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Research article

Kinetic modeling of the direct synthesis of dimethyl ether over a CuO-ZnO-MnO/SAPO-18 catalyst and assessment of the CO_2 conversion

Ainara Ateka*, Javier Ereña, Javier Bilbao, Andrés T. Aguayo

Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Spain

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ABSTRACT

A kinetic model has been established for the direct synthesis of dimethyl ether (DME) from syngas and CO_2 feeds. The kinetic parameters have been determined fitting the experimental results obtained using a CuO-ZnO-MnO/SAPO-18 (CZMn/S) bifunctional catalyst in a fixed-bed isothermal reactor, under a wide range of operating conditions: 250–350 °C; 10–40 bar; CO_2/CO molar ratio in the feed, between 0 and 1; H_2/CO_X molar ratio in the feed, 3/1 and 4/1; space time, from 1.25 $g_{cat}h(mol_C)^{-1}$, up to 20 $g_{cat}h(mol_C)^{-1}$; time on stream, up to 30 h. The model considers the kinetic equations of the individual reactions of methanol synthesis from CO and CO_2, the dehydration of methanol to DME, the water gas shift reaction (WGS) and the formation of paraffins, along with the deactivation kinetics. The attenuation of the reaction rates of methanol and paraffins synthesis has been considered by the competitive adsorption of CO_2 and H_2O in the metallic sites with respect to the adsorption of CO (more reactive than CO_2 in the synthesis of methanol). The deactivation by coke has been quantified by a kinetic equation dependent on the concentrations of methanol and DME, and the attenuation of the deactivation by the competitive adsorption of CO_2 and H_2O has also been considered in this equation. The kinetic model allows predicting satisfactorily the evolution with time on stream of the concentration of the components in the reaction medium (methanol, DME, unreacted CO and CO_2, and paraffins formed as by-products). In addition, the model has been used to simulate the reactor, determining the effect of the reaction conditions on the conversion of CO_2. This conversion, in contrast to the yield of DME, increases with increasing CO_2 concentration in the reactor feed.

1. Introduction

Given the forecasts of growth of CO_2 emissions, up to a concentration of 570 ppm of CO_2 by the end of the 21st century, and in order to mitigate the devastating consequences of climate change, developed countries have adopted regulations to promote the efficient use of energy and the progressive replacement of fossil fuels by renewable sources (http://www.epa.gov/climatechange/ghgemissions/gases (co2.html), Climate change). In this scenario, the catalytic and electrocatalytic routes that use CO_2 as a raw material receive great attention, and especially the routes for fuel production, due to their potential capability for large-scale CO_2 valorization, through hydrogenation reactions (Fischer-Tropsch synthesis, synthesis of C_{2+} alcohols and of gasoline/isoparaffins among others) [1,2]. Olah et al. [3] consider that the synthesis of dimethyl ether (DME) in a single stage co-feeding CO_2 together with syngas is an interesting alternative for replacing the industrial process for its production in two stages. These authors emphasize the environmental interest of this reaction when the syngas is produced from lignocellulosic biomass.

The main application of DME (CH_3-O-CH_3) nowadays is as domestic and automotive fuel, based on its properties (vapor pressure similar to that of liquefied petroleum gases, cetane number between 55 and 60) [4,5] and the reduced emissions of NO_x, SO_x and particulate matter in its combustion [6,7]. Based on a life cycle analysis (LCA), Lerner et al. [8] emphasize the interest of methanol and DME as clean transport fuels and determine that they can be economically competitive with oil derived fuels, due to the availability of natural gas. In addition, the economy of DME is also based on its future as intermediate raw material, progressively replacing petroleum derivatives and methanol for the production of olefins [9–13] or issoparaffin-rich gasoline [14] and as H_2 vector [15–20].

The synthesis of DME involves the following reactions:

Methanol synthesis:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (2)$$

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* Corresponding author.
E-mail address: ainara.ateka@ehu.eus (A. Ateka).

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Methanol dehydration to DME:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{3}$$

Reverse water gas shift (rWGS):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{4}$$

The secondary reaction of paraffins formation (mainly methane) also takes place:

$$nCO + (2n + 1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O \quad (n = 1 - 3) \tag{5}$$

The interest of synthesizing DME from syngas (STD process), using bifunctional catalysts has grown in the last decade, due to several factors: i) the lower production cost of DME and methanol (byproduct) than the synthesis of methanol and the synthesis of DME in two stages [21]; ii) the possibility of producing syngas from different raw materials, such as coal, natural gas (from growing reserves), biomass and wastes from the consumer society (plastics, tires); iii) the promotion of the biomass gasification technology [22–24]. The most widely studied catalysts for the direct synthesis of DME use CuO-ZnO-Al_2O_3 (CZA) as metallic function [25], although Al_2O_3 has been completely or partially replaced by other metallic oxides, such as MnO or ZrO_2 [26], and ZnO (used to stabilize Cu) has been replaced by La_2O_3 [27] among others. For the acid function, catalysts of different porous structure are used (γ-Al_2O_3, silica-alumina, HZSM-5, NaHZSM-5, mordenite, HY, ferrierite, HMCM-22, SAPOs and ZrO_2). All those acid functions have in common a very low acid strength, a pursued characteristic in this process in order to avoid the formation of hydrocarbons [28]. Due to its relevance for the viability of the process, considerable attention has also been paid to the deactivation of the catalyst, whose main cause is considered to be the partial blockage of the metallic sites by coke [29], although coke formation is a consequence of a synergy between the mechanisms in each function of the catalyst [30]. It has also been established that the increase in the H_2O content in the reaction medium attenuates coke deposition, due to the limitation of methoxy ions formation [31]. In addition, the catalyst is prone to irreversible deactivation, by Cu sintering above 300 °C [32].

