1. Introduction

The CO₂ emissions of our modern society into the atmosphere has reached alarming levels, which have led to ocean acidification and climate change [1–3]. These catastrophic consequences have originated the idea to recycle the emitted CO₂ to prevent its accumulation in atmosphere. The recycled CO₂ should be used for the production of value-added bulk chemicals and fuels because the demand for these products is so high that it can use almost all CO₂ emitted from all power plants worldwide and significantly contribute to the solution of the CO₂ problem (Fig. 1a) [4]. However, regarding the established processes in the chemical industry, synthetic fuels and most chemicals are produced from CO and hydrogen (syngas). Processes that use CO₂ directly to form value-added fuels and chemicals as well as their corresponding production plants are missing. Moreover, syngas is currently formed mostly from coal gasification (Fig. 1b). Therefore, production of syngas from recycled CO₂ by means of green hydrogen would be a major step forward to close the carbon loop in the future. In addition to that, synthetic fuels excel by their purity and narrow specifications enabling high engine efficiencies and lower emissions compared to their oil-based counterparts. Some chemicals, such as formic acid, dimethyl ether, methyl formate, and methanol are produced by catalytic CO₂ hydrogenation already today and there have been great improvements in catalyst design for these processes [5–7]. However, CO is still an intermediate in many of these CO₂ hydrogenation processes, such as methanol and DME synthesis [8,9]. The conversion of CO₂ to the intermediate CO needs high temperatures and low pressures unlike the consecutive reaction to methanol and DME. Therefore, formation of CO is not thermodynamically favored at the reaction conditions required for methanol and DME synthesis, which results in low yields of these products in direct CO₂ hydrogenation. A single-step commercial process for the production of methanol/DME from CO₂ has not yet been developed. This behavior reflects the higher reactivity of CO compared to CO₂ and explains the use of CO in the form of syngas for many existing processes in chemical industry such as methanol, higher alcohols or Fischer-Tropsch fuels [10].

The missing link between CO₂ and CO in these processes is known as the reverse water-gas shift (RWGS) reaction (Eq. 1) that allows entering the carbon recycling economy without a fundamental change of the existing infrastructure in chemical industry.

\[
CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = +41.2 \text{kJ.mol}^{-1}
\]

Due to the endothermicity of this reaction, CO formation is favorable...
at high temperatures. This can be also noticed from the changes of the Gibbs free energy with temperature and the increase of the equilibrium constant at higher temperatures [13]. Therefore, relatively high temperatures are required for this reaction, as well as stable catalysts that exhibit high activity and selectivity. However, it is a challenge to design a catalyst, which meets all these criteria, simultaneously. Certain metals supported on metal oxides are known to be highly active and relatively stable in CO2 hydrogenation reaction producing either CO or CH4. In particular, Pd, Ru, Rh, Ni and Pt have shown high activity in CO2 conversion through methanation while others such as Cu, Au, Ag, and Mo are known to selectively produce CO or methanol. Monometallic and bimetallic catalysts seem to perform differently and metal nanoparticle size plays an important role in the CO selectivity. In this review, we will discuss the recent findings on catalyst design and the catalysts performance in the RWGS reaction. We will also review the proposed reaction mechanisms and active sites participating in the RWGS reaction and the controversial findings presented in the literature. By discussing the opportunities and potential improvements, we will conclude this review.

2. Recent advances in catalyst design

High activity and high CO selectivity are among the main criteria for designing a catalyst for the RWGS reaction. Many researchers have recently designed new catalysts with these goals in mind. Table 1 presents some of these recently designed catalysts for the RWGS reaction.

2.1. Selectivity and reactivity of monometallic catalysts

2.1.1. Catalysts with high CO adsorption energy

CO2 hydrogenation on group 11 transition metals (Cu, Ag, and Au) leads to the formation of CO and/or alcohols and aldehydes through a non-dissociative C–O bond mechanism. This stands in contrast to other studied transition metals, namely Pt, Pd, Ni, Rh, Fe, Co and Ru that tend to form CH4 due to C–O bond dissociation followed by C–H bond formation [3]. CO is formed on the surface of the catalysts in both cases, which desorbs as final product in case of the RWGS reaction, but is only an intermediate that is further hydrogenated to methane in case of the so-called Sabatier reaction, respectively [3,4]. It is generally accepted that the bond strength of the formed CO on the surface of the metal nanoparticles can determine the product selectivity. Strong interaction of CO with the nanoparticles results in C–O bond dissociation, which helps the formation of CH4 while weak interaction of CO with the metal nanoparticles results either in desorption of CO as the final product or the formation of alcohols and aldehydes [11,32]. Therefore, we have calculated the adsorption energy of CO on the (1 1 1) surface of various fcc metal nanoparticles, which are investigated in the CO2 hydrogenation reaction. The (1 1 1) surface is chosen since this is the thermodynamically most stable surface of fcc metals [46]. This is a simplified approach applied in this review only to categorize the monometallic catalysts using a simple but useful descriptor for the observed selectivities. Details of the computational approach can be found in the SI. We have calculated the adsorption energy of CO on Cu, Au, Pd, Pt, Rh, Ni and Mo. We did not include Ru in our computational set since it is the only non-fcc metal in the series and therefore, its comparison to other metals would be inhomogeneous. However, a strong Ru–CO interaction is already known from other studies [47]. As indicated in Fig. 2, the metal nanoparticles with relatively high CO desorption energy tend to catalyze both the RWGS reaction and the methanation reaction, simultaneously. These metals include Pd, Pt, Ni, and Rh. Ru shows the same behavior when used as monometallic catalyst. CO desorption energy on Ni is relatively lower compared to Rh, Pd, and Pt. However, it is still higher than the group 11 metals (Cu, Au, and Ag) which produce CO selectively. While Ni-based catalysts are well-known for Sabatier reaction, they also form CO as a by-product in most cases [48–52].

