

Review



Transition Metal Carbides (TMCs) Catalysts for Gas Phase CO₂ Upgrading Reactions: A Comprehensive Overview

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Received: 21 July 2020; Accepted: 14 August 2020; Published: 20 August 2020



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: CO₂ utilization; carbide catalysts; low-carbon catalysis; CO₂ 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].



Figure 1. Various pathways for CO₂ utilization reprinted from [12] with permission from Elsevier.

Converting CO_2 into valuable chemicals and fuels is another one of the practical routes (chemical routes) for reducing CO_2 emissions (as shown in the right-hand side of Figure 1). In terms of these CO_2 fixation processes, some reactions such as reverse water gas shift (rWGS, Equation (1)), CO_2 methanation (Equation (2)), dry reforming of methane (DRM, Equation (3)), and CO_2 selective hydrogenation (Equation (4)) have been studied extensively.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = 41 \text{ kJ/mol}$$
 (1)

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H = -165 \text{ kJ/mol}$$
⁽²⁾

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \quad \Delta H = 247.3 \text{ kJ/mol}$$
 (3)

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H = -53.7 \text{ kJ/mol}$$
(4)

With regard to products of these reactions, there are three main different valuable molecules that can be obtained: CH_4 , 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 H_2/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 CO_2 utilization reactions such as rWGS and DRM are endothermic reactions which are favoured at high temperatures, whereas the others are exothermic, such as CO_2 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 CO_2 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 CO₂ utilization reactions due to its reducibility and high intrinsic activity towards CO₂ adsorption [16]. Many metal oxides such as CeO₂ [17–25], ZrO₂ [19,24,25], TiO₂ [26,27], Al₂O₃ [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 CO₂ 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 CO₂ 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, Mo₂C was proved to have great catalytic performance for NH₃ decomposition [45]. Metal-semiconductor Mo/Mo₂C/N-CNFs hybrids were used as heterojunction electrocatalysts with satisfied hydrogen evolution reaction (HER) performance [46]. Phase-pure ε (')-Fe₂C 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].

III	IV	V	VI	VII		VIII	
Sఆ⊴C ScC₂ SఴCు	TiC	V2C VC	C123C6 C17C3 C13C2	Mn23C6 Mn3C Mn5C2 Mn7C3	FesC FesC2 Fe2C Fe22C	C03C C02C	Ni3C
Y2C Y2C3 YC2	ZrC	Nb₂C NbC	Mo2C MoC MoC1-x	TeC	Ru	Rh	Pd
LaC ₂	HfC	Ta2C TaC	W2C WC W3C2	ReC	OsC	Ir	Pt

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_2 upgrading fields, such as Mo₂C [53–55], Fe_xC [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 CO₂ 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 CO₂ 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_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 CO₂ reduction, such as TiC. Meanwhile, TMCs with lower OBE, such as Mo₂C, are more active because they allow both the adsorption and subsequent removal of oxygen from CO_2 dissociation [62,63]. So far, Mo₂C 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 H₂ dissociation and C=O bond scission. Normally, it has a variety of crystal structures, such as α -MoC_{1-X}, β -Mo₂C, γ -MoC, η -MoC. Among these four different molybdenum carbides, β -Mo₂C, γ -MoC and η -MoC have very similar hexagonal crystal structures but different stacking sequences. The cubic α -MoC_{1-X} is isostructural with NaCl which has an ABCABC stacking sequence (Table 1).

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

Phase	Structures	Stacking Sequence	Crystal View			
α-MoC _{1-X} (NaCl type)	Cubic	ABCABC				
β-Mo ₂ C (Fe ₂ N type)	Hexagonal	ABAB				
γ-MoC (WC type)	Hexagonal	АААА				
η-MoC (MoC type)	Hexagonal	ABCABC				

From a catalysis point of view, the most common types are β -MoC_y (y = 0.5) and α -MoC_{1-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 CoMoC_yO_z formed after reduction, which has been identified as the critical active phase that dissociates CH₄ and CH_x intermediate that leads to CO formation [2].

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].

Catalyst	CO ₂ Conversion (%)	TOF (min ⁻¹)	CO:CH ₄ Ratio
PtCo/CeO ₂	6.6	14.6	4.5
PdNi/CeO ₂	2.5	5.6	0.6
Mo ₂ C	8.7	25.7	14.5
Co-Mo ₂ C	9.5	16.1	51.3

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_2C is an excellent substrate to disperse metal, Zhang et al. developed a series of Cu/β -Mo₂C with different Cu contents and compared the performances of Cu/β -Mo₂C catalysts with a Cu catalyst with a reference oxidic material (36 wt % Cu/ZnO/Al₂O₃). 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 -Mo₂C exhibits superior activity over $Cu/ZnO/Al_2O_3$ 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 -Mo₂C 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/Al₂O₃ 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 -Mo₂C can be ascribed to the strong interaction between Cu and β -Mo₂C 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/Mo₂C, Ni/Mo₂C and Co/Mo₂C and compared the CO₂ conversion and CO selectivity among these catalysts. The CO selectivity decreases following the sequence: $Cu/Mo_2C > \beta -Mo_2C > Ni/Mo_2C > Co/Mo_2C$ [68]. By contrast, the conversion of CO_2 on these four catalysts increased following the sequence: Cu/Mo_2C $<\beta$ -Mo₂C < Ni/Mo₂C < Co/Mo₂C. 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/Mo₂C and Co/Mo₂C catalysts have been used in this reaction. Hence, the CO₂ conversion and CH₄ 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/Mo₂C 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-Mo₂C, Cu-Cs-Mo₂C) 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-Mo₂C, β -Mo₂C and a commercial Mo₂C). All the studied catalysts were tested at the feed gas mixture of H₂: CO₂ = 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-Mo₂C 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. Cu-containing materials and β -Mo₂C catalyst show very similar conversion levels. However, in terms of the selectivity, Cu-Mo₂C has higher selectivity to CO than that of β -Mo₂C and Cu-Cs-Mo₂C. This is because of the presence of Cu⁺ and Cu⁰ species in the Cu-Mo₂C which favours the rWGS reaction. Cu⁰ provides the active sites to dissociate CO₂ 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-Mo₂C, the concentration of Cu^{2+} species increased notably; however, Cu²⁺ species do not favour the rWGS reaction. Hence, the richer concentration of Cu²⁺ species on the Cu-Cs-Mo₂C surface accounts for its poorer CO selectivity.

