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A Modeling Study on Reaction and Diffusion in MTO Process over SAPO-34 Zeolites

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Highlights

- A reaction-diffusion model was proposed for MTO process on SAPO-34.
- A methodology to derive diffusion coefficient of gases at high temperature is developed
- The influence of diffusion to MTO process under reaction conditions could be revealed

1. Introduction

Methanol-to-olefins (MTO) has received considerable attention since 1970s due to its importance in the production of light olefins from resources other than oil. Despite significant progress in fundamental research in the past decades, a recent milestone is that in 2010 the world's first commercial MTO unit based on the fluidized bed reactor-regenerator configuration was successfully commissioned in north China[1]. This stimulated the rapid development of coal to chemicals industry in China.

In commercial MTO units, catalyst used is exclusively based on SAPO-34 zeolites. The 8-ring windows with size of about 0.38 nm inside SAPO-34 zeolites restrict the diffusion of large and branched hydrocarbons, which is favorable for selectivity to light olefins. It is accepted that in MTO process these large and branched species will further react to form even heavier molecules, i.e. coke, which would possess negative influence on the life time of catalyst and cause a rapid decrease of conversion of methanol [2,3]. However, the direct and *in-situ* experimental study of the reaction and diffusion inside SAPO-34 catalyst remains a non-trivial challenge for scientists and engineers. The measurement of diffusion inside SAPO-34 catalyst has been mostly carried out under non-reactive conditions. How the diffusion affects the product distribution in MTO reaction over SAPO-34 catalyst is yet to be understood.

In this paper, for the first time, we try to use a modeling approach to study the reaction-diffusion process inside SAPO-34 zeolite under MTO reaction conditions.

2. Experimental and simulation methods

In our reaction-diffusion model, the reaction kinetics was based on the dual-cycle mechanism[3] while the diffusion was modeled by the Maxwell-Stefan equation. The diffusion coefficients for methanol and major product were first measured under relatively low temperature range through sorption kinetics method by use of IGA. A correlation between diffusion coefficient and molecular diameter, molecular loading, and coke content was developed. This correlation was further extended to predict the diffusion coefficients of species in MTO at higher temperature. The MTO reaction experiments were carried out in a fixed-bed quartz tubular reactor and the detailed species confined in the catalyst cavities were identified with *ex-situ* GC-MS analysis. A modification and validation of the correlation has been made according to our experimental data. This improved correlation was then used to investigate the reaction and diffusion process inside SAPO-34 zeolites under reactive conditions, with a focus on its influence on life time and product selectivity of catalyst.

Figure 1(a) shows the simplified scheme of the dual-cycle mechanism. In our reaction network, coke has been classified either as active (for example, methyl benzene) or non-active coke (for example, methyl pyrene). A comprehensive single particle model was developed to characterize the reaction and diffusion process within a SAPO-34 catalyst particle under MTO reaction conditions.

3. Results and discussion

Figure 1(b) compares the simulation results with experimental data, which shows a good agreement. The diffusion of methanol molecules under real reaction conditions is shown in Figure 1(c) as a function of coke content on catalyst. As can be seen, with the increase of coke content, the diffusion of methanol first rises and then drops, passing a maximum. This can be explained as that, at initial stage the coke deposited inside the cage is mainly activated coke, which would result in an enhanced interaction between molecules. Beerdsen et al.[4] also found that the diffusivity would go higher with a larger molecule loading. However, as long as the non-active coke forms, the free space inside cage decreases dramatically, causing a rapid drop of diffusivity. The diffusivity for large product molecules is also shown in Figure 1(d) as a function of coke content. Apparently, the coke deposition will limit the diffusivity of large molecules. This can lead to more side reactions inside crystal then accelerates the formation rate of non-active coke. In fact, the space distribution of coke species inside SAPO-34 zeolites could also be obtained, as shown in Figure 1(e).

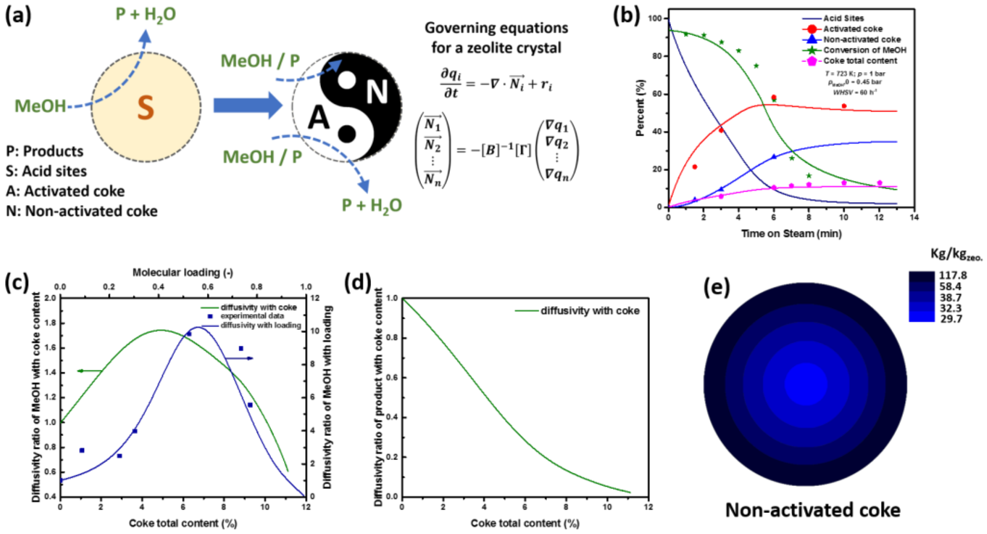

Figure 1. Reaction-diffusion model and simulation results for MTO process over SAPO-34. (a) The simplified scheme of MTO kinetics based on dual-cycle mechanism; (b) Comparison between experimental data and simulation results, (c) The diffusivity of MeOH as a function of coke content and molecule loading; (d) The diffusivity of large molecules as a function of coke content; (e) The distribution of non-active coke inside SAPO-34 zeolites.

4. Conclusions and outlook

A reaction-diffusion model for MTO process over SAPO-34 zeolites was developed, in which the reaction kinetics was based on the dual-cycle mechanism[2,3] while the diffusion was modeled by use of Maxwell-Stefan equation. A correlation between diffusion coefficient and molecular diameter, molecular loading, and coke content was developed, and further extended to predict the diffusion coefficients of methanol and major product gases at higher temperature. Preliminary results show that the relation between methanol diffusion and coke content is in accordance with mechanism reported in literature. In the absence of effective measurement tool, this model can be used to investigate the influence of diffusion on product distribution in MTO process. As the first step towards our ambition to find out the role of diffusion in product selectivity in MTO process, a detailed study on the diffusion of all major gas components is undergoing.

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Keywords
Reaction-diffusion model; MTO; Dual-cycle mechanism; SAPO-34