Various values for CH4 and CO selectivity have been reported in the literature using these catalysts [53,54]. However, there are recently studied monometallic catalysts, which can selectively produce CO [32,55]. For example, while Pd is not generally used for the RWGS reaction, due to its selectivity towards CH4, monometallic, atomically dispersed Pd/Al2O3 was reported to selectively produce CO through CO2 hydrogenation [8]. It was stated that the difference between atomically dispersed Pd sites supported on Al2O3 and Pd clusters can be sought in the active site for CO2 activation. While CO2 activation on Al2O3 led to the formation of weakly bound CO, which desorbed as the product, activation of CO2 on Pd clusters formed strongly bound CO, which then was hydrogenated further to form CH4. Although most supported monometallic Pd clusters have shown to produce CH4 in a considerable amount, there are catalysts, which have been designed to prove otherwise. SiH supported Pd nanoparticles were shown to selectively produce CO through active participation of SiH in the reaction [55]. Pd catalyzed the dissociative adsorption of H2 while SiH reacted with CO2. The reaction mechanism will be presented later in more details. Selective passivation of the CH4 production sites can also lead to high selectivity towards CO. In a recent study by Du et al., a ZrO2–Pd–ZrO2 catalyst was

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**Fig. 1.** a) Capacity for CO2 usage for various industries calculated based on the values given in ref. [11]. b) Sources of syngas production. Figure reproduced form ref [12], with permission from the Global Syngas Technologies Council. All rights reserved.
synthesized using the liquid phase layer deposition technique [58]. Initially, both methanation and the RWGS reaction were observed to take place on the catalyst. However, with time, coke selectively reduces CO as opposed to CH₄ [59]. Ni nanoparticles supported on CeO₂ [60, 61] and Au/CeO₂ [62] are also active for methanol synthesis from CO. It is well known that the presence of oxygen vacancies on the catalyst surface is vital for the catalyst activity to maintain the product selectivity. While relatively large Pt nanoparticles are known to form CH₄, the active site for CO formation is suggested to be the combination of Pt and the adjacent oxygen vacancy on the support (Pt-O₂) [63, 64]. Ni is another metal known to produce methane from CO₂ hydrogenation [65–67]. Ni nanoparticles supported on various metal oxides such as alumina, titania, and ceria-zirconia have been used as the active sites for the methanation reaction [63–66]. However, atomically dispersed Ni sites were found to selectively produce CO as opposed to CH₄ [67]. This remarkable influence of the metal particle size on the selectivity will be discussed below in more detail.

### Table 1
Summary of reported reaction conditions, CO₂ conversion and CO selectivity for the recent catalysts designed for the RWGS reaction.

| Catalyst | H₂:CO₂ molar ratio | Temperature (°C) | Pressure (MPa) | CO₂ Conversion (%) | CO selectivity (%) | WHSV (L·g⁻¹·h⁻¹) | Ref. |
|----------|---------------------|------------------|----------------|--------------------|-------------------|-------------------|------|
| Au/Al₂O₃ | 4:1                 | 400              | –              | 11                 | 100               | 7.5               | [14] |
| Au/TiO₂  | 4:1                 | 400              | –              | 35                 | 100               | 7.5               | [14] |
| Au@UiO-67⁺ | 3:1               | 408              | 2              | 30                 | ~95               | 12                | [15] |
| Au/TiO₂  | 3:1                 | 400              | 0.1            | 50                 | ~99               | 15                | [16] |
| Cu/CeO₂  | 3:1                 | 300              | 0.1            | 4                  | 39                | 36                | [17] |
| Cu/SiO₂  | 3:1                 | 300              | 0.1            | 6                  | 98                | 1.12*             | [18] |
| Cu/CeO₂  | 3:1                 | 300              | 0.1            | 18                 | 100               | 1.12*             | [18] |
| Cu/CeO₂ ×ₙ | 3:1            | 600              | 0.1            | 50                 | ~100              | 300               | [19] |
| CuCe(rod) | 4:1                 | 400              | 0.1            | >40                | ~100              | 60                | [20] |
| Cu/CeO₂-nanorods | 9:1 | 400 | 0.1 | 55 | 97 | 30 | [21] |
| Cu/CeO₂-nanocubes | 9:1 | 400 | 0.1 | 50 | >98 | 30 | [21] |
| Cu–CuO₂ | 9:1                 | 500              | 0.1            | 70                 | >90               | 30                | [22] |
| Cr₂O₃/Cu | 4:1                 | 600              | 0.1            | 45                 | 100               | 150               | [23] |
| 8% Cu/CeO₂(O₃) | 4:1 | 400 | 0.1 | 2 | 95 | 60 | [24] |
| Cu–Mo₂C | 4:1                 | 500              | –              | 52                 | ~100              | 12                | [25] |
| Cs-Mo₂C | 4:1                 | 500              | –              | 42                 | ~90               | 12                | [25] |
| Cu(1)/FAU | 1:1                | 500              | 0.1            | 8                  | 98                | 7.5               | [26] |
| 4Ca/Al₂O₃ | 2:1               | 600              | 0.1            | 47                 | 100               | 300               | [27] |
| CuMnOₓ | 2:1                 | 350              | 0.1            | 8                  | 100               | 15                | [28] |
| Cu-Al₂O₃ | 3:1                 | 600              | 0.1            | >50                | 100               | –                 | [29] |
| 1%Cu/β-Mo₃C | 2:1 | 600 | 0.1 | 41 | 100 | 300 | [30] |
| 5Wir/CeO₂ | 4:1                | 300              | 1.0            | 7                  | >99               | 11.4              | [31] |
| 20Wir/CeO₂ | 4:1                | 300              | 1.0            | 9                  | 12                | 11.4              | [31] |
| Pd/SiO₂ | 1:1                 | 600              | 0.1            | 29                 | 82                | 60                | [32] |
| Pt/CeO₂ | 1:1                 | 300              | 0.1            | 7                  | –                 | 30                | [33] |
| Pt/SiO₂ | 2:1                 | 300              | 0.1            | 3                  | 100               | 24.7*             | [34] |
| Pt/TiO₂ | 2:1                 | 300              | 0.1            | 5                  | 99                | 119.7*            | [34] |
| Pt/mullite | 1:1                | 340              | 0.1            | 23                 | 84                | 27                | [35] |
| Rh/S-1 | 3:1                 | 500              | 1.0            | 52                 | 80                | 3.6               | [36] |
| Rh@HZSMS⁺ | 3:1                | 500              | 1.0            | 68                 | 2                 | 3.6               | [36] |
| Rh/S-1 | 3:1                 | 500              | 1.0            | 47                 | 69                | 3.6               | [36] |

* Value given in h⁻¹.

