



Excellent catalytic performance of Cu⁺ modified HZSM-5 to produce *para*-xylene via the toluene methylation reaction: High catalytic active site combining with channel shape selectivity

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ABSTRACT

The toluene methylation reaction via methanol is an important process to produce high-value *para*-xylene (PX), it has always been our goal to explore a catalyst with high activity and selectivity for PX. Cu⁺ is used to modify HZSM-5 (BAS/Cu⁺-HZSM-5) zeolite, and the microscopic reasons for the excellent catalytic performance to produce PX on BAS/Cu⁺-HZSM-5 are investigated according to the intrinsic reaction and molecular diffusion. The intrinsic activation energies of methanol dissociation and xylene formation on BAS/Cu⁺-HZSM-5 are obtained by the density functional theory (DFT). Calculations indicate that the energy required for methanol dissociation is 109.7 kJ mol⁻¹, which is lower than that on pure HZSM-5. In addition, PX, *meta*-xylene (MX) and *ortho*-xylene (OX) formed with little activation energies of 12.7, 11.8 and 14.2 kJ mol⁻¹, respectively. Therefore, the formation of these xylenes on BAS/Cu⁺-HZSM-5 has high activity and strong competition. On the other hand, the self-diffusion coefficients of three xylenes on BAS/Cu⁺-HZSM-5 are analyzed by molecular dynamics (MD) simulation. And the self-diffusion coefficient of PX is found to be much larger than that of MX and OX in all cases, which indicates that the channel characteristics of BAS/Cu⁺-HZSM-5 are beneficial to the diffusion and separation of PX. Therefore, it can be concluded that BAS/Cu⁺-HZSM-5 has better catalytic performance and high PX selectivity for the toluene methylation reaction via methanol.

1. Introduction

Xylene is widely used in various petrochemical industries. Especially *para*-xylene (PX) has become an important organic chemical raw material in daily production and life due to its excellent characteristics. Toluene methylation reaction via methanol can directly convert low-value toluene and methanol into high-value PX, which is considered to be an efficient and sustainable technology that can meet the growing demand for aromatics [1–3]. However, the low yield of xylene and the difficulty in separating PX from mixed xylenes are the key points and difficulties during this reaction process [4]. Therefore, exploring better catalysts to enhance xylene yield and PX selectivity is the most

challenging [5].

A lot of research has been done to explore the suitable zeolites for producing xylene. The TNU-9, SSZ-33, ZSM-5 and MOR zeolites were used as catalysts for the toluene methylation reaction via methanol by Odedairo et al. [6], and it was found that ZSM-5 with microporous channels had the highest selectivity for xylene. By comparing with the performances of MOR, MCM-22, SAPO-11, SAPO-5 and ZSM-5 zeolites in the toluene methylation reaction, Zhu et al. [7] also found that the ZSM-5 zeolite with 10-membered ring channels and moderately strong acids exhibited higher selectivity to xylenes and conversion rate of toluene than other zeolites. In addition, as reported by Joshi et al. [8], ZSM-5 zeolite exhibited higher yield of xylene and PX selectivity in the

