**Abstract:** Increasing demand for CO$_2$ utilization reactions and the stable character of CO$_2$ have motivated interest in developing highly active, selective and stable catalysts. Precious metal catalysts have been studied extensively due to their high activities, but their implementation for industrial applications is hindered due to their elevated cost. Among the materials which have comparatively low prices, transition metal carbides (TMCs) are deemed to display catalytic properties similar to Pt-group metals (Ru, Rh, Pd, Ir, Pt) in several reactions such as hydrogenation and dehydrogenation processes. In addition, they are excellent substrates to disperse metallic particles. Hence, the unique properties of TMCs make them ideal substitutes for precious metals resulting in promising catalysts for CO$_2$ utilization reactions. This work aims to provide a comprehensive overview of recent advances on TMCs catalysts towards gas phase CO$_2$ utilization processes, such as CO$_2$ methanation, reverse water gas shift (rWGS) and dry reforming of methane (DRM). We have carefully analyzed synthesis procedures, performances and limitations of different TMCs catalysts. Insights on material characteristics such as crystal structure and surface chemistry and their connection with the catalytic activity are also critically reviewed.

**Keywords:** CO$_2$ utilization; carbide catalysts; low-carbon catalysis; CO$_2$ hydrogenation; reforming

1. Introduction

With the development of modern society, the amount of CO$_2$ emitted in human activities is growing and cannot be balanced by global fixation. As a result, the concentration of CO$_2$ in the atmosphere has kept steadily increasing in the last 200 years, rising to 380 ppm from ca. 270 ppm in the pre-industrial era [1]. The increased concentration of CO$_2$ caused a series of environmental issues, such as global warming and ocean acidification [2]. Among the various artificial solutions, the different forms of CO$_2$ utilization can be divided into two categories: the first one is direct utilization of CO$_2$ (physical routes), such as dry ice, fire extinguisher, welding, foaming, and propellants, as well as the use of supercritical CO$_2$ as a solvent [3,4]. In addition to these small-scale applications, it can also be used in large-scale industries to boost processes in enhanced oil recovery (EOR) [5,6], enhanced gas recovery (EGR) [7,8] and enhanced geothermal systems (EGS) [9–11]. In the above applications, the CO$_2$ molecule does not crack or react with other reactants. The physical utilization of CO$_2$ is illustrated in the left-hand side of Figure 1 [12].
Converting CO2 into valuable chemicals and fuels is another one of the practical routes (chemical routes) for reducing CO2 emissions (as shown in the right-hand side of Figure 1). In terms of these CO2 fixation processes, some reactions such as reverse water gas shift (rWGS, Equation (1)), CO2 methanation (Equation (2)), dry reforming of methane (DRM, Equation (3)), and CO2 selective hydrogenation (Equation (4)) have been studied extensively.

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H = 41 \text{ kJ/mol} \quad (1)
\]

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165 \text{ kJ/mol} \quad (2)
\]

\[
\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H = 247.3 \text{ kJ/mol} \quad (3)
\]

\[
\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H = -53.7 \text{ kJ/mol} \quad (4)
\]

With regard to products of these reactions, there are three main different valuable molecules that can be obtained: CH4, CO and methanol. From the energetic point of view, methane is an excellent fuel, with higher volumetric energy content than hydrogen [13]. CO can be added to hydrogen (leading to H2/CO mixtures aka syngas) to form methanol or liquid hydrocarbons by Fischer–Tropsch synthesis (FTS). Then, the products of FTS can be used as synthetic fuel [14]; and methanol can be used as one of the alternatives to fossil fuels and help decrease the pollutant emissions [15].

Currently, these reactions all share a common problem: they all occurred in conjunction with side reactions. In addition, from the perspective of thermodynamics, some CO2 utilization reactions such as rWGS and DRM are endothermic reactions which are favoured at high temperatures, whereas the others are exothermic, such as CO2 methanation. Although the exothermicity of methanation favours the reaction taking place at low temperature it is still a complex process with high kinetic barrier involving an eight-electron reduction process [13]. Therefore, considerable efforts have been made by the catalysis community to develop thermally stable catalysts with high activities and selectivities for all the described gas-phase CO2 utilization processes.

Normally, highly effective catalysts are composed of well isolated and dispersed active nanoparticles supported on the carrier materials, and both the active phase and support can be involved in the CO2 utilization chemistry [16]. Among the active sites and support materials, metal oxide is the...
most common category for CO\textsubscript{2} utilization reactions due to its reducibility and high intrinsic activity towards CO\textsubscript{2} adsorption [16]. Many metal oxides such as CeO\textsubscript{2} [17–25], ZrO\textsubscript{2} [19,24,25], TiO\textsubscript{2} [26,27], Al\textsubscript{2}O\textsubscript{3} [28,29] have been studied in depth showing promising results.

Aside from metal oxide catalysts, numerous endeavours have been made in the search for new active catalysts. Since transition metal carbides (TMCs) have properties similar to Pt-group precious metals, these materials have received considerable attention in catalysis [30]. Besides, many studies show that TMCs are a promising class of catalysts in a wide range of reactions like reforming [31], hydrogenation [32], and CO oxidation [33]. Hence, they are believed to have a positive function for the CO\textsubscript{2} utilization process and many research projects revolving around TMCs catalysts have been launched.

However, despite the surge in investigations dealing with TMCs catalysts, conclusive overviews concerning the catalytic performance of TMCs towards CO\textsubscript{2} utilization process are relatively scarce. Hence the genesis of this work was to address this literature gap by providing a comprehensive overview of recent advances on TMC catalysts. Our discussion will be divided into three sections: Firstly, the general properties of TMCs are carefully presented. Then, different TMCs catalysts are listed by category. The synthesis procedures, enhanced performances and limitations of listed TMCs catalysts are critically reviewed and hence a better understanding of how TMCs catalysts works can be obtained. To make it easier to compare, a summary table and conclusions are provided at the end of the analysis.

