A new concept for a microreactor with intense light/mater and gas/liquid interaction

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Highlights

- Light transmission combined with gas-liquid saturation along the Teflon AF tubular reactor
- *In situ* spectroscopy of redox reactions and/or photo-activation
- Ultra-high sensitivity for working at low concentrations

1. Introduction

Optical micro-devices are an effective tool to study catalytic reactions *in situ* or activate photochemical reactions. They are unique as they combine the microreactor properties, such as very high surface area-to-volume ratio, short molecular diffusion distance, improved safety, minimal sample consumption with an enhanced light-sample interaction. However, gas/liquid reactions can only be studied to a limited extend, as gas bubbles impede the light transmission. Thus, for studying gas/liquid reactions the liquid is normally pre-saturated, which due to the missing gas/liquid interaction can lead to a depletion of the gas phase component within these devices [1]. Employing commercial Teflon AF tubes seems to be an alternative to overcome those limitations as the very low refractive index of the polymer (1.29) [2] allows light guidance for most solvents especially for water. Interestingly, this is combined with remarkable gas permeation properties of the polymer [3]. This work shows the applicability of liquid filled Teflon AF tube as microreactor allowing for fast gas (N_2, O_2) to liquid mass transfer through the permeable wall and high light/matter interaction. Reaction studies are the photo-activated degradation of methylene blue (MB), and redox chemistry of heteropolyacids (HPAs) with different degree of vanadium-substitution: $H_5[PV_2Mo_{10}O_{40}]$ (HPA-2) and $H_8[PV_5Mo_7O_{40}]$ (HPA-5).

2. Optofluidic setup

The basic optofluidic setup of our LCWM (liquid core wave guide membrane) microreactor is shown in Figure 1. Firstly, both ends of the LCW are fixed to custom-made fluidic cells to introduce the reactants and connect the light source and spectrometer via standard optical fibers. Secondly, embedding the LCW in a stainless-steel tube and the permittivity of the Teflon AF allows continuous dosing of gases into the LCW.

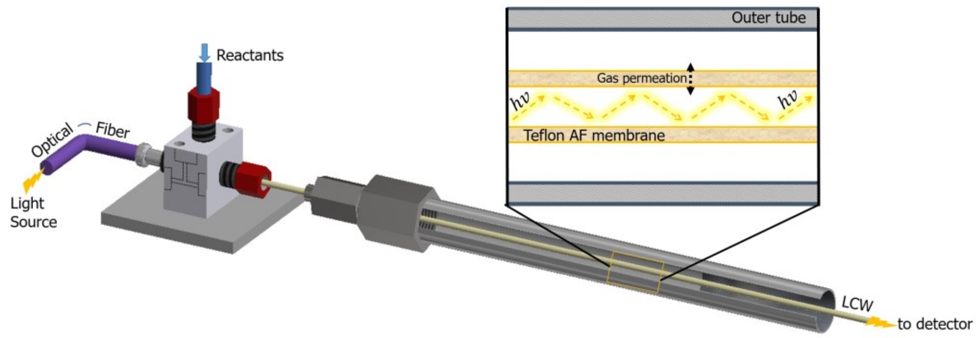

Figure 1. Schematic LCWM setup for *in situ* sensing and permeation using a Teflon AF tube (not to scale drawing)

3. Results and discussion

It could be proven that transmission/detection can be carried out in a wide spectral range (220 to 1.600 nm) with relatively low optical losses (≈1.44 dB m^{-1}) in the presence or absence of permeated gas. Residence time distribution (RTD) studies gave Bodenstein numbers from 5 to 60 in the studied flow range regime.

Studying the Methylene Blue degradation and/or reduction in glucose-alkaline solutions revealed (Figure 2a), the observable first order degradation rate of MB is highly reduced by the presence of oxygen molecules dissolved in the reaction media. Combining the possibility to change the gas phase from O_2 to N_2, to switch on and off the light source inducing photo-activation, and the available high spectral resolution allows to reveal competing processes taking place: re-oxidation of different MB species formed (Leuco-MB, Methylene Violet, etc.); formation of singlet oxygen; and mineralization of MB by oxygen.

Studying the reduction patterns of the HPA catalysts with different degree of vanadium during the oxidation of glucose to formic acid under anaerobic and aerobic conditions, it was possible to obtain kinetic information about the reduction processes of the two catalysts. The oxidation reaction rate with the HPA-5 catalysts was nearly twice as high compared to that with HPA-2. Moreover, as observed in Figure 2b, the HPA-2 showed a similar activation energy compared to HPA-5 for this reaction system.

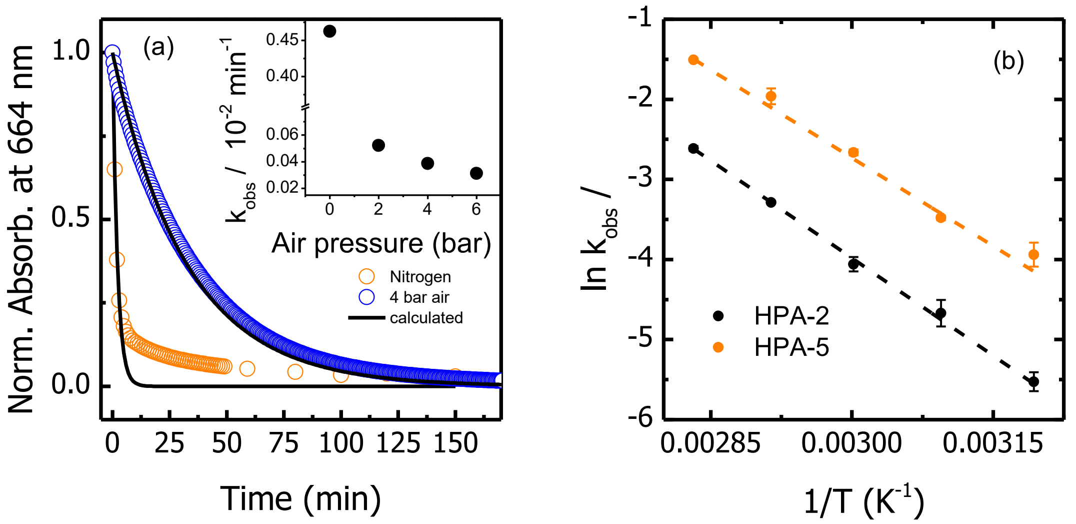

Figure 2. (a) MB degradation vs. time in anaerobic and aerobic conditions (inset: decrement of k_{obs} at different saturation air values), and (b) Arrhenius plot for the oxidation of glucose (0.75 mM) by HPA-2 and HPA-5 (15 μM, pH ~ 4.0).

4. Conclusion

LCWM microreactors are a novel optofluidic system allowing to combine intensive light/matter and gas/liquid interaction to combine photoactivation, spectroscopy and gas/liquid reactions.

References

[1] A.M. Cubillas, S. Unterkofler, T.G. Euser, B.J. Etzold, A.C. Jones, P.J. Sadler, P. Wasserscheid, P.S.J. Russell, , Chem. Soc. Rev. 42 (2013) 8629-8648.
[2] L. Kröckel, T. Frosch, M.A. Schmidt, Anal. Chim. Acta. 875 (2015) 1-6.
[3] M. O'Brien, I.R. Baxendale, S.V. Ley, Org. Lett. 12 (2010) 1596-1598.

Keywords
LCW; optical microreactor; *in situ* sensing; gas-liquid reactions