Recent Progress in Thermal Conversion of CO₂ via Single-Atom Site Catalysis

Qishun Wang, Xiaobo Zheng, Jiabin Wu, Yao Wang, Dingsheng Wang,* and Yadong Li

1. Introduction

The current CO₂ emission rate hovers about 35 billion tons annually (Figure 1a), with the predominant emissions from fossil fuels.[1] Despite that land and ocean each sink about one-quarter of the emission, there is still nearly one-half entered the atmosphere. Even more, this trend increases dramatically since 1950s. Reducing the greenhouse gas CO₂ emissions is a common goal of all mankind. Using fewer fossil fuels is a direct and significant method but impractical. Although the energy gap can be replaced by clean energy, the chemical industries are still highly dependent on petroleum products. Carbon capture and storage/ utilization (CCS/CCU) serves as important way for reducing carbon footprint of chemical industry, replacing the nonrenewable petroleum has profound implications.

Methods for of CO₂ utilization include biotechnological approaches via traditional crops or marine algae to produce fermentation products (ethanol, etc.), biofuels and bioplastics, and more constructive catalytical approaches. Among thermo-,[3] photo-,[4] and electrocatalysis,[5–7] the thermal catalytic approach has enormous industrial potential, through which CO₂ can be reduced to CO as a syngas component for Fischer–Tropsch (F–T) synthesis or CH₄ as composition of natural gas.

What is more, directly obtaining high value products, e.g., formic acid, methanol, and dimethyl ether, or C₂+ products is highly desired.

Hydrogen is the most feasible reductant to convert CO₂ to value-added industrial feedstock for CCU system. To quantitatively assess the actual impacts to the environment, the life cycle analysis must be considered. Some CCU systems may still emit more CO₂ than non-CCU system in extreme cases.[8] Currently, mass production of hydrogen still depends on fossil energy via water–gas reaction, water–gas shift reaction, or reforming. By using green hydrogen from renewable energy, CCU technique generally decreases the carbon footprint compared to the traditional petrochemical industries. However, the cost of green hydrogen produced from electrolysis and photolysis of water is still uncompetitive if no carbon tax adopted; meanwhile, the robustness and efficiency of catalysts still need to be improved for these reactions. It should be noticed that even the production of green hydrogen causes slight carbon footprint.

Reactions with low energy efficiency will cause double disadvantages, both poor CO₂ emission reduction and unnecessary energy dissipation. Due to the complexity of elementary reactions and high activation energies, catalysts are of vital importance in catalytical approaches of CO₂ utilization. As the research has become increasingly systematic, single-atom site catalysis serves as a potential industrial catalyst. Here, we review the recent progress of the SAC for CO₂ activation (Figure 1b).

SAC was first proposed in 2011[9] and the concept was quickly adopted and expanded to widened scope of materials in heterogeneous catalysis. A variety of materials are used as the substrate by now,[10,11] not limited to carbon materials[12–18] and oxides,[19] such as transition-metal dichalcogenides (TMD),[20] carbides,[21,22] coordinated polymers,[23,24] MXenes,[25] etc., and

© 2022 Wiley-VCH GmbH
the elements of supported atoms have spread all over the periodic table.\textsuperscript{26–28} Related to the basis “isolated atom active sites, not closely connected with each other but interacted with the substrate,” some concepts with subtle differences were also commonly used, such as single-atom site catalysis, single-atom catalyst (SAC), single-site heterogeneous catalyst (SSHC), atomically dispersed catalyst, and dual/tri-atom catalyst (DAC/TAC) for the specific condition with dimer/trimer of isolated atoms, which all have diverse or even unexpected catalytic properties compared to the pervious nanocatalysts. Although there are many different concepts, the underlying factors are common. The isolated atoms generate the discontinuous electron orbitals and the multiformality of the localized atomic site-substrate environments\textsuperscript{29} behind the size effect, providing the tunability of electronic structure. These distinctions set SACs apart from the bulk, nanoparticles or clusters type of catalysts. Due to the variable valency\textsuperscript{30} and the different coordination environment\textsuperscript{31–37} the SAC may generate more than one type of reactive sites.\textsuperscript{38–42} Some CO\textsubscript{2} activation reactions such as alcohols and C\textsubscript{2} production have complex elementary reactions and demand various active sites, which could be achieved by SAC or coexisting\textsuperscript{43} catalysts via synergy effect by carefully designing the structure and precisely adjustment of the isolated atoms. In most cases, we use the common expression SAC to refer all above concepts, regardless of the emphasis to specific definitions. For coexisting materials, quasiatomic dispersed materials or suspected samples but not stated by the author, we will also discuss partially, at the same time indicate their status.

2. Reactions

CO and CH\textsubscript{4} are the most facile and simple product in CO\textsubscript{2} reduction (Figure 2), proved by thermodynamics data and high proportion of researches. Directly using hydrogen as reductant, the CO formation reaction and methanation reaction are commonly known as the reverse water–gas shift reaction (rWGS) and Sabatier reaction, respectively. Both CO and CH\textsubscript{4} are low-priced, mainly obtained from fossil fuels, and their major application is gaseous fuel currently. Industrial production using rWGS or Sabatier reaction seems not a good idea unless forbidding fossil fuels, especially for the quite high energy dissipation of Sabatier reaction. Worse still, CH\textsubscript{4} is a far stronger greenhouse gas than CO\textsubscript{2}; meanwhile, CO is toxic and hard to liquefy.\textsuperscript{44} Handling the storage and transportation problems will limit its widespread use. CO and CH\textsubscript{4} are also obtained as byproducts in value-added CO\textsubscript{2} reduction reactions. CO\textsubscript{2} could assist the dehydrogenation reactions as a weak oxidizer, improve the selectivity and avoid the formation of coke, with reduction products of CO. Dry reforming of methane (DRM) uses the abundant natural gas to reduce CO\textsubscript{2} and produce the mixture of H\textsubscript{2} and CO, also known as the syngas. Apart from the fuel use, CH\textsubscript{4} could be used

\begin{align*}
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{CH}_4 & \rightarrow 2\text{CO} + 2\text{H}_2 \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{HCOOH} \\
\text{CO}_2 + 3\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
2\text{CO}_2 + 6\text{H}_2 & \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}
\end{align*}
Catalysts for CO₂ Activation

Dispersing the active component, usually the precious metal, to atom sites allows reducing the usage, thus cutting down the cost of catalyst by maximizing the atomic utilization. Most CO₂ reduction reactions activate under gas phase with hydrogen as reductant, which is compatible with existing plants but also produces considerable water and CO. These byproducts have strong migration ability to isolated atoms, leading to sintering and deactivation. The relative high temperature, strong reducing and migration atmospheres have been a big challenge to the stability of SACs. The substrates are the first to be considered, which play important role not only in anchoring the atoms, but also in providing specific chemical environment. Their diverse capabilities could regulate the catalytic activities. At present, the most reported SACs used in CO₂ thermocatalysis are supported on oxides, which is totally different from the electrocatalysis with majority of carbon-based materials. Since most studies focus on gas phase reaction with react at high
temperature, oxide substrates provide ultrahigh thermal stability, but with relative low surface area and limitation in coordination adjustment. The weaker bonding of atoms in carbon materials better suits the liquid phase reaction. Some new types of substrates are also adopted, such as sulfide, hydride, MOF, polymer, etc. exhibiting the diverse chemical environments and shape-selectivity through reticular chemistry. SACs for CO2 activation are summarized according to their substrates.

3.1. In2O3

Pure In2O3 could effectively catalyze the hydrogenation of CO2 to methanol with high selectivity even at room temperature but with quite low activities. The surface of In2O3 provides oxygen vacancies, as well as the adjacent In ions dissociate the hydrogen molecules heterolytically and form formate species as the intermediate.[53] The addition of transition metals serving as the promoter could improve the activities due to the synergistic interactions. Additionally, In2O3-based catalysts show good water resistance and bring high durability in hydrogenation of CO2.

Shrotri’s group compared the STY of methanol catalyzed by transition metals in group 8–10 doping in the In2O3 matrix. Among these metals (Fe, Ru, Co, Rh, Ni, Pd, Pt), the Rh sample exhibited the highest STY.[54] The existence of Rh3+ changed the chemical environment of In2O3. The partially reduced In2O3 stabilized the Rh3+ ions through the charge transfer and avoided sintering under industrially relevant conditions, indicated from the H2 temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) spectra. Rh ions promoted oxygen vacancies for CO2 adsorption, observed by the CO2 temperature programmed desorption (TPD) of the used catalyst.