Liu et al. proved that polycrystalline α -Mo₂C is also an economically viable, highly efficient, and selective catalyst for CO generation using CO₂ as a feedstock via rWGS reaction. A CO₂ conversion of about 16% with CO selectivity of 99.5% was achieved at 400 °C at a CO₂/H₂ = 1/1 reaction mixture. Besides, the formation of CO was observed when CO₂ contacts with the α -Mo₂C catalyst even at a very low temperature (35 °C). The authors monitored CO and CO₂ 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 Mo₂C (201)-Mo/C (displaying Mo and C surface atoms) and Mo-terminated Mo₂C (001)-Mo surface facets. Very low energy barriers were obtained by DFT on these two surface facets. However, an ab initio thermodynamics consideration of reaction conditions demonstrates that these facets bind CO_2 and CO + O intermediates too strongly for a subsequent removal. In contrast, Mo_2C (101)-Mo/C exhibits balanced binding properties, activating CO_2 well toward dissociation, while a subsequent release of CO seems viable from a thermodynamic point of view. Hence, the further presence of Mo_2C (101)-Mo/C served as an explanation of the observed reactivity [66].



Figure 3. (A) CO₂ conversion (B) CO and CH₄ selectivity for the β -Mo₂C, Cu-Mo₂C, Cs-Mo₂C, Cu-Cs-Mo₂C and commercial Mo₂C.

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].

 CO_2 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 CO_2 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 $CO_2 + 3H_2 - CH_3OH + H_2O$ 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 CO_2 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 -MoC_{1-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 -Mo₂C mixture and β -Mo₂C, respectively. However, under flowing H₂ gas, all the precursors were converted to β -Mo₂C, 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% CH₄ conversion, ~94% CO₂ conversion and ~82% H₂ 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 -Mo₂C, single-phase β -Mo₂C, 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 -Mo₂C > β -Mo₂C. 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 -Mo₂C, 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_2C catalysts. The catalytic performances in DRM towards β -Mo₂C with different pressure were tested. The conversion of CH₄ 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 -Mo₂C was converted to MoO₂, 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 Mo₂C catalysts in DRM reaction. Shi et al. studied DRM over Ni-Mo₂C catalysts with Ni/Mo molar ratios of 1/3, 1/2, and 1/1 (denoted as Ni-Mo₂C (1/3), Ni-Mo₂C (1/2), and Ni-Mo₂C (1/1), respectively). Characterizations of the spent samples revealed that the deactivation of Ni-Mo₂C (1/1) was due to coke formation whereas that of Ni-Mo₂C (1/3) was due to bulk oxidation of Mo₂C into MoO₂. The CO₂ 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 CO₂ utilization process, such as DRM, rWGS, CO₂ 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 to 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, $CH_4/CO_2 = 1$, and weight hourly space velocity (WHSV) = 6000 cm³g⁻¹h⁻¹) reproduced from reference [75] with permission from The Royal Society of Chemistry.

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/recarburization 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 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. 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 CH₄/CO₂ 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_6W_6C 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_6W_6C on the surface is converted to metallic oxide(s) (CoWO₄) (Equation (5)). The oxides are ineffective for DRM.

$$Co_6W_6C + (26-x)Os \leftrightarrow 6CoWO_4 + xCO + (1-x)CO_2$$
(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)).

$$CoWO_4 + 2CH_4 \leftrightarrow Co + WC + C + H_2O$$
(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.



Figure 7. Catalytic performance of Co₆W₆C at 850 °C and 3.4 bar adapted with permission from [77] Copyright (2005) American Chemical Society.

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/y-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 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 CO_2 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 -Fe₃C (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 -Fe₃C have proven to be active for CO₂ direct dissociation. CO₂ direct dissociation to *CO and *O is favorable on χ -Fe₅C₂ and θ -Fe₃C. Furthermore, H-assisted pathways exist in parallel. This work indicates that χ -Fe₅C₂ and θ -Fe₃C 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 CO_2 methanation. As mentioned before, CO_2 methanation is a reversible and exothermic reaction. Although it is thermodynamically favourable at low temperatures, the high kinetic barrier for the activation of CO_2 is the main challenge to achieve high CH_4 yields when a low temperature range is considered [85]. Traditionally, CO_2 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 $Fe_{2,2}C$ -Ni/SiRAIO_x or Fe_{2.2}C/Co-Ni/SiRAlO_x catalysts. They demonstrated that combining a magnetically hard (Co NRs) and a magnetically soft material (Fe_{2.2}C 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 Fe2.2C/Co-Ni/SiRAIO_x 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 CO_2 because it is able to strongly trap and activate CO_2 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 CO_2 . 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 CO_2 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

for methanol production on Cu/TiC (001) are 170–500 times much larger than those on Cu (111). 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 admetals are highly depended on their coverage on the carbide surface. Small two-dimensional particles or clusters of the admetals 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 CO_2 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 CO_2 through the WGS reaction with subsequent hydrogenation of CO_2 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 (Fe_{1-x}Co_x)₅C₂ 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 Fe_xC [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. Mehdad 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 Mo₂C passivation in this case because high temperature is required for the passivation process when H₂O and CO₂ were used as agents. H₂O reacted with the carbide surface only at 505 °C, and then it removed carbon from the surface at this temperature. CO₂ needed a temperature of 580 °C to dissociate on the surface of molybdenum carbide. At lower temperatures, neither H₂O nor CO₂ 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_2 reduced its activity for CO_2 hydrogenation to form CO and CH₄ [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_2 . The passivation of unpromoted Mo_2C/Al_2O_3 decreased the overall activity of the catalyst, whereas passivation of Rb promoted Mo_2C/Al_2O_3 did not significantly influence the activity [99]. In our previous work, the addition of Cs in Mo_2C 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 CO₂ 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, Mo₂C and WC are the most widely studied materials which can be applied directly for CO₂ 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_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.

