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Microcapillary enabled direct conversion of methane to methanol

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Methane valorization typically proceeds via the cost- and energy-intensive production of synthesis gas as an intermediate step. A low-temperature single-step approach for the conversion of methane into value-added chemicals such as methanol is therefore considered a “holy grail”. Methanol is a valuable commodity and a fuel itself. It is a versatile liquid intermediate which can be easily shipped and is readily converted to liquid hydrocarbons and olefinic building blocks for polymers and other chemicals [1].

The direct oxidation of methane to methanol using H\textsubscript{2}O\textsubscript{2} at low temperature over Au-Pd nanoparticles has been successfully demonstrated by Agarwal et al. [2]. However, the yields remain very low, and the current understanding of the reaction mechanism is limited. Additionally, in-situ generation of H\textsubscript{2}O\textsubscript{2} is industrially and environmentally more desirable than using pre-synthesized H\textsubscript{2}O\textsubscript{2} as the oxidant [3]. However, due to the explosive nature of H\textsubscript{2}, O\textsubscript{2} and CH\textsubscript{4} mixtures, the concept of coupling the direct synthesis of H\textsubscript{2}O\textsubscript{2} with the in-situ oxidation of methane to methanol has not received sufficient attention. This study aims to investigate this process using a catalytic microchannel reactor, which offers the opportunity to explore the process under a wide range of concentrations.

The catalytic microchannel, which showed an outstanding performance for the direct H\textsubscript{2}O\textsubscript{2} synthesis in our previous work [4], is obtained by embedding Au-Pd nanoparticles on the silica-coated walls of a microcapillary. The experiments are conducted under a broad range of H\textsubscript{2}:O\textsubscript{2}:CH\textsubscript{4} ratios at 20 bar and 42 °C. Direct conversion of methane to methanol with in-situ generated H\textsubscript{2}O\textsubscript{2} is successfully demonstrated. Partial pressures low in H\textsubscript{2} and O\textsubscript{2} and high in CH\textsubscript{4} leads to higher methanol yields. Deactivation on stream is also identified and can be overcome by regeneration in O\textsubscript{2} at mild conditions. Figure 1 represents the time-on-stream formation of methanol and H\textsubscript{2}O\textsubscript{2} in a microcapillary reactor of 1 m length at gas and liquid flow rates of 5 NmL min\textsuperscript{-1} and 0.1 mL min\textsuperscript{-1}, respectively. The yellow areas in the figure represent regeneration with 5 NmL min\textsuperscript{-1} of O\textsubscript{2} at 20 bar and 42 °C. This study sheds light on the one-step oxidation of methane to methanol with in-situ generated H\textsubscript{2}O\textsubscript{2}, and can be conducive towards a better catalyst design for this conversion.

![Diagram](image-url)

Time-on-stream formation of methanol and hydrogen peroxide in an AuPd coated capillary micro reactor. Yellow areas represent regeneration conditions.


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