



## Mechanistic studies in alkane oxidation

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Propane conversion over nano-structured transition metal oxide catalysts is a complex multi-step process occurring *via* several intermediates to desired and unwanted products as well as an oxygen reduction process taking place over the active catalytic site of a complex structure and involving multi-scale temporal behaviour. Although carbon oxide formation is thermodynamically favored, fundamental understanding of the kinetics through the investigation of activity and selectivity maps allows for the formation of desired products, such as acrylic acid. Insights gained *via* an understanding of the underlying reaction and transport phenomena would allow for catalyst and structured reactor design necessary for product selectivity optimization.



Over MoVTeNb oxide (M1 phase) catalysts, the partial pressure of oxygen controls activity in propane oxidation while auxiliary steam increases both activity and selectivity without changing the chemical nature of the active sites, and facilitates acrylic acid desorption.<sup>1</sup> Kube *et al.*<sup>2</sup> proposed similar reaction networks over MoVTeNb oxide and silica supported vanadium oxide catalysts and revealed, using isotope labelling, that while the abstraction of the first hydrogen atom at the methylene group of the propane molecule is rate limiting over silica-supported vanadium oxide, activation of propane over M1 involves both methyl and methylene groups simultaneously in rate-limiting processes. Sprung *et al.*<sup>3</sup> proposed four routes for product formation following transient experiments. Strong coupling between acrylic acid and carbon oxide formation was observed, such that fast rates of carbon oxide formation bridged by a slow oxidation step to the route of acrylic acid formation was proposed. Notable transition metal oxide catalysts such as  $\text{Sm}_{0.95}\text{MnO}_3$ , and  $\text{MnWO}_4$  are potential candidates for the selective oxidation of light alkanes. However, their reaction networks and pathways are not firmly established.

Mechanistic studies are carried out over these nano-structured transition metal oxide catalysts under stoichiometric, oxidizing and reducing conditions. These studies involve steady-state and transient kinetic experiments (SSITKA, isotope labelling, temperature programmed methods, step and pulse response, and kinetic modelling investigations. The reaction pathways involving intermediates such as allyl alcohol and propionic acid, hitherto not studied, are investigated. These mechanistic studies are conducted to propose and compare reaction networks, determine kinetically significant steps and extent of surface coverage, observe most abundant reaction intermediate (MARI) and the rate determining step, and develop a global rate formalism that could be used to predict activity and desired product selectivity outside laboratory conditions.

### References

- <sup>1</sup>R. Naumann D'Alnoncourt, L.I. Csepei, M. Hävecker, F. Girgsdies, M.E. Schuster, R. Schlögl, and A. Trunschke, *Journal of Catalysis*, **2014**, *311*, 369-385.
- <sup>2</sup>P. Kube, B. Frank, R. Schlögl, and A. Trunschke, *ChemCatChem*, **2017**, *9*, 3446-3455.
- <sup>3</sup>C. Sprung, G.S. Yablonsky, R. Schlögl, and A. Trunschke, *Catalysts*, **2018**, *8*, 330.