1																	18
1 H 1.00794	2											13	14	15	16	17	2 He 4.00260
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 0 15.9994	9 F 18.9984032	10 Ne 20.179
11 Na 22.989770	12 Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.94
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 CO 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 TC (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 126.90447	54 Xe 131.2
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 TI 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uu((277)
			57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	
			89 Ac 232.0381	90 Th	91 Pa	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es	100 Fm (257)	101 Md (258)	102 No (259)	

Figure 9. The distribution of elements in periodic table for the catalysts used in CO₂ utilization process. Red: active components; Yellow: supports.

Supports	Active Metals	Promoters	Reactions	Comments
	Со			$CoMoC_yO_z$ phase in Co-Mo ₂ C is an active phase which can dissociate CH_4 hence improve the catalytic performance (especially CO selectivity) of Mo ₂ C [2].
0 Ma C	Cu			The strong interaction between Cu and β -Mo ₂ C can effectively promote the dispersion of supported copper and prevent the aggregation of Cu particles [67].
p-1402C	Cu, Ni, Co		rWGS (reverse water gas shift)	$ \begin{array}{l} CO \ selectivity: Cu/Mo_2C > \beta \cdot Mo_2C > Ni/Mo_2C > Co/Mo_2C. \\ CO_2 \ conversion: Cu/Mo_2C < \beta \cdot Mo_2C < Ni/Mo_2C < Co/Mo_2C \ [68]. \end{array} $
	Cu	Cs		The electropositive character of Cs facilitates the electronic transfer from Cs to Mo and leads to an electronically rich surface which favours the selectivity towards CO [54].
α-Mo ₂ C				CO_2 dissociation toward CO can happen at ambient temperature at the surface of α -Mo ₂ C and the presence of Mo ₂ C (101)-Mo/C surface facet can be serve as a possible explanation of the observed reactivity [66].
Al ₂ O ₃	Mo ₂ C/Mo	Ni	CO ₂ methanation	The carburization process enhances the basicity of Ni-Mo $_2$ C/Al $_2$ O $_3$ and thus CO $_2$ absorption on their surface [70].
β -Mo ₂ C, δ -MoC and TiC			Methanol synthesis	TMC catalysts with a metal/carbon ratio of 1 (δ -MoC and TiC) were considered to be more selective than the catalysts with a metal/carbon ratio of 2 (β -Mo ₂ C) [59].
α-MoC _{1-x} β-Mo ₂ C			DRM	The phase of the molybdenum carbides obtained depended considerably on the precursor preparation method and flowing gas composition (Ar or H ₂). α -MoC _{1-x} phase showed better stability than β -Mo ₂ C phase in the DRM reaction [72].
β-Mo ₂ C			(dry reforming of methane)	Testing pressure is one of the critical reasons for catalyst deactivation. Clear deactivation occurred at β -Mo ₂ C after 8h test at ambient pressure. At same condition, high activity was maintained for 144 h with no bulk carbon deposition at 8 bar [73].
Mo ₂ C	Ni		DRM	The ratio of active metal sites (Ni) and Mo will influence the deactivation of Mo_2C catalysts in DRM reaction. The Ni-Mo ₂ C catalyst with Ni/Mo molar ratios of 1/2 is the most stable one [74].
SiRAlO _x	Co, Ni	Fe _{2.2} C	CO ₂ methanation	As a magnetically soft material, $Fe_{2.2}C$ NPs (nanoparticles) can be used as heating agent in a magnetic hyperthermia system for CO ₂ methanation [56].
TiC	Cu, Au		Methanol synthesis	Charge polarization happened between Au, Cu particles and TiC (001) surface makes them very active for CO ₂ activation and the catalytic synthesis of methanol [90].
	Cu, Au, Ni		CO ₂ hydrogenation	Main product Au-TiC and Cu-TiC: CO, methanolNi-TiC: CO, methanol, methane [42]
WC Mo ₂ C	Ni			Ni-WC is more stable than Ni-Mo ₂ C in DRM reaction due to the fact that compared with Ni-Mo ₂ C, the Ni-WC catalysts showed better ability to keep control of crystal structure and better resistance to sintering [75].
γ-Al ₂ O ₃	α-WC β-W ₂ C		DRM	β -W ₂ C nanoparticles exhibited higher stability than α -WC nanorods due to the inherent disorder and presence of carbon vacancies in the β -W ₂ C phase nanoparticles which can facilitate the reaction and prevent from coking [76].
biochar	WC			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].
Co ₆ W ₆ C				Co_6W_6C 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. Summary of CO₂ utilization process using different transition metal carbide (TMC) catalysts.

Supports	Active Metals	Promoters	Reactions	Comments
γ-Al ₂ O ₃	WC	К	rWGS	K acted as a structural and electronic promoter in K-WC/γ-Al ₂ O ₃ , attenuating surface chemistry and catalyst dispersion hence improve the CO selectivity in rWGS [78].
CNT	CoFe ₂ O ₄	Na	CO ₂ hydrogenation	$(Fe_{1-x}Co_x)_5C_2$ with a Hägg carbide structure is the active site in the catalyst for enhanced activity and preferential chain growth hence improve the catalytic performance [93].
VC/V ₈ C ₇			rWGS	V_8C_7 shows a higher CO_2 conversion and CO selectivity and C vacancies in V_8C_7 are responsible for the better catalytic behavior [94].

