Synthesis of Stable Zinc Oxide Based Catalysts for Carrying out Direct Dehydrogenation of Methanol to Obtain (a) Anhydrous Formaldehyde and (b) Highly Selective Hydrogen as By-product

A. Ghosh Chowdhury[1], U. Arnold[1], J. Sauer[1], M. Bender[2]
[1]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, [2]BASF SE, Ludwigshafen am Rhein, Germany

Abstract

There is a growing demand for renewable hydrogen in recent years with climate change attaining the highest priority in today's high energy consuming societies. In industry, a significant amount of hydrogen is used in the production of methanol (CH_3OH). Successively, the produced methanol is used to manufacture formaldehyde (CH_2O), which is one of the most extensively used raw materials for further synthesis of many other types of chemicals. Some of these are glycolic acid, dyes, melamine and various plastics. However, most of these synthesis routes require it's anhydrous form. Therefore, the currently and most widely used industrial oxidative dehydrogenation processes are disadvantageous, because of the formation of water during the manufacturing process. Not only is the separation chemistry of the formaldehyde-water-methanol mixture a complex unit operation, but it is also relatively energy intensive. Moreover, the hydrogen used in the beginning of the supply chain to produce methanol is lost since it reacts to water. The topic of direct dehydrogenation is therefore of real interest, since the two main products, viz. anhydrous monomeric formaldehyde and hydrogen are commercially of great interest. Zinc oxide (ZnO) is known to catalyze the direct methanol dehydrogenation. However, the volatilization of ZnO at high temperatures is a major problem leading to a significant drop in the catalyst activity over time. This investigation initially compares the dehydrogenation chemistry of ZnO catalyst to the methanol pyrolysis, wherein the formed hydrogen and water have also been quantified. To the best of our knowledge, a very few number of studies have been published catering to the quantification of the trace amount of water produced during the dehydrogenation reaction. All types of ZnO catalyst yielded a maximum of 0.8% water inside the investigated temperature range. Experiments have been carried out to stabilize the activity of the catalyst with the help of mild oxidizing agents such as carbon dioxide (CO_2). Although a minimal stabilizing effect was observed, it did not completely hinder the catalyst deactivation. Consequently, the focus was laid upon binding the ZnO chemically to the support matrix by sol-gel method and calcining it at temperatures up to 900°C in an oven under dynamic air flow. A time on stream study revealed the higher stability of the new catalyst, which surpasses ZnO stability with a relatively lower but constant methanol conversion (~30%) and formaldehyde selectivity (~60%).