⁺ Core-shell structure.

⁻ Yolk-shell structure.

#### 2.1.2. Catalysts with low CO adsorption energy
Unlike metals with strong CO adsorption energy, using monometallic catalysts with weak CO adsorption does not lead to CH₄ formation. For example, Au nanoparticles form methanol [68, 69] and CO [70, 71] from CO₂. Monometallic Au nanoparticles encapsulated in Zr-based MOFs (Au@UiO-67) selectively produce CO, [15] and Au/CeO₂ is an active catalyst for both methanol synthesis and the RWGS reaction [72]. CeO₂ is a well-known reducible catalytic support with the ability to create oxygen vacancies on the surface, [73] but the presence of Au is required for surface reduction [74]. This reduction is easier achieved by using CO as the reducing agent than H₂. It is well known that the presence of oxygen vacancies on the catalyst surface is vital for the catalyst activity in CO₂ hydrogenation reactions [5, 75]. Therefore, adding Au to the CeO₂ surface not only increases the ability to form oxygen vacancies by surface reduction, but also creates active sites for H₂ adsorption. Au/CeO₂ is also active for methanol synthesis from CO₂ hydrogenation. In another study, Behm’s group demonstrated that while both CO and methanol are initially produced on the Au/CeO₂ surface, inhibition of
the CO formation is faster than methanol, which leads to higher methanol selectivity through the reaction [72]. The catalyst deactivation is proposed to occur through formation of stable carbonate species on the catalyst active sites. The formation of such highly stable carbonates were also observed on other types of catalysts used for the RWGS reaction [28]. Au-based catalysts were also studied for the RWGS reaction under plasmon-enhanced conditions [70,71]. Huber’s group reported more than an order of magnitude improvement in catalyst activity by using localized surface plasmon resonance (LSPR). The decrease in apparent activation energies due to the change in intrinsic reaction kinetics by surface plasmon, as well as the increase in apparent reaction orders due to the decrease in spectator concentration on the catalyst surface, are the main reasons for such improvements in Au-based catalyst activities under plasmon-enhanced conditions.

Copper is another metal with weak CO adsorption energy, which is very well-known for its high selectivity towards CO when used as a catalyst in the CO₂ hydrogenation reaction [76,77]. However, the major drawback of using Cu is its low thermal stability, which leads to fast deactivation of the catalyst particularly at high temperatures. Recently, however, many modifications have been proposed to design highly active and relatively stable copper-based catalysts. Improving the dispersion of copper nanoparticles on β-MoO₃ was shown to have a significant effect on the catalyst stability compared to Cu/ZnO/Al₂O₃, a commercial Cu-based catalysts used for WGS reaction [30]. While the initial activity was only slightly improved, the stability was significantly enhanced when compared after 40 h time-on-stream at 600 °C. Cu/β-MoO₃ was found to lose only 15 % of its initial activity while Cu/ZnO/Al₂O₃ lost more than 60 %. The same operating conditions were used to test a catalyst with a surface Cu-Al spinel for the RWGS reaction and it was found to be highly stable during the 40 h test with no sign of deactivation [27]. The found formation of Cu-Al spinel oxide on the surface was attributed to the SMSI between isolated Cu²⁺ ions and Al₂O₃. The SMSI between Cu and metal oxides has been linked to the synthesis of other Cu-based catalysts for the RWGS reaction. An inverse nanoporous Cr₂O₃/Cu catalyst was designed by Shen et al., which was found to be active for the RWGS reaction with rates higher than supported noble-metal catalysts [23]. Synthesis of the catalyst was done through de-alloying of CrCuAl alloy forming a Cr₂O₃ layer on nanoporous Cu with high surface area (Fig. 3).

An inverse metal oxide/metal structure has been formed using CeO₂ and copper oxide (forming CeO₂/CuO₂), which has been used for various reactions such as CO oxidation and the WGS reaction [78]. The formation of both Cu⁺ and Cu²⁺ in this configuration was reported to be favorable for these reactions [79]. The activity of catalysts for the RWGS reaction is strongly linked to their ability to form oxygen vacancies on their surface. This is demonstrated, for example, by the results of Konsolakis et al. who showed that Cu/CeO₂-nanorods are more active in CO₂ conversion compared with Cu/CeO₂-nanocubes because nanorods have a higher potential in forming oxygen vacancies under reducing conditions [21]. In another example, Chen’s group managed to design a highly active Cu/CoO₂ hollow sphere catalyst, which benefits from a high density of oxygen vacancies [19]. This catalyst was tested for the RWGS reaction and proved to be more active than other Cu/CoO₂ catalysts used in the same study with lower oxygen vacancy density. The same conclusions were derived from the work of Zhou et al. [24] They proposed a Cu/CoO₂ and catalyst, on which Cu⁺ and oxygen vacancies were found to be actively participating in the reaction. The role of oxygen vacancies was proven by comparing Cu-Al and Co-Al spinel oxides as catalysts for the RWGS reaction [28]. The formation of a higher degree of mixed spinel oxides (normal spinel and inverse spinel) in Cu-Al structure forms more oxygen vacancies, which in turn results in higher activity of the Cu-Al spinel oxide compared to the Co-Al one. There are also other spinel-type mixed oxides (AB₂O₄) that are favorable for catalytic reactions due to the formation of defect sites [80]. The role of oxygen vacancies on the spinel oxide surfaces in the RWGS reaction is the adsorption and activation of CO₂ [28,81]. This is supported by CuO/In₂O₃ that was also found to be highly active for the CO₂ reduction due to its ability to form oxygen vacancies, on which CO₂ can be adsorbed and activated [82]. In fact, various factors such as metal particle size, metal-support interaction, metal particle dispersity, and the participation of the support in the reaction can influence the performance of a catalyst. However, the outstanding significance of oxygen vacancies was demonstrated by Jones group, which managed to keep all these variables constant to only monitor the effect of the support on the activity of the supported Cu nanoparticles in the RWGS reaction [18]. They studied Cu/SiO₂ and Cu/CoO₂ with the same above-mentioned characteristics and confirmed, besides the four times higher activity of Cu/CoO₂ than Cu/SiO₂ that the active sites participating in the RWGS reaction on this catalyst are indeed oxygen vacancies and Cu⁺.