2. General Properties of Transition Metal Carbides (TMCs)

Historically, in 1973, Levy and Boudart first discovered that the addition of carbon to tungsten modified the electronic properties of the metal, leading to behaviour similar to Pt-group metals [30]. Clearly, transition metal carbides altered physical and chemical properties from the parent metals due to the incorporation of carbon in the metal lattice [34]. In most cases, the formation of carbides appears to “tame” the high chemical activity of the transition metal surfaces and reduces the degree of interaction between adsorbates and TMC surfaces, leading to a modified surface activity that more closely resembles the Pt-group metals than the parent metals [35]. It is well known that precious metals are highly active catalytic materials; hence, interest in the catalytic properties of TMCs has been inspired by their “Pt-like” properties. However, subsequent studies have revealed that the description of “Pt-like” oversimplifies the chemical and catalytic properties of the TMCs surface. In reactions involving the transformation of C–H bonds of hydrocarbons, such as dehydrogenation and hydrogenation, the catalytic performances of TMCs are approaching or surpassing those of Pt-group metals. For instance, in the case of the selective dehydrogenation of cyclohexene to produce benzene, the desorption temperature and the desorption mechanism on TMCs are different to those on the Pt-group metal surfaces [36]. In addition, the TMCs surfaces are more active than the Pt-group metal surfaces in reactions involving oxygen-containing molecules [37].

Despite these studies having revealed that the reaction pathways towards TMCs catalysts are significantly different between TMCs and Pt-group metals, research dealing with catalytic behaviour of TMCs and its similarities to Pt-group is still underway. Compared with transition metals and carbon, TMCs can not only offer metallic conductivity, but also exhibit excellent catalytic activity. Indeed, some intriguing physical and chemical properties of TMCs have been found. They exhibit extreme hardness, very high melting points, simple crystal structures, electrical and thermal conductivities and good corrosion resistance [38–40]. These properties have been viewed as resulting from a combination of those of covalent solids, ionic crystals, and transition metals [41–43]. The combination of such properties has led to numerous technical applications and theoretical investigations, with most efforts focusing on the catalytic activity of TMCs [44]. For example, Mo\textsubscript{2}C was proved to have great catalytic performance for NH\textsubscript{3} decomposition [45]. Metal-semiconductor Mo/Mo\textsubscript{2}C/N-CNFs hybrids were used as heterojunction electrocatalysts with satisfied hydrogen evolution reaction (HER) performance [46]. Phase-pure \(\epsilon\) \((\epsilon\))-Fe\textsubscript{2}C catalysts was shown to be a stable and selective catalyst for the Fischer–Tropsch
(FT) reaction [47]. Furthermore, TMCs have generated interest in the fields of capacitors and batteries both experimentally and theoretically in recent years [48–50]. The TMCs are excellent supports for the dispersion of metals [51]. Since the addition of promoting metal species to supports can further improve performance by attenuating the structural and electronic properties of the catalyst [52], the combination of active metals and TMC supports provides lots of possibilities for the design of catalysts. However, it is worth noting that TMCs can be used not only as supports, but also as active sites or promoters.

Transition metals are known as a big group, for the categories of carbide formation, it is fairly common among the transition metals, except for the second and third rows of the group VIII (as shown in Figure 2) [41].

![Transition metal carbide formation in periodic table](image)

**Figure 2.** Transition metal carbide formation in periodic table. Blue: Transition metal carbides; Red: elements that do not form carbide.

Among these TMCs, some TMCs have been proved to be active in CO\textsubscript{2} upgrading fields, such as Mo\textsubscript{2}C [53–55], Fe\textsubscript{x}C [56], TiC [42] and WC [57], others are less active or not active at all [58]. Hence, the properties of TMCs which can be used as descriptors for carbide activities towards CO\textsubscript{2} conversion attract lots of attention. Previous studies show that the carbon to metal ratio could be served as an important descriptor [59] because metal carbides with a carbon/metal ratio below one are highly reactive towards CO\textsubscript{2} easily breaking its C–O bonds [42]. By contrast, carbides with a higher content of carbon such as TiC and MoC are less active [60,61]. However, this descriptor is not so practical because many TMCs have a metal to carbon ratio of 1, which means the value cannot be used to predict their activity. Recently, Porosoff and co-workers proposed a more appropriate descriptor: oxygen binding energy (OBE). Because oxy-carbide formation and the subsequent removal of oxygen are critical steps in completing the catalytic cycle of CO\textsubscript{2} conversion, it is likely that the strength of the interaction of oxygen with the TMCs surface plays an important role for controlling the catalytic activity. They found that the TMCs with high OBE do not allow facile removal of oxygen from the surface to complete the catalytic cycle for CO\textsubscript{2} reduction, such as TiC. Meanwhile, TMCs with lower OBE, such as Mo\textsubscript{2}C, are more active because they allow both the adsorption and subsequent removal of oxygen from CO\textsubscript{2} dissociation [62,63]. So far, Mo\textsubscript{2}C and WC were the most stable and investigated carbides within the TMCs catalysts family [57]. The performance and characterization of each specific catalyst will be detailed as listed in the following section.

3. TMC Catalysts

3.1. Molybdenum Carbide

Among the available TMCs, molybdenum carbide is a popular one because of its dual functionality for H\textsubscript{2} dissociation and C=O bond scission. Normally, it has a variety of crystal structures, such as α-MoC\textsubscript{1–x}, β-Mo\textsubscript{2}C, γ-MoC, η-MoC. Among these four different molybdenum carbides, β-Mo\textsubscript{2}C,
γ-MoC and η-MoC have very similar hexagonal crystal structures but different stacking sequences. The cubic α-MoC1-x is isostructural with NaCl which has an ABCABC stacking sequence (Table 1).

| Phase             | Structures | Stacking Sequence | Crystal View |
|-------------------|------------|-------------------|--------------|
| α-MoC1-x (NaCl type) | Cubic     | ABCABC             | ![Image](image1) |
| β-Mo2C (Fe2N type)          | Hexagonal | ABAB              | ![Image](image2) |
| γ-MoC (WC type)           | Hexagonal | AAAA              | ![Image](image3) |
| η-MoC (MoC type)          | Hexagonal | ABCABC             | ![Image](image4) |

From a catalysis point of view, the most common types are β-MoCy (y = 0.5) and α-MoC1-x (x < 0.5) with a face-centred cubic structure [65]. Both of them have been proven to be highly effective and selective catalysts for CO₂ upgrading reactions.

