

Supporting Information: Catalysis Science & Technology

High performance $(\text{VO}_x)_n\text{-(TiO}_x)_n/\text{SBA-15}$ Catalyst for the Oxidative Dehydrogenation of Propane - Lessons Learnt in Fundamental Research.

Carlos Carrero, Markus Kauer, Arne Dinse, Till Wolfram, Neil Hamilton, Annette Trunschke, Robert Schlögl, and Reinhard Schomäcker.

Selectivity for undesired products

CO

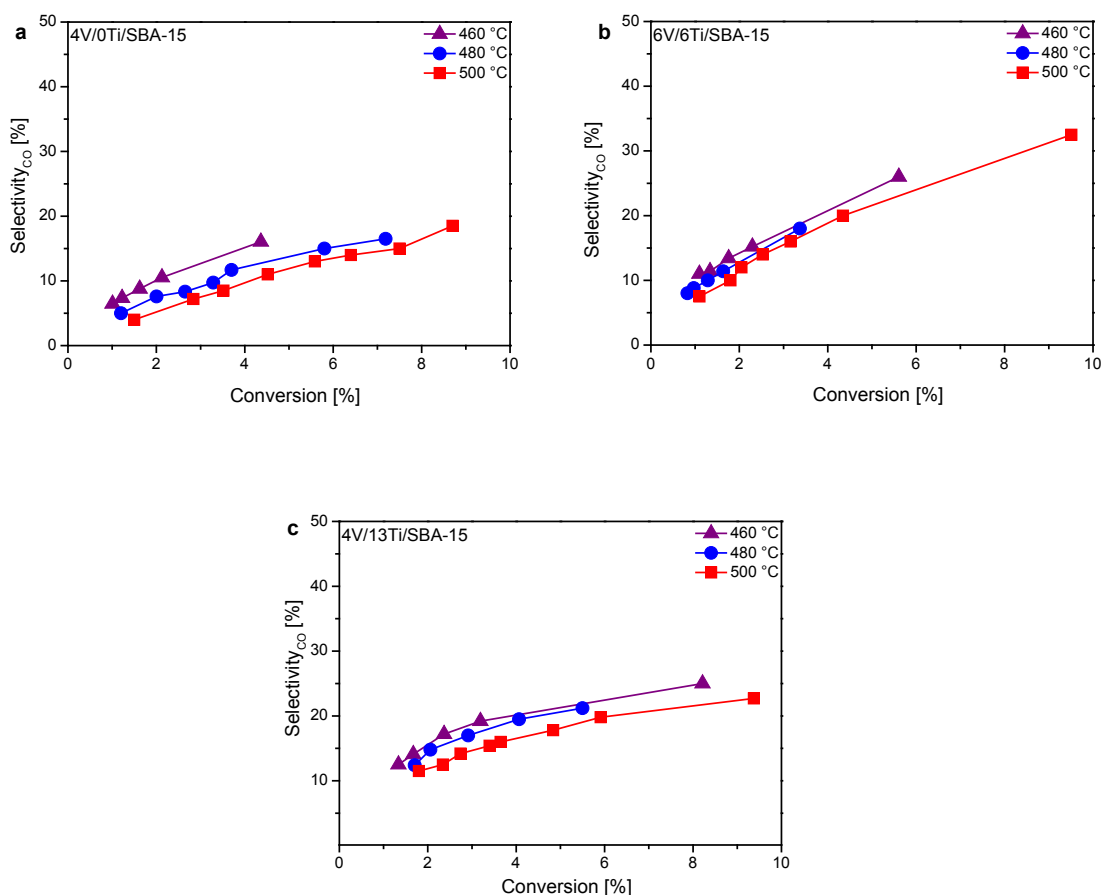


Figure S1. CO selectivity as a function of propane conversion at different temperatures for (a) 4V/0Ti/SBA-15 (b) 6V/6Ti/SBA-15 (c) 4V/13Ti/SBA15 . Catalyst mass: 2 – 150 mg, total flow rates: 120 – 20 ml*min⁻¹, and C₃H₈:O₂=2.