2.2. Selectivity and reactivity of bimetallic catalysts

As shown above, most monometallic catalysts with high CO adsorption energy favor the formation of CH₄ in CO₂ hydrogenation
reaction while the ones, which weakly adsorb CO, more selectively form CO as the final product. However, using the metals presented in Fig. 2 in bimetallic catalysts can highly affect their activity, stability, and CO selectivity. Recently, it has been shown that Pd-based bimetallic nanoparticles shift the selectivity from the formation of both CH₄ and CO towards higher CO formation. Ye et al. presented a uniformly mixed Pd-In catalyst supported on SiO₂, which can selectively form CO as the CO₂ hydrogenation product [32]. This feature is proposed to be linked to the non-dissociative adsorption of H₂ and weak binding energy of CO while using this bimetallic catalyst. Braga et al. used the same concept of weakening the CO binding energy by synthesizing a bimetallic Ni-Pd catalyst with the direct decomposition method. The catalyst showed much higher selectivity towards CO compared to monometallic Pd, which was synthesized as reference material with the same method [83]. In-situ CO-DRIFTS studies allowed to identify strongly bonded and weakly bonded CO molecules, but only the latter were able to desorb as the final product of the RWGS reaction. Xu’s group showed that Au-Pd nanoparticles encapsulated in the structure of the Zn-based and Zr-based MOFs improve the CO selectivity by 8% through CO₂ hydrogenation [37,38]. While the reason behind the effect of Au on Pd selectivity towards CO was not discussed, it can be suspected that the higher CO selectivity is caused by the increased electron density of Au in the presence of Pd. The activity of Au nanoparticles for CO₂ adsorption and activation can also be influenced by tuning the Au-metal oxide interface. Yang et al. studied this concept by adding small amounts of CeO₂ to Au/TiO₂ [84]. Not only does the addition of CeO₂ to Au/TiO₂ help the formation of small Au nanoparticles, which selectively form CO, but it also forms an Au-CeO₂-TiO₂ interface. While no charge transfer was observed between Au and TiO₂, the addition of CeO₂ helped the charge transfer from Au nanoparticles to the support. The electric polarization of the Au-CeO₂ interface helped to form carboxylate species as the intermediate products on the surface of the catalyst, which were then converted to CO and methanol. The main effects of the addition of a second metal or promoter, which have been discussed in the literature, are changes in the electron density or the creation of new active sites. However, other effects such as the change in energy of vacancies formation and the acid/base properties have been also reported as effects caused by the addition of a second metal or promoter [22,85,86]. It should be noted that these effects are related either to the electron density change or the creation of new active sites, i.e. the effects are not completely independent from each other and therefore not further discussed.

The selectivity of bimetallic Ru catalysts can also be shifted towards CO. Le Saché et al. have designed a bimetallic Ru-Ni/CeO₂-ZrO₂ catalyst, which produces CH₄ or CO depending on the operating temperature [87]. High CH₄ selectivity (93 %) is achieved at low temperatures (350 °C) while at high temperatures (750 °C) the CO selectivity is reported to be 91 %. When Ru is used as promoter, it enhances the activity of already CO-selective catalysts without hampering their selectivity. Simakov group improved the activity of Cu/ZnO/Al₂O₃ as a RWGS reaction catalyst by addition of 0.5 % Ru [88]. The catalyst characterization results showed that Ru forms a bond with Cu to convert to a core-shell Ru-Cu nanoparticle. While Ru is usually known as a CH₄-selective catalyst, the increase of the electron density of Ru due to its bond with Cu helps to shift the selectivity from CH₄ to CO.

Pt improves its selectivity to CO in CO₂ hydrogenation by adding a promoter as well. The promoter-Pt interface is regarded as the active site for CO₂ hydrogenation. Huber’s group showed the effect of adding K as the promoter to supported Pt-based catalysts [35,89]. They discovered that while Pt catalyzes both the RWGS reaction and the methanation reaction, the addition of K highly increases both the activity and CO selectivity. The K-Pt interface forms active sites for promoting the RWGS reaction, because the strong interaction between Pt nanoparticles and KO₂ weakens the adsorption energy of CO on Pt, which inhibits further hydrogenation of CO to form CH₄. Huber’s group reported the same effect by adding MoO₃ to Pt, [90] which increased the intrinsic activity of a single Pt site at 473 K from 0.4 to 22.7 min⁻¹. Similar to Au, the observed activity increase was explained by a plasmonic effect.

Non-noble metals have been used in bimetallic form to promote the RWGS reaction, too. Chen’s group recently discovered that addition of Fe to Ni, which normally promotes the methanation reaction, can form Ni-Fe₂O₃ interfaces, which selectively catalyze CO formation [39]. They discovered that this interface reduces the strength of the M—CO interaction, facilitating the desorption of CO, which in turn increases the CO selectivity. The same effect was found by Varvoutil et al. who reported that while the addition of Cs to Cu/CoO decreased the catalyst activity, it increased the selectivity towards CO [22]. Reina’s group reported in another example the positive effect of Cs on the CO selectivity of Fe/Al₂O₃. Besides Cs, they introduced Cu, which enhances the activity and stability of Fe-Cu/Al₂O₃ compared to Fe/Al₂O₃, Fe-Cu/Al₂O₃ and Fe-Cs/Al₂O₃ [91]. They reported in their study that while Cs addition enhances the activity and CO selectivity of FeO₃ for the RWGS reaction, addition of Cu prevents the FeO₃ phase from sintering. The same effect has been reported for Ni promotion by Cu, [41,92] as well as alkali and rare earth metals [40]. Ni promotion by Cu specifically suppresses the methanation reaction to increase CO selectivity [92]. Yolk-shell structures are also commonly used for catalyst stabilization and increased activity [93,94]. A bimetallic example of such structure used for the RWGS reaction is Ni-promoted Co yolk in an SiO₂ shell. Ni addition promotes the activity of Co as catalyst and helps to form the yolk-shell structure, which is evident from the catalyst characterization results presented by Price et al. [42].