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toluene methylation reaction via methanol compared with ZSM-12 zeolite. Therefore, ZSM-5 zeolite is widely used as a catalyst for the toluene methylation reaction via methanol due to excellent catalytic performance and channel shape selectivity [9–11]. Previous studies reported that the selectivity of aromatics on HZSM-5 could reach 30–40%, but the production of a large amount of alkanes was an important factor affecting selectivity [12–14]. Different metal species have been loaded in the channel of ZSM-5 to improve the yield of aromatics. The Ag modified ZSM-5 had better aromatic selectivity than Zn modified ZSM-5, and conditions such as reaction temperature, methanol partial pressure, and contact time had greater impact on the distribution of the products [15]. The researchers investigated the selectivity of aromatics by modifying ZSM-5 with various metals, including Ag, Ni, Ru, and Cu. And they found that the introduction of Ag could improve the selectivity for C6–C8 aromatic products compared with the initial ZSM-5, Ni modified ZSM-5 improved selectivity for naphthalene derivatives, and the Cu⁺ modified ZSM-5 had higher selectivity to C9–C11 aromatic products [16]. Aiming at improving the selectivity of PX during toluene methylation reaction via methanol, ZSM-5 zeolite was modified with Pt species by Aboul-Gheit et al. [17], and the results showed that the PX selectivity increased with the increase of Pt content. It was also showed that the dispersion of Pt not only could adjust the acidity strength and magnitude in ZSM-5, but also had a strong effect on the channel size. The use of La, Ce, and Nb species modification in HZSM-5 could tune the conversion rate of toluene. And since the excess metal species could block the channels of the catalyst and inhibit the activity of the active sites inside the catalyst, the La-ZSM-5 zeolite had the highest selectivity (98%) to xylene with the metal species loading of 10% [18]. Additionally, the HZSM-5 catalyst was modified with various metal species by Zhao et al. [19], and it could be observed that the modification with Pt, Pd, Co and Ni species could promote the selectivity of PX reaching more than 98.3%, and the conversion rate of toluene could reach 20.0% in the toluene methylation reaction via methanol, and the stability of the catalyst could be greatly improved. It can be seen that the metal modified ZSM-5 could significantly improve the selectivity and yield of PX.

Meanwhile, the metal species in the channels can affect the distribution of Brønsted acid (BAS) and Lewis acid (LAS) in ZSM-5, which affect the mechanism of intrinsic reaction and activation energy barrier, and regulate the performance of zeolite. BAS, the Si–OH–Al framework structure, is mainly the OH group bridged by the ZSM-5 framework [20]. While LAS generally refers to the extra-framework Al (EFAl) materials, which mainly releases Al from the ZSM-5 framework. Moreover, LAS can also be formed by metal ions exchange with protons bridged on the framework O in BAS during the modification process [21,22]. By using incipient wetness impregnation to prepare Cd modified HZSM-5 and studied its effect on aromatic generation, Zhang et al. [22] found that when Cd was used as modified metal, it could be exchanged with the protons on the framework O in BAS, leading to the formation of new LAS in the catalyst and the reduction of the number of BAS. As the number of LAS increased, the selectivity of PX was also increasing. In summary, metal modification can effectively increase the yield and selectivity of PX by introducing the LAS.

The experimental results showed that the modification of Cu⁺ in ZSM-5 was beneficial to promote methanol adsorption, enhance the catalytic performance of the zeolite, and the selectivity of PX had also been significantly improved. Zaidi et al. [23] implemented methanol to hydrocarbon reactions on HZSM-5, CuO/HZSM-5, ZnO/HZSM-5 and CuO/ZnO/HZSM-5, and found that after CuO was added to the ZnO/HZSM-5, the conversion of methanol and aromatics selectivity were improved. The bimetallic catalyst Zn–Cu-ZSM-5, which simultaneously supported Zn and Cu, not only had higher structural stability, but also had enhanced catalytic performance. At the same time, the yield of PX was increased, and the heavy aromatic products that had an adverse effect on the reaction were reduced [24]. The results of the methanol to aromatics conversion reaction under N₂ flow showed that

the Cu/ZSM-5 was beneficial to increase the yield of PX [25]. Similarly, HZSM-5 zeolite was modified with various metal oxides by Si et al. [26], and the results showed that the modification of HZSM-5 with 10% CuO could improve the selectivity to PX in the toluene methylation reaction via methanol. Adebajo et al. [27] also found that the CuZSM-5 could increase the conversion rate of methanol compared with HZSM-5. It can be concluded that the modification of Cu in ZSM-5 is the preferred catalyst for methanol toluene methylation: better stability, enhanced reactivity and higher PX selectivity make it become the focus of research gradually.