Recently, Li’s group reported a coexisting catalysts with SAC and cluster form of Pt embedded in the lattice of In2O3 for methanol synthesis with a selectivity up to 91.1%.[55] The XPS results indicated a relation between the chemical state and methanol selectivity. Single-atom Pt species were in the cationic state and maintained a majority of +2 valence state for the 0.58 wt% loading sample during the reaction, thus improving the methanol production. The selectivity was stable for more than 60 h with conversion decreasing slightly in the initial time for the stability test. In contrast, a 2.50 wt% loading control sample with Pt nanoparticles prepared by wet impregnation had a favor of rWGS and metallic Pt detected after reaction.

Pérez-Ramírez’s group studied the promotion effect with Pd for In2O3 in CO2 hydrogenation.[56] Series samples with different Pd loading were prepared by coprecipitation and dry impregnation synthesis methods and compared (Figure 3a–c). According to the extended X-ray absorption fine structure (EXAFS) and time of flight–secondary ions mass spectrometry (TOF-SIMS), Pd was doped into In2O3 matrix when prepared, and transformed into nanostructure with configurations of Pd2–In2 at the beginning of the reaction, thus improving the methanol selectivity, which fitted well with theoretical elucidation. The dispersion state appeared virtually unaltered for the coprecipitation sample after the long-time reaction, but the dry impregnation sample sintered significantly.

For other nonprecious metal dopants, Hensen’s group reported a Ni–In synergy catalytic system prepared by flame spray pyrolysis with controlled Ni–In interactions via varying the ratio for CO2 hydrogenation.[56] The low Ni loading promoted methanol formation and the Ni species were reduced to small clusters; meanwhile, partition of the Ni retained as isolated ion form with valence state of +3 during the CO2 hydrogenation reaction. A 5 wt% Ni loading sample processed the similar STY to Pd sample, outperforming the performance of Co and Cu system. Due to the higher rWGS activity and relatively low pressure, the optimized Ni–In catalyst encountered a slightly lower selectivity. The STY along with the selectivity fell with Ni loading increasing, and CH4 appeared in the products when the content is above 75%.

Huang’s group reported Ir1–In2O3 materials for ethanol synthesis in gas–liquid reaction by a wet chemistry synthetic method.[57] As indicated in the scanning transmission electron microscopy (STEM-HAADF) and EXAFS (Figure 3d–f), ultralow content of Ir (0.04 wt%) was loaded on partially reduced In2O3 with abundant oxygen vacancies served as distinct sites. CO2 was first reduced to the CH3O– active intermediate. Simultaneously, the isolated Ir and adjacent oxygen vacancies formed Lewis acid–base pair as catalytic centers and reduced CO2 to CO intermediates, evidenced by density functional theory (DFT) calculation and infrared spectra. Then the C–H coupling could be achieved after both steps. Higher temperature and metallic form of Ir from high loading led to the formation of methanol (Figure 3g).

As shown in Table 1, compared with other substrates, In2O3 is specialized alcohol production favoring. It is the intrinsic properties of In2O3 originated from the adjacent oxygen vacancies structure. The doping of transition metal, especially precious metal, induced partially reduction of In2O3, thus improving the density of defects and promoting CO2 adsorption. The H species are adsorbed and dissociated at metal sites, improving the reaction rate of the elementary step. The synergy between SAC and In2O3 promotes high efficiency and potential in industrial methanol production. The In2O3-based catalysts still face some problems. It is a trade-off between reaction temperature and methanol conversion; as the temperature improves, the conversion increases but the selectivity decreases significantly. The anchoring of atoms is quite well as revealed by the aggregation after reaction. Another problem is that the abundance of In is relatively low in earth crust. It is even lower than the rare-earth elements, and accordingly, the cost is rather high. Using In2O3 as the promoter and supported on other compatible oxides may cut the cost.

3.2. CeO2

CeO2 is a reducible rare-earth oxide and important substrate in heterogeneous catalysis. It has good stability and abundant oxygen vacancies due to the existence of Ce3+. CeO2 could be thermally reconstructed and traps migrant SA. Strong metal–support interaction (SMSI) is widely achieved between CeO2 and transition metals and promotes strong tunability for chemical environment. Size effect is a key factor for nanocatalysis. Amal’s group compared Pt SAC and clusters on CeO2 for CO2 reduction.[56] With ultralow loading, single-atom Pt was uniformly dispersed, inducing partially reduced Ce3+ of the CeO2.
substrate. The Pt species of the SAC sample had an intermediate valence between 0 and 2 after catalysis, presenting strong SMSI. Such Pt SAC had good selectivity toward rWGS reaction and exhibited good thermal stability as high as 500 °C.

Ma’s group reported Ir/CeO2 catalysts with tunable SMSI effects, and found that both SAC and small nanoparticles exhibited high selectivity toward CO while large nanoparticle favored methanation. Behind the size effect, the chemical structures of the active metal were found pivotal to the selectivity evidenced by EXAFS, XPS, and EELS. The partially oxidized Ir species had weaker interaction with CO, resulting in inhibition of methanation.

Another SMSI tuning phenomenon was reported by Zhang’s group; they investigated SMSI and H-spillover effects in CO2 methanation catalyzed by Ru/CeO2 in SAC, cluster, and NP forms. Activation of Ru–CO intermediate and dehydration are the key elementary steps, which is controlled by SMSI and H-spillover, respectively. As indicated in Raman, XPS, and chemisorption analyses, SMSI and H-spillover effects were competitive, and SAC sample had the strongest SMSI but no H-spillover among different size regimes, resulting in low CO activation and enhanced water removal. The cluster sample governed the best methanation activity with a good balance.

Supported Ru catalysts usually produce CH4 in CO2 hydrogenation. Interestingly, Cargnello’s group observed the restructuring of Ru nanoparticles supported on CeO2 into SAC during CO2 reduction, and the CO2 conversion switched from methanation to rWGS. The redispersion of Ru NPs was induced by oxidation atmosphere in rather low temperature (as low as 210 °C). The oxidative pretreatment changed the catalyst structure and
Recently, Liu’s group synthesized Pd atom dimers supported on oxygen vacancy-riched CeO$_2$ \cite{66}. By strictly controlling the pH, Pd complexes were obtained and loaded on CeO$_2$ nanorods. The dimer structure (DAC) is proved by the coordination structure from the EXAFS fitting and DFT simulated model (Figure 4i-f). The high homogeneity of reactive centers with unique Pd$_2$O$_4$ structure enabled CO$_2$ to CO dissociation and subsequent one-step C–C coupling. The C$_2$ formation was appropriately inhibited, thus achieving a selectivity of ethanol up to 99.2%.

Table 2 provides an overview on the CO$_2$ activation performances of CeO$_2$-based SACs. As a reducible oxide substrate, oxygen vacancies on surface of the CeO$_2$ provide plenty of anchoring sites for SAC. The atoms could stabilize under high temperature owing to the strong SMSI effects and thermal reconstruction. The oxophilicity and Ce$^{3+}$/Ce$^{4+}$ redox cycle of CeO$_2$ ensure CO$_2$ adsorption, forming the intermediate. As shown by these researches, chemical structures of CeO$_2$-supported SAC are regulated by different synthetic procedure and thermal treatment. It even induces the switchable selectivity from rWGS to Sabatier reaction. CeO$_2$ has high potential applied in industrial catalyst as substrates and its properties meet the demand for CO$_2$ reduction in both liquid phase and gas phase reaction.

### 3.3. TiO$_2$

TiO$_2$ has two common phases, anatase and rutile. And it is commercially available with various trade names, containing pure phase or the mixture of both phases. TiO$_2$ could be partially

---

Table 1. Catalytic activities of In$_2$O$_3$ based SACs for the hydrogenation of CO$_2$.

