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Understanding methanol synthesis from CO/H_2 feeds over Cu/CeO_2 catalysts

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ABSTRACT

Understanding copper-based methanol synthesis catalysts as a function of catalyst type and applied reaction conditions is an area of active industrial and academic research. In this work, results of a methanol synthesis study over a Cu/CeO_2 catalyst using CO/H_2 feeds are presented, using catalyst performance data combined with catalyst characterisation information (DRIFTS, XPS, TPR, XRD) obtained during start-up and under steady state methanol synthesis conditions. The results indicate that the active site and reaction mechanism for methanol synthesis over Cu/CeO_2 are different from the conventional Cu/ZnO/Al_2O_3 catalyst, with CO, rather than CO_2, being the carbon source for methanol. Fixed-bed micro reactors were employed to obtain catalyst performance data in discrete bed sectors using experimental spatial discretisation methods. Methanol synthesis activity over Cu/CeO_2 from CO/H_2 is preceded by transient CO_2 formation, with the onset of methanol synthesis activity observed when the CO_2 formation reaches its peak. Considerable differences between reactor bed sectors are observed during start-up, with CO_2 formation, CO_2 re-adsorption (as surface carbonates and formates), methanol formation and transient methanol decomposition occurring to different degrees and at different time scales.

The interfaces of defective CeO_{2-x} in contact with highly dispersed copper particles form the active site of the catalyst under steady-state methanol synthesis conditions, with the copper oxidation state being a combination of 0 and +1 states. The CeO_{2-x} defect sites are formed during start-up upon reaction of CeO_2 with CO. The CO_2 thus formed leads to catalyst deactivation due to build-up of carbonate and formate species on the catalyst surface. A gradient of progressive poisoning/deactivation is observed going further down the catalyst bed, where the level of deactivation can be controlled by modifying the CO content in the feed. CO_2 thus acts as a poison for the Cu/CeO_2 catalyst, and addition of even low levels of CO_2 to the feed leads to an evenly deactivated catalyst. During start-up in CO/H_2, transient CO_2 and H_2O formation is also observed in the case of Cu/ZnO/Al_2O_3, ascribed to partial reduction of ZnO, similar to the partial reduction of CeO_2 as seen in Cu/CeO_2. The key difference between the two systems is the absence of CO_2 and H_2O re-adsorption on Cu/ZnO/Al_2O_3, resulting in stable methanol production distributed equally over the catalyst bed. Introduction of CO_2 to the CO/H_2 feed in case of Cu/ZnO/Al_2O_3 leads to reduction of Cu^+ to Cu^0 and a change in methanol synthesis mechanism from CO to CO_2 hydrogenation.

1. Introduction

Methanol is an industrial chemical of high significance with an annual production of 62 million tonnes/year in 2014 [1]. Its main uses are as an intermediate in the production of other chemicals such as formaldehyde and methyl-*tert*-butyl ether (MTBE), and it is increasingly used in the methanol to olefins (MTO) process. Historically, methanol is produced on an industrial scale from CO, CO_2 and H_2 mixtures over a Cu/ZnO/Al_2O_3 catalyst, developed by ICI in the 1960s [2]. The methanol synthesis reaction mechanism has been studied extensively over the past decades, however the debate about reaction mechanism and chemical state of the active catalyst is still open. CO_2 has been identified as the carbon source from CO/CO_2/H_2 feeds based on ^{14}CO/$^{14}CO_2$ labelling studies [3]. A detailed mechanistic study by Froment and VandenBussche [4] using desorption techniques confirmed that CO_2 is the source of carbon and oxygen in methanol formed from CO_2/CO/H_2 mixtures [4,5], where CO acts as a source of CO_2 via the water gas shift (WGS) reaction [3,4]. IR studies showed that decomposition of CO_2 on the Cu metal surface results in partial coverage of the surface with oxygen. Surface CO_3^{2-} species are formed upon subsequent adsorption of

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CO_2 [4,6]. Model studies on the reaction of CO_2/H_2 mixtures on supported or unsupported Cu^0 confirmed formate formation via CO_3^{2-} intermediates, where the rate-determining step in methanol formation is the subsequent hydrogenation of these intermediate formates by adsorbed hydrogen (H_{ads}), formed by dissociative adsorption of H_2 on the Cu^0 surface [4,6].

Differing views exist regarding the nature of the active site. On the one hand, Twigg [5] and Chinchen et al. [7] claim that the correlation between Cu metal surface area and activity for a range of different materials is an indication that the critical steps occur on the surface of the Cu metal particles, regardless of the type of support used [5]. It is proposed that the reduced Cu phase is partially oxidised with adsorbed oxygen under $CO/CO_2/H_2$ methanol synthesis conditions, where the CO/CO_2 ratio determines the extent of oxygen coverage of Cu [7]. On the other hand, the activity of the copper phase is significantly enhanced by close interaction with the ZnO phase [8,9]. Herman et al. [9] showed that the high activity of $Cu/ZnO/Al_2O_3$ catalysts is related to an intimately mixed Cu/ZnO phase, as the activity of the mixed phase is at least three times higher than that of the individual components. Mechanical mixtures of Cu (metal) and ZnO are inactive [10]. Herman et al. proposed that Cu^+, which is iso-electronic to Zn^{2+}, could be incorporated into the ZnO structure, forming a solid solution [9]. The promoting effect of CO_2 on the activity was explained as it would keep the Cu in the active Cu^+ state [9]. However, EXAFS and XPS studies did not provide evidence for this Cu^+ in ZnO theory [11]. A different perspective on the possible role of Zn was reported in a recent study by Kuld et al. [12], who used a combination of different chemisorption techniques to discriminate surface copper and zinc species. Evidence for decoration of metallic copper particles with zinc atoms as a function of changes in gas composition was provided, resulting in a Cu-Zn surface alloy.

