INSIGHTS ON Mo_2C ACTIVITY

in deoxygenation reactions

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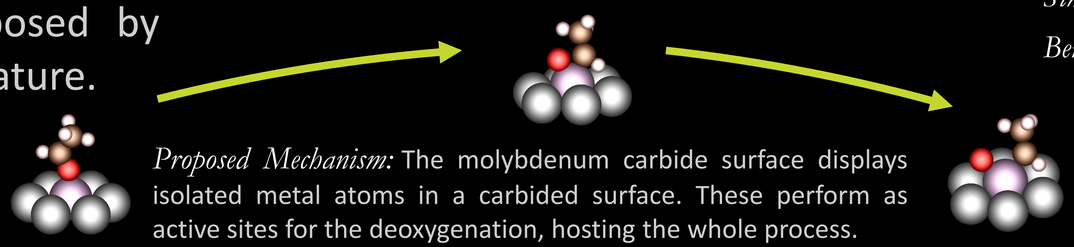
The **Hypothesis**

Experimental IR spectroscopic studies revealed the selective deoxygenation activity of Mo_2C surfaces.[1-3] A mechanism for carbonyl bond breaking was proposed by reference to the organometallic literature.



Proposed Mechanism: The molybdenum carbide surface displays isolated metal atoms in a carbided surface. These perform as active sites for the deoxygenation, hosting the whole process.

The **Challenge**

The objective is to computationally describe the process in atomistic detail.

The **Tools**

Computational method: DFT

Exchange and correlation functional: PBE

Simulated surfaces: C- and Mo-terminated α- and β-Mo_2C

Benchmark deoxygenations:

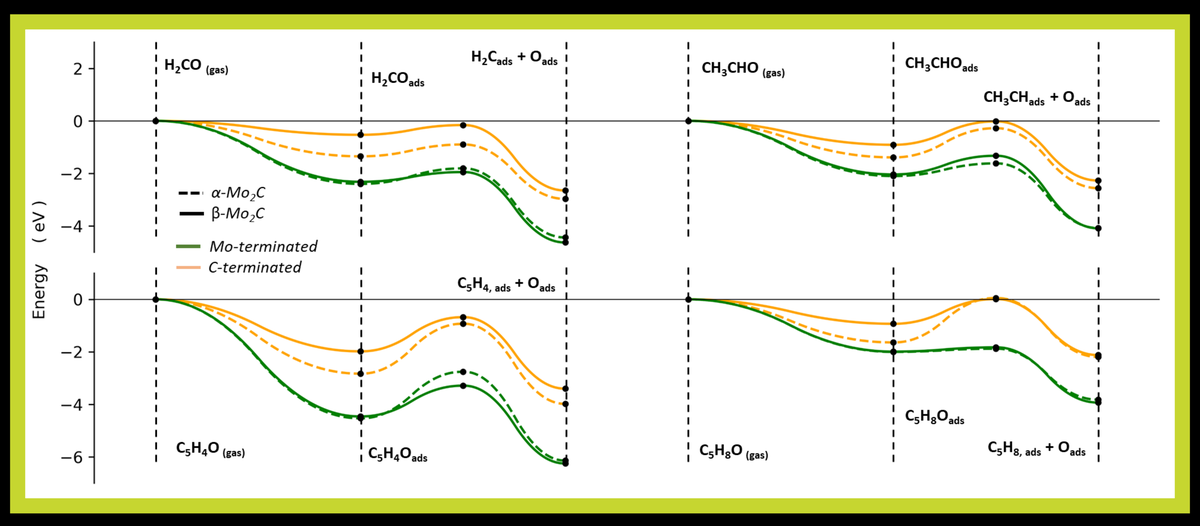
$CH_2O \longrightarrow CH_2 + O$

$CH_3CHO \longrightarrow CH_3CH + O$

$C_5H_4O \longrightarrow C_5H_4 + O$

$C_5H_8O \longrightarrow C_5H_8 + O$

Reaction profile



Catalytic activity confirmed

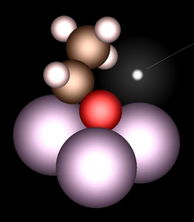
The lower energy of adsorbed products relative to adsorbed reactants in all the simulated deoxygenations confirms Mo_2C catalytic activity.

