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Kinetic model for the reaction of DME to olefins over a HZSM-5 zeolite catalyst

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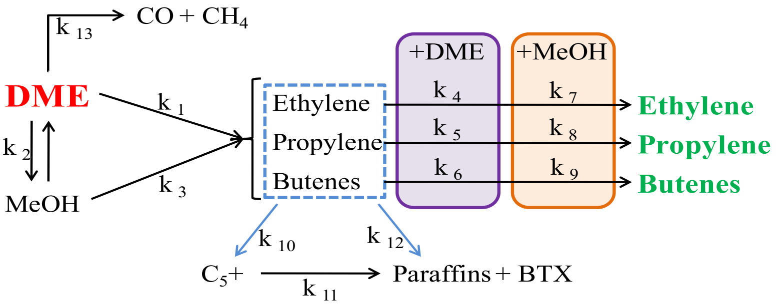
HIGHLIGHTS

- An 11 *lump* kinetic model characterizes the DME to olefins reaction.
- DME reacts at a lower temperature to olefins compared to methanol (350 °C vs. 450 °C).
- At the same temperature, DME reacts 20 times faster than methanol.
- Co-feeding water attenuates the reaction rate and modifies the product distribution.

GRAPHICAL ABSTRACT



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ABSTRACT

A kinetic model of 11 *lumps* (dimethyl ether, methanol, water, ethylene, propylene, butenes, C_2–C_4 paraffins, C_{5+} hydrocarbons, BTX aromatics, methane and CO) has been determined for the reaction of DME to olefins (DTO process) over a HZSM-5 zeolite catalyst ($SiO_2/Al_2O_3 = 280$) agglomerated with boehmite. The experiments have been carried out under a slightly above than at 1.5 bar in an isothermal fixed bed reactor under a wide range of operating conditions: 598–673 K; space time, 0.2–6 g_{cat} h mol_C^{-1}; feed, pure DME and co-fed with He, methanol and water. The model characterizes the effect of the reaction conditions (temperature, space time and feed composition) over the product distribution at zero time on stream.

The kinetic constant of DME conversion to olefins (at 623 K) is 20 times greater than that of methanol conversion. This result and the non-existence of the methanol dehydration step are the main differences between both processes. These differences have a great impact on the advance of the reaction and on the yield and distribution of product fractions.

1. Introduction

The reaction of dimethyl ether (DME) to olefins is interesting as a complementary route to the MTO (methanol to olefins) process to satisfy the growing demand of olefins, given the expected availability of DME. This availability is a consequence of: (i) the opportunity to value alternative raw materials to oil (carbon, natural gas, biomass, wastes of the consumer society) by reforming or gasification [1–3]; (ii) the progress in the knowledge of the DME synthesis in one step (with a bifunctional catalyst), which has thermodynamic advantages over the methanol synthesis and allows valorizing syngas with lower H_2/CO ratio (which facilitates the biomass valorization) and co-feeding CO_2 with syngas [4–6].

The studies in the literature regarding the reaction of DME to olefins have revealed the similarity of the reaction scheme with that of the reaction of methanol to olefins, with light olefins as primary hydrocarbon products, which are then transformed to

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Nomenclature

E_j	activation energy of each kinetic constant, kJ mol^{-1}
F	Fischer distribution
F_0, F_i, F_{Total}	molar flow rate of the feed, each *i lump* or compound and total, in carbon units, respectively, mol$_C$ h^{-1}
f_i	parameter for relating the reactivity of the olefins
K	equilibrium constant for the dehydration of methanol to DME
K_a	adsorption equilibrium constant of methanol and water
k_j, k_j^*	kinetic constant of *j* step in the reaction scheme at *T* temperature and at the reference temperature; the units are those corresponding to the kinetic equation
n_l, n_{exp}	number of *lumps* and experimental points (including repetitions), respectively
OF	objective function to be minimized for the calculation of the kinetic parameters, defined in Eq. (22)
p, q	number of experimental conditions and number of kinetic parameters to be estimated
p_i	partial pressure of *i lump*, atm
R_j	number of repetitions for each *j* experimental condition
$(r_i)_0$	rate of formation of *i lump* at zero time on stream, $(mol_i)_C$ $(g_{cat}\ h)^{-1}$
S_{BET}, S_m	BET surface area and micropore surface, respectively, m^2 g^{-1}
$s_a{}^2$, $s_e{}^2$	variance for the lack of fit and experimental error, respectively
T, T^*	temperature and reference temperature, respectively, K
V_m, V_P	micropore and pore volume, respectively, cm^3 g^{-1}
$y_{i,j}$, $y_{i,j}{}^*$	calculated and average experimental value of composition of *i lump* at *j* experimental condition, expressed as molar fraction referred to organic components, respectively
W	catalyst mass, g
W/F_0	space time, g$_{cat}$ h mol$_C^{-1}$

