

Supporting Information

Isotope studies in oxidation of propane over vanadium oxide

Pierre Kube,^[a] Benjamin Frank,^[a] Robert Schlögl,^[a] and Annette Trunschke^{*[a]}

Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin (Germany),
E-mail: trunschke@fhi-berlin.mpg.de

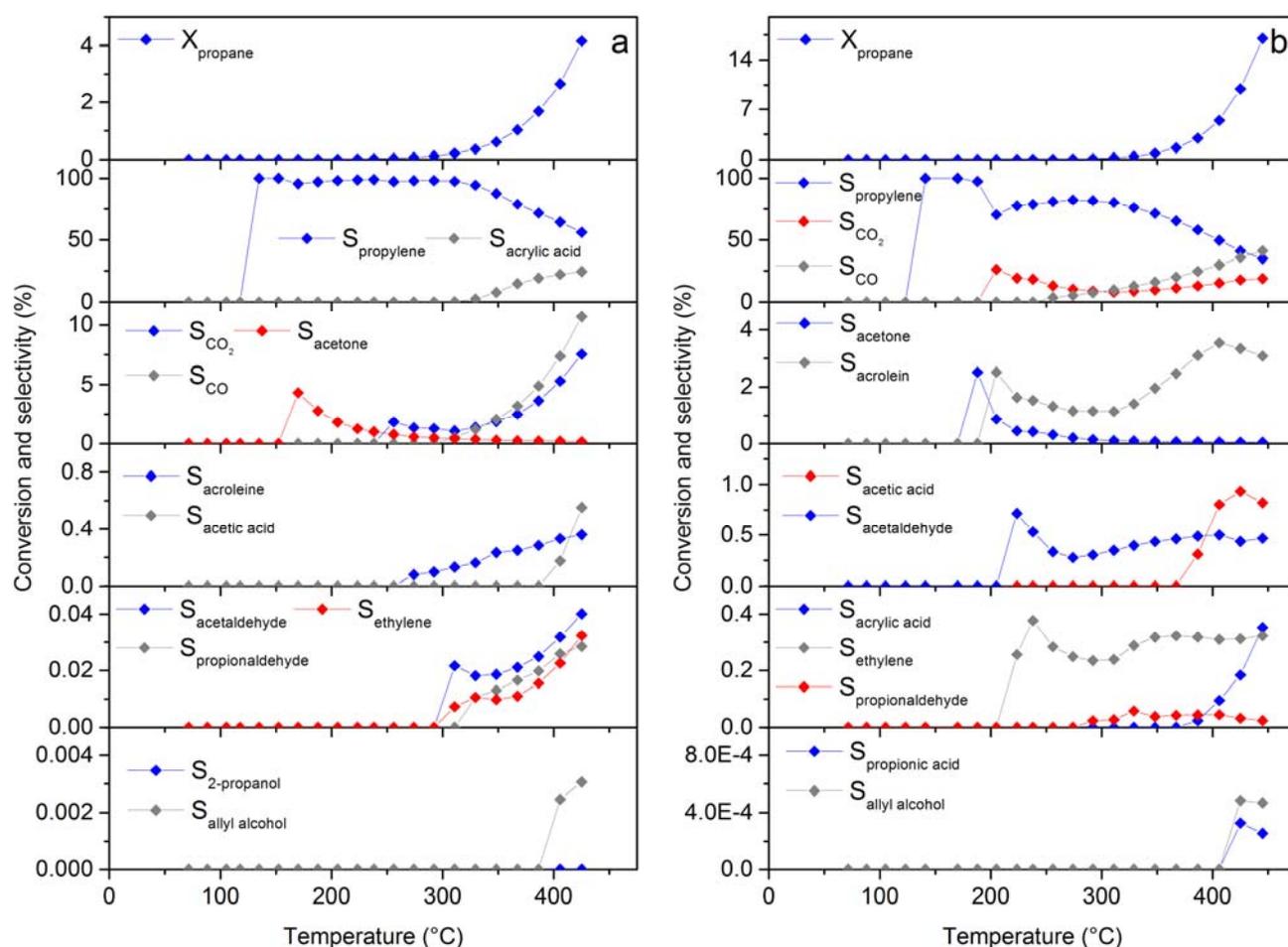
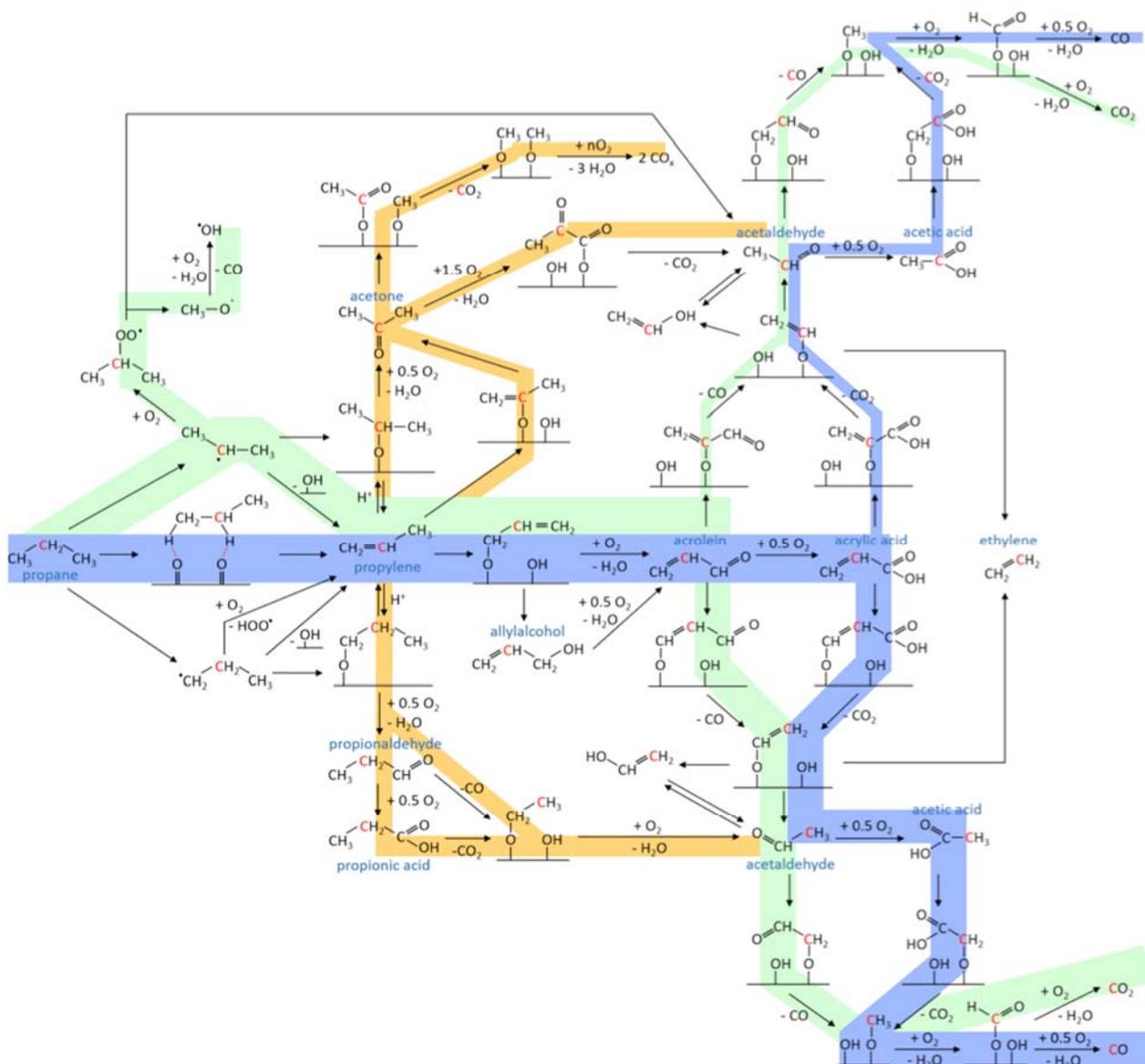


