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J. A. Rodriguez

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C₁ Chemistry on Metal Carbide Nanoparticles: Boosting the Conversion of CO₂ and CH₄

José A. Rodríguez,^{a,*} Carlos Jimenez-Orozco,^b Elizabeth Flórez,^b Francesc Viñes^c and Francesc Illas^{c,*}

^a *Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA.*

^b *Universidad de Medellín, Facultad de Ciencias Básicas, Grupo de Materiales con Impacto (Mat&mpac), Carrera 87 No 30-65, Medellín, Colombia.*

^c *Departament de Ciència dels Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain.*

*Corresponding authors: J.A. Rodríguez (rodriguez@bnl.gov); F. Illas (francesc.illas@ub.edu).

Abstract

The studies described in this perspective show that transition metal carbide (TMC) nanoparticles can be very useful for the activation of three molecules located at the heart of C₁ chemistry: H₂, CH₄, and CO₂. They also can play a major role in the trapping and conversion of two major greenhouse gases. A combination of experiment and theory has shed light on the physical and chemical properties of these systems, which can be very different from those of bulk carbides. Molecular clusters of these compounds, which can be inserted inside the cages of zeolites or carbon nanotubes, have unsaturated metal and carbon atoms that frequently work in a cooperative way when dealing with hard-to-activate molecules such as CH₄ and CO₂. These molecular clusters can evolve into nanoparticles of small to medium size (< 15 nm) that have unique carbon/metal ratios and structures not seen in the bulk metal carbides. Even when their structures are cut from bulk lattices, the TMC nanoparticles have corner or edge atoms that are active for the cleavage and conversion of C-H and C-O bonds. Here, we cover experimental and theoretical studies with well-defined metal carbide nanoparticles prepared by different methods, free and supported on diverse substrates. The perspective ends with a discussion of current challenges and potential applications.

Keywords: Carbon dioxide, methane, hydrogen, methanol, metal carbides

Introduction

Carbon dioxide (CO₂) and methane (CH₄) are among the worst greenhouse gases and main contributors to global warming and climate change.¹⁻³ Both molecules are highly stable, non-polar, and display a low reactivity.⁴⁻⁷ New initiatives emphasize the need to design and optimize processes for the trapping, storage, and conversion of CO₂ and CH₄.⁴⁻⁷ These processes involve three essential components: 1) A reactive center that binds and activates the CO₂ or CH₄ molecule, 2) a surrounding phase with reactants or solvents, and 3) a source of thermal, electrical or photochemical energy.⁴⁻⁷ Catalytic conversion of CO₂ or CH₄ to chemicals and fuels is a “two birds, one stone” approach towards solving the climate change problem and energy demand-supply deficit in the modern world.⁴⁻⁷ Conversion to oxygenates or light alkanes are promising processes for a large scale utilization of CO₂ and CH₄.⁸⁻¹⁰ These conversions are hampered by challenges associated with low activity and selectivity of currently used catalysts. In recent years, transition metal carbides (TMCs) have emerged as useful materials for the activation and transformation of CO₂ and CH₄.¹¹⁻²²

Since the pioneering work of Levy and Boudart, where the hydrogenation ability of TMCs was described as comparable to that of Pt-group elements,¹⁶ these materials have been the focus of many studies in catalysis.^{11-15,17-22} Transition metal carbides can display a unique combination of the physical properties characteristic of noble metals and ceramics.^{17,23} Many TMCs are good electrical and thermal conductors while possessing ultra-hardness and very high melting points.^{17,23} The degree of ionicity in a metal-carbon bond is much smaller than in a metal-oxide bond, opening the possibility for different catalytic properties.^{10,24} In a metal carbide, metal and carbon centers can participate in the binding an activation or CO₂ or CH₄.^{14, 18,25-27} The formation of C–C or C=C bonds can occur after adsorbing CO₂ or CH_x fragments on a metal carbide.^{14,25-27, 28} The carbon/metal ratio is an important variable that can be used to tune the breaking of one or two hydrogen bonds in the CO₂ molecule and favor the selectivity during hydrogenation towards oxygenates or alkanes.^{14,25-29} For a given carbon/metal ratio, different catalytic properties have been seen for bulk, two-dimensional (2D) and nanostructure systems.^{12,20,28,30} Furthermore, transition metal carbide surfaces can act as supports, having an useful ability to modify the catalytic properties of supported metals not seen in the case of metal oxide substrates.^{14,24,25,31}

In this perspective, we discuss recent developments and emerging trends for the conversion CO₂ and CH₄ on nanoparticles of transition metal carbides. For years it has been known that TMC nanoparticles supported inside zeolites can catalyze the conversion of CO₂ and CH₄ into oxygenates, light alkanes or aromatics.³²⁻³⁵ In principle, the size and structure of the TMC nanoparticles and their carbon/metal ratio could affect their ability to bind and transform CO₂ and CH₄. However, until recently, there was little information regarding these issues and no systematic review or perspective has been published so far examining this important topic. Here, we will cover studies with well-defined TMC nanostructures prepared by different methods, free and supported, that are able to activate CO₂ and CH₄ and carry out the C₁ chemistry associated with the production of high-value chemicals (Scheme I).^{20,28,30,36-44} We will compare the properties of these well-defined nanostructures to those reported for single-crystal surfaces, films, and bulk powders. Particular attention will be paid to the latest insights for the bonding and activation of CO₂ and CH₄, and to fundamental phenomena associated with the selective conversion of these molecules into oxygenates or alkanes. We end the article with a discussion of current challenges and potential applications.

Structural and morphological properties of TMC nanoparticles

Since the 1980s, methods have been reported in the literature for the synthesis of clusters, aggregates, and nanostructures of TMCs.³⁶⁻⁴⁴ These methods involve direct reaction of a given metal with C-containing molecules in the gas phase,^{42,43} metal deposition on layers of C-rich molecules,³⁶ reduction and carburization of oxide precursors,^{20,30,41} mechanochemical and ball milling approaches,³⁸ and sol-gel chemistry.³⁹ Molecular clusters, nanoparticles, and 2D systems frequently can adopt carbon/metal ratios and structures not seen in bulk TMCs.³⁶⁻⁴⁴ They exhibit an “abnormal” behavior that can be quite useful for the activation of key molecules like H₂,^{45,46} CO₂,^{18,31,37,47,48} CH₄²⁸ or C₂H₄.⁴⁹ Many interesting structural and electronic properties have been identified for clusters, aggregates, and nanostructures of TMCs,³⁶⁻⁴⁴ but only a few of these systems have been actually tested in the binding or activation of CO₂ and CH₄.^{18,20,28,37,47-50} In this section, we describe what is known about their structural and electronic properties.