The group 11 transition metals were also used in bimetallic structures for the RWGS reaction. They either have been used as active metals, which become more active by addition of another element, or they act as promoters themselves for shifting the selectivity toward CO. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper. Cu was investigated as a promoter in catalysts with lower initial activity towards CO formation. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper. Cu was investigated as a promoter in catalysts with lower initial activity towards CO formation. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper. Cu was investigated as a promoter in catalysts with lower initial activity towards CO formation. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper. Cu was investigated as a promoter in catalysts with lower initial activity towards CO formation. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper. Cu was investigated as a promoter in catalysts with lower initial activity towards CO formation. Copper-based catalysts are among the most attractive ones due to the remarkably high CO selectivity of copper.

While Cu is preferentially used as the non-noble metal for the RWGS reaction, other non-noble metal-based structures and catalysts have recently attracted the attention of many researchers in this field [95–97]. Carbide structures prepared with metals such as Ti, W and V were found to be active catalysts for the RWGS reaction [98–100]. Rodriguez et al. synthesized M/TiC (M = Au, Cu, Ni) as catalysts for CO₂ hydrogenation. They reported that CO₂ hydrogenation on these catalysts mostly go through HOCO production as an intermediate, which is then hydrogenated to produce CO and only traces of methanol [98]. WC/Al₂O₃ prepared by the evaporation-deposition method was reported by the Willauer group as an active and selective catalyst for the RWGS reaction [99]. They promoted WC/Al₂O₃ with alkali metals such as K and Na. H₂-treated K-WC/Al₂O₃ was found to be more active compared to the one promoted with Na. The catalyst activity, however, was negatively affected by addition of promoters compared to unpromoted WC/Al₂O₃. This effect might be due to the lower BET surface area of the promoted catalyst (87 m²·g⁻¹ and 95 m²·g⁻¹ for K promotion and Na promotion, respectively) compared to the unpromoted one (136 m²·g⁻¹). On the other hand, addition of K and Na boosted the CO
selectivity due to the formation of smaller WC particles. Besides WC/Al₂O₃, the same group also studied 2 % K-Mo₂C as another carbide-based RWGS catalyst that showed even higher activity [101]. Finally, Pajares et al. proposed VC as active and selective catalyst for the RWGS reaction [100]. Specifically, V₃C₇ was presented in this study and the activity of this catalyst was assigned to the carbon vacancies on the catalyst surface. Similar to oxygen vacancies, the carbon vacancies on V₃C₇ catalyst were used to explain the adsorption and activation of the reactants. The higher density of these vacancies helps to lower the activation energy of CO₂ and H₂ adsorption and the dissociation step.

There are several reasons for the observed shifts in product selectivity and enhancement of the catalyst activity in CO₂ hydrogenation on bimetallic catalysts. In some cases, the structure of the bimetallic catalysts redistributes the local charges and modifies the electron density of the catalyst, which alters the catalyst’s performance [102]. In many cases, the charge distribution alters the CO₂ adsorption since the electron-rich site more easily attracts the C=O and the electron-deficient site attracts O²⁻ as in the case of PtCo bimetallic catalyst [45]. In these cases, the charge transfer is observable from the change of oxidation state of the metals on the catalyst surface. XPS analysis showed that while Ni²⁺ and Co³⁺ are the dominant oxidation states for monometallic Ni and Co catalysts, respectively, the oxidation states of these two ions change to Ni³⁺ and Co²⁺ in a bimetallic NiCo catalyst [103]. Bimetallic catalysts can also enhance the production of the desirable products by addition of an active site. In the case of the K-promoted Pt catalyst, although the presence of KO₂ stabilized Pt in its high oxidation state, a new active site, namely PtKO₂, was created for decomposition of formate as the intermediate product to form the final products. The same effect was observed by addition of Fe to Ni to form Ni-FeOx as the active sites [39]. This will be discussed in more details in the following section. Hydrogen was found to bind more weakly on the bimetallic transition metal catalysts compared to the corresponding monometallic surfaces [104]. However, the effect of weak hydrogen adsorption on product selectivity has not been fully investigated yet.

2.3. Metal nanoparticle size effect

Like Pd, Ru and Rh strongly adsorb CO as an intermediate in CO₂ hydrogenation. These metals also catalyze CO₂ hydrogenation to form CH₄ [105–111]. However, based on recent studies, new Ru-based catalysts with high selectivity towards CO have been designed. Cargnello’s team has discovered that CeO₂ supported Ru catalyst can be tuned to selectively produce either CH₄ or CO [112]. While Ru nanoparticles on CeO₂ selectively produce CH₄ as expected, the nanoparticles decompose into atomically-dispersed Ru on CeO₂ upon reduction, shifting the selectivity completely towards CO. This behavior is reversible, as oxidation leads to the reformation of Ru nanoparticles that produce CH₄ again. The different product selectivity using supported Ru has been tested before through comparison of 5%Mn/Al₂O₃ (showing nanoparticles of Ru) and 0.1 %Ru/Al₂O₃ (showing atomic dispersion of Ru) [113]. The former selectively produced CH₄ and the latter produced CO with time, while the atomically-dispersed Ru sintered to form nanoparticles and, accordingly, the selectivity changed to CH₄. It should be noted that the effect of the support on the reaction is more prominent when the metal particle size is small due to the stronger influence of the support in small metal particles. However, with increasing metal particle sizes the catalyst performance is increasingly dominated by the metal particle characteristics [114].

