Tuning product selectivity in CO\textsubscript{2} hydrogenation over metal-based catalysts

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Conversion of CO\textsubscript{2} into chemicals is a promising strategy for CO\textsubscript{2} utilization, but its intricate transformation pathways and insufficient product selectivity still pose challenges. Exploiting new catalysts for tuning product selectivity in CO\textsubscript{2} hydrogenation is important to improve the viability of this technology, where reverse water-gas shift (RWGS) and methanation as competitive reactions play key roles in controlling product selectivity in CO\textsubscript{2} hydrogenation. So far, a series of metal-based catalysts with adjustable strong metal–support interactions, metal surface structure, and local environment of active sites have been developed, significantly tuning the product selectivity in CO\textsubscript{2} hydrogenation. Herein, we describe the recent advances in the fundamental understanding of the two reactions in CO\textsubscript{2} hydrogenation, in terms of emerging new catalysts which regulate the catalytic structure and switch reaction pathways, where the strong metal–support interactions, metal surface structure, and local environment of the active sites are particularly discussed. They are expected to enable efficient catalyst design for minimizing the deep hydrogenation and controlling the reaction towards the RWGS reaction. Finally, the potential utilization of these strategies for improving the performance of industrial catalysts is examined.

1. Introduction

Carbon dioxide (CO\textsubscript{2}), a major greenhouse gas, has been paid much attention recently due to the consumption of massive amounts of fossil fuel and increase of atmospheric CO\textsubscript{2} level, and a solution for this challenge is to suppress CO\textsubscript{2} emission.\textsuperscript{1} To this end, transformation of CO\textsubscript{2} into chemicals is extremely promising, which not only benefits the CO\textsubscript{2} elimination but also provides carbon resources for industrial processes.\textsuperscript{2–4} In these transformations, CO\textsubscript{2} hydrogenation over metal-based catalysts is a critical route, but the intricate transformation network and multiple active sites strongly influence the product selectivity.\textsuperscript{5–11} In recent years, various chemicals have been achieved via CO\textsubscript{2} hydrogenation, including CO,\textsuperscript{12–22} methane,\textsuperscript{23–27} methanol,\textsuperscript{28–37} olefins,\textsuperscript{38–41} gasolines,\textsuperscript{42–46} aromatics,\textsuperscript{47–51} and alcohols.\textsuperscript{52–58}

Among these products, CO formed by reverse water-gas shift (RWGS) and CH\textsubscript{4} formed by CO\textsubscript{2} methanation are the most fundamental products, which are usually chosen as model products for evaluating the performance of the catalysts, and the control of the ratio of these two products is a primary concern. To achieve this, the tuning of the catalytic sites and/or structure can be crucial. This perspective will focus on the recent advances in the fundamental understanding of the RWGS and methanation reactions in terms of emerging new catalysts which regulate the catalytic structure and switch reaction pathways, where the strong metal–support interactions, metal surface structure, and local environment of the active sites are particularly discussed.
products for investigations due to their strong competitiveness. From the viewpoint of chemical transformation, CO is preferred because of its potential for further applications, such as Fischer–Tropsch synthesis for hydrocarbons and oxygenates which possess higher economic value. In contrast, methane is relatively undesirable because of the limited applications and transformation routes. On the other hand, CO is a primary product and/or intermediate, which could be further transformed into other products. In contrast, methane is the completely hydrogenated product, which is basically stable in CO2 hydrogenation. Therefore, studying the selectivity control between CO and methane could provide deep understanding of reaction mechanisms of CO2 hydrogenation, which should be helpful for designing highly efficient catalysts. This understanding even helps to improve the catalysis in methanol and C2, product synthesis from CO2 hydrogenation.

As shown in Fig. 1, the RWGS is thermodynamically favorable at high temperature because of its endothermic nature, while CO2 methanation is thermodynamically favorable at relatively low temperature. However, the eight-electron transfer process of CO2 to CH4 is hindered by the high kinetic barrier. To overcome the kinetic limitation, a large number of catalysts have been employed for efficient CO2 hydrogenation. The CO2 hydrogenation proceeds via primary hydrogenation to *CO, and deep hydrogenation of *CO to methane. Based on this knowledge, the adsorption strength of *CO on the catalyst surface is regarded as a crucial factor (Fig. 2a). For example, Cu catalysts prefer to catalyze the RWGS reaction, while Co and Ni catalysts are favorable for CO2 methanation. These results are attributed to the fact that Co and Ni exhibit stronger adsorption for the *CO intermediate than Cu, thus leading to efficient C–O bond cleavage to form methane. The surface electronic states of the supported metal nanoparticles could optimize the *CO adsorption, which could be significantly controlled by strong metal–support interactions (SMSI) on reducible oxide supports. With the discovery of SMSI on non-oxides, the strategy of *CO-adsorption control for tuning product selectivity in CO2 hydrogenation is expanded to phosphates. Based on the transformation routes of *CO to CH4, as far as inhibiting C–O dissociation and deep hydrogenation of *CO species is concerned, new catalysts including bimetallic alloys and carbides are exploited (Fig. 2b). In addition, during SMSI construction, O vacancies easily form on the reducible oxide supports and play a crucial role in a series of charge transfer processes. The O vacancies could result in positively charged metal nanoparticles, which reduces the back-donation of d-electrons to the antibonding orbital of CO, and the interaction between metal and *CO species is weakened.