Methanol synthesis in the absence of CO_2, *i.e.* from CO/H_2 mixtures, occurs at a significantly reduced rate compared to CO_2 hydrogenation [13] and is generally believed to involve a different active site and mechanism [13–15]. Kinetic modelling studies by ourselves [16] and others [17] confirmed that methanol synthesis from CO_2-free CO/H_2 mixtures proceeds via a different rate-determining step (and hence reaction mechanism) than CO_2 hydrogenation from $CO_2/CO/H_2$ mixtures. Enhanced CO adsorption is observed in the binary Cu/ZnO system in comparison with the Cu and ZnO pure components [18]. The valency of the copper phase under CO/H_2 conditions has been postulated to be between zero and one, based on CO chemisorption [18] and DFT [19] studies. Charge transfer from copper metal to partially reduced ZnO occurs under methanol synthesis conditions in CO/H_2, providing a $Cu^{\delta+}/ZnO_{1-x}$ active site [19]. The reducible ZnO phase therefore serves as a stabiliser for the $Cu^{\delta+}$ phase, which is essential for CO adsorption and subsequent hydrogenation to methanol to occur. *In situ* DRIFTS experiments confirm that the stability of Cu^+ carbonyls is higher relative to Cu^0 and Cu^{2+} carbonyls [20]. The importance of reducible supports has been discussed by Frost, who proposed that methanol synthesis activity is proportional to the metal–support oxide interfacial contact area for systems including a wide range of metals and support oxides [11]. Direct hydrogenation of CO species adsorbed to $Cu^{\delta+}$, via CHO, CH_2O and CH_3O (methoxy) intermediates, has been postulated as the most likely mechanism for methanol synthesis from CO [15,19].

Other metal–reducible support combinations have been reported as methanol synthesis catalyst from CO/H_2. CeO_2-supported Cu catalysts have been known for over 30 years in this respect and were first reported by Lambert et al. [21]. The catalyst was prepared by activation of a $CeCu_2$ alloy precursor in CO/H_2 (1:2). The methanol synthesis activity was found to be highly sensitive to the activation procedure applied. The active phase formed was analysed by XRD and, apart from a metallic Cu phase, CeO_2 with the fluorite structure was observed. The CeO_2 was thought to be sub-stoichiometric in oxygen due to the reducing conditions present in the activation stage [21]. The presence of 2% CO_2 in the CO/H_2 feed gas was found to be detrimental for methanol synthesis, it was therefore concluded that the mechanism proposed for methanol synthesis from $CO_2/CO/H_2$ on the Cu component in the $Cu/ZnO/Al_2O_3$ system was not applicable to the Cu/CeO_2 system. In support of this, no correlation between methanol synthesis activity and Cu surface area was found [21]. It was speculated that very small Cu clusters, embedded in the CeO_2 matrix, are the active phase, in line with Frost's theory [11]. This initial report was followed by a series of papers by the Japanese research institute AIST in 2002, reporting methanol formation from CO/H_2 at 195 °C and 20 bar, over Pd/CeO_2 and Cu/CeO_2, with activities comparable to that of the commercial $Cu/ZnO/Al_2O_3$ catalyst, but operated at a 60 °C lower temperature [22,23]. The reducible CeO_2 support in these catalysts was identified to play a key role in the reaction mechanism and active site and the oxidation state of the copper phase was reported to be +1 [23].

In the present study, CO hydrogenation over Cu/CeO_2 is investigated with the aim to identify key differences and similarities with the $Cu/ZnO/Al_2O_3$ system. The main questions that will be addressed are:

- Understand formation and loss of methanol synthesis active sites from a CuO/CeO_2 precursor in a CO/H_2 feed;
- Reveal deactivation mechanisms occurring on the catalyst surface, both under quasi steady state CO/H_2 conditions and under CO_2 poisoning conditions;
- Study activity profiles along the catalyst bed by using experimental techniques (parallel difference testing) that allow discretisation of activity in different catalyst bed sectors;
- Develop understanding of the interplay between metal, support and gas phase at different stages of the reaction by combining (*in situ*) characterisation techniques with activity data.

The results obtained in this study will be put into perspective by comparison with results reported in our previous studies on the model $Cu/ZnO/Al_2O_3$ catalyst under $CO/CO_2/H_2$ [24] and CO/H_2 [16] conditions.

2. Experimental

2.1. Catalyst preparation

2.1.1. 10 wt% Cu/CeO_2-DP

A 10 wt% Cu/CeO_2 sample was prepared by deposition precipitation (DP) of CuO onto a CeO_2 support. A 1.0 M K_2CO_3 solution (Alfa Aesar) was added to a slurry of 11.0 g CeO_2 (Rhodia HSA-5) in aqueous $Cu(OAc)_2$ solution (3.83 g $Cu(OAc)_2 \cdot H_2O$, Alfa Aesar, 98+%, 19.2 mmol) in 1.0 L water at 70 °C over a period of 10 min, until pH = 9.0 was reached. The mixture was stirred at 1200 rpm using an overhead stirrer. After base addition was completed, the slurry was aged for 1 h at 70 °C and then filtered hot. The product was washed three times with 2.5 L hot (55–60 °C) demineralised water and finally dried at room temperature in air. The dried material was calcined at 450 °C (4h, heating ramp rate 3 °C min^{-1}).

2.2. Catalyst testing

Catalytic tests were performed using a set-up comprising of six parallel fixed-bed micro-reactors, operated under identical conditions (temperature, pressure, inlet gas composition). Samples for catalytic testing were prepared by compacting, crushing and sieving the calcined mixed oxide precursor, using the 600–1000 μm particle size fraction. In order to carry out parallel difference test-