Supported Nanostructured Mo$_x$C Materials for the Catalytic Reduction of CO$_2$ through the Reverse Water Gas Shift Reaction

Arturo Pajares$^{1,2,†}$, Xianyun Liu$^{1,4}$, Joan R. Busacker$^1$, Pilar Ramírez de la Piscina$^1$ and Narcís Homs$^{1,2,*}$

$^1$ Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica & Institut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain
$^2$ Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Barcelona, Spain
$^*$ Correspondence: nbhomes@irec.cat or narcis.homs@qi.ub.edu
$†$ Present address: Sustainable Materials Management, Flemish Institute for Technological Research (VITO NV), Boeretang 200, 2400 Mol, Belgium.
$‡$ Present address: College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China.

Abstract: Mo$_x$C-based catalysts supported on γ-Al$_2$O$_3$, SiO$_2$ and TiO$_2$ were prepared, characterized and studied in the reverse water gas shift (RWGS) at 548–673 K and atmospheric pressure, using CO$_2$:H$_2$ = 1:1 and CO$_2$:H$_2$ = 1:3 mol/mol reactant mixtures. The support used determined the crystalline Mo$_x$C phases obtained and the behavior of the supported nanostructured Mo$_x$C catalysts in the RWGS. All catalysts were active in the RWGS reaction under the experimental conditions used; CO productivity per mol of Mo was always higher than that of unsupported Mo$_x$C prepared using a similar method in the absence of support. The CO selectivity at 673 K was above 94% for all the supported catalysts, and near 99% for the SiO$_2$-supported. The Mo$_x$C/SiO$_2$ catalyst, which contains a mixture of hexagonal Mo$_2$C and cubic MoC phases, exhibited the best performance for CO production.

Keywords: CO$_2$ catalytic reduction; syngas; RWGS; supported molybdenum carbide; Mo$_x$C-based catalysts

1. Introduction

In addition to capture and storage of CO$_2$, nowadays there is a clear interest in its use as an out-stream chemical feedstock in order to actively contribute to the reduction of CO$_2$ emissions; CO$_2$ can be considered a cheap carbon C1 source for upgrading rather than a waste with consequences in global warming [1–4]. However, the direct transformation of CO$_2$ to useful products is difficult. The high chemical stability of CO$_2$ difficult its catalytic transformation, the developing of new materials capable of efficiently bind and activate this molecule is nowadays an active research area. An interesting CO$_2$ utilization approach is its reduction to CO, employing H$_2$ as a reducing agent via the reverse water gas shift (RWGS) reaction [5–8]:

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (1)$$

The reduction of CO$_2$ to CO with renewable H$_2$ can be regarded as a simple and easy path for CO$_2$ recycling, which would allow its reuse at a large scale. After the RWGS step and H$_2$O separation, a CO$_2$/CO/H$_2$ out-stream mixture can be produced. This out-stream can be used as syngas input for other well-established chemical processes, such as Fischer-Tropsch (FT) or methanol synthesis [9–15].

The RWGS reaction can be carried out using noble metal-based catalysts [5,10,16]. Due to the similar properties of transition metal carbides (TMCs) and Pt-based catalysts, the formers have been proposed as catalysts for different processes in which Pt-based catalysts are active [17,18]. One of these processes is the CO$_2$ reduction to CO, which has been analyzed over different TMCs using theoretical and experimental approaches [19–25].
The preparation of TMCs is usually carried out using carburization methods. These methods apply high temperature and/or pressure conditions in the presence of a reducing atmosphere, usually mixtures of H₂ and carbon-containing gases (CO, CH₄, C₂H₄) [25–28]. Due to the increased interest in TMC-based catalysts, in recent years, greener preparation methods have been explored [21,22,29–31]. In an earlier investigation, we studied the preparation of bulk Mo₃C catalysts using different molybdenum and carbon precursors and following sol-gel based routes; the bulk Mo₃C catalysts generated, contained different crystalline phases, which influenced their catalytic behavior in the RWGS reaction [31].

The deposition onto a support of the appropriate TMC active phase can be an interesting approach to improve the catalytic behavior of bulk TMCs materials, which usually show low surface area values. Supported Mo₃C phases have been used as catalysts in different processes such as CH₄ dry reforming [32], hydrazine decomposition [33], thiophene hydrodesulfurization [34], propene and tetralin hydrogenation [35] and Fischer-Tropsch synthesis [36]. However, supported Mo₃C catalysts have not been much studied in the RWGS reaction [37–39]. Porosoff et al. have reported the promoter effect of K in Al₂O₃-supported Mo₂C-based catalysts containing MoO₂ and/or metallic Mo, which were prepared by carburization with CH₄/H₂ at 873 K [38]. Sub-nanosized molybdenum carbide clusters highly dispersed onto N-doped carbon/Al₂O₃, prepared by carbonization of MoO₃ with glucose, were more performant in the RWGS than bulk β-Mo₂C [39]. Recently, the preparation of SiO₂- and SBA-15-supported Mo₂C-based catalysts (20% wt Mo), using different routes of Mo incorporation to the support and a final carburization process with CH₄/H₂, has been studied [40]. The preparation method and the support influenced the composition of Mo₃C crystalline phases developed and therefore the catalytic performance of the material in the RWGS [40]. The preparation of Mo₃C-based catalysts supported onto γ-Al₂O₃, SiO₂ and MFI-type zeolites by incipient wetness impregnation of ammonium molybdate and carburization with CH₄/H₂ have led to catalysts with different Mo-containing species such as Mo₃C, MoO₃ and Mo⁰; the phases developed and the catalytic performance in the RWGS of the materials depended also on the support characteristics [41].

