Molybdenum Oxide Supported on Ti₃AlC₂ is an Active Reverse Water-Gas Shift Catalyst


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**Molybdenum Oxide Supported on Ti$_3$AlC$_2$ is an Active Reverse Water–Gas Shift Catalyst**

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

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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$_3$AlC$_2$ 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$_3$/TiO$_2$ and MoO$_3$/Al$_2$O$_3$ catalysts, due to the outstanding electronic properties of the Ti$_3$AlC$_2$ support. We observed a charge transfer effect from the electronically rich Ti$_3$AlC$_2$ MAX phase to the catalyst surface, which in turn enhances the reducibility of MoO$_3$ species during reaction. The redox properties of the MoO$_3$/Ti$_3$AlC$_2$ catalyst improve its RWGS intrinsic activity compared to TiO$_2$- and Al$_2$O$_3$-based catalysts.

**KEYWORDS:** CO$_2$ hydrogenation, MAX phases, RWGS, syn gas, molybdenum

**INTRODUCTION**

There is a global interest in reducing anthropogenic CO$_2$ emissions into the atmosphere.$^{1,2}$ The main sources of CO$_2$ are power generation and manufacturing, which emitted 12.4 and 3.9 Gt of CO$_2$ in 2015.$^{3,4}$ However, CO$_2$ is a valuable C$_1$ feedstock that should not be thrown away. After CO$_2$ capture, either from the atmosphere or from industrial flue gases, it should be efficiently converted into high value-added products via catalytic processes.$^{5-8}$

The reverse water–gas shift (RWGS) reaction (eq 1) using renewable hydrogen is a sustainable way for converting CO$_2$.$^9$ This reaction produces CO, a basic building block for a variety of valuable chemicals and fuels, such as methanol, paraffins, and olefins.$^{10}$ However, RWGS is an equilibrium-limited reaction, favored at high temperatures (>700 °C) because it is endothermic.$^{11}$ At lower temperatures, the exothermic CO methanation (eq 2) and Sabatier reaction (eq 3) also take place, consuming a substantial amount of H$_2$ and producing undesired methane. Therefore, catalyst development is focused on improving the catalytic performance at <500 °C.$^{12,13}$

\[
\begin{align*}
\text{CO}_2 + H_2 & \rightleftharpoons \text{CO} + H_2O \quad \Delta H_{25^\circ C} = 41.2 \text{kJ mol}^{-1} \\
\text{CO} + 3H_2 & \rightleftharpoons CH_4 + H_2O \quad \Delta H_{25^\circ C} = -206.5 \text{kJ mol}^{-1} \\
\text{CO}_2 + 4H_2 & \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{25^\circ C} = -165.0 \text{kJ mol}^{-1}
\end{align*}
\]

Traditionally, RWGS catalysts are based on Cu, Pt, and Rh nanoparticles supported on metal oxides (Al$_2$O$_3$, TiO$_2$, and CeO$_2$, among others).$^{5,14,15}$ 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,$^{16-20}$ we are interested in molybdenum oxide as an active phase itself due to its redox properties.$^{21,22}$ The oxygen vacancies created when reducing MoO$_3$ will affect the reaction performance, whether it takes place via the redox mechanism (where CO$_2$ adsorbs and dissociates on the reduced sites previously created by H$_2$) or via the associative pathway (where oxygen vacancies can stabilize adsorbed carbon-containing intermediates), see Figure 1.$^{10,23,24}$

Another important factor is the choice of support. Although typically inert, supports can enhance the reaction performance...
Figure 1. Scheme of the formation of oxygen vacancies on MoO$_3$ particles during RWGS, and its ability to dissociate CO$_2$ via the redox pathway and/or to stabilize carbon-containing species (indicated by R) via the associative pathway.

Thermogravimetric analysis (TGA) was carried out using an NETZSCH Jupiter STA 449F3 instrument, under air (20 mL·min$^{-1}$, O$_2$:N$_2$ 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 $^\text{TM}$ 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. 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 Ife 1.2.12). We used Athena for background subtraction of long-range oscillations and linear combination fitting (LCF) of supported catalyst spectra using Python-based graphical interface ProQEXAFS software.