Molecular clusters with a M₈C₁₂ stoichiometry, metcars, have been prepared for a large number of metals (M= Ti, V, Zr, Hf, Cr, Mo, and Fe).^{42,43,51} The typical structure of the metcars is shown at the top of Figure 1. For comparison, we also include the typical rock salt structure for bulk 1:1 TMCs surface and other carbide clusters. The metcars have

a carbon/metal ratio of 1.5, which is larger than that seen in most bulk TMCs where this ratio typically falls in the range of 0.5 to 1.0. As we will see below, in spite of a large carbon/metal ratio, the metcars display a good ability to bind key molecules in C1 chemistry like H₂, CO, H₂O, and CO₂.^{37,45,47,50} The M₈C₁₂ compounds adopt a T_d-like structure that includes low- and high-coordinated M atoms and six C₂ groups (Figure 1). In principle, the four M atoms located in edge sites of the structure are expected to be the most active centers for binding but, depending on the nature of a reactant, the C atoms also can be active.^{37,45,47,50} Over the years, different types of M_xC_y molecular clusters have been synthesized and also studied in theoretical calculations.^{15,37,48-52} Figure 1 displays the structures of several molecular clusters. The large clusters at the bottom are derived from cuts in the rock-salt lattice of bulk δ-MoC. The small to medium size clusters have the proper size to be inserted in the cages of zeolites or mesoporous structures used in C1 catalysis.^{32-35,53} For example, binding geometries for Mo₂C_x (x = 1, 2, 3, 4, and 6) and Mo₄C_x (x = 2, 4, 6, and 8) nanoparticles inside the ZSM-5 zeolite were identified by combining DFT cluster calculations with hybrid quantum mechanical and molecular mechanical (QM/MM) periodic structure calculations (Figure 2).⁵³ In the clusters shown in Figures 1 and 2, the carbon/metal ratio changes and we can see a large diversity of M and C atoms that appear at corner or edge sites with a low coordination number. These structural characteristics open the door to interesting reaction channels for the activation of CO₂ and CH₄.^{28,37,48,53}

Nanoparticles of molybdenum carbide have been prepared on an inert Au(111) substrate, Figure 3.³⁶ The MoC_y nanoparticles were generated by deposition of Mo metal onto a reactive multilayer of ethylene, which was physisorbed on the Au(111) surface at 100 K. Upon heating to 750 K, the unreacted ethylene desorbed and MoC_y nanoparticles were present on the gold surface.³⁶ Following this synthetic procedure, by changing the initial amounts of Mo and C₂H₄ deposited on the Au(111) substrate, it was possible to control the carbon/molybdenum ratio in the carbide nanoparticles, varying between 0.6 and 1.1.^{24,28,36} Images acquired by scanning tunnelling microscopy (STM), see Figure 3, showed that the MoC_x nanoparticles were small (0.6-1.5 nm) and nucleated on the face-centred cubic (*fcc*) troughs located on either side of the elbows of the reconstructed Au(111) surface, Figure 2.³⁶ The STM images indicated that the TMC nanoparticles were essentially amorphous and did not have the typical structures of bulk MoC or Mo₂C.³⁶ Thus, due to their morphology and electronic structure,³⁶ special chemical properties can be expected from these carbide systems.

Several approaches are available to produce TMC nanoparticles in powder-like form.^{20,30,38,39,41,54,55} A major aim is the rational design of functional materials with eco-friendly and cost-effective approaches. Oxygen contamination and the formation of oxycarbides can be a major problem.^{17,21,23} Due to their low cost, the carbides of early transition metals have received a lot of attention.^{20,38,53} Figure 4a displays an image of transmission electron microscopy (TEM) for nanoparticles of (hexagonal) α - MoC_{1-x} prepared by a mild-approach that involved the decomposition and carburization of $\text{Mo}(\text{CO})_6$.²⁰ These systems were crystalline with an average size close to 2 nm (Figure 4b). The XRD pattern of these nanoparticles matched that of bulk α - MoC_{1-x} (Figure 4c).²⁰ The results of XRD, pair distribution function (PDF), and EXAFS pointed to the existence of a large number of C vacancies and defects in the lattice of the nanoparticles.²⁰ This is typical of nanoparticles of molybdenum carbide, which can adopt the structures of bulk (hexagonal) α - MoC_{1-x} or (orthorhombic) β - Mo_2C , but have a very large concentration of lattice imperfections and a wide range of carbon/metal ratios.^{20,30,53} Furthermore, in powder-like TMC nanoparticles, crystalline and amorphous regions usually coexist,^{38-41,53} showing edges defined by metal and carbon atoms that have a low coordination number, as seen in the molecular clusters of Figure 1. The nanostructures seen in Figures 1-4 provide an excellent platform to investigate the performance of TMC nanoparticles in C_1 chemistry.

Adsorption and activation of H_2 on TMC nanoparticles

The interaction of hydrogen with TMC nanoparticles is important due to the role that this element plays in C_1 catalysis^{4,5,56,57} and in the hydrogen evolution reaction (HER).⁵⁸⁻⁶⁴ TMCs also have been proposed as materials for hydrogen storage.^{45,65-67} An early study examined at a theoretical level the interaction of a series of H_2 molecules with the Ti_8C_{12} metcar.⁴⁵ H_2 molecules were bound with different configurations to the molecular cluster seen at the top of Figure 1. It was found that a single Ti atom at a corner site of the cluster could bind three H_2 molecules, while a Ti atom on the center of a structural face was able to bind only one molecule.⁴⁵ After considering binding to the Ti and C sites of the metcar, a total of 16 H_2 molecules could be attached to the cluster. Thus, the Ti_8C_{12} system can be considered as a high-capacity hydrogen storage medium.⁴⁵ The high ability that all the elements in a metcar have to bind hydrogen also has been found for the atoms in a $\text{TiC}(001)$ surface.⁶⁶ On $\text{TiC}(001)$, the hydrogen saturation coverage is above one

monolayer as a consequence of bonding H and H₂ species to Ti and C centers. The results of DFT calculations predict that at low coverages the H₂ molecules easily dissociates on TiC(001) and the H adatoms prefer bonding to C sites, producing CH_x species that are detected by XPS.⁶⁶ At medium to high hydrogen coverages, the Ti sites are populated and bound H₂ molecules (Kubas-type complexes) appear,⁶⁵ which are similar to the hydrogen entities bound to the Ti₈C₁₂ metcar.⁴⁵

