of noble metal catalytic activity follows in the order of Rh > Ru > Ir > Pd > Pt,[30,36,37] where the superior activity of Rh, Ru, and Ir is reasoned to be due to their high dispersion and small particle size. Pd and Pt were relatively less active because of sintering at high temperatures. The main challenge, however, is their prohibitive costs and limited availability, which restrict their practical use.[38−41] The leading features for a DRM process catalyst to meet industrial specifications are being highly active, resistant to coking, robust, and long-lasting and having minimal synthetic steps from commercially available precursors. Particularly, coke resistance is often overlooked.[30] Considering these parameters, a non-noble metal, nickel, emerged as a viable choice for DRM reactions (Table 2). Despite the problem of coke formation, nickel usually shows initial conversion rates that are higher than those of Ru, Ir, Pd, and Pt.[30] Therefore, the current research direction in DRM has been and should be to develop a coke-resistant nickel-based catalyst.

In order to explore the next-generation DRM catalysts, the key element is to understand the complexity and limiting factors, particularly the principle of coke formation on nickel-based catalysts. Investigations on coke formation showed that methane decomposition and carbon dioxide dissociation form the surface carbon species, and they subsequently dissolve into the nickel clusters to form nickel carbide.[42] A close look at the interface of coke formation on nickel catalysts indicates whisker (filamentous) carbon, which generally occurs at higher temperatures and is structure dependent in the order of aromatics > olefins > branched alkanes.[43] The deactivation of nickel catalyst, therefore, is explained by the diffused carbon originating from the various dissociation and decomposition reactions, which soon nucleates around the nickel by creating whisker layers, reaches the pores, and pushes the particles out of the catalyst structure.[44] Temperature gradients facilitate the coke formation, which in turn alters the shape of the metal particle to a more conical feature, ultimately leading to a deactivation by uprooting the metal particles. It is also known that step edges on nickel crystals are more prone to coke formation and deposition. The coke formation generally increases as the feed ratio (CH$_4$/CO$_2$) increases. Moreover, the size of the nickel particle plays a huge role in coke deposition and thereby affects the catalytic activity.[45−47] To generate whisker carbon, a minimum diameter

of about 7 nm is required.[42,48] It was also observed that the dispersion of nickel particles affects the rate of deactivation of catalysts. For example, well-dispersed, aerogel nickel showed continuous activity for 30 h, whereas others deactivated after an hour.[49−51]

> Recycling CO$_2$ back to fuels requires eight electrons per molecule with steep activation barriers. Nonredox fixation would be easier to implement in remote or mobile applications but not at large-scale markets and point sources, where redox is the ultimate solution. A variety of paths need to be explored for effective CO$_2$ sequestration.

Effect of Catalyst Support. DRM is known to follow a bifunctional mechanism with four steps: (1) dissociative adsorption of methane, (2) dissociative adsorption of CO$_2$, (3) hydroxyl group formation, and (4) oxidation of intermediates and desorption (Figure 2).[30,63] A number of catalyst supports were studied for DRM, including neutral (e.g., SiO$_2$), acidic (e.g., Al$_2$O$_3$), and basic (e.g., MgO) supports. Among those supports, neutral or acidic supports show slower reaction rate and faster deactivation compared to basic supports because of less availability of adsorbed CO$_2$.[64] In general, neutral supports are found to be less active compared to acidic and basic supports.[65,66] In the case of acidic supports, the limitation of CO$_2$ adsorption and accumulation of coke that blocks the active metal sites seem to hinder their applicability.[40] On the other hand, basic supports increase the rate of dissociative adsorption of CO$_2$, which improves the coke formation by faster gasification of carbon species in comparison to acidic supports.[53]

The nature and activity of the catalyst support strongly depends on the type of active metal used.[67] Basic MgO is widely studied as a support for nickel-based DRM reactions.[68] The main function of the support is to enhance the DRM reaction by suppressing the unwanted side reactions such as the Boudouard reaction (2CO $\rightleftharpoons$ C + CO$_2$, $\Delta H_{298}° = -172$ kJ·mol^{-1}) or excessive methane decomposition (CH$_4$ $\rightleftharpoons$ C + 2H$_2$, $\Delta H_{298}°= 75$ kJ·mol^{-1}). The advantages of using MgO as a support for DRM reaction include enhanced CO$_2$ adsorption due to its Lewis basicity; faster gasification of carbonaceous species; and interestingly, the similar ionic radii of Mg and Ni, which lead to the formation of NiO−MgO solid solution at any molar ratio.[69,70] The solid solution has significant influence over the size and formation of Ni(0) particles. However, the formation of solid solution strongly depends on the preparation method, such as calcination temperature and loading of nickel.[71] For example, a NiO−MgO catalyst with varied NiO content was synthesized by the sol−gel method exhibited mesoporous framework, and the nanosized Ni particles showed good coke resistance for DRM reaction.[72] However, the catalyst stability test in terms of methane and carbon dioxide conversion clearly revealed that higher Ni content suffered more degradation upon coke formation.[72] Also, mixed metal oxides with a well-balanced composition of Ce, Mg, and alumina assisted in achieving nickel particles with average diameter less than 5 nm, and this composite catalyst was found to be efficient (99% conversion of

both CO_2 and CH_4).[73] It was confirmed that the enhanced activity is due to the presence of magnesium on the surface of alumina that enhances the CO_2 conversion, while ceria suppresses the coke formation and results in enhanced CH_4 reactivity.[74] In cases where MgO was used to modify other supports such as alumina and zirconia, MgO was identified for its influence in enhancing the metal dispersion, catalytic activity, stability, and anticoking capability.[75−77] Despite the excellent supportive role, it was found in some cases that even >20 mol % of MgO had no pronounced effect on the suppression of coke formation.[78] Clearly, the numerous efforts in support optimization have not yet led to a phenomenal catalyst system, and there is considerable need for finding the right balance in active catalyst and support interactions.

Effect of Promoters. The high-temperature DRM reaction favors coke deposition on the active catalyst; however, incorporation of promoters (low-quantity additives) may prove effective in increasing the lifetime of the catalysts by reducing the coke deposition. The catalytic promoters could alter the surface structure, improve the dispersion of active metals over the support, and inhibit the coke formation through redox control over the heterogeneous system. Alkali and alkaline earth metals were commonly investigated as promoters for the DRM where nickel is the active metal.[79−81] These promoters not only facilitate the interactions with carbon dioxide but also block the step sites and significantly decrease the nucleation site for coke formation.[44] Potassium is found to be an active promoter within a Ca/Ni catalytic system (Ca/Ni/K is in the ratio of 2:1:0.1) and showed no deactivation for nearly 360 h.[82] DFT calculations suggested that the potassium binds to oxygen along the step edges ($-K-O-K-O-$) and becomes more stable than when on the surface,[44] effectively preventing the coke formation. This assembly will work as long as the promoters are sufficiently available at the step edges. In this context, the noble metal promoters tend to segregate to the step sites and eliminate the ability of neighboring sites for the coke deposition. For example, Ag promotes the gasification of coke formed by altering the recalcitrant whisker to amenable amorphous carbon species[83] in a silver-promoted Ni/CeO_2 catalyst. In a different mechanism, promoters like V_2O_5 enhance the catalytic activity of Rh/SiO_2 nearly 20-fold.[23,84] This is due to a VOx layer formation, which breaks down the larger Rh particles and increases the dispersion of active metal sites for the activation of CH_4. Apart from these, bimetallic catalysts have also been investigated to prevent coke formation and to overcome the economic and operational limitations. In general, if the chemical potential of carbon is higher than the promoter, then the latter will be displaced and lead to coke formation. However, it is worth mentioning that the impregnation procedure, ratio of promoter to active catalyst, and poisoning effect should be taken into account to design an active and robust catalyst for a successful DRM reaction. The difficulty lies in controlling every parameter over a bulk structure, where any modifications also impact the parameters that are held constant. This is why serendipity is generally more common in new catalyst discoveries, especially through high-throughput experimentation.