Here, Mo₃C phases were generated onto γ-Al₂O₃, SiO₂ and TiO₂ by a thermal treatment of the solid obtained from the interaction between a MoCl₅/urea solution and the corresponding oxide. The crystalline Mo₃C phases obtained depended on the support used in the preparation and determined the catalytic behavior of materials in the RWGS.

2. Experimental

2.1. Preparation of Catalysts

Commercial γ-Al₂O₃ (Alfa Aesar, Haverhill, MA, US, 226 m² g⁻¹), SiO₂ (Degussa, Frankfurt, Germany, 200 m² g⁻¹) and TiO₂ (Tecnan, Navarra, Spain, 117 m² g⁻¹, anatase/rutile, 78/22% wt) were employed as supports. Urea (Alfa Aesar, Haverhill, MA, US, 99%), which was used as carbon source, was added to a solution of MoCl₅ (Alfa Aesar, Haverhill, MA, US, 99.6%) in ethanol with a urea/MoCl₅ = 7 molar ratio [21,29,31]. The viscous solution was contacted with the respective powdered support. The resulting solid was dried at 333 K, and then treated under Ar flow up to 1073 K for 3 h. The samples were cooled down to room temperature under Ar and then exposed to air without passivation. Mo₅C/Al₂O₃, Mo₅C/TiO₂ and Mo₅C/SiO₂ catalysts with about 26% wt of Mo were prepared by using the proper amount of molybdenum and carbon precursors. A reference catalyst (unsupported), containing only bulk hexagonal Mo₂C was prepared following a similar method but in the absence of support [21]. For characterization purposes, the commercial supports were also separately treated up to 1073 K (3 h) under Ar.

2.2. Characterization of Catalysts

The Mo content of samples was determined by inductively coupled plasma mass spectrometry using a Perkin Elmer Optima 3200RL apparatus (Santa Clara, CA, US). The N₂ adsorption-desorption isotherms were recorded at 77 K using a Micromeritics Tristar II 3020 equipment. Prior to the measurements, the samples were outgassed at 523 K for
The specific surface area ($S_{BET}$) was calculated by multi-point BET analysis of $N_2$ adsorption isotherms. The X-ray powder diffraction (XRD) analysis was performed using a PANalytical X’Pert PRO MPD Alpha1 powder diffractometer (Malvern, UK) equipped with a CuKα1 radiation. The XRD profiles were collected in the $2\theta$ range of 4°–100° with a step size of 0.017° and counting 50 s at each step. Transmission electron microscopy (TEM-HRTEM) images and energy dispersive X-ray analysis (EDX) were collected employing a JEOL J2010F microscope (Tokyo, Japan) with a 532 nm laser and a CCD detector. Raman spectra of the samples were collected using a Jobin-Yvon LabRAM HR 800, fitted to an optical Olympus BXFM microscope (Kyoto, Japan) with a 532 nm laser and an optical microscope. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Perkin Elmer PHI-5500 Multitechnique System (Physical Electronics, Chanhassen, MN, US) with an Al X-ray source ($h\nu = 1486.6$ eV and 350 W). Samples were kept in an ultra-high vacuum chamber during data acquisition ($5 \times 10^{-9}$–$2 \times 10^{-8}$ Torr). Before XPS measurements, the C 1s BE of adventitious carbon was determined in the same equipment and conditions using Au as reference. The BE values were referred to the mentioned C 1s BE at 284.8 eV.

2.3. RWGS Catalytic Tests

The RWGS reaction tests were carried out in a Microactivity-Reference unit (PID Eng&Tech) using a tubular fixed-bed reactor under atmospheric pressure. Approximately, 150 mg of catalyst were diluted with inactive SiC up to 1 mL of catalytic bed. The RWGS was studied at 0.1 MPa, between 548 K and 673 K, by following the temperature sequence: 598 K (3 h) → 573 K (3 h) → 548 K (10 h) → 548 K (3 h) → 598 K (3 h) → 573 K (3 h) → 548 K (3 h) → 623 K (3 h) → 648 K (3 h) → 648 K (10 h). The first part of the catalytic test: 598 K (3 h) → 573 K (3 h) → 548 K (10 h) was carried out in order to condition the catalyst under RWGS. The gas hourly space velocity (GHSV) was $3000 \text{ h}^{-1}$. The effluent was analysed on-line with a gas chromatograph Varian 450-GC equipped with a methanizer and TCD and FID detectors. $CO_2$ conversion and product distribution at each temperature were determined by the average of at least three measures.