Minor effects of surface carbon

The presence of surface carbon reduces the reaction energy but does not quench Mo_2C's reactivity.

Similarities between α and β

Both phases are stable under normal conditions, so thermal treatments, commonly used to clean surfaces, might induce a phase transition. Computational results predict that it would not be a problem from a catalytic point of view.



In the absence of surface carbon, reactants and products find their most stable adsorption sites in hollows.

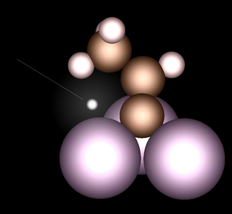
Reactants E_{ads}: $\sim 2\ eV$

Oxygen E_{ads}: $\sim 7.5\ eV$

Hydrocarbon E_{ads}: $\sim 5\ eV$

Reaction barrier: $\sim 0.1 - 0.5\ eV$

On carbided surfaces, reactants are adsorbed on Mo. The preferred interaction of oxygen is on a hollow site, whereas the hydrocarbon fragment preferently interacts with surface carbon. This represents an **important breakthrough**.



Reactants E_{ads}: $\sim 1.4\ eV$

Oxygen E_{ads}: $\sim 6\ eV$

Hydrocarbon E_{ads}: $\sim 4.8\ eV$

Reaction barrier: $\sim 0.5 - 1.5\ eV$

Infrared Spectra

$\nu(CO) \sim 1600\ cm^{-1}$: **Ketone reactants η_1 adsorbed on a Mo atom**

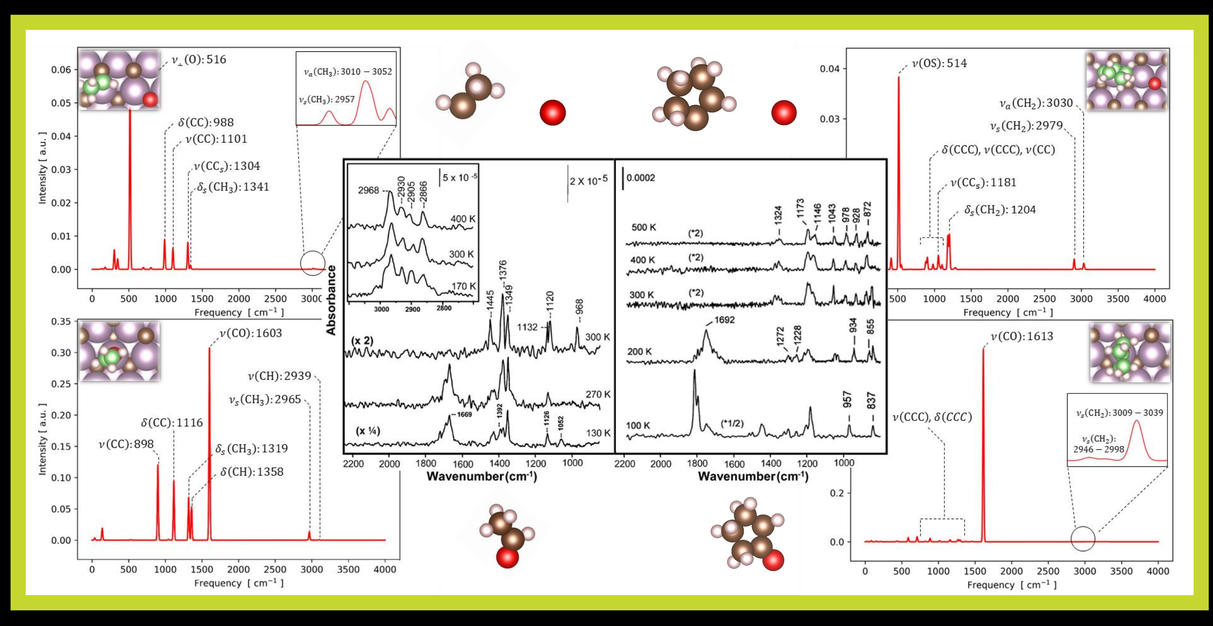
The adsorbed reactants are characterized by a $\nu(CO)$ band at 1600 cm^{-1} in the experimental spectra. The simulated spectra attribute this band to an η_1 interaction with a surface Mo atom.