DRM Catalyst Design Parameters. The lack of an industrially feasible catalyst remains a challenge for DRM, and in the quest for developing one, we highlight the following parameters for an optimal design based on nickel:

(1) Homogeneous Dispersion of Nickel Particles. Well-dispersed catalyst particles delay deactivation time, limit coke formation, and prolong the stability and time on stream by preventing interaction between nickel clusters.[85,86]

(2) Size and Concentration of Metal Catalyst Particles. The smaller the nickel particles, the better they are exposed to reactants and are in good thermal contact throughout the catalyst bed.[42] Smaller particles also favor the initial activation of methane, particularly in sizes smaller than 6 nm, and display superior coke resistance.[18] As the concentration of the metal catalyst increases, solid solution of bimetallic species increases and thereby the catalytic activity, although there is always an optimal range.[87]

(3) Support and Basicity of the Catalyst. DRM requires effective CO_2 sorption, and therefore, basic supports will significantly increase the adsorption of CO_2 for a steady formation of CO.[75] A basic support increases the oxygen availability through CO_2 scission, assists in oxidation of surface carbon, and thereby increases the catalyst resistance.[88−90]

(4) High Surface Area of Catalyst. A high contact surface area improves reaction rate and yields. Porous supports, therefore, improve the dispersion of nickel metal; confine the nickel particles inside the pores; prevent the inhibition of diffusion; provide better coke resistance; and through their micro- and macropores would produce a robust, active catalyst.[91,92]

(5) Bimetallic Catalysts and Promoters. Although pure nickel catalysts are ideal, the presence of a small amount of alloying metals increases the reducibility of nickel by hydrogen spillover, prolongs the stability of the catalyst, and promotes dissociative adsorption of H_2.[53,93−95] Dopants and promoters may improve catalyst performance tremendously if they block coke formation pathways.

(6) Catalyst Preparation Methods. Synthesis methods of the catalyst systems control the homogeneous dispersion and how well the metal and support interact. Among the methods, sol−gel was found to be better than coprecipitation and impregnation methods.[77] In the coprecipitation method, the precipitating agents adversely affect the catalytic activity, and in the impregnation method, sequential impregnation was better.[18,96] Advanced preparation methods such as atomic layer deposition[97] and nonthermal plasma-treated catalyst preparations allow size control (even below 3 nm) and highly dispersed metal particles, leading to considerable contributions in catalytic activity.

Recently, we have developed a new Ni−Mo−MgO-based DRM catalyst (NiMoCat), which shows exceptional stability and activity toward dry reforming of methane.[62] The NiMoCat exhibits all the parameters needed for an industrially feasible catalyst. The nickel−molybdenum bimetallic nanoparticles are, therefore, synthesized in the presence of single-crystal MgO nanocubes through a polyol method. The as-synthesized catalyst was further activated under carbon dioxide and methane, in which we found that as-synthesized nickel−molybdenum nanoparticles migrate to the high-energy sites and step edges of single-crystal MgO above the Tammann temperature of nickel (691 °C). As a result, NiMoCat features no coking from the support or unassociated Ni−Mo nanoparticles. Because of the general applicability of this approach, we named this phenomenon the nanocatalysts on single crystal edges (NOSCE) technique. We believe that this method could be applied in other catalytic reactions with a myriad of possible combinations of active metals and single crystal supports.

Low-Energy, Nonredox Process: Cyclic Carbonate Formation from CO_2 and Epoxides. In contrast to the DRM reaction, cyclic

> Dry reforming of methane could provide scalable, redox CO_2 reclamation but requires coke- and sintering-resistant nickel catalysts. Ideally those catalysts should feature homogeneity, high surface area, nanoscale morphologies, and easy preparation.

carbonate formation is an exothermic reaction. It is also 100% atom economical and frequently associated with wider applications involving them as versatile synthetic intermediates, aprotic polar solvents, precursors for biomedical applications, raw materials for engineering plastics, and electrolytes in batteries.[98] For these reasons, cyclic carbonate synthesis has slowly but steadily drawn attention and is expected to grow significantly in the near future.[99,100] The main bottleneck, however, is the fact that activation of CO_2 is challenging because of its thermodynamic stability $(\Delta H_f^{\circ} = -394 \text{ kJ mol}^{-1})$, which impedes its utility as a reagent.[101,102] DFT studies calculated the activation barrier to be between 50 and 70 kcal/mol. This barrier can be best overcome by an appropriate catalytic system, and consequently, a handful of catalysts have been developed.[103]

In the industrial production of cyclic carbonates metal-free catalysts are desirable. Apart from the economic reasons, metals bring unwanted toxicity, contamination, and chemical sensitivity (being prone to hydrolysis and oxidation), and their limited availability raises the question of sustainability for the production of cyclic carbonates.[104] Because of this, studies focused on developing charged organic (quaternary ammonium and phosphonium) catalytic systems as alternatives.[105−108] These catalysts are synthesized by the reaction of tertiary amines (or phosphines) with appropriate alkyl halides because of the reactivity difference in halides $(I^- > Br^- > Cl^- > F^-)$.[101] Easy exchange of anions allows employing suitable acid or alkali metal salts.[109] Thus, the reactivity can be increased, but then the complete removal of halide impurity is challenging.[110] Regardless, they exhibited higher activity because of the presence of nucleophilic counteranions.[111]

Among the wide range of ionic, metal-free catalysts, 1,8-diazabicyclo [5.4.0]undec-7-enium chloride ([HDBU]Cl) showed excellent catalytic activity and resulted in propylene carbonate in 97% yield using 10 bar of CO_2 at 140 °C.[112] The quaternary ammonium center in the catalyst was suspected to stabilize the ring-opened epoxide (oxy anion species) leading to higher activity (Figure 3).[113] Theoretical studies also confirm the decrease in energy barrier associated with the activation of epoxide by the quaternary ammonium centers.[111,113,114] Although these catalysts are active, the additional need for separation of catalyst and product purification make the process industrially undesirable. More recently, Byun and Zhang provided heterogeneous properties to imidazolium ionic liquids by varying the length of the alkyl substituent on the imidazolium ring.[115] Despite these efforts, immobilization of the active catalysts is considered a feasible fail-safe strategy[116] and therefore received considerable attention. However, loss of activity during recycling[117] and the requirements of cocatalysts and elevated pressure are known to be major drawbacks of these systems.[118,119]

In an effort to move metallic catalysts into heterogeneous systems, metal organic framework (MOF)-based catalysts were designed and reported to have significant catalytic activity for cycloaddition of epoxide to CO_2.[102] For example, postsynthetic modified imidazole containing MOF with the coexistence of basic/acidic sites acted as an efficient catalyst for the coupling of CO_2 and epoxide at ambient pressures and was recyclable up to six times without the need for a cocatalyst.[120] However, this catalytic system showed very high conversion for only two substrates, and challenging epoxides like styrene oxide, 1,2-epoxy hexane, and others showed low conversion (range of 38−77%) and selectivity (34−93%).

Nanoporous polymers incorporating N-heterocyclic carbenes (NHCs) can also function as an efficient catalyst at atmospheric pressure with excellent yields up to 98% for epichlorohydrin in 24 h (Figure 4a). The reaction proceeds via the formation of a carbene-CO_2 adduct followed by the nucleophilic addition, and intramolecular cyclization of alkoxide intermediate results in the cyclic carbonate product.[122] However, the catalyst is efficient only for aliphatic substrates, and also the synthesis of the catalyst involves costly palladium catalysis with multiple steps.

