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Understanding the generation of methanol synthesis and water gas shift activity over copper-based catalysts – A spatially resolved experimental kinetic study using steady and non-steady state operation under $CO/CO_2/H_2$ feeds

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ABSTRACT

Understanding the mechanism and generation of activity for methanol synthesis and the water gas shift reactions over copper-based catalysts remains a significant area of study in heterogeneous catalysis. In this work, steady and non-steady state experimental and kinetic modelling methods are presented to demonstrate changes in functionality of a $Cu/ZnO/Al_2O_3$ catalyst based on gas composition.

Steady-state testing of a $Cu/ZnO/Al_2O_3$ catalyst, using experimental spatial discretisation approaches with fixed-bed, integral-operation micro reactors, has generated performance data over a range of P_{CO}/P_{CO2} ratios (1–10). The data showed a mixture of observations where forward or reverse water gas shift was kinetically favourable, and also where the reaction was significantly limited by thermodynamic equilibrium. A steady state Langmuir–Hinshelwood model based on micro kinetics was most appropriate which includes kinetic descriptions of both directions of the water gas shift reaction. Using this method, the entire dataset could be predicted and an internal consistency within the kinetic model of the key adsorption constants was demonstrated.

Non-steady state, 'reactor start-up', testing of a $Cu/ZnO/Al_2O_3$ catalyst marked a novel approach to further understanding the functionality of the catalyst. Initial changes in surface carbon and oxygen populations were quantified and linked to subsequent dynamic changes in methanol synthesis and water gas shift activity. Cu/ZnO and Cu/Al_2O_3 formulations were also evaluated and tested using kinetic models, permitting a structural and compositional comparison with $Cu/ZnO/Al_2O_3$.

1. Introduction

Methanol (CH_3OH) has a long history as a key industrial chemical, chiefly serving as an intermediate in the production of other chemicals such as formaldehyde and methyl-tert-butyl ether (MTBE). Methanol has also recently found increased use in alternative fuel applications such as fuel cells [1]. The world production of methanol was ~62 million metric tonnes in 2014,[1] a figure which is increasing annually. The industrial production of methanol via catalytic technologies has been carried out for over 90 years, following the original commercialisation of a process by BASF in 1923. Since then, the production of methanol has seen significant developments on a practical level (in terms of catalyst and process improvements) but also on a scientific level, to understand the fundamentals of how this catalytic process actually works.

The catalytic synthesis of methanol from mixtures of $CO/CO_2/H_2$ (termed 'syngas') was the second major industrial application of catalysis, following that of ammonia synthesis [2]. Unlike ammonia synthesis however, it is critical to deliver a catalyst that is both *active* and *selective* to the methanol synthesis reaction as unwanted reactions may occur. Under $CO/CO_2/H_2$ conditions the following catalytic reactions may be prevalent:

$$CO_2 + 3H_2 \Longleftrightarrow CH_3OH + H_2O \quad (\Delta H_{298} = -41.17\ \text{kJ mol}^{-1}) \tag{1}$$

$$CO_2 + H_2 \Longleftrightarrow CO + H_2O \quad (\Delta H_{298} = +49.47\ \text{kJ mol}^{-1}) \tag{2}$$

$$CO + 2H_2 \Longleftrightarrow CH_3OH \quad (\Delta H_{298} = -90.64\ \text{kJ mol}^{-1}) \tag{3}$$

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Nomenclature

a_i	power dependency on methanol synthesis rate expression (–)
A	pre-exponential factor (s^{-1} (for 1st order))
b_i	power dependency on reverse water gas shift rate expression (–)
$B(t)$	sensitivity function (–)
CC	parameter cross correlation matrix (–)
d_p	particle size diameter (μm)
E_a	activation energy (kJ mol^{-1})
F	F-value (–)
k	rate constant (s^{-1} (for 1st order))
K	adsorption equilibrium constant (bar^{-1} (for 1st order))
K^*	thermodynamic constant (–)
P	partial pressure (bar)
Par	number of parameters (–)
r	rate of reaction (mol m^{-3} s^{-1} (for intrinsic rates unless noted))
R	universal gas constant (J K^{-1} mol^{-1})
s	active site (–)
t	time (s)
T	temperature (K)
v_m	molar volume (m^3)
y	model response (–)
Z	compressibility factor (–)

Greek letters

β^*	thermodynamic equilibrium value (–)
ΔH_{ads}	heat of adsorption (kJ mol^{-1})
ΔH_{298K}	heat of reaction (kJ mol^{-1})
κ_{CC}	condition number (–)