Based on this understanding, the advantages of alloy and carbide catalysts are maximized, because alloy catalysts have adjustable electronic structures for optimizing reaction intermediate adsorption, and carbide catalysts can provide a functional catalytic surface for new reaction routes (Fig. 2c). These unique structures and surface properties show more opportunities for selective CO2 hydrogenation. In addition to *CO-adsorption, *H spillover on the catalytic surface is equally remarkable. Under the precondition of moderate H2 dissociation, inhibiting *H spillover efficiently avoids deep hydrogenation of *CO, which might provide new insights for selectivity control in CO2 hydrogenation.

With regard to the rapid growth of investigations in selective CO2 hydrogenation, and the requirements for in-depth understanding of reaction mechanisms, we believe that it is time to summarize recent achievements in tuning product selectivity in CO2 hydrogenation. Previous reviews have focused on applications of the catalysts and the reaction mechanisms from CO2 to specific products, but strategies for selectivity control and principles for catalyst design are rarely discussed. In this perspective, the structural features of oxide, phosphate, metal alloy, and carbide-based catalysts are briefly summarized.

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Furthermore, the principles for controlling the product selectivity are proposed.

2. Oxide-supported metal nanoparticle catalysts

2.1 Crystal phase of oxides

A typical phenomenon is observed on titania-supported cobalt catalysts, where Co/r-TiO₂ (rutile) selectively catalyzes CO₂ methanation, but CO is predominant on the Co/a-TiO₂ (anatase) catalyst. Calculation at 800 °C results in a partial transition from anatase to rutile, enhancing the adsorption of the *CO intermediate that leads to deep hydrogenation to CH₄. Similarly, CO selectivity in In₂O₃ catalyzed CO₂ hydrogenation can be improved by crystal phase transition from hexagonal In₂O₃ (h-In₂O₃) to cubic In₂O₃ (c-In₂O₃). The h-In₂O₃ is reduced by H₂ and oxidized by CO₂ to form c-In₂O₃. The rearrangement of surface O species makes it more active for H₂ dissociation to form O vacancies. CO₂ adsorbs on the O vacancies and heals the vacancies by desorbing CO, resulting in higher RWGS activity.

2.2 SMSI on oxides

SMSI was firstly reported by Tauster and Fung in the 1970s to study the suppressed CO and H₂ adsorption on the supported metals. TiO₂- and CeO₂-supported Rh, Ru and Ir catalysts with high loadings can selectively catalyze CO₂ methanation. With lower metal loadings to reduce the nanoparticle size, these catalysts yield CO as the predominant product. These results are reasonably attributed to the chemical features of the small nanoparticles. Li et al. reported the SMSI on an Ir/CeO₂ catalyst, where the partially oxidized Ir nanoparticles exhibit relatively weak CO adsorption, resulting in rapid CO desorption rather than hydrogenation to CH₄. Similarly, the atomically dispersed RuOₓ species, which might be generated during the oxidative treatment, could maintain the oxidized state even under the reaction conditions with a reductive atmosphere, because of the strong bonding with the CeO₂ support.

DFT calculations provide mechanistic understanding of the SMSI-controlled product selectivity. Fig. 3e shows the difference between CO dissociation barriers and CO desorption free energies of single-atom Ir (Ir₁) and stepped Ir (Ir₃). The stepped Ir shows a much lower value than that of the single atom Ir, suggesting preferentially occurring CO desorption on the single-atom Ir, which could explain the highly selective RWGS reaction. In addition, the difference between C–O dissociation to *CH and dehydrogenation of *CHO to *CO on the single-atom Ir is greatly increased compared to that of the stepped
classical SMSI overlayer on the TiO2 support by H2 treatment, spillover is important for the reaction. The H atoms from H2, as mentioned in the aforementioned discussion, it is found that the hydrogen atoms competitively catalyze RWGS and methanation, respectively. In addition, a mixture of Ti species (Ti4+/Ti3+ at 7/3), different from the general Rh catalyst in CO2 methanation. The Rh nanoparticles with small size at 1.1 nm are uniformly dispersed on the NbOPO4 support, exhibiting CO as the main products of the Rh/NbOPO4 catalyst with phosphate-based SMSI for CO oxidation.