β-Mo₂C is capable of strongly binding and subsequently dissociating CO₂ [66]. As for rWGS shift reaction, Porosoff et al. synthesized β-Mo₂C and Co-Mo₂C catalysts via impregnation method and tested them at 300 °C. PtCo/CeO₂ (6.6%) and PdNi/CeO₂ catalysts were tested at same condition for sake of comparison. The performance of these four catalysts can be seen below (Table 2). Compared with traditional metal-oxide PtCo/CeO₂ and PdNi/CeO₂ catalysts, Mo₂C exhibit better performance in both CO₂ conversion and CO selectivity. The better performance is attributed to the ability of Mo₂C to break the C=O bond, as well as to dissociate hydrogen to either perform hydrogenation of CO₂ or remove oxygen from Mo₂C-O. Thereafter, the catalytic performance of Mo₂C was further improved by impregnating Co. As shown in Table 2, the addition of 7.5 wt % Co to Mo₂C leads to an increase in conversion from 8.7% to 9.5% while the CO:CH₄ ratio improves from 15 to 51. The enhanced performance is assigned to an amorphous CoMoₓCᵧOz formed after reduction, which has been identified as the critical active phase that dissociates CH₄ and CHₓ intermediate that leads to CO formation [2].

| Catalyst         | CO₂ Conversion (%) | TOF (min⁻¹) | CO:CH₄ Ratio |
|------------------|--------------------|-------------|--------------|
| PtCo/CeO₂        | 6.6                | 14.6        | 4.5          |
| PdNi/CeO₂        | 2.5                | 5.6         | 0.6          |
| Mo₂C            | 8.7                | 25.7        | 14.5         |
| Co-Mo₂C         | 9.5                | 16.1        | 51.3         |

Table 1. Information of four phase of molybdenum carbide adapted with permission from [64].

Table 2. Summary of conversion, turnover frequency (TOF) and selectivity of selected bimetallic catalysts, Mo₂C and 7.5 wt % Co-Mo₂C, adapted with permission from [2].
Normally, Cu-oxide catalysts have a tendency to deactivate dramatically in the rWGS reaction due to the aggregation of supported copper particles at high temperatures. Since Mo$_2$C is an excellent substrate to disperse metal, Zhang et al. developed a series of Cu/β-Mo$_2$C with different Cu contents and compared the performances of Cu/β-Mo$_2$C catalysts with a Cu catalyst with a reference oxidic material (36 wt % Cu/ZnO/Al$_2$O$_3$). The results show that the optimized Cu loading is 1 wt %, excessive Cu leads to the gradual drop of activity. Meanwhile, 1 wt % Cu/β-Mo$_2$C exhibits superior activity over Cu/ZnO/Al$_2$O$_3$ under relatively high weight hourly space velocity (WHSV = 300,000 mL/g/h) over the whole temperature range (300–600 °C). The stability of 1 wt % Cu/β-Mo$_2$C catalyst is also excellent. It maintains 85% of its initial activity after 40 h under conditions of WHSV = 300,000 mL/g/h at 600 °C. In comparison, the Cu/ZnO/Al$_2$O$_3$ catalyst loses more than 60% of its original activity (from 42.5% to 15%) within 15 h reaction under the same reaction conditions. The excellent stability and activity of Cu/β-Mo$_2$C can be ascribed to the strong interaction between Cu and β-Mo$_2$C which effectively promotes the dispersion of supported copper and prevents the aggregation of Cu particles [67]. In order to explore the influence of different metal sites in the rWGS reaction, Xu et al. prepared Cu/Mo$_2$C, Ni/Mo$_2$C and Co/Mo$_2$C and compared the CO$_2$ conversion and CO selectivity among these catalysts. The CO selectivity decreases following the sequence: Cu/Mo$_2$C > β-Mo$_2$C > Ni/Mo$_2$C > Co/Mo$_2$C [68]. By contrast, the conversion of CO$_2$ on these four catalysts increased following the sequence: Cu/Mo$_2$C < β-Mo$_2$C < Ni/Mo$_2$C < Co/Mo$_2$C. As regards this totally opposite trend, the author considers that there is a clear tendency towards the cleavage of both C–O bonds in the molecule when Ni/Mo$_2$C and Co/Mo$_2$C catalysts have been used in this reaction. Hence, the CO$_2$ conversion and CH$_4$ selectivity increased but the selectivity of CO decreased. The function of Cu in the carbide catalyst is to prevent the cleavage of both C–O bonds in the reactant molecule. Therefore, the CO selectivity towards Cu/Mo$_2$C is the highest compared to the remaining three. Aside from Cu, Ni and Co, alkali metals have proved to be active in the CO$_2$ utilization process because their CO$_2$ adsorptive capacity [69]. In our recent work, a series of novel multi-component Cs-doped catalysts (Cs-Mo$_2$C, Cu-Cs-Mo$_2$C) for CO$_2$ conversion via rWGS reaction have been developed [31]. The catalytic performance and the physicochemical properties of these two catalysts have been compared to reference materials (Cu-Mo$_2$C, β-Mo$_2$C and a commercial Mo$_2$C). All the studied catalysts were tested at the feed gas mixture of H$_2$: CO$_2$ = 4:1 at a constant WHSV of 12,000 mL g$^{-1}$ h$^{-1}$. The performance of all the tested catalysts can be seen below (Figure 3). Cs-Mo$_2$C catalyst reaches 100% CO selectivity in the low-temperature range (400–500 °C) that the key asset of this catalysts is the electropositive character of Cs which facilitates the electronic transfer from Cs to Mo and leads to an electronically rich surface which favours the selectivity towards CO. Co-containing materials and β-Mo$_2$C catalyst show very similar conversion levels. However, in terms of the selectivity, Cu-Mo$_2$C has higher selectivity to CO than that of β-Mo$_2$C and Cu-Cs-Mo$_2$C. This is because of the presence of Cu$^+$ and Cu$^{0}$ species in the Cu-Mo$_2$C which favours the rWGS reaction. Cu$^{0}$ provides the active sites to dissociate CO$_2$ and the role of Cu$^+$ is to stabilize the intermediate formate species when the formate mechanism prevails over the redox or takes place simultaneously. For the surface of Cu-Cs-Mo$_2$C, the concentration of Cu$^{2+}$ species increased notably; however, Cu$^{2+}$ species do not favour the rWGS reaction. Hence, the richer concentration of Cu$^{2+}$ species on the Cu-Cs-Mo$_2$C surface accounts for its poorer CO selectivity.