Phosphonium-based porous ionic polymers (PIPs) also exhibited excellent catalytic activity for cycloaddition of CO_2 to epoxides (Figure 4b). Advantages included being metal- and cocatalyst-free and effective under atmospheric CO_2 pressure conditions. These catalysts also showed high yields of cyclic carbonate product (87−93%) and recyclability for 10 times with retention of activity.[123] PIPs feature many fitting parameters for an effective cyclic carbonate formation catalyst, but their synthesis involves costly air-sensitive Grignard reagents and lengthy purifications.
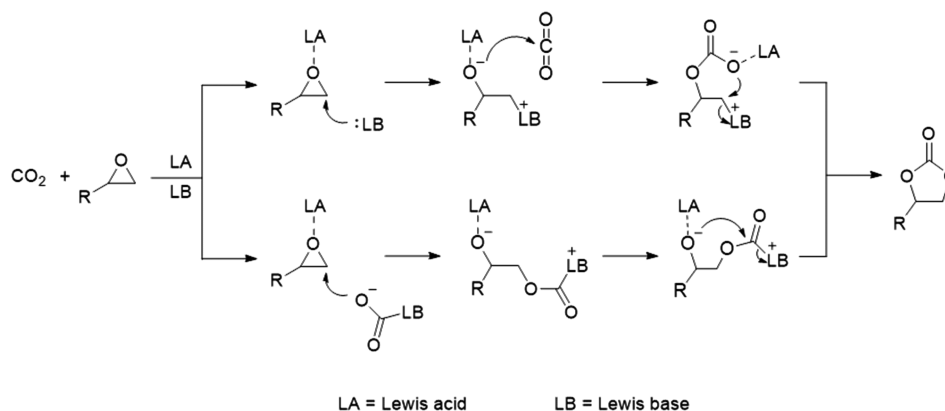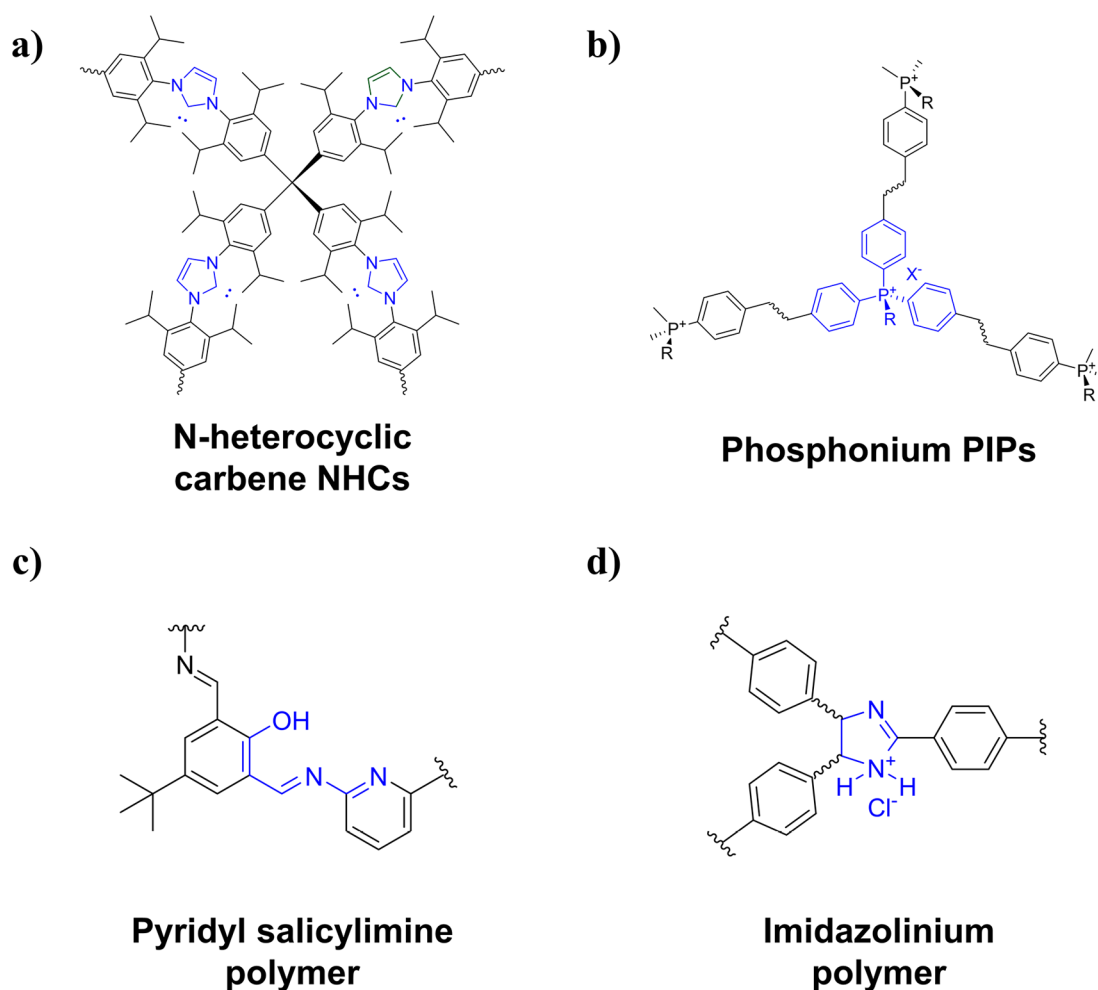

Figure 3. Two generally accepted mechanisms for the cyclic carbonate formation from CO_2 and epoxides.[121]

Figure 4. Representative catalysts for cycloaddition of CO_2 to epoxides under ambient reaction conditions without the need for cocatalysts. Imidazolinium polymer (d) so far presents the best conversion conditions and products, providing a new state-of-the-art.

We have shown that polymeric pyridyl salicylimines are remarkably effective for both aliphatic and aromatic substrates at near quantitative yields[124] (Figure 4c). Styrene oxide, for example, was converted to styrene carbonate in 99% yield and >99% selectivity without the need for a cocatalyst, metal or solvent, and the reaction proceeded under atmospheric pressure of CO_2. Although these are promising developments, it is clear that there is still plenty of room for developing better and sustainable catalytic systems for cyclic carbonate formation.

> Cyclic carbonates offer widespread use of CO_2 without redox processes. Current catalysts fall short of being free of metals, cocatalysts, high pressures, or temperatures. A bifunctional Lewis acid/base heterogeneous catalyst is needed.

Cyclic Carbonate Formation Catalyst Selection Parameters. In the light of the above considerations, we highlight the following parameters in selecting the optimal catalyst design and activity:

(1) Coexisting Lewis Acid and Basic Sites. A promising CO_2 cycloaddition catalyst has to do both activation of epoxides and CO_2 capture. This can best be achieved by the combination of Lewis acid and basic sites. For a successful, sustainable, industrial-scale utilization, well-defined bifunctional catalysts are desired and should synergistically activate both the reactants under mild conditions. They should also be chemically robust, highly compatible with each other and the reactants, and thermally stable under a wide range of conditions.[125]

(2) Heterogeneity, Recyclability, and Contamination-Free. To prevent problems such as product−catalyst separation, active metal leaching, and the subsequent contamination in the final product, metal-free heterogeneous catalysts offer better cyclability and product purity while preserving feasible TON and TOFs.

