

Selective Oxidation of Methanol to Green Oxygenates - Influence of Calcination Temperature on a VO_x/TiO_2 Catalyst

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Supplementary Information

1 Adsorption Isotherms

In Fig. S1 the nitrogen sorption isotherms are shown, which provide the basis for the determination of the specific surface area according to the method of Brunauer, Emmett and Teller (BET) [1] and the pore size distribution according to the method of Barrett, Joyner and Halenda (BJH) [1], which are discussed in the main manuscript.

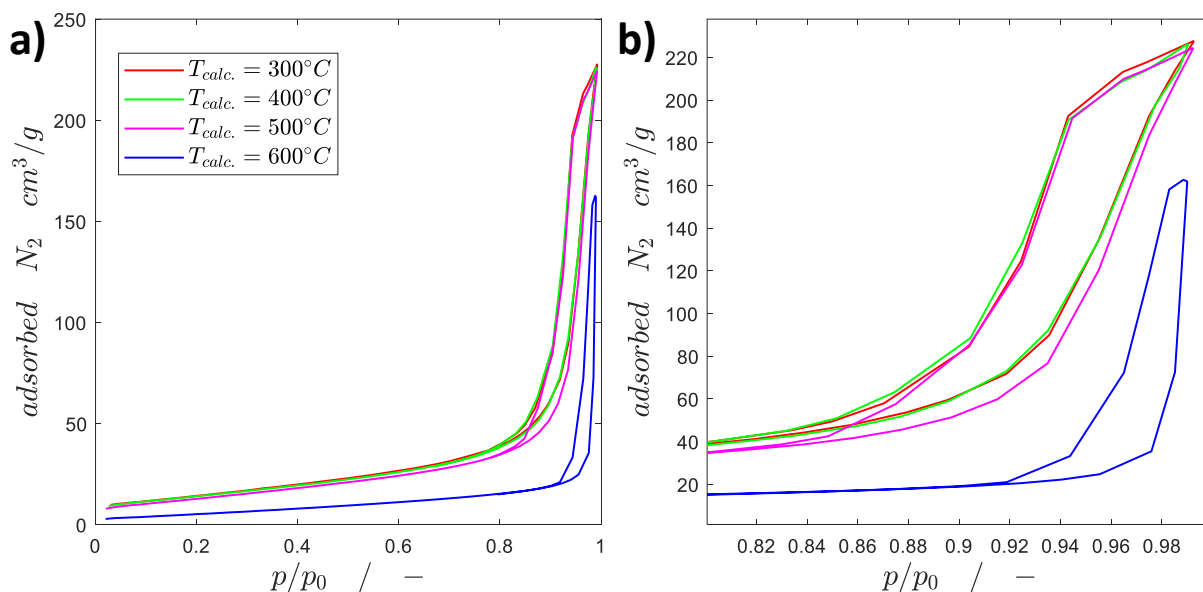


Figure S1: Nitrogen adsorption-desorption isotherms a) original data, b) zoom; $T=77\text{ K}$

The measured sorption isotherms can be classified as Type IV(a), which is characteristic of mesoporous materials with pore diameters larger than 4 nm. No pronounced increase in adsorbed volume at low relative pressures was observed. All samples exhibit an H_2 -type hysteresis loop, reflecting a dominant fraction of mesopores with a relatively narrow size distribution. For the VO_x/TiO_2 -600 sample, the

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hysteresis loop shifts from $p/p_0 \approx 0.80$ to $p/p_0 \approx 0.92$, which can be attributed to a pore size shift caused by sintering. In addition, the isotherm is shifted downward due to the loss of micro- and small mesopores and a resulting decrease in total surface area [1].

2 UV-Vis

Fig. S2 shows the UV-Vis spectra of the catalysts (a), the supports (b) and the difference spectra (c). The catalysts and supports were calcined at the same temperature to ensure comparability. The scale of the subfigures is equal.