CO₂

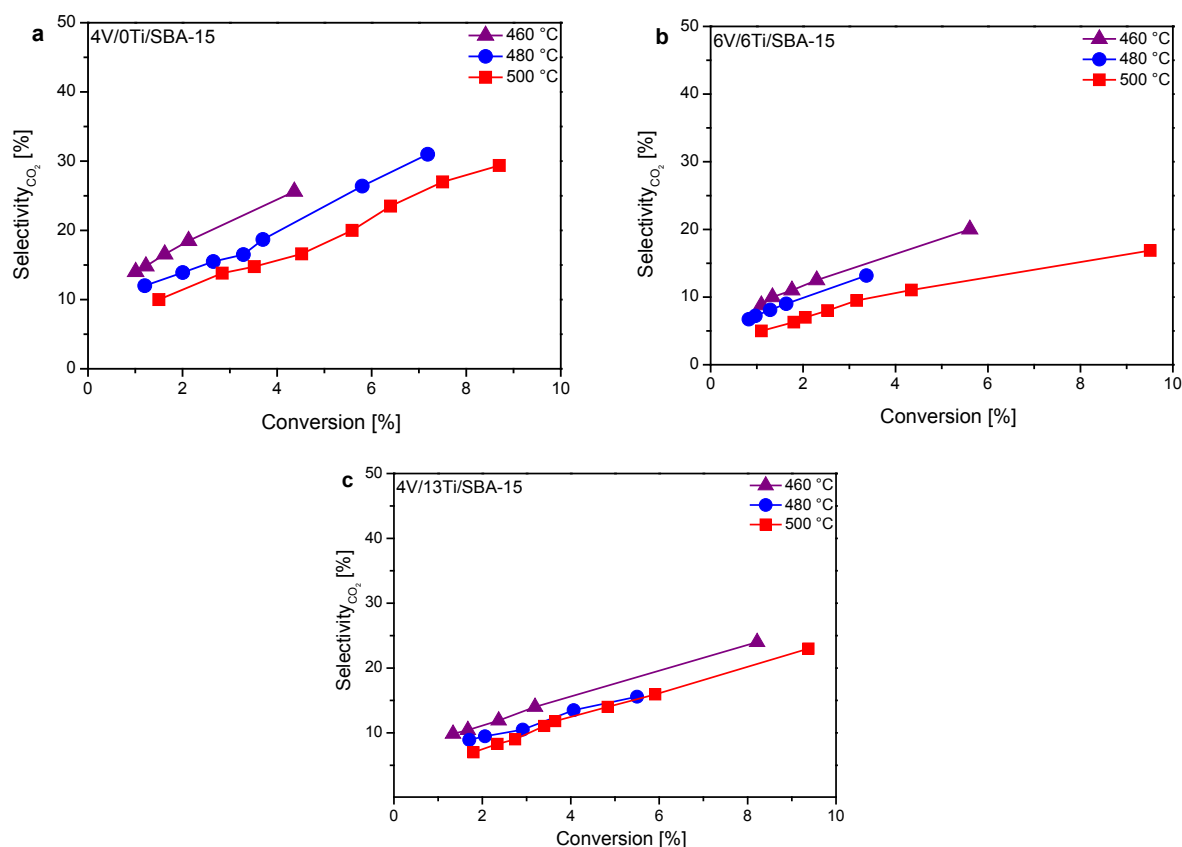


Figure S2. CO₂ selectivity as a function of propane conversion at different temperatures for (a) 4V/0Ti/SBA-15 (b) 6V/6Ti/SBA-15 (c) 4V/13Ti/SBA-15. Catalyst mass: 2 – 150 mg, total flow rates: 120 – 20 ml*min⁻¹, and C₃H₈:O₂=2.

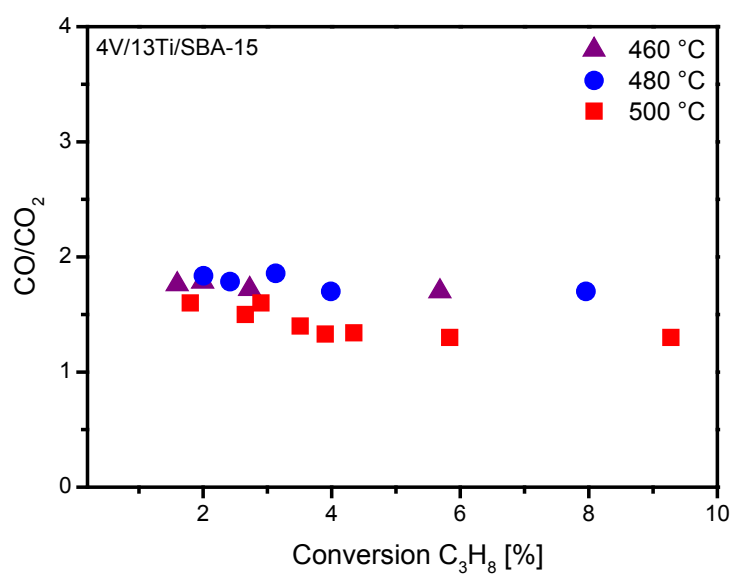


Figure S3. Molar ratio of CO to CO₂ at three different temperatures for 4V/13Ti/SBA-15 catalyst.