(3) High Surface Area. Introduction of porosity in a bifunctional catalytic material helps in amplifying the CO_2 uptake capacity and thus accelerates the substrate−active site interactions. High surface area is beneficial for the energy and mass transfer during the reactions.[123] The selectivity of the desired product can also be tuned by the pore openings through sieving, and by the structural properties like grain boundaries, which depend on the judicious construction of building blocks and deliberate synthetic strategies.[126]

(4) Avoidance of Cocatalyst, Pressure, and Temperature. Most of the Lewis acid catalytic systems require cocatalysts, mostly ammonium salts, to couple CO_2 into the formed oxy intermediates.[127] Cocatalysts are usually used more than the catalytic amounts and under elevated reaction conditions (>100

°C and 5 bar CO_2 pressure). Single-catalyst, ambient pressure, and low-temperature reactions are needed for widespread industrial implementation.

(5) **Metal-Free Catalysts**. Among the elements in the periodic table, only six metals are classified as abundant,[104,128] which clearly indicates the necessity of developing metal-free catalysts for a sustainable future. In addition, metal leaching and product separation issues hinder their viability. To replace the metals, organic quaternary nitrogen systems, hydrogen bond donors (HBDs), N-donor bases, and phosphonium salts can be used which also can remarkably facilitate reducing the energy barrier associated with the activation of reactants which was confirmed by both theoretical and experimental results.[107,109,129]

(6) **Scope of Substrates**. Varying the electronic and steric nature of the substrates may change the properties and applications of the cyclic carbonate products for their wide-spread use. Thus, to access the synthetically useful cyclic carbonate products, the catalyst should be outright superior and efficient to convert even unconventional substrates.

(7) **Cost and Scalability**. All CO_2 conversion processes need to be in the scale of at least millions of tons to make an impact for climate change reversal. The cost and scalability must be plausible if a new process is offered. Therefore, the catalysts are expected to be abundantly available, cost-effective, and easily synthesized.

Very recently, we developed an environmentally benign, metal-free (not even during the synthesis!), commercially attractive, robust, heterogeneous imidazolinium catalyst[130] that possesses 6 out of 7 of the above-mentioned qualities for an ideal design of optimum catalyst (Figure 4d). The imidazolinium structure produced through a one-pot reaction of terephthaldehyde and ammonium chloride features the coexistence of a quaternary and a basic amine functionalities. Complete investigations using in-depth physicochemical characterizations led us to confirm the unexpected imidazolinium construct that turned out to be a promising catalyst that does not require any cocatalyst, solvent, or high CO_2 pressure. The catalytic performance was tested for the conversion of simple to extremely challenging epoxides, and good to excellent activity was found. The density functional theory calculations suggested nucleophilic attack-driven epoxide ring-opening reactions (ND-ERO) and calculated the energy requirements for the catalytic reaction. It is remarked that[131] a noncrystalline solid structure with low porosity showed an outstanding catalytic activity with retention of its activity over 15 cycles and potential for its rapid implementation for CO_2 reclamation studies.

Outlook. Although many CO_2 utilization processes exist, the sheer scale of emissions dictate reclamation on the scale of megatons, and unfortunately, there are only a handful of processes that can make a credible impact. Injecting CO_2 back into the fuel production cycles for a "circular carbon economy" is a must in the interim, and dry reforming has a unique position to achieve such a foothold. Catalyst designs are not yet sufficiently mature to realize this, but recent research is very promising. Similarly, low-energy processes are needed to address low-cost CO_2 recycling. Cyclic carbonates from CO_2 is a powerful reaction, despite the lack of highly efficient but sustainable heterogeneous catalysts. We envision that intensive research could bring out these viable solutions for reclaiming the greenhouse gas emissions. If CO_2 avoidance is coupled with postemissions processing, we may be able to slow global warming before it is too late.

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■ REFERENCES

(1) Stern, P. C.; Sovacool, B. K.; Dietz, T. Towards a science of climate and energy choices. *Nat. Clim. Change* **2016**, 6, 547.

(2) Mac Dowell, N.; Fennell, P. S.; Shah, N.; Maitland, G. C. The role of CO_2 capture and utilization in mitigating climate change. *Nat. Clim. Change* **2017**, 7, 243.

(3) Porosoff, M. D.; Yan, B.; Chen, J. G. Catalytic reduction of CO_2 by H_2 for synthesis of CO, methanol and hydrocarbons: challenges and opportunities. *Energy Environ. Sci.* **2016**, *9* (1), 62−73.

(4) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, *532*, 435−437.

(5) Sustainable Development Goals: Sustainable Development Knowledge Platform (United Nations). https://sustainabledevelopment.un.org/sdgs. Available in the UN report "Transforming our world: the 2030 Agenda for Sustainable Development, 21 October 2015, A/RES/70/1.

(6) Patel, H. A.; Byun, J.; Yavuz, C. T. Carbon Dioxide Capture Adsorbents: Chemistry and Methods. *ChemSusChem* **2017**, *10* (7), 1303−1317.

(7) Aresta, M.; Dibenedetto, A.; Angelini, A. The changing paradigm in CO_2 utilization. *J. CO2 Util.* **2013**, *3−4*, 65−73.

(8) Patel, H. A.; Karadas, F.; Canlier, A.; Park, J.; Deniz, E.; Jung, Y.; Atilhan, M.; Yavuz, C. T. High capacity carbon dioxide adsorption by inexpensive covalent organic polymers. *J. Mater. Chem.* **2012**, *22* (17), 8431−8437.

(9) Dogan, N. A.; Ozdemir, E.; Yavuz, C. T. Direct Access to Primary Amines and Particle Morphology Control in Nanoporous CO_2 Sorbents. *ChemSusChem* **2017**, *10* (10), 2130−2134.

(10) Noorden, R. V. Two plants to put 'clean coal' to test. *Nature* **2014**, *509* (7498), 20.

(11) Peters, G. P.; Le Quéré, C.; Andrew, R. M.; Canadell, J. G.; Friedlingstein, P.; Ilyina, T.; Jackson, R. B.; Joos, F.; Korsbakken, J. I.; McKinley, G. A.; Sitch, S.; Tans, P. Towards real-time verification of CO_2 emissions. *Nat. Clim. Change* **2017**, *7* (12), 848−850.

(12) Naims, H. Economics of carbon dioxide capture and utilization—a supply and demand perspective. *Environ. Sci. Pollut. Res.* **2016**, *23* (22), 22226−22241.

(13) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An overview of CO_2 capture technologies. *Energy Environ. Sci.* **2010**, *3* (11), 1645−1669.

(14) Aresta, M.; Dibenedetto, A.; Quaranta, E. State of the art and perspectives in catalytic processes for CO_2 conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology. *J. Catal.* **2016**, *343*, 2−45.

(15) Alper, E.; Yuksel Orhan, O. CO_2 utilization: Developments in conversion processes. *Petroleum* **2017**, *3* (1), 109−126.

(16) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2. *Chem. Rev.* **2014**, *114* (3), 1709−1742.

(17) Dokania, A.; Ramirez, A.; Bavykina, A.; Gascon, J. Heterogeneous Catalysis for the Valorization of CO_2: Role of Bifunctional Processes in the Production of Chemicals. *ACS Energy Lett.* **2019**, *4* (1), 167−176.

(18) Arora, S.; Prasad, R. An overview on dry reforming of methane: strategies to reduce carbonaceous deactivation of catalysts. *RSC Adv.* **2016**, *6* (110), 108668−108688.

(19) Iulianelli, A.; Liguori, S.; Wilcox, J.; Basile, A. Advances on methane steam reforming to produce hydrogen through membrane reactors technology: A review. *Catal. Rev.: Sci. Eng.* **2016**, *58* (1), 1−35.

(20) Usman, M.; Wan Daud, W. M. A.; Abbas, H. F. Dry reforming of methane: Influence of process parameters—A review. *Renewable Sustainable Energy Rev.* **2015**, *45*, 710−744.