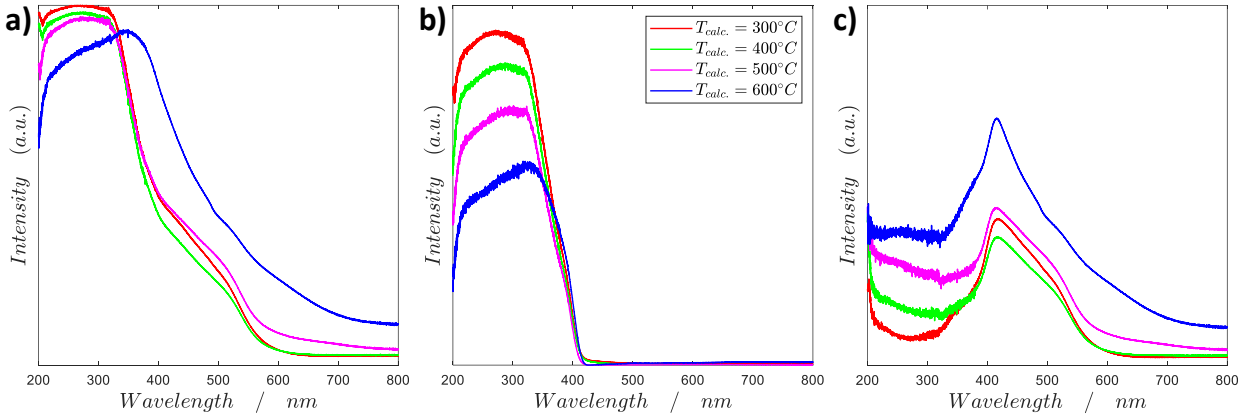


Figure S2: UV-Vis spectra of a) VO_x/TiO_2 catalysts, b) TiO_2 support and c) difference between VO_x/TiO_2 catalysts and TiO_2 catalysts support

The spectra of the TiO_2 support calcined at different temperatures show a pronounced decrease in band intensity between 200–400 nm with increasing calcination temperature, which can be attributed to particle growth and the formation of a rutile phase [2]. Additionally, a red shift is observed for the VO_x/TiO_2 -600 catalyst, consistent with the increase in particle size [3].

Fig. S3 shows the deconvolution of the UV-Vis spectra.

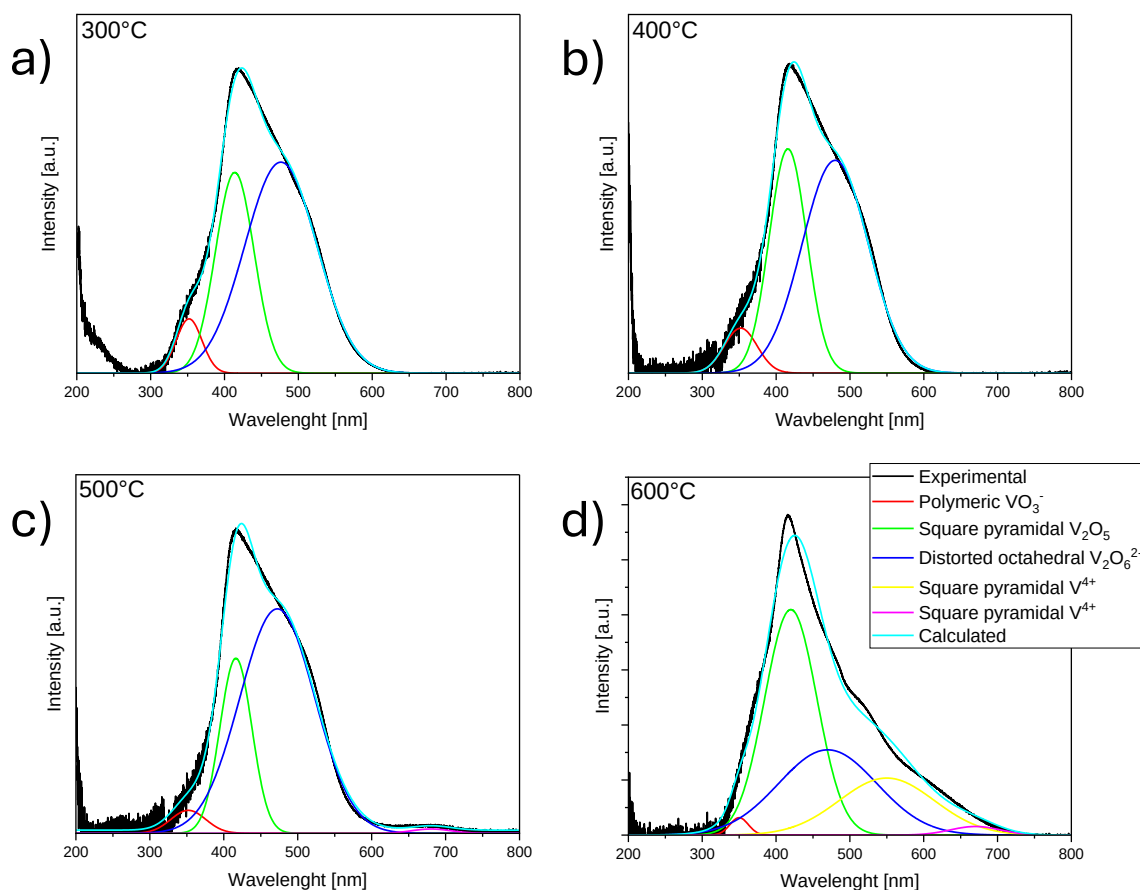


Figure S3: Deconvolution of UV-Vis spectra of the 4.6 wt.-% VO_x/TiO_2 catalysts calcined at a) 300 °C; b) 400 °C; c) 500 °C; d) 600 °C. Bands have been assigned according to [4,5]

