PARTIAL OXIDATION OF METHANOL TO FORMALDEHYDE OVER AN ELECTROLYTIC SILVER CATALYST

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A thesis submitted to the University of Auckland in fulfilment of the requirement for the Degree of Doctor of Philosophy in Chemistry

August 2003

The University of Auckland

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ABSTRACT

The partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst is a large-scale industrial process that provides the feedstock for the manufacture of synthetic resins, plastics and important chemical intermediates such as 1,4-butanediol and methylene diphenyl diisocyanate (MDI). The process is carried out at atmospheric pressure by passing CH_3OH vapour, in the presence of air and steam, through a thin bed of electrolytic silver catalyst operating adiabatically at temperatures between 873-973 K. Process yields of CH_2O may be as high as 88-90 %. Competing reactions lead to the formation of CO_2, HCOOH and CO. The objective of this thesis was to gain a better understanding of the reaction mechanism and those factors which influence silver catalyst activity and selectivity to CH_2O during CH_3OH oxidation.

Through the application of a variety of experimental techniques it is shown that the dissociative chemisorption of O_2 activates electrolytic silver catalysts for CH_3OH oxidation. Over the temperature range 448-1073 K, the oxygen inventory of silver catalysts comprises three distinct atomic oxygen species: two surface species (denote O_α and O_γ) and a bulk-dissolved species (O_β). The surface species are distinguishable by their Ag-O bonding, thermal stability and reactivity differences. O_α is formed by the dissociative chemisorption of O_2 on Ag(110) or Ag(111) planes. The species is weakly bound, possesses bridging Ag-O-Ag bonding and strong nucleophilic character, and opens reaction pathways towards CH_2O, CO_2 and HCOOH. Recombinative desorption of O_α as O_2 commences at temperatures above 580 K. O_γ formation occurs exclusively on reconstructed Ag(111) planes. The species possesses a highly covalent Ag=O bonding interaction and exists to temperatures in excess of 923 K in the presence of gas phase O_2. O_γ activates silver catalysts for the oxidative-dehydrogenation of CH_3OH to $CH_2O + H_2O$, but shows no selectivity towards CO_2 or HCOOH production. Bulk-dissolved oxygen (O_β) exchanges reversibly with the O_α and O_γ species. The product distribution of CH_3OH oxidation over electrolytic silver catalysts is controlled by the relative surface populations of the O_α and O_γ states. Formaldehyde selectivity and yield increase with temperature up to 923 K, CH_3OH/O_2 feed ratio from 1.5-2.25 and catalyst grain boundary density, all of which reflect a corresponding increase in the surface O_γ / O_α ratio on the catalysts. An optimum formaldehyde yield of 84.3 % was obtained

during testing of the silver catalysts, under conditions close to those employed industrially (temperature = 923 K, molar feed composition $CH_3OH/O_2/H_2O/He$ = 2.25/1/1.7/20, GHSV = 1.25×10^5 h^{-1}). Above 923 K, yields decreased due to the homogeneous decomposition of CH_2O to CO + H_2. Pronounced thermal and catalytic etching of the silver catalyst occurred during activation under conditions of industrial CH_2O synthesis. Critically, structures created by these processes promote O_β and O_γ formation, and improve catalyst performance. Results were used to develop comprehensive reaction schemes for CH_3OH oxidation over electrolytic silver catalysts.

The thermal decomposition of $Ag^IAg^{III}O_2$ in air was examined in relation to the industrial practice of adding silver oxides to silver catalyst beds to facilitate 'light off' during start up operations. $Ag^IAg^{III}O_2$ was thermally reduced to metallic silver via two non-reversible steps, with the intermediate formation of Ag_2O. The transformation of $Ag^IAg^{III}O_2$ to Ag_2O occurred with heating in the 373-473 K region, while the product of this reaction remained stable to temperatures in excess of 623 K. Complete thermal decomposition of the Ag_2O intermediate to Ag and O_2 occurred at 673 K.

The oxidation of several silver substrates by reaction with ozone (5 mol % O_3 in O_2) was examined as potential route to the production of silver catalysts of high initial activity towards CH_3OH oxidation. At 300 K, the Ag substrates were oxidised by O_3 to yield Ag_2O and monoclinic $Ag^IAg^{III}O_2$. The $Ag^IAg^{III}O_2$ formed at the gas/oxide interface, via the oxidation of Ag_2O.

Acknowledgments

The following people and organizations deserve recognition for their contribution to this work.

TERMS AND DEFINITIONS

The following terms and definitions are used throughout this thesis:

- **Conversion** is the molar fraction of methanol (or O_2) transformed per reactor pass, expressed as a percentage.

$$\text{Conversion (\%)} = \frac{[CH_3OH]_{in} - [CH_3OH]_{out}}{[CH_3OH]_{in}} \times 100$$

- **Selectivity** is the number of moles formed of a specific product per mole of methanol reacted, expressed as a percentage.

$$\text{Selectivity (\%)} = \frac{[product]_{out}}{[CH_3OH]_{in} - [CH_3OH]_{out}} \times 100$$

In the previous equations, $[CH_3OH]_{in}$ and $[CH_3OH]_{out}$ denote the molar concentrations of methanol at the reactor inlet and outlet, respectively.

- **Yield** of a specific product is obtained by multiplying conversion and selectivity.

$$\text{Yield (\%)} = (\text{conversion} \times \text{selectivity})/100$$

- **Activity** or **reaction rate** (mol CH_3OH s^{-1}) is the conversion rate of methanol.

- **Specific activity** (mol CH_3OH s^{-1} m^{-2}) is the molar conversion rate of methanol per m^2 of catalyst surface area.

- **Methanol loading** (tonne CH_3OH h^{-1} m^{-2}) is the mass flow rate of CH_3OH to the reactor per square metre of catalyst bed.

- **Gas hourly space velocity** (h^{-1}) is the total volume feed rate to the reactor per cubic metre of catalyst bed.

- **Contact time** or **residence time** (s) is the time taken by a molecule to traverse the catalyst bed.

$$\text{Contact time (s)} = \frac{3600\,(\text{s h}^{-1}) \times \alpha \times 273\,\text{K}}{\text{GHSV}\,(\text{h}^{-1}) \times T(\text{K})}$$

Where α is the bulk volume of the catalyst = catalyst volume/geometric bed volume = (1-voidage). The overall voidage in carefully packed beds of granular particles is ~ 0.4.

- **Linear velocity** (m/s) is the speed at which gases traverse the catalyst bed and is the volume feed rate to the reactor per square metre of catalyst bed.

- **Time-on-stream** is the duration between the beginning of catalyst testing and the time of catalytic activity measurements.

- **Sticking probability** is the ratio of adsorbing to impinging gas molecules.

- **'Light off' temperature** is the temperature at which the conversion of methanol exceeds a specified value (specified in this thesis as 30 %).