Exploring the dynamic behavior of gas-solid catalytic reactions using feed switching experiments – *Case study of Cu-based methanol synthesis catalyst functionality under CO/H₂ and CO/CO₂/H₂ feeds*

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Abstract

In heterogeneous catalysis, it can be very easy to trvialise description of underpinning reaction mechanism(s) for a given catalytic process. One example is in the generation of activity on a catalyst surface as a function of the reaction conditions (composition, temperature) employed. A case study of methanol synthesis over Cu-based catalysts is presented; in this system, significant changes in behavior are seen between CO/H_2 and $CO/CO_2/H_2$ feeds.

A steady state kinetic model description is developed for feeds with P_{CO}/P_{CO2} ratios between 1 and 10 based using the micro-kinetic based model of Vanden Bussche and Froment, (1996) over metallic Cu. Meanwhile, behaviour under CO/H_2 conditions (i.e. no CO_2 in feed) was found to be significantly different. Only Cu-based catalysts with a reducible support (e.g. ZnO) showed methanol synthesis activity in these conditions, suggesting Cu surface area alone is not the only metric in generating activity in this scenario. Dynamic switching experiments between CO/H_2 and $CO/CO_2/H_2$ are then demonstrated to bridge these two modes of operation and the nature of the catalyst surface and surface species. In all cases, the use of spatially resolved, integral micro reactor operation was instrumental in providing clarity to the observations.

Keywords: micro kinetics, transient, active site, surface species, methanol synthesis

Introduction

For a given heterogeneous catalytic process, it can be very easy to trivialise the descriptions of underpinning reaction mechanism(s). Examples include simplifications of micro-kinetic models, particularly in delivering a steady state description, or in the lumping of multiple reaction mechanisms. In recent years, increased use of transient kinetic analysis techniques has improved this position, allowing the fundamentals of catalytic performance to be understood both as a function of catalyst composition but also the feed conditions imposed on it. Both factors are often intrinsically linked and the generation of active sites on a catalytic surface can be strongly driven by the reaction conditions employed.

The synthesis of methanol (CH_3OH) from syngas (mixtures of $CO/CO_2/H_2$) exemplifies this as it features a catalyst whose active sites are generated *in situ*. The industrial process uses a $Cu/ZnO/Al_2O_3$ catalyst which operates at elevated pressure (50 – 80 bar) and mild temperatures (< 573 K). Three key reactions can take place which can be equilibrium limited in the conditions of interest:

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O \qquad (1)$$
$$CO_2 + H_2 \longleftrightarrow CO + H_2O \qquad (2)$$
$$CO + 2H_2 \longleftrightarrow CH_3OH \qquad (3)$$

Significant mechanistic research (Liu *et al.*, (1985), Chinchen *et al.,* (1986) demonstrated the prevalence of producing methanol via CO_2 over $Cu/ZnO/Al_2O_3$ and that activity of these catalysts were directly related to the copper surface area of the catalyst. The choice of support (e.g. Al_2O_3, ZnO, SiO_2) was purely seen as a means to maintain a stable dispersion of metallic copper. A robust, mechanistically driven kinetic model was later developed by Vanden Bussche and Froment (1996) to for a wide range of conditions (Pressure = 15 – 51 bar, Temp. = 453 – 553 K, $P_{CO}/P_{CO2} = 0 – 4$).

Such descriptors are effective to a point but do not fully explain observations at high (≥10) P_{CO}/P_{CO2} ratios observed by Klier *et al.,* (1982) and Sahibzada *et al.*, (1995). Here, an increase of intrinsic methanol productivity is seen in *low*-CO_2 content feeds but a sudden drop to a much lower productivity is observed in CO_2-*absent* feeds. This non-linearity suggests that the catalyst surface or mechanistic pathways to methanol may be altered in this range of conditions.

Aims

In this study, a methodology is presented using discretised micro-reactor testing and kinetic analysis to probe the linkage between catalyst formulation and reaction conditions. In light of the prior art, there is a need to develop a more encompassing framework for methanol synthesis catalysis over Cu-based catalysts at industrially relevant conditions. The aims of this paper are thus:

- Develop tools to probe the link between catalyst formulation (physical descriptors), catalyst functionality and feed conditions.
- Understand the feed condition limits of describing methanol synthesis via CO_2 hydrogenation over metallic copper.
- Develop experimental and modeling methods to probe catalyst state and functionality under CO/H_2 feed conditions.
- Discriminate between mechanisms for methanol synthesis under $CO/CO_2/H_2$ and CO/H_2 feeds via switching experiments.