3. Results and Discussion

As stated above, $Al_2O_3$, $SiO_2$, and $TiO_2$-supported $Mo_xC$ catalysts with about 26% wt Mo were prepared, characterized and tested in the RWGS reaction. Table 1 shows the Mo content and the $S_{BET}$ of fresh catalysts. For comparison, $S_{BET}$ values of the supports treated at 1073 K under Ar, which are the conditions used in the preparation of catalysts, are also included. In all cases, the $S_{BET}$ of the supports after the thermal treatment at 1073 K was lower than that of the corresponding commercial pristine material; the diminution was about 10% for $Al_2O_3$ and $SiO_2$, meanwhile for $TiO_2$ the $S_{BET}$ decreased from 117 $m^2g^{-1}$ to 13 $m^2g^{-1}$. For $TiO_2$, a phase change occurred during the thermal treatment; the rutile weight percentage increased from 22% (pristine material) until 95% after the treatment at 1073 K, as determined from XRD analysis [42]. On the other hand, except for the $Mo_xC/TiO_2$, the $S_{BET}$ of supported catalysts was lower than that of the corresponding support treated at 1073 K; the formation of $Mo_xC$ could prevent in some extension the surface area decrease of the $TiO_2$ support, which could be related with a different extent of the rutile formation from anatase.

Table 1. Mo content, determined by chemical analysis and surface area ($S_{BET}$) of fresh and post-reaction catalysts.

| Catalyst         | Mo (%wt) | $S_{BET}$ ($m^2g^{-1}$) |
|------------------|----------|--------------------------|
|                  | Fresh    | Post-Reaction b          | Post-Reaction c |
| $Mo_xC/Al_2O_3$  | 25.1     | 119 (204)                | 93              | 97              |
| $Mo_xC/SiO_2$    | 25.5     | 129 (181)                | 115             | 107             |
| $Mo_xC/TiO_2$    | 27.5     | 39 (13)                  | 32              | 25              |

$^a$ between brackets $S_{BET}$ of supports treated at 1073 K; $^b$ $CO_2/H_2/N_2 = 1/3/1$ reactant mixture; $^c$ $CO_2/H_2/N_2 = 1/1/3$ reactant mixture.
The supported catalysts were analyzed by XRD, and the corresponding XRD patterns are shown in Figures 1–3; XRD patterns of the respective supports treated at 1073 K under Ar are also displayed for comparison. From the XRD pattern of MoₓC/Al₂O₃ (Figure 1), characteristic diffraction peaks of γ-Al₂O₃ are observed, and the main presence of hexagonal Mo₂C (JCPDS 00-035-0787) can be deduced; a crystallite size of 28 nm was calculated. The XRD analysis of MoₓC/SiO₂ (Figure 2) indicates the presence of hexagonal Mo₂C; however, the observation of diffraction peaks with maxima at 2θ = 36.9° and 2θ = 42.1° are attributed to the presence of cubic MoC (JCPDS 03-065-0280). From the intensity of diffraction peaks of both phases and that in reference files, a semiquantitative analysis was performed [43]; the presence of 65% cubic MoC and 35% hexagonal Mo₂C is determined in the MoₓC/SiO₂ catalyst. Figure 3 shows the corresponding XRD profile of TiO₂-supported catalyst. Characteristic diffraction peaks of both anatase and rutile TiO₂ phases are clearly observed. The rutile weight percentage with respect to TiO₂ phases calculated from XRD pattern is 51% [42]. As commented above, the formation of MoₓC could prevent the anatase transformation, having the MoₓC/TiO₂ catalyst a higher amount of anatase and a higher surface area than the support treated at 1073 K (Table 1). From the XRD pattern of MoₓC/TiO₂, the main presence of cubic MoC with poor crystallinity can be proposed, even if the presence of hexagonal Mo₂C could not be ruled out (Figure 3).

The catalysts were also characterized by Raman spectroscopy, TEM-HRTEM, STEM-EDX and XPS. Raman spectroscopy was used in order to determine the presence of molybdenum oxide species and/or carbonaceous residues (Figure S1). The very low intensity bands in the zone 815–990 cm⁻¹ points to the presence of residual MoO₃ [44–46], which could be formed by surface oxidation when the samples were exposed to air. For MoₓC/TiO₂, Raman bands at 260, 429 and 610 cm⁻¹, assigned to rutile, and at 150 cm⁻¹ assigned to anatase, are clearly visible [47–49]. In all cases, the intensity of the bands in the 1200–1700 cm⁻¹ region characteristic of carbonaceous species (D and G bands), is negligible (Figure S1).

![Figure 1](image_url)  
**Figure 1.** XRD patterns of MoₓC/Al₂O₃ catalyst and the Al₂O₃ support after thermal treatment at 1073 K.
The catalysts were also characterized by Raman spectroscopy, TEM-HRTEM, STEM-EDX and XPS. Raman spectroscopy was used in order to determine the presence of molybdenum oxide species and/or carbonaceous residues (Figure S1). The very low intensity bands in the zone 815–990 cm\(^{-1}\) points to the presence of residual MoO\(_3\) [44–46], which could be formed by surface oxidation when the samples were exposed to air. For MoxC/TiO\(_2\), Raman bands at 260, 429 and 610 cm\(^{-1}\), assigned to rutile, and at 150 cm\(^{-1}\) assigned to anatase, are clearly visible [47–49]. In all cases, the intensity of the bands in the 1200–1700 cm\(^{-1}\) region characteristic of carbonaceous species (D and G bands), is negligible (Figure S1).

