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Increasing the selectivity to ethylene in the MTO reaction by enhancing diffusion limitation in the shell layer of SAPO-34 catalyst†

Jiawei Zhong, [ID] ‡[abc] Jingfeng Han,‡[a] Yingxu Wei,*[a] Shutao Xu,[a] Yanli He,[a] Yijun Zheng,[a] Mao Ye,[a] Xinwen Guo, [ID] [b] Chunshan Song[bd] and Zhongmin Liu [ID] *[ae]

The zinc cation accommodation in the cavities of the shell layer and the facilitated aromatic formation over the zinc cation modified SAPO-34 with a core–shell like structure introduce extra diffusion limitation for bulky hydrocarbons, which increases the selectivity to ethylene and the ethylene to propylene ratio at the initial stage of the MTO reaction.

Light olefins are important basic chemicals in the petrochemical industry. Owing to the increasing demand for light olefins and the limited reserve of crude oil, the last few decades have witnessed the rapid development of methanol-to-olefin (MTO) conversion processes.[1] In particular, the SAPO-34 catalyst exhibits excellent catalytic performance in the MTO reaction due to its eight-membered ring pore opening, medium to strong acidity and good thermal stability. It is accepted that the MTO reaction follows the hydrocarbon pool (HCP) mechanism, with poly-methylbenzenes and the corresponding carbenium ions as the active HCP species, and the H-transfer reactions between the HCP intermediates with olefin or methanol result in coke formation.[2] SAPO-34 with deposited coke species in the cavity exhibits more remarkable product shape selectivity than the fresh catalyst, and the enhanced selectivity of ethylene and ethylene-to-propylene ratio with time on stream are observed with the proceeding of the reaction.[3] Therefore, in the industrial MTO process, precoked SAPO-34 with suitable carbonaceous deposits is adopted to increase the selectivity to light olefins.[4] Nowadays, ethylene is shown to have a higher economical value compared with propylene, thus, besides employing the precoking process, a new strategy is also required to achieve higher selectivity to light olefin, especially the selectivity of ethylene in the initial period of the MTO reaction, during which ethylene is not predominant.

The cavity structure and acidity of SAPO-34 are important for the MTO reaction. *Via* controlling the coordination states of Si atoms in SAPO-34, suitable acidity can be achieved for light olefin production.[1] Through occupation of the cage (*e.g.* precoking) or the isomorphous substitution of T-atoms in the framework,[5] the modifications of the cavity structure also adjust the product distribution. By contrast to MeASPO-34 synthesis through isomorphous substitution, few investigations are devoted to ion-exchanged SAPO-34, since unsatisfying results are often obtained.[6] The improved catalytic performance of the metal cation modified SAPO-34 is mainly attributed to the adjustment of acidity. However, the mild acidity achieved usually favours the propylene generation, which is attributed to the depression of H-transfer reactions that consume olefin products, especially propylene, and the improvement of the olefin-based reaction route for the production of propylene and higher olefins.[2,7]

The cavity structure of SAPO-34 plays a vital role in product formation.[3b,8] At the beginning of the reaction, upon the contact of methanol with the catalyst, the MTO reaction occurs in the supercages near the external surface of the SAPO-34 catalyst. The fresh catalyst without modification of cavity at this moment cannot exert enough diffusion impacts on the products, which results in the low light olefin selectivity during the initial stage of the MTO reaction.[1–3] So, to improve the initial catalytic performance, metal cation modification was employed to adjust the cavity structure of SAPO-34. Herein, zinc cations were incorporated *via* an ion-exchange method, mainly into the shell layer cavities of SAPO-34 with non-uniform Si distribution and

[a] *National Engineering Laboratory for Methanol to Olefins, State Energy Low Carbon Catalysis and Engineering R&D Center, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: liuzm@dicp.ac.cn, weiyx@dicp.ac.cn; Fax: +86 411 84691570; Tel: +86 411 84379335*

[b] *State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China*

[c] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[d] *EMS Energy Institute, Departments of Energy and Mineral Engineering, and of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

[e] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China*

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‡ J. Zhong and J. Han contributed equally to this work.