Integrating methanol dehydration (Eq. 3) in the same reactor displaces the thermodynamic equilibrium of methanol synthesis (Eqs. 1 and 2), and allows to work at lower pressure, higher temperature and lower H_2/CO ratio in the feed than in the synthesis of methanol [33–35]. This latter advantage is important to valorize the syngas derived from biomass [3]. Besides, the lower thermodynamic limitation is favorable for the incorporation of CO_2 in the feed, increasing its conversion respect to that in the synthesis of methanol under the same conditions. However, the required conditions of pressure and temperature in the direct synthesis of DME are intermediate to the optimum conditions for the individual stages, and therefore, the direct synthesis requires catalysts and kinetic models suitable for these conditions. In addition, the incorporation of CO_2 in the feed has a remarkable influence on the composition of the reaction medium, as it leads to an increase in the content of H_2O in the reaction medium (by displacement of the WGS reaction, Eq. 4).

Among the initiatives on tailoring the catalysts used in the synthesis of DME to the conditions required when co-feeding CO_2 with syngas, the increase in the activity and stability of the CuO-ZnO sites of the CZA metallic function have been studied with different strategies. In this regard, the CO_2 hydrogenation rate has been improved substituting ZnO by Fe_2O_3 and using CeO_2 as promoter [36,37]. The activity for the reverse WGS reaction (to potentiate the greater activity of CO than of CO_2) has been upgraded by substituting Al_2O_3 by MnO [38,39], and ZrO_2 has been incorporated to increase the stability of the $Cu^{\delta+}$ sites [40–45]. The improvements in the acid function have been addressed by reducing the hydrophilicity with respect to the conventionally used γ-Al_2O_3, which has been replaced by the HZSM-5 zeolite (modified for the passivation of its strong acid sites, responsible for the formation of hydrocarbons) [30,46,47], and silicoaluminophosphates (SAPO-18, SAPO-11) [26,35,48–51], among others (as WO_x/ZrO_2) [52].

In a previous work [26] the good performance of the CuO-ZnO-MnO (CZMn) metallic function and of the SAPO-18 (S) acid function in the valorization of CO_2 (co-fed together with syngas) has been verified, determining as optimal the mass ratio (metallic function)/(acid function) of 2/1 and emphasizing the lower cost of the CZMn/S catalyst and its regenerability [49]. In addition, relevant effects derived from the presence of CO_2 in the feed have been determined, which are essentially attributed to: i) the increase in the H_2O concentration, and ii) the relevance of the reverse WGS reaction (Eq. 4). Besides, it is important to point out that the adequate reaction conditions for the valorization of CO_2 correspond to those of lower production of DME, therefore, for the economic viability of the process a commitment between both objectives must be achieved [53]. The activity for the reverse WGS reaction (Eq. 4) is a key feature of the metallic function of the catalyst to achieve high CO_2 conversion values, since its conversion into CO is necessary (more active in the synthesis of methanol) to enhance DME yield [49,54].

These features of the direct synthesis of DME must be taken into account in the design of suitable reactors. Among the reactors studied by means of simulation, multitubular fixed-bed reactors (used in the synthesis of methanol) [55] and fixed-bed reactors with hydrophilic membranes (to remove the formed H_2O and displace the limiting thermodynamic equilibrium of methanol synthesis and rWGS reactions) stand out [56,57]. The design requires suitable kinetic models for CO_2 containing feeds and reaction conditions. However, most studies regarding the kinetic modeling of the direct synthesis of DME [58,59] have not been determined from experimental results of the direct synthesis of DME, but have been developed combining kinetic models previously established in the literature for the individual reactions of methanol synthesis [60,61], methanol dehydration to DME [62,63] and WGS reaction [64–74]. These kinetic models provide remarkable information on the mechanisms of the reactions considered and have allowed the design of industrial reactors for each of the mentioned reactions. Nevertheless, they are based on experimental results corresponding to the suitable conditions for each of these individual reactions, whereas the reaction conditions in the direct synthesis of DME and in particular when co-feeding CO_2 with syngas, are different. Thus, in the direct synthesis of DME, it is convenient to prepare the catalysts with an excess of acid function, in order to facilitate the progress of methanol dehydration, so that the overall reaction is conditioned by the progress of the methanol synthesis stage and by the WGS reaction. This characteristic of the catalyst prevents the advance of the overall reaction from being limited by the adsorption of H_2O on the acid function. It should also be noted that catalyst deactivation has not been considered in the kinetic modeling studies available in the literature.

In the present paper, a kinetic model has been established for the synthesis of DME over a CZMn/S catalyst (specifically suitable for the conversion of CO_2) [49] and this model has been used for the simulation of the reactor (isothermal fixed-bed), focusing on the valorization of the CO_2 co-fed together with syngas. This objective is complementary to the usual goal in the studies on the direct synthesis of DME, which are mainly addressed in the literature towards maximizing the yield and selectivity of this product. Some fundamental aspects of the kinetic model (such as considering CO_2 co-feeding together with syngas, the effect of the high H_2O concentration and the features of deactivation kinetics) have been established progressively in partial kinetic studies with different catalysts, of lower activity for the conversion of CO_2 and lower stability [34,54,75].

2. Experimental

2.1. Catalyst

The CuO-ZnO-MnO (CZMn) metallic function (for the synthesis of