TEM-HRTEM and STEM-EDX analysis of MoxC/Al\(_2\)O\(_3\), MoxC/SiO\(_2\) and MoxC/TiO\(_2\) are shown in Figures 4–6, respectively. For MoxC/Al\(_2\)O\(_3\) (Figure 4), the presence of hexagonal Mo\(_2\)C with a mean particle size of 21 nm was determined in agreement with XRD results. TEM-HRTEM analysis of MoxC/SiO\(_2\) (Figure 5) allowed to confirm the presence of hexagonal Mo\(_2\)C and cubic MoC particles with bimodal distribution and mean particle sizes of 18 nm and 5 nm, respectively (Figure 5A–C). For MoxC/TiO\(_2\) (Figure 6), only the presence of the cubic MoC phase with a mean particle size of 4 nm could be determined. The supported MoxC materials studied in this work follow the recently predicted general trend of size-dependent phase diagrams for bulk Mo and W carbides: fcc phases are generally found at small particle size and hcp phases are prevalent at large particle size [50].

In all cases, STEM-EDX results (see Figures 4C, 5D, and 6C) indicate a homogeneous distribution of Mo on the corresponding support. Figures 4D, 5E and 6D, show the corresponding EDX spectra; N- and Cl-containing species were not detected.
TEM-HRTEM and STEM-EDX analysis of Mo$_x$C/Al$_2$O$_3$, Mo$_x$C/SiO$_2$ and Mo$_x$C/TiO$_2$ are shown in Figures 4–6, respectively. For Mo$_x$C/Al$_2$O$_3$ (Figure 4), the presence of hexagonal Mo$_2$C with a mean particle size of 21 nm was determined in agreement with XRD results. TEM-HRTEM analysis of Mo$_x$C/SiO$_2$ (Figure 5) allowed to confirm the presence of hexagonal Mo$_2$C and cubic MoC particles with bimodal distribution and mean particle sizes of 18 nm and 5 nm, respectively (Figure 5A–C). For Mo$_x$C/TiO$_2$ (Figure 6), only the presence of the cubic MoC phase with a mean particle size of 4 nm could be determined.

The supported Mo$_x$C materials studied in this work follow the recently predicted general trend of size-dependent phase diagrams for bulk Mo and W carbides: fcc phases are generally found at small particle size and hcp phases are prevalent at large particle size [50].

Figure 4. (A,B) TEM−HRTEM micrographs of Mo$_x$C/Al$_2$O$_3$ catalyst; (C) STEM−EDX mapping; (D) EDX spectrum.

Figure 5. (A–C) TEM−HRTEM micrographs of Mo$_x$C/SiO$_2$ catalyst; (D) STEM−EDX mapping; (E) EDX spectrum.
As stated above, the catalysts were also analyzed by XPS. Al 2p, Si 2p and Ti 2p BE at 74.8, 104.0 and 459.3 eV, characteristic of Al2O3, SiO2, and TiO2, were found for MoxC/Al2O3, MoxC/SiO2 and MoxC/TiO2, respectively (Figure S2). Figure 7 shows the C 1s and Mo 3d XP spectra. The C 1s core level spectra (Figure 7A) show a maximum at 284.8 eV associated to the adventitious carbon, the component at 283.7–283.8 eV is associated to surface molybdenum carbide species [21,31,51–54]. Components extended above 284.8 eV are related to different oxygen containing species [52–56]. The Mo 3d spectra are complex (Figure 7B); however, they can be deconvoluted into four doublets (Mo 3d5/2 and Mo 3d3/2). According to literature, the Mo 3d5/2/Mo 3d3/2 intensity ratio was fixed to be 1.5, and the Mo 3d5/2-Mo 3d3/2 BE splitting was set at 3.1 eV [57–59]. The 3d5/2 peaks at the lowest BE region, 228.5–228.7 eV, are attributed to Mo2+ and Mo3+ in Mo2C and/or oxycarbide species [19,21,31,51]. The Mo 3d5/2 components at 229.4–229.5, 231.3–232.6 and 233.2 eV, can be assigned to Mo4+, Mo5+ and Mo6+ surface species, respectively [19,58–61], which could be related to the presence of MoC, oxycarbide and/or oxide species. Table 2 shows the contribution of Mo2+/Mo3+ and Mo4+ species to the total surface Mon+ species; the MoxC/SiO2 catalyst having both Mo2C and MoC shows the highest values.

Table 2. Apparent Ea determined for MoxC/support catalysts and surface characteristics determined from XPS.

| Catalyst       | Ea (kJ·mol⁻¹) | (Mo²⁺,³⁺/Total Moⁿ⁺)XPS | (Mo²⁺,³⁺,⁴⁺/Total Moⁿ⁺)XPS |
|----------------|--------------|--------------------------|-----------------------------|
| MoxC/Al₂O₃    | 77.7 ± 1.7   | 0.277                    | 0.347                       |
| MoxC/SiO₂     | 64.9 ± 3.2   | 0.431                    | 0.690                       |
| MoxC/TiO₂     | 77.9 ± 4.1   | 0.098                    | 0.316                       |

Reaction conditions: CO₂/H₂/N₂ = 1/1/3, GHSV = 3000 h⁻¹, P = 0.1 MPa and T = 598–648 K.
Figure 7. XP spectra of Mo₅C/support catalysts: (A) C 1s level; (B) Mo 3d level.