Nanoparticles of MoC_x dispersed on Au(111), see Figures 3 and 5, displayed a larger reactivity towards H₂ than bulk δ-MoC.⁴⁶ On the bulk carbide, dissociative adsorption of H₂ at room temperature led to the population of Mo and C sites by H adatoms with some formation {< 0.2 monolayer (ML)} of CH_x species, which were all removed by heating to 400 K.⁴⁶ Figure 5A shows C 1s XPS spectra collected after dosing H₂ to a Au(111) substrate recovered by 0.3 ML of MoC_{1.1}, prepared following the methodology that produced the carbide nanoparticles seen in Figure 3.^{36,46} In the case of a MoC_{0.6}/Au(111) system, only a limited fraction (~30%) of the C atoms present in the system reacted with hydrogen to yield CH_x species, probably due to the strong bonds between C and Mo atoms in the nanoparticles which were necessary to maintain the cluster integrity.⁴⁶ In contrast, C atoms in MoC_{1.1} nanoparticles were significantly more reactive towards hydrogen than the atoms in the MoC_{0.6} nanoparticles or in the bulk δ-MoC.⁴⁶ In Figure 5A, the strong signal at binding energy near 284.6 eV with respect to the Fermi level, implies that ~ 50% of the C atoms transformed into CH_x groups. This process was fully reversible while heating from 350 to 500 K, where H₂ desorbed into the gas phase without the evolution of methane or any other light alkanes.⁴⁶ Experiments identical to those shown in Figure 5A were done several times and they did not change the C/Mo ratio of the nanoparticles, giving C 1s XPS spectra with the same features. Thus, the MoC_{1.1} nanoparticles can act as a reservoir for the storage and release of H atoms that can be used in hydrogenation processes.⁴⁶

To explain the remarkable behavior of MoC_{1.1}/Au(111), a DFT study was carried out using a stoichiometric Mo₁₂C₁₂ nanoparticle supported on Au(111), Figures 5B-C.⁴⁶ On the supported Mo₁₂C₁₂ system, molecular H₂ and H adatoms were bound with similar strength (see a set of adsorption places in Figure 5B), with H₂ preferring low-coordinated Mo sites, undergoing dissociation to H adatoms, which then moved to adjacent C and Mo sites of the nanoparticle following a complex network of diffusion steps.⁴⁶ Kubas CH₂ structures could be easily formed by diffusion of H adatoms, as shown in Figure 5C, freeing Mo sites that could be used to dissociate additional H₂.⁴⁶ This is important for the

hydrogen storage capacity of the nanoparticle that can behave as a sponge. In the carbide structure in Figure 5B-C, since the carbon/metal ratio is not small (> 0.5), the C atoms are not tightly bound to Mo sites and are chemically active towards CH_x formation.⁴⁶ Compared to flat $\beta\text{-Mo}_2\text{C}(001)$ and $\delta\text{-MoC}(001)$ surfaces, the nanoparticle exhibits a good carbon/metal ratio and a large concentration on unsaturated Mo and C sites.

In principle, the H diffusion and formation of Kubas CH_2 structures can be useful for the HER in electrocatalysis. Indeed, metal carbides are active for this process.⁵⁸⁻⁶⁴ Special attention has received nanoparticles of Mo and W carbides.^{54,56,58,59,68} Figure 6 displays the electrocatalytic HER performance of tungsten or tungsten carbide embedded in N-doped nanoporous carbon (denoted as W@NPC and WC@NPC) in 0.5 M H_2SO_4 .⁶⁸ As the corresponding HER polarization curves shown in Figure 6a, the plain NPC displayed negligible catalytic activity whereas W@NPC showed weak HER activity. Remarkably, WC@NPC showed exceptionally high HER catalytic activity in the aspects of exchange current density, overpotential, and Tafel slope among all tungsten-based catalysts.⁶⁸ To understand better the difference between WC@NPC and W@NPC as catalysts for HER, their adsorption free energies (ΔG_{H^*}) for H^* (intermediate state from H^+ to H_2 during HER) adsorption were studied by DFT calculations.⁶⁸ Six model structures for H^* adsorption were considered: W_3C_3 cluster, W_6 cluster, Graphene, N-Graphene (N-doped graphene), $\text{W}_3\text{C}_3@\text{Graphene}$, and $\text{W}_3\text{C}_3@\text{N-Graphene}$. The calculated ΔG_{H^*} are plotted in Figure 6d together with the results for a Pt model. The $\text{W}_3\text{C}_3@\text{Graphene}$ composite exhibits Pt-like HER activity.⁶⁸ Interestingly, in their landmark article of 1973,¹⁶ Levy and Boudart, after examining a reaction that also involved the transfer of hydrogen, already pointed out the similarities in the catalytic performances of tungsten carbide and platinum.

Adsorption and conversion of CH_4 on TMC nanoparticles

Methane is the major component of natural gas. A major goal in the chemical industry is to use CH_4 as a C_1 feedstock for the synthesis of commodity chemicals such as methanol, ethylene, or benzene, an appealing approach for closing the C-cycle.³ The high strength of the C–H bonds in CH_4 and the non-polar character of the molecule make the activation of this hydrocarbon particularly difficult.^{2,4} Furthermore, to avoid the decomposition of the produced CH_x fragments and competing reactions, methane activation should take place at low or medium temperatures.^{69,70} These difficulties have motivated a large number of studies aimed at examining fundamental and practical aspects associated with

methane activation by different kinds of inorganic catalysts: Plain transition metals, oxides, sulfides, carbides, and zeolites.^{2,4,32-35,69-71}

On late transition metal surfaces, methane binds very weakly and the probability for dissociation is low.^{72,73} For example, on Ni well-defined surfaces, methane dissociation is significant only at temperatures above 450 K,⁷² with similar trends reported for Pt and Pd surfaces.⁷³ Some metal-oxide interfaces are able to activate methane near room temperature (< 400 K) due to cooperative interactions between metal and oxygen centers.^{4,74,75} Can a similar phenomenon occur on TMC nanoparticles?

