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# Molybdenum Oxide Supported on Ti<sub>3</sub>AlC<sub>2</sub> is an Active Reverse Water–Gas Shift Catalyst

Maria Ronda-Lloret, Liuqingqing Yang, Michelle Hammerton, Vijaykumar S. Marakatti, Moniek Tromp, Zdeněk Sofer, Antonio Sepúlveda-Escribano, Enrique V. Ramos-Fernandez, Juan Jose Delgado, Gadi Rothenberg, Tomas Ramirez Reina, and N. Raveendran Shiju\*



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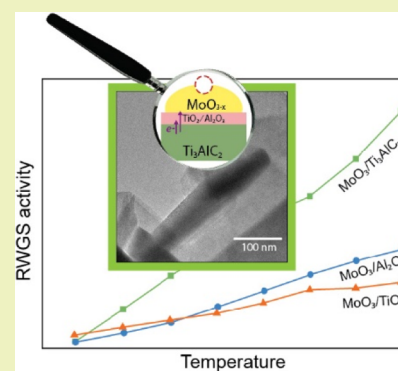


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**ABSTRACT:** MAX phases are layered ternary carbides or nitrides that are attractive for catalysis applications due to their unusual set of properties. They show high thermal stability like ceramics, but they are also tough, ductile, and good conductors of heat and electricity like metals. Here, we study the potential of the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase as a support for molybdenum oxide for the reverse water–gas shift (RWGS) reaction, comparing this new catalyst to more traditional materials. The catalyst showed higher turnover frequency values than MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, due to the outstanding electronic properties of the Ti<sub>3</sub>AlC<sub>2</sub> support. We observed a charge transfer effect from the electronically rich Ti<sub>3</sub>AlC<sub>2</sub> MAX phase to the catalyst surface, which in turn enhances the reducibility of MoO<sub>3</sub> species during reaction. The redox properties of the MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> catalyst improve its RWGS intrinsic activity compared to TiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-based catalysts.

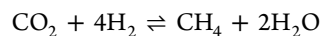
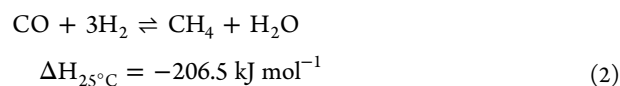
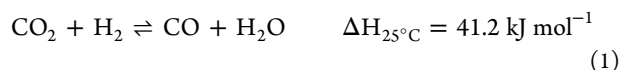


**KEYWORDS:** CO<sub>2</sub> hydrogenation, MAX phases, RWGS, syn gas, molybdenum

## INTRODUCTION

There is a global interest on reducing anthropogenic CO<sub>2</sub> emissions into the atmosphere.<sup>1,2</sup> The main sources of CO<sub>2</sub> are power generation and manufacturing, which emitted 12.4 and 3.9 Gt of CO<sub>2</sub> in 2015.<sup>3,4</sup> However, CO<sub>2</sub> is a valuable C<sub>1</sub> feedstock that should not be thrown away. After CO<sub>2</sub> capture, either from the atmosphere or from industrial flue gases, it should be efficiently converted into high value-added products *via* catalytic processes.<sup>5–8</sup>

The reverse water–gas shift (RWGS) reaction (eq 1) using renewable hydrogen is a sustainable way for converting CO<sub>2</sub>.<sup>9</sup> This reaction produces CO, a basic building block for a variety of valuable chemicals and fuels, such as methanol, paraffins, and olefins.<sup>10</sup> However, RWGS is an equilibrium-limited reaction, favored at high temperatures (>700 °C) because it is endothermic.<sup>11</sup> At lower temperatures, the exothermic CO methanation (eq 2) and Sabatier reaction (eq 3) also take place, consuming a substantial amount of H<sub>2</sub> and producing undesired methane. Therefore, catalyst development is focused on improving the catalytic performance at <500 °C.<sup>12,13</sup>



$$\Delta H_{25^\circ\text{C}} = -165.0 \text{ kJ mol}^{-1} \quad (3)$$

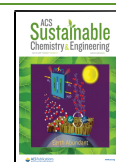
Traditionally, RWGS catalysts are based on Cu, Pt, and Rh nanoparticles supported on metal oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub>, among others).<sup>9,14,15</sup> Molybdenum is more abundant and cheaper than precious metals, increasing the potential for the large-scale industrial application of Mo-based catalysts. While previous work only focused on its promoting effect,<sup>16–20</sup> we are interested in molybdenum oxide as an active phase itself due to its redox properties.<sup>21,22</sup> The oxygen vacancies created when reducing MoO<sub>3</sub> will affect the reaction performance, whether it takes place *via* the redox mechanism (where CO<sub>2</sub> adsorbs and dissociates on the reduced sites previously created by H<sub>2</sub>) or *via* the associative pathway (where oxygen vacancies can stabilize adsorbed carbon-containing intermediates), see Figure 1.<sup>10,23,24</sup>

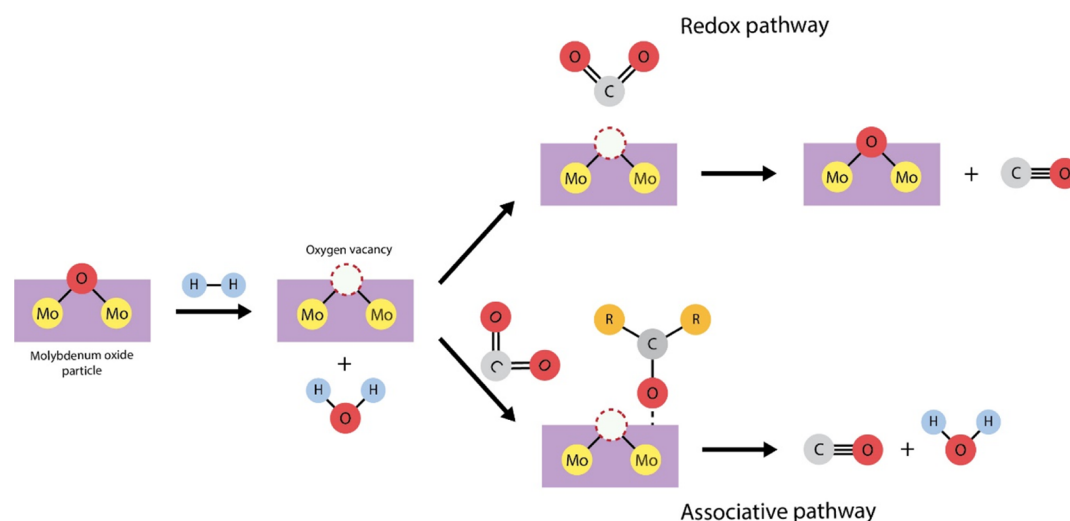
Another important factor is the choice of support. Although typically inert, supports can enhance the reaction performance

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**Figure 1.** Scheme of the formation of oxygen vacancies on MoO<sub>3</sub> particles during RWGS, and its ability to dissociate CO<sub>2</sub> via the redox pathway and/or to stabilize carbon-containing species (indicated by R) via the associative pathway.

by increasing the active sites' dispersion, facilitating charge transfer, and modifying the morphology of the supported particles.<sup>25–27</sup> More importantly, the support can prevent catalyst deactivation and boost the industrial application of high-temperature reactions.<sup>26</sup> Here, we explored a new type of supports, MAX phases, and their application in catalysis. MAX phases (M<sub>n+1</sub>AX<sub>n</sub>) are a group of layered ternary carbides or nitrides, where M is an early transition metal, A is an element mostly from groups 13 and 14, X is carbon or nitrogen, and  $n = 1, 2,$  or  $3.$ <sup>28</sup> MAX phases stand out by their unusual set of properties. They are stiff and high-temperature shock resistant like ceramics, but they are also tough, ductile, and good conductors of heat and electricity like metals.<sup>29–31</sup> They are typically used in mechanical and thermal applications, such as high-temperature structural components and protective coatings.<sup>32–34</sup> Their potential as catalysts has recently emerged, as we reported the activity and improved selectivity of the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase during butane oxidative dehydrogenation.<sup>35</sup> We also showed that MAX phases are promising supports for CO<sub>2</sub> conversion reactions.<sup>36</sup> The thermal stability and acid–base properties of the Ti<sub>2</sub>AlC MAX phase increased the stability and coking resistance of a Co<sub>3</sub>O<sub>4</sub>/Ti<sub>2</sub>AlC catalyst during dry reforming of butane.<sup>36</sup> Elsewhere, Trandafir *et al.* recently showed the potential of Pd/Ti<sub>3</sub>SiC<sub>2</sub> as a chemo-selective catalyst in the hydrogenation of functionalized nitrile derivatives.<sup>37</sup>

Here, we use for the first time the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase as a support for molybdenum oxide RWGS catalysts. We study the properties and the RWGS activity of the MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> catalyst and compare it to titania and alumina-based catalysts.