Subscripts

base	of base temperature
i	of species
melting	melting point

Acronym

FWGS	forward water gas shift
IR	infrared
MFC	mass flow controller
RWGS	reverse water gas shift
STP	standard temperature and pressure

Eqs. (1) and (3) describe methanol synthesis via hydrogenation of CO_2 and CO respectively and are both mildly exothermic. Eq. (2) is the reverse water gas shift (RWGS) reaction and is mildly endothermic. The industry standard catalyst for this process is a $Cu/ZnO/Al_2O_3$ formulation which was developed by ICI in the 1960s. This catalyst formulation enabled higher activity than its ZnO/Cr_2O_3 predecessor whilst operating at much lower pressures and temperatures (<100 bar, <573 K), therefore increasing plant efficiency and greatly reducing operating costs.

The methanol synthesis process over a $Cu/ZnO/Al_2O_3$ catalyst has attracted great research interest and debate over the past 40 years. Central to this has been the pursuit of the nature of the active site(s) for the methanol synthesis and RWGS reactions and also the reaction mechanisms by which these reactions proceed. Early kinetic studies for this system assumed that CO was the source of carbon in the synthesis of methanol [3]. Subsequent works [4,5] noticed discrepancies in catalyst performance based on the CO_2 content of the syngas feeds, leading to a maximum in the methanol production rate over integral operation reactors at P_{CO}/P_{CO2} ratios of 5–10. The key argument placed at the time was that CO_2 could help maintain a degree of oxidised copper sites on the catalyst surface.

The works of Liu and co-workers, Chinchen and co-workers [6,7] greatly altered the views on the reaction pathway for methanol synthesis over $Cu/ZnO/Al_2O_3$ catalysts. In the former, an isotope labelling study using ^{18}O CO_2 found that the source of carbon in methanol under $CO/CO_2/H_2$ conditions was in fact CO_2 not CO. In the latter, a linear trend between copper metal surface areas and CO_2 hydrogenation activity of a wide range of copper-based formulations was found. Linked to this, CO_2 partial pressure has a linear relationship with methanol production rate under differential conditions [8].

From this link of copper metal surface area with CO_2 hydrogenation pathway as the critical step in determining methanol synthesis activity, the rest of this introduction will examine kinetics and mechanistic developments. The main focus will be to identify gaps in understanding of the linkage between catalyst formulation, functionality and feed content under reaction conditions.

1.1. Kinetic modelling of copper-based catalysts in the literature under $CO/CO_2/H_2$ conditions

Table 1 shows a selection of key kinetic models proposed in the literature based on operation under $CO/CO_2/H_2$ conditions. The model of Mochalin and co-workers [9] was unique at the time of writing as it completely disregarded the CO hydrogenation to methanol route, owing to the fact the authors were never able to synthesise methanol over a $Cu/ZnO/Al_2O_3$ catalyst under CO/H_2 conditions. Water inhibition is apparent in both the methanol synthesis (from CO_2) and RWGS routes described but the work expanded no further on this or the physical basis of the overall model. Similar models have been proposed subsequently [10,11].

The model of Graaf and co-workers [12] was proposed based on a statistical discrimination approach whereby experimental data from a spinning basket reactor were fitted to 48 different kinetic models. A similar model more recently was also proposed by Lim and co-workers [13]. The concerns with the final model lie in its physical basis, which does not acknowledge that certain surface intermediates can feature in more than one overall reaction [14]. Instead all reactions are assumed to proceed via individual routes.

In the work of Graaf and co-workers [12] the magnitude of the estimated value of $\Delta H_{ads,CO}$ is close to a number of estimations in the literature for the adsorption of CO on a Cu^0 surface which are in the range of 42–53 kJ mol^{-1} [15,16]. CO coverage under methanol synthesis conditions was shown to be low in these works, however, which brings the significance of this parameter into question. The value is also similar to the reaction of CO with surface oxygen on a $Cu/ZnO/Al_2O_3$ surface to form $CO_2(ads)^-$ in the range of 64–80 kJ mol^{-1} [17,18]. Many works support a redox mechanism for the WGS reaction, of which the formation of $CO_2(ads)^-$ occurs in the forward direction [14,19]. It is therefore plausible that r_3 in this network is a lumped descriptor of forward water gas shift (FWGS) and CO_2 hydrogenation to methanol activity, rather than a separate mechanistic route for methanol synthesis from adsorbed CO. This may also explain the error in the fitted RWGS pre-exponential factor if the reaction network is over-determined.

The work of Coteron and Hayhurst [20] refuted the existence of a CO hydrogenation route under $CO/CO_2/H_2$ conditions and instead