3 Activity Tests

In Fig. S3a the yield of FA is given. A similar trend of VO_x/TiO_2 -300, VO_x/TiO_2 -400, and VO_x/TiO_2 -500 is observed, with a maximum at 160 °C. No FA is detected between 130 and 160 °C with the VO_x/TiO_2 -600 catalyst. Between 170 and 190 °C the yield of FA increases linearly with temperature. The yield of FA is constant between 190 and 200 °C at 35%. Fig. S3b depicts the yield of FAc. Similar trends of VO_x/TiO_2 -300, VO_x/TiO_2 -400, and VO_x/TiO_2 -500 are observed with a maximum of 14% at 160 °C, following the maximum of FA. For VO_x/TiO_2 -600, FAc is only detected at 200 °C. The yield is 10%. VO_x/TiO_2 -300, VO_x/TiO_2 -400, and VO_x/TiO_2 -500 form CO between 160 and 200 °C (Fig. S3c). The trends of VO_x/TiO_2 -300 and VO_x/TiO_2 -400 are similar, with an increasing yield of CO with increasing temperature, with 86% at 200 °C. The yield of CO of VO_x/TiO_2 -500 increases exponentially between 160 and 190 °C and remains constant at 46% between 190 and 200 °C. VO_x/TiO_2 -600 forms a small amount of CO between 180 and 200 °C with an exponential increase up to 8% at 200 °C.

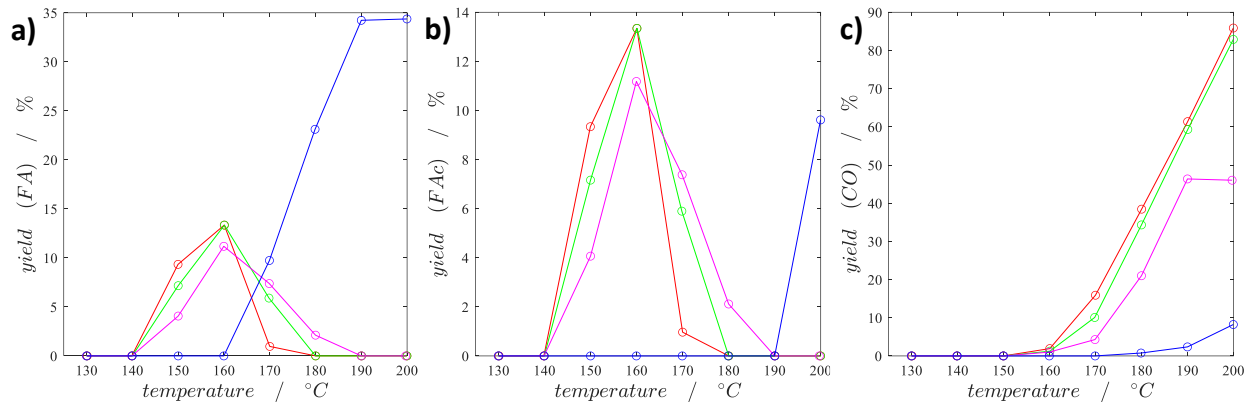


Figure S4: Influence of calcination temperature of the catalyst on a) yield of FA, b) yield of Fac, and c) yield of CO; $WHSV = 1000 \text{ kg} \cdot \text{s} \cdot \text{m}^{-3}$; $x_{MeOH}^{in}/x_{O_2}^{in}=1$

4 Calculations

The conversion and yield are calculated as follows:

$$X_{MeOH} = \frac{\dot{n}_{MeOH}^{in} - \dot{n}_{MeOH}(z=L)}{\dot{n}_{MeOH}^{in}}; Y_i = \frac{\dot{n}_i(z=L)}{\dot{n}_{MeOH}^{in}} \cdot \frac{|v_{MeOH,j}|}{v_{i,j}}, \text{ with} \quad (1)$$

the molar flow rate at the inlet of the reactor $\dot{n}_i^{in}$, the molar flow rate at the outlet of the reactor $\dot{n}_i(z=L)$ and the stoichiometric coefficient of component i in reaction j $v_{i,j}$.

References

- [1] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure and Applied Chemistry 87 (2015) 1051–1069.
- [2] J.M. Won, M.S. Kim, S.C. Hong, Effect of vanadium surface density and structure in VOx/TiO2 on selective catalytic reduction by NH3, Korean J. Chem. Eng. 35 (2018) 2365–2378.
- [3] C. Retamoso, N. Escalona, M. González, L. Barrientos, P. Allende-González, S. Stancovich, R. Serpell, J. Fierro, M. Lopez, Effect of particle size on the photocatalytic activity of modified rutile sand (TiO2) for the discoloration of methylene blue in water, Journal of Photochemistry and Photobiology A: Chemistry 378 (2019) 136–141.
- [4] R. Bulánek, L. Čapek, M. Setnička, P. Čičmanec, DR UV–vis Study of the Supported Vanadium Oxide Catalysts, J. Phys. Chem. C 115 (2011) 12430–12438.
- [5] U. Scharf, M. Schraml-Marth, A. Wokaun, A. Baiker, Comparison of grafted vanadia species on ZrO2, TiO2, SiO2 and TiO2/SiO2 mixed oxides, Faraday Trans. 87 (1991) 3299.