Tailoring Macropores in Titania Monoliths for Optimized Flow-Through Properties

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Introduction

Titanium dioxide (TiO_2) monoliths with a hierarchical pore structure are very suitable for separation and catalysis applications:

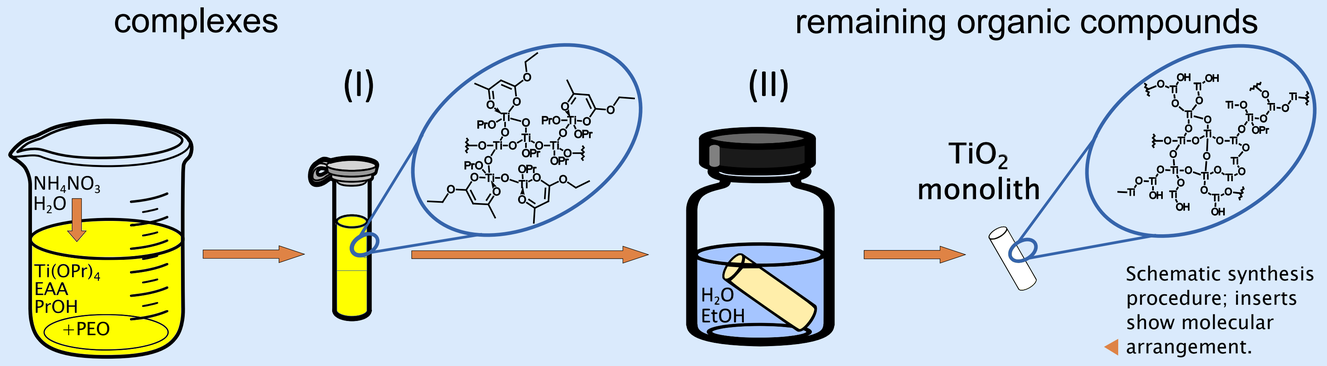
- ★ High surface area due to mesopores
- ★ Good flow-through properties due to macropores
- ★ High stability, even in harsh pH conditions
- ★ Possibility of surface functionalization

To optimize the performance, an application specific adjustment of the pore sizes may be necessary. Therefore, the influences of the synthesis parameters need to be investigated in detail.

Synthesis

The synthesis is based on a partially inhibited sol-gel process.[1]

- ★ Ligands required to decrease reactivity
- ★ Initial gelation for 24 h
  - → loose network of Ti-O-Ti bridged complexes
- ★ Final gelation in a mixture of EtOH and water at 60 °C (II)
  - → ligand degradation enables further condensation
- ★ Calcination at 350 °C removes remaining organic compounds

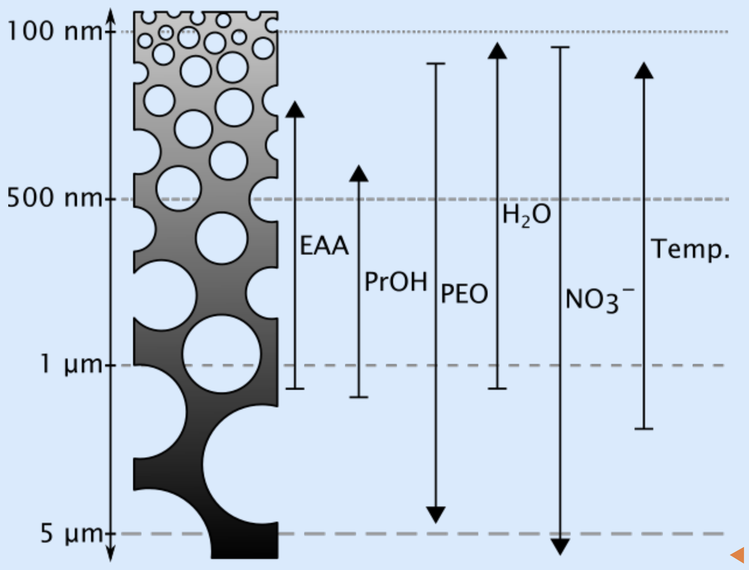


Schematic synthesis procedure; inserts show molecular arrangement.

