Zn-based catalyst route for Pentaerythritol synthesis: Process related CO_2 reduction

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Significance and Relevance

To date industrially production of penta has relied on a homogeneous catalysis process that requires numerous post-separation steps to achieve high purity. This approach is energy intensive and results in significant CO_2 emissions. However, there are no published papers where a heterogeneous catalyst has been used for penta synthesis. We have therefore, for the first time, developed a novel heterogeneous catalysis route to form penta from aldehydes by using a Zn-based catalyst. This is an attractive alternative for producing penta with less solvent and simpler separation steps as shown in Figure 1(b).

Preferred and 2nd choice for the topic: Preferred "Catalysis to electrify the chemical production" and 2nd choice "Green chemistry and biomass transformation, renewable resources conversion"
Preferred presentation: *(Oral preferred/Short Oral preferred. If not selected, then can go for Poster.*

Introduction and Motivations

Pentaerythritol (Penta) is a common platform chemical used in the production of resins, plastics, paints, and various other commercial products [1]. Industrially, penta is produced with high over-all yields and a good product grade through a homogeneous catalysis system in which formaldehyde and acetaldehyde undergo three sequential cross condensation reactions followed by the cannizzaro reaction in the presence of a liquid alkaline solution. In this existing liquid alkaline homogeneous catalysis system, an excess of formaldehyde and alkaline solution is needed due to the formation of sodium formate salt as a byproduct during the reaction [2]. As an alternative, a heterogeneous catalytic system is introduced in this work, in which a solid catalyst can make the process less complicated by reducing the amount of water solvent and replacing the alkaline solution. Moreover, this can also decrease formaldehyde usage which can potentially reduce CO_2 emissions, since formaldehyde synthesis produces process related CO_2.

For this purpose, Zn based non-alkaline catalysts were prepared and tested for the synthesis of penta. There are several studies which explain the potential of Zn-based catalysts for many hydrogenation and aldol reactions [3]. However, there is limited literature that explains the bifunctionality of Zn based catalysts to initiate aldol and cannizzaro reactions simultaneously. It is found in this study that Zn based catalysts such as ZnO and Zn over different supports prepared through different methods have different catalytic activity towards aldol condensation products and for penta synthesis.

Materials and Methods

Zn/SnO_2 (WI), Zn/Al_2O_3 (WI), and Zn/ZSM-5 (WI) were prepared by a conventional wet impregnation method, and Zn/ZSM-5(IE) was prepared by an ion exchange method. All the catalyst activity tests were performed in a 300 ml stainless steel batch reactor (Buchiglas). Formaldehyde and acetaldehyde were mixed with the solid catalysts and the reactor was flushed to contain N_2 at atmospheric pressure before heating up to 200 ^oC, while continuously stirred at 500 rpm for 2 h when the reaction temperature was reached. After cooling down the reaction mixture, the solid catalysts

were separated out from the liquid reaction mixtures. Products were then analyzed and quantified by GC/MS.

Results and Discussion

High surface area ZnO was used as catalyst, and it can be seen in the figure that it shows high activity towards penta formation as selectivity reached 46% with 100% conversion of formaldehyde. Among all the tested catalysts, MeOH was formed predominantly along with penta derivatives that mainly consisted of dipentaerythritol and cyclic monoformals of penta (CPF). Other by-products included mainly 2-butenal, acetic acid and 2-buten-1,4-diol named as (oxys+acids+diols) in the graph. Except the liquid product distribution shown in the graph by columns, gas products were also produced due to the cracking reactions reported as gas yield (C%) which accounted for 14-18% of the carbon contained in the feed reactants. Amongst the catalysts that were prepared by the WI method, Zn/SnO_2 showed the best performance for penta synthesis with less by-product formation. Moreover, catalyst Zn/ZSM-5 (IE) prepared by ion exchange showed the least activity towards penta formation which might be due to the poor activity of Zn ions for catalyzing the reaction. In control experiments without the catalysts there was undetectable yield of penta or its derivatives.

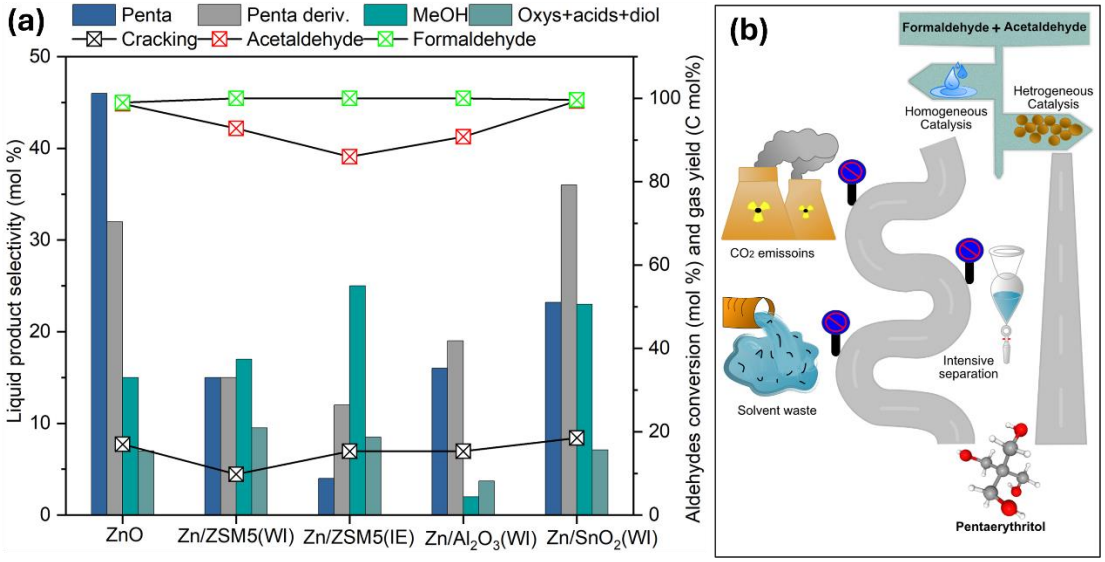

Figure 1. (a) Performance of Zn-based catalysts, Reaction conditions: formaldehyde: acetaldehyde 5:1 (mol:mol), formaldehyde 37 wt% in water, 200 °C, 0.5 g catalyst, 500 rpm, 2 h reaction time, **(b)** Schematic diagram of pentaerythritol synthesis by homogeneous and heterogeneous catalysis routes.

References

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