| Catalyst            | H2 : CO2 ratio | Temperature (°C) | Pressure (MPa) | CO2 conversion (%) | Selectivity (%) | Rate (mmol gcat⁻¹ h⁻¹) |
|---------------------|----------------|------------------|----------------|-------------------|----------------|------------------------|
| Rh/TiO2 (ref. 13)   | 1 : 1          | 200              | 0.1            | 0.4               | 92.3           | 0.48 0.04              |
| Ir/CoO (ref. 14)    | 4 : 1          | 300              | 1.0            | 6.8               | 100            | 6.9 0                  |
| Ru/CoO (ref. 15)    | 4 : 1          | 240              | 0.1            | <5                | 92.1           | 7.9 1.8                |
| PtCo/TiO2 (ref. 16) | 2 : 1          | 300              | 0.1            | 8.2               | 98.8           | 1.2 43.4               |
| PtCo/CoO (ref. 16)  | 2 : 1          | 300              | 0.1            | 9.1               | 92.3           | 7.7 40.5               |
| PtCo/ZrO2 (ref. 16) | 2 : 1          | 300              | 0.1            | 7.8               | 92.5           | 10.5 39.3              |
| Co3O4 (ref. 17)     | 3 : 1          | 350              | 0.1            | 10.0              | 95.0           | 5.0 38.1               |
| Mo2C18              | 2 : 1          | 300              | 0.1            | 8.7               | 93.5           | 6.5 43.6               |
| Co/Mo2C18           | 2 : 1          | 300              | 0.1            | 9.5               | 98.1           | 1.9 49.9               |
| Rh/S-1 (ref. 19)    | 3 : 1          | 500              | 1.0            | 51.6              | 79.8           | 20.2 13.2              |
| NiIn-Cu10           | 3 : 1          | 550              | 0.1            | 50.7              | 100            | 0.3 181.1              |
| Ni–Au21             | 3 : 1          | 600              | 0.1            | 18.0              | 95.0           | 5.0 109.9               |
| Rh/NbOPO4 (ref. 22) | 3 : 1          | 500              | 2.0            | 39.9              | 98.9           | 1.1 58.1               |
| Co/r-TiO2 (ref. 69) | 4 : 1          | 400              | 3.0            | 85.0              | 1.0            | 99.0 0.5               |
| Co/a-TiO2 (ref. 69) | 4 : 1          | 400              | 3.0            | 15.0              | 90.0           | 10.0 8.7               |
| Ru/r-TiO2 (ref. 85) | 4 : 1          | 400              | 0.1            | 57.0              | 3.0            | 97.0 0.05              |
| Ru/a-TiO2 (ref. 85) | 4 : 1          | 400              | 0.1            | 23.0              | 100            | 0.0 0.66               |
| Ni2Fe2ZrO2 (ref. 101)| 2 : 1         | 400              | 0.1           | 18.6              | 95.8           | 3.7 22.1               |
| Cu/b-Mo2C109        | 2 : 1          | 600              | 0.1            | 40.0              | 99.2           | 0.8 1771.4             |
| InNi3Co0.5 (ref. 111)| 3 : 1         | 500              | 0.1            | 53.0              | 97.0           | 3.0 117.6              |
| Ni/SiO2 (ref. 112)  | 4 : 1          | 750              | 0.1            | 58.0              | 100            | 0.0 2071.4             |

Ir. C–O bond cleavage of the main intermediates (*HCOO, *COOH, and M–CO) strongly determines the CO2 hydrogenation selectivity.

In addition, *H spillover also plays a significant role in this reaction. For example, Ru/a-TiO2 and Ru/r-TiO2 could selectively catalyze RWGS and methanation, respectively. In addition, to the influence of the crystalline phase on *CO adsorption in the aforementioned discussion, it is found that the hydrogen spillover is important for the reaction. The H atoms from H2 dissociation at metallic sites could spill to the TiO2 surface and form Ti–O(H)–Ti species, leading to electron donation into shallow trap states in the band gap of TiO2.90,91 Identified by the band at 1740 cm⁻¹ in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), *H spillover is more likely to occur on the Ru/a-TiO2 compared with Ru/r-TiO2. That leads to charge transfer from Ru to a-TiO2, reducing the π backdonation from Ru to adsorbed *CO, which results in quick desorption of *CO and hinders deep hydrogenation to methane.

Besides the classical SMSI, a new type of SMSI was developed by Matsubu et al.,11 which is realized by pretreating the Rh/TiO2 catalyst in mixed gases of CO2 and H2 with a ratio of 10 : 1 to form carbonate-containing species in the overlayer (Fig. 3f and g). It is denoted as adsorbate-induced SMSI (A-SMSI). The amorphous overlayer on the Rh nanoparticles contains a mixture of Ti species (Ti4+/Ti3+ at 7/3), different from the classical SMSI overlayer on the TiO2 support by H2 treatment, where the Ti species are dominantly in the Ti3⁺ state.92–93 It is proposed that the adsorbed HCOOH species might coordinate with TiO2 in the overlayer, and change the surface properties of the Rh nanoparticles. The redshift and decreased intensity of the linear CO in DRIFTS indicate the weakened CO adsorption, because of the physically blocked Rh nanoparticles and the polarization of CO bonds induced by charge transfer to Rh. In the CO2 hydrogenation, the Rh/TiO2 catalyst with A-SMSI shows 90% selectivity for CO formation, which is different from the general Rh catalysts with dominant CO2 methanation (Fig. 3h and i).

As observed in these examples, the adjustments of crystal phases of oxides and construction of SMSI on supported catalysts are efficient routes for hindering the CO2 deep hydrogenation. The features of SMSI, including weakening *CO adsorption, inhibiting C–O dissociation and deep hydrogenation, and optimizing *H spillover, are emphasized.

These examples for SMSI show great success on the selectivity control in CO2 hydrogenation over oxide-supported catalysts. However, the formation of the SMSI still relies on the reducible oxides. In addition, high CO selectivity is always obtained at low conversion of CO2 (<5%). Also, the classical SMSI could be destroyed by re-oxidation from water or oxygen at high temperature.12–15 To overcome this limitation, exploiting new supports or catalysts for this reaction is always important.