Liu et al. proved that polycrystalline α-Mo$_2$C is also an economically viable, highly efficient, and selective catalyst for CO generation using CO$_2$ as a feedstock via rWGS reaction. A CO$_2$ conversion of about 16% with CO selectivity of 99.5% was achieved at 400 °C at a CO$_2$/H$_2$ = 1/1 reaction mixture. Besides, the formation of CO was observed when CO$_2$ contacts with the α-Mo$_2$C catalyst even at a very low temperature (35 °C). The authors monitored CO and CO$_2$ adsorption by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature-programmed desorption (TPD), microcalorimetry and a series of density functional theory (DFT)-based calculations. The computational results show that the phenomenon can be explained by the presence of Mo$_2$C (201)-Mo/C (displaying Mo and C surface atoms) and Mo-terminated Mo$_2$C (001)-Mo surface facets. Very low energy barriers were obtained by DFT on these two surface facets. However, an ab initio thermodynamics
Beyond the rWGS reaction, molybdenum carbide can be used in CO₂ methanation too. Yao et al. synthesized Ni-Mo₂C/Al₂O₃ catalysts via a temperature-programmed method; Ni-Mo/Al₂O₃ catalyst was prepared for comparison. The CO₂ conversion within the CO₂ methanation for the Ni-Mo₂C/Al₂O₃ increased from 1.8% to 27.3% when temperature increased from 250 °C to 500 °C while the CO₂ conversion for the reference Ni-Mo/Al₂O₃ only increased from 1.2% to 22.3%. Meanwhile, the CH₄ selectivity for Ni-Mo₂C/Al₂O₃ was higher than 86% among all temperature range while the selectivity for the Ni-Mo/Al₂O₃ catalysts was lower than 25%. Hence there is clear connection between the carbide structure and the enhanced CO₂-methanation performance is deemed to be ascribed to the carburization process. Generally, carburisation enhances the basicity of the resulting Ni-Mo₂C/Al₂O₃ catalyst and thus CO₂ absorption/activation on its surface is favoured [70].

CO₂ selective hydrogenation (Equation (4)) can be catalysed by molybdenum carbide too. A series of DFT calculations towards β-Mo₂C (001) and δ-MoC (001) were conducted by Posada-Pérez et al. The DFT results indicate that Mo-terminated β-Mo₂C (001) surface can provoke the spontaneous cleavage of a C–O bond in CO₂ and carbon monoxide formation. Hence, this surface is active for the hydrogenation of CO₂ to CO, methanol and methane. By contrast, δ-MoC does not dissociate C–O bonds on its own, but it binds CO₂ better than transition metal surfaces and is an active and selective catalyst for the CO₂ +3H₂ → CH₃OH + H₂O reaction [71]. In order to explore the relationship between the metal/carbon ratio of TMC catalysts and methanol selectivity, experimental data was collected from the hydrogenation of CO₂ on the β-Mo₂C (001), δ-MoC (001) and TiC (001) surface. Only CO and methanol were detected on the surface of δ-MoC (001) and TiC (001). By contrast, the products of a large amount of methane in addition to CO and methanol were observed on the sample of β-Mo₂C (001). It is clear that there is no methane formation on the system in which the carbide has a metal/carbon ratio of 1. Hence, δ-MoC (001) and TiC (001) was considered as a more selective support than β-Mo₂C (001) towards methanol synthesis. A new set of Au/δ-MoC and Cu/δ-MoC catalysts were subsequently synthesized and it turns out that they are highly active, selective, and stable for the reduction of CO₂ to CO with some further selective hydrogenation toward methanol [59].

Molybdenum carbides are also extremely active and stable catalysts for the dry reforming of methane (DRM) to produce synthesis gas using stoichiometric feedstock. Liang et al. proved that the phase of the molybdenum carbides obtained considerably depended on the precursor preparation method and flowing gas composition. In addition, α-MoC₁₋ₓ phase showed better stability than β-Mo₂C phase in the DRM reaction. According to their research, under flowing Ar gas, the precursors...
prepared by ion-exchange (IE), incipient wetness impregnation (IWI) and mechanical mixture (MM) methods were transformed into a α-MoC$_{1-x}$, α-MoC$_{1-x}$/β-Mo$_2$C mixture and β-Mo$_2$C, respectively. However, under flowing H$_2$ gas, all the precursors were converted to β-Mo$_2$C, regardless of the precursor preparation method. The illustrating figure can be seen below (Figure 4). In the sequent test, the catalyst prepared by ion-exchange at 900 °C at Ar (IE-Ar-900 catalyst) showed high activity (~87% CH$_4$ conversion, ~94% CO$_2$ conversion and ~82% H$_2$ selectivity) and stability within 12 h. By contrast, under the same test condition, the performance of catalysts prepared by incipient wetness impregnation and mechanical mixture at 900 °C at Ar (IWI-Ar-900 and MM-Ar-900 catalysts) showed a gradual decline and rapid decline, respectively. Since the main Mo carbide phases in these three samples are α-MoC$_{1-x}$, mixed-phase α-MoC$_{1-x}$ and β-Mo$_2$C, single-phase β-Mo$_2$C, respectively, the results indicated that the carbide catalyst stability ranked in the order of α-MoC$_{1-x} >$ mixed-phase α-MoC$_{1-x}$ and β-Mo$_2$C >β-Mo$_2$C. The authors proposed the following explanation: it was widely accepted that there were two possible mechanisms of DRM, the redox mechanism, and the noble metal-type mechanism. The noble metal type mechanism is preferable for DRM over carbide catalysts. Meanwhile, the contribution of the noble metal-type mechanism to the DRM activity on the α-MoC$_{1-x}$ was more than that on the β-Mo$_2$C, which accounted for the fact that the former showed better stability than the latter [72].

**Figure 4.** Schematic illustrating the reaction pathways during the carburization of different Mo oxide precursors in Ar or H$_2$ gas reproduced from reference [72] with permission from The Royal Society of Chemistry.