All catalysts were tested in the RWGS using CO₂:H₂ = 1/3 and CO₂/H₂ = 1/1 ratios. Catalytic data of unsupported Mo₂C, prepared using a similar method to that used in this work but in the absence of support, are also included for comparison [21]. As stated in the experimental section, the first part of the catalytic test: 598 K (3 h)→573 K (3 h)→548 K (10 h) was carried out in order to condition the catalyst under RWGS. Next, when the temperature was increased to 598 K, the CO₂ conversion was in all cases higher than that obtained at 598 K in the conditioning step (Figure 8A and Figure 10A). This behavior could be related with the removal of initially adsorbed surface species. After this first step and regardless the catalyst and the conditions, CO₂ conversion increases with the rising of reaction temperature from 598 K to 673 K (Figure 8A and Figure 10A).
Figure 8. Catalytic behavior of Mo\textsubscript{x}C/support and unsupported reference Mo\textsubscript{2}C catalysts in the RWGS reaction as a function of reaction temperature; (A) CO\textsubscript{2} conversion, (B) CO selectivity. Reaction conditions: m\textsubscript{cat} = 150 mg, CO\textsubscript{2}/H\textsubscript{2}/N\textsubscript{2} = 1/3/1, GHSV = 3000 h\textsuperscript{−1}, P = 0.1 MPa.

Figures 8 and 9 show the RWGS behavior of catalysts when CO\textsubscript{2}:H\textsubscript{2} = 1/3 is used. Mo\textsubscript{x}C/SiO\textsubscript{2} presented the highest value of CO\textsubscript{2} conversion (27.5%) at 673 K (Figure 8A); the corresponding equilibrium CO\textsubscript{2} conversion for RWGS at the experimental conditions used is about 37% (at 673 K). Mo\textsubscript{x}C/Al\textsubscript{2}O\textsubscript{3} showed a catalytic activity close to that of the unsupported Mo\textsubscript{2}C catalyst. Meanwhile, Mo\textsubscript{x}C/TiO\textsubscript{2} showed lower values of CO\textsubscript{2} conversion than those of unsupported Mo\textsubscript{2}C [21]. These results contrast with those usually reported for supported metallic catalysts [62,63]. The activity of SiO\textsubscript{2}- and Al\textsubscript{2}O\textsubscript{3}-supported metals in the RWGS is usually lower than that found when reducible supports such as TiO\textsubscript{2} or CeO\textsubscript{2} are used, which can generate oxygen vacancies that strengths the CO\textsubscript{2} adsorption and then the activity in the RWGS [63]. In this work, besides the difference in the surface-
area of catalysts, the composition and characteristics of generated Mo\textsubscript{x}C nanoparticles change as a function of the support.

![CO Production graph](image_url)

**Figure 9.** CO production per mol of Mo as a function of reaction temperature in RWGS over Mo\textsubscript{x}C/support and unsupported reference Mo\textsubscript{2}C catalysts. Reaction conditions: m\textsubscript{cat} = 150 mg, CO\textsubscript{2}/H\textsubscript{2}/N\textsubscript{2} = 1/1, GHSV = 3000 h\textsuperscript{-1}, P = 0.1 MPa.

A key process in the RWGS is the cleavage of C-O bond with CO + O formation. In this context molybdenum oxycarbide has been proposed as an intermediate in the RWGS over Mo\textsubscript{x}C that likely enhances the RWGS rate [25]. We have demonstrated that over a polycrystalline α-Mo\textsubscript{2}C catalyst, prepared with the method used in the present work, the enhanced CO\textsubscript{2} dissociation toward CO + O results from specific surface facets [21]. Next, the easy release of CO and the continuous O removal by H\textsubscript{2} to form H\textsubscript{2}O, results in high RWGS activity. The existence of both, hcp Mo\textsubscript{2}C and fcc MoC phases in the SiO\textsubscript{2}-supported catalyst, could result in interphases regions with appropriate characteristics to enhance RWGS on Mo\textsubscript{x}C/SiO\textsubscript{2} catalyst. In this context, for different Mo\textsubscript{x}C bulk catalysts, the lowest activation energy in the RWGS was found for a catalyst containing several Mo\textsubscript{2}C and MoC phases [31].

All the supported catalysts showed high CO selectivity values. When CO\textsubscript{2}/H\textsubscript{2} = 1/3 was used, CO selectivity were always higher than 92% (Figure 8B). The highest CO selectivity was observed for the Mo\textsubscript{x}C/SiO\textsubscript{2} catalyst, achieving at 673 K, 98.5%. Only Mo\textsubscript{x}C/Al\textsubscript{2}O\textsubscript{3} showed CO selectivity values slightly lower than that of unsupported Mo\textsubscript{2}C (Figure 8B). CH\textsubscript{4} was the main byproduct and only very small amounts of ethylene were formed.