3. Phosphate-based catalysts

SMSI has been reported on phosphates such as hydroxyapatite (HAP) and LaPO4 for CO oxidation.94–96 It also plays a role in tuning the selectivity of CO2 hydrogenation. Wang et al.22 reported a Rh/NbOPO4 catalyst with phosphate-based SMSI for highly active and selective RWGS reaction, which is quite different from the general Rh catalyst in CO2 methanation. The Rh nanoparticles with small size at 1.1 nm are uniformly dispersed on the NbOPO4 support, exhibiting CO as...
a predominant product in CO₂ hydrogenation in a wide temperature range of 200–500 °C (Fig. 4a). The catalyst with Rh loading at 0.7% gives CO₂ conversion of 39.9% with CO selectivity of 98.9%. Such performance remarkably outperforms the Rh nanoparticles on CeO₂, TiO₂, and Nb₂O₅ supports with SMSI. The SMSI between Rh and a NbOPO₄ support is explored by H₂-TPR and CO-TPD tests, where the reduction temperatures of Rh⁺/Rh⁰ are increased and the desorption temperatures of CO are decreased, compared with the generally supported Rh catalysts. In addition, the Rh/NbOPO₄ sample gives the lowest Rh⁺/Rh⁰ ratio among these catalysts identified by XPS, due to the electronic interactions on the Rh–NbOPO₄ interface to stabilize the positively charged Rh.⁸² The Rh/NbOPO₄ catalyst also exhibits decreased CO adsorption, where only the weak stretches of gem-dicarbonyl Rh(CO)₂ species¹²,¹³,⁹⁷,⁹⁸ are observed in CO-adsorption DRIFTS (Fig. 4b). In the CO₂ hydrogenation process, the specific interaction between Rh and NbOPO₄ supports the SMSI to inhibit CO hydrogenation, thus enhancing CO selectivity.

Fig. 3  (a–c) HAADF-STEM images of catalysts: (a) 5 Ir/Ce used, (b) 15 Ir/Ce used, and (c) 20 Ir/Ce used. (d) The coordination number of Ir—Ir and Ir—O shells (data, right axis) relative to catalytic selectivity (bars, left axis) of Ir/Ce catalysts with different Ir loadings. Reproduced with permission from ref. 14. Copyright (2017) Wiley-VCH. (e) HAADF-STEM images of catalysts: (a) 5 Ir/Ce used, (b) 15 Ir/Ce used, and (c) 20 Ir/Ce used. (d) The coordination number of Ir—Ir and Ir—O shells (data, right axis) relative to catalytic selectivity (bars, left axis) of Ir/Ce catalysts with different Ir loadings. Reproduced with permission from ref. 14. Copyright (2017) Wiley-VCH. (f) In situ STEM images of (f) an SMSI overlayer, a TiO₂ crystalline bilayer containing exclusively Ti³⁺, and (g) an A-SMSI overlayer, an amorphous TiO₂ overlayer containing a mixture of Ti³⁺ and Ti⁴⁺, on the surface of Rh nanoparticles. (h) CH₄ and (i) CO generation rates on 2% Rh with various supports after reduction or 20CO₂ : 2H₂ treatment. Reproduced with permission from ref. 13. Copyright (2017) Springer Nature.

Fig. 4  (a) Dependence of CO selectivity on CO₂ conversion over various catalysts at 200–500 °C. (b) DRIFTS peak intensities characterizing the different CO species adsorbed on various catalysts. (c) Correlation of DRIFTS peak intensity and selectivity in CO₂ hydrogenation over various catalysts. Reproduced with permission from ref. 22. Copyright (2020) Wiley-VCH.
hydrogenation (Fig. 4c), in situ DRIFTS shows that the *CH₄ species, a crucial intermediate for CH₄ formation, can be observed on the other catalysts, but is undetectable on the Rh/NbOPO₄ catalyst, in agreement with the highly selective RWGS.

Therefore, the high CO selectivity for the Rh/NbOPO₄ catalyst in CO₂ hydrogenation could be explained by the decreased *CO adsorption, resulting from the SMSI between Rh and NbOPO₄, which is similar to the phenomena on the general oxide-supported catalysts with SMSI. Although it is observed that phosphate-based SMSI tunes the Rh catalyst from CO₂ methanation to RWGS, the influence on CO₂ hydrogenation still needs further *operando characterization and theoretical investigations. This observation still provides a new type of catalyst for CO₂ hydrogenation with optimized selectivity.

4. Alloy-based catalysts

Inspired by the catalysts with SMSI for weak adsorption of the *CO intermediate to selectively obtain the CO product in CO₂ hydrogenation, it is reasonable that construction of alloyed metal catalysts with variable adsorption of the *CO intermediate could be adjusted by the alloyed compositions and supports. Recently, alloys of PtCo, NiFe, CuNi and PtCo/ZrO₂ have been reported for tuning product selectivity in CO₂ hydrogenation.