## EXPERIMENTAL SECTION

**Materials and Instrumentation.** X-ray diffraction (XRD) patterns were recorded on a MiniFlex II X-ray diffractometer, described previously by Ronda-Lloret *et al.*<sup>36</sup> X-ray photoelectron spectroscopy (XPS) was performed using a K- $\alpha$  spectrometer from Thermo Scientific (Al–K radiation), with a source of electrons and ions for automated charge balancing. The binding energies were referenced to the C 1s line at 284.6 eV, with an accuracy of  $\pm 0.2$  eV (a detailed description of the analysis procedure is published elsewhere<sup>36</sup>).

Thermogravimetric analysis (TGA) was carried out using an NETZSCH Jupiter STA 449F3 instrument, under air (20 mL·min<sup>-1</sup>, O<sub>2</sub>:N<sub>2</sub> mixture) between 30 and 1000 °C.

Scanning transmission electron microscopy (STEM) spectra combined with high-angle annular dark field (HAADF) images were obtained using a double Cs aberration-corrected FEI Titan<sup>3</sup> Themis 60–300 microscope (operated at 200 kV).

We performed X-ray absorption spectroscopy (XAS) using the SuperXAS beamline of the SLS Synchrotron at the PSI (Switzerland). We prepared the samples by mixing with cellulose and pressing into pellets of approximately one absorption length in thickness. We performed the measurements at the Mo K-edge (20,000 eV) in the QEXAFS mode using an oscillating monochromator and collected spectra with a fluorescence detector (sensor silicon drift detector) and with a transmission detector (ionization chambers) simultaneously. A spectrum was recorded every second and averaged over 1 min to improve the signal-to-noise ratio. We calibrated with respect to the edge position of a metal foil measured simultaneously and normalized spectra using Python-based graphical interface ProQEXAFS software.<sup>38</sup> The edge position ( $E_0$ ) of each sample spectrum was set to the most intense peak of the first derivative (see Figure S7). Further processing of X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) was carried out using the Demeter software package (0.9.25, using Ifeffit 1.2.12).<sup>39</sup> We used Athena for background subtraction of long-range oscillations and linear combination fitting (LCF) of supported catalyst spectra using  $\alpha$ -MoO<sub>3</sub> and MoO<sub>3</sub>-NP references. We then used Artemis to carry out EXAFS fitting using scattering paths generated from crystallographic  $\alpha$ -MoO<sub>3</sub> data (COD ID 1537654) which were summed to simulate the EXAFS spectrum.<sup>40</sup> Fitting parameters are reported in Tables S3–S5, where Debye-Waller factors ( $\Delta\sigma^2$ ), path distances ( $R$ ), and energy shift ( $\Delta E_0$ ) were refined, but coordination numbers ( $N$ ) were set according to the crystal structure. The amplitude reduction factor ( $S_0^2$ ) was determined by first fitting Mo<sup>0</sup> foil data measured at the same time as the sample spectra. We carried out the fits in the ranges indicated in  $R$  in Tables S3–S5 and evaluated the quality of fit using an  $R$ -factor.

N<sub>2</sub> adsorption–desorption analysis was performed in a Thermo Scientific Surfer instrument at 77 K. The samples were previously evacuated in vacuum at 200 °C for 16 h.

CO chemisorption analyses were performed with a Micromeritics Pulses Chemisorb 2705 apparatus. Before the analysis, the samples were pretreated under a helium gas flow of 80 mL·min<sup>-1</sup> at 350 °C for 3 h and then reduced at 500 °C for 6 h under pure hydrogen. More details on the analysis procedure can be found in Ronda-Lloret *et al.*<sup>36</sup>

**Procedure for Catalyst Synthesis.** 10 wt % molybdenum (in metal-basis) materials were prepared using the wet impregnation method.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Sigma Aldrich) was used as a metal oxide precursor.  $\text{Ti}_3\text{AlC}_2$ ,  $\text{TiO}_2$  (Hombikat M311), and  $\gamma\text{-Al}_2\text{O}_3$  (CK-300, Ketjen) were used as supports. In a typical procedure, 0.40 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and 2 g of support were mixed in 20 mL of water and stirred at 65 °C for 24 h. The resulting solid was dried at 120 °C for 2 h and then calcined under air at 350 °C for 4 h (heating rate 4 °C·min<sup>-1</sup>). The  $\text{Ti}_3\text{AlC}_2$  MAX phase was prepared by mixing the elemental powders purchased from STRTEM chemicals: Ti (325 mesh, 99.5%), Al (325 mesh, 99.5%), and graphite (325 mesh, 99.9%). The composition corresponding to  $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$  was mixed in a 3D blender (40 rpm) in hexane for 8 h, using 5 mm zirconia balls. The resulting mixture was placed in an alumina crucible covered with an alumina lid and heated to 1450 °C for 2 h under an argon atmosphere (heating and cooling rate was 2 °C·min<sup>-1</sup>). The resulting powder was mechanically ground in an agate mortar. The  $\text{Mo}_2\text{TiAlC}_2$  MAX phase was prepared by mixing the elemental powders purchased from STRTEM chemicals: Ti (325 mesh, 99.5%), Mo (2–4 microns, 99.9%), Al (325 mesh, 99.5%), and graphite (325 mesh, 99.9%). The composition corresponding to  $\text{Mo}_2\text{Ti}_{1.1}\text{AlC}_2$  was mixed in a 3D blender (40 rpm) in hexane for 8 h, using 5 mm zirconia balls. The resulting mixture was placed in an alumina crucible covered with an alumina lid and heated to 1550 °C for 2 h under an argon atmosphere (heating and cooling rate was 2 °C·min<sup>-1</sup>). The resulting powder was mechanically ground in an agate mortar. A bulk  $\text{MoO}_3$  sample was obtained from the calcination of  $\text{Mo}_2\text{C}$  using compressed air (50 mL·min<sup>-1</sup>) at 600 °C for 2 h (heating ramp 5 °C·min<sup>-1</sup>).

**Procedure for Catalytic Testing.** The catalysts were tested in the RWGS reaction in a vertical fixed bed reactor. A total of 200 mg of catalyst was placed on quartz wool in the middle of the reactor, which had 7 mm inner diameter. The samples were heated under  $\text{N}_2$  to 400 °C. The catalytic tests were then performed at atmospheric pressure and at a  $\text{H}_2$ : $\text{CO}_2$  ratio of 4:1. We performed temperature screening tests between 400 and 750 °C using 100 mL·min<sup>-1</sup> total flow (30,000 mL·g<sup>-1</sup>·h<sup>-1</sup>) and stability tests for 48 h at 550 °C using 50 mL·min<sup>-1</sup> total flow (15,000 mL·g<sup>-1</sup>·h<sup>-1</sup>). The reactants and products were analyzed using an online ABB AO2020 advanced optima process gas analyzer, equipped with thermal conductivity and infrared detectors.

The conversion and selectivity values were calculated using eqs 4 and 5

$$\text{CO}_2 \text{ conversion (\%)} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \cdot 100 \quad (4)$$

$$\text{CO selectivity (\%)} = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}} \cdot 100 \quad (5)$$

The number of active sites was calculated from CO chemisorption analysis (see the Experimental Section for details). Using the CO uptake values obtained from this analysis, we estimated the turnover frequency (TOF) values (eq 6).

$$\begin{aligned} \text{TOF reactant (moles reactant converted site}^{-1}\cdot\text{min}^{-1}) \\ = \frac{\text{flow reactant (in)} \cdot \text{conversion reactant}}{\text{CO uptake} \cdot \text{weight catalyst}} \end{aligned} \quad (6)$$

The CO production rate was calculated using eq 7

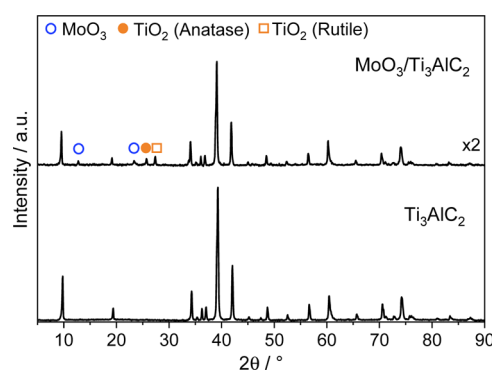
$$\begin{aligned} \text{CO production rate (mol}_{\text{CO}} \cdot \text{g}_{\text{catalyst}}^{-1} \cdot \text{min}^{-1}) \\ = \frac{\text{flow CO}_2(\text{in}) \cdot \text{yield CO}}{\xi_{\text{catalyst}}} \end{aligned} \quad (7)$$

## RESULTS AND DISCUSSION

**Catalyst Synthesis.** We compared the properties and activity in RWGS of  $\text{MoO}_3$ -based catalysts, using the  $\text{Ti}_3\text{AlC}_2$  MAX phase,  $\gamma\text{-Al}_2\text{O}_3$ , and  $\text{TiO}_2$  as supports. The catalysts, each containing 10 wt % on Mo metal basis, were prepared by wet

impregnation, using ammonium molybdate tetrahydrate as a precursor.  $\gamma\text{-Al}_2\text{O}_3$  and anatase  $\text{TiO}_2$  were purchased from commercial sources.  $\text{Ti}_3\text{AlC}_2$  was prepared by mixing elemental powders of Ti, Al, and graphite, followed by heating at 1450 °C under argon. Samples of a molybdenum-containing MAX phase,  $\text{Mo}_2\text{TiAlC}_2$ , and bulk  $\text{MoO}_3$  were also tested as reference materials (see the Experimental Section for details).