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition  | STY | Method   | References |
|------------|---------|------------|------------|-------------|------------|------------|-----|----------|------------|
| In$_2$O$_3$ Rh SAC | 0.96 wt% | – | Methanol ≈75%$^a$ | 300 | 5 MPa H$_2$/CO$_2$ = 4 | GHSV = 60 | L h$^{-1}$ g$^{-1}$ | ≈1.0$^a$ g h$^{-1}$ g$^{-1}$ | Sol–gel | [54] |
| In$_2$O$_3$ Ni SAC | ≈10%$^a$ | Methanol ≈63%$^a$ | 270 | 5 MPa H$_2$/CO$_2$ = 4 | GHSV = 30 | L h$^{-1}$ g$^{-1}$ | ≈0.5$^a$ g h$^{-1}$ g$^{-1}$ |
| In$_2$O$_3$ Pt SAC+cluster | <1% | Methanol 91.1% | 220 | 2 MPa CO$_2$/H$_2$/Ar = 24/72/4 | GHSV = 24 | L h$^{-1}$ g$^{-1}$ | – | Coprecipitation | [53] |
| In$_2$O$_3$ Pd SAC (fresh) Cluster (used) | >9%$^a$ | Methanol ≈65%$^a$ | 300 | 4 MPa CO$_2$/H$_2$/Ar = 24/72/4 | GHSV = 24 | L h$^{-1}$ g$^{-1}$ | ≈0.48$^a$ g h$^{-1}$ g$^{-1}$ | >60 h | Coprecipitation | [55] |
| In$_2$O$_3$ Ni SAC+cluster | ≈3%$^a$ | Methanol 53%$^a$ CO 47%$^a$ | 250 | 3 MPa CO$_2$/H$_2$/N$_2$ = 10:30:10 | GHSV = 60 | L h$^{-1}$ g$^{-1}$ | 0.25$^a$ g h$^{-1}$ g$^{-1}$ | Flame spray pyrolysis | [56] |
| In$_2$O$_3$ Ir SAC | – | – Methanol 72% | 200 | 6.0 MPa H$_2$/CO$_2$ = 5, 3.0 mL H$_2$O | TOF$_{\text{Ir}}$ up to 481.2 h$^{-1}$ | 0.046$^a$ g h$^{-1}$ g$^{-1}$ | Impregnation | [57] |

$^a$Approximate data obtained from chart. $^b$After unit conversion.
Figure 4. a) Schematic representation of relation between size and methanation activity. b) H₂-TPR profiles and c) in situ DRIFTS results of (1, 4) Ru(SA)/CeO₂, (2, 5) Ru(NC)/CeO₂, and (3, 6) Ru(NP)/CeO₂. Reproduced with permission.© 2018, American Chemical Society. d) Schematic representation of two sets of single-atom sites on CeO₂ substrate. e) TOF of DRM in terms of hydrogen production per M₁ site (number of atoms on the topmost layer measured under kinetics control regime). f) Corresponding microscopy analysis of Ce₀.⁹⁵Ni₀.₀²⁵Ru₀.₀²⁵O₂ catalyst after DRM. Reproduced with permission.© 2019, American Chemical Society. g) Activities of different catalysts in formic acid formation. g₁) Formation rate calculated by total Pd atoms and g₂) TOFs calculated by surface Pd atoms. g₃-₄) Successive reaction rate for the formation of formic acid. h₁) CO₂-TPD of the substrate materials. h₂-₃) H₂-TPR profiles of different catalysts. Reproduced with permission.© 2019, Elsevier. i) Microscopy analysis and j) fits of the EXAFS spectrum of Pd₀.₉₃Ce₀.₀₇O₂. k) Catalytic performance of different catalysts for CO₂ hydrogenation. l) Elementary steps involved in the catalytic cycle for ethanol formation over Pdₓ/CeO₂(110). Red spheres: O atoms; blue spheres: Pd atoms. Reproduced with permission.© 2021, Elsevier.
reduced in hydrogen-rich atmosphere, producing abundant oxygen vacancies, which also induces thermal reconstruction and strong SMSI effect as the reducible CeO₂.

Christopher’s group studied the size effect of Rh supported on TiO₂ substrate, drawing quantitative relationships.[67] The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique was used to determine the atom site fractions (Figure 5a–c), which decreased along with the increasing of Rh loading. The Rh sites were dynamic and nanoparticles disintegrated during the reaction. Various CO₂:H₂ ratios were tested, exhibiting entirely different selectivity owing to the competing parallel reaction pathways (Figure 5d).

Combining theoretical modeling and experiment was also adopted in Ir/TiO₂ system by Zhang’s group.[45] Coordination number is the key factor for size effect and tuned the rWGS activity and methanation during the CO₂ hydrogenation.[69] Transition metal Ni and Ru were stabilized on defective carbon nanotube (CNT) or reduced TiO₂ in blue color. The defects on both substrates were the key for avoiding clusters or nanoparticles. Ni samples showed good rWGS selectivity for both substrates and Ru samples processed an intermediate electronic distribution leading to the fresh SAC. The SAC could be reactivated through redispersion but large particles were too stable to redispersed in the redox cycle.

Serp’s group found regulation of charge transfer important in CO₂ hydrogenation.[60] Transition metal Ni and Ru were stabilized on defective carbon nanotube (CNT) or reduced TiO₂ in blue color. The defects on both substrates were the key for avoiding clusters or nanoparticles. Ni samples showed good rWGS selectivity for both substrates and Ru samples processed an interesting correlation between the selectivity and Ru⁵⁺ binding energy of XPS, indicating the tuning effect of electron density. It should be noticed that trace Na was retained in the blue color. The defects on both substrates were the key for avoiding clusters or nanoparticles. Ni samples showed good rWGS selectivity for both substrates and Ru samples processed an interesting correlation between the selectivity and Ru⁵⁺ binding energy of XPS, indicating the tuning effect of electron density. It should be noticed that trace Na was retained in the blue TiO₂, and the activities of CNT sample improved significantly with Na modification.

Piccolo’s group evaluated several Mo-modified commercial TiO₂ for methanol synthesis.[30] Rutile-type samples (trade name: RNR, RL11A) had better methanol selectivity than anatase (trade name: PC500, DTS1D) or their mixture (trade name: P25, P90), which was related to the nature of supported Mo (Figure 5f). Decreasing oxidation state was observed from anatase to rutile and most Mo ions were reduced to +4 or +5 valence. The Mo coverage also influenced the activities with Mo oxo species favoring methanol formation. RNR-supported 3 wt% Mo has the highest methanol STY at 35 g₂MeOH·kgcat⁻¹·h⁻¹ among all tested catalysts.

Table 2. Catalytic activities of CeO₂-based SACs for CO₂ activation.

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition | STY | Method | References |
|------------|---------|------------|------------|-------------|------------|-----------|-----|--------|------------|
| CeO₂       | Pt 0.05 wt% SAC | ≈10%       | CO 100%    | 250         | 0.1 MPa H₂/CO₂/N₂ = 62.5/32.5/5 | GHSV = 48 L·gcat⁻¹·h⁻¹ | 5.96 mol CO₂·g⁻¹·h⁻¹ | So–gel | [60]    |
| CeO₂       | Ir 0.7 wt% SAC   | 2.9%       | CO <99%    | 300         | 1.0 MPa H₂/CO₂/Ar = 76/19/5 | GHSV = 12 L·gcat⁻¹·h⁻¹ | 81.1 mol CO₂·mol⁻¹·h⁻¹ | Ligand-free adsorption | [61]    |
| CeO₂       | Ru 0.89 wt% SAC  | <10%       | CH₄ 100%   | 190         | 0.1 MPa H₂/CO₂/He = 8/2/30 | GHSV = 48 L·gcat⁻¹·h⁻¹ | TOF = 4.59 × 10⁻³ s⁻¹ | Impregnation | [62]    |
| CeO₂       | Ru 0.5 SAC       | <5%        | CO 90%     | 240         | 1 atm CO₂/H₂/Ar = 1/49 | GHSV adjusted by CO₂ conversion | TOF = 20 × 10⁻³ mol·s⁻¹·gcat⁻¹ | Oxidative redispersion | [63]    |
| CeO₂       | Ru/SnOₓ SAC, alloy | 1.63%     | CO 98%     | 330         | 1 atm H₂/CO₂/He = 76/19/6 | TOF = 0.22 mol CO₂·mol⁻¹·s⁻¹·gcat⁻¹ | Incipient wetness | Imregnation | [64]    |
| CeO₂       | Ni 5 at% SAC     | 63%        | DRM 80.0%  | 600         | 1 atm CH₄/CO₂/Ar = 1/1/78 | GHSV = 48 L·gcat⁻¹·h⁻¹ | – | Hydrothermal | [65]    |
| CeO₂       | Ru 5 at% SAC     | 81%        | DRM 82.9%  | 81%        | 41 mol Ru⁺⁺·mol⁻¹·s⁻¹ | @ 560 °C | – | – | [66]    |
| CeO₂       | Ru 2.5 at% Ni 2.5 at% SAC | 93%      | DRM 98.5%  | 93%        | 41 mol Ru⁺⁺·mol⁻¹·s⁻¹ | @ 560 °C | – | – | [66]    |
| CeO₂       | Pd 0.049 wt% SAC | –         | Formic acid | 100         | 2 MPa H₂, 2 mL 2 M NaHCO₃ | catalyst 10-20 mg, 1 h | 41 mol Na⁺·mol⁻¹·s⁻¹ | Coprecipitation | [50]    |
| CeO₂       | Pd 0.13 wt% DAC  | 9.2%       | Ethanol 99.2% | 240         | 3 MPa H₂/CO₂/N₂ = 27.7/24.3/3 | GHSV = 4 L·gcat⁻¹·h⁻¹ | 10.6 g_2 ethanol·g⁻¹·h⁻¹ | Impregnation | [66]    |

