
Revisiting Industrial Cu/ZnO/Al₂O₃ Catalyst: Function of Each Component

Jesse Cole, Desirae Haluk, Zhong He*

Primus Green Energy, Hillsborough, NJ 08844, USA

*Corresponding Authors: Zhong He, Primus Green Energy, Hillsborough, NJ 08844 USA, Tel: 908-281-6000 ext: 131; E-mail: zhe@primusge.com

Introduction

Primus Green Energy (PGE) is a green energy company converting natural gas into syngas through methane reforming and then into methanol. Global demand for methanol is expected to increase from 60.7 MMT in 2013 to more than 109 MMT in 2023, with an average annual growth rate of 6 percent (IHS). As one of the most versatile chemical compounds, methanol is used in numerous applications, including for fuel, solvent, antifreeze and for making biodiesel fuels. Methanol production, however, is currently limited to only a few large-scale plants around the world, resulting in high transportation costs for users who are not located within close proximity to a production facility. Primus Green Energy's gas-to-methanol (GTM) STG+™ System can produce methanol meeting IMPCA specification onsite in any location where there is a feed gas source or where methanol is in demand. Primus' STG+™ units produce methanol at small, medium or large scales. The simple, economical process accommodates a range of feedstock types, including associated gas, natural gas, ethane and natural gas liquids. Due to its integrated design, the system is cost-effective at scales as small as 160 metric tons per day of methanol, providing users with an ideal opportunity to capitalize on their

natural gas resources while meeting local methanol demand [1].

Methanol synthesis is a key step in utilizing natural gas into valuable chemicals and polymers. Methanol was identified as the major product in hydrogenation of CO over mixed Cr₂O₃ and ZnO by BASF in 1923 [2]. ICI discovered a preparation method of Cu/ZnO/Al₂O₃ [3] to overcome the intrinsic instability of Cu-based catalysts in 1966, which is still the most popular catalyst in industrial practices for the established methanol synthesis process from syngas.

The active sites of industrial Cu/ZnO/Al₂O₃ are still in dispute. However, many recent studies [4] have demonstrated that the methanol production rate linearly correlates with copper surface area in the reduced form. Therefore, methanol synthesis from syngas over Cu appears to be structure sensitive. Distorted (or stepped) metallic Cu is active for methanol synthesis. However, the synergy between ZnO and distorted metallic Cu increases the reaction rate even further due to dynamic strong metal support interaction effect resulting in partial coverage of Cu with ZnO_x [5].

ZnO is frequently coupled with Cu in industry as a very efficient catalyst for the production of methanol from syngas. ZnO has a low activity (<673K) for methanol formation without the synergistic effects of Cu. However, once paired with Cu, this activity increases by several orders of magnitude [6]. Three common theories have been used to explain these effects: the creation of active sites through Cu/Zn alloys, morphological synergies, and a hydrogen reservoir formed on ZnO through hydrogen spillover [6]. This hydrogen spillover effect is very effective in promoting high CO₂ conversion on co-precipitated Cu-ZnO structures, but only when Cu and ZnO are paired. All three theories can be explained through Zn migration which allows for the formation of the bronze-like Cu_xZn_(1-x)O_y active phase which occurs solely on the boundary between Cu and ZnO particles [7]. The migration can be best explained through the Kirkendall effect which illustrates that differing diffusion rates will cause a movement of the boundary between two metallic surfaces, thereby leading to a more uniformly active catalyst and preventing clusters of Cu or ZnO [7]. Three morphological structures have been examined to be effective in promoting the bronze-like active phase of Cu_xZn_(1-x)O_y: mechanical mixtures, co-precipitates and core-shell morphologies, where the latter one is the most effective with 100% methanol selectivity by inhibiting reverse water gas shift and methanol decomposition reactions [7]. With respect to the electronic effects of ZnO, Frost indicated that Schottky junctions, created through the contact between ZnO and Cu, promote electron transfer between the conduction band of ZnO and the Fermi level of Cu, which leads to the creation of oxygen vacancies. These vacancies improve the effectiveness

of the reduction of the ZnO and thereby add to its activity as a site [8].

Al₂O₃ used in commercial methanol synthesis is primarily featured as a structural promoter, which increases solubility ranges of Zn and thermal stability of the catalyst. When examined further, it has been found to weakly participate in the reaction of methanol synthesis from syngas. In a study by Liu et al, Cu-Zn-Al catalyst without the use of promoters was examined before and after reaction to determine the changes in catalytic performance [9]. The Cu-Zn-Al catalyst had a significant drop in activity when exposed to 523K conditions and 120h time on stream. However, this decrease in methanol selectivity was coupled with an increase in the selectivity of DME and higher alcohols which are largely considered detrimental by methanol suppliers due to the added and tedious step of removing the impurities prior to completion of the process. When examined through FT-IR, it was determined that there was a conversion of aluminum species between AlOOH and Al₂O₃. AlOOH has detrimental effects to the formation of methanol from syngas as the mechanism takes up valuable active sites and causes CO dissociation and promotes the formation of longer chain alcohols by functioning as a bi-functional catalyst. Hence, AlOOH is useful for higher alcohol synthesis but not methanol production.

As the global demand of methanol continues to grow, industrial methanol synthesis is expected to be more prosperous. Although many different strategies are emerging in the innovation of catalyst materials or its composition [10], Cu/ZnO/Al₂O₃ originally developed by ICI, is projected to dominate the industrial practice. Future efforts should be focused

on higher activity and mechanical strength of the catalyst, as well as the mechanism of methanol synthesis.

References

- 1 Primus Green Energy, Methanol Brochure, available from <http://www.primusge.com/>
- 2 BASF (1923) US Patent 1,569,775
- 3 Davies P, Snowden F F, Bridger G W, Hughes D O, et al. (1966) UK Patent 1,010,871
- 4 Natesakhawat S, Lekse J W, Baltrus J P, Ohodnicki P R, et al. (2012) Active Sites and Structure-Activity Relationships of Copper-Based Catalysts for Carbon Dioxide Hydrogenation to Methanol, 2: 1667-1676
- 5 Behrens M, Studt F, Kasatkin I, Kühl S, et al. (2012) The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts, 336: 893-897
- 6 Le Valant A, Comminges C, Tisseraud C, Canaff C, et al. (2015) The Cu-ZnO synergy in methanol synthesis from CO₂, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu+ZnO mechanical mixtures, 324: 41-49
- 7 Tisseraud C, Comminges C, Pronier S, Pouilloux Y, et al. (2016) The Cu-ZnO synergy in methanol synthesis Part 3: Impact of the composition of a selective Cu@ZnO_x core-shell catalyst on methanol rate explained by experimental studies and a concentric spheres model,
- 8 Frost J C (1988) Junction effect interactions in methanol synthesis catalysts, 334: 577-580
- 9 Liu Y, Liu C, Deng X, Huang W (2015) A study on deactivation of Cu-Zn-Al catalyst for higher alcohols synthesis, 5: 99023-99027
- 10 Martin O, Martín A J, Mondelli C, Mitchell S, et al. (2016) Indium Oxide as a Superior Catalyst for Methanol Synthesis by CO₂ Hydrogenation, n/a-n/a

Copyright: © 2016 Zhong H, et al. This is an open-access article which is distributed under Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.