Synthesis of DME from (H₂+CO₂). Effect of feed composition on catalyst deactivation

I. Sierra, A. Ateka, J. Ereña, A. T. Aguayo and J. Bilbao
Departamento de Ingeniería Química, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

Dimethyl ether (DME) is a clean fuel for diesel engines and an excellent source for obtaining H₂ by catalytic steam reforming, especially for vehicles, given that it is suitable for storage and transport and may be fed into cells without the need for pumping. DME is also a key intermediate to produce automotive fuels and raw materials (olefins and BTX aromatics) from alternative sources to oil (natural gas, coal, biomass) [1].

The synthesis in a single step following the syngas to DME process (STD) has advantages over the two-step process (synthesis of methanol and its dehydration to DME), due to the lower thermodynamic limitation of methanol synthesis. This thermodynamic advantage favours the incorporation of CO₂ as a co-feed with the syngas, or the transformation of (H₂+CO₂) mixtures into DME. Considerable attention has been paid in the literature to the use of CO₂ as a raw material in the synthesis of chemicals and liquid energy carriers, in order to mitigate the accumulation of CO₂ in the atmosphere. Amongst the different alternatives, STD process is an interesting route to combine the upgrading (via gasification) of alternative sources to oil, particularly lignocellulosic biomass, with the large-scale CO₂ sequestration.

The bifunctional catalyst used is composed of a CuO-ZnO-Al₂O₃ metallic function for the hydrogenation of CO₂ to methanol, and a γ-Al₂O₃ acid function for the dehydration of methanol to DME. The reaction equipment is provided with a fixed bed, and allows for operating at high temperatures and pressures. The combustion of the coke deposited on deactivated catalyst has been carried out in a tapered element oscillating microbalance (TEOM) coupled to a gas micro-chromatograph.

A kinetic model has been established for the transformation of (H₂+CO₂) into DME on a CuO-ZnO-Al₂O₃/γ-Al₂O₃ bifunctional catalyst, with excess of γ-Al₂O₃ acid function [2]. This model fits the experimental data in a wide range of operating conditions. A fact to be noted in the kinetic model is the presence of a term with CO₂ concentration to quantify the attenuation of both the reaction rate of methanol and paraffin synthesis and the deactivation by coke of the metallic function.

In this work, a parametric study of the process has been conducted, in order to establish a suitable value of H₂/CO₂ molar ratio in the feed. The aim is to maximize DME production with catalyst deactivation being as low as possible. Runs have been carried out feeding mixtures of (H₂+CO₂) under the following conditions: 275 ºC; 40 bar; space time, 42.0 (g of catalyst) h (mol of carbon)-1; time on stream, 30 h.

When the amount of H₂ in the feed is increased, the conversion of CO₂ and the yield of products (DME, methanol and paraffins) steadily increases. This increase is attributed to the competition between the water gas shift reaction and the hydrogenation of CO₂ to methanol. Moreover, the conversion of CO₂ undergoes a very slight decrease with time on stream. Coke deposition after 30 h of time on stream is very low: 0.12 wt% for a H₂/CO₂ molar ratio of 2/1, 0.09 wt% for 3/1 and 0.08 wt% for 4/1. A high concentration of hydrogen in the reaction medium limits the deposition of coke on the metallic phase, following the same trend observed by feeding (H₂+CO). This effect is explained by the relatively high partial pressures of H₂ inhibiting the development of coke.

According to these results, the most suitable value of H₂/CO₂ molar ratio in the feed is 4/1 in the range of operating conditions studied, since although the catalyst undergoes a slight loss of activity with time on stream, DME yield peaks for this composition of the feed.

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References

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