Experimental and theoretical studies have investigated the interaction of methane with FeC_6^- and Ta_2C_4^- carbide clusters.^{71,76} Time-of-flight (TOF) mass spectra for the interactions of laser ablation generated, mass-selected, and thermalized Ta_2C_4^- clusters with CH_4 , CD_4 , CH_2D_2 , or $^{13}\text{CH}_4$ are shown in Figure 7.⁷⁶ The Ta_2C_4^- was reactive towards the methane and there was a clear isotope effect with a reduction in the reaction rate when switching from CH_4 to CD_4 . Upon the interaction of the carbide cluster with CH_4 in a linear ion trap (LIT) reactor, a strong product peak assigned to $\text{Ta}_2\text{C}_5\text{H}_2^-$ was observed, suggesting the following dehydrogenation channel: $\text{Ta}_2\text{C}_4^- + \text{CH}_4 \rightarrow \text{Ta}_2\text{C}_5\text{H}_2^- + \text{H}_2$.⁷⁶ DFT calculations were performed to determine the structure of Ta_2C_4^- and study the path for its reaction with methane. In the initial stage of the process, the C–H bond activation occurs mainly around one Ta atom and, in the second stage, the other Ta atom receives the H atom coming from the C–H bond cleavage (see top of Figure 7).⁷⁶ Vibrational spectra agree well with the reaction path predicted by the theoretical simulations. The last stage in this path involved the cleavage of another C–H bond and the evolution of H_2 . A comparison of the behavior of Ta_2C_4^- , Ta_2C_3^- , and Ta_2C_2^- showed that the cooperative effect of the two metal atoms to perform methane activation depends on the number of C ligands.⁷⁶ For the reaction of methane with the FeC_6^- cluster, the final product was $\text{FeC}_6\text{CH}_4^-$, with a CH_3 group bound to the Fe and a H attached to a C in the carbide cluster structure.⁷¹ DFT calculations indicated that the initial binding of methane and the cleavage of one C–H bond occurred on the Fe site: H-Fe-CH_3 , with a final migration of the produced H to a C atom in the carbide cluster.⁷¹ As in the case of Ta_2C_4^- , there was a kinetic isotope effect and the rate of activation of CD_4 was slower than that of CH_4 .⁷¹

Methane interacts weakly with surfaces of bulk $\delta\text{-MoC}$ and $\beta\text{-Mo}_2\text{C}$.^{14,28} In contrast, a series of experiments, combining XPS and thermal desorption mass spectroscopy (TDS), for MoC_y ($y = 0.5\text{--}1.3$) nanoparticles dispersed on an inert substrate like Au(111), Figure

3, have shown show that these carbide systems are able to bind and dissociate CH₄ at room temperature and low partial pressures.²⁸ Figure 8 displays the C 1s XPS spectra collected after dosing CH₄ at 300 K to a Au(111) surface pre-covered with 0.3 ML of MoC_{1.1}. Initially, the as-prepared surface exhibits the typical C 1s features for a carbide, and exposure to methane induces the appearance of a second peak, towards higher binding energy, due to the existence of adsorbed CH_x.²⁸ The intensity of this new feature decreases when the sample temperature is raised from 300 to 500 K. In TDS spectra, the desorption of methane (79%), ethane (15%), and ethylene (7%) was observed.²⁸ Thus, the CH_x groups generated by methane dissociation were chemically active and could be used to produce C–C bonds and more complex hydrocarbons. During many CH₄ adsorption/desorption cycles, the MoC_{1.1}/Au(111) system maintained an essentially constant C/Mo ratio and its reactivity towards CH₄ did not decay.²⁸ Thus, the MoC_{1.1} nanoparticles had the right balance of activity and stability for being useful as catalysts.

To study the chemistry behind the XPS and TDS experiments for the CH₄/MoC_{1.1}/Au(111) systems, methane adsorption and first C–H bond cleavage were investigated with DFT on eight MoC_y nanoparticles with C/Mo ratios ranging from 0.67 to 1.50, Figure 8.²⁸ In general, CH₄ prefers to adsorb on low-coordinated Mo atoms, see Figure 8, featuring surprisingly high adsorption energies, ranging from -0.38 to -1.16 eV, that is much bigger than those seen on surfaces of bulk δ -MoC and β -Mo₂C.²⁸ Figure 9 compares the energy barriers for the dissociation of methane on a large set of molybdenum carbide systems. These results indicate that the reactivity of the finite carbide nanoparticles cannot be extrapolated from the behavior seen for the extended bulk surfaces. In general, the breakdown of the correlation is mainly a consequence of a lowering in the energy barrier for the CH₄ → CH₃ + H dissociation on the carbide nanoparticles, a product of the presence of special low-coordinated Mo atoms in the corners or vertices of the nanostructures (Figure 8). This type of site is very active in interacting with methane and other hydrocarbons.^{28,49}

The structure and chemical changes of Mo species in MoO₃/H–ZSM-5 during catalytic CH₄ reactions were monitored using *in-situ* XAFS, temperature-programmed oxidation after the reaction, and isotopic exchange of D₂ with OH groups in H–ZSM-5 before and after CH₄ reaction.³³ Exposure of MoO₃/H–ZSM-5 to methane led to reduction and carburization of molybdenum with the C/Mo ratio reaching a value close (~ 0.4) to that expected for Mo₂C (Figure 10). The corresponding changes in the Mo K-edge pointed to a MoO_x → MoC_y conversion. These studies revealed that the conversion involved

$\text{Mo}_2\text{O}_5^{2+}$ dimers which were reduced and carburized to form small (0.6–1 nm) MoC_x clusters. In this active phase, methane transformed into benzene, ethane, and ethylene.³³ The last two being molecules also observed after exposing the $\text{MoC}_x/\text{Au}(111)$ systems seen in Figure 3 to methane.²⁸ Inside the H-ZSM-5 zeolite, catalytically inactive MoO_x species reacted with CH_4 to form the two types of sites necessary for the transformation of methane to benzene: MoC_x for C–H bond rupture and starting C–C bond formation,^{28,33,49} and acid sites in the zeolite for addition and cyclization of C_2^+ hydrocarbons to yield a highly stable aromatic ring.³³ Depending on the methodology followed to prepare the $\text{MoC}_x/\text{ZSM-5}$ active phase, the selectivity in the methane to benzene conversion could be as high as 85%.³²⁻³⁵