Greek symbols

α	confidence level
ΔH_a	adsorption heat of methanol and water, kJ mol^{-1}
θ	term that quantifies the attenuation of the reaction rates by the adsorption of water and methanol
σ^2	variance
υ_a, υ_e, υ	degrees of freedom for the lack of fit, experimental error and residual, respectively
ω_i	weight factor for each *i lump* or compound

Abbreviations of compounds

B, E, P	butenes, ethylene and propylene, respectively
BTX	aromatics (benzene, toluene, xylenes)
C_{5+}	aliphatics with 5 or more carbon atoms
D, M	dimethyl ether and methanol, respectively
Pa	C_2–C_4 light paraffins
W	water

aromatics, paraffins and high olefins by secondary reactions [7,8]. However, the results of DME conversion, product distribution and deactivation do not match with those of methanol, which has been attributed to the different concentration of methanol in the reaction medium [9] or to the higher conversion of DME [10]. This higher conversion of DME than that of methanol can be attributed to the major affinity to the catalyst protons [11] and to the differences in the reaction mechanism [12,13]. The non-existence of the methanol dehydration step in the DME to olefins reaction should be considered, thus the real capacity of the catalyst for the production of olefins is greater. Moreover, the water content in the reaction medium is lower, which favors all the reaction steps. These differences suggest that the catalyst and the suitable conditions (especially temperature) of the process of reaction of DME to olefins (DTO process) will be different from that of the MTO process, therefore justifying the interest of the kinetic modeling of the DTO process.

The DME to hydrocarbons reaction has been studied in the literature mainly due to its interest in the methanol to hydrocarbons reaction, which is quickly dehydrated to DME, so that, the mixture of methanol and DME in the equilibrium has been considered as the reactant. Consequently, it is well established that the formation of C_2–C_4 olefins from both oxygenates follows the dual cycle reaction mechanism, which occurs by two routes: (i) methylation–dealkylation of intermediate aromatics (polymethylbenzenes); (ii) methylation-cracking of olefins [14–17]. Moreover, secondary reactions of isomerization, cyclization and hydrogen transfer take place, which give as by-products: light paraffins, BTX aromatics, C_5^+ aliphatics and coke. Due to the complexity of the reaction scheme, with numerous individual steps, the selectivity of olefins is very sensitive to the properties of the catalyst (acidity and shape selectivity) and to the reaction conditions.

HZSM-5 zeolite has received great attention as a catalyst in the reaction of methanol to olefins to maximize the olefin yield and in particular the propylene yield, therefore, this catalyst is interesting for the DTO process. Among its advantages over other acid materials, the following should be noted: (i) its stability and, (ii) facility of tailoring its acidity through different actions, such as the selection of SiO_2/Al_2O_3 ratio, decreasing the crystal size, hydrothermal treatment, treatment with alkali and doping with different metals (Na, K, P, Fe, Ni, etc) [18–24]. Moreover, the performance of HZSM-5 zeolite can be improved by generating a hierarchical porous structure, with the formation of mesopores in the outside of the microporous crystalline channels of the zeolite [11,12], and also by agglomerating the zeolite into a matrix with mesopores [13]. Al-Dughaiter and de Lasa [8] have proven the effect of the HZSM-5 zeolite acidity in the reaction of DME to olefins, with a good compromise of activity, olefin selectivity and stability for a high SiO_2/Al_2O_3 ratio, as a consequence of the moderate acidity in these conditions. In a previous work, it has been proven the good behavior of a catalyst prepared with HZSM-5 zeolite (SiO_2/Al_2O_3 = 280) agglomerated with boehmite as a binder, so that, after the calcination, a mesoporous matrix of γ-Al_2O_3 is generated [25].

In this paper, a kinetic model for the reaction of DME to olefins over the latter catalyst has been established, taking as reference the models reported in the literature for the reaction of methanol to olefins over HZSM-5 zeolite and taking into account the particular characteristics of the reaction of DME. Several kinetic models proposed for the reaction of methanol to olefins consider the reaction mechanisms [26,27], but most of them are models of *lumps* (simpler), which facilitates the calculation of the kinetic parameters and the subsequent use of the model in the reactor design and simulation. The pioneer model of *lumps* established by Chang [28] to quantify the formation of olefins is based on a reaction mechanism with carbene ions as intermediates. Aguayo et al. [29] proposed a model based on the previous model to quantify the fractions of olefins and gasoline in the products, and considered an autocatalytic step of gasoline fraction formation, as indicated by