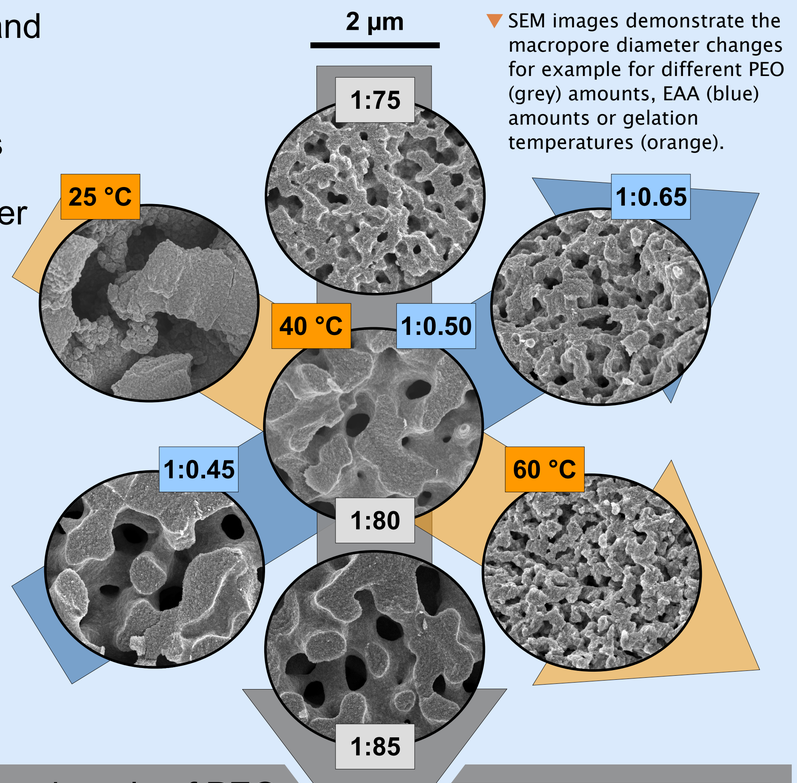
Characterization of the Porosity

The porosity of all monoliths was characterized by SEM, MIP and N_2 physisorption measurements.

- ★ Strong correspondence between different analysis methods
- ★ Macropore sizes and volumes influenced by every parameter
  - → broad range of accessible pores
- ★ Mesopore diameter unchanged
  - → independent high surface area ($S_{BET} \leq 260\ m^2/g$)



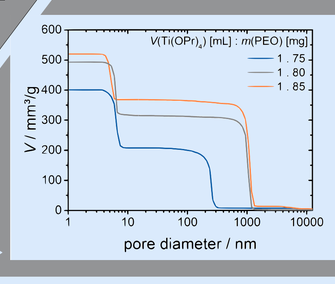
Macropore ranges obtained by the different synthesis parameter. Arrow points in the direction of increasing amounts.



SEM images demonstrate the macropore diameter changes for example for different PEO (grey) amounts, EAA (blue) amounts or gelation temperatures (orange).

The major role of PEO is known in literature.[2]

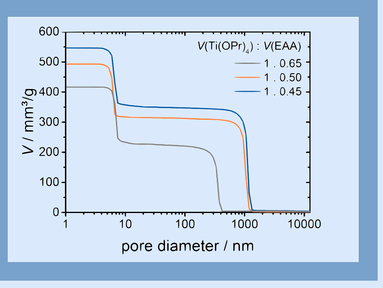
- → spinodal decomposition
- ★ no effect on mesopores



Influence of PEO. With an increasing amount the macropore diameter and volume increase.

EAA has several effects:

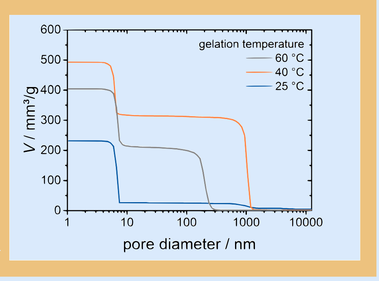
- ★ Stabilization against hydrolysis
- ★ Sterical inhibitor in Ti-O-Ti network
- ★ Change in polarity



Influence of EAA. With increasing ligand amount the macropore size and volume decrease.