For a proper comparison of the catalysts, the values of CO production were calculated per mol of Mo in the samples; results are shown in Figure 9. All the supported catalysts showed a higher CO production per mol of Mo compared to the unsupported Mo\textsubscript{2}C catalyst [21]. At the end of the catalytic test, Mo\textsubscript{x}C/SiO\textsubscript{2} and Mo\textsubscript{x}C/Al\textsubscript{2}O\textsubscript{3} showed a higher CO production at 648 K than before reaction at 673 K (Figure 9). This could be related with the removal of remaining oxygen surface species during the reaction at 673 K. The highest CO production in the whole range of reaction temperature tested was obtained for Mo\textsubscript{x}C/SiO\textsubscript{2}; it reached about 17.0 mol CO/mol Mo•h at 673 K.

Catalysts were also tested in the RWGS using a stoichiometric ratio of the reactant mixture, CO\textsubscript{2}/H\textsubscript{2}/ = 1/1. Figure 10 shows the variation of CO\textsubscript{2} conversion and CO selectivity values. As expected, the CO\textsubscript{2} conversion (Figure 10A) was lower and the CO
selectivity (Figure 10B) higher when a mixture CO$_2$/H$_2$ = 1/1 was used than when the reactant mixture was CO$_2$/H$_2$ = 1/3. Using the CO$_2$/H$_2$ = 1/1 reactant mixture, the highest CO$_2$ conversion (Figure 10A) and the highest CO production per mol of Mo (Figure 11), in the whole range of reaction temperature tested, were also found over the Mo$_x$C/SiO$_2$ catalyst. In this case, at the end of the catalytic test, only for Mo$_x$C/SiO$_2$ a slightly higher CO production at 648 K than before reaction at 673 K was observed (Figure 11).

Figure 10. Catalytic behavior of Mo$_x$C/support and unsupported reference Mo$_2$C catalysts in the RWGS reaction as a function of reaction temperature; (A) CO$_2$ conversion, (B) CO selectivity. Reaction conditions: m$_{\text{cat}}$ = 150 mg, CO$_2$/H$_2$/N$_2$ = 1/1/3, GHSV = 3000 h$^{-1}$, P = 0.1 MPa.
were similar. Meanwhile, the presence of MoO$_2$ was detected by XRD in post-reaction catalysts after the test with CO$_2$/H$_2$/N$_2$ = 1/1/3 (Figure S3) due to an easier removal of the O surface species formed from the CO$_2$ activation over these materials under CO$_2$/H$_2$/N$_2$ = 1/1/3 conditions [21,31].

Figure 11. CO production per mol Mo as a function of reaction temperature in RWGS over Mo$_x$C/support and unsupported reference Mo$_2$C catalysts. Reaction conditions: m$_{\text{cat}}$ = 150 mg, CO$_2$/H$_2$/N$_2$ = 1/1/3, GHSV = 3000 h$^{-1}$, P = 0.1 MPa.

It is noteworthy, that after the overall RWGS study carried out, all supported catalysts, showed quite constant values of CO$_2$ conversion and CO selectivity during the last step at 648 K (5 h), under both CO$_2$/H$_2$/ = 1/3 and CO$_2$/H$_2$/ = 1/1 conditions.

The apparent activation energies (E$_a$) for CO production over supported catalysts were calculated according to the Arrhenius plots in the temperature range of 598–648 K; values between 65–78 kJ/mol were obtained (Table 2). These values are in the range of that recently reported for an alumina supported Mo$_2$C cluster-based catalyst (76.4 kJ/mol) [39]. Mo$_x$C/SiO$_2$ showed the lowest E$_a$ for CO production. As stated above, the best performance of Mo$_x$C/SiO$_2$ could be related with the coexistence in this catalyst of different Mo$_x$C phases, hexagonal Mo$_2$C and cubic MoC, as has been recently suggested for unsupported Mo$_x$C catalysts [31]. Moreover, Mo$_x$C/SiO$_2$ showed the highest contribution of Mo$^{2+}$/Mo$^{3+}$ and Mo$^{4+}$ species to the total surface Mo$^{n+}$ species. For Mo$_x$C-based catalysts, an easy reduction under reaction conditions of molybdenum species has been related with their performance in RWGS [41].

Post-reaction catalysts were characterized by BET and XRD. Only a slight decrease in the BET surface area was found after the RWGS reaction (Table 1). The XRD patterns of fresh (Figures 1–3) and post-reaction catalysts after the test with CO$_2$/H$_2$ = 1/3 (Figure S3) were similar. Meanwhile, the presence of MoO$_2$ was detected by XRD in post-reaction Mo$_x$C/SiO$_2$ and Mo$_x$C/TiO$_2$ when the reactant mixture was CO$_2$/H$_2$ = 1/1 (Figure S4); the oxidation could be prevented under a richer hydrogen atmosphere (CO$_2$/H$_2$ = 1/3) due to an easier removal of the O surface species formed from the CO$_2$ activation over these materials under CO$_2$/H$_2$ = 1/3 conditions [21,31].

4. Conclusions

Using urea and MoCl$_5$ as carbon and molybdenum sources, different Mo$_x$C phases were successfully supported over Al$_2$O$_3$, SiO$_2$ and TiO$_2$. The support determined the developed Mo$_x$C phases on the materials and their catalytic behavior in the RWGS. Hexagonal Mo$_2$C nanoparticles on Mo$_x$C/Al$_2$O$_3$ and cubic MoC nanoparticles on Mo$_x$C/TiO$_2$ were found. Over Mo$_x$C/SiO$_2$ both hexagonal Mo$_2$C and cubic MoC nanoparticles were present. In all cases, supported hexagonal Mo$_2$C nanoparticles were larger than cubic MoC ones.
All catalysts showed a stable catalytic behavior and exhibited higher CO production per mol of Mo than the unsupported hexagonal Mo$_2$C similarly prepared, under the reaction conditions used (CO$_2$/H$_2$ = 1/3 and CO$_2$/H$_2$ = 1/1; T = 548–673 K).