[45] Approximate data obtained from chart. [48] After unit conversion. [50] The loading of RuSn₉ is 1.0 wt% nominal and 1.21 wt% determined by ICP. [49] Conversion based on CH₄ and selectivity based on H₂.
Similar to CeO$_2$, chemical structures of TiO$_2$ are highly related to the activities in CO$_2$ hydrogenation (Table 3). Besides the regulations from size effect, oxygen vacancies and SMSI effects, the phase of TiO$_2$ substrates also show important role in the production selectivity. TiO$_2$ has weak acid sites on its surface, thus the Na modification is found effective improving CO$_2$ adsorption. TiO$_2$ has good stability and SAC on it could be redispersed by oxidative calcination, which regenerates the catalysts and benefits in industrial application.

### 3.4. Other Oxides

Table 4 provides an overview on the CO$_2$ activation performances based on oxides except In$_2$O$_3$, CeO$_2$, and TiO$_2$. Other reducible oxides are also used in CO$_2$ reduction researches. Llorca’s group synthesized Pd/Fe$_3$O$_4$ catalyst with different size regimes and found the SAC sample processed good selectivity to value-added product ethanol. Due to the reaction condition at rather low temperature and even atmospheric pressure, the CO$_2$ conversion is quite low. Pd single atom sintered and deactivated if the temperature above 350 °C, exhibiting a CO favored activity as cluster and nanoparticles samples. Increasing the pressure also decreased the selectivity to ethanol, and produced more methanol, propanol, or CO. Pd/Al$_2$O$_3$ SAC was prepared by the same procedure with CO as main product in CO$_2$ hydrogenation.

Oxide-supported SACs are widely used in CO$_2$ activation limited to reducible oxides. Inert oxides are found not inert in complex catalyst systems, and serve as critical components. The inert oxides still have the ability to activate CO$_2$ and influence the reaction by chemical environment adjustment. Szanyi’s group compared two inert substrates, Al$_2$O$_3$ and CNT supported Pd for CO$_2$ hydrogenation (Figure 6a). Two loadings (0.5 and 10 wt%) of Pd/Al$_2$O$_3$ were synthesized and determined as clusters and isolated atoms, respectively. Pd is able to dissociate H$_2$, as a result the CO$_2$ reduction activity was slightly higher with more Pd but the SAC sample produced more CO among the tested temperature. The small fraction of CH$_4$ may be attributed by partial sintering of the 0.5 wt% Pd, deduced by the authors. But unlike the oxide substrate, CNT could not active CO$_2$, thus causing very low activity (onset temperature of ~400 °C). Indeed, the La$_2$O$_3$ was required as promoter for activation of CO$_2$ in hydrogenation and the onset temperature dropped down to ~200 °C, which was almost same as Pd/Al$_2$O$_3$. A good rWGS selectivity was processed for Pd/La$_2$O$_3$/CNT, compared to Pd/Al$_2$O$_3$. Condition was different for Ru/Al$_2$O$_3$ system in their subsequent progress (Figure 6b,c). Ru/Al$_2$O$_3$ with various Ru loading was synthesized using similar method. The 0.1 wt% low loading had mostly atomically dispersion of Ru species, which exhibited high rWGS selectivity at onset temperature of ~300 °C, which is higher than both Pd/Al$_2$O$_3$ samples of ~200 °C. Interestingly, selectivity to methanation increased
significantly in long-term test along with the sintering of Ru, indicating the size effect. But the atomic dispersion of Pd sample could stabilize in oxidation and reduction pretreatment under 500 °C. CO was determined not an intermediate of the methanation reaction, and the activation energy of which is higher than that of CO hydrogenation.

As for other inert oxides, Liu’s group synthesized ZnO nanowire-supported Pd SAC and evaluated several reactions.[73] In CO2 hydrogenation, the SAC showed rWGS activity and no methane formation detected. Another Pd/ZnO SAC showed formic acid selectivity in liquid phase bicarbonate hydrogenation, as discussed in the CeO2 section.[50]

Shrotri’s group prepared Co SAC doped in ZrO2 with up to 15 atom% loading for rWGS reaction.[74] The Co ions maintained divalent revealed by EXAFS. Due to the imbalance of charge, plenty of oxygen vacancies formed and promoted CO2 adsorption as the Co loading increased, resulting in high CO selectivity under wide experimental condition via formate intermediate (Figure 6d–g). Increasing the Co loading to 50% caused the formation of Co3O4 and predominant of methanation activity.

Frei’s group replaced 1-10 atom% Ni in MgO matrix by a solid solution approach with isolated dispersion and tendency locating on the surface.[75] The Ni ions favored low coordination number, as proofed by XRF and XPS results and predicted by DFT, which decreased the CO2 adsorption energy. The selectivity was restricted to rWGS for Ni SAC and as a matter of fact, 2e− redox was applied, while multielectron reaction to methanol or methane required clusters. After Ni sintering at 350 °C, CH4 generated as a byproduct, accompanied with higher CO formation rate in CO2 hydrogenation.

Lauterbach’s group used Co/SiO2 as models to probe CO2 hydrogenation, even the temperature was adjusted back. Liu’s group combined theoretical modeling and experiment, tuning the DRM activity in Ni/MgO catalyst.[76] The atomic dispersion of Ni4 site could be strongly anchored on MgO with strong SMSI according to the calculation, thus preventing Ni sintering and coke of the active sites during the reaction. The dispersed sample performed low DRM activity and rWGS occurred as by-reaction. The Ni4 site generated as a product, accompanied with higher CO formation rate in CO2 hydrogenation.

Table 3. Catalytic activities of TiO2-based SACs for the hydrogenation of CO2.

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition | STY | Method | References |
|------------|---------|------------|------------|-------------|------------|-----------|-----|--------|------------|
| TiO2 P25   | Rh      | 65% SAC    | <10%       | CO 97%<sup>a</sup> | 200        | 1 atm H2/CO2/ N2=1/10/89 | TOF = 0.029 s<sup>−1</sup> | Impregnation | [67] |
|            | 0.5 wt% | 35% particles |            | CO 82%<sup>a</sup> |            | 1 atm H2/CO2/ N2=1/3/96 | TOF = 0.016<sup>a</sup> s<sup>−1</sup> |            | |
|            |         |            |            | CO 35%<sup>a</sup> |            | 1 atm H2/CO2/ N2=4/1/95 GHSV = 45-90 L·g<sub>cat</sub>·h<sup>−1</sup> | TOF = 0.0049 s<sup>−1</sup> |            | |
| TiO2 rutile| Ir      | SAC 2.1%   | CO almost 100% | 350 | 0.1 MPa H2/CO2/ He=45/45/10 GHSV=10 L·g<sub>cat</sub>·h<sup>−1</sup> | TOF = 0.042<sup>a</sup> s<sup>−1</sup> | Incipient-wetness impregnation | [45] |
| TiO2 anatase| Pt     | 0.025 wt% | SAC <2%    | CO 100% | 250 | 1 atm CO2/H2/ He =1/4/15 GHSV = 90 L·g<sub>cat</sub>·h<sup>−1</sup> | TOF = 0.094<sup>a</sup> s<sup>−1</sup> | Strong electrostatic adsorption | [68] |
| TiO2 P25   | Ni      | SAC 11.8%  | CO 99.6%  | 340 | 0.61 MPa N2/H2/ CO2=1/4/1 GHSV = 16.5 L·g<sub>cat</sub>·h<sup>−1</sup> | 109.5 mol MeOH·mol<sub>M</sub>·h<sup>−1</sup> | Impregnation | [69] |
|            | 0.71 wt%| SAC <2%    | CO 100%   | 340 | 0.61 MPa N2/H2/ CO2=1/4/1 GHSV = 16.5 L·g<sub>cat</sub>·h<sup>−1</sup> | 177 mol CO<sub>2</sub>·mol<sub>M</sub>·h<sup>−1</sup> | Oxidative redispersion | [68] |
| TiO2 anatase| Ru     | 1.0 wt% | SAC <2%    | CH4 97.3% | 210 | 3.5 MPa H2/CO2/ N2=3/1/1 GHSV = 7.5 L·g<sub>cat</sub>·h<sup>−1</sup> | 3.57 mol MeOH·mol<sub>M</sub>·h<sup>−1</sup> | Impregnation | [30] |
| TiO2 rutile| Mo      | SAC <2%    | CH4 12.0% | 275 | 3.5 MPa H2/CO2/ N2=3/1/1 GHSV = 7.5 L·g<sub>cat</sub>·h<sup>−1</sup> | 3.61 mol MeOH·mol<sub>M</sub>·h<sup>−1</sup> |           |       |        |