(21) Mondal, K.; Sasmal, S.; Badgandi, S.; Chowdhury, D. R.; Nair, V. Dry reforming of methane to syngas: a potential alternative process for value added chemicals—a techno-economic perspective. *Environ. Sci. Pollut. Res.* **2016**, *23* (22), 22267−22273.

(22) Ross, J. R. H. Natural gas reforming and CO_2 mitigation. *Catal. Today* **2005**, *100* (1), 151−158.

(23) Pakhare, D.; Spivey, J. A review of dry (CO_2) reforming of methane over noble metal catalysts. *Chem. Soc. Rev.* **2014**, *43* (22), 7813−7837.

(24) Zhao, S.; Jin, R.; Jin, R. Opportunities and Challenges in CO_2 Reduction by Gold- and Silver-Based Electrocatalysts: From Bulk Metals to Nanoparticles and Atomically Precise Nanoclusters. *ACS Energy Lett.* **2018**, *3* (2), 452−462.

(25) Pakhare, D.; Shaw, C.; Haynes, D.; Shekhawat, D.; Spivey, J. Effect of reaction temperature on activity of Pt- and Ru-substituted lanthanum zirconate pyrochlores ($La_2Zr_2O_7$) for dry (CO_2) reforming of methane (DRM). *J. CO2 Util.* **2013**, *1*, 37−42.

(26) Fischer, F.; Tropsch, H. Conversion of methane into hydrogen and carbon monoxide. *Brennst.-Chem.* **1928**, *9*, 39−46.

(27) Reitmeier, R. E.; Atwood, K.; Bennett, H.; Baugh, H. Production of Synthetic Gas - Reaction of Light Hydrocarbons with Steam and Carbon Dioxide. *Ind. Eng. Chem.* **1948**, *40* (4), 620−626.

(28) Hou, Z.; Chen, P.; Fang, H.; Zheng, X.; Yashima, T. Production of synthesis gas via methane reforming with CO_2 on noble metals and small amount of noble-(Rh-) promoted Ni catalysts. *Int. J. Hydrogen Energy* **2006**, *31* (5), 555−561.

(29) Luo, J. Z.; Yu, Z. L.; Ng, C. F.; Au, C. T. CO_2/CH_4 Reforming over Ni-La_2O_3/5A: An Investigation on Carbon Deposition and Reaction Steps. *J. Catal.* **2000**, *194* (2), 198−210.

(30) Aramouni, N. A. K.; Touma, J. G.; Tarboush, B. A.; Zeaiter, J.; Ahmad, M. N. Catalyst design for dry reforming of methane: Analysis review. *Renewable Sustainable Energy Rev.* **2018**, *82* (Part 3), 2570−2585.

(31) Kehres, J.; Jakobsen, J. G.; Andreasen, J. W.; Wagner, J. B.; Liu, H.; Molenbroek, A.; Sehested, J.; Chorkendorff, I.; Vegge, T. Dynamical Properties of a Ru/$MgAl_2O_4$ Catalyst during Reduction and Dry Methane Reforming. *J. Phys. Chem. C* **2012**, *116* (40), 21407−21415.

(32) Zhang, Z.; Verykios, X. E.; MacDonald, S. M.; Affrossman, S. Comparative Study of Carbon Dioxide Reforming of Methane to Synthesis Gas over Ni/La_2O_3 and Conventional Nickel-Based Catalysts. *J. Phys. Chem.* **1996**, *100* (2), 744−754.

(33) Ferreira-Aparicio, P.; Márquez-Alvarez, C.; Rodríguez-Ramos, I.; Schuurman, Y.; Guerrero-Ruiz, A.; Mirodatos, C. A Transient Kinetic Study of the Carbon Dioxide Reforming of Methane over Supported Ru Catalysts. *J. Catal.* **1999**, *184* (1), 202−212.

(34) Sutthiumporn, K.; Kawi, S. Promotional effect of alkaline earth over Ni-La_2O_3 catalyst for CO_2 reforming of CH_4: Role of surface oxygen species on H_2 production and carbon suppression. *Int. J. Hydrogen Energy* **2011**, *36* (22), 14435−14446.

(35) Lanzafame, P.; Perathoner, S.; Centi, G.; Gross, S.; Hensen, E. J. M. Grand challenges for catalysis in the Science and Technology Roadmap on Catalysis for Europe: moving ahead for a sustainable future. *Catal. Sci. Technol.* **2017**, *7* (22), 5182−5194.

(36) Rezaei, M.; Alavi, S. M.; Sahebdelfar, S.; Yan, Z.-F. Syngas Production by Methane Reforming with Carbon Dioxide on Noble Metal Catalysts. *J. Nat. Gas Chem.* **2006**, *15* (4), 327−334.

(37) Tsyganok, A. I.; Inaba, M.; Tsunoda, T.; Hamakawa, S.; Suzuki, K.; Hayakawa, T. Dry reforming of methane over supported noble metals: a novel approach to preparing catalysts. *Catal. Commun.* **2003**, *4* (9), 493−498.

(38) Zhang, Z.; Verykios, X. E. Carbon dioxide reforming of methane to synthesis gas over Ni/La_2O_3 catalysts. *Appl. Catal., A* **1996**, *138* (1), 109−133.

(39) Crisafulli, C.; Scirè, S.; Minicò, S.; Solarino, L. Ni-Ru bimetallic catalysts for the CO_2 reforming of methane. *Appl. Catal., A* **2002**, *225* (1), 1−9.

(40) Fan, M.-S.; Abdullah, A. Z.; Bhatia, S. Catalytic Technology for Carbon Dioxide Reforming of Methane to Synthesis Gas. *ChemCatChem* **2009**, *1* (2), 192−208.

(41) Zhao, Y.; Pan, Y.-x.; Xie, Y.; Liu, C.-j. Carbon dioxide reforming of methane over glow discharge plasma-reduced Ir/Al_2O_3 catalyst. *Catal. Commun.* **2008**, *9* (7), 1558−1562.

(42) Bian, Z.; Das, S.; Wai, M. H.; Hongmanorom, P.; Kawi, S. A Review on Bimetallic Nickel-Based Catalysts for CO_2 Reforming of Methane. *ChemPhysChem* **2017**, *18* (22), 3117−3134.

(43) Bartholomew, C. H. Mechanisms of catalyst deactivation. *Appl. Catal., A* **2001**, *212* (1), 17−60.

(44) Rostrup-Nielsen, J. R.; Sehested, J.; Nørskov, J. K. Hydrogen and synthesis gas by steam- and CO_2 reforming. In *Adv. Catal.*; Academic Press, 2002; 65−139.

(45) van Dillen, A. J.; Terörde, R. J. A. M.; Lensveld, D. J.; Geus, J. W.; de Jong, K. P. Synthesis of supported catalysts by impregnation and drying using aqueous chelated metal complexes. *J. Catal.* 2003, *216* (1), 257−264.

(46) Chen, D.; Christensen, K. O.; Ochoa-Fernández, E.; Yu, Z.; Tøtdal, B.; Latorre, N.; Monzón, A.; Holmen, A. Synthesis of carbon nanofibers: effects of Ni crystal size during methane decomposition. *J. Catal.* 2005, *229* (1), 82−96.

(47) Bengaard, H. S.; Nørskov, J. K.; Sehested, J.; Clausen, B. S.; Nielsen, L. P.; Molenbroek, A. M.; Rostrup-Nielsen, J. R. Steam Reforming and Graphite Formation on Ni Catalysts. *J. Catal.* 2002, *209* (2), 365−384.

(48) Kim, J.-H.; Suh, D. J.; Park, T.-J.; Kim, K.-L. Effect of metal particle size on coking during CO_2 reforming of CH_4 over Ni-alumina aerogel catalysts. *Appl. Catal., A* 2000, *197* (2), 191−200.