Matsubu et al. have shown the same effect for Rh/TiO₂ [115]. They have identified Rh nanoparticles and isolated Rh atoms on their catalyst surface. The Rh nanoparticles form CH₄ while isolated atomic Rh sites produce CO. They observed that the nanoparticles disintegrate during reaction into atomically-dispersed isolated Rh sites, which results in a shift of the selectivity towards CO as expected. While many have reported this effect, not many researchers discussed the reason behind such observation. Matsubu et al. explained that the single atom Rh is more likely to form and desorb CO since it is not surrounded with other Rh atoms, which can provide H for further hydrogenation of CO to form CH₄. What we observe is that the active sites for CH₄ formation in these catalysts is a metal-metal entity, whereas the active sites for CO formation are the metal-metal oxide interface. The lower the size of the nanoparticles, the higher the number of metal-metal oxide sites to increase the CO selectivity. It is therefore understandable that atomically dispersed Pd on carbon nanotubes did not produce CO due to the absence of a metal oxide support [8]. Metal-metal oxide sites are also responsible for the increased RWGS activity of K-promoted Pt by forming Pt-KO₂ sites [90]. With this concept, we can also explain the superior activity of materials, such as SiH or γ-Ga₂O₃, which adsorb CO₂ and activate hydrogen themselves or are able to diffuse hydrogen from the metal nanoparticle via the interface to far distant CO₂ adsorption sites, where the final product CO is formed. This property differentiates these materials from the above-described metal-metal oxide systems, which require hydrogen activation on the metal sites, from where hydrogen can only spill over to CO₂ adsorption sites in close vicinity to the interface [55,116].

3. Reaction mechanism

3.1. General reaction mechanisms

The RWGS reaction mechanism has been a topic of intensive debate between researchers. Despite the numerous studied catalysts, two reaction mechanisms are most common when searching the literature: First, a redox mechanism, in which H₂ does not participate directly in CO₂ reduction, but reduces the catalyst surface to form H₂O after CO₂ releases one of the oxygen atoms on the catalyst surface (Eq. 2 and 3) [117–119].

\[
\text{CO}_2 + \text{M} - \text{CO} + \text{M} - \text{O} - \text{M}
\]

(2)

\[
\text{H}_2 + \text{M} - \text{O} - \text{M} \rightarrow \text{H}_2\text{O} + \text{M} - \text{M}
\]

(3)

The second most common mechanism proposed is the formation of formate as the intermediate product [120–123]. In this mechanism, H₂ directly reacts with CO₂ to form formate on the catalyst surface, followed by further hydrogenation to form CO and H₂O. Here in this section, we will review the recent advances in understanding the RWGS reaction mechanism on various catalysts and the origin of selectivity for this reaction on the catalyst surface.

3.2. Recent advances in understanding the RWGS reaction mechanism

Pd-based catalysts are extensively investigated for this purpose. Pd usually shows both CO and CH₄ formation, which makes it an interesting case for selectivity studies. By investigating two different loadings of Pd on Al₂O₃, the Szanyi group reported that CH₄ and CO are formed on different surface sites [124]. Based on their findings from in-situ DRIFTS-MS studies, they noted that Pd/Al₂O₃ works as a bi-functional catalyst. CO₂ is adsorbed on the hydroxyl groups of the Al₂O₃ surface to form formate intermediates while H₂ is dissociatively adsorbed on the Pd nanoparticles. The formed formate species, which are close to the nanoparticles (i.e. at the interface) are further hydrogenated to form CO, which is then transferred to Pd. Two sets of sites for either CO or CH₄ formation are postulated on the Pd surface: Pd sites with weak interaction with CO desorb CO while the ones with strong interaction with CO keep this molecule to hydrogenate it further to produce CH₄ (mechanism is illustrated in Fig. 4). The difference in CO selectivity between catalysts with high and low Pd loading is determined by the concentration of sites, which form strong CO bond.

In a separate study, the Szanyi group reported that the sites with strong CO bond are filled first [125]. Only when these sites are saturated, the sites with weak CO bonds are filled. Therefore, CH₄ formation on Pd/Al₂O₃ is prioritized (Fig. 5). In another study, however, they
claimed that the majority of CO formation on Pd/Al₂O₃ comes from the hydrogenation of carboxyl intermediates, whereas formate molecules only partly participate in this reaction due to their high thermal stability [126]. The formation of formate species is also confirmed on a Pd/Ga₂O₃ catalyst during the RWGS reaction. However, whether formate is formed as a stable species on the catalyst surface or if it reacts as an intermediate product to form CO is difficult to decide with standard spectroscopy techniques. Therefore, Aguirre and Collins used modulation-excitation spectroscopy (MES) combined with phase sensitive detection (PSD) to study the Pd/Ga₂O₃ catalyst surface during H₂ and CO₂ adsorption [116]. Contrary to Al₂O₃, Ga₂O₃ was found to be reduced by H₂ to form Ga-H. The H atoms were transferred from Pd to the Ga₂O₃ support through the spillover effect. Various forms of formate species, namely monodentate, bidentate and bridged formate were formed, out of which, monodentate formate was found to act as the intermediate product that was further hydrogenated to CO.

Unlike Pd/Al₂O₃ and Pd/Ga₂O₃, a redox mechanism is proposed for the RWGS reaction on Pd/SiH by Qian et al [55]. In this study, Si–H bonds were found to be oxidized by CO₂ and form Si–OH and Si=O. CO₂ was therefore reduced to CO. The oxidized surface then accepted H atoms from Pd to desorb water and re-form Si–H bonds. In general, Pd was found to catalyze CO₂ hydrogenation by dissociative H₂ adsorption upon which either CO or CH₄ are formed and desorbed. Gold nanoparticles in Au/Al₂O₃ were also reported to have a similar role in CO₂ hydrogenation in regard to H₂ dissociation [14]. Surface hydroxyl groups on Al₂O₃ were reported to actively participate in this reaction to form bicarbonate species by their reaction with CO₂. The formed bicarbonate species on the Au-Al₂O₃ interface were claimed to react with atomic H on the Au nanoparticles to form formate. The formates could either decompose to CO and H₂O₂, or are transferred to other Al₂O₃ surface sites and stay there as spectator. Bobadilla et al. did not consider the presence of oxygen vacancies on Al₂O₃ surface because Al₂O₃ is not a reducible support and therefore, they ruled out the possibility of formation of CO in this way. However, for Pt/Al₂O₃, the prominent role of oxygen vacancies on the Al₂O₃ support in the vicinity of Pt nanoparticles were discussed, where they act as active sites for CO₂ adsorption and activation [60]. On the Au/TiO₂ surface, the situation is more complicated as shown by Bobadilla et al., who reported that Ti₃⁺, oxygen vacancies, as well as hydroxyl groups are active sites for the RWGS reaction, besides the Au nanoparticles. Based on their study, two major mechanisms can be proposed for the RWGS reaction on Au/TiO₂. Either CO₂ can react with the oxygen vacancies to form a carbonate intermediate on the surface, which then reacts with H atoms on the Au nanoparticles as well as the surface hydroxyl groups to form CO and H₂O, or as Rodriguez et al. also proposed for the WGS reaction, [127] CO₂ reacts with adsorbed H atoms on the Au/TiO₂ interface to form a hydroxycarbonyl (OCOH) intermediate, which then decomposes to form CO and a hydroxyl group. The hydroxyl group then reacts with the second H to form and desorb water. These mechanisms are illustrated in Fig. 6.