**Characterization of the Fresh Catalysts.** The XRD pattern of the fresh  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst shows the characteristic peaks of the  $\text{Ti}_3\text{AlC}_2$  MAX phase structure (Figure 2), indicating that the bulk of the support remains

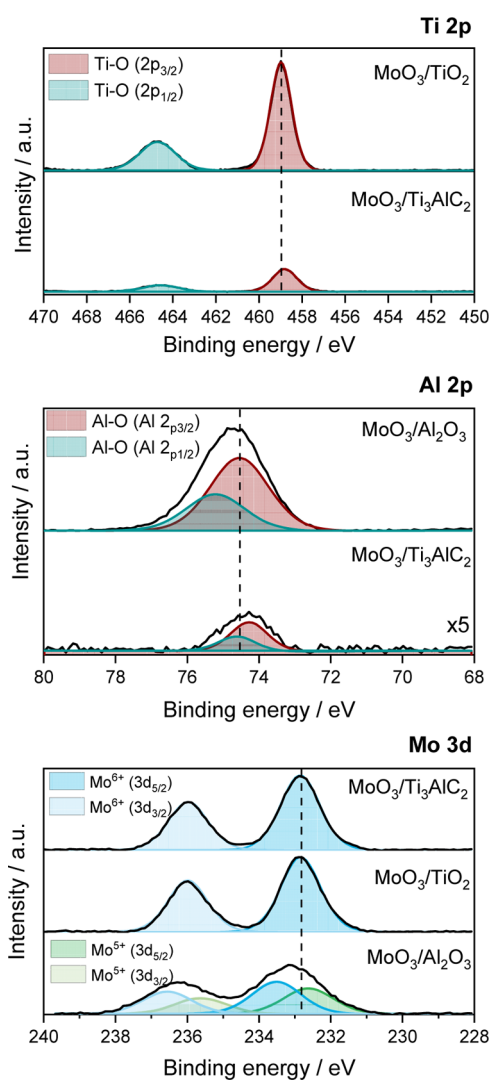


**Figure 2.** XRD patterns of the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst and the  $\text{Ti}_3\text{AlC}_2$  MAX phase used as a support.

stable after calcination. Anatase and rutile  $\text{TiO}_2$  peaks are also present at  $2\theta = 25.7$  and  $27.4^\circ$ , indicating a slight oxidation of  $\text{Ti}_3\text{AlC}_2$ .<sup>41</sup> The characteristic peaks of  $\text{MoO}_3$  are also visible at  $2\theta = 12.8$  and  $23.5^\circ$ .<sup>42</sup> The pattern of  $\text{MoO}_3/\text{TiO}_2$  only shows broad peaks of anatase  $\text{TiO}_2$  at  $2\theta = 25.4, 38.2, 48.1, 54.8, 62.7, 70.0, 75.4,$  and  $82.9^\circ$ .<sup>41</sup> Similarly, the pattern of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  only shows the peaks of  $\gamma\text{-Al}_2\text{O}_3$  at  $2\theta = 37.8, 45.8, 60.7,$  and  $67.0^\circ$  (Figure S1).<sup>43,44</sup> The absence of  $\text{MoO}_3$  diffraction peaks indicates that molybdenum particles are small and well-dispersed over the oxide supports.

We studied the surface composition of the fresh catalysts with XPS. The Ti 2p and Al 2p spectra of the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst only show the Ti–O and the Al–O bonds at 458.8 eV (Ti 2p<sub>3/2</sub>) and 74.3 eV (Al 2p<sub>3/2</sub>), respectively (Figure 3). The distinctive peaks of the  $\text{Ti}_3\text{AlC}_2$  structure (Ti–C bond at 454 eV (Ti 2p<sub>3/2</sub>) and Al–Ti bond at 72 eV (Al 2p<sub>3/2</sub>)) are absent.<sup>35,45</sup> This indicates that the  $\text{Ti}_3\text{AlC}_2$  surface completely oxidizes to titania and alumina under our calcination conditions (*i.e.*, under air at 350 °C for 4 h).<sup>46</sup> The Ti–O and Al–O peaks of  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  shift to lower binding energies compared to  $\text{MoO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$ . This indicates a charge transfer effect from the bulk MAX phase to the surface oxide layer, enriching the surface with electrons.<sup>47</sup>

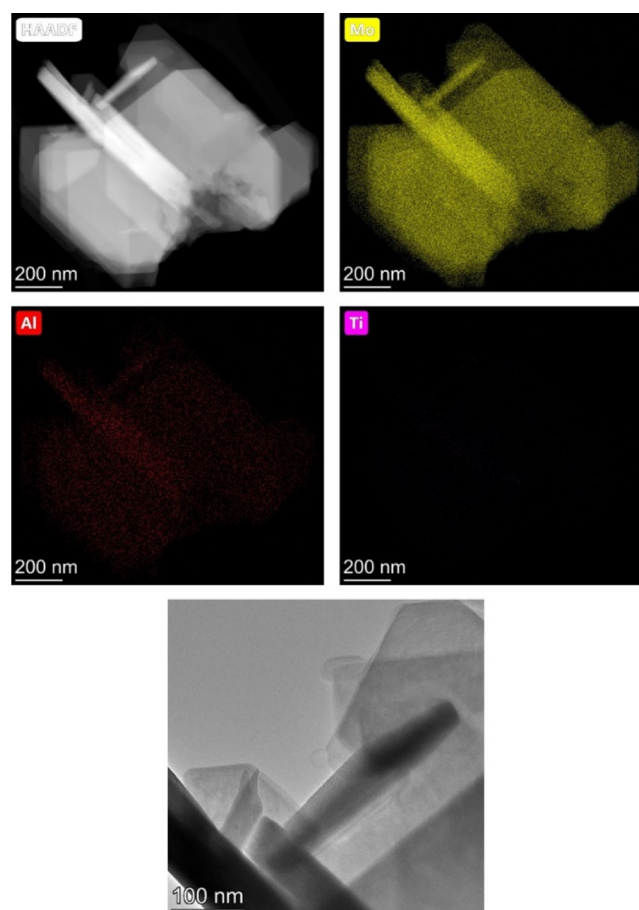
The Mo 3d spectra of the catalysts (Figure 3) show two spectral lines, assigned to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> spin–orbit components. The Mo 3d<sub>5/2</sub> binding energy in  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  and  $\text{MoO}_3/\text{TiO}_2$  spectra is 232.8 eV, which corresponds to  $\text{MoO}_3$  species ( $\text{Mo}^{6+}$ ).<sup>48,49</sup> The Mo 3d spectrum of the  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst shows two contributions at Mo 3d<sub>5/2</sub> binding energies of 232.6 and 233.6 eV, corresponding to  $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$  species. In the O 1s spectrum,  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  and  $\text{MoO}_3/\text{TiO}_2$  also show similar Mo–O binding energies (*ca.* 530.4 eV, *cf.* Figure S2).<sup>50</sup> This indicates that the surface of the  $\text{Ti}_3\text{AlC}_2$  undergoes oxidation and Mo predominantly sits on the oxidized titanium, as expected by the excess of titanium



**Figure 3.** Ti 2p, Al 2p, and Mo 3d XPS spectra of  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$ ,  $\text{MoO}_3/\text{TiO}_2$ , and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts.

in this compound (Ti/Al ratio is 3 to 1). The excess of titanium on the MAX phase surface is also confirmed by the  $I_{\text{Ti}}/I_{\text{Al}}$  intensity ratio obtained from XPS (Table S1). Previous work showed that during oxidation below 700 °C,  $\text{Ti}_3\text{AlC}_2$  predominantly converts to titania rather than to alumina.<sup>46</sup> While the three catalysts have the same metal loading, the Mo and support intensity ratio ( $I_{\text{Mo}}/I_{\text{Ti}}$  or  $I_{\text{Mo}}/I_{\text{Al}}$ ) is the largest for the MAX phase-based catalyst (Table S1). This indicates that this catalyst has the largest Mo-containing particles on the surface.