Cu-based catalysts are exposed to different 'steps' in conditions to track behaviour, as shown in Figure 1:
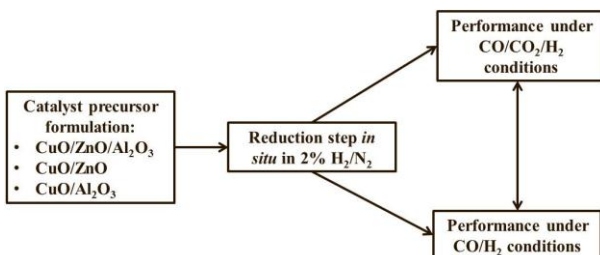

Figure 1: Conditions Cu-based catalysts are exposed to in this study

Results

Steady state testing of $Cu/ZnO/Al_2O_3$ under $CO/CO_2/H_2$ conditions ($P_{CO}/P_{CO2} = 1 - 10$; $P_{tot} = 15 - 35$ bar; Temp $= 453 - 493$ K) provided data which was most adequately described by the micro-kinetically based steady state model of Vanden Bussche and Froment (1996). The experimental discretisation of this dataset revealed regions of operation where either forwards or reverse water gas shift were kinetically rather than thermodynamically driven. The final model captures both of these reactions based on the same micro kinetic scheme.

The testing of Cu-based formulations under CO_2-*absent* conditions showed markedly different behavior. During initial exposure to 3% CO / 67% H_2 / bal. N_2 feeds, the catalyst shows highly transient behavior, including a strong initial elution of H_2O and CO_2. The final steady state of the catalyst is strongly driven by the exposed conditions. Due to this time dependent, condition driven effect, dynamic kinetic analysis was employed. Surface carbon species were calculated to accumulate over time. This amount increased with operation temperature, suggesting a build-up of reaction intermediates rather than simple adsorption.

In terms of formulation used, the methanol productivities of the materials shown in Table 1 largely follows the classic Cu surface area-activity relationship for $P_{CO}/P_{CO2} = 1$. This is not the case for $P_{CO}/P_{CO2} = \infty$; the ZnO containing catalysts are similar and the Cu/Al_2O_3 sample produces no methanol at all, suggesting the choice of support is important.

Table 1: Steady state methanol observed in exit stream for different Cu-based formulations as f(P_{CO}/P_{CO2}) ratio. 500 mg catalyst, 473 K, 25 bar

Catalyst	$P_{CO}/P_{CO2} = 1$ (μmol_{MeOH} g^{-1} s^{-1})	$P_{CO}/P_{CO2} = \infty$ (μmol_{MeOH} g^{-1} s^{-1})
$Cu/ZnO/Al_2O_3$	1.04	0.22
Cu/ZnO	0.44	0.19
Cu/Al_2O_3	0.06	0.00

Dynamic switching experiments can be shown to bridge understanding of both feed conditions. As Figure 2 shows, a switch from CO_2-absent to CO_2-containing feeds result in a transient over-production of methanol. This is very different to the behavior when switching from a H_2/N_2 conditioned catalyst. In both cases however, transient H_2O production is the same. The link between the overproduction of methanol and surface species built up during CO/H_2 exposure will be discussed.
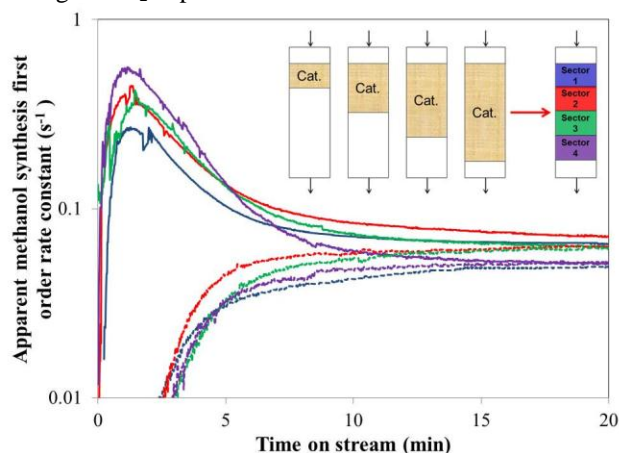

Figure 2: Evolution of apparent rate constant for methanol synthesis (1st order in CO_2) at 473 K, 25 bar, 7.5 L h^{-1} (STP) flow during initial operation of catalyst fixed bed sectors under a ($CO_2/CO/H_2/N_2$: 3/3/67/27) feed. Solid lines denote catalyst pre-treated in ($CO/H_2/N_2$: 3/67/30) and dotted lines denote pre-treatment in (H_2/N_2:2/98) respectively.

Conclusion

The findings from this study suggest a strong interplay between gas phase conditions and catalyst formulation. By exploring feed switching experiments under relevant process temperatures and pressures, a detailed kinetic analysis of this system has been possible to understand the generation of catalyst functionality.

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