Kettel et al. reported CO₂ hydrogenation over PtCo bimetallic catalysts supported on oxides of CeO₂, ZrO₂, and TiO₂, which all give RWGS as a dominant reaction. Particularly, PtCo/TiO₂ gives a much higher CO/CH₄ ratio than those of PtCo/CeO₂ and PtCo/ZrO₂. On the PtCo/TiO₂ catalyst, the energy barrier of *CO desorption is much lower than that for hydrogenation to *CHO, leading to the generation of gas phase CO (Fig. 5a and b). In contrast, energy for *CO hydrogenation is comparable with that of *CO desorption on the PtCo/ZrO₂ catalyst, resulting in the formation of CH₄ or CH₄OH as competitive reactions, evidenced by DRIFTS and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).

These PtCo catalysts provide an example for tuning the product selectivity in CO₂ hydrogenation, which combines the advantages of alloys and oxide supports. Investigations on ZrO₂-supported NiFe catalysts reveal the structure–performance relationship of catalyst interfaces. Ni₃/ZrO₂ is highly active for CO₂ methanation (CO₂ conversion of 34.2% and CH₄ selectivity of 84.7%), while Fe₁/ZrO₂ shows low activity, but is highly selective for CO production (CO₂ conversion of 31% and CO selectivity of 100%). Interestingly, upon introducing Ni to an Fe-based catalyst, the activity is markedly increased, and the CO selectivity can be tuned from 11.5% to 91.8% by adjusting the Ni/Fe ratios. Generally, the Ni–ZrO₂ interface is regarded as the active site for CO₂ methanation. However, when a large amount of Fe species is introduced, the dispersed Fe species would cover the Ni particles to form Ni–FeO₄ interfaces, which changes the product selectivity in the CO₂ hydrogenation. Therefore, CO₂ methanation occurs on the Ni/ZrO₂ catalyst via the RWGS + CO hydrogenation pathway, but fails on the NiFe/ZrO₂ catalyst which gives CO as the predominant product.

Because of the structural nonuniformity of the catalysts, it is still difficult to investigate the relationship between the catalyst structure and catalytic performance. Moreover, addition of promoters/additives might result in the formation of new active sites and interfaces for CO₂ adsorption and transformation. Wang et al. reported a CuNi alloy-based catalyst (Ni-in-Cu), showing highly dispersed Ni incorporated into the Cu lattice, which combines the advantages of high activity of Ni and high selectivity of Cu. The Ni-in-Cu catalyst gives a CO₂ conversion of 1.1–50.7%, and the CO selectivity always remains at 100%. The superior CO selectivity is obtained even under conditions with H₂/CO₂ ratios in a wide range of 1–9 (Fig. 5c). In comparison, the general Cu (ref-Cu) and Ni (ref-Ni) catalysts show much lower CO₂ conversion and CO selectivity than those of the Ni-in-Cu catalyst. In these cases, the atomic dispersion of Ni in the Cu lattice is crucial for such performance, and the ref-CuNi catalyst with the same composition but partially separated Cu and Ni phases yields the methane product under equivalent reaction conditions.

More importantly, the simple and uniform structure of the Ni-in-Cu catalyst provides a model for mechanistic investigation to identify the reaction routes and active sites. By in situ DRIFTS and XPS studies, the CO₃²⁻, CO₂⁺ and HCO₃⁻ species are observed on the catalyst surface, giving decreased signals during the CO₂ hydrogenation, which indicate their important roles as the intermediates for CO formation. In contrast, *HCOO is formed and remains unchanged during this process, which is attributed to the fact that this species is stable and difficult to be hydrogenated. Combining various characterization techniques, it has been found that the CO₂ molecules simultaneously interact with Cu and Ni sites on the surface of the CuNi alloy. When CO is formed from the C=O cleavage of CO₂, it rapidly desorbs from the catalyst surface to avoid deep hydrogenation (Fig. 5d). DFT calculations reveal the easy C=O cleavage of CO₂ to form CO on the CuNi(111) surface. Because CO can easily desorb from the catalytic surface, it is difficult to form *HCO by hydrogenation (Fig. 5e), which is due to the fact that H atoms preferentially remove the isolated O atoms on the CuNi(111) surface via an exothermic process with energy barriers of ~0.31–0.75 eV. In contrast, *CO hydrogenation to *HCO is an endothermic step with energy barriers of 1.40/0.78 eV. These results demonstrate the multifunctionality of CuNi alloy sites on the Ni-in-Cu catalyst, which embodies the efficient CO₂ activation and H₂ dissociation, and accelerates the CO desorption, benefiting the RWGS reaction but switching off the methanation.