HAADF–STEM imaging showed that  $\text{MoO}_3$  is predominantly dispersed in the form of rods when deposited on  $\text{Ti}_3\text{AlC}_2$  (Figure 4, see also Figures S3 and S4 in the Supporting Information). Some rods are in contact with the support, while others are “free” (*i.e.*, unsupported). These rods are  $480 \pm 138$  nm long and  $88 \pm 11$  nm wide. The large size of  $\text{MoO}_3$  particles when supported on  $\text{Ti}_3\text{AlC}_2$  results from the low surface area of this support (*ca.* 1  $\text{m}^2/\text{g}$ ). In agreement with XRD and XPS results, we see that the  $\text{MoO}_3$  particles are very small and highly dispersed when supported on  $\text{TiO}_2$  (average particle size: 0.42 nm,  $\sigma = 0.11$  nm) and  $\gamma\text{-Al}_2\text{O}_3$  (average particle size: 0.67 nm,  $\sigma = 0.19$  nm, Figure S5). The  $\text{MoO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts are mesoporous, with

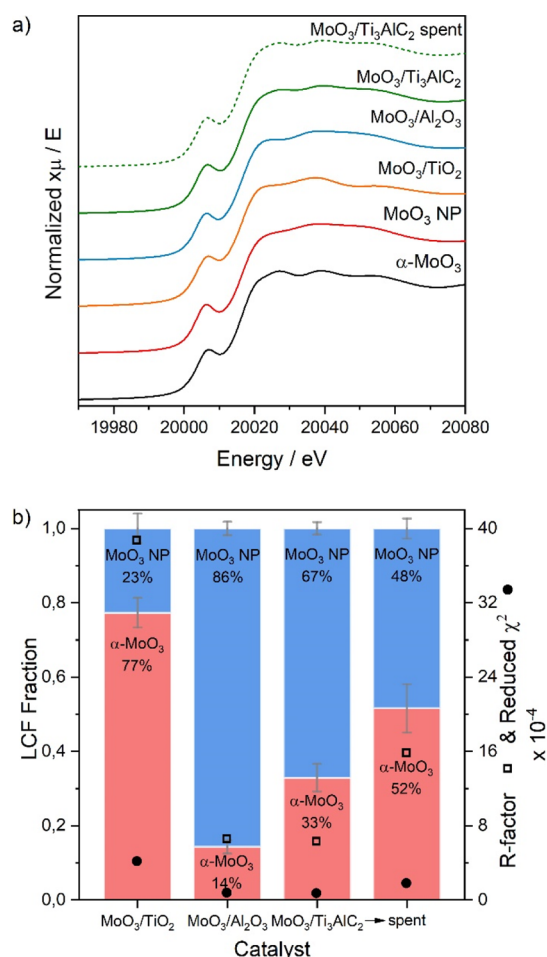


**Figure 4.** HAADF–STEM images of the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst.

a BET surface area of 208  $\text{m}^2\cdot\text{g}^{-1}$  and 145  $\text{m}^2\cdot\text{g}^{-1}$ , respectively (Figure S6 and Table S2).

We then studied the local structure of the molybdenum on each support using Mo K-edge XANES and EXAFS spectroscopy. We also measured  $\text{MoO}_3$  nanoparticles ( $\text{MoO}_3\text{-NPs}$ ) and bulk  $\alpha\text{-MoO}_3$  references for comparison. In the XANES spectra (Figure 5a), all catalysts show the edge position at 20016.4 eV, characteristic of  $\text{Mo}^{6+}$  ( $1s \rightarrow 5p$ , measured at the maximum of the second peak of the first derivative, see Figure S7), and a triple peak feature above the edge. The distinct pre-edge corresponds to the quadrupole  $1s\text{-}4d$  transition, indicating a distorted octahedral environment.<sup>51</sup> The triple peak feature above the edge in the XANES is slightly different for each catalyst. The  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  spectrum is similar to that of bulk  $\alpha\text{-MoO}_3$ , whereas the features of the  $\text{MoO}_3/\text{Al}_2\text{O}_3$  spectrum are dampened similarly to that of  $\text{MoO}_3\text{-NPs}$ .  $\text{MoO}_3/\text{TiO}_2$  shows the largest discrepancy from the reference spectra, with a more intense central peak compared to the first and third features. These differences can be partially explained by differences in nanoparticle size and shape, which affect the ratio of surface sites to bulk sites, as well as by particle–support interactions.

We used the  $\text{MoO}_3$  nanoparticles and the bulk  $\alpha\text{-MoO}_3$  samples as references for LCF (Figure 5b) to get an indication of the relative amounts of surface versus internal Mo sites in the studied catalysts. The absolute numbers obtained from the LCF cannot be directly related to the number of surface versus bulk sites, since (i) we only have two reference samples and (ii) the NP reference consists of a combination of surface and



**Figure 5.** (a) Mo K-edge XANES spectra of the supported catalysts and reference structures. (b) Summary of the LCF analysis of the supported catalysts using reference spectra. The quality of the fit is indicated by the  $R$ -factor and reduced  $\chi^2$  value.

bulk atoms and the exact proportion of those is unknown. For this study, we are interested in the trends observed when using different supports; thus, we use the LCF analyses to infer the differences in particle sizes between samples. Moreover, the XAS measures all Mo atoms in the sample. This means that Mo atoms present in amorphous compounds and/or present as single site species, which are not detected with other techniques such as XRD and HAADF-STEM, are also taken into account in this analysis. We cannot correct for these contributions as we have no insights into the amount of Mo forming rods or other species (amorphous and/or single site species). Figure 5b shows that the MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst can be fitted to a mixture of bulk  $\alpha$ -MoO<sub>3</sub> and MoO<sub>3</sub>-NPs, suggesting that the average nanoparticle size in this catalyst is slightly larger than in the MoO<sub>3</sub>-NP reference. The contribution from bulk  $\alpha$ -MoO<sub>3</sub> increases in the MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> catalyst, due to the presence of large rod-shaped MoO<sub>3</sub> particles (as seen in STEM-HAADF). The shape of the XANES spectrum of the MoO<sub>3</sub>/TiO<sub>2</sub> catalyst is slightly different to either reference spectra, resulting in a poorer fit (as indicated by the relatively high  $R$ -factor and  $\chi^2$  value). This suggests that there is a contribution to the spectrum that is not accounted for by the nanoparticle or bulk  $\alpha$ -MoO<sub>3</sub> data.<sup>52</sup> More details on the LCF results are given in Figure S8 and Table S3.

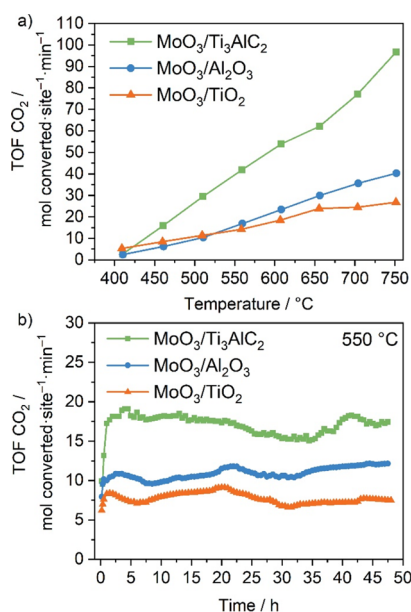
In the EXAFS spectra (Figure S9), we observe in more detail the structural differences between MoO<sub>3</sub> nanoparticles and bulk  $\alpha$ -MoO<sub>3</sub>. In  $k$ -space, the oscillations of the MoO<sub>3</sub>-NP spectrum are dampened compared to  $\alpha$ -MoO<sub>3</sub>, especially at higher wavenumbers, as expected. This results in an  $R$ -space spectrum in which the amplitude of the second shell is suppressed. The shape of the first shell in the MoO<sub>3</sub>-NP spectrum is also affected, with just one main peak compared to the complex first shell of  $\alpha$ -MoO<sub>3</sub>. The EXAFS spectrum of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is very similar to the MoO<sub>3</sub> nanoparticle reference. The spectrum of MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> is more similar to the bulk  $\alpha$ -MoO<sub>3</sub> reference, indicating that MoO<sub>3</sub> has bulk-like properties, interacting only weakly with the support. The MoO<sub>3</sub>/TiO<sub>2</sub> spectrum exhibits dampened oscillations compared to the other spectra. This could result from destructive interference by an additional, non-MoO<sub>3</sub>, contribution to the spectrum or a different coordination geometry in this catalyst. From the EXAFS fitting (Figure S10), we can see that the supported catalysts can be fitted in the same way as  $\alpha$ -MoO<sub>3</sub>, using three doubly degenerate O paths at three different distances from Mo (Tables S4–S6). This suggests that the {MoO<sub>6</sub>} octahedra are distorted in the supported MoO<sub>3</sub> catalysts.<sup>53</sup> The MoO<sub>3</sub>/TiO<sub>2</sub> spectrum was fitted with an additional Ti path at 2.76 Å, giving rise to the destructive interference that dampens the EXAFS oscillations and indicating that there is a close metal–support interaction. More details on the EXAFS fitting are reported in the Supporting Information

**Catalytic Tests.** We then tested the catalysts in the RWGS reaction. A total of 200 mg of catalyst was placed in a vertical fixed bed reactor. As high H<sub>2</sub>:CO<sub>2</sub> ratios improve CO<sub>2</sub> conversion,<sup>54,55</sup> we set the H<sub>2</sub>:CO<sub>2</sub> ratio to 4:1. We ran temperature-screening tests between 400–750 °C (100 mL·min<sup>-1</sup> total flow) and long-term stability tests at 550 °C for 48 h (50 mL·min<sup>-1</sup> total flow).