Brønsted acidity. The aromatic formation in the cavity was facilitated by the zinc ion, thus enhanced ethylene selectivity is preferably obtained over the zinc cation modified SAPO-34. Based on the elucidation of the structure modification–diffusion restriction–product selectivity relationship in the MTO reaction, a new strategy was proposed for efficient catalyst development with enhanced ethylene selectivity.

The SAPO-34 is a cubic crystal with an average size of approximately 7 µm (Fig. S1 and S2, ESI†). The zinc cation modified SAPO-34 prepared *via* an ion exchange method is denoted as Zn-SAPO-34. The crystallinity of Zn-SAPO-34 is maintained well, and no phases related to the corresponding metal species are observed (Fig. S3, ESI†). Zn-SAPO-34 exhibits a very slight decrease in surface area and pore volume compared with H-SAPO-34 (Fig. S4 and Table S1, ESI†). The intensity of the absorbance bands at 3620 and 3593 cm^{-1} measured using DRIFTS decreases slightly for Zn-SAPO-34 (Fig. S5, ESI†), indicating the substitution of part of protons from Brønsted acid sites by zinc cations,[9] which is in accordance with the ^{1}H MAS NMR (Fig. S6 and Table S2, ESI†).

H_2–TPR profiles (Fig. S7, ESI†) show that the H_2 consumption signal from the reduction of ZnO is absent over Zn-SAPO-34.[10] In the XPS analysis (Fig. S8, ESI†), Zn-SAPO-34 exhibits a binding energy of the Zn $2p_{3/2}$ core level at 1023.2 eV and that of the Zn $2p_{1/2}$ core level at 1046.3 eV.[11] Therefore, the combined analysis indicates that the Zn species exist in the form of zinc cations instead of ZnO. The Zn content in the subsurface determined using XPS is 0.70 wt%, which is higher than that in the bulk (0.34 wt%) determined with XRF (Table S3, ESI†), implying that the exchanged zinc cations mainly located on the subsurface. This is related to the nonuniform distribution of Si atoms in SAPO-34.[1,12] The Si-enrichment at the periphery of the crystal leads to more ion-exchangeable acid sites in the layer near the external surface, thus more zinc cations can be incorporated into this more acidic layer with Si-enrichment. After metal modification, parts of the acidic cavities near the external surface evolve into Zn^{2+}-cavities. Therefore, Zn-SAPO-34 exhibits a core–shell like structure, with a thin Si-rich, Zn-rich and more acidic subsurface, which has also been proved by the EDX analysis (Fig. S9, ESI†).

The MTO reaction was conducted over H-SAPO-34 and Zn-SAPO-34 at 475 °C with WHSV of 2 h^{-1}. Complete methanol conversion can be realized over the two catalysts, and the Zn modification shifts the product distribution and small-sized hydrocarbon products, especially ethylene become more predominant. As shown in Fig. 1 and Fig. S10 (ESI†), compared with SAPO-34 after methanol reaction for 2 min (H-SAPO-34-2min), a remarkable increase in ethylene selectivity of about 40% is realized over the zinc cation modified SAPO-34 (Zn-SAPO-34-2min), and the total selectivity to light olefins after 2 min is enhanced to nearly 75% over Zn-SAPO-34-2min. At this moment, by comparison with Zn-SAPO-34, the initial selectivity of ethylene and light olefins over H-SAPO-34 is approximately 8% and 5% lower, respectively. And the highest selectivity (HS) of light olefins of 81% is attained over Zn-SAPO-34 in a much shorter reaction time than H-SAPO-34. With the predominant generation
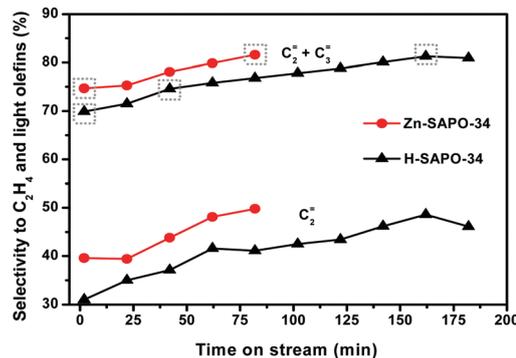