As mentioned above, methane coupling to ethane and ethylene has been seen on free and supported TMC nanoparticles.^{28,33,49} This chemical transformation has been optimized on catalysts containing molybdenum and tungsten carbides.⁷⁷ Fast carbon diffusion on/in the carbide is a key factor.⁷⁷ TMC nanoparticles also can catalyze the dry reforming of methane with carbon dioxide (DRM, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$), bringing down the temperature of operation and preventing deactivation by carbon deposition.⁷⁸⁻⁸¹ This is possible thanks to the large reactivity of the TMCs towards the two reactants in the DRM process: CH_4 and CO_2 . In the next section of the perspective, we will examine the interaction of these carbide systems with carbon dioxide and their ability to cleave C—O bonds.

Adsorption and conversion of CO_2 on TMC nanoparticles

On plain metal centers, the activation of carbon dioxide usually involves a charge transfer and the formation of a CO_2^- species that usually has an O–C–O angle in the range of 120–140° and weaker C–O bonds with respect to the free linear molecule.^{6,82} Depending on the nature of the metal, CO_2 can dissociate into $\text{CO} + \text{O}$ or disproportionate to yield $\text{CO}_3 + \text{CO}$.^{6,82} Noble metals such as copper and gold interact poorly with CO_2 ,^{6,82} but they can be activated by deposition on the surface of a TMC.^{24,25} This phenomenon is a consequence of electronic polarizations at the copper-carbide and gold-carbide interfaces that facilitate bonding to CO_2 .^{24,25} Thus, in general, electrons are available in a metal carbide to interact with CO_2 .

Experiments with well-defined surfaces such as $\beta\text{-Mo}_2\text{C}(001)$ or $\text{TiC}(001)$ provide very valuable reference points for the bonding and conversion of CO_2 .^{18,83} At room temperature, the CO_2 molecule dissociates on $\beta\text{-Mo}_2\text{C}(001)$ to yield CO and O atoms

(Figure 11a).⁸³ The results of DFT calculations showed that there was only a small energy barrier for the $\text{CO}_2 \rightarrow \text{CO} + \text{O}$ dissociation and the process was highly exothermic (Figure 11b).⁸³ Eventually, the adsorbed CO could dissociate at higher temperatures to yield C adatoms. The hydrogenation of the CO and C adatoms produced methanol and methane, respectively (Figure 11c). The dominant product was methane. A result in agreement with the trends seen for CO_2 hydrogenation on powders of Mo_2C .^{13,20,21,24,83}

A drastic change is seen in the surface chemistry when moving to MoC or other 1:1 metal-to-carbon systems that adopt a rock-salt structure.^{25-27,83} On these 1:1 compounds, the CO_2 molecules did not dissociate spontaneously as seen on $\beta\text{-Mo}_2\text{C}(001)$. A typical bonding configuration is seen at the top of Figure 12.²⁵⁻²⁷ CO_2 binds to the surface forming a $\text{C}=\text{C}$ bond, the $\text{C}-\text{O}$ bonds are elongated, but there is no spontaneous cleavage. In the presence of hydrogen, there was partial dissociation into CO without C formed.²⁵ Upon hydrogenation, CO and methanol were the only products seen.^{25,83} For TiC, ZrC, HfC, NbC, TaC, and cubic $\delta\text{-MoC}$, the most stable (001) surface has been usually investigated from both experiment and theory.^{25-27,83} Quesne *et al.*⁸⁴ considered a total of thirteen TMCs and for each of them they carried out calculations for the (001), (011), and (111) surfaces, the latter with two different terminations, in all cases using appropriate periodic models. Their analysis suggests that the shifts in the density of states and *d*-band centers govern the ability to donate electron density to adsorbed molecules, in particular to CO_2 . WC has a 1:1 metal-to-carbon ratio but in its hexagonal phase does not adopt a rock-salt structure.⁵⁶ This hexagonal phase has W-terminated surfaces where CO_2 can easily dissociate.⁵⁶ Porosoff *et al.*^{18,21} investigated experimentally and computationally the activity of six TMCs (TiC, ZrC, NbC, TaC, WC, and Mo_2C) for the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$). From the experimentally determined catalytic activity on powders and DFT calculated data, these authors found that the activity can be correlated with the oxygen binding energy: The TMCs binding atomic oxygen too strongly tend to show low activity. In powders, the presence of defects enhances the stability of oxy-carbides that usually decrease catalytic activity for CO_2 conversion.^{21,31,83} Nevertheless, in some situations, DFT calculations have shown that group 4 TMCs can be efficient for CO_2 capture even in the presence of oxygen and despite the formation of oxy-carbides.⁸⁵

The molecular clusters displayed in Figure 1 offer a large number of metal and carbon adsorption sites not seen in bulk surfaces of TMCs. Figure 13 summarizes the results of DFT studies for the interaction of CO_2 with a Ti_8C_{12} metcar.⁴⁷ The geometry of the

carbide cluster makes impossible the bonding configuration seen at the top of Figure 12 for CO₂ on TiC(001),²⁵ but there are some similarities. In both cases, CO₂ is attached with its C on top of a carbide C site and O interacts with Ti.^{25,47} The O–C–O angle is in the range of 120–140° and there is a significant elongation of the C–O bonds. However, on Ti₈C₁₂ and TiC(001), the dissociation of CO₂ is hampered by large energy barriers and must be assisted by H atoms.^{25,47} In Figure 14, we can see DFT results for the bonding of CO₂ to the MoC_x clusters of Figure 1.³⁷ On the carbide systems that had a relatively large degree of symmetry {Mo₈C₁₂, Mo₁₂C₁₂, Mo₁₄C₁₃ (nanocube), δ-MoC(001)}, the bonding energy of the molecule was substantial (-1 to -1.5 eV), but not as large as seen on clusters that had Mo centers with a very low coordination number.³⁷ On those Mo centers, the energy barriers for CO₂ dissociation could be below 0.7 eV, opening the route to spontaneous C-O bond cleavage at room temperature.³⁷