$\nu_{\perp}(O) \sim 900 - 1000\ cm^{-1}$: **On-top oxygen**

Dissociation of the CO bond is indicated in the experimental data by the disappearance of the $\nu(CO)$ band and the emergence of of a new band at $\sim 900 - 1000\ cm^{-1}$. DFT simulations attribute the latter band to surface Mo-oxo (on-top O). A band for hollow-site O is predicted to appear at $\sim 500\ cm^{-1}$.

$\nu_s(surface = CR) \sim 1300 - 1400\ cm^{-1}$: **Formation of a C=C bond**

The comparison of the experimental data and the DFT-simulated spectra reveal the novel binding of the hydrocarbon fragment to C in the surface.



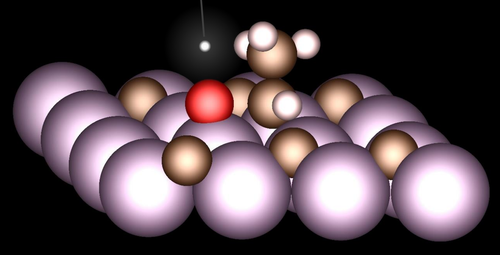
IR confirms computational predictions

and shows that the surface is carbon rich.

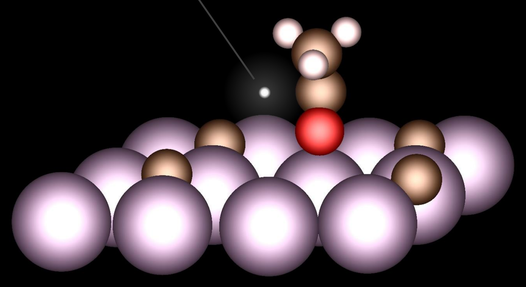
Reaction mechanism

Reactant is rearranged and places its **C=O bond horizontally** (in a η_2 configuration). The bond breaking process occurs by displacing the hydrocarbon fragment to the nearest active site.

Mo is essential: The process only takes place if there is molybdenum available.



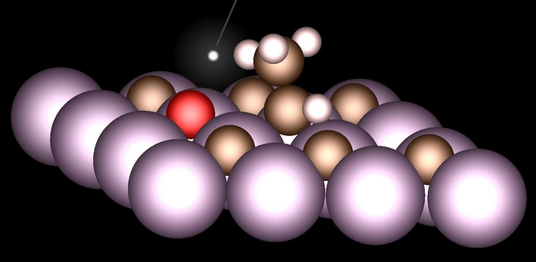
Reactant is η_1 **adsorbed on Mo.** Surface carbon prevents it from adsorbing in a hollow, which is the most stable site in non-carbided surfaces.



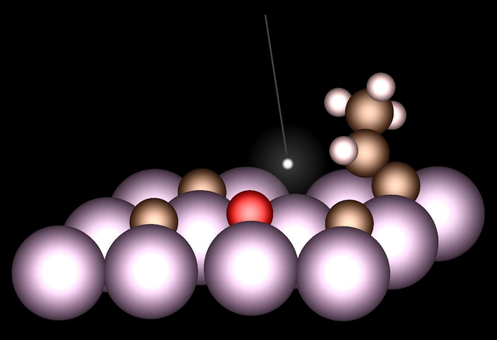
The previously **proposed mechanism** missed the **active role of surface carbon** in the adsorption of deoxygenated hydrocarbons.

Reaction products fall into the closest active adsorption sites. Local carbon coverage and arrangement determines whether these are **hollows** or η_1 **adsorbed on Mo**.

50% C coverage: The preferred local sites are **hollows**.



Deoxygenated hydrocarbon ***diffuses*** to its most stable adsorption site, and **bonds to a surface carbon**.



A carbon rich molybdenum carbide surface is catalytically active as long as it displays at least **small Mo-terminated clusters**.

References:

1. Temprano, I., Goubert, G., Behan, G., Zhang, H. & McBreen, P. H., *Catal. Sci. Technol.* **1**, 1449–1455 (2011).
2. Siaj, M., Temprano, I., Dubuc, N. & Mcbreen, P. H., *J. Organomet. Chem.* **691**, 5497–5504 (2006).
3. Siaj, M. & McBreen, P. H., *Science* **309**, 588–590 (2005).

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