

Performance and predictions of kinetic models for MgO-catalyzed ethanol conversion to 1,3-butadiene

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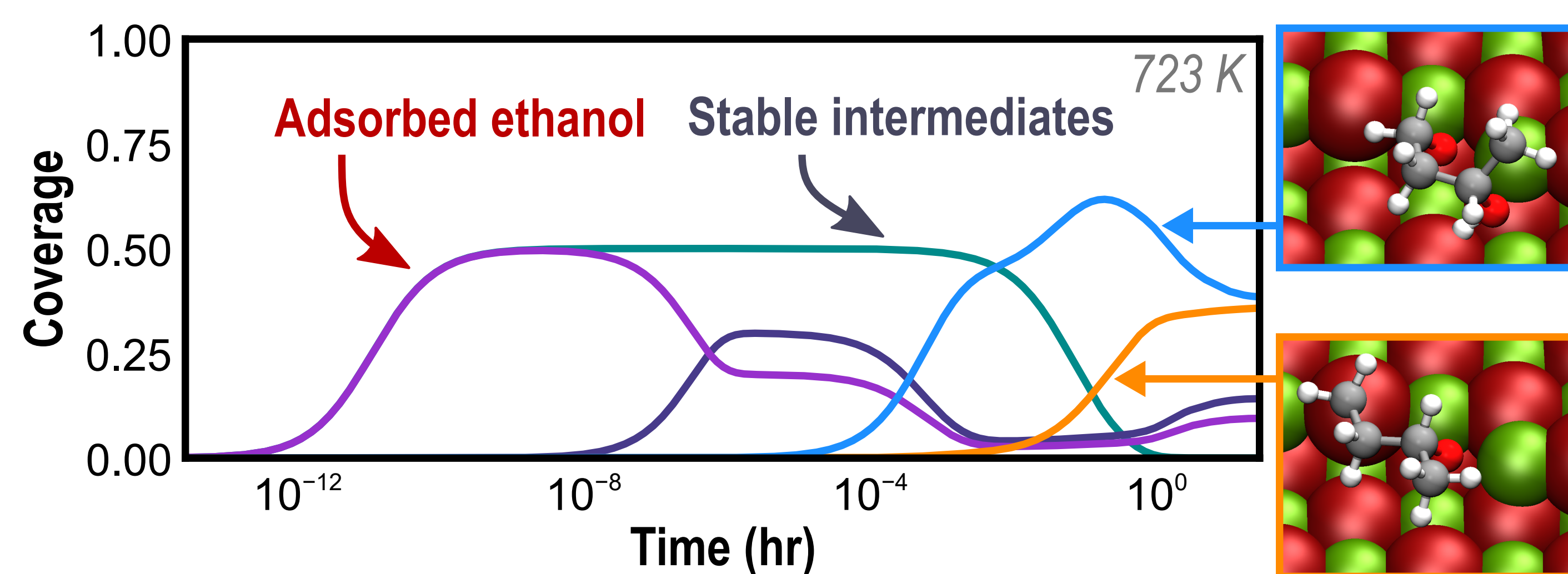
Introduction

Ethanol conversion to 1,3-butadiene is a **sustainable** route to an important organic intermediate. Challenges include low **selectivity** and **sensitivity** to both conditions and catalyst composition.

We study the kinetics on an **MgO (100) step-edge** using first-principles-informed **energy span** (ES) [1] and **microkinetic** (MK) models based on the detailed mechanism proposed by Taifan *et al.* [2]. This includes several pathways, involving **dehydrogenation** and **dehydration** of ethanol, followed by **condensation** and **MPV reduction**. DFT calculations used VASP at a PBE level of theory.