Kinetic Investigations

Experimental runs were carried out at temperatures between 673 and 773 K using u-shaped fixed bed quartz reactors (i.d. 6 mm) at atmospheric pressure. For the measurements, catalyst sample amounts between 200 - 900 mg were portioned to the reactor. Using synthetic air as oxygen source, propane and oxygen were fed in the ratio 1:1 ($C_3H_8/O_2/N_2 = 16.9/16.9/67.5$), 2:1 ($C_3H_8/O_2/N_2 = 29.1/14.5/56.4$) and 4:1 ($C_3H_8/O_2/N_2 = 45/11.3/45$) with a gas hourly space velocity (GHSV) of $6.6 \cdot 10^2 - 6.6 \cdot 10^3 \text{ h}^{-1}$. For initial rate determination the propane conversion was kept below 10 %, which enables isothermal and differential conditions. Mass transfer limitations were avoided by working with particle sizes of 200 to 300 μm . This is described in more details elsewhere [B. Frank et. al. Appl. Catal. 323 (2007) 66]. In addition, to check for diffusional limitations the Weisz modulus Ψ' considering propane as the limiting reactant was estimated. The Weisz modulus describes the ratio of reaction rate to reactant diffusion rate and is defined by eq. 1

$$\Psi' = L^2 \cdot \frac{m+1}{2} \cdot \frac{r_{\text{eff}} \cdot \rho_{\text{cat}}}{D_{\text{eff}, C_3H_8} \cdot c_{C_3H_8}} \quad (1)$$

L	: Characteristic length of catalyst particle	= 10^{-4} m
m	: Reaction order of propane	= 1
r_{eff}	: Measured reaction rate	= $6 \times 10^{-3} \text{ mol s}^{-1} \text{ kg}^{-1}$
ρ	: Catalyst density	= $2 \times 10^3 \text{ kg m}^{-3}$
D_{eff}	: Effective diffusivity	= $10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$
c	: Concentration	= 8 mol m^{-3}

With an effective rate of $6 \times 10^{-3} \text{ mol s}^{-1} \text{ kg}^{-1}$ estimated for 500 °C, 10 % propane conversion and the data given above a Weisz modulus of 0.15 is calculated indicating that the reaction proceeds much slower than the propane diffusion and no mass transfer limitation needs to be considered at 500 °C or lower temperatures.

Concentrations of the individual components were calculated from a GC analysis of the product gas and expressed in mol m^{-3} .

Parameter determination

Propane conversion X and propene selectivity S as functions of the respective concentration c_i were calculated from eqs. (2) and (3)

$$X = 1 - \frac{c_{C_3H_8}}{c_{C_3H_8,0}} \quad (2)$$

$$S = \frac{c_{C_3H_6}}{c_{C_3H_8,0} - c_{C_3H_8}} \quad (3)$$

Initial reaction rates at low propane conversions were calculated according to eq. 4

$$r_0 = c_{0,C_3H_8} \cdot \frac{dX}{d\tau} \quad (4)$$

with

r_0 being the initial reaction rate, c_0 the respective initial reactant concentration and τ the modified residence time calculated from catalyst mass and gas flow rate m_{cat}/F . The material balances for the stable reactants and products in the applied tube reactor is given by

$$dc_{C_3H_8}/d\tau = -r_1 \quad (5)$$

$$dc_{C_3H_6}/d\tau = r_1 - r_2 \quad (6)$$

$$dc_{CO_2}/d\tau = 3r_2 \quad (7)$$

$$(8) \quad dc_{O_2}/d\tau = 0.5r_1 - 3.5r_2$$

Rate expressions for ODH and consecutive propene combustion r_1 and r_2 , respectively, are:

$$r_1 = k_{\infty,1} \exp(-E_{A1}/RT) C_{C_3H_8}^{m_1} C_{O_2}^{m_2} \quad (9)$$

$$r_2 = k_{\infty,2} \exp(-E_{A2}/RT) C_{C_3H_6}^{m_3} C_{O_2}^{m_4} \quad (10)$$

The rate constants $k_{1,eff}$ and $k_{2,eff}$ are effective rate constants combining the rate constants of the reaction (A) and (C) (see ODP reaction network in page 6) with the binding constant of

the substrates and the catalyst concentration. Numerical integration for data evaluation was done by using “Presto Kinetics” Version 4.0 which uses the least square method for fitting.