Control experiments showed that Ti<sub>3</sub>AlC<sub>2</sub> alone is active only above 700 °C, converting between 10–18% of CO<sub>2</sub> (Figure S11). A Mo<sub>2</sub>TiAlC<sub>2</sub> MAX phase, which contains molybdenum in the layered MAX phase structure,<sup>56</sup> showed no activity within the entire temperature range. This confirms that a metal or metal oxide available on the surface as active sites are required to improve CO<sub>2</sub> activation in RWGS. The prereduction of a MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at 750 °C did not improve CO<sub>2</sub> conversion and CO selectivity compared to the unreduced catalyst (Figure S12). Therefore, we focused on the catalytic tests of the pristine catalysts after calcination, without prereduction. This is an interesting advantage of our MAX phase-supported catalyst, as avoiding the preactivation step results in significant process savings in a real industrial application.

The temperature-screening tests show that the MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> catalyst is already active at 450 °C, reaching 50% conversion at 750 °C (Figure S13). Despite the low surface area and large particle size of this catalyst, its conversion is similar to MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>/TiO<sub>2</sub>. All catalysts were highly selective to CO above 550 °C. Since the three catalysts show a similar conversion and selectivity, their CO production rate values are also similar (Table S7). Due to its low surface area, the Ti<sub>3</sub>AlC<sub>2</sub>-based catalyst has fewer available active sites compared to the other catalysts, as quantified by CO chemisorption (Table S8). Thus, we compared the catalyst in terms of their intrinsic activity, using their TOF (Figure 6a). MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> shows higher TOF values from 450 °C

onward, indicating that it is intrinsically more active than  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{TiO}_2$ .



**Figure 6.** TOF values of the catalysts during (a) temperature-screening tests (reaction conditions: 200 mg catalyst,  $\text{H}_2$ : $\text{CO}_2$  ratio = 4:1, 100  $\text{mL}\cdot\text{min}^{-1}$  total flow,  $\text{WHSV} = 30,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ) and (b) stability tests (reaction conditions: 550 °C, 200 mg catalyst,  $\text{H}_2$ : $\text{CO}_2$  ratio = 4:1, 50  $\text{mL}\cdot\text{min}^{-1}$  total flow,  $\text{WHSV} = 15,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ).

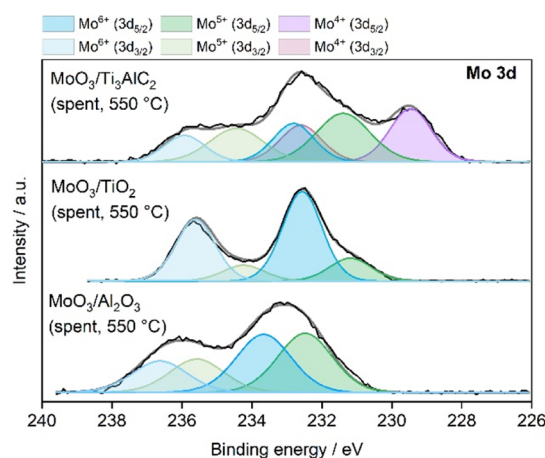
We also studied the long-term stability of the catalysts at a  $\text{WHSV}$  of  $15,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , which is a relatively high space velocity that would result in a compact RWGS reactor, potentially reducing the capital costs of a continuous  $\text{CO}_2$  conversion unit. In addition, the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst shows higher  $\text{CO}_2$  conversion with considerable  $\text{CO}$  selectivity at lower space velocity (Figure S14). To be far from equilibrium conditions and study the potential of the MAX phase catalyst in low-temperature RWGS, we performed the stability tests at 550 °C. The  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst is stable over time and it converts 20%  $\text{CO}_2$  (Figure S15).  $\text{MoO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts give 20–25% and 30%  $\text{CO}_2$  conversion, respectively. The increase in conversion at the start of the reaction might be related to the reduction of the  $\text{MoO}_3$  species upon exposure to the hydrogen-rich reaction mixture ( $4\text{H}_2:1\text{CO}_2$ ). Under these conditions,  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  showed a lower  $\text{CO}$  production rate ( $0.01 \text{ mol CO produced}\cdot\text{g}_{\text{catalyst}}^{-1}\cdot\text{min}^{-1}$ ) than  $\text{MoO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts ( $0.02 \text{ mol CO produced}\cdot\text{g}_{\text{catalyst}}^{-1}\cdot\text{min}^{-1}$ ), see Table S9. When comparing their intrinsic activity by means of TOF (Figure 6b),  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  stands out as the most active catalyst. It converts 18  $\text{mol CO}_2\cdot\text{site}^{-1}\cdot\text{min}^{-1}$ , while  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{TiO}_2$  convert 10 and 7  $\text{mol CO}_2\cdot\text{site}^{-1}\cdot\text{min}^{-1}$ , respectively. Control experiments showed that a bulk  $\text{MoO}_3$  sample is significantly less active than  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  (Figure S16). This indicates that the activity of the Mo sites is enhanced in the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst due to metal–support interactions and/or the exposure of a particular set of planes when  $\text{MoO}_3$  grows as rods.<sup>57,58</sup>

In the stability tests,  $\text{CO}$  selectivity followed the order  $\text{MoO}_3/\text{TiO}_2$  (70–100%) >  $\text{MoO}_3/\text{Al}_2\text{O}_3$  (60–80%) >  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  (60–65%), indicating the formation of side products (Figure S15). Methane was not detected. TGA analysis (Figure

S17) of the spent catalysts shows the absence of carbon deposits, indicating the inhibition of coking reactions. We hypothesize that alcohols are produced as side products, as previous work reported the formation of alcohols from  $\text{CO}$  hydrogenation and  $\text{CH}_4$  oxidation reactions when using  $\text{MoO}_3$ -based catalysts under similar conditions.<sup>59–62</sup> In addition, the  $\text{CO}$  selectivity profiles oscillate with time (Figure S15). We hypothesize that this is due to changes in the molybdenum oxidation state during reaction. Depending on the balance of reduced/oxidized states,  $\text{CO}$  hydrogenation to alcohols can also occur, thus decreasing  $\text{CO}$  selectivity. The decrease in  $\text{CO}$  concentration in the reaction mixture might shift the equilibrium toward  $\text{CO}_2$  consumption, giving higher  $\text{CO}_2$  conversion with lower  $\text{CO}$  selectivity. To understand the working of the catalysts better, we also characterized them after the reaction. The XRD patterns of the spent catalysts show that the  $\text{Ti}_3\text{AlC}_2$  MAX phase is stable under reaction conditions (Figure S1). As expected, the  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  supports were also stable (Figure S1).

In the LCF analysis of the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  sample XANES spectrum (Figure 5), the percentage of bulk  $\alpha$ - $\text{MoO}_3$  increases after stability testing. The EXAFS spectrum of the spent sample is also more similar to bulk  $\alpha$ - $\text{MoO}_3$  compared to the fresh sample (Figure S9). This reflects a change in the molybdenum oxide particle morphology that increases the volume-to-surface ratio. HAADF–STEM images of the spent catalyst confirm that the size and morphology of  $\text{MoO}_3$  particles change during the reaction, from large rods to agglomerates (Figures S17 and S18). These agglomerates are smaller than the rods, but their varied shape does not allow us to calculate the particle size. The nanoparticle sizes on  $\text{MoO}_3/\text{TiO}_2$  (average particle size: 0.51 nm,  $\sigma = 0.18$  nm) and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  (average particle size: 0.70 nm,  $\sigma = 0.15$  nm) catalysts do not significantly change during the reaction compared to the fresh samples (Figure S19).