As mentioned for Au-TiO₂, hydroxycarbonyl or carboxyl species were found to be the intermediate product for CO₂ hydrogenation in various studies [127,128]. Some researchers believe that formate is only formed as a spectator on the catalyst surface while the RWGS reaction in fact takes place through formation of carboxyl groups [129]. Such a carboxyl mechanism, in which CO₂ and H are formed by carboxyl dissociation on the catalyst surface, is discussed for the WGS reaction, making it also a possible pathway for the reverse reaction [130,131]. On Au/CeO₂ however, Behm’s group reported the possibility of a redox mechanism for the RWGS reaction [118]. Based on their study, CO₂ has the possibility to release one oxygen atom on the pre-reduced Au/CeO₂ surface, which is the condition for a redox mechanism.

For investigation of the reaction mechanism on Pt, it is important to consider the catalyst morphology as well as the operating conditions. Huang’s group reported that while small Pt particles (0–2 nm) favor the formation of CO, CH₄ is formed on the larger nanoparticles (2–5 nm) [59]. Specially with larger nanoparticles, the CO selectivity reduces significantly when operating at higher temperatures compared to lower ones: CO selectivity was > 95 % at 250 °C and ~65 % at 400 °C for the highest loading, which represents the largest Pt nanoparticles. In a separate study, they investigated the role of Pt nanoparticles on CeO₂ for the RWGS reaction [33]. They found that addition of Pt on CeO₂ surface increases the formation of Ce³⁺ sites, which are responsible for CO₂ adsorption. They also discovered that while CO₂ adsorption on Ce³⁺ sites form Ce³⁺–O–Bonds, CO cannot be desorbed without addition of H from an adjacent Pt site. They realized that although the adsorption of CO₂ on the CeO₂ surface resembles a redox mechanism for the RWGS reaction, it actually proceeds via formation of an intermediate formate on the Pt-CeO₂ interface before decomposition to CO and water. Kopac et al. studied the RWGS reaction on the metal surface, interface, and support of a Cu/SrTiO₃ catalyst [132]. They reported that formation of CO is favored on the interface of the catalyst and, most importantly, reducing the size of the Cu nanoparticles can boost the activity in the RWGS reaction by increasing the metal-support interface. In agreement with previous studies on the role of Pt, Pd and Au, they concluded that also Cu acts as adsorption sites for H₂ dissociation, providing H atoms for formation of intermediates. However, direct desorption of CO from the catalyst surface without engagement of H₂ was found to be the case for other types of supported copper-based catalysts such as Cu/ β-MoC [30]. Zhang et al. tested their catalyst by exposing it to pulses of CO₂ and monitored the potential CO formation. This is one of the few remarkable examples, which experimentally showed CO formation upon CO₂ dosage without hydrogen. While CO desorption from the catalyst surface was not observed using β-MoC, addition of Cu to the support showed the formation of CO at the moment when CO₂ was introduced to the catalyst in the absence of H₂ at 250 °C (Fig. 7).

While the metal nanoparticles are usually known to act as the hydrogen source for hydrogenation of the adsorbed CO₂ species, Zhang
et al.’s observation and similar studies, which claim a redox mechanism, show that the role of the metal nanoparticles in the RWGS reaction mechanism depends on the structure of the catalyst, the type of support and the presence of hydroxyl groups. The latter will be explained in detail below. Another factor, which has been considered for CO formation is the type of the intermediate, which is formed on the catalyst surface through CO_{2} and H_{2} adsorption. Schneck et al. showed how the structure of the intermediate could be controlled resulting in a change of catalyst selectivity. Upon normal adsorption of CO_{2} on metal hydrides, formates are formed, which are intermediates for forming methanol as
well as formic acid [128]. However, they managed by photochemical manipulation to change the way CO2 and H2 were adsorbed, which resulted in the formation of the hydroxycarboxyls as the intermediates for the formation of CO. Other studies also confirmed that the routes for formate formation and CO formation are different. However, unlike Schneck et al., they reported that methanol is formed via the CO formation route [129,133]. Arguments for [14,134] and against [133] the formation of CO from a formate species as an intermediate have been presented in the literature. The main role of the metal nanoparticles as well as the detected potential intermediates on the catalyst surface are therefore yet to be confirmed.

### 3.3. The effect of hydroxyl groups

As stated above, various reaction mechanisms have been proposed for the formation of CO by CO2 hydrogenation. However, upon closer inspection, we realized that one of the crucial factors in determining the RWGS reaction mechanism is the presence/absence of the hydroxyl groups on the catalyst surface. This becomes clearer when we investigate the same active metal, Cu for example, in various catalysts structures. When CO2 adsorption is considered on the Cu (1 0 0), (1 1 0), and (1 1 1) surfaces without support, CO2 is reduced to CO leaving an oxygen on the Cu surface, [135,136] which is the main step of the redox mechanism. This redox mechanism was proposed by several researchers for unsupported Cu [137] or Cu on metal oxide supports without hydroxyl groups on the surface, such as ZnO or MoO3 [30,119,138]. However, when Cu is used with supports exposing hydroxyl groups, such as Al2O3 or SiO2, the formation of oxygen-terminated intermediate products are reported [120,121]. The same holds for Au as a catalyst in the RWGS reaction: on Au/CO2, the reaction occurs according to the redox mechanism and on Au/Al2O3 the formate mechanism is observed [14,118]. This has been proven in the theoretical study of Cu/ZnO and Cu/ZnOH for methanol synthesis from CO2 hydrogenation. Wu et al. discovered that the direct reduction of CO2 to CO (without hydrogen interaction) is more dominant when Cu/ZnO is used. However, on Cu/ZnOH they discovered that CO2 hydrogenation to HCOO and CH3O is promoted showing the effect of the hydroxyl groups on the adsorption of CO2 [133]. It appears that the surface hydroxyl groups react with the adsorbed CO2 to form oxygenated species such as formate or bicarbonate, which consequently convert/decouple to CO. Other researchers have confirmed the significant promoting effect of surface hydroxyl groups on CO2 adsorption and hydrogenation [139,140].