(49) Lavoie, J.-M. Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation. *Front. Chem.* 2014, *2* (81), 1−17.

(50) Jiang, Z.; Liao, X.; Zhao, Y. Comparative study of the dry reforming of methane on fluidised aerogel and xerogel Ni/Al_2O_3 catalysts. *Appl. Petrochem. Res.* 2013, *3* (3), 91−99.

(51) Alipour, Z.; Rezaei, M.; Meshkani, F. Effect of alkaline earth promoters (MgO, CaO, and BaO) on the activity and coke formation of Ni catalysts supported on nanocrystalline Al_2O_3 in dry reforming of methane. *J. Ind. Eng. Chem.* 2014, *20* (5), 2858−2863.

(52) Khajenoori, M.; Rezaei, M.; Meshkani, F. Dry reforming over CeO_2-promoted Ni/MgO nano-catalyst: Effect of Ni loading and CH_4/CO_2 molar ratio. *J. Ind. Eng. Chem.* 2015, *21*, 717−722.

(53) Singha, R. K.; Shukla, A.; Sandupatla, A.; Deo, G.; Bal, R. Synthesis and catalytic activity of a Pd doped Ni-MgO catalyst for dry reforming of methane. *J. Mater. Chem. A* 2017, *5* (30), 15688−15699.

(54) Abd Ghani, N. A.; Azapour, A.; Muhammad, S. A. F. S.; Ramli, N. M.; Vo, D. V. N.; Abdullah, B. Dry reforming of methane for syngas production over Ni-Co-supported Al_2O_3-MgO catalysts. *Appl. Petrochem. Res.* 2018, *8* (4), 263−270.

(55) Al-Doghachi, F. A. J.; Taufiq-Yap, Y. H. CO_2 Reforming of Methane over Ni/MgO Catalysts Promoted with Zr and La Oxides. *ChemistrySelect* 2018, *3* (2), 816−827.

(56) Akbari, E.; Alavi, S. M.; Rezaei, M. Synthesis gas production over highly active and stable nanostructured Ni-MgO-Al_2O_3 catalysts in dry reforming of methane: Effects of Ni contents. *Fuel* 2017, *194*, 171−179.

(57) Chai, R. J.; Fan, S. Y.; Zhang, Z. Q.; Chen, P. J.; Zhao, G. F.; Liu, Y.; Lu, Y. Free-Standing NiO-MgO-Al_2O_3 Nanosheets Derived from Layered Double Hydroxides Grown onto FeCrAl-Fiber as Structured Catalysts for Dry Reforming of Methane. *ACS Sustainable Chem. Eng.* 2017, *5* (6), 4517−4522.

(58) Usman, M.; Daud, W. M. A. W. An investigation on the influence of catalyst composition, calcination and reduction temperatures on Ni/MgO catalyst for dry reforming of methane. *RSC Adv.* 2016, *6* (94), 91603−91616.

(59) Zhang, Q.; Feng, X. Q.; Liu, J.; Zhao, L. P.; Song, X. F.; Zhang, P.; Gao, L. Hollow hierarchical Ni/MgO-SiO_2 catalyst with high activity, thermal stability and coking resistance for catalytic dry reforming of methane. *Int. J. Hydrogen Energy* 2018, *43* (24), 11056−11068.

(60) Meshkani, F.; Rezaei, M.; Andache, M. Investigation of the catalytic performance of Ni/MgO catalysts in partial oxidation, dry reforming and combined reforming of methane. *J. Ind. Eng. Chem.* 2014, *20* (4), 1251−1260.

(61) Yu, M. J.; Zhu, K. K.; Liu, Z. C.; Xiao, H. P.; Deng, W.; Zhou, X. G. Carbon dioxide reforming of methane over promoted $Ni_xMg_{1-x}O$ (111) platelet catalyst derived from solvothermal synthesis. *Appl. Catal., B* 2014, *148*, 177−190.

(62) Song, Y.; Ozdemir, E.; Ramesh, S.; Adishev, A.; Subramanian, S.; Harale, A.; Albuali, M.; Fadhel, B. A.; Jamal, A.; Moon, D.; Choi, S. H.; Yavuz, C. T. Dry reforming of methane by stable Ni-Mo nanocatalysts on single-crystalline MgO. *Science* 2020, *367* (6479), 777−781.

(63) Papadopoulou, C.; Matralis, H.; Verykios, X. Utilization of Biogas as a Renewable Carbon Source: Dry Reforming of Methane. In *Catalysis for Alternative Energy Generation*; Guczi, L., Erdôhelyi, A., Eds.; Springer: New York, NY, 2012; pp 57−127.

(64) Kawi, S.; Kathiraser, Y.; Ni, J.; Oemar, U.; Li, Z. W.; Saw, E. T. Progress in Synthesis of Highly Active and Stable Nickel-Based Catalysts for Carbon Dioxide Reforming of Methane. *ChemSusChem* 2015, *8* (21), 3556−3575.

(65) Djinović, P.; Batista, J.; Pintar, A. Efficient catalytic abatement of greenhouse gases: Methane reforming with CO_2 using a novel and thermally stable Rh-CeO_2 catalyst. *Int. J. Hydrogen Energy* 2012, *37* (3), 2699−2707.

(66) Ferreira-Aparicio, P.; Guerrero-Ruiz, A.; Rodrıguez-Ramos, I. Comparative study at low and medium reaction temperatures of syngas production by methane reforming with carbon dioxide over silica and alumina supported catalysts. *Appl. Catal., A* 1998, *170* (1), 177−187.

(67) Wang, H. Y.; Ruckenstein, E. Carbon dioxide reforming of methane to synthesis gas over supported rhodium catalysts: the effect of support. *Appl. Catal., A* 2000, *204* (1), 143−152.

(68) Dębek, R.; Motak, M.; Grzybek, T.; Galvez, M.; Da Costa, P. A Short Review on the Catalytic Activity of Hydrotalcite-Derived Materials for Dry Reforming of Methane. *Catalysts* 2017, *7* (1), 32.

(69) Titus, J.; Goepel, M.; Schunk, S. A.; Wilde, N.; Gläser, R. The role of acid/base properties in Ni/MgO-ZrO_2-based catalysts for dry reforming of methane. *Catal. Commun.* 2017, *100*, 76−80.

(70) Yu, M.; Zhu, K.; Liu, Z.; Xiao, H.; Deng, W.; Zhou, X. Carbon dioxide reforming of methane over promoted $Ni_xMg_{1-x}O$ (111) platelet catalyst derived from solvothermal synthesis. *Appl. Catal., B* 2014, *148−149*, 177−190.

(71) Usman, M.; Daud, W. M. A. W. Microemulsion based synthesis of Ni/MgO catalyst for dry reforming of methane. *RSC Adv.* 2016, *6* (44), 38277−38289.

(72) Jafarbegloo, M.; Tarlani, A.; Mesbah, A. W.; Sahebdelfar, S. One-pot synthesis of NiO-MgO nanocatalysts for CO_2 reforming of methane: The influence of active metal content on catalytic performance. *J. Nat. Gas Sci. Eng.* 2015, *27* (Part 2), 1165−1173.

(73) Das, S.; Thakur, S.; Bag, A.; Gupta, M. S.; Mondal, P.; Bordoloi, A. Support interaction of Ni nanocluster based catalysts applied in CO_2 reforming. *J. Catal.* 2015, *330*, 46−60.

(74) Das, S.; Thakur, S.; Bag, A.; Gupta, M. S.; Mondal, P.; Bordoloi, A. Support interaction of Ni nanocluster based catalysts applied in CO_2 reforming. *J. Catal.* 2015, *330*, 46−60.