The Mo 3d XPS spectra of the spent catalysts show the reduction of  $\text{MoO}_3$  species during the reaction (Figure 7). Interestingly,  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  shows  $\text{MoO}_2$  ( $\text{Mo}^{4+}$ ),  $\text{Mo}_4\text{O}_{11}$  ( $\text{Mo}^{5+}$ ), and  $\text{MoO}_3$  ( $\text{Mo}^{6+}$ ) species on the surface, while the other two catalysts only contain  $\text{Mo}_4\text{O}_{11}$  and  $\text{MoO}_3$ .<sup>48,63</sup> The percentage of reduced species is significantly higher on the  $\text{MoO}_3/\text{Ti}_3\text{AlC}_2$  catalyst surface (Table 1), indicating that this catalyst is reduced more during the reaction. The higher



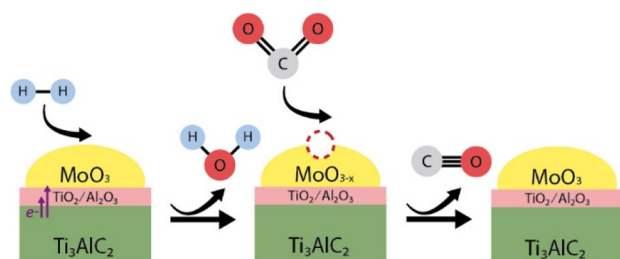
**Figure 7.** Mo 3d XPS spectra of the catalysts after the stability test at 550 °C.

**Table 1. Atomic Percentage of MoO<sub>2</sub> (Mo<sup>4+</sup>), Mo<sub>4</sub>O<sub>11</sub> (Mo<sup>5+</sup>), and MoO<sub>3</sub> (Mo<sup>6+</sup>) Species on the Spent Catalyst Surface, based on Mo 3d XPS**

catalyst	atomic percentage on the surface (%)		
	Mo <sup>6+</sup>	Mo <sup>5+</sup>	Mo <sup>4+</sup>
MoO <sub>3</sub> /Ti <sub>3</sub> AlC <sub>2</sub> (spent)	24	41	35
MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (spent)	50	50	0
MoO <sub>3</sub> /TiO <sub>2</sub> (spent)	80	20	0

activation percentage observed with MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> during the stability test (around 8%, Figure S15) can be related to its higher reduction degree under reaction conditions. These results indicate that a more reduced MoO<sub>3</sub> surface leads to the formation of more oxygen vacancies, which in turn increases the RWGS activity.

Typically, RWGS results in catalyst reduction, especially in hydrogen-rich mixtures.<sup>64</sup> Hydrogen can remove active oxygen sites from MoO<sub>3</sub>, creating water and leaving surface oxygen vacancies. The CO<sub>2</sub> can regenerate the oxygen vacancies by dissociating on the surface to CO and O.<sup>65</sup> The ability of the catalyst to enhance this redox cycle determines its activity. In this study, MoO<sub>3</sub> nanoparticles in close interaction with the support lead to poor redox properties, as seen with the MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The low surface area of the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase leads to large bulk-like MoO<sub>3</sub> rods. Nevertheless, MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> is the most intrinsically active catalyst in terms of TOF (Figure 5). We attribute this to the electronically rich Ti<sub>3</sub>AlC<sub>2</sub>, which transfers the charge to the active site. This charge transfer effect enhances the redox properties of MoO<sub>3</sub>, facilitating the formation of surface oxygen vacancies that participate in the reaction (see Figure 8).<sup>66</sup> In addition, electronically richer molybdenum sites are



**Figure 8.** Cartoon showing the composition of the MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> catalyst under reaction conditions and the proposed RWGS reaction pathway.

ideal for CO<sub>2</sub> activation, as the charge transfer from Mo to CO<sub>2</sub> antibonding orbitals can weaken the C–O bond, facilitating its reduction to CO.<sup>67</sup>

## CONCLUSIONS

In this work, we show for the first time the potential of MAX phase-based catalysts for application in CO<sub>2</sub> conversion *via* the RWGS reaction. When supporting molybdenum oxide on the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase, the low surface area of the MAX phase leads to the formation of large MoO<sub>3</sub> rods with bulk-like properties. Nevertheless, the presence of electronically rich Ti<sub>3</sub>AlC<sub>2</sub> enhances the redox properties of MoO<sub>3</sub> under RWGS conditions, resulting in a highly reduced surface that contains a large amount of oxygen vacancies. The MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts contain small and highly dispersed

MoO<sub>3</sub> nanoparticles, but their close contact with the support inhibits the formation of oxygen vacancies during the reaction. As MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub> forms more oxygen vacancies under reaction, this catalyst showed the highest intrinsic activity in terms of TOF during the catalytic experiments. The electronically richer Mo sites when supported on MAX phases are ideal activation sites for CO<sub>2</sub> *via* electron transfer to CO<sub>2</sub> antibonding orbitals. Such an interaction weakens the C–O bond and favors its reduction to CO. All catalysts are selective to CO, inhibiting the formation of undesired methane and coke. However, unidentified side products, most likely alcohols, also form. This study, which brings more insights into the workings of MAX phase catalysts on CO<sub>2</sub> conversion reactions, shows the high potential of MAX phases as catalyst supports.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c07881>.

Characterization of the fresh and spent catalysts (XRD patterns, XPS, temperature-programmed reduction profiles, nitrogen adsorption–desorption isotherms, CO chemisorption, TGA, and HAADF–STEM images); detailed analysis of XANES and EXAFS spectra; CO<sub>2</sub> conversion and CO selectivity values of control samples (Ti<sub>3</sub>AlC<sub>2</sub>, Mo<sub>2</sub>TiAlC<sub>2</sub>, reduced MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and bulk MoO<sub>3</sub>) and studied catalysts (10 wt % MoO<sub>3</sub>/Ti<sub>3</sub>AlC<sub>2</sub>, MoO<sub>3</sub>/TiO<sub>2</sub>, and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>), and CO formation rates of the studied catalysts (PDF).