<sup>a</sup>Approximate data obtained from chart. <sup>b</sup>Trace Na retained as promoter.
Table 4. Catalytic activities of other oxide-based SACs for CO₂ activation.

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition | STY | Method | Ref. |
|------------|---------|------------|------------|-------------|-----------|-----------|-----|--------|-----|
| Fe₂O₄      | Pd 0.11 wt% | SAC        | 0.3%       | Ethanol 97.5% | 300       | 0.1 MPa H₂/CO₂ | 413 mmolH₂O₂·g₁⁻¹·h⁻¹ | Linker-assisted adsorption | [70] |
|            |         |            |            |             |           | N₂ = 40/10/50 | GHSV = 60 L·g⁻¹·h⁻¹ |                     |     |
|            |         |            |            |             |           |             | 440 mmolH₂O₂·g₁⁻¹·h⁻¹ |                     |     |
| Al₂O₃      | Pd 0.1 wt% | SAC        | 2.3%       | Ethanol 98.0% | 300       | 0.1 MPa H₂/CO₂ | 117 mmolH₂O₂·g₁⁻¹·h⁻¹ | Linker-assisted adsorption | [70] |
|            | (nominal)| | | | | N₂ = 40/10/50 | GHSV = 60 L·g⁻¹·h⁻¹ |                     |     |
| Al₂O₃      | Pd 0.5 wt% | SAC | ≈43%⁺¹ | CH₄ ≈37%⁺¹ | 500       | 1 atm H₂/CO₂ | – | Incipient wetness impregnation | [72] |
|            |         |            |            |             |           | He = 15/5/80 |                     |     |
| Al₂O₃      | Ru 0.1 wt% | SAC | ≈43%⁺¹ | CH₄ ≈37%⁺¹ | 300       | 1 atm H₂/CO₂ | – | Incipient wetness impregnation | [71] |
|            |         |            |            |             |           | He = 15/5/80 |                     |     |
| ZnO        | Pd 0.05 wt% | SAC | ≈16%⁺¹ | CO | 440       | 1 atm H₂/CO₂ | – | Impregnation | [73] |
|            |         |            |            |             |           | He = 5/0.6/94.4 |                     |     |
| ZrO₂       | Co 10 atom% | SAC | 19% | CO 97% | 340       | 3 MPa H₂/CO₂ | 3.8 μmol·g⁻¹·s⁻¹ | Coprecipitation | [74] |
| MgO        | Ni 10 atom% | SAC | <3% | CO 100% | 300       | 3 MPa H₂/CO₂ | CO formation rate = 0.09³¹⁻¹ | Coprecipitation | [75] |
| ZnO        | Pd 0.049 wt% | SAC | – | Formic acid 100 | 2 MPa H₂, 2 mL NaHCO₃ | 66 molₐₕ₂O₂·g₁⁻¹·h⁻¹ | Coprecipitation | [50] |
| MgO        | Ni 2.5 wt% | SAC or cluster²⁹ | CO₂/CH₄ ≈16/55⁺¹ | DRM 800 | 1 atm CH₄/CO₂ | H₂/CO Production | Coprecipitation | [76] |
| Ni 5 wt%   | cluster²⁹ | ≈68/60%⁺¹ | | | N₂ = 1/1/1 | H₂/CO Production | <0.01/0.04³¹⁻¹·L·min⁻¹ | Coprecipitation | [76] |
| Ni 10 wt%  | cluster²⁹ | ≈90/83%⁺¹ | | | | | 0.29³¹⁻¹·L·min⁻¹ | Strong electrostatic adsorption | [77] |
| SiO₂       | Co 1.82 wt% | SAC | 7% | CO >95% | 400       | 1 MPa H₂/CO₂ | H₂/CO ratio ≈0.9³¹⁻¹ | Calcination | [78] |
| La₂Zr₂O₇  | Rh 1.23 wt% | SAC | ≈56%⁺¹ | DRM 800 | 0.1 MPa CO₂/CH₄ | H₂/CO ratio ≈0.9³¹⁻¹ | Calcination | [78] |
| HEO J14    | Ru 2 wt%  | SACₜ | 40.1% | CO >95% | 500       | 0.1 MPa CO₂/H₂ = 1 | H₂/CO ratio ≈0.9³¹⁻¹ | Calcination | [78] |
| Pt 2 wt%   | 45.4% | | | | | Ball-milling | [80] |
| Pt 5 wt%   | 47.8% | | | | | Ball-milling | [80] |

⁺¹Approximate data obtained from chart. ²NI-Calculated by surface nickel concentration from XPS. ³Ni/0.3 nm (1–2 Ni atoms) for 2.5% Ni/MgO and 0.6–0.8 nm (3–4 Ni atoms) for both 5% and 10% Ni/MgO.

Ternary oxides are also used as catalyst substrates, such as spinel (AB₂O₄) and perovskite (ABO₃). Researches about ternary oxide pyrochlore (A₂B₂O₇) become active in recent years. Yao’s group evaluated a Rh-substituted pyrochlore in DRM.²⁷⁸ By citric acid-assisted calcination synthetic procedure, Ru ions formed solid solution in the La₂B₂O₇ oxide and dispersed as single atoms or clusters substituting to the Zr with pyrochlore structure or Ti with perovskite structure at B site, respectively. In DRM reaction, Rh SAC/La₂Zr₂O₇ led to rapid carbon, resulting from the fast CH₄ dissociation. In contrast, Rh cluster/La₂Ti₂O₇ had better performance in CO₂ activation, owing to the oxygen vacancies accelerating electron transport, which contributed to the excellent activity and long-term stability of DRM.
High entropy oxide (HEO) is a type emerging material, which provides new possibility of metastable substrates of catalysts among enormous possible compositions. Dai’s group used mechanochemical method to prepare rocksalt-structured J14 HEO with (NiMgCuZnCo)O composite. Owing to the new entropic tuning strategy, HEO with up to 5 wt% Pt or Ru doping exhibited good activity to rWGS and thermal stability even after 700 °C calcination (Figure 6h). Limited to our understanding, the mechanism of high entropic tuning is still hard to explain and unpredictable by far, but such materials endow a new field for heterogeneous catalysis including CO2 activation.

3.5. Carbon-Based Materials

Carbon-based SACs are widely used in electrocatalysis, especially for N-doped carbon. N-contained groups provide strong anchoring ability to the metal among the periodic table. But there are rarely reports on carbon-supported SACs for the CO2 thermal reduction comparing with the oxide substrates. Some preliminary results are listed here (Table 5). CNTs are often used as reference to show the effect of SMSI, such as La2O3-promoted Pd/CNT reported by Szanyi and defective CNT-supported Ni or Ru reported by Serp’s group, already discussed in TiO2 and Other oxides part, respectively. Indeed, the CNT substrate is inert for CO2 adsorption and activation. The SACs with transition metal supported on CNT only exhibit poor activity if no promoter existed in rWGS reactions. Ji’s group used a mechanochemistry method (Figure 7a) preparing DACs on N-doped carbon (NC). The metal and interatomic distances were controllable by mixing nitrogen-doped porous carbon and various bimetal organometallic complexes. The synthetic procedure could be extended to FePd and FeNi DACs. The Ni2 DAC had a distance around 3.7 Å (Figure 7b), and keep mostly unchanged after catalysis despite partial Ni species sintered to cluster. The DAC structure remarkably improved the conversion in CO2 hydrogenation and maintained good rWGS selectivity comparing with Ni SAC sample.
Table 5. Catalytic activities of carbon-based SACs and SAs for CO2 activation.