(75) Zhang, R.-j.; Xia, G.-f.; Li, M.-f.; Wu, Y.; Nie, H.; Li, D.-d. Effect of support on the performance of Ni-based catalyst in methane dry reforming. *J. Fuel Chem. Technol.* 2015, *43* (11), 1359−1365.

(76) Xu, L.; Song, H.; Chou, L. Ordered mesoporous MgO-Al_2O_3 composite oxides supported Ni based catalysts for CO_2 reforming of CH_4: Effects of basic modifier and mesopore structure. *Int. J. Hydrogen Energy* 2013, *38* (18), 7307−7325.

(77) Min, J.-E.; Lee, Y.-J.; Park, H.-G.; Zhang, C.; Jun, K.-W. Carbon dioxide reforming of methane on Ni-MgO-Al_2O_3 catalysts prepared by sol-gel method: Effects of Mg/Al ratios. *J. Ind. Eng. Chem.* 2015, *26*, 375−383.

(78) Titus, J.; Roussière, T.; Wasserschaff, G.; Schunk, S.; Milanov, A.; Schwab, E.; Wagner, G.; Oeckler, O.; Gläser, R. Dry reforming of methane with carbon dioxide over NiO-MgO-ZrO_2. *Catal. Today* 2016, *270*, 68−75.

(79) Shah, Y. T.; Gardner, T. H. Dry Reforming of Hydrocarbon Feedstocks. *Catal. Rev.: Sci. Eng.* 2014, *56* (4), 476−536.

(80) Hu, Y. H.; Ruckenstein, E. Catalytic Conversion of Methane to Synthesis Gas by Partial Oxidation and CO_2 Reforming. In *Adv. Catal.*; Academic Press, 2004; 297−345.

(81) Juan-Juan, J.; Román-Martínez, M. C.; Illán-Gómez, M. J. Effect of potassium content in the activity of K-promoted Ni/Al_2O_3 catalysts for the dry reforming of methane. *Appl. Catal., A* 2006, *301* (1), 9−15.

(82) Shamsi, A. Partial Oxidation and Dry Reforming of Methane Over Ca/Ni/K(Na) Catalysts. *Catal. Lett.* 2006, *109* (3), 189−193.

(83) Yu, M.; Zhu, Y.-A.; Lu, Y.; Tong, G.; Zhu, K.; Zhou, X. The promoting role of Ag in Ni-CeO2 catalyzed CH4-CO2 dry reforming reaction. *Appl. Catal., B* **2015**, *165*, 43−56.

(84) Sigl, M.; Bradford, M. C. J.; Knözinger, H.; Vannice, M. A. CO2 reforming of methane over vanadia-promoted Rh/SiO2 catalysts. *Top. Catal.* **1999**, *8* (3), 211−222.

(85) Zeng, S.; Zhang, L.; Zhang, X.; Wang, Y.; Pan, H.; Su, H. Modification effect of natural mixed rare earths on Co/γ-Al2O3 catalysts for CH4/CO2 reforming to synthesis gas. *Int. J. Hydrogen Energy* **2012**, *37* (13), 9994−10001.

(86) Zhang, M.; Ji, S.; Hu, L.; Yin, F.; Li, C.; Liu, H. Structural Characterization of Highly Stable Ni/SBA-15 Catalyst and Its Catalytic Performance for Methane Reforming with CO2. *Chin. J. Catal.* **2006**, *27* (9), 777−781.

(87) Wang, S.; Lu, G. Q.; Millar, G. J. Carbon Dioxide Reforming of Methane To Produce Synthesis Gas over Metal-Supported Catalysts: State of the Art. *Energy Fuels* **1996**, *10* (4), 896−904.

(88) Chen, P.; Zhang, H.-B.; Lin, G.-D.; Tsai, K.-R. Development of coking-resistant Ni-based catalyst for partial oxidation and CO2-reforming of methane to syngas. *Appl. Catal., A* **1998**, *166* (2), 343−350.

(89) Trimm, D. L. Catalysts for the control of coking during steam reforming. *Catal. Today* **1999**, *49* (1), 3−10.

(90) Ghelamallah, M.; Granger, P. Impact of barium and lanthanum incorporation to supported Pt and Rh on α-Al2O3 in the dry reforming of methane. *Fuel* **2012**, *97*, 269−276.

(91) García-Diéguez, M.; Pieta, I. S.; Herrera, M. C.; Larrubia, M. A.; Alemany, L. J. Nanostructured Pt- and Ni-based catalysts for CO2-reforming of methane. *J. Catal.* **2010**, *270* (1), 136−145.

(92) Tao, K.; Zhang, Y.; Terao, S.; Tsubaki, N. Development of platinum-based bimodal pore catalyst for CO2 reforming of CH4. *Catal. Today* **2010**, *153* (3), 150−155.

(93) Lucrédio, A. F.; Assaf, J. M.; Assaf, E. M. Methane conversion reactions on Ni catalysts promoted with Rh: Influence of support. *Appl. Catal., A* **2011**, *400* (1), 156−165.

(94) Steinhauer, B.; Kasireddy, M. R.; Radnik, J.; Martin, A. Development of Ni-Pd bimetallic catalysts for the utilization of carbon dioxide and methane by dry reforming. *Appl. Catal., A* **2009**, *366* (2), 333−341.

(95) Pawelec, B.; Damyanova, S.; Arishtirova, K.; Fierro, J. L. G.; Petrov, L. Structural and surface features of PtNi catalysts for reforming of methane with CO2. *Appl. Catal., A* **2007**, *323*, 188−201.

(96) Tomishige, K.; Kanazawa, S.; Sato, M.; Ikushima, K.; Kunimori, K. Catalyst Design of Pt-Modified Ni/Al2O3 Catalyst with Flat Temperature Profile in Methane Reforming with CO2 and O2. *Catal. Lett.* **2002**, *84* (1), 69−74.

(97) Rahemi, N.; Haghighi, M.; Babaluo, A. A.; Jafari, M. F.; Estifaee, P. Synthesis and physicochemical characterizations of Ni/Al2O3-ZrO2 nanocatalyst prepared via impregnation method and treated with non-thermal plasma for CO2 reforming of CH4. *J. Ind. Eng. Chem.* **2013**, *19* (5), 1566−1576.

(98) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933.

(99) Sopena, S.; Fiorani, G.; Martin, C.; Kleij, A. W. Highly Efficient Organocatalyzed Conversion of Oxiranes and CO2 into Organic Carbonates. *ChemSusChem* **2015**, *8* (19), 3248−3254.

(100) North, M.; Pasquale, R.; Young, C. Synthesis of cyclic carbonates from epoxides and CO2. *Green Chem.* **2010**, *12* (9), 1514−1539.

(101) Alves, M.; Grignard, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies. *Catal. Sci. Technol.* **2017**, *7* (13), 2651−2684.

(102) Beyzavi, M. H.; Stephenson, C. J.; Liu, Y.; Karagiaridi, O.; Hupp, J. T.; Farha, O. K. Metal-Organic Framework-Based Catalysts: Chemical Fixation of CO2 with Epoxides Leading to Cyclic Organic Carbonates. *Front. Energy Res.* **2015**, *2* (63), 1−10.

(103) Martín, C.; Fiorani, G.; Kleij, A. W. Recent Advances in the Catalytic Preparation of Cyclic Organic Carbonates. *ACS Catal.* **2015**, *5* (2), 1353−1370.

(104) North, M.; Styring, P. Perspectives and visions on CO2 capture and utilisation. *Faraday Discuss.* **2015**, *183* (0), 489−502.

(105) Sun, J. M.; Fujita, S.; Arai, M. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. *J. Organomet. Chem.* **2005**, *690* (15), 3490−3497.

