

Mechanism and Modelling of the Partial Oxidation of Methanol over Silver

**A thesis submitted to the Faculty of Engineering for the degree of
Doctor of Philosophy**

By

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I hereby declare that the work presented in this thesis is solely my own work. To the best of my knowledge the work presented is original except where otherwise indicated by reference to other authors. No part of this work has been submitted for any other degree.

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Summary

This work involves an experimental and kinetic modelling study of the silver catalysed reaction of methanol to formaldehyde. The motivation for this was the desire to investigate the potential for Process Intensification in formaldehyde production. Formaldehyde production from methanol over silver catalyst is a fast, exothermic process where dilution is used to control heat release, and these properties are both indicators of Process Intensification potential. The process is run adiabatically and produces hydrogen (which is currently burnt). Oxygen is consumed during the reaction but is also required to activate the catalyst and is fed in under-stoichiometric quantities.

The central overall reactions in the silver catalysed process for formaldehyde production are oxydehydrogenation $\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$ ($\Delta H = -159\text{kJ/mol}$) and dehydrogenation $\text{CH}_3\text{OH} \leftrightarrow \text{CH}_2\text{O} + \text{H}_2$ ($\Delta H = 84\text{kJ/mol}$). When sufficient oxygen is available, formaldehyde can be further oxidised to carbon dioxide $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ($\Delta H = -519\text{kJ/mol}$). Formaldehyde can decompose to carbon monoxide and hydrogen $\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ ($\Delta H = 12.5\text{kJ/mol}$). Oxidation of methanol and hydrogen also occurs and other minor products of the reaction are methyl formate, methane and formic acid. These overall reactions do not adequately describe the silver catalysed reaction mechanism. In particular, the overall dehydrogenation reaction does not include oxygen as a reactant, but it will not occur over silver that does not have active atomic oxygen species adsorbed on the surface, and these atomic oxygen species are formed from gas phase oxygen.

In the absence of a complete mechanism for silver catalysed formaldehyde production, the intensification of the process was investigated using a thermodynamic model (based on the overall oxydehydrogenation and dehydrogenation reactions, not reaction kinetics). It was found that by using heat exchange (rather than heat generated from the exothermic oxydehydrogenation path) and a lower oxygen concentration in the feed stream, hydrogen selectivity could be increased while maintaining the required methanol conversion. Before this

opportunity could be further investigated, a complete reaction mechanism that would allow the requirement of oxygen for catalyst activation to be included was required.

There is agreement in the literature that two active atomic oxygen species react with methanol on silver. These are weakly bound atomic oxygen (O_α) and strongly bound atomic oxygen (O_γ). The location of O_α is on the surface of the silver, while the location of O_γ has been described as being in the silver surface (where it substitutes for silver atoms). Both species react with methanol to form formaldehyde. When the concentration of O_α is high enough, O_α will also react with formaldehyde forming carbon dioxide (while O_γ will not). The literature presents differing views on the extent of involvement of each atomic oxygen species in industrial formaldehyde production. There is also disagreement on the pathways for water and hydrogen formation.

An extensive experimental investigation of the partial oxidation of methanol to formaldehyde was carried out using a flow reactor. The effect of temperature (250-650°C), reactant concentration (7000-40000ppm methanol) and the feed ratio of methanol to oxygen (2.5-5.5) were studied. The extreme case of methanol reaction with O_γ in the absence of gas phase oxygen was also investigated. To isolate the effect of secondary reactions, the oxidation of formaldehyde, carbon monoxide and hydrogen were investigated, both in the presence and absence of silver catalyst.

When methanol was exposed to silver catalyst that had been activated by being covered in O_γ (with this being the only source of oxygen) the catalytic nature of O_γ was demonstrated by the high selectivity to formaldehyde and hydrogen that was achieved (with very little carbon dioxide or water production).

When gas phase oxygen was fed to the reactor along with methanol, hydrogen selectivity over silver increased up to about 40% as the concentration of reactants was increased. This result is consistent with the general rule of thumb from industrial practice that hydrogen selectivity is about 50%. When formaldehyde and oxygen were exposed to silver in the flow reactor, the only reaction products were carbon

dioxide and water and the combination of high temperature and excess oxygen was required for complete conversion of formaldehyde.

A pseudo-microkinetic model (based on a Langmuir-Hinshelwood mechanism) for the partial oxidation of methanol to formaldehyde (over silver) was taken from the literature and investigated. This model predicts formaldehyde production using only O_α (no other active atomic oxygen species are included) but lacks pathways for reactions between O_α and adsorbed hydrogen or hydroxyl (so the only possible fate of adsorbed H atoms is to desorb as H_2). The O_α model was combined with literature models for hydrogen desorption and the reactions involving adsorbed hydroxyl (desorption, self reaction, decomposition and reaction with adsorbed hydrogen). Comparison of this Hybrid model with experimental data showed that reactions involving O_α will predict formaldehyde formation and oxidation, but not hydrogen formation (because the rate of hydrogen desorption is too slow compared with the rate of water formation). It is concluded that any detailed model must include the reaction between methanol and O_γ (producing hydrogen). Although the reaction between two adsorbed $O_\gamma H$ species has been suggested as the pathway for hydrogen formation from O_γ , this is not certain and so all possible reactions involving O_γ and hydrogen need be investigated and the appropriate pathways added to the Hybrid model.

Once a complete microkinetic mechanism for the partial oxidation of methanol to formaldehyde over silver is available it can be used to further investigate the process intensification of this process. In particular, the use of staged addition of oxygen (to keep the catalyst active) combined with heat exchange (to replace the heat normally supplied by the oxydehydrogenation path) with the aim of simultaneously maximizing methanol conversion and selectivity to formaldehyde and hydrogen.

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