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition | STY | Method | References |
|------------|---------|------------|------------|-------------|------------|-----------|-----|--------|------------|
| CNT        | Ni 1.06 wt% | SAC       | 5.4%       | CO 93.7%    | 340        | 0.61 MPa H2/CO2/ N2 = 4/1/1 | 32.4 molCO/molH2·h⁻¹ | Reactive deposition | [69] |
|            |         |           | 8.1%       | CO 95.5%    |            | GHSV = 16.5 L·g⁻¹·h⁻¹ | 50.7 molCO/molH2·h⁻¹ |             |            |
|            | Ru 0.95 wt% | SAC       | 8.4%       | CO 56.0%    |            |            | 100.5 molCO/molH2·h⁻¹ |             |            |
|            |         |           | 20.2%      | CO 79.5%    |            |            | 247.1 molCO/molH2·h⁻¹ |             |            |
| CNT        | Pd 1 wt% | SAC       | ≥36%        | CO ≥97%     | 500        | 1 atm H2/CO2/ He = 15/5/80 | – | Impregnation | [72] |
|            | La2O3 2.3 wt% | SAC   | ≈36%        | CO ≈97%     |            | GHSV = 72 L·g⁻¹·h⁻¹ |             |             |            |
| N-doped C  | Ni 0.09 wt% | DAC, SAC | 14%        | CO 98%      | 500        | 0.1 MPa H2/CO2 = 1 | TOF = 1209.3 h⁻¹ | Ball-milling and pyrolysis | [84] |
|            |         |           |            | CO 97%      |            | GHSV = 27 L·g⁻¹·h⁻¹ | TOF = 831.9 h⁻¹ |             |            |
| N-doped C  | Co–Fe nanoparticles | SAA    | 51.7%      | C5, 42.4%   | 300        | 2.5 MPa H2/ CO2 = 3 (10% Ar) | Yield = 23% | Co precursor: Co/NC | [51] |
|            | Co 20 atom% | SAC       |            | CH4, 21.6%  |            | GHSV = 2 L·g⁻¹·h⁻¹ |             |             |            |
|            | Co–Fe nanoparticles | SAC    | ≈42%       | C5–, ≈39%   |            | Yield = 17% | Co precursor: salt |             |            |
|            | Co 2 atom% | SAC       |           | CH4, ≈19%   |            |             |             |             |            |
| SiO2       | Pt–Ni nanoparticles | SAC    | 11.5%      | DRM         | 500        | 1 atm CO2/CH4/ N2 = 1/1/1 | H2/CO yield = 5.4/10.8% | Reverse microemulsion method | [90] |
|            | Pt 0.22 wt%/0.6 at% | SAC |             | H2/CO = 0.49 |            | GHSV = 60 L·g⁻¹·h⁻¹ |             |             |            |

*Trace Na added as promoter. Approximate data obtained from chart.

Kim’s group synthesized Co–Fe single-atom alloy (SAA) derived from N-doped carbon-supported Co SAC for CO2 F–T synthesis (Figure 7c–g). Fe salt was impregnated on Co SAC/NC and SAA was induced in the following calcination. DFT results indicated the suppressing effect of methanation for FeCo alloy. Stepwise synthetic procedure could stabilize SAC and inhibit migration of Co. Although the strong anchoring from pyridinic groups of the substrates, the SAA catalyst prepared via coimpregnation still dealloyed after the CO2 hydrogenation regeneration.

Carbon-based materials seem inadequate in thermocatalysis for its inertness toward CO2, unlike the oxides in which defects and lattice oxygen could assist the reactions. Another important factor is stability. The SACs anchored by M–N or M–C bonds trend to mirage and the carbon supports may be instable in the catalytic condition due to the Boudouard reaction with onset temperature of ≈400 °C. Despite these disadvantages, some theoretical researches[85,86] also prove that in relative low temperature, carbon-supported SAC has the potential for the reduction of CO2 into high-value production.

### 3.6. Single-Atom Alloys

Even small fraction of doping atoms in alloy could significantly change its property.[87] SAA is an expanded concept of SAC and also has potential application in CO2 activation (Table 5), as revealed by theoretical researches[88,90] and experiment from Sasmz’s group. They reported Pt–Ni SAC and CeO2 cores confined in nanotubular SiO2 structure for DRM.[91] Ce species had strong interaction with both components in Ni–Pt SAC and may enter the lattice evidenced by the HRTEM and TPR. The oxygen vacancies improved the Ni dispersion. No Pt–Pt bonds were detected in 0.25 wt% Pt concentration. The confined structure is similar to yolk–shell and exhibited excellent resistance to carbon deposition for over 120 h. Mechanism researches further support the properties of SAA. Pd SAC on Cu surface was found having lowest dissociation barrier and promoting hydrogen-spillover.[92] Single Pt atom on Cu(111) promotes rWGS reaction, evidenced by in situ XPS and the produced CO molecules also assist in the dispersion of Ni species but the isolated atoms decreased both Brønsted/Lewis acid sites and basic sites evidenced by in situ XPS and the produced CO molecules also assist in the dispersion of Ni species but the isolated atoms decreased both Brønsted/Lewis acid sites and basic sites.

### 3.7. Porous Materials

Porous materials have unique advantages in catalysis. Its high surface area is benefit for anchoring SAC and its pores and channels could tune the products via shape-selective catalysis. Zeolites are inorganic material and widely used in industrial catalysis. De Jong’s group developed a 13X zeolite confined Ni catalyst for CO2 methanation and CeO2 was added as promoter.[94] CeO2 assisted in the dispersion of Ni species but the isolated atoms were not specified according to the energy dispersive X-ray spectroscopy (EDX). TPR indicated strong H-spillover effect of Ni and reduction of CeO2 (Figure 8a). The 2.5 w% CeO2 as promoter decreased both Brønsted/Lewis acid sites and basic sites compared to other additive amount or fresh 13× (Figure 8b), achieving high methanation selectivity and long-term stability. A balance of acidity and basicity should prevail for adsorption and activation of CO2.
Ordomsky’s group encapsulated Ru in MCM-4 for formic acid synthesis.[95] Isolated Ru\(^{3+}\) sites were incorporated to the channel wall with coordination of CTAB, forming solid micelle. A proposed mechanism involving that the H\(_2\) molecule heterolytically splitted in Ru sites and formed formate intermediate was suggested by DFT modeling. With the aid of tertiary amine, the catalyst reached high TOF = \(143\) h\(^{-1}\) in water free condition or high formate concentration of 4M in aqueous solution of CO\(_2\) hydrogenation.

Reticular chemistry endows the new field of organometallic or organic materials with structure similar to zeolite. MOF is an organometallic complex with micropores. By tuning the secondary building unit (SBU) and ligand, MOFs with different structures and properties are widely reported. SAC could also be loaded on MOFs,[96,97] but the experimental studies about CO\(_2\) activation are still limited. Zeng’s group used Cr-based MIL-101 anchoring isolated Pt at ultralow loading by slow syringe pumping.[98] Pt\(^{2+}\) ions were coordinated with oxygen atoms in the SBU (Figure 8c-e). The SAC had good methanol selectivity via formate intermediate and formic formed as the main byproduct. By simply increasing the amount of Pt and reductant, Pt nanoparticles were obtained, which processed totally different reaction pathway and CO was formed via carboxyl intermediate.