(106) Ma, D.; Liu, K.; Li, J.; Shi, Z. Bifunctional Metal-Free Porous Organic Framework Heterogeneous Catalyst for Efficient CO2 Conversion under Mild and Cocatalyst-Free Conditions. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 15050−15055.

(107) Xie, Y.; Liang, J.; Fu, Y.; Huang, M.; Xu, X.; Wang, H.; Tu, S.; Li, J. Hypercrosslinked mesoporous poly(ionic liquid)s with high ionic density for efficient CO2 capture and conversion into cyclic carbonates. *J. Mater. Chem. A* **2018**, *6* (15), 6660−6666.

(108) Zhang, Y.; Liu, K.; Wu, L.; Zhong, H.; Luo, N.; Zhu, Y.; Tong, M.; Long, Z.; Chen, G. Silanol-Enriched Viologen-Based Ionic Porous Hybrid Polymers for Efficient Catalytic CO2 Fixation into Cyclic Carbonates under Mild Conditions. *ACS Sustainable Chem. Eng.* **2019**, *7* (19), 16907−16916.

(109) Bobbink, F. D.; Dyson, P. J. Synthesis of carbonates and related compounds incorporating CO2 using ionic liquid-type catalysts: State-of-the-art and beyond. *J. Catal.* **2016**, *343*, 52−61.

(110) McCamley, K.; Warner, N. A.; Lamoureux, M. M.; Scammells, P. J.; Singer, R. D. Quantification of chloride ion impurities in ionic liquids using ICP-MS analysis. *Green Chem.* **2004**, *6* (7), 341−344.

(111) Cokoja, M.; Wilhelm, M. E.; Anthofer, M. H.; Herrmann, W. A.; Kühn, F. E. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts. *ChemSusChem* **2015**, *8* (15), 2436−2454.

(112) Yang, Z. Z.; He, L. N.; Miao, C. X.; Chanfreau, S. Lewis Basic Ionic Liquids-Catalyzed Conversion of Carbon Dioxide to Cyclic Carbonates. *Adv. Synth. Catal.* **2010**, *352* (13), 2233−2240.

(113) Foltran, S.; Alsarraf, J.; Robert, F.; Landais, Y.; Cloutet, E.; Cramail, H.; Tassaing, T. On the chemical fixation of supercritical carbon dioxide with epoxides catalyzed by ionic salts: an in situ FTIR and Raman study. *Catal. Sci. Technol.* **2013**, *3* (4), 1046−1055.

(114) Foltran, S.; Mereau, R.; Tassaing, T. Theoretical study on the chemical fixation of carbon dioxide with propylene oxide catalyzed by ammonium and guanidinium salts. *Catal. Sci. Technol.* **2014**, *4* (6), 1585−1597.

(115) Byun, J.; Zhang, K. A. I. Controllable Homogeneity/Heterogeneity Switch of Imidazolium Ionic Liquids for CO2 Utilization. *ChemCatChem* **2018**, *10* (20), 4610−4616.

(116) Du, Y.; Wang, J.-Q.; Chen, J.-Y.; Cai, F.; Tian, J.-S.; Kong, D.-L.; He, L.-N. A poly(ethylene glycol)-supported quaternary ammonium salt for highly efficient and environmentally friendly chemical fixation of CO2 with epoxides under supercritical conditions. *Tetrahedron Lett.* **2006**, *47* (8), 1271−1275.

(117) Ochiai, B.; Endo, T. Polymer-supported pyridinium catalysts for synthesis of cyclic carbonate by reaction of carbon dioxide and oxirane. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45* (23), 5673−5678.

(118) Amaral, A. J. R.; Coelho, J. F. J.; Serra, A. C. Synthesis of bifunctional cyclic carbonates from CO2 catalysed by choline-based systems. *Tetrahedron Lett.* **2013**, *54* (40), 5518−5522.

(119) Meng, X.-L.; Nie, Y.; Sun, J.; Cheng, W.-G.; Wang, J.-Q.; He, H.-Y.; Zhang, S.-J. Functionalized Dicyandiamide-formaldehyde polymers as efficient heterogeneous catalysts for conversion of CO2 into organic carbonates. *Green Chem.* **2014**, *16* (5), 2771−2778.

(120) Liang, J.; Chen, R.-P.; Wang, X.-Y.; Liu, T.-T.; Wang, X.-S.; Huang, Y.-B.; Cao, R. Postsynthetic ionization of an imidazole-containing metal-organic framework for the cycloaddition of carbon dioxide and epoxides. *Chem. Sci.* **2017**, *8* (2), 1570−1575.

(121) Wu, X.; Castro-Osma, J. A.; North, M. Synthesis of Chiral Cyclic Carbonates via Kinetic Resolution of Racemic Epoxides and Carbon Dioxide. *Symmetry* **2016**, *8* (1), 4.

(122) Talapaneni, S. N.; Buyukcakir, O.; Je, S. H.; Srinivasan, S.; Seo, Y.; Polychronopoulou, K.; Coskun, A. Nanoporous Polymers

Incorporating Sterically Confined N-Heterocyclic Carbenes for Simultaneous CO_2 Capture and Conversion at Ambient Pressure. *Chem. Mater.* **2015**, *27* (19), 6818−6826.

(123) Sun, Q.; Jin, Y.; Aguila, B.; Meng, X.; Ma, S.; Xiao, F.-S. Porous Ionic Polymers as a Robust and Efficient Platform for Capture and Chemical Fixation of Atmospheric CO_2. *ChemSusChem* **2017**, *10* (6), 1160−1165.

(124) Subramanian, S.; Park, J.; Byun, J.; Jung, Y.; Yavuz, C. T. Highly Efficient Catalytic Cyclic Carbonate Formation by Pyridyl Salicylimines. *ACS Appl. Mater. Interfaces* **2018**, *10* (11), 9478−9484.

(125) Coletti, A.; Whiteoak, C. J.; Conte, V.; Kleij, A. W. Vanadium Catalyzed Synthesis of Cyclic Organic Carbonates. *ChemCatChem* **2012**, *4* (8), 1190−1196.

(126) Zhong, H.; Su, Y.; Chen, X.; Li, X.; Wang, R. Imidazolium- and Triazine-Based Porous Organic Polymers for Heterogeneous Catalytic Conversion of CO_2 into Cyclic Carbonates. *ChemSusChem* **2017**, *10* (24), 4855−4863.

(127) Comerford, J. W.; Ingram, I. D. V.; North, M.; Wu, X. Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings. *Green Chem.* **2015**, *17* (4), 1966−1987.

(128) Izatt, R. M.; Izatt, S. R.; Bruening, R. L.; Izatt, N. E.; Moyer, B. A. Challenges to achievement of metal sustainability in our high-tech society. *Chem. Soc. Rev.* **2014**, *43* (8), 2451−2475.

(129) Liu, M.; Li, X.; Liang, L.; Sun, J. Protonated triethanolamine as multi-hydrogen bond donors catalyst for efficient cycloaddition of CO_2 to epoxides under mild and cocatalyst-free conditions. *J. CO2 Util.* **2016**, *16*, 384−390.

(130) Subramanian, S.; Oppenheim, J.; Kim, D.; Nguyen, T. S.; Silo, W. M. H.; Kim, B.; Goddard, W. A.; Yavuz, C. T. Catalytic Non-redox Carbon Dioxide Fixation in Cyclic Carbonates. *Chem.* **2019**, *5* (12), 3232−3242.

(131) Gascon, J. Co-catalyst and Metal-free CO_2 Fixation into Cyclic Carbonates: COPs to the Rescue. *Chem.* **2019**, *5* (12), 3015−3016.