Zhang et al. reported a Ni–Au bimetallic catalyst with a core–shell structure, where the Au shell is always in contact with the Ni core. The core–shell structure kinetically transforms to a NiAu alloy during the CO₂ hydrogenation, and reverses after the reaction. In this process, CO is a dominant product with selectivity higher than 95%. In the environmental transmission electron microscopy (ETEM) characterization (Fig. 6a) at near-ambient pressure (9 ± 0.1 mbar, 25% CO₂/75% H₂), the ultra-thin Au shell is observed around the Ni@Au nanoparticles at 400–500 °C, and disappears to form a NiAu alloy at 600 °C. The segregation energy (Eseg) of the Ni atom from the bulk to the
The surface Au layer was calculated. The $E_{\text{seg}}$ can be reduced by the adsorbed species, such as $\text{H}_2$, $\text{H}^*$, $\text{OH}^*$ and $\text{CO}^*$, on the Au surface (Fig. 6b). Particularly, the minimized $E_{\text{seg}}$ is obtained under CO adsorption, which helps Ni transfer to the Au layer to form a NiAu alloy. These results are also in agreement with the fact that the NiAu alloy is detected during the CO$_2$ hydrogenation, but disappears after the reaction. Moreover, the CO$_2$ hydrogenation on the NiAu alloy undergoes a two-step pathway. In the first step, CO$_2$ hydrogenation to CO occurs on Ni sites with an energy barrier of 0.89 eV. In the second step, CO prefers to diffuse from Ni to Au sites and desorbs, with energy barriers of 1.23 and 0.45 eV, respectively. In contrast, both dissociation and deep hydrogenation of CO need to overcome higher energy barriers. Therefore, CO could benefit the formation of the NiAu alloy, which is evidenced by NiAu alloy formation after quenching in CO rather than $\text{H}_2$ or $\text{N}_2$ (Fig. 6c).

The metal alloy based-catalysts play a role in decreasing the energy barriers of the $^*$CO desorption, to a level below $^*$CO dissociation or deep hydrogenation. Compared to the SMSI that also has similar functions in weakening CO adsorption, the alloyed interfaces exhibit more adjustable properties, because of their precisely controllable metal compositions and electronic structures. These observations on the alloy based-catalysts convincingly demonstrate that an appropriate binding strength of intermediates, throughout the CO$_2$ hydrogenation, is a key to controlling product selectivity.

5. Carbide-based catalysts

Transition metal carbides (TMCs) are well known to have excellent catalytic properties, which are similar to those of noble metal catalysts. The high activity of carbides originates from the carbon, and results in modulating the electronic properties, and tuning the binding energies of reaction intermediates. Metal carbides have been extensively used in reforming and WGS reactions. Also, they are promising for CO$_2$ hydrogenation because of the dual functions of $\text{H}_2$ dissociation and C=O bond scission.

Porosoff et al. reported CO$_2$ hydrogenation on defined Mo$_2$C surfaces, which are highly active and selective for CO production. The Mo$_2$C catalyst shows a CO$_2$ conversion of 8.7% and CO/CH$_4$ ratio of 14.5 for CO$_2$ hydrogenation at 300 °C, outperforming noble metal bimetallic catalysts. The catalytic performance can be further improved by modification with Co, a well-known catalyst for methanation or Fischer–Tropsch synthesis to produce alkanes. CO$_2$ conversion and CO selectivity of 9.5% and 51.3% (CO/CH$_4$ product ratio of 51.3) were obtained on the Co–Mo$_2$C catalyst. By employing temperature-programmed surface reaction (TPSR), the Mo$_2$C surface is proved to be the active phase. In AP-XPS experiments (Fig. 7), when CO$_2$ gas is introduced into the Mo$_2$C catalyst, a signal assigned to O–Mo–C at 283.6 eV appears, rather than CO$_2$ and HOO$^*$ species, suggesting a different pathway for CO$_2$ activation on the Mo$_2$C. It is proposed that CO$_2$ directly reacts with Mo$_2$C through the lone-pair electrons on the O atom to produce CO and an oxycarbide surface (Mo$_2$C–O), which is
subsequently reduced by H2 to regain the Mo2C surface. Notably, the unreduced MoOx species always exists in the Mo2C catalyst, with a ratio of 16.8% identified by in situ X-ray absorption near edge spectroscopy (XANES). Introducing Co into the Mo2C catalyst leads to the formation of a new CoMoCo phase during the reduction process. The CoMoCo phase is highly active for CH4 dissociation,114 which further increases the CO selectivity, in agreement with the much higher CO/CH4 ratio obtained on the Co–Mo2C catalyst. Because of the excellent properties, Mo2C was further coupled with other metals, such as Cu, a classical catalyst for CO2 hydrogenation. Zhang et al.109 reported a Cu/b-Mo2C catalyst, which shows extraordinary RWGS activity, selectivity, and stability. The Cu/b-Mo2C exhibits acceptable deactivation after six-cycle start-up–cool-down tests, and maintains 85% of its initial activity after 40 h reaction at a high reaction temperature of 600 °C. Cu+ species are detected on the Cu/b-Mo2C catalyst, suggesting a strong interaction between Cu and Mo2C, resulting in electron transfer from Cu to Mo2C. Such interaction helps in Cu nanoparticle stabilization, modulates the electronic structure for efficient CO2 activation and hinders Cu sintering. In the CO2 dissociation experiments without H2, the Cu/b-Mo2C catalyst exhibits much higher CO production than that of b-Mo2C.
and Cu/ZnO/Al₂O₃. These results support the mechanism of the RWGS reaction on Mo₂C catalysts involving two steps, CO₂ dissociation on the catalytic surface and H₂ reduction of the residual O species.¹⁸,¹¹⁵