Lin’s group synthesized Zr-MOFs with Zr\(_{12}\) SBUs, in which 11 Cu\(^{1+}\) ions and 3 alkaline metal ions were loaded on the blinding site of Zr-SBU.[99] The two adjacent Cu sites with short distance of 2.7 Å formed DAC, processing C–C coupling activation (Figure 8f-h). With the basicity of alkaline metal increased, the selectivity to ethanol increased and the Cs sample had >99% selectivity and highest TON among Li, Na, K, and Cs. Apart from the SBU, the ligand could also coordinate metal ions. In another research they anchored Cu and Zn by ligand and SBU in a UiO-67 derivation, respectively, and in situ reduced to small nanoparticles. Such SAC-derived catalyst had almost 100% methanol selectivity.[100] Porous organic polymer (POP) is an amorphous material with pores formed by covalent bonds. Zhang’s group used an aminopyridine POP to fabricate Ir SAC for liquid phase CO\(_2\) hydrogenation with an ultrahigh TON = 25 135 (\(\approx\)0.66 wt% loading).[101] The POP has plenty of C=O and N–H groups, accompanied with strong chemical interaction with noble metal and formed amorphous structure with mesopores of 7.6 nm. The Ir species were partially reduced by NaBH\(_4\) and presented the less positive oxidation state. Ir was
fully reduced if using active carbon or C₃N₄ supported via same synthetic procedure and formed metallic nanoparticles. The Ir SAC had similar coordination environment to the pincer ligand Ir complexes (Figure 8i,j), exhibiting similar catalytic behavior and high activity as homogeneous catalysis, however combined with good stability and recyclability.

All the above porous materials present relative high loading of SACs and good activities (Table 6), owing to their high surface areas. Although porous materials usually present shape-selectivity in catalysis, which doesn’t take effort in CO₂ hydrogenation and partially relates to the small size of the production molecules. But the uniform pore structure provided by porous materials like zeolites, MOFs, and COFs could construct identical sites in each pore units. Porous materials confined SACs not only have great potential in industrial CO₂ activation, but also are ideal models for mechanism researches.

### 3.8. Other Substrates

Some nonoxide compounds are used as SAC substrates. Zhou’s group reported an Al-doped MgH₂ methanation catalyst via reactive ball-milling. The isolated Al atoms weakened the Mg–H and provide lattice H for CO₂ hydrogenation through formate intermediate. Comparing with the undoped MgH₂ with the same treatment, the conversion was slightly improved, with fewer byproduct of C–C coupling formed.

Ajayan’s group used porous hexagonal boron nitride (h-BN) to support isolated Ru via vacuum filtration. The Ru complex was trapped by hydroxyl groups on mesopores of h-BN and formed bonds with B, N, and O atoms after annealing. An intermediate valence of Ru was detected in Ru/BN, which slightly increased after calcination due to electron-withdrawing effect in Ru–O bond. Comparing to the Ru species with high valence,
the Ru SAC exhibited better activity and selectivity toward methanation.

Huang’s group reported C₃N₄-supported Cu SACs with tailored coordination structures, which led to two distinct reduction products (Figure 9a–c). The Cu–N₄ and Cu–N₃ structures were prepared by simple pyrolysis methods and identified by XPS and EXAFS, with mean Cu valences of +1.05 and +1.64, respectively. Such coordination structures processed different reaction pathways (Figure 9d), formate intermediate for Cu–N₄ with methanol productivity, and carbonyl intermediate for Cu–N₃ with RWGS activity in liquid phase base-free CO₂ hydrogenation.

Zeng’s group found the neighboring effect of SAC for altering the reaction pathway of liquid phase CO₂ hydrogenation in Pt/MoS₂ system. The ratio of isolated/neighboring/patch of Pt monomers was counted based on HAADF-STEM images. Due to the layered structure of MoS₂, the apparently adjacent atoms could represent the actual neighboring condition in 3D space. The neighboring Pt atoms decreased the activation energy and achieved higher catalytic activity in methanol production comparing with isolated Pt atoms (Figure 9e–g). Unexpectedly, reaction pathway was different according to in situ DRIFT and DFT modeling. Interaction of Pt atoms sequentially transformed CO₂ into formic acid and then methanol while isolated Pt atom favored the CO₂ to methanol path through COOH* to C(OH)₂* transformation as intermediates (Figure 9h–i). If the feed ratio of H₂/CO₂ gas was switched from 3/1 to 1/3, the main product switches to formic acid at the same time.

Tsang’s group developed a complex assisted deposition method for preparation of various transition metals supported on TMDs. Taking Fe/MoS₂ as example, the monolayered MoS₂ exfoliated by n-BuLi intercalation had plenty of sulfur vacancies, allowing the SMSI with Fe ions. Only Fe–S scattering was appeared in wavelet transformation spectra of EXAFS for 3–10 wt% loading sample, exhibiting high RWGS activity and selectivity, meanwhile maintaining good stability over 500 h.

Yamashita’s group presented isolated Ru anchored on base substrate layered double hydroxides (LDH) for liquid phase CO₂ hydrogenation. Ru formed hydride species indicated by EXAFS and its electronic state was tuned by electronic metal–support interaction (EMSI), showing a correlation between Ru₁sp binding energy and TON based on Ru. The reaction activity was also related to CO₂ adsorption capacity, which originated from the basicity of LDHs and could be easily tuned by varying the metal components and ratio.

The nonoxide substrates could anchor the metal atoms with enough strength and high loading; meanwhile, the more coordination structures other than M–O bonds extend the chemistry environments for SACs. Nonoxide compounds are beneficial supplement besides oxides and carbon materials, but to a large extent, their properties in thermocatalysis are not clear and undiscovered. Still big efforts need to be made for the structure–performance relationship and industrial application.

Table 6 provides an overview on the CO₂ activation performances of SACs based on these less common substrates. The hydrogen activation ability from hydride-supported SAC provides new thoughts for CO₂ hydrogenation. And coincidently, the rest SACs are all 2D layered materials and exhibit good properties in
CO2 activation, which represent an ideal platform for SAC research, owing to the high surface areas and defect-rich interface\textsuperscript{107} for anchoring SA. As these materials are not conventional substrates in industry, the stability and robustness still need inspection. Further studies on the mechanism of these substrates are necessary and instructive.

4. Conclusion and Perspective

SACs have been one of the most promising material concepts at the moment, and adopted in variety fields among heterogeneous catalysis. Mechanism studies have confirmed the relation between the high activity and single-atom sites. Despite constructive progress on SAC in CO2 activation to date, there are still many challenges to be solved. Most studies evaluated specific reactions lack of industrial prospect and thankfully, SACs show high potential in a variety of CO2 activation reactions not limited to rWGS and Sabatier reaction. More studies should focus on value-added products.

Methanol economy draws the future of chemical industry and olefins or even starch have been obtained from methanol. Moreover, directly synthesizing of C\textsubscript{2} productions such as ethene, alcohols, and dihydroxyacetone for building blocks of fine chemicals or even carbohydrate could reduce the synthetic steps and improve the atomic efficiencies.

It is challenging to regulate the selectivity of these products during CO2 activation. SACs provide the opportunity in rationally designing and precisely controlling the active sites in atomic level by tuning the metal–support interactions or coordination environment. More tuning methods could be adopted for SACs. Hybridization and surface modification of various substrates combine the advantages. Additionally, basic sites play a particularly key role in CO2 activation. Even trace alkali metal ions act as promoter for improving the activity and are considered effective in stability of some metal oxide-supported SACs. In liquid phase reaction, SACs cooperated with organic ligands could also enhance the conversion and selectivity, which could take the place of homogeneous catalysis, with similar chemical structure of the organometallic complex. Developing

**Figure 9.** a) Schematic representation of C\textsubscript{3}N\textsubscript{4}-supported Cu SAC with different coordination structure and corresponding b) XPS and c) STEM. Scale bar: 2 nm. d) Proposed mechanism of methanol and CO formation over Cu/C\textsubscript{3}N\textsubscript{4} SAC. Reproduced under the terms of the Creative Commons CC BY license.\textsuperscript{104} Copyright 2021, The Authors. Published by Springer Nature. e) Microscopy analysis of 7.5 wt\% Pt/MoS\textsubscript{2}. Detailed images of isolated and neighboring Pt SACs and the corresponding structure. f) EXAFS spectra in r-space and g) histogram of the contents of different Pt/MoS\textsubscript{2}. Proposed mechanism of addition of H\textsuperscript{+} to COOH\textsuperscript{−} over isolated and patch of Pt SACs. Reproduced with permission.\textsuperscript{20} Copyright 2018, Springer Nature.
promoters for SACs is worth studying and has promising industrial application.

Stability remains the crucial issue for SACs. A majority of CO₂ activation reactions process under relative high temperature and high pressure, accompanied with strong reducible atmosphere. Most metal oxide substrates show good durability or beneficially partial reduction under such condition. The metal–support interactions play a decisive role in anchoring the SA, but the side products water or CO may still affect them. The long-term stability of SACs is rarely tested and still far away from the demand of industry. On the other side, the SAC and traditional catalysts are not distinct from each other. Even partial of activities in some traditional catalysts are originated from SAC without being recognized as active sites in the past. Strong migration tendency becomes effective under the reaction condition, which promotes not only the aggregation but also redispersion of active metal dynamically. For example, Pt can be trapped as isolated atoms in reducible substrates via covalent metal oxide bonds. If the aggregation is hard to overcome, developing renewable catalysts by thermal reconstruction is accepted and should be well considered.

