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Kinetic modelling of methanol conversion to light olefins process over silicoaluminophosphate (SAPO-34) catalyst

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ABSTRACT

The MTO process over SAPO-34 catalyst was modelled with the consideration of functionality against coke deposition for products distribution, consisting of 11 reactions involving 13 reaction species and used in the assessment of experimental data acquired in a fixed bed reactor in a temperature range from 400 to 460 °C using weight hour space velocity (WHSV) of 1, 2 and 4 g MeOH g catalyst^{-1} h^{-1} and at atmospheric pressure. The results showed that olefins carbon selectivity increases with space velocity, suggesting that the secondary reactions which take part in the MTO reaction for the paraffinic components production are reduced by decreasing contact time. Calculation of the kinetic model parameters of best fit was performed by particle swarm optimization algorithm through solving the mass conservation equations of the reaction products of the kinetic scheme. Pre-exponential factors and apparent activation energies were then calculated based on the Arrhenius equation using the optimized rate constants. The kinetic model gave a good representation of MTO experimental data at conditions close to industrial practice.

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1. Introduction

Todays, the shortage of oil resources has attracted the attention of the scientists to develop a technology for light olefins production from the abundant and relatively cheap resources of natural gas, coal and biomass (Sun et al., 2014). Among the alternative routes, the zeolite catalysed methanol to olefins (MTO) has shown to be a promising process, because methanol can be efficiently produced from syngas obtained through natural gas reforming or carbon gasification (Álvaro-Muñoz et al., 2014). Among molecular sieve catalysts applied in MTO reaction (Bhawe et al., 2012; Castro et al., 2009; Lee et al., 2010; Park et al., 2008; Svelle et al., 2007; Teketel et al., 2011; Wang et al., 2011), the small pore silicoalomonophosphate molecular

sieve SAPO-34, with mild acid strength has shown to have the best catalytic performance (Chen et al., 2005; Wang et al., 2015; Yang et al., 2013). The successful development of commercially applicable MTO technology has been provided in China using the DMTO technology developed by the Dalian Institute of Chemical Physics (DICP) (Tian et al., 2015).

Although the commercialization and technological development of this process has been considerable, kinetic modeling of this complex reaction network with heterogeneous reaction steps has yet needed to be more developed (Gayubo et al., 2005). Kinetic studies are important means to gain a better insight of the overall process so that it can be modified for optimum operating conditions and better yields. For reactor design, simulation of processes that are carried

out at large-scale and from an economic perspective a kinetic model is an indispensable tool. The development of a realistic kinetic model for a process of this type requires detailed information on the mechanism of the reactions. But, due to the extremely complicated reaction route, the reaction mechanism remains a great challenge (Chen et al., 2014). The huge number of fit parameters corresponding to each elementary step contributing to MTO reaction network and the lacking quantitative information on every individual intermediate and product species results in kinetic expressions of high complexness, but of low accuracy and robustness (Van Speybroeck et al., 2014).

The researcher approach when dealing with this complex mixture is to apply lumping, in reaction network and species. In these global kinetic models, the mechanistic aspects are considered in a generic way, and as they are simpler, they benefit from less complicated kinetic parameters estimation and simple use in reactor design (Olsbye et al., 2012). Several kinetic modeling efforts have been reported in the literature for MTO.

Mihail et al. (1983) proposed a kinetic model based on carbenoid intermediates, involving 27 reactions and 18 molecular species. According to the proposed mechanism, dimethyl ether (DME) generates a carbene species which reacts with oxygenates to form the first C—C bond, that subsequently further reacts to form higher olefins. Bos et al. (1995) developed a model with 6 lumps plus coke reacting through 12 reactions. The Bos et al. (1995) reaction network was further simplified by eliminating slower steps, and a kinetic model was developed on SAPO_34, which takes into account four individual steps for the production of ethene, propene, butenes, and remaining hydrocarbons (pentenes + paraffins) (Gayubo et al., 2000). Single event kinetic modeling of MTO on SAPO_34 was developed based on the surface-bonded oxonium methylide mechanism by Alwahabi and Froment (2004). Chen et al. (2007) have distinguished the type of product (stable or unstable, primary or secondary) and the type of deactivation (selective or nonselective) using the yield-conversion plot. Based on the obtained results, the kinetic of MTO reaction was modelled with 7 reactions involving 7 lumps [ethene, propene, butenes (C_4), C_5, C_6, oxygenates, ethane + propane]. Langmuir–Hinshelwood mechanism was also applied in MTO kinetic modeling and methanol, DME, ethylene, propylene and paraffin were taken into account as the reaction species (Fatourehchi et al., 2011).