Table 3. Cont.

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.

References

- 1. Aressta, M.; Dibenedetto, A. Utilisation of CO₂ as a chemical feedstock: Opportunities and challenges. *J. Chem. Soc. Dalton Trans.* **2007**, *28*, 2975–2992. [CrossRef] [PubMed]
- Porosoff, M.D.; Yang, X.; Boscoboinik, J.A.; Chen, J.G. Molybdenum carbide as alternative catalysts to precious metals for highly selective reduction of CO₂ to CO. *Angew. Chem. Int. Ed.* 2014, *53*, 6705–6709. [CrossRef] [PubMed]
- 3. Huang, C.H.; Tan, C.S. A review: CO₂ utilization. Aerosol Air Qual. Res. 2014, 14, 480–499. [CrossRef]
- 4. Muradov, N. Industrial Utilization of CO₂: A Win–Win Solution. In *Liberating Energy from Carbon: Introduction* to *Decarbonization*; Lecture Notes in Energy; Springer: New York, NY, USA, 2014; Volume 22. [CrossRef]
- 5. Ettehadtavakkol, A.; Lake, L.W.; Bryant, S.L. CO₂-EOR and storage design optimization. *Int. J. Greenh. Gas Control* **2014**, *25*, 79–92. [CrossRef]
- 6. Nicot, J.P.; Duncan, I.J. Review: Common attributes of hydraulically fractured oil and gas production and CO₂ geological sequestration. *Greenh. Gases Sci. Technol.* **2012**, *2*, 352–368. [CrossRef]
- 7. Shi, Y.; Jia, Y.; Pan, W.; Huang, L.; Yan, J.; Zheng, R. Potential evaluation on CO₂-EGR in tight and low-permeability reservoirs. *Nat. Gas Ind. B* **2017**, *4*, 311–318. [CrossRef]
- Lin, T.K.; Hsieh, B.Z. Prevention of seabed subsidence of class-1 gas hydrate deposits via CO₂-EGR: A numerical study with coupled geomechanics-hydrate reaction-multiphase fluid flow model. *Energies* 2020, 13, 1579. [CrossRef]
- Bongole, K.; Sun, Z.; Yao, J.; Mehmood, A.; Yueying, W.; Mboje, J.; Xin, Y. Multifracture response to supercritical CO₂-EGS and water-EGS based on thermo-hydro-mechanical coupling method. *Int. J. Energy Res.* 2019, 43, 7173–7196. [CrossRef]
- 10. Zhang, F.Z.; Jiang, P.X.; Xu, R.N. System thermodynamic performance comparison of CO₂-EGS and water-EGS systems. *Appl. Therm. Eng.* **2013**, *61*, 236–244. [CrossRef]
- 11. Borgia, A.; Pruess, K.; Kneafsey, T.J.; Oldenburg, C.M.; Pan, L. Simulation of CO₂-EGS in a fractured reservoir with salt precipitation. *Energy Procedia* **2013**, *37*, 6617–6624. [CrossRef]
- 12. Rafiee, A.; Khalilpour, K.R.; Milani, D.; Panahi, M. Trends in CO₂ conversion and utilization: A review from process systems perspective. *J. Environ. Chem. Eng.* **2018**, *6*, 5771–5794. [CrossRef]
- 13. Su, X.; Xu, J.; Liang, B.; Duan, H.; Hou, B.; Huang, Y. Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. *J. Energy Chem.* **2016**, *25*, 553–565. [CrossRef]
- 14. Daza, Y.A.; Kent, R.A.; Yung, M.M.; Kuhn, J.N. Carbon dioxide conversion by reverse water-gas shift chemical looping on perovskite-type oxides. *Ind. Eng. Chem. Res.* **2014**, *53*, 5828–5837. [CrossRef]
- 15. Verhelst, S.; Turner, J.W.; Sileghem, L.; Vancoillie, J. Methanol as a fuel for internal combustion engines. *Prog. Energy Combust. Sci.* **2019**, *70*, 43–88. [CrossRef]
- 16. Porosoff, M.D.; Yan, B.; Chen, J.G. Catalytic reduction of CO₂ by H₂ for synthesis of CO, methanol and hydrocarbons: Challenges and opportunities. *Energy Environ. Sci.* **2016**, *9*, 62–73. [CrossRef]
- 17. Wang, F.; Wei, M.; Evans, D.G.; Duan, X. CeO₂-based heterogeneous catalysts toward catalytic conversion of CO₂. *J. Mater. Chem. A* **2016**, *4*, 5773–5783. [CrossRef]
- 18. Yang, Y.; Wang, S.; Jiang, Y.; Wu, X.; Xia, C.; Peng, R.; Lu, Y. CO₂ Activation and Reduction on Pt-CeO₂-Based Catalysts. *J. Phys. Chem. C* **2019**, *123*, 17092–17101. [CrossRef]
- 19. Wang, W.; Qu, Z.; Song, L.; Fu, Q. CO₂ hydrogenation to methanol over Cu/CeO₂ and Cu/ZrO₂ catalysts: Tuning methanol selectivity via metal-support interaction. *J. Energy Chem.* **2020**, *40*, 22–30. [CrossRef]
- le Saché, E.; Santos, J.L.; Smith, T.J.; Centeno, M.A.; Arellano-Garcia, H.; Odriozola, J.A.; Reina, T.R. Multicomponent Ni-CeO₂ nanocatalysts for syngas production from CO₂/CH₄ mixtures. *J. CO₂ Util.* 2018, 25, 68–78. [CrossRef]