York et al. explored the relationship between DRM test pressure and stability of Mo$_2$C catalysts. The catalytic performances in DRM towards β-Mo$_2$C with different pressure were tested. The conversion of CH$_4$ can reach 92.4% at 847 °C under conditions of gas hourly space velocity (GHSV) = 2.8 × 10$^3$ h$^{-1}$ at 1 bar. However, when the pressure was set at 8.3 bar the sample displayed a conversion drops to 62.5%. Interestingly, at ambient pressure catalyst deactivation occurred, and this was clearly observed after 8 h. This is because the initial β-Mo$_2$C was converted to MoO$_2$, which has only very low activity for DRM reaction. By contrast, when the experiment was run at slightly elevated pressure (about 8 bar), high activity was maintained for the duration of the experiments (typically 144 h) with no bulk carbon deposition occurring on the catalyst [73]. Sometimes, the ratio of metal sites and Mo will also influence the deactivation of Mo$_2$C catalysts in DRM reaction. Shi et al. studied DRM over Ni-Mo$_2$C catalysts with Ni/Mo molar ratios of 1/3, 1/2, and 1/1 (denoted as Ni-Mo$_2$C (1/3), Ni-Mo$_2$C (1/2), and Ni-Mo$_2$C (1/1), respectively). Characterizations of the spent samples revealed that the deactivation of Ni-Mo$_2$C (1/1) was due to coke formation whereas that of Ni-Mo$_2$C (1/3) was due to bulk oxidation of Mo$_2$C into MoO$_2$. The CO$_2$ conversion over these two catalysts in the DRM reaction decreased a lot after less than 4 h testing. Only at a Ni/Mo molar ratio of 1/2, a catalytic oxidation–reduction cycle could be established [74].

In summary, as one of the most popular TMC catalysts, molybdenum carbides can be used as both supports and active sites in different CO$_2$ utilization process, such as DRM, RWGS, CO$_2$ methanation and methanol synthesis. When it was used as support, the addition of active metals can improve
the catalytic activity and sometimes lead the reaction to different products. Some other factors also have combined effects in the catalytic performance, such as the ratio of active metal sites and Mo, the different phases, the metal/carbon ratio of the molybdenum carbides, and testing conditions.

3.2. Tungsten Carbide

Since 1973, when Levy and Boudart reported that α-WC displayed reactivity similar to Pt for neo-pentane isomerization, tungsten carbide catalysts started to attract a lot of attention [20]. Unlike molybdenum carbides that can be used in a variety of reactions, tungsten carbides are mainly applied in DRM. They show high DRM activity and good resistance to coke formation. According to some precious literatures, the relative activities of a number of the DRM catalysts were established to be Mo2C > Ir > WC > Pd > Pt (reaction pressure = 2 bar) and Mo2C = WC > VC > NbC > TaC (reaction pressure = 8.0 bar) [75].

Yao et al. compared the different performance of Ni-WC and Ni-Mo2C with various Ni/M (M = Mo and W) molar ratios for DRM. The results are as shown below (Figure 5). For the Ni-WC and Ni-Mo2C catalysts with high Ni/M molar ratios (1:2 and 1:9), the catalytic performance and stability are similar during the test period. However, the performance of Ni-Mo2C with 1:21 Ni/M ratio decreased rapidly after 5 h, whereas the performance of Ni-WC with same Ni/M ratio remained active and stable over a 12 h test. The superior stability of Ni-WC is attributed to the better ability of Ni-WC to keep control of the crystal structure than the Ni-Mo2C (1/21) catalyst in the DRM reaction. As pointed out by many researchers, bulk oxidation of Mo2C into MoO2 is the main reason for deactivation of Ni-Mo2C, but Ni-WC (1/21) remained resistant to oxidation. In addition, severe sintering of Ni-Mo2C particles occurred during the high-temperature DRM reaction. As for Ni-WC particles, there was no obvious size change after reaction, which could also account for their stable catalytic performance [75].

![Figure 5. Lifetime study of the Ni-Mo2C and Ni-WC catalysts with various Ni/M (M = Mo and W) ratios in dry reforming of methane (DRM) (T = 800 °C, P = 1 bar, CH4/CO2 = 1, and weight hourly space velocity (WHSV) = 6000 cm3g−1h−1) reproduced from reference [75] with permission from The Royal Society of Chemistry.](image)

In order to investigate the morphological impacts on the catalytic performance for DRM reaction, two geometries of tungsten carbide nanomaterials, nanorods, and nanoparticles with different exposed facets were synthesized by Mounfield et al. γ-Al2O3 was chosen as the support due to its high thermal and mechanical stability. Reactions were carried out under a mixture of 1:1 CH4/CO2 with a total flow rate of 30 mL/min at 900 °C and 1 bar. The results show that β-W2C nanoparticles maintained high activity and exhibited less coke formation for more than 40,000 turnovers, while α-WC nanorods began to deactivate after only 8000 turnovers. The extraordinary stability can be assigned to the inherent disorder and presence of carbon vacancies in the β-W2C phase nanoparticles. By contrast, α-WC nanorods do not have the same degree of defects. These inherent carbon vacancies in the carbide lattice likely facilitate the oxidation/recarburation reaction that leads to higher activity while preserving the active catalyst and minimizing coke deposition [76].
Yan et al. synthesized tungsten-promoted biochar by impregnation method. The catalytic performance of DRM towards the tungsten-promoted biochar catalyst has been tested at a CH$_4$/CO$_2$ ratio of 1, 5 bar and GHSV of 6000 h$^{-1}$. Low feed conversion (8.9% for CH$_4$ and 20% for CO$_2$) was observed at a low temperature (600 °C). When the temperature reached at 750 °C, the conversion of CO$_2$ and CH$_4$ increased to 65% and 33% respectively. In addition, the catalyst was found to be very stable at 850 °C for a period of over 500 h (Figure 6). The CH$_4$ and CO$_2$ conversions decreased steadily during the first 20 h at 850 °C and then stabilized at 93% and 83%, respectively, with a CO yield of 91% and a H$_2$/CO ratio after 500 h run-time remaining at around 0.87–0.91. The extraordinary stability of the WC/biochar catalyst could be explained by the transmission electron microscopy (TEM) result. The spent WC/biochar catalyst sample showed that the particles were more uniform with size range 5–10 nm after 500 h testing, and no significant sintering of WC nanoparticles and coking on the WC nanoparticles was observed [58]. As a caveat it should be mentioned that the stability tests was conducted under conditions not really far from equilibrium conversions so the apparent stability should be taken with caution.

![Figure 6](image.png)

**Figure 6.** The lifetime test of DRM over the tungsten carbide nanoparticle in biochar matrix at 850 °C, 5 bar, gas hourly space velocity (GHSV) of 6000 h$^{-1}$ and a constant feed CH$_4$/CO$_2$ ratio of 1 reproduced from reference [58] with permission from The Royal Society of Chemistry.