Materials and Instrumentation. X-ray diffraction (XRD) patterns were recorded on a MiniFlex II X-ray diffractometer, described previously by Ronda-Lloret et al.$^{36}$ X-ray photoelectron spectroscopy (XPS) was performed using a K-α 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 ±0.2 eV (a detailed description of the analysis procedure is published elsewhere$^{36}$).

*EXPERIMENTAL SECTION*

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impregnation, using ammonium molybdate tetrahydrate as a precursor. γ-Al2O3 and anatase TiO2 were purchased from commercial sources. Ti3AlC2 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, Mo7TiAlC2, and bulk MoO3 were also tested as reference materials (see the Experimental Section for details).

Characterization of the Fresh Catalysts. The XRD pattern of the fresh Mo3O12/Ti3AlC2 catalyst shows the characteristic peaks of the Ti3AlC2 MAX phase structure (Figure 2), indicating that the bulk of the support remains stable after calcination. Anatase and rutile TiO2 peaks are also present at 2θ = 25.7 and 27.4°, indicating a slight oxidation of Ti3AlC2.41 The characteristic peaks of MoO3 are also visible at 2θ = 12.8 and 23.5°.42 The pattern of Mo3O12/Ti3AlC2 only shows broad peaks of anatase TiO2 at 2θ = 25.4, 38.2, 48.1, 54.8, 62.7, 70.0, 75.4, and 82.9°.41 Similarly, the pattern of MoO3/Al2O3 only shows the peaks of γ-Al2O3 at 2θ = 37.8, 45.8, 60.7, and 67.0° (Figure S1).43,44 The absence of MoO3 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 Mo3O12/Ti3AlC2 catalyst only show the Ti–O and the Al–O bonds at 458.8 eV (Ti 2p3/2) and 74.3 eV (Al 2p3/2), respectively (Figure 3). The distinctive peaks of the Ti3AlC2 structure (Ti–C bond at 454 eV (Ti 2p3/2) and Al–Ti bond at 72 eV (Al 2p3/2)) are absent.45,46 This indicates that the Ti3AlC2 surface completely oxidizes to titania and alumina under our calcination conditions (i.e., under air at 350 °C for 4 h).46 The Ti–O and Al–O bonds of Mo3O12/Ti3AlC2 shift to lower binding energies compared to MoO3/TiO2 and MoO3/Al2O3. This indicates a charge transfer effect from the bulk MAX phase to the surface oxide layer, enriching the surface with electrons.47

The Mo 3d spectra of the catalysts (Figure 3) show two spectral lines, assigned to Mo 3d5/2 and Mo 3d3/2 spin–orbit components. The Mo 3d5/2 binding energy in Mo3O12/Ti3AlC2 and MoO3/TiO2 spectra is 232.8 eV, which corresponds to MoO3 species (Mo6+).48,49 The Mo 3d spectrum of the Mo3O12/Al2O3 catalyst shows two contributions at Mo 3d5/2 binding energies of 232.6 and 233.6 eV, corresponding to Mo6+ and Mo5+ species. In the O 1s spectrum, Mo3O12/Ti3AlC2 and Mo3O12/TiO2 also show similar Mo–O binding energies (ca. 530.4 eV, cf. Figure S2).46 This indicates that the surface of the Ti3AlC2 undergoes oxidation and Mo predominantly sits on the oxidized titanium, as expected by the excess of titanium.