Mo$_x$C/SiO$_2$ exhibited the highest surface ratio of Mo species with low oxidation states (Mo$^{2+,3+,4+}$) and the best performance in the RWGS reaction. Over Mo$_x$C/SiO$_2$, CO$_2$ conversion of 27.5% and CO selectivity of 98.5% were achieved at 673 K under CO$_2$/H$_2$ = 1/3; for CO production, an apparent activation energy of 64.9 ± 3.2 kJ mol$^{-1}$ was determined at 598–648 K under CO$_2$/H$_2$ = 1/1. The catalytic behavior is proposed to be governed by the supported Mo$_x$C phase. The simultaneous presence of hexagonal Mo$_2$C and cubic MoC nanoparticles in Mo$_x$C/SiO$_2$ plays a main role on the catalytic behavior of this catalyst.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/xxxxxx/s1, Figure S1. Raman spectra of fresh Mo$_x$C/support catalysts; Figure S2. XP spectra of Mo$_x$C/support catalysts. (A) Al 2p level registered for Mo$_x$C/Al$_2$O$_3$, (B) Si 2p level registered for Mo$_x$C/SiO$_2$, (C) Ti 2p level registered for Mo$_x$C/TiO$_2$; Figure S3. XRD patterns of Mo$_x$C/support catalysts after RWGS reaction (CO$_2$/H$_2$ = 1/3); reaction conditions: m$_{\text{cat}}$ = 150 mg, GHSV = 3000 h$^{-1}$, P = 0.1 MPa.; Figure S4. XRD patterns of Mo$_x$C/support catalysts after RWGS reaction (CO$_2$/H$_2$ = 1/1); reaction conditions: m$_{\text{cat}}$ = 150 mg, GHSV = 3000 h$^{-1}$, P = 0.1 MPa.

**Author Contributions:** Methodology, experimental and formal analysis A.P., X.L., J.R.B., P.R.d.l.P. and N.H.; writing—original draft, A.P., X.L., P.R.d.l.P. and N.H.; writing—review and editing, A.P., P.R.d.l.P. and N.H.; supervision, P.R.d.l.P. and N.H.; project administration and funding acquisition, P.R.d.l.P. and N.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by MAT2017-87500-P and PID2020-116031RB I00/AEI/10.13039/501100011033/FEDER projects.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data present in this study are available on request from the corresponding author.

**Acknowledgments:** The authors thank MAT2017-87500-P and PID2020-116031RB I00/AEI/10.13039/501100011033/FEDER projects, for financial support. J.R.B. acknowledges the Spanish SECAT for his master thesis grant. X.L. is grateful to the China Scholarship Council and the University of Barcelona (IN2UB) for her PhD grants. A.P. thanks MINECO for his PhD grant (BES-C-2015-074574).

**Conflicts of Interest:** The authors declare no conflict of interest.
9. Boot-Handford, M.E.; Abanades, J.C.; Anthony, E.J.; Blunt, M.J.; Brandani, S.; Mac Dowell, N.; Fernández, J.R.; Ferrari, M.C.; Gross, R.; Hallett, J.P.; et al. Carbon Capture and Storage Update. Energy Environ. Sci. 2014, 7, 130–189.

10. Daza, Y.A.; Kuhn, J.N. CO₂ Conversion by Reverse Water Gas Shift Catalysis: Comparison of Catalysts, Mechanisms and Their Consequences for CO₂ Conversion to Liquid Fuels. RSC Adv. 2016, 6, 49675–49691. [CrossRef]

11. Liu, X.M.; Lu, G.Q.; Yan, Z.F.; Bellamini, J. Recent Advances in Catalysts for Methanol Synthesis Via Hydrogenation of CO and CO₂. Ind. Eng. Chem. Res. 2003, 42, 6518–6530. [CrossRef]

12. Jahangiri, H.; Bennett, J.; Mahjoubi, P.; Wilson, K.; Gu, S. A Review of Advanced Catalyst Development for Fischer–Tropsch Synthesis of Hydrocarbons from Biomass Derived Syn-Gas. Catal. Sci. Technol. 2014, 4, 2210–2229. [CrossRef]

13. Saeidi, S.; Amin, N.A.S.; Rahimpour, M.R. Hydrogenation of CO to Value-Added Products—A Review and Potential Future Developments. J. CO₂ Util. 2014, 5, 66–81. [CrossRef]

14. Elsermagawy, O.Y.H.; Hoadley, A.; Patel, J.; Bhatelia, T.; Lim, S.; Haque, N.; Li, C. Thermo-Economic Analysis of Reverse Water-Gas Shift Process With Different Temperatures for Green Methanol Production as a Hydrogen Carrier. J. CO₂ Util. 2020, 41, 101280. [CrossRef]

