

## **Optimization of the oxidative dehydrogenation of methanol to formaldehyde: a combined theoretical, experimental and simulative approach.**

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### **Abstract**

With production capacities exceeding 30 million tons per annum,<sup>1</sup> formaldehyde is one of the most important platform molecules in today's chemical industry and is also a key intermediate in the production of synthetic fuels like oxymethylene ethers. One of the major industrial synthesis routes for formaldehyde is the oxidative dehydrogenation (ODH) of methanol over polycrystalline silver catalysts.<sup>2</sup> Hydrogen is a valuable byproduct of this process. Within this study, we address various approaches at different scale to identify optimization potentials in methanol ODH.

As a basis for comparison to the industrial process, methanol ODH over polycrystalline silver catalysts was studied in an electrically heated, continuous flow reactor at temperatures between 773 K and 953 K. By optimizing the reaction parameters, distinct trends in hydrogen formation could be identified and used to increase the hydrogen yield. Our experiments showed that the selectivity to hydrogen was increased and the selectivity to water reduced by increasing the molar ratio of methanol to oxygen in the feed, while the selectivity of the main product formaldehyde remained constant.

To compare the activity of silver and copper species in methanol ODH, Strong Electrostatic Adsorption (SEA) was applied to manufacture supported coinage-metal catalysts. The catalysts were extensively characterized before and after reaction by XRD, TEM/EDX, SEM/EDX and N<sub>2</sub> physisorption. All systems were stable under methanol ODH conditions for more than 400 min TOS.

To enhance the understanding of the underlying reaction mechanism in methanol ODH, density functional theory calculations were applied to generate Gibb's free energy reaction diagrams. Methanol partial oxidation and direct dehydrogenation were compared on both silver and copper surfaces. The results indicated that the energy barriers for methanol partial oxidation were very low for silver and slightly higher for copper catalysts. On the other hand, the process of direct methanol dehydrogenation was highly energy demanding over silver while copper was shown to exhibit lower methanol dissociation barriers.

By process simulation and economic evaluation, various separation procedures for hydrogen from the off-gas of the silver process were evaluated on the process scale. In addition, the effect of changes in inert gas circulation on the hydrogen separation efficiency were studied. The results indicated that the separation of hydrogen from the off-gas of the industrial methanol ODH process could be economically beneficial, especially if the process was adapted to facilitate hydrogen separation without changing the catalytic performance.

1 Merchant Research&Consulting Ltd., <https://mcgroup.co.uk/news>

2 G.J. Millar and M. Collins, Ind. Eng. Chem. Res. 2017, 56, 9247–9265.