- 21. Stroud, T.; Smith, T.J.; le Saché, E.; Santos, J.L.; Centeno, M.A.; Arellano-Garcia, H.; Odriozola, J.A.; Reina, T.R. Chemical CO₂ recycling via dry and bi reforming of methane using Ni-Sn/Al₂O₃ and Ni-Sn/CeO₂-Al₂O₃ catalysts. *Appl. Catal. B Environ.* **2018**, 224, 125–135. [CrossRef]
- 22. Rood, S.C.; Ahmet, H.B.; Gomez-Ramon, A.; Torrente-Murciano, L.; Reina, T.R.; Eslava, S. Enhanced ceria nanoflakes using graphene oxide as a sacrificial template for CO oxidation and dry reforming of methane. *Appl. Catal. B Environ.* **2019**, *242*, 358–368. [CrossRef]
- 23. Centeno, M.A.; Reina, T.R.; Ivanova, S.; Laguna, O.H.; Odriozola, J.A. Au/CeO₂ catalysts: Structure and CO oxidation activity. *Catalysts* **2016**, *6*, 158. [CrossRef]
- 24. Pastor-Pérez, L.; le Saché, E.; Jones, C.; Gu, S.; Arellano-Garcia, H.; Reina, T.R. Synthetic natural gas production from CO₂ over Ni-x/CeO₂-ZrO₂(x = Fe, Co) catalysts: Influence of promoters and space velocity. *Catal. Today* **2017**, *2*, 10–15. [CrossRef]
- 25. Pastor-Pérez, L.; Patel, V.; le Saché, E.; Reina, T.R. CO₂ methanation in the presence of methane: Catalysts design and effect of methane concentration in the reaction mixture. *J. Energy Inst.* **2020**, *93*, 415–424. [CrossRef]
- 26. Shi, Z.; Tan, Q.; Wu, D. Enhanced CO₂ hydrogenation to methanol over TiO₂ nanotubes-supported CuO-ZnO-CeO₂ catalyst. *Appl. Catal. A Gen.* **2019**, *581*, 58–66. [CrossRef]
- Liu, C.; Nauert, S.L.; Alsina, M.A.; Wang, D.; Grant, A.; He, K.; Weitz, E.; Nolan, M.; Gray, K.A.; Notestein, J.M. Role of surface reconstruction on Cu/TiO₂ nanotubes for CO₂ conversion. *Appl. Catal. B Environ.* 2019, 255, 117754. [CrossRef]
- 28. Pastor-Pérez, L.; Shah, M.; le Saché, E.; Reina, T.R. Improving Fe/Al₂O₃ catalysts for the reverse water-gas shift reaction: On the effect of cs as activity/selectivity promoter. *Catalysts* **2018**, *8*, 608. [CrossRef]
- 29. Duyar, M.S.; Ramachandran, A.; Wang, C.; Farrauto, R.J. Kinetics of CO₂ methanation over Ru/γ-Al₂O₃ and implications for renewable energy storage applications. *J. CO*₂ *Util.* **2015**, *12*, 27–33. [CrossRef]
- Levy, R.B.; Boudart, M. Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis. *Science* 1973, 181, 547–549. [CrossRef]
- 31. Oshikawa, K.; Nagai, M.; Omi, S. Characterization of molybdenum carbides for methane reforming by TPR, XRD, and XPS. *J. Phys. Chem. B* **2001**, *105*, 9124–9131. [CrossRef]
- 32. Prats, H.; Piñero, J.J.; Viñes, F.; Bromley, S.T.; Sayós, R.; Illas, F. Assessing the usefulness of transition metal carbides for hydrogenation reactions. *Chem. Commun.* **2019**, *55*, 12797–12800. [CrossRef] [PubMed]
- 33. Qi, K.Z.; Wang, G.C.; Zheng, W.J. A first-principles study of CO hydrogenation into methane on molybdenum carbides catalysts. *Surf. Sci.* **2013**, *614*, 53–63. [CrossRef]
- 34. Ramanathan, S.; Oyama, S.T. New catalysts for hydroprocessing: Transition metal carbides and nitrides. *J. Phys. Chem.* **1995**, *99*, 16365–16372. [CrossRef]
- 35. Kitchin, J.R.; Nørskov, J.K.; Barteau, M.A.; Chen, J.G. Trends in the chemical properties of early transition metal carbide surfaces: A density functional study. *Catal. Today* **2005**, *105*, 66–73. [CrossRef]
- 36. Hwu, H.H.; Chen, J.G. Surface chemistry of transition metal carbides. *Chem. Rev.* 2005, 105, 185–212. [CrossRef]
- 37. Stottlemyer, A.L.; Kelly, T.G.; Meng, Q.; Chen, J.G. Reactions of oxygen-containing molecules on transition metal carbides: Surface science insight into potential applications in catalysis and electrocatalysis. *Surf. Sci. Rep.* **2012**, *67*, 201–232. [CrossRef]
- Rodriguez, J.A.; Liu, P.; Dvorak, J.; Jirsak, T.; Gomes, J.; Takahashi, Y.; Nakamura, K. Adsorption of sulfur on TiC(001): Photoemission and first-principles studies. *Phys. Rev. B Condens. Matter Mater. Phys.* 2004, 69, 1–10. [CrossRef]
- Darujati, A.R.S.; LaMont, D.C.; Thomson, W.J. Oxidation stability of Mo₂C catalysts under fuel reforming conditions. *Appl. Catal. A Gen.* 2003, 253, 397–407. [CrossRef]
- 40. Liu, P.; Rodriguez, J.A.; Muckerman, J.T. Sulfur adsorption and sulfidation of transition metal carbides as hydrotreating catalysts. *J. Mol. Catal. A Chem.* **2005**, 239, 116–124. [CrossRef]
- 41. Toth, E.L. Transition Metal Carbides and Nitrides; Academic Press: New York, NY, USA, 1971; ISBN 9780323157223.
- 42. Rodriguez, J.A.; Evans, J.; Feria, L.; Vidal, A.B.; Liu, P.; Nakamura, K.; Illas, F. CO₂ hydrogenation on Au/TiC, Cu/TiC, and Ni/TiC catalysts: Production of CO, methanol, and methane. *J. Catal.* **2013**, 307, 162–169. [CrossRef]