Fig. 1 The selectivity to light olefins and ethylene of methanol conversion over H-SAPO-34 and Zn-SAPO-34 (after methanol reaction for a certain time, these catalysts (in the boxes) were used for further measurements: H-SAPO-34-2min and H-SAPO-34-42min: SAPO-34 after reaction for 2 and 42 min; Zn-SAPO-34-2min: zinc ion modified SAPO-34 after reaction for 2 min; H-SAPO-34-HS and Zn-SAPO-34-HS: H-SAPO-34 and Zn-SAPO-34 with the highest selectivity to light olefins).

of ethylene, the selectivity to C_3H_8, C_4, C_5 and C_6 decreases markedly, though the selectivity to CH_4 increases slightly over Zn-SAPO-34 (Fig. S11, ESI†). Moreover, the methanol reaction over Zn-SAPO-34 for 2 min (Zn-SAPO-34-2min) exhibits similar product distribution to that over H-SAPO-34 for 42 and 62 min (H-SAPO-34-42min and H-SAPO-34-62min) (Fig. S12, ESI†), indicating that zinc cation incorporation efficiently facilitates the transition of a fresh catalyst into a working catalyst. Detailed analysis of the effluent products shows that the metal ion modification does not result in decomposition of CH_3OH, since only a trace amount of CO and CO_2 is detected (Table S4, ESI†).[13] However, the catalyst lifetime is slightly shortened over the catalyst with zinc cation modification (Fig. S13, ESI†).

The acidity of the molecular sieve catalyst plays an important role in olefin generation in the MTO reaction. It is widely acknowledged that the decreased acid density of the SAPO catalyst enhances the selectivity of propylene and higher olefins, which are generated mainly *via* the alkene-based reaction route.[2,7] In the present work, the methanol reaction over the SAPO-34 catalyst with lowered acid strength and acid site density after zinc cation modification leads to an improved selective production of C_2H_4. Therefore, the enhanced selectivity to C_2H_4 over Zn-SAPO-34 cannot be attributed to the adjustment of catalyst acidity with metal cation modification.

It is well recognized that during the MTO reaction over SAPO-34, the selectivity to light olefins, especially C_2H_4, is enhanced with time on stream, which is ascribed to the increased diffusion restriction for the generated hydrocarbon products, stemming from the accumulation of the bulky hydrocarbons, such as polyaromatics, in the cavity during the reaction.[1–3] Therefore, the diffusivities of the hydrocarbon molecule in fresh catalysts, H-SAPO-34 and Zn-SAPO-34, and the methanol-reacted catalysts after different reaction times, H-SAPO-34-2min, Zn-SAPO-34-2min and H-SAPO-34-42min, were evaluated and calculated from the adsorption kinetics curves measured using IGA (eqn (S1), ESI†).[14] Ethane, propane and *n*-butane are used as the probe molecules representing the diffusion properties of C_2, C_3 and

C_4 hydrocarbon products. The diffusivity of ethane, propane and *n*-butane in Zn-SAPO-34 is lower than that in H-SAPO-34 (Table S5, ESI†), which is possibly related with the zinc cation accommodation in the CHA cavities. The decreased diffusivity in Zn-SAPO-34, as the indicator of the introduced diffusion restriction, would contribute to the increase of ethylene production. The organic species deposition in H-SAPO-34 and Zn-SAPO-34 imposes more severe diffusion restriction for the mass transfer of the probe molecules. The diffusivity of ethane in the catalysts after reaction for 2 min, H-SAPO-34-2min and Zn-SAPO-34-2min, was largely reduced, and further decline in diffusivity of ethane is presented at a prolonged reaction time in the catalyst of H-SAPO-34-42min (Table S6, ESI†).

Moreover, for revealing the diffusion restriction caused by the cation exchange in catalyst modification and coke species deposition on the catalyst during methanol conversion, the diffusion properties of ethylene and propylene, the main products of the MTO reaction over the fresh and methanol-reacted catalysts, were evaluated using a chromatographic method. Using ethylene and propylene as the probe molecules provides more realistic mass transport properties of the target products, which is very useful to clarify the critical issue of product selectivity.