Most studies agree that the metal nanoparticles act as a source of H reservoir for hydrogenation of the intermediate product, which is formed on the metal-support interface. However, some researchers reported that CO can be formed on the catalyst surface through pulsing CO2 and without direct interference of H2 [117–119]. Besides the fact, that the mechanism of the RWGS reaction is still controversially discussed, we also have to consider that more than one reaction mechanism might be involved in this reaction and, therefore, a kinetic study can help to identify the prevailing mechanism. For example, parallel cycles for CO2 adsorption and reaction were detected on the In2O3 catalyst surface [141]. Therefore, the mere possibility of CO formation through direct CO2 reduction on the surface does not necessarily mean that a redox mechanism dominates the reaction. On the other hand, formation of formate and carbonate species have been reported on the catalyst surface. It was found that the majority of the carbonate species formed on the Cu-Al spinel surface upon CO2 adsorption do not participate in the RWGS reaction [28]. Other researchers reported that formates on the Al2O3 surface were found to be adsorbed too strongly to decompose to CO [14]. Therefore, the detection of these compounds cannot be interpreted as proof for their involvement as intermediate products, since they can also be spectators. Specifically, formate, carbonate, and hydroxycarboxyl isomers have been proposed as the intermediates in various reports [14,116,128]. However, it is generally accepted that only the intermediates, which form in the vicinity of the H supply, i.e. on the metal-support interface, can contribute to the reaction and the rest of the catalyst surface is not involved in the catalytic cycle. Therefore, increasing the metal-support interface is generally a strategy to increase the activity of a catalyst for the RWGS reaction. Another catalyst feature to consider is its capacity to generate vacancies on the surface. Vacancies have been found to participate in the CO2 hydrogenation reactions through adsorption of CO2. Therefore, vacancy creation on the catalyst surface can help the activation of CO2 molecules if the vacancy is located next to the metal-support interface [66].

### 4. Conclusions and future opportunities

In this review, we presented the latest findings in the literature on catalyst design and synthesis for the hydrogenation of CO2 to CO. We also discussed in detail the reaction mechanisms for this reaction. In the following, we summarize the main results of our review:

1. In the search for common properties of catalysts, active for the RWGS reaction, we identified the CO adsorption/desorption energy on the metal surface as useful descriptor to classify their selectivities to CO and CH4. As an intermediate product before desorption (as CO) or further hydrogenation to CH4, the strength of the M=CO bond can be used as a criterion for categorizing the metallic nanoparticles that form either CO or CH4. According to our calculations, metal nanoparticles such as Cu, Au and Ag, which show low tendency to form CH4 in monometallic catalysts, have a lower CO adsorption energy compared to Pd, Pt, Ni, and Rh.

2. The selectivity of the CO2 hydrogenation reaction can be strongly influenced by the use of bimetallic catalysts. This implies that the changes in the structure of the active sites, which can affect the strength of the bond between the metal and the intermediate, plays a major role in determining the selectivity in these cases [125,142]. Based on the cases evaluated in the literature, we found that this phenomenon can mainly occur in two ways: One way is the effect of the addition of the second metal on the local charge of the first metal. In this case, the charge transfer may create a scenario for easier adsorption of CO2 (through creating partial positive and negative charges) or affect the strength of the formed CO on the metal (since metal atoms and ions have different CO adsorption energies). The second way is to create a new active site in the form of metal-metal oxide entities as we have seen in the case of K promoted Pt, were Pt-KO2 was identified as the active site.

3. Significant progress has been achieved recently in understanding the reaction mechanism of the RWGS reaction. In most studies, researchers reported that CO2 and H2 form hydrogenated intermediates on the catalyst surface such as formate, carboxylate or bicarbonate. These intermediates then are further hydrogenated/decomposed to form the final products. It is commonly agreed that the intermediate products, which are only formed on the interface of the support and the metal nanoparticles can participate in the reaction, since the adsorbed hydrogen atom on the metal nanoparticle can then react with the intermediate to desorb it as CO and H2O. Vacancies on the catalyst surface are also generally known to facilitate CO2 adsorption and activation [28,100]. Therefore, a catalyst with high concentration of oxygen vacancies as well as weak metal-intermediate bond strength can perform well for the RWGS reaction. Based on the available literature, we propose that the mechanistic differences on the different metal oxide supports can be traced back to the presence or absence of surface hydroxyl groups. Hydroxyl groups adsorb CO2 to form oxygen-hydrogenated intermediate products, whereas in the absence of these hydroxyl groups, CO is formed in a redox mechanism without intermediate formation.

4. Cu-based spinel oxides and spinel-type mixed oxides are particularly promising for CO2 hydrogenation reactions due to their high activity and stability [81,143]. The observed high activity is caused by a high number of oxygen vacancies and high concentration of Cu2+ ions, which can potentially form well-dispersed Cu sites for hydrogen adsorption [27,28,144]. However, the high calcination temperatures that are needed for the formation of this phase leads to the reduction of...
the surface area of the active phase, which limits the activity of the catalyst. There are several options to solve this problem. One solution is to stabilize the metals during the calcination process by surface coating, which has been demonstrated very recently [144]. While the surface area can be retained in this method, some deactivation still can be noticed. Another potential solution for hindering the Cu sintering process is to use perovskite structure, which can be reactivated through an oxidation-reduction sequence. These options can be further explored in future studies on catalyst design for the RWGS reaction.

The findings of these studies will be essential for designing potential catalysts, which are not only active, stable, and selective, but also cost effective and suitable for commercialization.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

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