- 43. Oyama, S.T. Introduction to the chemistry of transition metal carbides and nitrides. In *The Chemistry of Transition Metal Carbides and Nitrides*; Oyama, S.T., Ed.; Online; Springer: Dordrecht, The Netherlands, 1996; ISBN 978-94-009-1565-7. [CrossRef]
- 44. Xiao, Y.; Hwang, J.Y.; Sun, Y.K. Transition metal carbide-based materials: Synthesis and applications in electrochemical energy storage. *J. Mater. Chem. A* **2016**, *4*, 10379–10393. [CrossRef]
- Zheng, W.; Cotter, T.P.; Kaghazchi, P.; Jacob, T.; Frank, B.; Schlichte, K.; Zhang, W.; Su, D.S.; Schüth, F.; Schlögl, R. Experimental and theoretical investigation of molybdenum carbide and nitride as catalysts for ammonia decomposition. *J. Am. Chem. Soc.* 2013, *135*, 3458–3464. [CrossRef] [PubMed]
- 46. Li, M.; Wang, H.; Zhu, Y.; Tian, D.; Wang, C.; Lu, X. Mo/Mo₂C encapsulated in nitrogen-doped carbon nanofibers as efficiently integrated heterojunction electrocatalysts for hydrogen evolution reaction in wide pH range. *Appl. Surf. Sci.* **2019**, *496*, 143672. [CrossRef]
- 47. Wang, P.; Chen, W.; Chiang, F.K.; Dugulan, A.I.; Song, Y.; Pestman, R.; Zhang, K.; Yao, J.; Feng, B.; Miao, P.; et al. Synthesis of stable and low-CO₂ selective ε-iron carbide Fischer-Tropsch catalysts. *Sci. Adv.* 2018, 4, 1–7. [CrossRef] [PubMed]
- 48. Yang, Y.; Qin, Y.; Xue, X.; Wang, X.; Yao, M.; Huang, H. Intrinsic Properties Affecting the Catalytic Activity of 3d Transition-Metal Carbides in Li-O₂ Battery. *J. Phys. Chem. C* **2018**, *122*, 17812–17819. [CrossRef]
- 49. Zhu, K.; Zhang, H.; Ye, K.; Zhao, W.; Yan, J.; Cheng, K.; Wang, G.; Yang, B.; Cao, D. Two-Dimensional Titanium Carbide MXene as a Capacitor-Type Electrode for Rechargeable Aqueous Li-Ion and Na-Ion Capacitor Batteries. *ChemElectroChem* **2017**, *4*, 3018–3025. [CrossRef]
- 50. Tackett, B.M.; Sheng, W.; Chen, J.G. Opportunities and Challenges in Utilizing Metal-Modified Transition Metal Carbides as Low-Cost Electrocatalysts. *Joule* **2017**, *1*, 253–263. [CrossRef]
- 51. Feria, L.; Rodriguez, J.A.; Jirsak, T.; Illas, F. Interaction of SO₂ with Cu/TiC(0 0 1) and Au/TiC(0 0 1): Toward a new family of DeSO_x catalysts. *J. Catal.* **2011**, 279, 352–360. [CrossRef]
- 52. Dorner, R.W.; Hardy, D.R.; Williams, F.W.; Willauer, H.D. Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons. *Energy Environ. Sci.* **2010**, *3*, 884–890. [CrossRef]
- Porosoff, M.D.; Baldwin, J.W.; Peng, X.; Mpourmpakis, G.; Willauer, H.D. Potassium-promoted molybdenum carbide as a highly active and selective catalyst for CO₂ conversion to CO. *ChemSusChem* 2017, *10*, 2408–2415. [CrossRef]
- 54. Zhang, Q.; Pastor-Pérez, L.; Jin, W.; Gu, S.; Reina, T.R. Understanding the promoter effect of Cu and Cs over highly effective β-Mo₂C catalysts for the reverse water-gas shift reaction. *Appl. Catal. B Environ.* **2019**, 244, 889–898. [CrossRef]
- 55. Liu, P.; Rodriguez, J.A. Water-gas-shift reaction on molybdenum carbide surfaces: Essential role of the oxycarbide. *J. Phys. Chem. B* 2006, *110*, 19418–19425. [CrossRef] [PubMed]
- Kale, S.S.; Asensio, J.M.; Estrader, M.; Werner, M.; Bordet, A.; Yi, D.; Chaudret, B. Iron carbide or iron carbide/cobalt nanoparticles for magnetically-induced CO₂ hydrogenation over Ni/SiRAlO_x catalysts. *Catal. Sci. Technol.* 2019, 9, 2601–2607. [CrossRef]
- Brungs, A.J.; York, A.P.E.; Green, M.L.H. Comparison of the group V and VI transition metal carbides for methane dry reforming and thermodynamic prediction of their relative stabilities. *Catal. Lett.* 1999, 57, 65–69. [CrossRef]
- 58. Yan, Q.; Lu, Y.; To, F.; Li, Y.; Yu, F. Synthesis of tungsten carbide nanoparticles in biochar matrix as a catalyst for dry reforming of methane to syngas. *Catal. Sci. Technol.* **2015**, *5*, 3270–3280. [CrossRef]
- Posada-Pérez, S.; Ramírez, P.J.; Evans, J.; Viñes, F.; Liu, P.; Illas, F.; Rodriguez, J.A. Highly Active Au/δ-MoC and Cu/δ-MoC Catalysts for the Conversion of CO₂: The Metal/C Ratio as a Key Factor Defining Activity, Selectivity, and Stability. J. Am. Chem. Soc. 2016, 138, 8269–8278. [CrossRef]
- 60. Ono, L.K.; Sudfeld, D.; Cuenya, B.R. In situ gas-phase catalytic properties of TiC-supported size-selected gold nanoparticles synthesized by diblock copolymer encapsulation. *Surf. Sci.* 2006, 600, 5041–5050. [CrossRef]
- 61. Rodriguez, J.A.; Illas, F. Activation of noble metals on metal-carbide surfaces: Novel catalysts for CO oxidation, desulfurization and hydrogenation reactions. *Phys. Chem. Chem. Phys.* **2012**, *14*, 427–438. [CrossRef]
- 62. Porosoff, M.D.; Kattel, S.; Li, W.H.; Liu, P.; Chen, J.G. Identifying trends and descriptors for selective CO₂ conversion to CO over transition metal carbides. *Chem. Commun.* **2015**, *51*, 6988–6991. [CrossRef]
- 63. Kunkel, C.; Viñes, F.; Illas, F. Transition metal carbides as novel materials for CO₂ capture, storage, and activation. *Energy Environ. Sci.* **2016**, *9*, 141–144. [CrossRef]