Estimation of reaction orders

Reactions rates were determined from conversions of less than 10% in order to assure differential conditions with the reactor. The partial pressures of oxygen and propane were varied at a constant partial pressure of the other reactant by adjusting to partial pressure of the inert gas N_2 . From a plot of the logarithmic rates at initial feed composition against the $\log c_{\text{reactants}}$ the reaction orders were estimated and used as starting values for the fitting procedures described below.

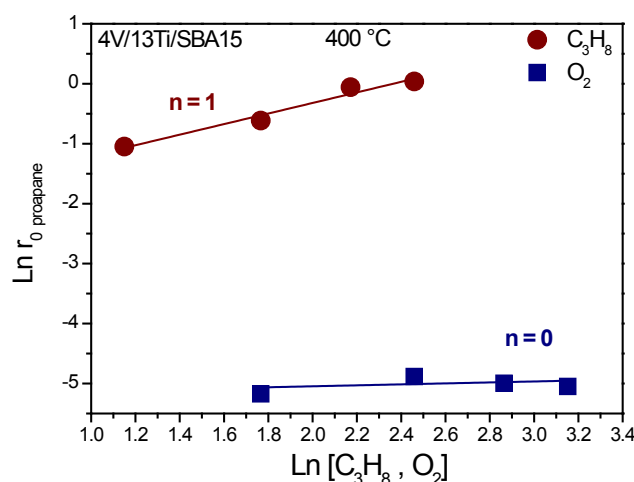


Figure S4. Determination of reaction orders for oxygen and propane in the dehydrogenation step at 400°C.

Determination of kinetic parameters

For the determination of the kinetic parameters the oxidative dehydrogenation was carried out at six different temperatures, six different residence times and eight different feed compositions. Two different strategies were applied for parameter fitting. First single dependencies were studied in order to determine the reaction order for the composition variation and the rate constants for individual temperatures from the residence time variation. The apparent activation energies were subsequently calculated from an Arrhenius plot. Finally a multi parameter fit for all parameters, namely reaction orders, apparent activation energies

and pre-exponential factors was performed fitting all data sets simultaneously using the previously determined parameters as starting values.

The formation of both by-products is lumped in reaction rate law 2 because both products are formed simultaneously during the catalytic total oxidation of propene, as seen in experiments with propene as feed, see Figure S3. This mechanism and the almost constant ratio of the two products do not allow a further resolution of the kinetic model without monitoring further intermediates of this combustion reaction. The weak increase in CO/CO₂ ratio is most likely caused by the depletion of oxygen.

The total oxidation of propane contributes less than 8% to the conversion of propane in the absence of propene. As soon propene is produced its higher reactivity will compete with the propane for the oxygen and will further reduce the fraction of propane that is directly oxidized to CO_x. The introduction of this minor contribution into the evaluation of the kinetic data causes large errors on all kinetic parameters, due to the insignificant contribution of this reaction.

The obtained parameter were validated on the basis of the "Condition" of the mathematical problem. This is an automatic subroutine of the tool "Presto Kinetes" applied for the data analysis. The condition of the problem is a reference number for assessment of the actual parameter estimation's run. The higher the condition the worse-posed is the problem, leading automatically to problems for the algorithm. The condition's optimal value is close to one. Mathematically the condition is defined as the ratio of the biggest to the smallest Eigenvalue of the Fisher matrix. If one or several of the Eigenvalues are much smaller than the biggest Eigenvalue this indicates arbitrary insensitivity of the corresponding parameters. This phenomenon may find its cause in dependencies between parameters and/or insufficient experimental values. If the condition goes up to values larger than 1000 (red bitmap) the selected coefficients should be checked. It is recommended to discard the coefficient with the highest index and perform the analysis again.