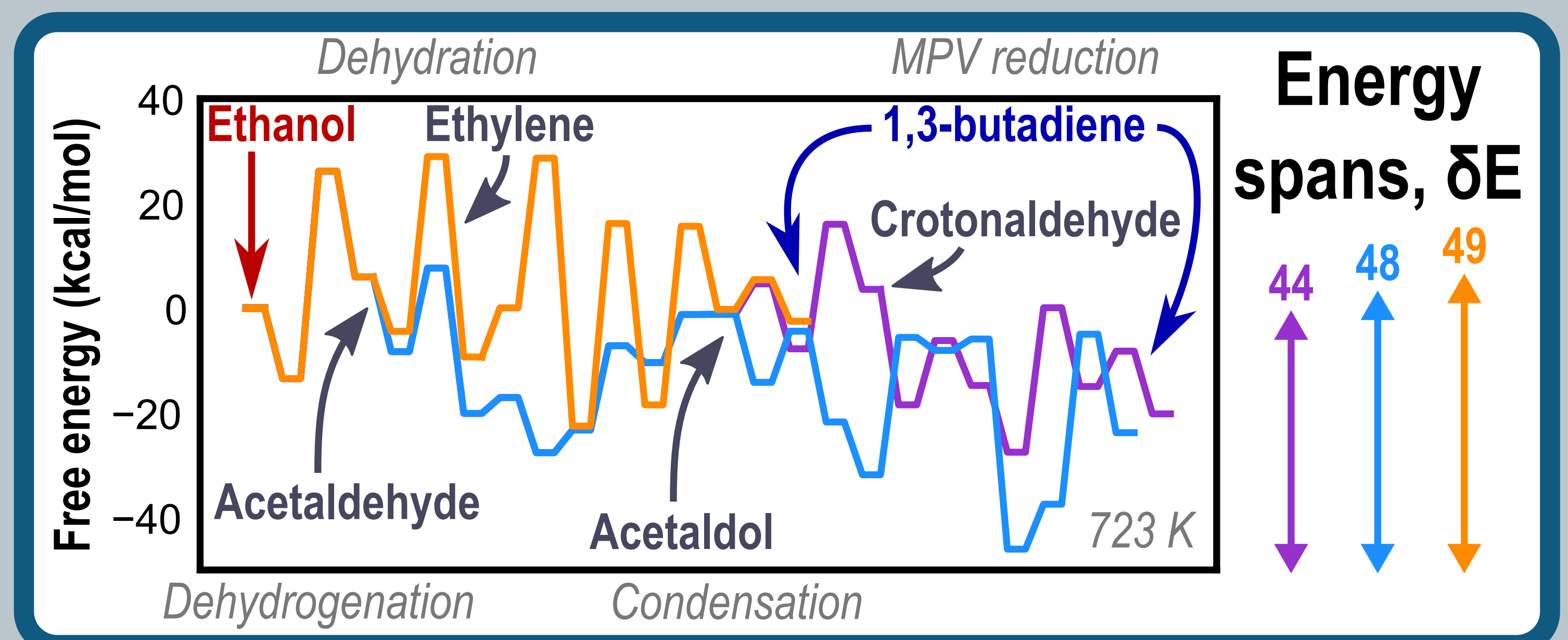
