Reaction kinetics in formulated industrial catalysts

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Solid catalysts are structured products which are invaluable in assisting a wide range of chemical processes on an industrial scale (Fig. 1). Important benefits include permitting chemical reactions to occur at lower temperatures and increasing selectivity towards desired products vs. unwanted by-products. A multi-level understanding is required to formulate effective catalysts for industrial processes, from the nm scale catalyst microstructure through to mm/cm scale catalyst pellet structure and overall reactor scale operation in itself.

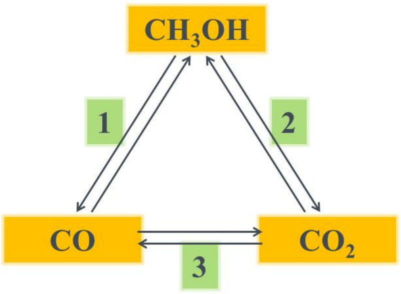
Fig. 1: Examples of formulated catalysts: A) Heavy duty diesel emissions control catalyst, B) Fuel cells, C) Methanol synthesis catalysts [1].

Under operating conditions, ‘active sites’ on the catalyst surface form the heart of the catalytic process. These are functional centres whereby specific reactions (whether desired or undesired) can take place; understanding their development during the catalyst formulation process is critical. The catalyst formulation process itself is multi-stage, incorporating formulation of a catalyst precursor, activation of that precursor (typically in a controlled gas atmosphere) and final conditioning of the ‘activated’ catalyst under operating conditions.

Reaction kinetics is a powerful tool in understanding the functional behaviour of a catalyst under reaction conditions. Reaction kinetics incorporate building mechanistically based mathematical descriptions of catalyst behaviour. These descriptions involve fitting parameters (such as pre-exponentials and activation energies) which are estimated when experimental data are fitted. A good kinetic model reveals the rate determining step in a catalytic reaction and alludes to quantities of active sites for different reactions.

Previously, the conditioning period of a model vanadium phosphorus oxide selective oxidation catalyst was explored [2]. Catalytic reaction performance was seen to change during this period and kinetic modelling was successfully applied to understand relative changes in quantities of active sites for all reaction pathways in the system. The catalyst lost activity with time but this chiefly involved the almost complete removal of a product over-oxidation pathway.

In this paper, transient reaction behaviour of a copper-zinc oxide-alumina ($Cu/ZnO/Al_2O_3$) catalyst will be explored. This catalyst can produce methanol from syngas (CO/H_2 or $CO/CO_2/H_2$) mixtures at elevated pressures (typically > 15 bar) and temperatures (typically 180 - 250°C). Fig. 2 shows the possible reactions which can take place: the reaction network features 3 interdependent reactions which can also be subject to thermodynamic limitations.



1) $CO + 2H_2 \leftrightarrow CH_3OH \quad (\Delta H_r = -90\ kJ/mol)$

2) $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O\ (\Delta H_r = -49\ kJ/mol)$

3) $CO + H_2O \leftrightarrow CO_2 + H_2\ (\Delta H_r = -41\ kJ/mol)$

Fig. 2: Reaction network for syngas conversion over $Cu/ZnO/Al_2O_3$

Previous literature has probed the dynamic nature of catalyst surface morphology under different gas phase compositions of CO, CO_2, H_2 and H_2O [3]. Such works (and in-house data, Fig. 3) have observed that pre-treatment of a $Cu/ZnO/Al_2O_3$ catalyst under CO/H_2 feed conditions results in a transient over-production of methanol when switching to a $CO/CO_2/H_2$ feed. This is not seen for CO or H_2 only pre-treatments. In all three cases however, the catalyst reaches a similar steady state performance after a few hours on stream, suggesting that these pre-treatment effects could be reversible.

It is believed that CO/H_2 conditions alter the morphology of surface copper metal on the catalyst, increasing metal surface area by inducing greater 'flatness'. Previous work has demonstrated a link between CO_2 hydrogenation to methanol and copper surface area [4], which may rationalise the initially high methanol yield when CO_2 is added to the feed stream.

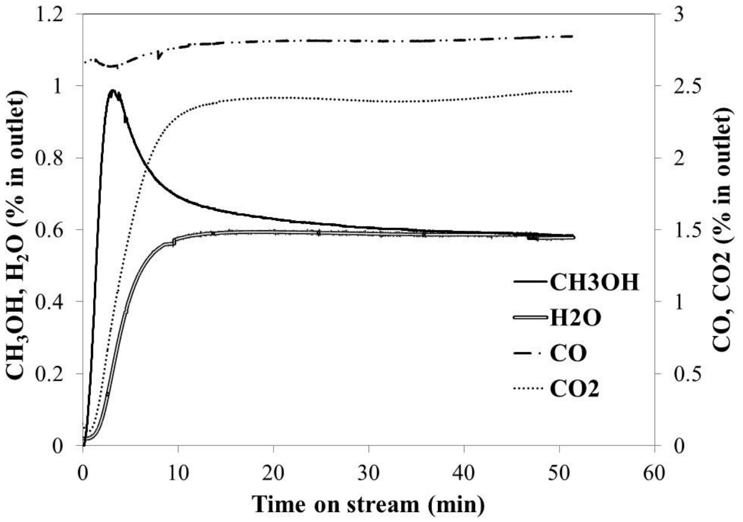


Fig. 3: Transient methanol production observed when switching from a 3% CO / 67% H_2 / Bal. N_2 feed to 3% CO / 3% CO_2 / 67% H_2 / Bal. N_2 feed. Conditions: 25 bar, 200°C, 7.5 L hr^{-1} flow rate, 500 mg $Cu/ZnO/Al_2O_3$ catalyst, d_{tube} = 3 mm

To date, no kinetic modelling has been carried out to understand the above phenomena (in particular under industrially relevant conditions). The aim of this work is to demonstrate changes in active site populations on a $Cu/ZnO/Al_2O_3$ catalyst under these dynamic periods of operation and link this through to functional behaviour of the catalyst. Other catalysts (binary formulations: Cu/ZnO and Cu/Al_2O_3) will also be probed to further understand which components (metal and/or support) are critical in generating different active sites under different gas phase conditions.

[1]: http://www.matthey.com/ [Accessed: 22nd Feb 2013]
[2]: Wilkinson S.K., Simmons M.J.H., Stitt E.H., Baucherel X., Watson M.J., *Journal of Catalysis*, (2013), 299, 249-260
[3]: Vesborg P.C.K., Chorkendorff I., Knudsen I., Balmes O. Nerlov J., Molenbroek A.M., Clausen B.S., Helveg S., *Journal of Catalysis*, (2009), 262, 65-72
[4]: Chinchen G.C., Waugh K.C., Whan D.A., *Applied Catalysis*, (1986), 25, 101-107