Figure S1. Selectivity of reaction products as a function of temperature for the temperature-programmed oxidation of propane (heating rate 1K/min, measurement isothermal every 20 K) over a) M1 ($C_3H_8/O_2/He = 10/5/85$, $W/F = 0.06 \text{ g s ml}^{-1}$, $m_{\text{cat}} = 10 \text{ mg}$, $F_{\text{total}} = 10 \text{ ml min}^{-1}$), and b) 6V/SBA-15 ($C_3H_8/O_2/He = 10/5/85$, $W/F = 1.33 \text{ g s ml}^{-1}$, $m_{\text{cat}} = 222 \text{ mg}$, $F_{\text{total}} = 10 \text{ ml min}^{-1}$).



Scheme S1. Coloured version of Scheme 3 presented in the main text that highlights the major principal agreements and differences in the reaction networks over 6V/SBA-15 (green path), and M1 (blue path); The pathways highlighted in orange occur on both catalysts in a similar way.

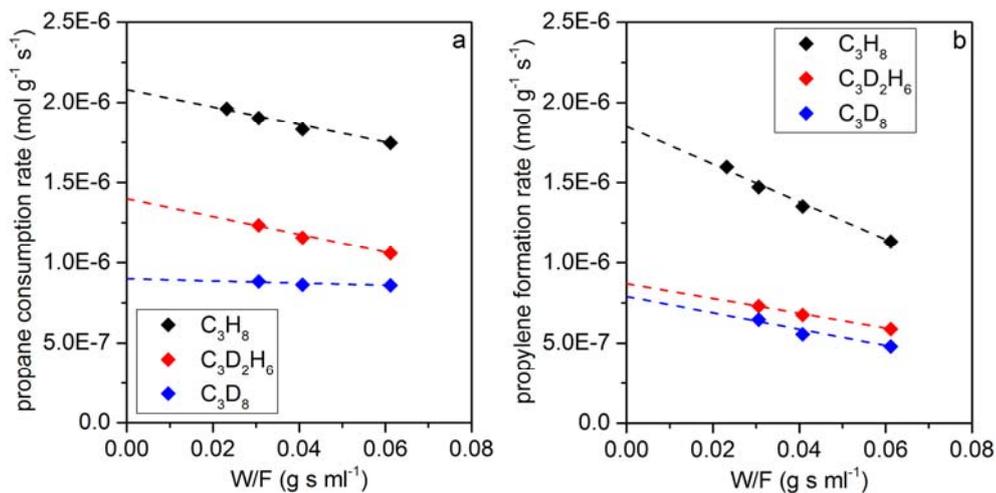


Figure S2. Propane consumption rates (a) and propylene formation rates (b) as function of W/F (0.02-0.06 g s ml⁻¹) for M1 in the feed C₃H₈/O₂/He = 10/5/85 at T=400°C for different isotopes.