Some bimetallic transition metal carbides are also active for DRM. The catalytic performance of cobalt tungsten carbide was explored by Shao et al. Co$_6$W$_6$C catalyst was tested at temperature range from 500 °C to 850 °C and then back down to 500 °C. It turns out that this catalyst is ineffective below 850 °C. This is because the surface oxidation happened during the low temperature range reaction (500 °C–850 °C), Co$_6$W$_6$C on the surface is converted to metallic oxide(s) (CoWO$_4$) (Equation (5)). The oxides are ineffective for DRM.

$$\text{Co}_6\text{W}_6\text{C} + (26-x)\text{Os} \leftrightarrow 6\text{CoWO}_4 + x\text{CO} + (1-x)\text{CO}_2 \quad (5)$$

However, during the reaction process at 850 °C or greater, the material goes through a transformation to an active phase containing Co, WC, and C as bulk phases (Equation (6)).

$$\text{CoWO}_4 + 2\text{CH}_4 \leftrightarrow \text{Co} + \text{WC} + \text{C} + \text{H}_2\text{O} \quad (6)$$

Once these phases are formed, the material is active, selective and stable even at lower temperatures. As can be seen from Figure 7, it takes around 30 h for the catalyst to finish stabilization. During the unstable periods, the carbon balance value increased from 70% to 90%. The 20% difference is probably caused by the carbon deposition on the surface of the catalysts.
In addition, tungsten carbide can be used in rWGS reaction. Unpromoted and alkali metal promoted WC supported on high surface area γ-Al₂O₃ (WC/γ-Al₂O₃) were studied for the low-temperature rWGS reaction by Morse et al. The activity and selectivity for the synthesized catalysts were tested for the rWGS at 350 °C with a weight hourly space velocity (WHSV) of 1.01 mL g⁻¹ s⁻¹ and an H₂: CO₂ ratio of 3:1 at a pressure of 20 bar. The CO₂ conversion over WC/γ-Al₂O₃ and K-WC/γ-Al₂O₃ are 24.3% and 20.3%, respectively, which are commendable results given the selected low temperatures. However, the CO selectivity towards K-WC/γ-Al₂O₃ (98.1%) is more than 10% higher than the value over WC/γ-Al₂O₃ (88%). Such changes to catalyst performance may be rationalized by structural and electronic effects from the addition of alkali metal promoters. Scanning electron microscopy (SEM) reveals significant differences in the morphology of the catalysts (Figure 8). As for unpromoted WC/γ-Al₂O₃, clear segregation between tungsten-rich regions and the γ-Al₂O₃ support can be observed. On the other hand, the K-promoted catalysts are composed of much smaller, better dispersed tungsten-rich regions. In addition, X-ray photoelectron spectroscopy (XPS) results indicates a greater extent of carburization of the K-promoted catalysts, pointing out that potassium acts as a structural and electronic promoter, attenuating surface chemistry and catalyst dispersion, while increasing the extent of tungsten carburization [78].

**Figure 7.** Catalytic performance of Co₆W₆C at 850 °C and 3.4 bar adapted with permission from [77]
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In most instances, iron carbide is known to catalyse the Fischer–Tropsch synthesis [79–82] and it is believed to be the active phase for hydrocarbon production [69,83]. The performance of iron carbide over CO₂ utilization process are less discussed. However, some attempts have been made

**Figure 8.** Scanning electron microscopy (SEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) maps for the “H₂ treated” (A) unpromoted, (B) K-promoted WC/γ-Al₂O₃ reprinted from [78] with permission from Elsevier.

### 3.3. Iron Carbide

In most instances, iron carbide is known to catalyse the Fischer–Tropsch synthesis [79–82] and it is believed to be the active phase for hydrocarbon production [69,83]. The performance of iron carbide over CO₂ utilization process are less discussed. However, some attempts have been made...
to apply this kind of material for CO₂ hydrogenation reactions recently. Liu et al. investigated the CO₂ activation mechanism over thermodynamically stable χ-Fe₅C₂ (510) and θ-Fe₅C (031) facets by performing periodic density functional theory (DFT) calculations. Four major pathways of CO₂ activation were examined, including the direct dissociation of CO₂ and the H-assisted intermediates of *COOH, *HCOO, and *CO + *OH. Both χ-Fe₅C₂ and θ-Fe₅C have proven to be active for CO₂ direct dissociation. CO₂ direct dissociation to *CO and *O is favorable on χ-Fe₅C₂ and θ-Fe₅C. Furthermore, H-assisted pathways exist in parallel. This work indicates that χ-Fe₅C₂ and θ-Fe₅C are promising candidates for direct CO₂ dissociation and hydrogenation with lower activation barriers compared to metallic Fe and magnetite [84].

In addition, iron carbide can be used in CO₂ methanation. As mentioned before, CO₂ methanation is a reversible and exothermic reaction. Although it is thermodynamically favourable at low temperatures, the high kinetic barrier for the activation of CO₂ is the main challenge to achieve high CH₄ yields when a low temperature range is considered [85]. Traditionally, CO₂ methanation is performed in a continuous flow reactor using conventional external heating. Recently, magnetic hyperthermia has been applied in heterogeneous catalysis. The concept is based on the fact that ferromagnetic materials placed in a high-frequency alternating magnetic field release heat through hysteresis losses. Therefore, the heat can be directly and evenly distributed within the catalyst by using magnetic nanoparticles (NPs). Then, the requirement for heating the whole reactor system is no longer needed. Furthermore, the target temperature can be reached by magnetic induction heating in a few seconds [86,87]. Based on this heating system, Kale et al. explored the catalytic performance towards Fe₅ₓCₓ-Ni/SiRAIOₓ or Fe₅ₓCₓ/Co-Ni/SiRAIOₓ catalysts. They demonstrated that combining a magnetically hard (Co NRs) and a magnetically soft material (Fe₅ₓCₓ NPs) as heating agents permit exploiting the soft material to attain a temperature necessary for the hard material to start heating. Therefore, for the combined Fe₅ₓCₓ/Co-Ni/SiRAIOₓ system, excellent catalytic performances (90% of CO₂ conversion and 100% CH₄ selectivity) are achieved even at a very low field, namely 16 mT [56].