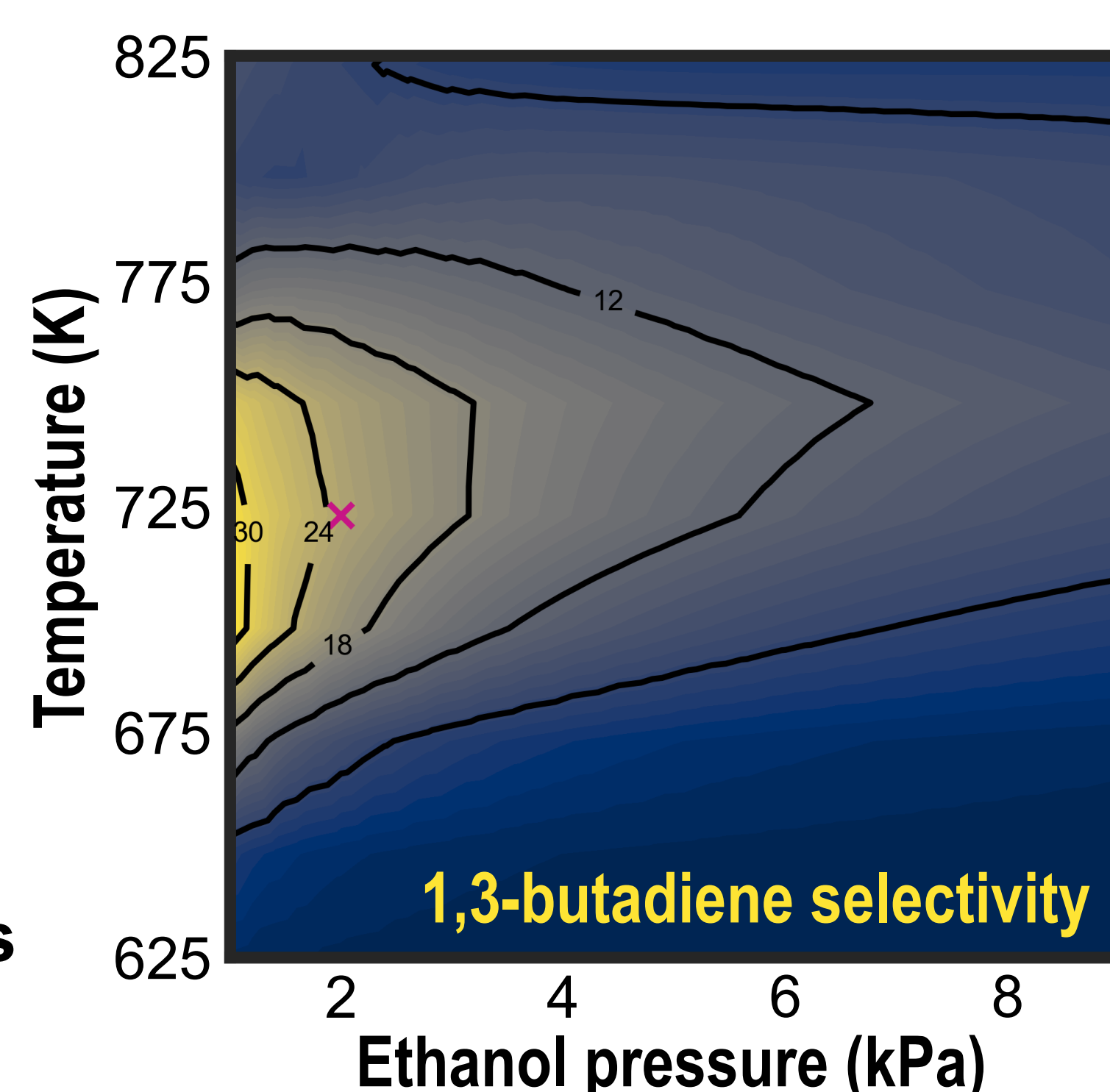
Microkinetic model