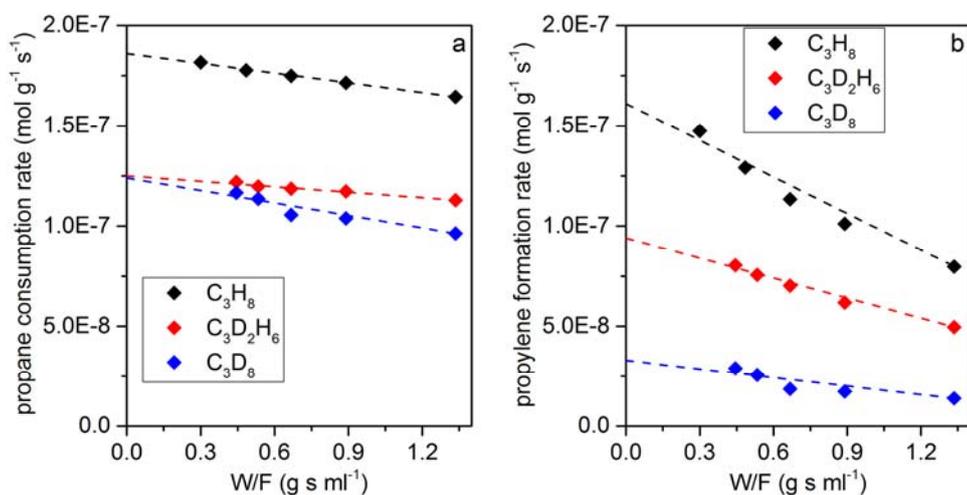
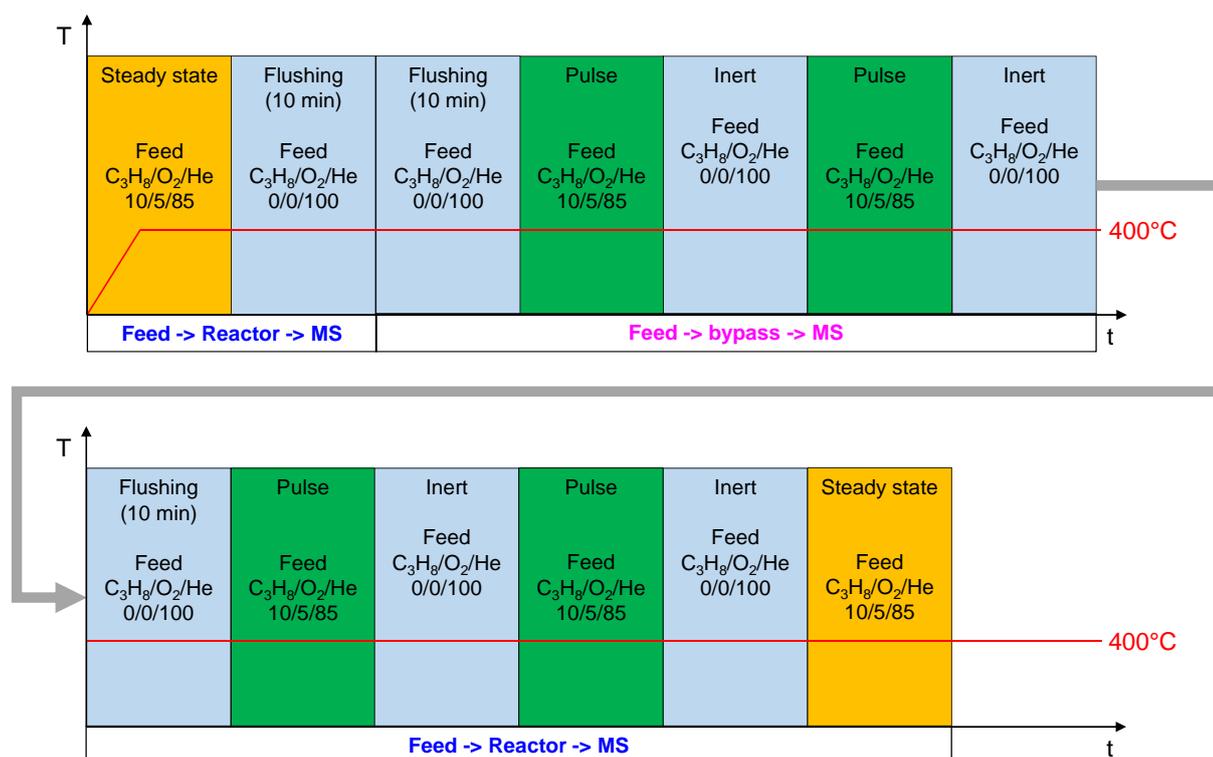


Figure S3. Propane consumption rates (a) and propylene formation rates (b) as function of W/F (0.30-1.34 g s ml⁻¹) for 6V/SBA-15 in the feed C₃H₈/O₂/He = 10/5/85 at T=400°C for different isotopes.



Scheme S2. Schematic illustration of ^{13}C -labelled/unlabelled propane pulse sequence.