### 3.4. Titanium Carbide

As one of the TMCs, TiC can be used as a high active catalyst for the catalytic hydrogenation of CO₂ because it is able to strongly trap and activate CO₂ as the above three TMCs catalysts [63]. Among the methods which can enhance the catalytic activity of TiC, doping is the mostly widely used. This strategy has already been successfully applied to enhance the catalytic performance of metal oxides. The investigations dealing with TiC catalysts can be divided into two categories: theoretical research and experimental study.

For the theoretical research, López et al. firstly investigated the possible effects of surface metal doping of TiC by using transition metal (Cr, Hf, Mo, Nb, Ta, V, W, and Zr) as dopants. According to the periodic slab models with large supercells and state-of-the-art density functional theory (DFT) based calculations, CO₂ adsorption is enhanced by doping with transition metals [88]. After that, the authors explored other possibilities which include non-transition metals elements (Mg, Ca, Sr, Al, Ga, In, Si, Sn) as well as late transition metals (Pd, Pt, Rh, Ir) and lanthanides (La, Ce). As with the results from previous study, the introduction of dopants replacing one Ti surface atom makes significant difference on the CO₂ adsorption properties. In all the studied cases, CO₂ appears as bent and, hence, activated. The effect is especially pronounced for dopants with large ionic crystal radii. The larger the ionic crystal size of the dopant, the larger the CO₂ adsorption energy. This finding provides a useful descriptor that allows one to predict the effect on the adsorption energy of other dopants without needing to carry out any DFT calculation. Hopefully further experimental works can be triggered in this field [89].

For the experimental studies, catalysts combined Au, Cu particles with TiC (001) display a very high activity for the catalytic hydrogenation of CO₂. Vidal et al. found that small Cu and Au particles in contact with a TiC (001) surface undergo a charge polarization that makes them very active for CO₂ activation and the catalytic synthesis of methanol. The apparent activation energy for methanol synthesis decreases from 25.4 kcal/mol on Cu (111) to 11.6 kcal/mol on Cu/TiC (001). The TOFs
Also, the catalytic activities for methanol synthesis between Cu/TiC (001), Au/TiC (001) systems and conventional Cu/ZnO catalysts have been compared in their work. Cu/TiC (001) and Au/TiC (001) systems exhibit better performance than the traditional one, indicating that TiC can be an excellent support for enhancing the ability of noble metals to bond and activate CO2 [90]. After that, Rodriguez et al. explored the specific products of catalytic CO2 hydrogenation over Cu/TiC, Au/TiC, Ni/TiC catalysts. CO is found to be the main product which is produced by rWGS reaction due to the small two-dimensional particles or clusters which were in close contact with TiC. In the cases of Au/TiC (001) and Cu/TiC (001), a substantial amount of methanol is also produced, but no methane is detected. Ni/TiC (001) produces a mixture of CO, methanol, and methane. The authors also proved that the catalytic activities of the admets are highly depended on their coverage on the carbide surface. Small two-dimensional particles or clusters of the admets in close contact with TiC (001) were found to be the most active formation [42]. Since Au/TiC was proved to be active for the rWGS reaction and CO2 hydrogenation to methanol, Asara et al. further explored the catalytic activity of Au/TiC towards the hydrogenation of CO or CO2 with periodic DFT calculations on model systems. The result shows that direct hydrogenation of CO to methanol is hard to achieve on Au/TiC due to the high activation barriers. Hence, when dealing with mixtures of syngas (CO/CO2/H2/H2O), CO could be transformed into CO2 through the WGS reaction with subsequent hydrogenation of CO2 to methanol [91].

3.5. Other Carbides

As noted before, the above four TMCs have been used widely due to their superior performance, some other TMCs catalysts are rarely reported because they are less active or not active in CO2 utilization field. For instance, TaC is almost inactive as CO2 hydrogenation catalysts [92]. However, there are still some relevant references and inspiring results in the less-researched areas, such as the application of cobalt carbide and vanadium carbide.

Kim et al. reported a Na-promoted CoFe2O4 catalysts supported on carbon nanotubes (Na–CoFe2O4/CNT) which exhibited high CO2 conversion (~34%) and light olefin selectivity (~39%), outperforming other reported Fe-based catalysts under similar reaction conditions. The author attributed the superior performance to the facile formation of a unique bimetallic alloy carbide (Fe1-xCox)Sc2 with a Hägg carbide structure, which was the active catalytic site for enhanced activity and preferential chain growth. The carburization reaction was facilitated by Na promoter [93]. In addition to cobalt carbide, two vanadium carbides, one mostly containing stoichiometric VC and the other being C-defective V8C7, were synthesized for the rWGS reaction by a gel-like method by Pajares et al. The rWGS reactions were tested at following conditions: mcat = 150 mg, CO2/H2/N2 = 1/3/1, GHSV = 3000 h−1, p = 1 bar. The sample containing more V8C7 shows a higher CO2 conversion and CO selectivity at all temperature range (350–500 °C), especially at low temperature. DFT calculations confirm that C vacancies in V8C7 are responsible for the observed catalytic behavior, allowing reactants to adsorb more strongly and lowering the energy barrier for both H2 and CO2 dissociation steps [94].

4. Limitations of TMCs

Although TMCs are desirable materials for CO2 utilization reactions due to their extraordinary catalytic properties, some of their inherent properties still hindered the maximization of their performance. For example, the fresh surfaces of most TMCs catalysts are very reactive to air, such as Mo2C [95] and Fe3C [80]. To avoid violent oxidation, passivation on the surfaces of TMCs is a common solution. The majority of the literature on carbide catalysts reports results obtained with carbides that are passivated by flowing low concentrations of O2 in an inert diluent over the fresh carbide, and it is common practice to use 0.5 or 1% O2 [96,97]. However, the degree of oxidation is not always easy to control. Therefore, some other agents and conditions of passivation have been explored. Mehad et al. investigated the toluene hydrogenation activity of Mo2C catalysts which used CO2, H2O or O2 as passivation agents respectively. The result shows that H2O and CO2 are
unsuitable for Mo\textsubscript{2}C passivation in this case because high temperature is required for the passivation process when H\textsubscript{2}O and CO\textsubscript{2} were used as agents. H\textsubscript{2}O reacted with the carbide surface only at 505 °C, and then it removed carbon from the surface at this temperature. CO\textsubscript{2} needed a temperature of 580 °C to dissociate on the surface of molybdenum carbide. At lower temperatures, neither H\textsubscript{2}O nor CO\textsubscript{2} adsorbed strongly enough to passivate the carbide surfaces [95].