Although considerable studies have been performed on MTO reaction over SAPO_34, there is no user friendly kinetic model in terms of reaction mechanism, taking into account the effects of coke deposition on products distribution as well as the initial reaction conditions (i.e. temperature, WHSV . . .). In the present work, a lumped (in terms of reaction steps) kinetic model was established based on the simple and reliable reaction network with the consideration of functionality against coke deposition for products distribution, consisting of 11 reactions involving 13 reaction species.

2.   Experimental

The details of experimental reaction setup and the catalyst are identical to those described in our previous works (Behbahani et al., 2014; Rostami et al., 2014). The experimental data was carried out in a stainless steel tubular, fixed-bed reactor (12 mm I.D., 20 cm length). 2 g of SAPO-34 catalyst in powder form with the average particle sizes of 1.6 μm and surface area of 468 m^2 gCatalyst^{-1} was loaded into the reactor in each run. The experiments were performed in a temperature range from 400 to 460 °C using weight hour space velocity (WHSV) of 1, 2 and 4 gMeOH gCatalyst^{-1} h^{-1} and at atmospheric pressure. In order to measure the deposited coke on SAPO_34 during MTO reaction, a set of experiment has been conducted at different initial reaction condition in which the tests were cut off at different times on stream (different coke content) and the partial/complete deactivated catalyst was unloaded from the reactor's bed. Then the samples were sent to Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology at Tsinghua University for quantitative test.

3.   Product distribution analysis

The evolution of different hydrocarbons mole fractions with the time on stream at different industrial operating conditions (different temperature and contact time) is shown in Figs. 1–4. The results clearly show that the ethylene and methane mole ratio increase in the whole time during reaction as TOS increases. As it can be seen in, higher temperature favours ethylene and methane production. Propylene molar fraction has no considerable change by TOS, but according to Fig. 1 decreasing temperature results in more propylene formation. The propane mole ratio was high at the beginning, but it came down with intensive slope. Ethane also had a similar trend with less intensity. This shows that hydride transferring reaction in MTO leading ethane and propane formation from ethylene and propylene, respectively, decreases by coke deposition. This could be due to the fact that acid sites are responsible for hydride transferring reaction and increasing coke content results in lower contribution of these acid sites
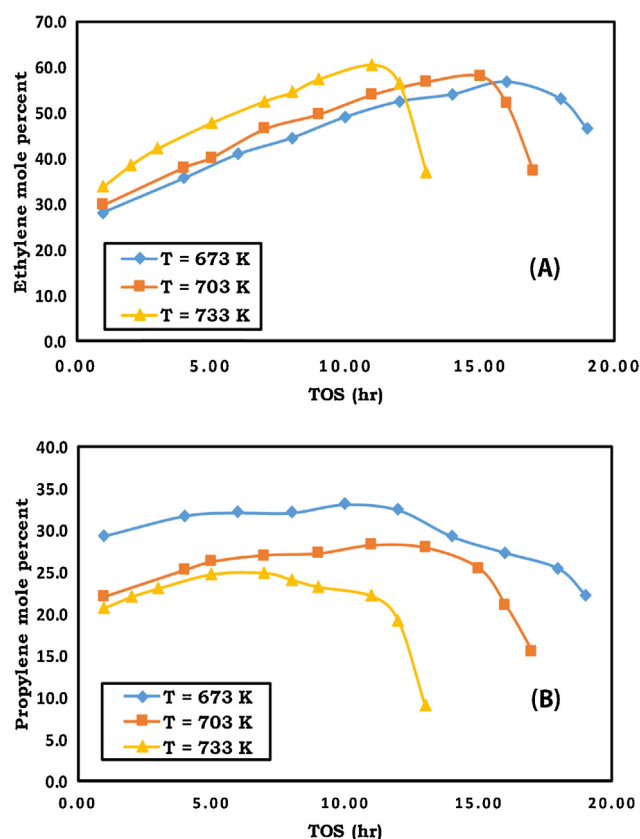

Fig. 1 – Effects of temperature on ethylene (A) and propylene (B) mole percent at WHSV = 2 h^{-1}.