Pulses containing ethylene or propylene were injected onto the catalyst bed, and then the concentration of probe molecules ($C(t)$) escaping from the catalyst bed was detected using a mass spectrometer. The residence time distribution (RTD) of the component in the catalyst bed was obtained by eqn (S2) (ESI†), and the RTD curves of ethylene and propylene diffusion in fresh catalysts, H-SAPO-34 and Zn-SAPO-34, and two methanol-reacted catalysts, H-SAPO-34-42min and Zn-SAPO-34-2min, are plotted in Fig. 2.

For the fresh catalysts, H-SAPO-34 and Zn-SAPO-34, the RTD of ethylene and propylene is more dispersive and the mean residence time is longer compared with the catalysts after the methanol reaction, implying the intracrystal diffusion in the fresh catalyst. Ethylene and propylene probing in the SAPO-34 and zinc cation modified catalyst exhibits very close RTD profiles, with a slight difference in the sharper RTD for propylene probing, indicating greater diffusion resistance encountered in propylene diffusion compared with that for ethylene.

With the occurrence of the methanol reaction, coke deposition in the catalyst sets up obstacles for the intracrystal diffusion

in the catalyst (Zn-SAPO-34-2min), and the cut-off of ethylene or propylene molecular transport into the catalyst crystal partially occurs; just a portion of ethylene and propylene penetrates into the catalyst bed *via* diffusion inside the catalyst crystal, while the majority of the probe molecules go through the catalyst bed with intercrystal transport. Therefore, when probing Zn-SAPO-34 after the reaction for 2 min, a sharper RTD profile and a shorter residence time are observed, indicating the severe diffusion hindrance and even the transport cut-off of ethylene and propylene through the eight-membered ring of the catalyst crystals. The cut-off of the entrance of the probe molecule into the catalyst is also a strong signal of the coke location in the cavities of the subsurface of the catalyst crystals.

In the case of severe diffusion resistance from the catalyst with higher coke deposition (H-SAPO-34-42min), the sharp and narrow residence time distribution confirms that the direct penetration with intercrystal transport should be the main mass transport mode of ethylene and propylene, and the intracrystal diffusion is almost prohibited. However, in the case of the MTO reaction, the intracrystal transport of the generated olefin products from the cavities inside the SAPO-34 catalyst to the effluent phase is one of the critical steps for product generation. Among the olefin products, propylene and higher olefins, the relatively large-sized products compared to ethylene, would encounter more severe diffusion resistance and their generation as the effluent products would be depressed. By comparison, small-sized products, such as methane and ethylene, would beneficially appear as the main effluent products.

An interesting performance has been noticed that the selectivity of ethylene over Zn-SAPO-34-2min is close to that over H-SAPO-34-42min. This means that compared to H-SAPO-34, an extra enhancement in ethylene generation was provided by Zn-SAPO-34, besides the contribution from the diffusion limitation with coke deposition over the two catalysts in common.

In methanol conversion over SAPO-34, according to the HCP mechanism, the formed cyclic organic species retained in the catalyst function as the critical intermediates for the olefin generation. The retained compounds in H-SAPO-34 and Zn-SAPO-34 after the reaction were investigated to clarify the important HCP species and coke species. At the beginning of the reaction for 2 min, a chemical environment is quickly established over Zn-SAPO-34 for an efficient MTO reaction with selective production of ethylene. At this moment, the two catalysts with initial organics deposition, H-SAPO-34-2min and Zn-SAPO-34-2min, present very close weight losses in retained organics removal in TG analysis (Fig. 3), but the analysis of the retained organic compounds using GC-MS (Fig. S14, ESI†) shows differences in the deposited aromatic hydrocarbons. As shown in Fig. 3 and Fig. S14 (ESI†), for H-SAPO-34-2min and Zn-SAPO-34-2min, the retained materials are mainly composed of methylbenzenes and methylnaphthalenes, while lower methylbenzenes and methylnaphthalene are more predominantly formed over Zn-SAPO-34-2min than H-SAPO-34-2min. Compared to higher methylbenzenes, the lower methylbenzenes and methylnaphthalenes have been proposed as the important intermediates for ethylene generation in the MTO reaction.[15]
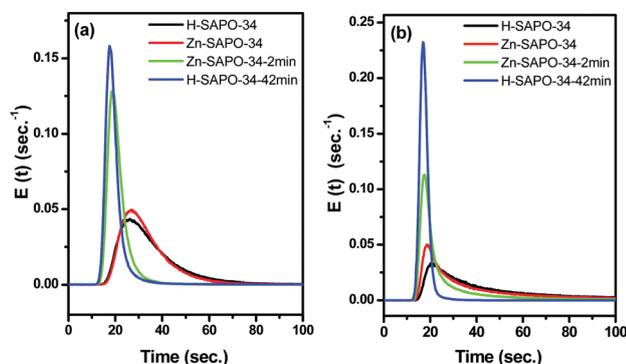