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Hartmann, D. L. Anthropogenic Climate Change. *Global Physical Climatology*, 2nd ed.; Elsevier Inc., 2016; pp 397–425.
- (2) Vallero, D. A. Air Pollution Biogeochemistry. *Air Pollution Calculations*; Elsevier Inc., 2019; pp 175–206.
- (3) Shell International B. V. Shell Scenarios. The Numbers behind Sky. 2018, <https://www.shell.com/energy-and-innovation/the-energy-future/scenarios/shell-scenario-sky.html> (accessed August 2020).
- (4) Lüthi, D.; Le Floch, M.; Bereiter, B.; Blunier, T.; Barnola, J.-M.; Siegenthaler, U.; Raynaud, D.; Jouzel, J.; Fischer, H.; Kawamura, K.; Stocker, T. F. High-Resolution Carbon Dioxide Concentration Record 650,000–800,000 Years before Present. *Nature* **2008**, *453*, 379–382.
- (5) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO<sub>2</sub> from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840–11876.
- (6) Kothandaraman, A.; Nord, L.; Bolland, O.; Herzog, H. J.; McRae, G. J. Comparison of Solvents for Post-Combustion Capture of CO<sub>2</sub> by Chemical Absorption. *Energy Procedia* **2009**, *1*, 1373–1380.
- (7) Gnanakumar, E. S.; Chandran, N.; Kozhevnikov, I. V.; Grauatienza, A.; Ramos Fernández, E. V.; Sepulveda-Escribano, A.; Shiju, N. R. Highly Efficient Nickel-Niobia Composite Catalysts for Hydrogenation of CO<sub>2</sub> to Methane. *Chem. Eng. Sci.* **2019**, *194*, 2–9.
- (8) Ronda-Lloret, M.; Wang, Y.; Oulego, P.; Rothenberg, G.; Tu, X.; Shiju, N. R. CO<sub>2</sub> Hydrogenation at Atmospheric Pressure and Low Temperature Using Plasma-Enhanced Catalysis over Supported Cobalt Oxide Catalysts. *ACS Sustainable Chem. Eng.* **2020**, *8*, 17397–17407.
- (9) Daza, Y. A.; Kuhn, J. N. CO<sub>2</sub> Conversion by Reverse Water Gas Shift Catalysis: Comparison of Catalysts, Mechanisms and Their Consequences for CO<sub>2</sub> Conversion to Liquid Fuels. *RSC Adv.* **2016**, *6*, 49675–49691.
- (10) Ronda-Lloret, M.; Rothenberg, G.; Shiju, N. R. A Critical Look at Direct Catalytic Hydrogenation of Carbon Dioxide to Olefins. *ChemSusChem* **2019**, *12*, 3896–3914.
- (11) Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40*, 3703–3727.
- (12) Wei, J.; Ge, Q.; Yao, R.; Wen, Z.; Fang, C.; Guo, L.; Xu, H.; Sun, J. Directly Converting CO<sub>2</sub> into a Gasoline Fuel. *Nat. Commun.* **2017**, *8*, 15174.
- (13) Yang, L.; Pastor-Pérez, L.; Gu, S.; Sepúlveda-Escribano, A.; Reina, T. R. Highly Efficient Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Catalysts for CO<sub>2</sub> Upgrading via Reverse Water-Gas Shift: Effect of Selected Transition Metal Promoters. *Appl. Catal., B* **2018**, *232*, 464–471.
- (14) Su, X.; Yang, X.; Zhao, B.; Huang, Y. Designing of Highly Selective and High-Temperature Endurable RWGS Heterogeneous Catalysts: Recent Advances and the Future Directions. *J. Energy Chem.* **2017**, *26*, 854–867.
- (15) Ronda-Lloret, M.; Rico-Francés, S.; Sepúlveda-Escribano, A.; Ramos-Fernandez, E. V. CuOx/CeO<sub>2</sub> Catalyst Derived from Metal Organic Framework for Reverse Water-Gas Shift Reaction. *Appl. Catal., A* **2018**, *562*, 28–36.
- (16) Gharibi Kharaji, A.; Shariati, A. Performance Comparison of Two Newly Developed Bimetallic (X-Mo/Al<sub>2</sub>O<sub>3</sub>, X=Fe or Co) Catalysts for Reverse Water Gas Shift Reaction. *China Pet. Process. Petrochem. Technol.* **2016**, *18*, 51–58.
- (17) Kharaji, A. G.; Shariati, A.; Takassi, M. A. A Novel  $\gamma$ -Alumina Supported Fe-Mo Bimetallic Catalyst for Reverse Water Gas Shift Reaction. *Chin. J. Chem. Eng.* **2013**, *21*, 1007–1014.
- (18) Kharaji, A. G.; Shariati, A.; Ostadi, M. Development of Ni-Mo/Al<sub>2</sub>O<sub>3</sub> Catalyst for Reverse Water Gas Shift (RWGS) Reaction. *J. Nanosci. Nanotechnol.* **2014**, *14*, 6841–6847.
- (19) Carrasquillo-Flores, R.; Ro, I.; Kumbhalkar, M. D.; Burt, S.; Carrero, C. A.; Alba-Rubio, A. C.; Miller, J. T.; Hermans, I.; Huber, G. W.; Dumesic, J. A. Reverse Water-Gas Shift on Interfacial Sites Formed by Deposition of Oxidized Molybdenum Moieties onto Gold Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 10317–10325.
- (20) Ro, I.; Sener, C.; Stadelman, T. M.; Ball, M. R.; Venegas, J. M.; Burt, S. P.; Hermans, I.; Dumesic, J. A.; Huber, G. W. Measurement of Intrinsic Catalytic Activity of Pt Monometallic and Pt-MoOx Interfacial Sites over Visible Light Enhanced PtMoOx/SiO<sub>2</sub> Catalyst in Reverse Water Gas Shift Reaction. *J. Catal.* **2016**, *344*, 784–794.
- (21) Akande, S. O.; Chroneos, A.; Vasilopoulou, M.; Kennou, S.; Schwingschlögl, U. Vacancy Formation in MoO<sub>3</sub>: Hybrid Density Functional Theory and Photoemission Experiments. *J. Mater. Chem. C* **2016**, *4*, 9526–9531.
- (22) Borgschulte, A.; Sambalova, O.; Delmelle, R.; Jenatsch, S.; Hany, R.; Nüesch, F. Hydrogen Reduction of Molybdenum Oxide at Room Temperature. *Sci. Rep.* **2017**, *7*, 40761.
- (23) Wang, L. C.; Widmann, D.; Behm, R. J. Reactive Removal of Surface Oxygen by H<sub>2</sub>, CO and CO/H<sub>2</sub> on a Au/CeO<sub>2</sub> Catalyst and Its Relevance to the Preferential CO Oxidation (PROX) and Reverse Water Gas Shift (RWGS) Reaction. *Catal. Sci. Technol.* **2015**, *5*, 925–941.
- (24) Chen, Y.; Wang, H.; Burch, R.; Hardacre, C.; Hu, P. New Insight into Mechanisms in Water-Gas-Shift Reaction on Au/CeO<sub>2</sub> (111): A Density Functional Theory and Kinetic Study. *Faraday Discuss.* **2011**, *152*, 121–133.
- (25) Deelen, T. W.; Mejia, C. H.; Jong, K. P. Control of Metal-Support Interactions in Heterogeneous Catalysts to Enhance Activity and Selectivity. *Nat. Catal.* **2019**, *2*, 955–970.