- 64. Wan, C.; Regmi, Y.N.; Leonard, B.M. Multiple phases of molybdenum carbide as electrocatalysts for the hydrogen evolution reaction. *Angew. Chem. Int. Ed.* **2014**, *53*, 6407–6410. [CrossRef] [PubMed]
- Xu, W.; Ramirez, P.J.; Stacchiola, D.; Rodriguez, J.A. Synthesis of α-MoC_{1-x} and β-MoC_y catalysts for CO₂ hydrogenation by thermal carburization of Mo-oxide in hydrocarbon and hydrogen mixtures. *Catal. Lett.* 2014, 144, 1418–1424. [CrossRef]
- Liu, X.; Kunkel, C.; de la Piscina, P.R.; Homs, N.; Viñes, F.; Illas, F. Effective and Highly Selective CO Generation from CO₂ Using a Polycrystalline α-Mo₂C Catalyst. *ACS Catal.* 2017, *7*, 4323–4335. [CrossRef]
- Zhang, X.; Zhu, X.; Lin, L.; Yao, S.; Zhang, M.; Liu, X.; Ma, D. Highly Dispersed Copper over β-Mo₂C as an Efficient and Stable Catalyst for the Reverse Water Gas Shift (rWGS) Reaction. ACS Catal. 2017, 7, 912–918. [CrossRef]
- Xu, W.; Ramírez, P.J.; Stacchiola, D.; Brito, J.L.; Rodriguez, J.A. The Carburization of Transition Metal Molybdates (M_xMoO₄, M = Cu, Ni or Co) and the Generation of Highly Active Metal/Carbide Catalysts for CO₂ Hydrogenation. *Catal. Lett.* 2015, *145*, 1365–1373. [CrossRef]
- 69. Prasad, P.S.S.; Bae, J.W.; Jun, K.W.; Lee, K.W. Fischer-Tropsch synthesis by carbon dioxide hydrogenation on Fe-based catalysts. *Catal. Surv. Asia* **2008**, *12*, 170–183. [CrossRef]
- Yao, L.; Wang, Y.; Galvez, M.E.; Hu, C.; da Costa, P. γ-Alumina-Supported Ni-Mo Carbides as Promising Catalysts for CO₂ Methanation. *Mod. Res. Catal.* 2017, 06, 135–145. [CrossRef]
- SPosada-Pérez, S.; Viñes, F.; Ramirez, P.J.; Vidal, A.B.; Rodriguez, J.A.; Illas, F. The bending machine: CO₂ activation and hydrogenation on δ-MoC(001) and β-Mo₂C(001) surfaces. *Phys. Chem. Chem. Phys.* 2014, 16, 14912–14921. [CrossRef]
- 72. Liang, P.; Gao, H.; Yao, Z.; Jia, R.; Shi, Y.; Sun, Y.; Fan, Q.; Wang, H. Simple synthesis of ultrasmall β-Mo₂C and α-MoC_{1-x} nanoparticles and new insights into their catalytic mechanisms for dry reforming of methane. *Catal. Sci. Technol.* **2017**, *7*, 3312–3324. [CrossRef]
- York, A.P.E.; Claridge, J.B.; Brungs, A.J.; Tsang, S.C.; Green, M.L.H. Molybdenum and tungsten carbides as catalysts for the conversion of methane to synthesis gas using stoichiometric feedstocks. *Chem. Commun.* 1997, 1, 39–40. [CrossRef]
- 74. Shi, C.; Zhang, A.; Li, X.; Zhang, S.; Zhu, A.; Ma, Y.; Au, C. Ni-modified Mo₂C catalysts for methane dry reforming. *Appl. Catal. A Gen.* **2012**, *431*, 164–170. [CrossRef]
- 75. Yao, Z.; Jiang, J.; Zhao, Y.; Luan, F.; Zhu, J.; Shi, Y.; Gao, H.; Wang, H. Insights into the deactivation mechanism of metal carbide catalysts for dry reforming of methane via comparison of nickel-modified molybdenum and tungsten carbides. *RSC Adv.* **2016**, *6*, 19944–19951. [CrossRef]
- 76. Mounfield, W.P.; Harale, A.; Román-Leshkov, Y. Impact of morphological effects on the activity and stability of tungsten carbide catalysts for dry methane reforming. *Energy Fuels* **2019**, *33*, 5544–5550. [CrossRef]
- Shao, H.; Kugler, E.L.; Ma, W.; Dadyburjor, D.B. Effect of temperature on structure and performance of in-house cobalt-tungsten carbide catalyst for dry reforming of methane. *Ind. Eng. Chem. Res.* 2005, 44, 4914–4921. [CrossRef]
- 78. Morse, J.R.; Juneau, M.; Baldwin, J.W.; Porosoff, M.D.; Willauer, H.D. Alkali promoted tungsten carbide as a selective catalyst for the reverse water gas shift reaction. *J. CO*₂ *Util.* **2020**, *35*, 38–46. [CrossRef]
- Bukur, D.B.; Okabe, K.; Rosynek, M.P.; Li, C.P.; Wang, D.J.; Rao, K.R.P.M.; Huffman, G.P. Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis. I. Characterization Studies. *J. Catal.* 1995, 155, 353–365. [CrossRef]
- 80. Shroff, M.D.; Datye, A.K. The importance of passivation in the study of iron Fischer-Tropsch catalysts. *Catal. Lett.* **1996**, *37*, 101–106. [CrossRef]
- 81. Yang, C.; Zhao, H.; Hou, Y.; Ma, D. Fe₅C₂ nanoparticles: A facile bromide-induced synthesis and as an active phase for Fischer-Tropsch synthesis. *J. Am. Chem. Soc.* **2012**, *134*, 15814–15821. [CrossRef]
- Chen, B.; Wang, D.; Duan, X.; Liu, W.; Li, Y.; Qian, G.; Yuan, W.; Holmen, A.; Zhou, X.; Chen, D. Charge-Tuned CO Activation over a χ-Fe₅C₂ Fischer-Tropsch Catalyst. *ACS Catal.* 2018, *8*, 2709–2714. [CrossRef]
- 83. Herranz, T.; Rojas, S.; Pérez-Alonso, F.J.; Ojeda, M.; Terreros, P.; Fierro, J.L.G. Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas. *J. Catal.* **2006**, *243*, 199–211. [CrossRef]
- 84. Liu, X.; Cao, C.; Tian, P.; Zhu, M.; Zhang, Y.; Xu, J.; Tian, Y.; Han, Y.F. Resolving CO₂ activation and hydrogenation pathways over iron carbides from DFT investigation. *J. CO*₂ *Util.* **2020**, *38*, 10–15. [CrossRef]
- 85. Wang, W.; Gong, J. Methanation of carbon dioxide: An overview. *Front. Chem. Eng. China* **2011**, *5*, 2–10. [CrossRef]