The adsorption and hydrogenation of CO₂ were investigated on the MoC_{1.1}/Au(111) nanostructures displayed in Figure 3.⁸⁶ Figure 15 compares Arrhenius plots for methanol synthesis on bulk δ-MoC and on Au(111) pre-covered with 0.3 ML of MoC_{1.1}. The Au(111) substrate was inactive as a catalyst for the CO₂ → CH₃OH reaction. As can be seen in Figure 15, the apparent activation energy for methanol production is reduced from 25 kcal/mol on Cu(111) to 17 kcal/mol on bulk δ-MoC and 14 kcal/mol on the MoC_{1.1}/Au(111) surface.⁸⁶ The atoms in the MoC_{1.1} nanoparticles are orders of magnitude more efficient for the CO₂ → CH₃OH hydrogenation than those in the Cu(111) benchmark system or in a surface of δ-MoC. This in part reflects the excellent ability that the MoC_{1.1} nanoparticles have to adsorb H₂ dissociatively (Figure 5)⁴⁶ but, in addition, they also have an enhanced reactivity towards CO₂. In the right side of Figure 15, three reaction paths over a Mo₁₂C₁₂ nanoparticle are shown that can lead to the dissociation of CO₂ at low or moderate temperatures.⁸⁶ These dissociation paths are not feasible on δ-MoC(001) and probably facilitate the high catalytic activity of MoC_{1.1}/Au(111).

The nanoparticles of (hexagonal) α-MoC_{1-x} seen in Figure 4 catalyzed the conversion of CO₂ into methane and C₂⁺ hydrocarbons.²⁰ This α-MoC_{1-x}/C catalyst exhibited a 2-fold increase in both activity on a per-site basis and selectivity to C₂⁺ products when compared to a bulk α-MoC_{1-x} analogue.²⁰ In general, the particular structure and content of carbon vacancies in α-MoC_{1-x} can lead to special catalytic properties not seen for other structures of molybdenum carbides.^{54, 87, 88, 89, 90} A hexagonal structure of a 2:1 molybdenum carbide (α-Mo₂C) also has singular catalytic properties for CO₂ conversion

to CO.⁹¹ Some of the facets in the α -Mo₂C structure may be difficult to obtain in a controlled manner, but they are actually similar to those exposed by a new class of two dimensional TMCs termed MXenes,⁹² increasingly used in catalysis.⁹³ Indeed, theoretical studies have shown that MXenes are indeed good candidate for carbon capture and utilization (CCU) technologies.⁹⁴

In the preparation of nanoparticles of tungsten carbide, the existence of mixtures of W₂C and WC is common.^{22,59} This can be problematic because the cubic and hexagonal phases of WC exhibit quite different reactivity towards CO₂.⁵⁶ Furthermore, the harsh synthesis conditions required for carburizing tungsten usually induce sintering, agglomeration, and carbon growth, making it very difficult to evaluate the intrinsic activity of any separate phase of W_xC.²² In a recent work, two methodologies {a micelle-based synthesis technique (M) and incipient wetness impregnation (IWI)} were compared for the preparation of nanoparticles of tungsten carbide.²² The samples were carburized at elevated temperatures and characterized with TEM (Figure 16), XRD, XPS, and catalytic testing. The micelle-based synthesis led to silica encapsulated nano-W_xC (top of Figure 16), with the largest content of carbide species and the highest catalytic activity seen for the sample carburized at 1000 °C (bottom of Figure 16).²²

In general, TMC nanoparticles encapsulated in silica, carbon nanotubes, nanodiamond@graphene (ND@G) composites, or zeolites display very good activity for CO₂ hydrogenation.^{22,30,44,53,68,95,96} Remarkably, the MoC_x/ND@G catalyst achieves the activation of CO₂ and a high selectivity for the reverse water-gas shift at a relatively low temperature compared to bulk β -Mo₂C due to a strong interaction between the carbide nanostructures and curved graphene layers on the surface of ND@G.⁹⁶

Summary and future work

The studies described above indicate that TMC nanoparticles can be very useful for the activation of three molecules located at the heart of C₁ chemistry: H₂, CH₄, and CO₂. They also can play a major role in the trapping and conversion of two major greenhouse gases. A combination of experiment and theory shed light on the physical and chemical properties of these systems. It is clear that the structure and reactivity of these nanoparticles can be very different from those of bulk metal carbides. Molecular clusters of the carbides, which can be inserted inside the cages of zeolites or carbon nanotubes, have unsaturated metal and carbon atoms that frequently work in a cooperative way when dealing with hard to activate molecules such as CH₄ and CO₂. These molecular clusters

can evolve into nanoparticles of small to medium size (< 15 nm) that have unique carbon/metal ratios and structures not seen in the bulk metal carbides. Even when their structures are cut from bulk lattices, the TMC nanoparticles have corner or edge atoms that are active for the cleavage and conversion of C–H and C–O bonds.

In the last twenty years, the progress made in the study of these systems has been impressive, but more systematic investigation needs to be done if one wants to achieve full potential when working with TMC nanoparticles in catalysis. Looking into the future, it has been proposed that the methodical optimization of catalysts should involve a combination of solid design and synthesis approaches, reliable data sets of activity, sophisticated theoretical modeling, and machine learning (Figure 17).⁹⁷⁻⁹⁹ At the present time, it is impossible to close the loop for optimization. The list of existing metal carbides is large,^{17,23} and many of them have not been studied at the nanosize regime. In the studies described above, most of the research has been focused on molecular clusters or nanoparticles of TiC_x , MoC_x , and WC_x , with a few works for TaC_x , ZrC_x , and VC_x . Thus, there is a clear need to expand the field of study into many more TMCs.

More experimental and theoretical research needs to be done examining the interaction of CH_4 and CO_2 with molecular clusters (Figures 1, 7, 9, 13, and 14) or with model nanoparticles (Figures 3, 5, 8, and 15). Working with these well-defined systems is essential for identifying in a clear way the phenomena behind catalytic conversion and for validating conceptual ideas. Furthermore, to close production cycles in C_1 chemistry, it is also necessary to investigate the performance of TMC nanoparticles as catalysts for reactions such as the forward water-gas shift⁹⁰ and methanol steam reforming.^{88,89}

It is expected that in technical applications, many TMC nanoparticles will be dispersed on oxide surfaces or encapsulated inside zeolites or carbon nanotubes. Very little is known about the fundamental interactions of metal carbide nanoparticles with these supports.^{32,53,54,81,96,100} From the results described above, very strong perturbations can be expected as a result of binding the nanoparticles to O or C centers of a particular support. These perturbations could change the catalytic properties of any given system.