■ RESULTS AND DISCUSSION

Catalyst Synthesis. We compared the properties and activity in RWGS of Mo3O12-based catalysts, using the Ti3AlC2 MAX phase, γ-Al2O3, and TiO2 as supports. The catalysts, each containing 10 wt % on Mo metal basis, were prepared by wet
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, Ti$_3$AlC$_2$ predominantly converts to titania rather than to alumina. 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 MoO$_3$ is predominantly dispersed in the form of rods when deposited on Ti$_3$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 ± 138 nm long and 88 ± 11 nm wide. The large size of MoO$_3$ particles when supported on Ti$_3$AlC$_2$ results from the low surface area of this support (ca. 1 m$^2$/g). In agreement with XRD and XPS results, we see that the MoO$_3$ particles are very small and highly dispersed when supported on TiO$_2$ (average particle size: 0.42 nm, $\sigma = 0.11$ nm) and $\gamma$-Al$_2$O$_3$ (average particle size: 0.67 nm, $\sigma = 0.19$ nm, Figure S5). The MoO$_3$/TiO$_2$ and MoO$_3$/Al$_2$O$_3$ catalysts are mesoporous, with a BET surface area of 208 m$^2$·g$^{-1}$ and 145 m$^2$·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 MoO$_3$ nanoparticles (MoO$_3$-NPs) and bulk $\alpha$-MoO$_3$ references for comparison. In the XANES spectra (Figure 5a), all catalysts show the edge position at 20016.4 eV, characteristic of 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 $\rightarrow$ 4d transition, indicating a distorted octahedral environment. The triple peak feature above the edge in the XANES is slightly different for each catalyst. The MoO$_3$/Ti$_3$AlC$_2$ spectrum is similar to that of bulk $\alpha$-MoO$_3$, whereas the features of the MoO$_3$/Al$_2$O$_3$ spectrum are dampened similarly to that of MoO$_3$-NPs. MoO$_3$/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 MoO$_3$ nanoparticles and the bulk $\alpha$-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
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 into account in this analysis. We cannot correct for these contributions as we have no insights into the amount of Mo

In the EXAFS spectra (Figure S9), we observe in more detail the structural differences between MoO3 nanoparticles and bulk \(\alpha\)-MoO3. In \(k\)-space, the oscillations of the MoO3-NP spectrum are dampened compared to \(\alpha\)-MoO3, 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 MoO3-NP spectrum is also affected, with just one main peak compared to the complex first shell of \(\alpha\)-MoO3. The EXAFS spectrum of MoO3/Al2O3 is very similar to the MoO3 nanoparticle reference. The spectrum of MoO3/Ti3AlC2 is more similar to the bulk \(\alpha\)-MoO3 reference, indicating that MoO3 has bulk-like properties, interacting only weakly with the support. The MoO3/TiO2 spectrum exhibits dampened oscillations compared to the other spectra. This could result from destructive interference by an additional, non-MoO3, 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 \(\alpha\)-MoO3, using three doubly degenerate O paths at three different distances from Mo (Tables S4–S6). This suggests that the \(\{\text{MoO}_6\}\) octahedra are distorted in the supported MoO3 catalysts. The MoO3/TiO2 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 H2:CO2 ratios improve CO2 conversion,54,55 we set the H2:CO2 ratio to 4:1. We ran temperature-screening tests between 400–750 °C (100 mL·min⁻¹ total flow) and long-term stability tests at 550 °C for 48 h (50 mL·min⁻¹ total flow).

Control experiments showed that Ti3AlC2 alone is active only above 700 °C, converting between 10–18% of CO2 (Figure S11). A MoO3/TiAlC2 MAX phase, which contains molybdenum in the layered MAX phase structure,56 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 CO2 activation in RWGS. The pre-reduction of a MoO3/Al2O3 catalyst at 750 °C did not improve CO2 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 pre-reduction. 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 MoO3/Ti3AlC2 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 MoO3/Al2O3 and MoO3/TiO2. 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 Ti3AlC2-based catalyst has fewer available active sites compared to the other catalysts, as quantified by CO chemisorption (Table S8). Thus, we compared the catalysts in terms of their intrinsic activity, using their TOF (Figure 6a). MoO3/Ti3AlC2 shows higher TOF values from 450 °C
onward, indicating that it is intrinsically more active than MoO3/Al2O3 and MoO3/TiO2.

We also studied the long-term stability of the catalysts at a WHSV of 15,000 mL·g⁻¹·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 CO2 conversion unit. In addition, the MoO3/Ti3AlC2 catalyst shows higher CO2 conversion with considerable CO selectivity at lower space velocity (Figure S14). To be far from equilibrium conditions and study the potential of the MAX phase catalyst that the activity of the Mo sites is enhanced in the MoO3/Ti3AlC2 catalyst due to metal-support interactions and/or the reaction might be related to the reduction of the MoO3 species.