The MK model accounts for **competition** between the pathways and limited availability of reactants due to finite **surface coverage** and gas **desorption**. Several **stable intermediates** dominated the coverage, primarily adsorbed ethanol and hydrogen at early times and **two four-carbon species** in the long term.



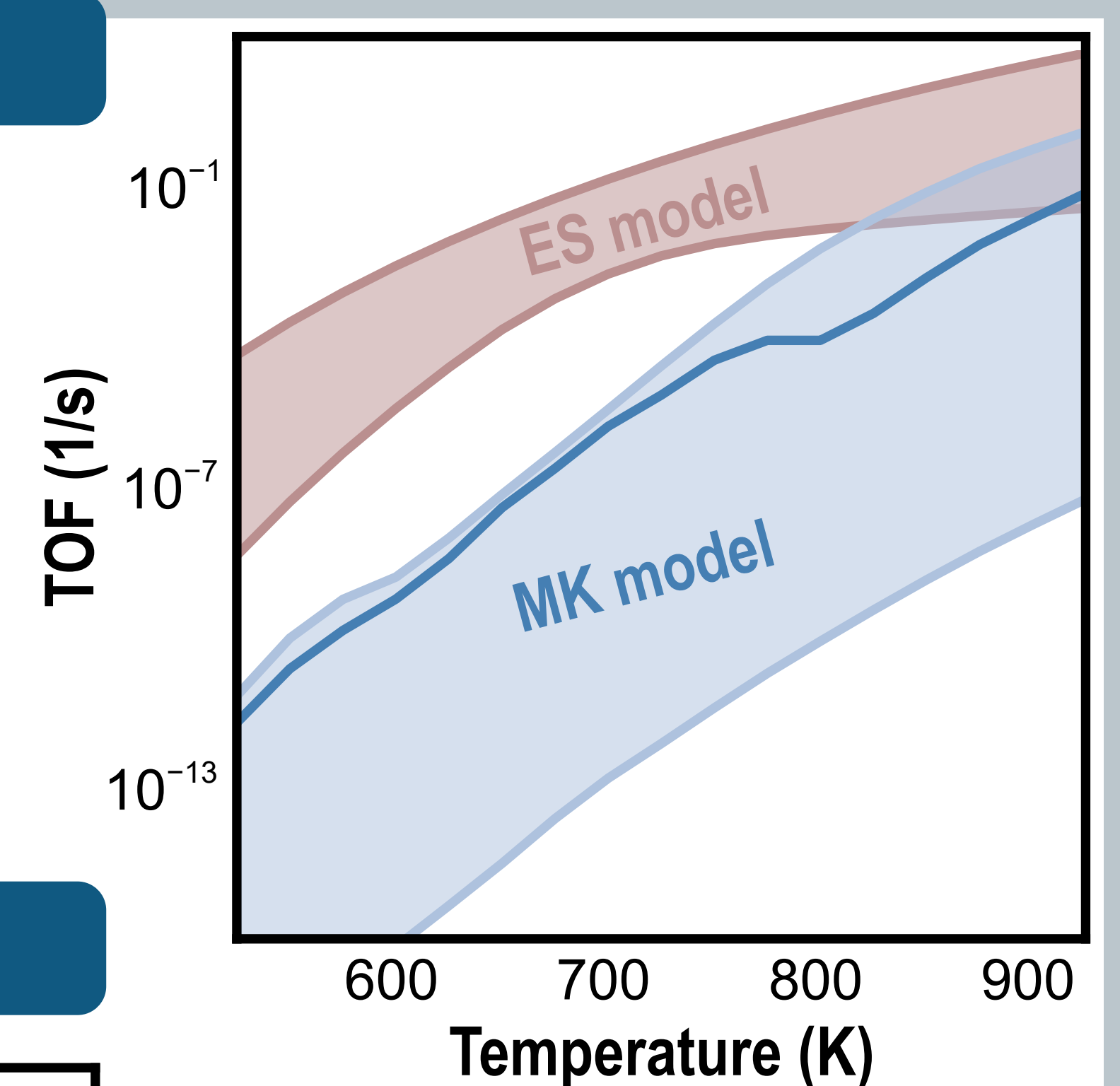
The four-carbon compounds form during competing condensation pathways, and their relative importance **changes with conditions**. Stable four-carbon species and variation of the main TOF-determining states were also predicted by the ES model. Experimental studies also report **surface poisoning** by longer hydrocarbons [3,4].

1,3-butadiene **selectivity** was found to be low, except in a narrow range of conditions. The highest selectivity was observed **near the conditions** used in experiments [4] (x).