Moreover, Zhang et al.¹¹⁰ coupled the high activity of Mo₂C and the non-thermal plasma (NTP) technique to produce CO. The TOF activity of β-Mo₂C nanorods in NTP-catalysis (applying NTP and the catalyst, without heating) is two orders of magnitude higher than that obtained under catalysis-only conditions (applying the catalyst and heating) (Fig. 8a and b), for example, 26.0 s⁻¹ and 0.55 s⁻¹ for NTP catalysis and thermal catalysis-only conditions, respectively. In the designed reaction between CO₂ and the catalyst surface, CO was detected immediately upon introducing a CO₂/Ar flow. It is suggested that the CO originates from direct CO₂ dissociation, which facilitates the high CO selectivity, in agreement with reports on carbide-based catalysts. In the NTP-catalysis, CO₂ and H₂ can be vibrationally excited and dissociated by plasma. In the first-step CO₂ dissociation test (Fig. 8c–e), β-Mo₂C nanorods under NTP-only conditions (applying NTP, without catalyst and heating) show a 20 times higher CO signal than that under catalysis-only conditions, indicating that NTP can promote CO₂ dissociation. In the meanwhile, an abundant O₂ signal is detected, which originates from the three-body (M) recombination of dissociative O atoms from split CO₂. NTP-catalysis also exhibits a stronger CO signal, in agreement with the high activity and weaker O₂ signal due to the O affinity of carbides.¹¹⁶ Overall, the NTP-catalysis exhibits a synergistic enhancement for the RWGS reaction. The NTP induces vibration, excitation and dissociation of reactants, which subsequently interact with β-Mo₂C. In this process, β-Mo₂C exists as a platform for various intermediates to accelerate the reaction. The highly porous structure of β-Mo₂C nanorods provides a large accessible surface, modifies the electron energy distribution, and expands the discharge region, which not only promote the formation of charge-induced intermediates, but also change the adsorption and desorption.¹¹⁷

Fig. 8  (a) CO₂ conversion under catalysis-only (at 350 °C), NTP-only, and NTP catalysis conditions (input power of ca. 36 W) over β-Mo₂C NP and β-Mo₂C nanorod catalysts (AP, CO₂ : H₂ = 1 : 2, WHSV = 1 500 000 mL g⁻¹ h⁻¹). (b) TOF comparison over β-Mo₂C NP and β-Mo₂C nanorod catalysts under catalysis-only (at 350 °C) and NTP-catalysis conditions (input power of ca. 36 W). (c–e) Surface reaction experiment with injection of 1% CO₂/Ar under (c) catalysis-only, (d) NTP-only and (e) NTP-catalysis conditions. Reproduced with permission from ref. 110. Copyright (2020) Elsevier.
surface interactions on the β-Mo2C lead to not only superior CO selectivity but also high productivity.

In addition to the Mo2C, other carbides such as Ni3C and InNi3C0.5 were explored for CO2 hydrogenation.111,112 Although Ni is highly selective for methanation, both Ni3C and InNi3C0.5 with carbide structures exhibit superior RWGS features. Chen et al.111 reported that InNi3C0.5 supported on Al2O3/Al-fibers shows over 97% CO selectivity in CO2 hydrogenation under wide reaction conditions. For example, the CO2 conversion is 53% at 540 °C, which is close to the equilibrium value of 54%. The InNi3C0.5 has an anti-perovskite-type structure containing a stable (111) surface with a hexagonal shape. DFT calculations reveal the dual active sites of 3Ni–In (h1) and 3Ni–C (h2), which give a richer electron density distribution, facilitating activated *H formation and CO2 dissociation to CO via a redox mechanism. CO2 prefers to adsorb on the h1 site, and the dissociated *CO and *O are adsorbed on h2 and h1 sites, respectively. The dissociated *H species are adsorbed on both h1 and h2 sites. The *O on the h1 site could react with *H+ to form *OH, and two *OH easily convert to H2O. The dual sites always provide lower energy barriers than those of the sole h1 site, demonstrating the advantages of the dual sites on InNi3C0.5.

Carbide phases, such as Ni3C, easily form in Ni catalysts at high reaction temperature, because carbon is highly miscible on the Ni surface.118 Galhardo et al.112 reported that the Ni3C phase, which forms in CO2 hydrogenation, can switch the selectivity from CH4 to CO. The fresh Ni/SiO2 catalysts show suppressed methanation activity in CO2 hydrogenation with CO as a dominant product at a wide temperature range (100–800 °C, Fig. 9a). Catalysts with different Ni loadings, particle sizes, or supports show similar catalytic features of methanation in Run 1, and suppressed selectivity of CH4 in Run 2. Under operando conditions, energy-dispersive X-ray absorption spectroscopy (ED-XAS) and EXAFS (Fig. 9b and c) reveal that the Ni–C scattering belongs to the Ni3C structure, which contributes to the selectivity changes. The Ni/SiO2 catalyst exhibits much lower CO-adsorption intensity in DRIFTS after Run 1, suggesting the weak CO-binding ability of the formed Ni3C surface, which benefits CO desorption. It is further evidenced by DFT calculations that various CO-adsorption modes give higher adsorption energies on the Ni3C(001) surface, compared to those on the Ni(111) surface (Fig. 9d and e). These results help to explain the suppressed methanation: because CO2 adsorption always occurs on the oxide supports, and the activated *H species can spill to reduce CO2, the CO2-to-CO process is not affected by the C atoms covered on Ni. However, the subsequent CO-to-CH4 process is suppressed, due to the weakened CO adsorption on the Ni3C phase.

