

# IN SITU RAMAN SPECTROSCOPY OF SOLID CATALYZED REACTIONS IN SUPERCRITICAL CO<sub>2</sub> WITHIN A SI/GLASS MICROREACTOR

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## ABSTRACT

We report the *in situ* monitoring of a solid catalyzed reaction by Raman spectroscopy in a packed bed Si/glass microreactor up to pressures of 10 MPa. Reactant and product concentrations in the microreactor are analyzed during the hydrogenation of cyclohexene mediated by supercritical CO<sub>2</sub> (scCO<sub>2</sub>) over Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. This study shows the novel opportunities in spectroscopic high pressure reaction profiling which can be performed directly on the presented microreactor. The fast temporal response on changes in flow rates, system pressure and reactor temperature makes the microreactor favorable for efficient optimization of reaction conditions and transient experiments.

**KEYWORDS:** high pressure, microreactor, *in situ*, Raman spectroscopy

## INTRODUCTION

Solid catalyzed gas-liquid reactions often suffer from mass transfer limitations. Therefore, the reaction performance can be greatly enhanced at high pressure using supercritical fluids as the reaction solvent to eliminate phase boundaries and increasing the solubility and diffusivity of reactants [1]. High pressure reactions in microreactor chips have been presented by [2-4], which all demonstrate the advantages of microscale high pressure systems. In large scale reactors (see Figure 1(a)) high pressure reactions are conducted under great safety precautions and suffer from large temperature and concentration gradients within the reaction zone, limiting the possibility of fast accurate measurements.

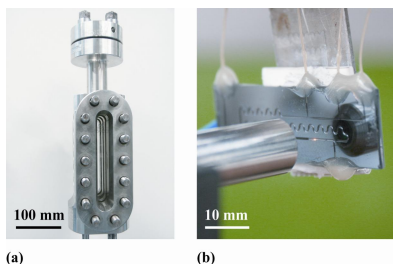


Figure 1. (a) Supercritical water oxidation (SCWO) reactor [5].  $V_R = 150$  mL,  $M = 35$  kg,  $p_{max} = 26$  MPa,  $T_{max} = 473$  K. (b) Microreactor with Raman probe.  $V_R = 15$   $\mu$ L,  $M = 1.6$  g.  $p_{max} = 14$  MPa,  $T_{max} = 323$  K.

Due to the reduced mechanical stress on small scales high pressure reactions can be easily performed in the presented continuous microreactor (Figure 1(b)).

## EXPERIMENTAL

Standard photolithographic, dry etching and anodic bonding techniques are used for the fabrication of the Si/glass chips with a channel cross-section of  $400 \times 390 \mu\text{m}^2$ . The microfluidic connections are realized with epoxy glued PEEK capillaries [3]. The temperature is controlled by resistive heating at 298 and 313 K. The molar ratio of reactants is constant at 90:5:5 ( $\text{CO}_2:\text{H}_2:\text{C}_6\text{H}_{10}$ ) and the mean residence time through the packed bed is between 0.3 – 0.5 s. Raman spectra are acquired using an Ocean Optics QE65000 spectrometer with a RIP-RPB fiber optic probe with a focal length of 7.5 mm placed in front of the microreactor. A continuous wave laser at a wavelength of 785 nm with 500 mW power serves as the light source. The spectra are accumulated for 7 s.

## RESULTS AND DISCUSSION

Fig. 2 shows a scheme of the microreactor and the corresponding measured Raman spectra at different measurement locations.

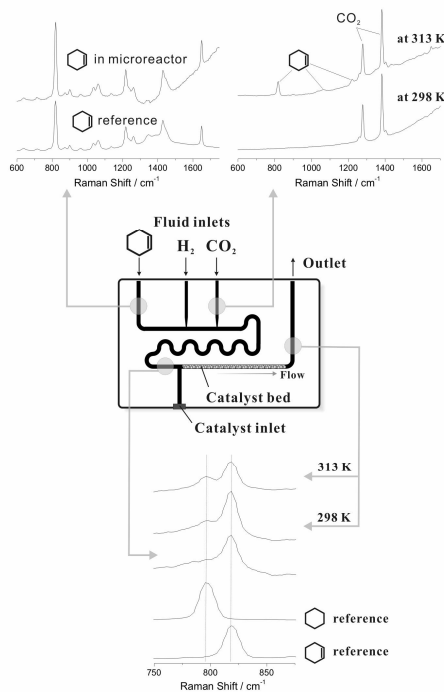


Figure 2. Raman spectra at different locations in the microreactor at 10 MPa.

The spectrum at the cyclohexene inlet is identical to that of a reference measurement where a characteristic band is at  $820 \text{ cm}^{-1}$ . A higher fluorescence signal is

recognized in the microreactor at higher wavenumbers possibly from the microreactor material Si and glass. At the CO<sub>2</sub> inlet the two characteristic signals of CO<sub>2</sub> symmetric stretching are observed at 298 and 313 K, while the signal of cyclohexene is observed at 313 K due to the back-mixing caused by the enhanced fluid diffusivity. No product is detected at the position before the catalyst bed where the Raman spectrum shows only the characteristic signal of reactant, cyclohexene. After the catalyst bed the characteristic signal of the product cyclohexane is appearing, indicating the hydrogenation of cyclohexene over the Pd catalyst particles, which is enhanced at higher temperature. Table 1 shows a good agreement between the conversions analyzed by Raman and offline gas chromatography (GC).

Table 1. Conversion of cyclohexene in the packed bed microreactor at 10 MPa.

Temperature [K]	Conversion GC analysis [-]	Conversion Raman [-]
305	0.25	0.27
309	0.27	0.30
313	0.31	0.31
318	0.34	0.33

## CONCLUSIONS

This first example of *in situ* Raman detection in a high pressure Si/glass microreactor shows the manifold possibilities of reaction analysis which can be performed in the presented system. High pressure reactions which have to be conducted under heavy safety precautions can be easily analyzed continuously at the micro scale with great improvement in safety.

## ACKNOWLEDGEMENTS

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