So far, good progress has been made in establishing a decent number of synthetic methods for the generation of free and supported TMC nanoparticles. In this area much more is needed. In general terms, we need to control with a high level of accuracy the structure and purity of the generated TMC nanoparticles. Systems with a special geometry may be required on the basis of previous experimental work, or predictions coming from theoretical calculations, and contamination with oxygen can be a serious issue.

Oxycarbides can lead to some special properties but,^{101,102} in general, they have a negative impact on the performance of TMCs.^{21,83}

Author Information

Corresponding Authors

Jose A. Rodriguez. Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA; E-mail: rodriguez@bnl.gov

Francesc Illas. Departament de Ciència dels Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain; francesc.illas@ub.edu

Authors

Carlos Jimenez-Orozco. Universidad de Medellín, Facultad de Ciencias Básicas, Grupo de Materiales con Impacto (Mat&mpac), Carrera 87 No 30-65, Medellín, Colombia,

Elizabeth Florez. Universidad de Medellín, Facultad de Ciencias Básicas, Grupo de Materiales con Impacto (Mat&mpac), Carrera 87 No 30-65, Medellín, Colombia.

Francesc Viñes. Departament de Ciència dels Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain

Author Contributions

A first draft of the text was written by J.A.R. Then, the manuscript was reshaped through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

Authors declare no competing financial interest.

Biographies

José A Rodriguez received BSc and MSc degrees in chemistry from *Simon Bolivar University* (Venezuela) and a Ph.D. in physical chemistry from *Indiana University*. He is currently the leader of the *Catalysis: Structure and Reactivity Group* at Brookhaven

National Laboratory. He does experimental work using in-situ synchrotron-based techniques (AP-XPS, XAFS, XRD, PDF) to study C1 catalysis.

Carlos Jimenez-Orozco obtained his PhD in Chemical Sciences at the *University of Antioquia* (Colombia). In 2019 he joined the *University of Medellin* (Colombia) where he holds a position of Assistant Professor in the Faculty of Basic Sciences. His research is focused on the molecular design of materials and their fundamental understanding by using computational modeling, with applications in heterogeneous catalysis and the removal of pollutants from water.

Elizabeth Flórez received a Ph.D. degree in Chemical Sciences from the *University of Antioquia* (Colombia). Since 2012, she is a Titular (Full) Professor at the Faculty of Basic Sciences of the *University of Medellín* (Colombia). Her research field is focused on the applications of density functional theory in the study of chemical catalysts, two-dimensional materials, adsorption/biosorption of contaminants from aqueous solutions, and wastewater treatment.

Francesc Viñes obtained his Ph.D. in chemistry at the *Universitat de Barcelona*, where he has been an Associate Professor in the Materials Science and Physical Chemistry Departments since 2019. His research is based in the theoretical and computational description of heterogeneously thermo-, photo-, or electrocatalyzed processes and the description of catalysts and materials through computational materials science.

Francesc Illas obtained his chemistry degree and Ph.D. at the *Universitat de Barcelona* where he became Full Professor of Physical Chemistry in 1992. His research focuses on theoretical and computational chemistry, computational heterogeneous catalysis and computational materials science. He is a leader in the *Institute of Theoretical and Computational Chemistry at the Universitat de Barcelona (IQTCUB)*.

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Scheme Caption

Scheme I. Nanostructures of metal carbides for the conversion of methane and carbon dioxide.

Figure Captions

Figure 1. Structures for the Mo_8C_{12} metcar, bulk $\delta\text{-MoC}(001)$, and a series of Mo_xC_y clusters. Color code: Large pink spheres: Mo; small black spheres: C.

Figure 2. Anchoring modes for a Mo_2C_3 nanoparticle on Al centers within the framework of a ZSM-5 zeolite. The carbide system is bound to 2 or 3 aluminum atoms inside the zeolite structure. Color code: Blue: Mo; Grey: C; Red: O; Purple: Al; Yellow: Si. Reproduced with permission from ref. 53. Copyright 2014 American Chemical Society.

Figure 3. Image of scanning tunneling microscopy collected after depositing nanoparticles of MoC_x on a Au(111) surface. The coverage of the carbide was ~ 0.1 monolayer. Reproduced with permission from ref. 36. Copyright 2005 American Chemical Society.

Figure 4. (a) TEM image of (hexagonal) $\alpha\text{-MoC}_{1-x}$ nanoparticles showing multipodal morphology; (b) high-resolution TEM image with FFT pattern (inset) of outlined region indexed to the [011] zone axis. (c) XRD patterns for nanoparticle MoC_{1-x} and bulk $\alpha\text{-MoC}_{1-x}$ with corresponding reference patterns. Reproduced with permission from ref. 20. Copyright 2020 American Chemical Society.

Figure 5. (A) C 1s XPS spectra collected after dosing H_2 to a $\text{MoC}_{1.1}/\text{Au}(111)$ surface at 300 K with subsequent heating to 500 K in vacuum. (B) Top view of a $\text{Mo}_{12}\text{C}_{12}$ particle supported on a Au(111) surface. Black, blue, and orange spheres denote C, Mo, and Au atoms, respectively. H_2 adsorption sites are shown in purple, accompanied by adsorption energies, E_{ads} . Adsorbed H_2 dissociation energies are shown by red arrows, implying that one H adatom remains on-site, while the other moves to occupy a nearby site. H adatom diffusions are shown by black arrows, signaling initial to final locations. For H_2 dissociation and H diffusion, forward and backward energy barriers, E_b , are given in normal or italics fonts, respectively. (C) Formation energies for Kubas CH_2 structures on low-coordinated C atoms are shown from gas-phase H_2 (blue) or through H adatoms recombination (red). In the latter a H adatom on a Mo site diffuses and interacts with the H-attaching a surface C atom. Forward and backward energy barriers, E_b , are given in normal or italics fonts, respectively. All energy values are given in eV. Reproduced with permission from ref. 46. Copyright 2020 American Chemical Society.