Fig. 2 The effect of coke species accumulation on residence time distribution of ethylene (a) and propylene (b) in the catalyst bed.
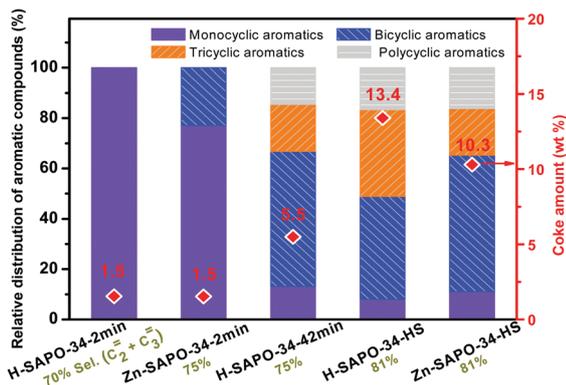
Fig. 3 Coke amount and relative distribution of aromatic compounds in H-SAPO-34 and Zn-SAPO-34 after the MTO reaction (the coked catalysts marked in Fig. 1 were analysed and the selectivity to light olefins is marked in olive-green).

With the proceeding of the reaction, the deposited coke species depress the intracrystal diffusion of large-sized hydrocarbon products and facilitate the production of ethylene. Based on the composition analysis of the coke species and effluent products over the Zn-SAPO-34 catalyst, which present a relatively large fraction of methylnaphthalene among the retained organics and a slight increase of methane selectivity in the effluents, it is speculated that the H-transfer reaction between the methylbenzene and methanol is promoted by the synergic effect from zinc cations as the Lewis acid site and the Brønsted acid sites from bridge hydroxyl groups nearby in Zn-SAPO-34.[16] Besides, zinc cations located in the cavity of SAPO-34 may facilitate the production of aromatics through dehydrogenation, corresponding to the previous report that zinc cation modified ZSM-5 promoted aromatics production.[11a] The quick accommodation of aromatic compounds, especially bicyclic aromatics and polycyclic aromatics, enhances the diffusion hindrance and contributes to the increase of ethylene production in the initial stage of methanol conversion,[3a] indicated by the enhanced ethylene selectivity of 40% over Zn-SAPO-34 after methanol reaction for 2 min (Fig. S10, ESI†). Moreover, the highest selectivity to light olefin is achieved over Zn-SAPO-34 in a short contact time and with a relatively low consumption of coke (Zn-SAPO-34-HS with a coke amount of 10.3 wt%) compared with H-SAPO-34 (H-SAPO-34-HS with a coke amount of 13.4 wt%) (Fig. S15, ESI†).

In conclusion, the MTO reaction using zinc cation modified SAPO-34 as the catalyst with a core–shell like structure showed enhanced ethylene selectivity. With zinc cation modification, an excellent chemical environment can be quickly established in Zn-SAPO-34 for methanol conversion, which contributes to the remarkable improvement of ethylene selectivity in the initial MTO reaction stage. The improved ethylene selectivity is ascribed to the increased diffusion hindrance for hydrocarbon products with a large molecular size. In the shell layer of the catalyst,

the incorporated zinc cation enrichment and the generated coke species accommodation result in the increased diffusion hindrance. Among the retained compounds over Zn-SAPO-34, lower methylbenzenes and methylnaphthalenes are more predominant, which induce the methanol reaction to light olefins with ethylene as the main product. An effective way for manipulating the olefin production from methanol conversion can be proposed, based on the development of the Zn-SAPO-34 catalyst and the correlation of the product selectivity variation to the organic species-induced reaction and mass transport in the dynamic process of the MTO reaction.

Conflicts of interest

There are no conflicts to declare.

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