Besides the intrinsic reaction, the unique channel structure of zeolite plays an important role in improving the diffusion of molecules in zeolite channels and achieving high selectivity to target species. The uniqueness of zeolite largely lies in its shape selection catalytic performance, because most of catalytic activity of zeolite are located in the channels of zeolite, so only the size and shape of zeolite channels matching molecules can be involved in the catalytic reaction process. When the modified metal cations form LAS on HZSM-5 framework, they would occupy the channel space of HZSM-5, increasing the space restriction on the products, which is manifested by the selectivity of channels to the products. This channel shape selectivity has huge impact on the adsorption and diffusion of products in HZSM-5. By studying the influence of different metal modification on HZSM-5, Zhu et al. [28] found that the introduction of Zn species greatly enhanced dehydro-cyclization reaction, and the modification of Mg increased the diffusion resistance of MX, OX and other PX isomers, thereby enhanced the selectivity to PX. Lai et al. [29] studied the influence of introduction of Ga on the channels structure and the activity of ZSM-5, found that the Brønsted acid sites combined with Ga species in synergy to improve the aromatization activity, and a large number of micropores improved aromatics selectivity via synthesizing Ga-doped ZSM-5. The above examples showed that the formation of aromatics was closely correlated with the acid sites and the size of ZSM-5 channels. Therefore, it is necessary to investigate the influence of BAS/LAS in metal modified ZSM-5 on the mechanism of the toluene methylation reaction via methanol to produce xylene from the perspective of intrinsic reaction, and to explore the influence of channel shape selectivity of metal modified ZSM-5 to the *para*-xylene from the perspective of molecular dynamics.

Taking Cu⁺ modified ZSM-5 as the main catalyst, the reaction route of toluene methylation reaction via methanol on BAS/Cu⁺-HZSM-5 will be studied in the first section by using the density functional theory (DFT), and the activation energy of each elementary reaction will be analyzed for the catalytic activity of BAS/Cu⁺-HZSM-5 for this reaction. And the second part is that the diffusion of three kinds of xylene in Cu⁺ modified ZSM-5 through molecular dynamics simulation will be investigated, and their self-diffusion coefficients at different temperatures and different concentrations will be analyzed. Hope to clarify the reason of excellent catalytic performance of Cu⁺ modified HZSM-5 to produce *para*-xylene via the toluene methylation reaction.

2. Computation details

2.1. DFT calculation

2.1.1. Calculation methods

This calculation based on DFT was completed by using the Vienna ab initio simulation package (VASP) program, and due to the advantages of the generalized gradient approximation (GGA) in surface and channel reaction studies, we used it for all calculations [30–34]. Perdew-Burke-Ernzerhof (PBE) was used as the exchange-correlation functions [35]. When representing electron-ion interactions we used projected augmented wave (PAW), and set 400 eV (1 eV = 96.485 kJ mol⁻¹) as the plane wave basis set cutoff energy [36,37]. The SIGMA value was set to 0.2 eV using the Gaussian smearing method and the ISPIN value was 2 for spin polarized calculation [38,39]. Γ -point was

more reasonable for the Brillouin zone sampling and was mentioned in many theoretical studies of toluene methylation reaction via methanols [40,41]. The force threshold in all optimizations was estimated to converge at $0.05 \text{ eV } \text{\AA}^{-1}$ ($1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$) and the energy of all atoms was converged to $1 \times 10^{-5} \text{ eV}$ [41,42].

The climbing-image nudged elastic band (CI-NEB) method was used to locate the transition structure, and this structure was optimized by using the dimer method to obtain the most stable transition states (TSs) between reactants and products in the elementary reaction [43–45]. When the force threshold on the reacting molecule was less than $0.07 \text{ eV } \text{\AA}^{-1}$, the transition state was considered to reach the convergence criterion [39]. The activation energy barrier (E_a) and reaction energy (E_r) of each step were calculated by the following equations (1) and (2), respectively:

$$E_a = E_{\text{TS}} - E_{\text{IS}} \quad (1)$$

$$E_r = E_{\text{FS}} - E_{\text{IS}} \quad (2)$$

where E_{TS} corresponded to the energy of the transition state, E_{IS} and E_{FS} were that of the reactant and product of the elementary reaction, respectively.