The catalysts ($\text{W/F} = 0.06 \text{ g s ml}^{-1}$ for M1 or 1.34 g s ml^{-1} for 6V/SBA-15) were heated to 400°C (heating rate of 2°C min^{-1}) in a feed of 10 % propane, 5 % oxygen, and 85 % helium and kept at this temperature and contact time for the entire pulse experiment. After 24 hours at steady state, the reactor was flushed with helium for 10 minutes and switched to bypass mode followed by flushing for 10 minutes with helium. 1 ml of a gas mixture, containing 10% propane, 5% oxygen 85% helium, was injected into the helium flow to determine the blank values of the setup. The system was then flushed for 1 min with helium. The injection of 1 ml gas mixture followed by flushing with helium was performed twice in bypass mode. Afterwards the setup was switched back to reactor mode and flushed for 10 minutes with helium. The injection of 1 ml of the same gas mixture followed by flushing with helium was performed twice in reactor mode on the catalyst. The effluent gas both in bypass and reactor mode were separated into permanent gases and hydrocarbons by a self-packed Porapak Q column. For preparation of the column, a stainless steel tube (1/8" outer diameter, 2 mm inner diameter, 20 cm long) was filled with Porapak Q material (Supelco, particle size 125 to 150 μm). The composition of the separated fractions was analysed with a QMA-400 mass spectrometer. Propane conversion and product selectivity were calculated based on calibration factors obtained by injection of 1ml of different test gases (1% CO , 1% CO_2 , 1% O_2 , 47% Ar and balance N_2 ; 1% propane, 1% propylene and balance N_2). After each pulse experiment, the catalysts were fed with a mixture of 10 % propane, 5 % oxygen, and 85 % helium to check if the steady state has changed. The pulse experiment was repeated with an injection gas mixture, containing 5% propane, 5% oxygen and balance helium and a steady state feed of 10 % propane, 5 % oxygen, and 85 % helium.

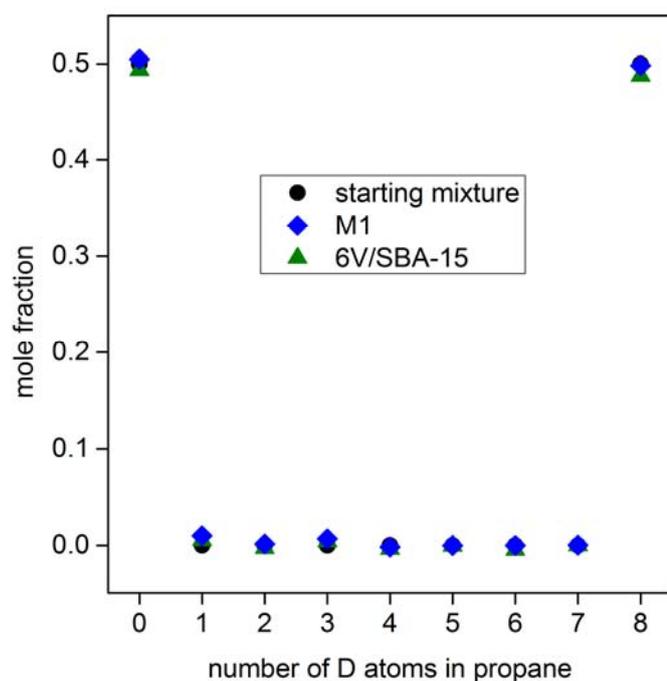


Figure S4. Deuterium distribution in propane during the reaction of $C_3H_8/C_3D_8/O_2/He$ over 6V/SBA-15 and M1 and for bypass measurement at $400^\circ C$, $W/F = 1.34 \text{ g s ml}^{-1}$ (6V/SBA-15) and 0.06 g s ml^{-1} (M1) and feed $C_3H_8/C_3D_8/O_2/He = 5/5/5/85$.

A test for H/D exchange of propane with the catalyst surface, which is also a test for reversibility of the C-H bond breaking, was performed to find out if H/D exchange plays a role during KIE experiments. A feed containing $C_3H_8/C_3D_8/O_2/He$ was pulsed over the catalyst and the product gas was measured by mass spectrometry to find a significant evidence for partial deuterated propane as product of H/D exchange. The results are summarized in Fig. S4 and show for both catalysts under the applied reaction conditions no significant H/D exchange of the reactant molecule, meaning that the mole fraction of partial deuterated propane is practically zero. These results also suggest that isotopic scrambling of H and D in partial deuterated propane plays no role.