- (26) Beckers, J.; Rothenberg, G. Redox Properties of Doped and Supported Copper-Ceria Catalysts. *Dalton Trans.* **2008**, *46*, 6573–6578.
- (27) Slot, T. K.; Yue, F.; Xu, H.; Ramos-Fernandez, E. V.; Sepúlveda-Escribano, A.; Sofer, Z.; Rothenberg, G.; Shiju, N. R. Surface Oxidation of  $Ti_3C_2T_x$  Enhances the Catalytic Activity of Supported Platinum Nanoparticles in Ammonia Borane Hydrolysis. *2D Mater.* **2020**, *8*, 015001.
- (28) Barsoum, M.; El-Raghy, T. The MAX Phases: Unique New Carbide and Nitride Materials. *Am. Sci.* **2001**, *89*, 334–343.
- (29) Boatemaa, L.; Bosch, M.; Farle, A. S.; Bei, G. P.; Zwaag, S.; Sloof, W. G. Autonomous High-Temperature Healing of Surface Cracks in  $Al_2O_3$  Containing  $Ti_2AlC$  Particles. *J. Am. Ceram. Soc.* **2018**, *101*, 5684–5693.
- (30) Barsoum, M. W. Physical Properties of the MAX Phases. *Encyclopedia of Materials: Science and Technology*, 2nd ed.; Elsevier Ltd, 2006; pp 1–11.
- (31) Medkour, Y.; Roumili, A.; Maouche, D.; Louail, L. Electrical Properties of MAX Phases. *Advances in Science and Technology of Mn +1AX<sub>n</sub> Phases*; Woodhead Publishing Limited, 2012; pp 159–175.
- (32) Wang, X. H.; Zhou, Y. C. Oxidation Behavior of  $Ti_3AlC_2$  at 1000–1400 °C in Air. *Corros. Sci.* **2003**, *45*, 891–907.
- (33) Sloof, W. G.; Pei, R.; McDonald, S. A.; Fife, J. L.; Shen, L.; Boatemaa, L.; Farle, A.-S.; Yan, K.; Zhang, X.; Van Der Zwaag, S.; Lee, P. D.; Withers, P. J. Repeated Crack Healing in MAX-Phase Ceramics Revealed by 4D in Situ Synchrotron X-Ray Tomographic Microscopy. *Sci. Rep.* **2016**, *6*, 23040.
- (34) Eklund, P.; Beckers, M.; Jansson, U.; Högberg, H.; Hultman, L. The  $M_{N+1}AX_n$  Phases: Materials Science and Thin-Film Processing. *Thin Solid Films* **2010**, *518*, 1851–1878.
- (35) Ng, W. H. K.; Gnanakumar, E. S.; Batyrev, E.; Sharma, S. K.; Pujari, P. K.; Greer, H. F.; Zhou, W.; Sakidja, R.; Rothenberg, G.; Barsoum, M. W.; Shiju, N. R. The  $Ti_3AlC_2$  MAX Phase as an Efficient Catalyst for Oxidative Dehydrogenation of n-Butane. *Angew. Chem., Int. Ed.* **2018**, *57*, 1485–1490.
- (36) Ronda-Lloret, M.; Marakatti, V. S.; Sloof, W. G.; Delgado, J. J.; Sepúlveda-Escribano, A.; Ramos-Fernandez, E. V.; Rothenberg, G.; Shiju, N. R. Butane Dry Reforming Catalyzed by Cobalt Oxide Supported on  $Ti_2AlC$  MAX Phase. *ChemSusChem* **2020**, *13*, 6401–6408.
- (37) Trandafir, M. M.; Neațu, F.; Chirica, I. M.; Neațu, Ș.; Kuncser, A. C.; Cuculea, E. I.; Natu, V.; Barsoum, M. W.; Florea, M. Highly Efficient Ultralow Pd Loading Supported on MAX Phases for Chemoselective Hydrogenation. *ACS Catal.* **2020**, *10*, 5899–5908.
- (38) Clark, A. H.; Imbao, J.; Frahm, R.; Nachttegaal, M. ProQEXAFS: A Highly Optimized Parallelized Rapid Processing Software for QEXAFS Data. *J. Synchrotron Radiat.* **2020**, *27*, 551–557.
- (39) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.
- (40) Andersson, G.; Magnéli, A.; Sillén, L. G.; Rottenberg, M. On the Crystal Structure of Molybdenum Trioxide. *Acta Chem. Scand.* **1950**, *4*, 793–797.
- (41) Liu, X.; Khan, M.; Liu, W.; Xiang, W.; Guan, M.; Jiang, P.; Cao, W. Synthesis of Nanocrystalline Ga-TiO<sub>2</sub> Powders by Mild Hydrothermal Method and Their Visible Light Photoactivity. *Ceram. Int.* **2015**, *41*, 3075–3080.
- (42) Inzani, K.; Nematollahi, M.; Vullum-Bruer, F.; Grande, T.; Reenaas, T. W.; Selbach, S. M. Electronic Properties of Reduced Molybdenum Oxides. *Phys. Chem. Chem. Phys.* **2017**, *19*, 9232–9245.
- (43) Papageridis, K. N.; Siakavelas, G.; Charisiou, N. D.; Avraam, D. G.; Tzounis, L.; Kousi, K.; Goula, M. A. Comparative Study of Ni, Co, Cu Supported on  $\gamma$ -Alumina Catalysts for Hydrogen Production via the Glycerol Steam Reforming Reaction. *Fuel Process. Technol.* **2016**, *152*, 156–175.
- (44) Jongsomjit, B.; Panpranot, J.; Goodwin, J. G. Co-Support Compound Formation in Alumina-Supported Cobalt Catalysts. *J. Catal.* **2001**, *204*, 98–109.
- (45) Chen, K.; Qiu, N.; Deng, Q.; Kang, M.-H.; Yang, H.; Baek, J.-U.; Koh, Y.-H.; Du, S.; Huang, Q.; Kim, H.-E. Cytocompatibility of  $Ti_3AlC_2$ ,  $Ti_3SiC_2$ , and  $Ti_2AlN$ : In Vitro Tests and First-Principles Calculations. *ACS Biomater. Sci. Eng.* **2017**, *3*, 2293–2301.
- (46) Wang, X. H.; Zhou, Y. C. Oxidation Behavior of  $Ti_3AlC_2$  Powders in Flowing Air. *J. Mater. Chem.* **2002**, *12*, 2781–2785.
- (47) White, R. T.; Thibau, E. S.; Lu, Z.-H. Interface Structure of MoO<sub>3</sub> on Organic Semiconductors. *Sci. Rep.* **2016**, *6*, 21109.
- (48) Xiang, D.; Han, C.; Zhang, J.; Chen, W. Gap States Assisted MoO<sub>3</sub> Nanobelt Photodetector with Wide Spectrum Response. *Sci. Rep.* **2015**, *4*, 4891.
- (49) Xie, F.; Choy, W. C. H.; Wang, C.; Li, X.; Zhang, S.; Hou, J. Low-Temperature Solution-Processed Hydrogen Molybdenum and Vanadium Bronzes for an Efficient Hole-Transport Layer in Organic Electronics. *Adv. Mater.* **2013**, *25*, 2051–2055.
- (50) Zhao, X.; Jia, W.; Wu, X.; Lv, Y.; Qiu, J.; Guo, J.; Wang, X.; Jia, D.; Yan, J.; Wu, D. Ultrafine MoO<sub>3</sub> Anchored in Coal-Based Carbon Nanofiber as Anode for Advanced Lithium-Ion Batteries. *Carbon* **2020**, *156*, 445–452.
- (51) Leliveld, R. G.; Van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. A Mo-K Edge XAFS Study of the Metal Sulfide-Support Interaction in (Co)Mo Supported Alumina and Titania Catalysts. *J. Catal.* **1997**, *165*, 184–196.
- (52) Wang, J.; Boelens, H. F. M.; Thathagar, M. B.; Rothenberg, G. In Situ Spectroscopic Analysis of Nanocluster Formation. *Chem-PhysChem* **2004**, *5*, 93–98.
- (53) Caro, C.; Thirunavukkarasu, K.; Anilkumar, M.; Shiju, N. R.; Rothenberg, G. Selective Autooxidation of Ethanol over Titania-Supported Molybdenum Oxide Catalysts: Structure and Reactivity. *Adv. Synth. Catal.* **2012**, *354*, 1327–1336.
- (54) Whitlow, J. E.; Parrish, C. E. Operation, Modeling and Analysis of the Reverse Water Gas Shift Process. *AIP Conf. Proc.* **2003**, *654*, 1116–1123.
- (55) Zhang, Q.; Pastor-Pérez, L.; Jin, W.; Gu, S.; Reina, T. R. Understanding the Promoter Effect of Cu and Cs over Highly Effective B-Mo<sub>2</sub>C Catalysts for the Reverse Water-Gas Shift Reaction. *Appl. Catal., B* **2019**, *244*, 889–898.
- (56) Anasori, B.; Dahlqvist, M.; Halim, J.; Moon, E. J.; Lu, J.; Hosler, B. C.; Caspi, E. a. N.; May, S. J.; Hultman, L.; Eklund, P.; Rosén, J.; Barsoum, M. W. Experimental and Theoretical Characterization of Ordered MAX Phases Mo<sub>2</sub>TiAlC<sub>2</sub> and Mo<sub>2</sub>Ti<sub>2</sub>AlC<sub>3</sub>. *J. Appl. Phys.* **2015**, *118*, 094304.
- (57) Shiju, N. R.; Liang, X.; Weimer, A. W.; Liang, C.; Dai, S.; Gulians, V. V. The Role of Surface Basal Planes of Layered Mixed Metal Oxides in Selective Transformation of Lower Alkanes: Propane Amoxidation over Surface Ab Planes of Mo-V-Te-Nb-O M1 Phase. *J. Am. Chem. Soc.* **2008**, *130*, 5850–5851.
- (58) Shiju, N. R.; Rondinone, A. J.; Mullins, D. R.; Schwartz, V.; Overbury, S. H.; Gulians, V. V. XANES Study of Hydrothermal Mo-V-Based Mixed Oxide M1-Phase Catalysts for the (Amm)Oxidation of Propane. *Chem. Mater.* **2008**, *20*, 6611–6616.
- (59) Spencer, N. D.; Pereira, C. J. Partial Oxidation of CH<sub>4</sub> to HCHO over a MoO<sub>3</sub>-SiO<sub>2</sub> Catalyst: A Kinetic Study. *AIChE J.* **1987**, *33*, 1808–1812.
- (60) Tatsumi, T.; Muramatsu, A.; Yokota, K.; Tominaga, H. Mechanistic Study on the Alcohol Synthesis over Molybdenum Catalysts. *J. Catal.* **1989**, *115*, 388–398.
- (61) Kim, H.-G.; Lee, K. H.; Lee, J. S. Carbon Monoxide Hydrogenation over Molybdenum Carbide Catalysts. *Res. Chem. Intermed.* **2000**, *26*, 427–443.
- (62) Muramatsu, A.; Tatsumi, T.; Tominaga, H. Active Species of Molybdenum for Alcohol Synthesis from Carbon Monoxide-Hydrogen. *J. Phys. Chem.* **1992**, *96*, 1334–1340.
- (63) Nacimiento, F.; Cabello, M.; Alcántara, R.; Pérez-Vicente, C.; Lavela, P.; Tirado, J. L. Exploring an Aluminum Ion Battery Based on Molybdate as Working Electrode and Ionic Liquid as Electrolyte. *J. Electrochem. Soc.* **2018**, *165*, A2994–A2999.
- (64) Karpenko, A.; Leppelt, R.; Cai, J.; Plzak, V.; Chuvilin, A.; Kaiser, U.; Behm, R. Deactivation of a Au/CeO<sub>2</sub> Catalyst during the

Low-Temperature Water-Gas Shift Reaction and Its Reactivation: A Combined TEM, XRD, XPS, DRIFTS, and Activity Study. *J. Catal.* **2007**, *250*, 139–150.

(65) Wang, L. C.; Tahvildar Khazaneh, M.; Widmann, D.; Behm, R. J. TAP Reactor Studies of the Oxidizing Capability of CO<sub>2</sub> on a Au/CeO<sub>2</sub> Catalyst-A First Step toward Identifying a Redox Mechanism in the Reverse Water-Gas Shift Reaction. *J. Catal.* **2013**, *302*, 20–30.

(66) Puigdollers, A. R.; Schlexer, P.; Tosoni, S.; Pacchioni, G. Increasing Oxide Reducibility: The Role of Metal/Oxide Interfaces in the Formation of Oxygen Vacancies. *ACS Catal.* **2017**, *7*, 6493–6513.

(67) Álvarez, A.; Borges, M.; Corral-Pérez, J. J.; Olcina, J. G.; Hu, L.; Cornu, D.; Huang, R.; Stoian, D.; Urakawa, A. CO<sub>2</sub> Activation over Catalytic Surfaces. *ChemPhysChem* **2017**, *18*, 3135–3141.