15. Kirsch, H.; Sommer, U.; Pfeifer, P.; Dittmeyer, R. Power-To-Fuel Conversion Based on Reverse Water-Gas-Shift, Fischer-Tropsch Synthesis and Hydropyrocracking: Mathematical Modeling and Simulation in Matlab/Simulink. Chem. Eng. Sci. 2020, 227, 115930. [CrossRef]

16. Liang, B.; Duan, H.; Su, X.; Chen, X.; Huang, Y.; Chen, X.; Delgado, J.J.; Zhang, T. Promoting Role of Potassium in the Reverse Water Gas Shift Reaction on Pt/Mullite Catalyst. Catal. Today 2017, 281, 319–326. [CrossRef]

17. Levy, R.B.; Boudart, M. Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis. Catal. Today 2017, 281, 319–326. [CrossRef]

18. Levy, R.B.; Boudart, M. Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis. Science 1973, 181, 547–549. [CrossRef] [PubMed]

19. Oyama, S.T. The Chemistry of Transition Metal Carbides and Nitrides; Blackie Academic & Professional: Glasgow, Scotland, 1996.

20. 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. Engl. 2014, 53, 6705–6709. [CrossRef]

21. Porosoff, M.D.; Kattel, S.; Li, W.; 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]

22. Pajares, A.; Prats, H.; Romero, A.; Viñes, F.; de la Piscina, P.; Sayrò, R.; Homs, N.; Illas, F. Critical Effect of Carbon Vacancies on the Reverse Water Gas Shift Reaction over Vanadium Carbide Catalysts. Appl. Catal. B 2020, 267, 118719. [CrossRef]

23. 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]

24. Posada-Pérez, S.; Viñes, F.; Ramírez, P.J.; Vidal, A.B.; Rodríguez, 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] [PubMed]

25. Reddy, K.P.; Dama, S.; Mhamane, N.B.; Ghosalya, M.K.; Raja, T.; Satyanarayana, C.V.; Gopinath, C.S. Molybdenum carbide catalyst for the reduction of CO₂ to CO: Surface science aspects by NAPPES and catalysis studies. Dalton Trans. 2019, 48, 12199–12209. [CrossRef]

26. Claridge, J.B.; York, A.P.E.; Brungs, A.J.; Green, M.L.H. Study of the Temperature-Programmed Reaction Synthesis of Early Transition Metal Carbide and Nitride Catalyst Materials from Oxide Precursors. Chem. Mater. 2000, 12, 132–142. [CrossRef]

27. Volpe, L.; Boudart, M. Compounds of Molybdenum and Tungsten with High Specific Surface Area. J. Solid State Chem. 1985, 59, 348–356. [CrossRef]

28. Naito, S.; Tsuji, M.; Sakamoto, Y.; Miyao, T. Marked Difference of Catalytic Behavior by Preparation Methods in CH₄ Reforming with CO₂ Over Mo₂C and WC Catalysts. Stud. Surf. Sci. Catal. 2000, 143, 415–423.

29. Giordano, C.; Erpen, C.; Yao, W.; Antonietti, M. Synthesis of Mo and W Carbine and Nitride Nanoparticles Via a Simple “Urea Glass” Route. Nano Lett. 2008, 8, 4659–4663. [CrossRef]

30. Gao, J.; Wu, Y.; Jia, C.; Zhong, Z.; Gao, F.; Yang, Y.; Liu, B. Controllable Synthesis of α-MoC₁₋ₓ and β-Mo₂C Nanowires for Highly Selective CO₂ Reduction to CO. Catal. Commun. 2016, 74, 148–150. [CrossRef]

31. Liu, X.; Pajares, A.; Matienzo, D.D.C.; Ramírez de la Piscina, P.; Homs, N. Preparation and Characterization of Bulk Mo₅C₃ Catalysts and Their Use in the Reverse Water-Gas Shift Reaction. Catal. Today 2020, 356, 384–389. [CrossRef]

32. Tsuji, M.; Miyao, T.; Naito, S. Remarkable Support Effect of ZrO₂ Upon the CO₂ Reforming of CH₄ Over Supported Molybdenum Carbide Catalysts. Catal. Lett. 2000, 60, 195–198. [CrossRef]

33. Chen, X.; Zhang, T.; Ying, P.; Zheng, M.; Wu, W.; Xia, L.; Li, T.; Wang, X.; Li, C. A Novel Catalyst for Hydrazine Decomposition: Molybdenum Carbide Supported on γ-Al₂O₃. Chem. Commun. 2002, 3, 288–289. [CrossRef] [PubMed]

34. Aegerter, P.A.; Quigley, W.W.C.; Simpson, G.J.; Ziegler, D.D.; Logan, J.W.; McCrea, K.R.; Glazier, S.; Bussell, M.E. Thiophene Hydrodesulfurization over Alumina-Supported Molybdenum Carbide and Nitride Catalysts: Adsorption Sites, Catalytic Activities, and Nature of the Active Surface. J. Catal. 1996, 164, 109–121. [CrossRef]

35. Da Costa, P.; Potvin, C.; Manoli, J.M.; Breyssse, M.; Djêga-Mariadassou, G. Novel Phosphorus-Doped Alumina-Supported Molybdenum and Tungsten Carbides: Synthesis, Characterization and Hydrogenation Properties. Catal. Lett. 2001, 72, 91–97. [CrossRef]