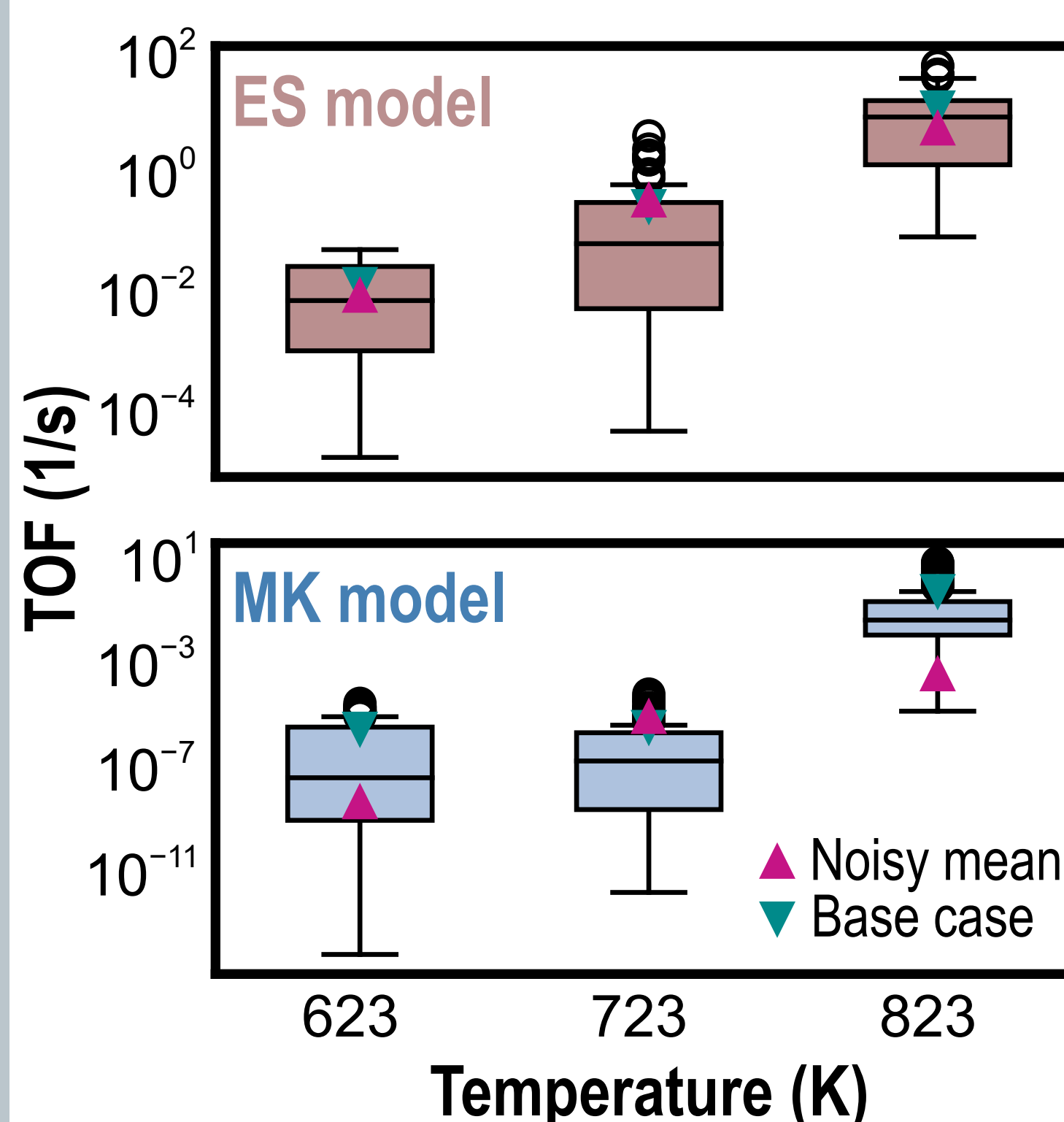


TOF predictions

The turnover frequency (TOF) predicted by the MK model is **significantly lower** than the ES TOF range over all paths due to the **competing reactions**, **gas dynamics**, and **coverage limitations**.



Model uncertainty



We **perturbed** the energy landscape using a **2 kcal/mol correlated error model**. The range of outcomes was **large**; however, the base case predictions were mostly **lower** than the corresponding **median**, and **similar trends** were observed with increasing temperature.

Conclusions

The **ES model** provides an estimate of the **maximum TOF** achievable across catalytic cycles and identifies **TOF-determining** intermediates and transition states. We further considered **competition** between pathways, **gas dynamics** and **coverage limitations** with the **MK model**. Both models provide insight into a complex chemical process. We found that perturbing the energy landscape by a **correlated noise** term can have a **large effect**, especially on the MK model.

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References:

- [1] Kozuch, S. and Shaik, S. *Accounts Chem. Res.* **44**, 101 (2010).
- [2] Taifan, W. E., *et al.* *J. Catal.* **346**, 78 (2017).
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- [4] Taifan, W. E., *et al.* *ACS Catal.* **9**, 269 (2019).

For more on this work:

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