Carbide-based catalysts effectively control the transformation pathways of *CO species. When the *CO adsorption is weakened, the C–O bond cleavage and *CO deep hydrogenation are hindered. The CO formation on the carbides always...
follows the pathway of direct dissociation of CO₂ to CO via a redox mechanism, and because of the strong interaction between the carbide surface and oxygen, an oxycarbide surface could form and subsequently be reduced by H₂. Sometimes, the unique active phases of carbides even show new functions of catalyzing CH₄ dissociation, further benefiting the selective formation of CO.

6. Conclusions and perspectives

In conclusion, the developments for metal-based catalysts to tune product selectivity in CO₂ hydrogenation are briefly summarized. Oxide-supported metal catalysts with classical SMSI show an effective strategy for weakening *CO and H₂ adsorption to hinder deep hydrogenation. Phosphate-supported metal catalysts with similar phenomena to classical SMSI show even more excellent catalytic performances. Alloy- and carbide-based catalysts exhibit multifunctionality, contributing to reducing the CO desorption energy barrier to a level lower than CO dissociation or deep hydrogenation. Alloy-based catalysts also exhibit satisfactory controllability of the structure–performance relationship by easily adjusting the metal compositions. Carbide-based catalysts can strongly bond with the O atom of CO₂, facilitating direct CO₂ dissociation. Sometimes, the unique CH₄ dissociation ability further inhibits CH₄ formation and improves the CO selectivity.

Based on this knowledge, active sites for tuning the CO adsorption and transformation are rationally designed. However, the local environments of the active sites are sometimes overlooked. The activation and diffusion of H₂, which determine the hydrogenation of the carbon-containing intermediates, could be controlled to optimize the reaction. Wang et al.¹⁹ showed a representative example of tuning the selectivity of CO₂ hydrogenation via controlling H spillover around the metal nanoparticles. The Rh nanoparticles fixed within siliceous zeolite (Rh@S-1) enable high CO selectivity in CO₂ hydrogenation, which is beyond the general expectation of Rh-catalyzed CO₂ methanation (Fig. 10a–d). The referenced catalyst of Rh@HZSM-5 prefers to produce CH₄, while both Rh@KZSM-5 (introducing K⁺ by ion exchange) and Rh@S-1–OH (introducing silanol groups to the zeolite micropores) catalysts mainly give CH₄ at high CO₂ conversion. Because of the same content and size of Rh nanoparticles, these different catalytic performances are attributed to the nanoporous environment of zeolite sheaths. Experiments of a WO₃-probe, H–D exchange and D₂O treatment demonstrate that the stronger H spillover in the zeolite micropores with protons or silanol (Rh@HZSM-5 and Rh@S-1–OH) could provide active *H species for deep hydrogenation, but studies on Rh@S-1 catalysts with weak hydrogen spillover ability are scarce (Fig. 10e–g).¹¹⁹–¹²¹ In addition, the weakened CO adsorption on the S-1 zeolite fixed Rh nanoparticles also contributes to the hindered methanation in CO₂ hydrogenation.

It is also expected that investigations on the competitive processes of the RWGS reaction and CO₂ methanation will help to elucidate the reaction mechanism of CO₃ hydrogenation, and guide the preparation and optimization of industrial catalysts. Compared with the simple products of CO and CH₄, the synthesis of methanol and even C₂+ compounds with higher economic value is more desired. However, in practice, the inevitable CO or CH₄ formation in CO₂ hydrogenation will not only consumes hydrogen feed, but will also lead to insufficient

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Fig. 10 (a–d) (a) Catalytic performance of (a) Rh@HZSM-5, (b) Rh@S-1, (c) Rh@S-1–OH and (d) Rh@KZSM-5 in CO₂ hydrogenation. Reaction conditions: 0.5 g of catalyst; 1 MPa feed gas pressure, CO₂/H₂/Ar = 1/3/1, molar; feed flow rate 30 mL min⁻¹. (e) Photographs of samples made with 1 g of WO₃ mixed with 0.02 g of various catalysts after treatment with H₂ at 30 °C for 10 min. (f) Results of H–D exchange experiments with various catalysts. (g) CH₄ and CO selectivity in CO₂ hydrogenation catalyzed by Rh@HZSM-5 treated with D₂O and H₂O. Reproduced with permission from ref. 19. Copyright (2019) American Chemical Society.
yield of target products. As a successful example, Yang et al. reported ethanol synthesis from CO$_2$ hydrogenation over a Cu/Co$_3$O$_4$ catalyst at high pressure (1–30 bar). These achievements expand the applications of the model reactions (RWGS and CO$_2$ methanation) to CO$_2$-to-valuable chemical processes, offering good opportunities for industrial applications in the future, particularly in carbon neutralization for global environmental protection.

**Author contributions**

L. W. and F.-S. X. conceived the topic and structure of the article. All authors reviewed and contributed to this paper.

**Conflicts of interest**

There are no conflicts to declare.

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