2.1.2. Calculation models

The HZSM-5 model used for the calculation is the cluster model, which is derived from the MFI structure in the crystallographic structural data. Because the cluster model can qualitatively describe the research related to the reaction compared with the periodic model [41]. Meanwhile, the 46T cluster model could not only simulated the confinement effect of periodic HZSM-5 zeolite, but also could more conveniently describe the transition state, therefore the 46T cluster HZSM-5 zeolite catalyst model was constructed for the study of toluene methylation reaction via methanol [46,47]. H atoms were used to replace the original terminal O atoms to eliminate the boundary effect of the cluster model, and the terminal Si–H bond length was set to 1.470 \AA [48]. There were 12 different T sites in HZSM-5. Among them, the Si at the T12 position was most easily to be substituted, and T12 was a site at the interconnection of straight channel and zigzag channel in ZSM-5, which could provide the largest reaction space for toluene methylation reaction, which was beneficial to the progress of this reaction [49]. Therefore, in HZSM-5, an Al atom was used to replace the Si atom at T12

site, then a H atom was used to compensate for the excess negative charge $-e$, forming Al12–O(H)–Si3 [50–52], as shown in Fig. 1.

The extra-framework Cu^+ was introduced in HZSM-5 zeolite to form BAS/ Cu^+ -HZSM-5 zeolite and the role of extra-framework Cu^+ was to balance the negative charge generated by the substitution of Al for Si to form LAS. Therefore, on the 10-MR of the zigzag channel of HZSM-5 zeolite, Al atom replaced the Si atom at T3 site between two framework O atoms to form the structure of Al–O–Si–O–Al. Subsequently, in order to maintain the electrical neutrality, the Cu^+ bonded with two framework O atoms adjacent to Al to forming the LAS site. As shown in Fig. 1, the distance between Cu^+ and BAS was 3.852 \AA [43,53]. The stoichiometric number of BAS/ Cu^+ -HZSM-5 zeolite with 46T was $\text{Si}_{44}\text{Al}_2\text{CuO}_{68}\text{H}_{49}$, the active sites $\text{O}_3\text{SiO}(\text{H})\text{Al}(\text{OSiO}_3)_3$, Cu^+ and $\text{Al}^{3+}(\text{OSiO}_3)_4$ were relaxed, the rest of the atoms were fixed. In addition, in order to consider the different LAS site according to the different Al substitution positions, Al was used to replace Si atom at T2 site to form the structure of Al–O–Si–O–Si–O–Al. And the structure of BAS/ Cu^+ -HZSM-5' with Al–O–Si–O–Si–O–Al was shown in Fig. S1. The activation energy of methanol dissociation was studied on the two zeolite models, and it was found that a higher energy barrier was needed to be overcome on BAS/ Cu^+ -HZSM-5' than that on BAS/ Cu^+ -HZSM-5, as shown in Fig. S2. Therefore, we did not consider this structure in the subsequent reaction process.

2.2. Molecular dynamics simulations

2.2.1. Simulation models

Periodic ZSM-5 zeolite model with the cell parameter of $1 \times 1 \times 2$ was used in molecular dynamics simulations [54]. This model was a pure silicon model with the cell contained 192 T sites. Subsequently, Al atom substituted Si atom at T12 position, and used H atom to compensate for the excess negative charge $-e$ to form BAS. Then extra-framework Cu^+ was introduced in HZSM-5 to form the BAS/ Cu^+ -HZSM-5 zeolite containing both BAS and LAS. This model ensured that the extra-framework Cu^+ existed in the cross cavity of each straight channel and zigzag channel, and its structural molecular formula was $\text{Si}_{184}\text{Al}_8\text{Cu}_4\text{O}_{384}\text{H}_4$, as shown in Fig. 2.