The gelation temperature is an important factor for the porosity:

- ★ Huge influence on the kinetic
- ★ No gelation below 25 °C



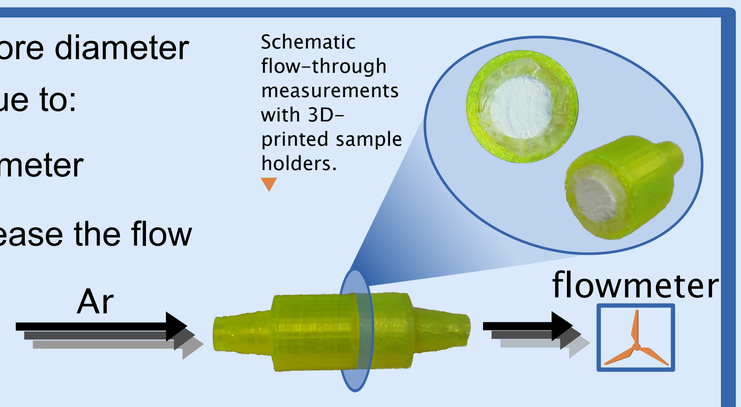
Influence of the temperature. While almost no macropores are formed at 25 °C, increasing the temperature leads to smaller macropores and lower volumes.

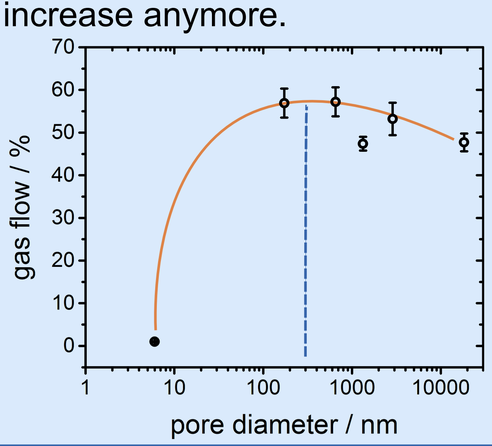
Flow-through Experiments

The independent tailoring of the macropore diameter and the pore volume is very important due to:

- ★ Maximized flow at ~ 300 nm pore diameter
  - → turbulences in bigger pores decrease the flow
- ★ Above a pore volume of 400 mm^3/g the gas flow does not significantly increase anymore.

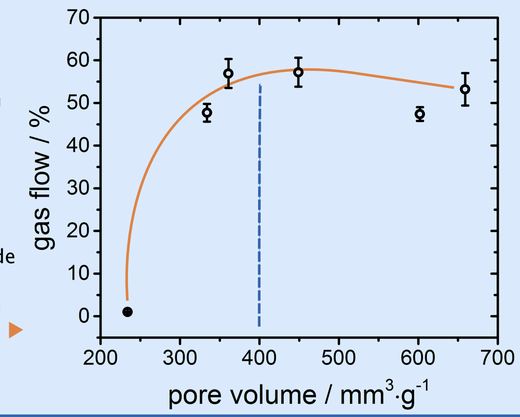
Schematic flow-through measurements with 3D-printed sample holders.





Resulting gas flow in dependance of the pore diameter. Orange guide line indicates a maximum at around 300 nm pore diameter (blue line).

Resulting gas flow in dependance of the total pore volume. Orange guide line indicates an flow increase until 400 mm^3/g (blue line).



Conclusion

The porosity of Titania monoliths can be influenced by various synthesis parameters.

- ★ **100 nm < d_{macro} < 18 µm: macropores adjustable**
  - → Further understanding of the mechanism
- ★ **150 mm^3/g < V_{pore} < 700 mm^3/g: porosity variable**
  - → optimized volume exploitation
- ★ **$d_{meso} \approx 7$ nm: mesopores constant**
  - → High surface area for further grafting

Flow-through experiments show the high dependency on the porosity.

- ★ **highest flow at $d_{macro} \approx 300$ nm**
  - → no turbulances
- ★ **flow increases until $V_{pore} \approx 400\ mm^3/g$**

Literature: [1] G. Hasegawa et al., J. Sol-Gel Sci. Technol. **2010**, 53, p. 59-66.
[2] G. Hasegawa et al., J. Am. Ceram. Soc. **2010**, 93, p. 3110-3115.

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