In addition, passivation is not always helpful to the catalysts’ performance. Nagai et al. showed that passivation of molybdenum carbide with dilute O\textsubscript{2} reduced its activity for CO\textsubscript{2} hydrogenation to form CO and CH\textsubscript{4} [98]. Hence, in some cases, the elements that have low electronegativity (such as alkali metals) can be used as a promoter to maintain metal carbide in low valence and diminish the impact of passivation. Shou et al. confirm that alkali metal can reduce the sensitivity of the catalyst to passivation by 1% O\textsubscript{2}. The passivation of unpromoted Mo\textsubscript{2}C/Al\textsubscript{2}O\textsubscript{3} decreased the overall activity of the catalyst, whereas passivation of Rb promoted Mo\textsubscript{2}C/Al\textsubscript{2}O\textsubscript{3} did not significantly influence the activity [99]. In our previous work, the addition of Cs in Mo\textsubscript{2}C catalyst has also been proved to have a reduction effect on the surface of the catalysts [33].

5. Conclusions

This overview summarized the recent advance of different TMC catalysts towards gas phase CO\textsubscript{2} utilization processes. The enhanced properties of TMC catalysts and the explanations are gathered in Table 3. From the composition perspective, TMCs could be used as active sites, promoters, and in most cases, supports. The yellow squares in Figure 9 show the elements which can form TMC compounds. Among these TMC materials, Mo\textsubscript{2}C and WC are the most widely studied materials which can be applied directly for CO\textsubscript{2} utilization reactions or combined with active metal sites to form enhanced catalysts. The elements in red squares are the most researched active metals. The combination of different TMCs and active metals could lead to different catalytic activities towards target reactions. The catalytic performance depends on many factors, such as the even distribution of active metals, the electronic interaction between active sites and TMC supports, the carburisation/decarburisation capacity as well as the resistance towards sintering. For a certain active site and TMC support, the catalytic activity is still subjected to many changes, such as the ratio of active site and transition metal, synthesis method and catalyst’s pre-conditioning.

Overall this work showcases the features of TMCs as a very promising family of catalytic materials for CO\textsubscript{2} conversion reactions. Certainly, the transition towards a low-carbon future in the context of a circular economy will rely on sustainable catalytic processes and engineered materials with tuneable properties such as TMCs will play a vital role in addressing this global challenge.

![Figure 9](image-url)
Table 3. Summary of CO₂ utilization process using different transition metal carbide (TMC) catalysts.

| Supports | Active Metals | Promoters | Reactions | Comments |
|----------|---------------|-----------|-----------|----------|
| Al₂O₃    | Mo₂C/Mo       | Ni        | CO₂ methanation | The carburization process enhances the basicity of Ni-Mo₂C/Al₂O₃ and thus CO₂ absorption on their surface [70]. |
| β-Mo₃C, β-Mo₃C and TiC | Mo₂C/Mo       | Ni        | Methanol synthesis | TMC catalysts with a metal/carbon ratio of 1 (β-Mo₃C and TiC) were considered to be more selective than the catalysts with a metal/carbon ratio of 2 (β-Mo₂C) [59]. |
| α-Mo₃C   | Cu            | Cs        | CO₂ methanation | CO₂ dissociation toward CO can happen at ambient temperature at the surface of α-Mo₃C and the presence of Mo₃C (101)-MoC surface facet can be serve as a possible explanation of the observed reactivity [66]. |
| Mo₂C     | Ni            |           | DRM        | Ni-WC is more stable than Ni-Mo₂C in DRM reaction due to the fact that compared with Ni-Mo₂C, the Ni-WC catalysts showed better ability to keep control of crystal structure and better resistance to sintering [75]. |
| SiRAO₃   | Co, Ni        | Fe₂₋₂C   | CO₂ methanation | As a magnetically soft material, Fe₂₋₂C NPs (nanoparticles) can be used as heating agent in a magnetic hyperthermia system for CO₂ methanation [56]. |
| TiC      | Cu, Au        | Ni        | Methanol synthesis | Charge polarization happened between Au, Cu particles and TiC (001) surface makes them very active for CO₂ activation and the catalytic synthesis of methanol [90]. |
| WC Mo₂C  | Ni            |           | DRM        | Uniform particle distribution with little coke formation after 500 h on stream, indicating that the small particle size contributed directly to the stability of the catalyst [58]. |
| γ-Al₂O₃  | α-WC β-W₂C    |           | DRM        | β-W₂C nanoparticles exhibited higher stability than α-WC nanorods due to the inherent disorder and presence of carbon vacancies in the β-W₂C phase nanoparticles which can facilitate the reaction and prevent from coking [76]. |
| biochar  | WC            |           | DRM        | Uniform particle distribution with little coke formation after 500 h on stream, indicating that the small particle size contributed directly to the stability of the catalyst [58]. |
| Co₃W₂C   |               |           | DRM        | Co₃W₂C is ineffective for DRM below 850 °C. It is active after 30 h DRM inlet gas treatment at 850 °C, because Co, WC were formed after the treatment. Co, WC are the actual active phase [77]. |
### Table 3. Cont.

| Supports   | Active Metals | Promoters | Reactions | Comments |
|------------|---------------|-----------|-----------|----------|
| γ-Al₂O₃    | WC            | K         | rWGS      | K acted as a structural and electronic promoter in K-WC/γ-Al₂O₃, attenuating surface chemistry and catalyst dispersion hence improve the CO selectivity in rWGS [78]. |
| CNT        | CoFe₂O₄       | Na        | CO₂ hydrogenation | (Fe₁₋ₓCoₓ)C₂ with a Hågg carbide structure is the active site in the catalyst for enhanced activity and preferential chain growth hence improve the catalytic performance [93]. |
| VC/N₄C₇   |               |           | rWGS      | V₈C₇ shows a higher CO₂ conversion and CO selectivity and C vacancies in V₈C₇ are responsible for the better catalytic behavior [94]. |
Author Contributions: Authors declare equal contributions to all sections of this work. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Department of Chemical and Process Engineering at the University of Surrey and the EPSRC grant EP/R001588/1. LPP acknowledge Comunitat Valenciana for her APOSTD2017 fellowship. This work was also partially sponsored by the CO2Chem through the EPSRC grant EP/P026435/1.

Conflicts of Interest: The authors declare no conflict of interest.

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