- 86. Abenojar, E.C.; Wickramasinghe, S.; Bas-Concepcion, J.; Samia, A.C.S. Structural effects on the magnetic hyperthermia properties of iron oxide nanoparticles. *Prog. Nat. Sci. Mater. Int.* **2016**, *26*, 440–448. [CrossRef]
- 87. Bordet, A.; Asensio, J.M.; Soulantica, K.; Chaudret, B. Enhancement of Carbon Oxides Hydrogenation on Iron-Based Nanoparticles by In-Situ Water Removal. *ChemCatChem* **2018**, *10*, 4047–4051. [CrossRef]
- López, M.; Broderick, L.; Carey, J.J.; Viñes, F.; Nolan, M.; Illas, F. Tuning transition metal carbide activity by surface metal alloying: A case study on CO₂ capture and activation. *Phys. Chem. Chem. Phys.* 2018, 20, 22179–22186. [CrossRef]
- López, M.; Viñes, F.; Nolan, M.; Illas, F. Predicting the Effect of Dopants on CO₂ Adsorption in Transition Metal Carbides: Case Study on TiC (001). *J. Phys. Chem. C* 2020, 124, 15969–15976. [CrossRef]
- 90. Vidal, A.B.; Feria, L.; Evans, J.; Takahashi, Y.; Liu, P.; Nakamura, K.; Rodriguez, J.A. CO₂ activation and methanol synthesis on novel Au/TiC and Cu/TiC catalysts. *J. Phys. Chem. Lett.* **2012**, *3*, 2275–2280. [CrossRef]
- 91. Asara, G.G.; Ricart, J.M.; Rodriguez, J.A.; Illas, F. Exploring the activity of a novel Au/TiC(001) model catalyst towards CO and CO₂ hydrogenation. *Surf. Sci.* **2015**, *640*, 141–149. [CrossRef]
- 92. Dubois, J.L.; Sayama, K.; Arakawa, H. CO₂ Hydrogenation over Carbide Catalysts. *Chem. Lett.* **1992**, *21*, 5–8. [CrossRef]
- Kim, K.Y.; Lee, H.; Noh, W.Y.; Shin, J.; Han, S.J.; Kim, S.K.; An, K.; Lee, J.S. Cobalt Ferrite Nanoparticles to Form a Catalytic Co–Fe Alloy Carbide Phase for Selective CO₂ Hydrogenation to Light Olefins. *ACS Catal.* 2020, 10, 8660–8671. [CrossRef]
- Pajares, A.; Prats, H.; Romero, A.; Viñes, F.; de la Piscina, P.R.; Sayós, R.; Homs, N.; Illas, F. Critical effect of carbon vacancies on the reverse water gas shift reaction over vanadium carbide catalysts. *Appl. Catal. B Environ.* 2020, 267, 118719. [CrossRef]
- 95. Mehdad, A.; Jentoft, R.E.; Jentoft, F.C. Passivation agents and conditions for Mo₂C and W₂C: Effect on catalytic activity for toluene hydrogenation. *J. Catal.* **2017**, *347*, 89–101. [CrossRef]
- 96. Hanif, A.; Xiao, T.; York, A.P.E.; Sloan, J.; Green, M.L.H. Study on the structure and formation mechanism of molybdenum carbides. *Chem. Mater.* **2002**, *14*, 1009–1015. [CrossRef]
- 97. Rocha, A.S.; Rocha, A.B.; da Silva, V.T. Benzene adsorption on Mo₂C: A theoretical and experimental study. *Appl. Catal. A Gen.* **2010**, *379*, 54–60. [CrossRef]
- 98. Nagai, M.; Kurakami, T.; Omi, S. Activity of carbided molybdena—Alumina for CO₂ hydrogenation. *Catal. Today* **1998**, *45*, 235–239. [CrossRef]
- Shou, H.; Ferrari, D.; Barton, D.G.; Jones, C.W.; Davis, R.J. Influence of Passivation on the Reactivity of Unpromoted and Rb-Promoted Mo₂C Nanoparticles for CO Hydrogenation. ACS Catal. 2012, 2, 1408–1416. [CrossRef]



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