Large-scale and universal routes for fabricating SACs need to be developed. So far, strategies like mechanochemical approach (ball-milling) and pyrolyzing coordinated polymer have been reported, but most synthetic procedures are not suitable for multisubstrates or unpractically applied in batch production. Meanwhile, processing high loading of SACs can be another challenge toward industry.

The precise structure and catalytic mechanism of SACs largely remain undiscovered yet. The observation of isolated atoms is highly depended by aberration-corrected TEM and X-ray absorption spectroscopy (XAS) technique, which provide apparently localized image or average spectra, respectively. The position of SAs and intermediates of catalysis. Moreover, comparing to highly depended by aberration-corrected TEM and X-ray absorption spectroscopy (XAS) technique, which provide apparently localized image or average spectra, respectively. The position of SAs and intermediates of catalysis. Moreover, comparing to Fourier transform infrared spectroscopy (FTIR), electron spin resonance (EPR), and Mössbauer spectra are helpful for structural analysis and should be properly adopted. Structure–performance relationship is of great importance for all catalysts, and pyrolyzing coordinated polymer has promising industrial application.

### Table 7: Catalytic activities of other substrate-supported SACs for the hydrogenation of CO₂

| Substrates | Loading | Dispersion | Conversion | Selectivity | Temp. [°C] | Condition | STY | Method | References |
|------------|---------|------------|------------|-------------|------------|-----------|-----|--------|------------|
| MgH₂       | 0.3 wt% | SAC, cluster 0.44 wt% | 27.1%      | CH₄ 88.4%   | 320        | 1.0 MPa H₂/CO₂ = 5 GHSV = 4.8 L·g⁻¹·h⁻¹ | –   | Reactive | [102]     |
| h-BN       | 0.58 wt% | SAC, cluster | 28.7%      | CH₄ 93.5%   | 350        | 1 MPa H₂/CO₂/Ar = 18/72/10 GHSV = 18 L·g⁻¹·h⁻¹ | 1.86 × 10⁻³ mol·g⁻¹·s⁻¹ | Electrostatic adsorption and calcination | [103]     |
| C₃N₄Cu     | 12.1 wt% | SAC Cu–N₄ | –          | Methanol    | 150        | 3.2 MPa H₂/CO₂/ N₂ = 24/72/4 | 4.2, | One-step thermal pyrolysis | [104]     |
| Cu          | 13.1 wt% | SAC Cu–N₄ | –          | CO ≈93%     | 10 mL water catalyst 10 mg, 3 h | 2.4 mmol·g⁻¹·h⁻¹ | Two-step thermal pyrolysis | –         |
| MoS₂       | 0.2 wt%  | SAC isolated | –         | Methanol    | 150        | 3.2 MPa H₂/CO₂ = 3/1, 30 mL DMF catalyst 200 mg, 3 h | Yield = 0.003/0.062 mmol TOF = ≈11⁹ h⁻¹ | Replacement | [20]      |
| Pt          | 7.5 wt%  | SAC isolated/ neighboring/ patch 10.8/ 65.5/23.7 | –          | Methanol    | 210        | 3.2 MPa H₂/CO₂ = 3/1, 30 mL DMF catalyst 5.33 mg, 3 h | Yield = 0.4/5.7 mmol TOF = ≈1000⁹ h⁻¹ | –         |
| Fe          | 9.34 wt% | SAC >96%   | 17.2%      | CO 99.9%    | 300        | 0.1 MPa H₂/CO₂ = 3 GHSV = 9 L·g⁻¹·h⁻¹ | 12.5 μmol·m⁻¹·s⁻¹ (intrinsic activity) | Hydrothermal reduction | [105]     |
| LDH         | 0.36%   | SAC        | /          | Formate     | 100        | 2 MPa H₂/CO₂ = 1, 1 M NaHCO₃ 24 h | TOF ≈19 h⁻¹ | Impregnation | [106]    |

*Approximate data obtained from chart.*
the time-consuming DFT, the high-throughput machine learning could assist in prediction and screening the SACs, which will hugely reduce the cost to screen a suitable catalyst. The in-depth understanding of structure–performance relationship will promote rational design new types of SACs.

CO$_2$ hydrogenation to value-added liquid products and other lucrative CO$_2$ activation over SACs are still far away from the satisfaction of industry. Despite this progress, we still believe that the emerging efforts on different directions of SAC fields will finally solve the problems of industrialization and help us understanding the structure–performance relationship originated from the active sites of small isolated atoms.

Acknowledgements

This work was supported by the National Key R&D Program of China (grant no. 2018YFA0702003), the National Natural Science Foundation of China (grant nos. 21890383, 21871159, and 22002185) and Science and Technology Key Project of Guangdong Province of China (2020B010188002), and the China Postdoctoral Science Foundation (grant no. 2021TQ0172). Q.W. acknowledges financial support from the Shuimu Tsinghua Scholar Program.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

CO$_2$ activation, CO$_2$ reduction, single-atom site catalyses, thermocatalyses

Received: March 29, 2022
Revised: April 28, 2022
Published online: June 15, 2022

[1] Global Carbon Project, Supplemental Data of Global Carbon Budget 2021 (Version 1.0), https://doi.org/10.18160/gcp-2021, (accessed: March, 2022).
[2] J. M. Thomas, K. D. M. Harris, Energy Environ. Sci. 2016, 9, 687.
[3] J. Xu, L. Li, J. Pan, W. Cui, X. Liang, Y. Yu, B. Liu, X. Wang, S. Song, H. Zhang, Adv. Sustain. Syst. 2022, 6, 2100439.
[4] B. Yu, L. Li, S. Liu, H. Wang, H. Liu, C. Lin, C. Liu, H. Wu, W. Zhou, X. Li, T. Wang, B. Chen, J. Jiang, Angew. Chem. Int. Ed. 2021, 60, 8983.
[5] X. Sun, Y. Tuo, C. Ye, C. Chen, Q. Lu, G. Li, P. Jiang, S. Chen, P. Zhu, Z. Ma, J. Zhang, J. H. Bitter, D. Wang, Y. Li, Angew. Chem. Int. Ed. 2022, 60, 23614.
[6] S. Chen, B. Wang, J. Zhu, L. Wang, H. Ou, Z. Zhang, X. Liang, L. Zheng, L. Zhou, Y.-Q. Su, D. Wang, Y. Li, Nano Lett. 2021, 7325.
[7] T. Cao, R. Lin, S. Liu, W.-C. Cheong, Z. Li, K. Wu, Y. Zhu, X. Wang, J. Zhang, Q. Li, X. Liang, N. Fu, C. Chen, D. Wang, Q. Peng, Y. Li, Nano Res. 2022, 15, 3959.
[8] N. von der Assen, J. Jung, A. Bardow, Energy Environ. Sci. 2013, 6, 2721.
[9] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Nat. Chem. 2011, 3, 634.
[10] X. Zheng, P. Li, S. Dou, W. Sun, H. Pan, D. Wang, Y. Li, Energy Environ. Sci. 2021, 14, 2809.
[11] Z. Zhuang, Q. Kang, D. Wang, Y. Li, Nano Res. 2020, 13, 1856.
Qishun Wang received his Ph.D. degree from the Changchun Institute of Applied Chemistry, in 2020, under the supervision of Prof. Hongjie Zhang. Currently, he is a postdoctoral in Prof. Yadong Li’s group in the Department of Chemistry, Tsinghua University. His current research interests are focused on the nanosynthesis and heterogeneous catalysis, especially the rational design of advanced single-atom site catalysts for thermocatalysis.

Dingsheng Wang received his B.S. degree from the Department of Chemistry and Physics, University of Science and Technology of China, in 2004, and his Ph.D. degree from the Department of Chemistry, Tsinghua University, in 2009, under the supervision of Prof. Yadong Li. He did his postdoctoral research at the Department of Physics, Tsinghua University, with Prof. Shoushan Fan. He joined the faculty of the Department of Chemistry, Tsinghua University in 2012. His research interests focus on the synthesis, assembly, and catalytic applications of nanomaterials, clusters, and single-atom catalysts.