Figure 6. (a) HER polarization curves at 5 mV s^{-1} in 0.5 M H_2SO_4 ; (b) Tafel curve calculated by $\eta = a \lg |j| + b$; (c) $i-t$ curve of WC@NPC (inset: HER LSV curves before and after stability test); (d) free energy of H^* adsorption on different surfaces by DFT calculation. RHE = reversible hydrogen electrode. Reproduced with permission from ref. 68. Copyright 2017 American Chemical Society.

Figure 7. TOF mass spectra for the reactions of mass-selected Ta_2C_4^- (a) with CH_4 (b), CD_4 (c), CH_2D_2 (d), and $^{13}\text{CH}_4$ (e) for 2.0 ms. The reactant gas pressures are shown. The label + X denotes $\text{Ta}_2\text{C}_4\text{X}^-$ (X = CH_2 , CH_4 , etc.). Reproduced with permission from ref. 76. Copyright 2017 American Chemical Society Copyright.

Figure 8. Left side panel: C 1s XPS spectra collected after dosing CH_4 to a $\text{MoC}_{1.1}/\text{Au}(111)$ surface at 300 K with subsequent heating to 500 K in vacuum. Right side: Side and top views for the bonding of methane to different MoC_x nanoparticles supported on $\text{Au}(111)$. Au, Mo, C, and H atoms are shown as yellow, blue, black, and white spheres, respectively. Reproduced with permission from ref. 28. Copyright 2020 Royal Society of Chemistry.

Figure 9. Energy barrier (E_b) for CH_4 to CH_3+H dissociation on different molybdenum carbide nanoparticles (black triangles) and extended surfaces (blue dots) versus the reaction energy (E_{reac}). The linear regression corresponds to the values from the extended surfaces only. Reproduced with permission from ref. 28. Copyright 2020 Royal Society of Chemistry.

Figure 10. Left-side panel: Ratio of C/Mo in the Mo/H-ZSM-5 sample as a function of reaction time. Right-side panel: K-edges of molybdenum. (a) physical mixture of MoO_3 with H-ZSM-5 heated at 973 K for 0.5 h; (b) *in-situ* synthesized Mo_2C ; (c) 4 wt % Mo/H-ZSM-5 reacted with methane at 950 K for 1.33 h; (d) 3.33 h; and (e) 6.33 h. Reproduced with permission from ref. 33. Copyright 2001 American Chemical Society.

Figure 11. (a) O 1s XPS intensities measured for CO and O after dosing CO_2 to $\beta\text{-Mo}_2\text{C}(001)$ at 300 K. (b) DFT calculated energy changes for the bonding and dissociation of CO_2 on $\beta\text{-Mo}_2\text{C}(001)$. (c) Arrhenius plots for the production of methane, CO, and methanol on a $\beta\text{-Mo}_2\text{C}(001)$ surface under 0.5 atm of CO_2 and 4.5 atm of H_2 . Reproduced with permission from ref. 83. Copyright 2014 Royal Society of Chemistry.

Figure 12. Top: Calculated bonding configuration for CO_2 on $\text{TiC}(001)$. Bottom: Arrhenius plots for the formation of methanol on $\text{Cu}(111)$, $\text{TiC}(001)$, $\text{Cu}/\text{ZnO}(000\bar{1})$, $\text{Au}/\text{TiC}(001)$ and $\text{Cu}/\text{TiC}(001)$ surfaces under 0.5 atm of CO_2 and 4.5 atm of H_2 . Reproduced with permission from ref. 25. Copyright 2012 American Chemical Society.

Figure 13. DFT calculated reaction path for the adsorption and dissociation of CO_2 on a Ti_8C_{12} metcar. C, O and Ti sites are shown as black, red and blue spheres, respectively. Reproduced with permission from ref. 47. Copyright 2021 Royal Society of Chemistry.

Figure 14. Top: Calculated CO_2 adsorption energy, E_{ads} , for the most stable CO_2 bonding mode on different MoC_x nanoparticles and bulk $\delta\text{-MoC}(001)$. Middle and bottom: Structures for CO_2 adsorption on stoichiometric nanoparticles with Mo_6C_6 (middle, left), $\text{Mo}_{12}\text{C}_{12}$ (middle, right), and $\text{Mo}_{24}\text{C}_{24}$ (bottom, left) in the most stable lateral bonding mode, and, finally, on $\text{Mo}_{32}\text{C}_{32}$ (bottom, right), where the most stable interaction involved a vertex site. C, Mo, and O atoms are represented by brown, magenta, and red color, respectively. For sake of clarity, the C atom of CO_2 is shown in black. Bonding modes and adsorption energy are included. Reproduced with permission from ref. 37. Copyright 2022 Royal Society of Chemistry.

Figure 15. Left panel: Arrhenius plots for CO₂ hydrogenation on Cu(111), bulk δ-MoC, and a Au(111) surface with 0.3 ML of MoC_{1.1}. P(CO₂)= 0.5 atm and P(H₂)= 4.5 atm. Right panel: Main considered paths for CO₂ direct dissociation on Mo₁₂C₁₂/Au(111). Blue, black, red, and yellow spheres correspond to Mo, C, O, and Au atoms, respectively. Listed on the left of the figure are calculated results for the adsorption energy (E_{ads}), energy barrier for CO₂ dissociation (E_b), and the reaction energy (E_{reac}). All energies are in eV. Reproduced with permission from ref. 86. Copyright 2021 American Chemical Society.

Figure 16. Top: TEM images with 50 nm scale bars of nano W_xC (M, micelle-based synthesis technique, with effective silica encapsulation) carburized at 1000, 835 and 600 °C. Center: TEM images with 50 nm scale bars of nano W_xC (IWI, incipient wetness impregnation) carburized at 1000, 835 and 600 °C. Bottom: Correlation between RWGS (CO₂ + H₂ → CO + H₂O) activity and XPS contributions of W_xC, including the C 1s signals for W₂C and WC. Reproduced with permission from ref. 22. Copyright 2022 Royal Society of Chemistry.

Figure 17. Scheme for the design of novel catalytic materials through the integration of experimental studies, theoretical calculations, and machine learning. Reproduced with permission from ref. 93. Copyright 2020 American Chemical Society.

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