Interestingly, MoO3/Ti3AlC2 shows MoO2 (Mo⁴⁺), Mo⁴O₁₁ and MoO₃ (Mo⁶⁺) species on the surface, while the other two catalysts only contain Mo⁴O₁₁ and MoO₃.48,63 The percentage of reduced species is significantly higher on the fresh samples (Figure S19). When comparing their intrinsic activity by means of TOF (Figure 6b), MoO3/Ti3AlC2 stands out as the most active catalyst. It converts 18 mol CO₂-site⁻¹·min⁻¹, while MoO3/Al2O3 and MoO3/TiO2 convert 10 and 7 mol CO₂-site⁻¹·min⁻¹, respectively. Control experiments showed that a bulk MoO3 sample is significantly less active than MoO3/Ti3AlC2 (Figure S16). This indicates that the activity of the Mo sites is enhanced in the MoO3/Ti3AlC2 catalyst due to metal-support interactions and/or the exposure of a particular set of planes when MoO3 grows as rods.57,58

In the stability tests, CO selectivity followed the order MoO3/TiO2 (70–100%) > MoO3/Al2O3 (60–80%) > MoO3/Ti3AlC2 (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 CO hydrogenation and CH₄ oxidation reactions when using MoO3-based catalysts under similar conditions.59–62 In addition, the 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, CO hydrogenation to alcohols can also occur, thus decreasing CO selectivity. The decrease in CO concentration in the reaction mixture might shift the equilibrium toward CO₂ consumption, giving higher CO₂ conversion with lower 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 Ti₃AlC₂ MAX phase is stable under reaction conditions (Figure S1). As expected, the Al₂O₃ and TiO₂ supports were also stable (Figure S1).

In the LCF analysis of the MoO3/Ti3AlC2 sample XANES spectrum (Figure 5), the percentage of bulk α-MoO₃ increases after stability testing. The EXAFS spectrum of the spent sample is also more similar to bulk α-MoO₃ 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 MoO3 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 MoO3/TiO2 (average particle size: 0.51 nm, σ = 0.18 nm) and MoO3/Al2O3 (average particle size: 0.70 nm, σ = 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 MoO3 species during the reaction (Figure 7). Interestingly, MoO3/Ti3AlC2 shows MoO2 (Mo⁴⁺), MoO4 (Mo⁵⁺), and MoO₃ (Mo⁶⁺) species on the surface, while the other two catalysts only contain MoO4 and MoO3.48,63 The percentage of reduced species is significantly higher on the MoO3/Ti3AlC2 catalyst surface (Table 1), indicating that this catalyst is reduced more during the reaction. The higher CO hydrogenation and CH₄ oxidation reactions when using MoO3/Ti3AlC2...
MoO₃ nanoparticles, but their close contact with the support inhibits the formation of oxygen vacancies during the reaction. As MoO₃/Ti₃AlC₂ 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 CO₂ via electron transfer to CO₂ 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 CO₂ 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; CO₂ conversion and CO selectivity values of control samples (Ti₃AlC₂, MoO₃/TiAlC₂ reduced MoO₃/Al₂O₃, and bulk MoO₃) and studied catalysts (10 wt % MoO₃/Ti₃AlC₂, MoO₃/Al₂O₃, and MoO₃/Al₂O₃), and CO formation rates of the studied catalysts (PDF).

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**Table 1. Atomic Percentage of MoO₂ (Mo⁺⁺⁺), Mo₄O₁₁ (Mo⁺⁺), and MoO₃ (Mo⁺⁺⁺) Species on the Spent Catalyst Surface, based on Mo 3d XPS**

**Figure 8.** Cartoon showing the composition of the MoO₃/Ti₃AlC₂ catalyst under reaction conditions and the proposed RWGS reaction pathway.

**CONCLUSIONS**

In this work, we show for the first time the potential of MAX phase-based catalysts for application in CO₂ conversion via the RWGS reaction. When supporting molybdenum oxide on the Ti₃AlC₂ MAX phase, the low surface area of the MAX phase leads to the formation of large MoO₃ rods with bulk-like properties. Nevertheless, the presence of electronically rich Ti₃AlC₂ enhances the redox properties of MoO₃ under RWGS conditions, resulting in a highly reduced surface that contains a large amount of oxygen vacancies. The MoO₃/TiO₂ and MoO₃/Al₂O₃ catalysts contain small and highly dispersed
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Notes
The authors declare no competing financial interest.

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