2.2.2. Simulation methods

The Sorption module and Forcite module of Materials Studio 8.0

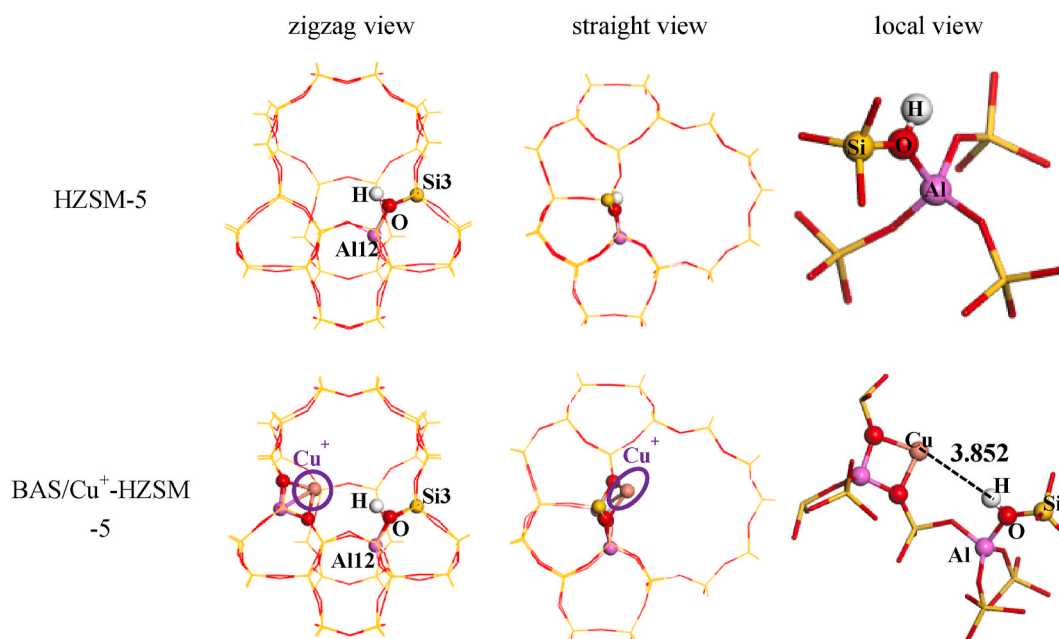


Fig. 1. The calculated models for HZSM-5 and BAS/ Cu^+ -HZSM-5 with the perspective of zigzag view, straight view and local view.

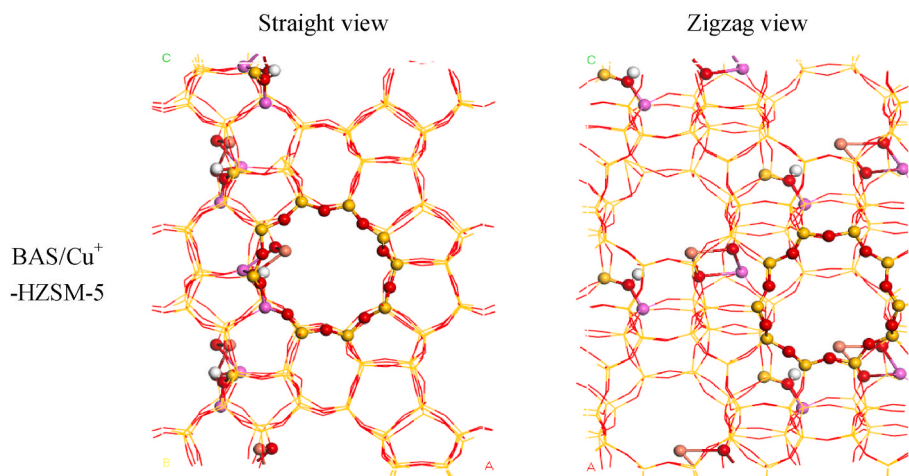


Fig. 2. The simulation model for BAS/Cu⁺-HZSM-5 with the perspective of straight view and zigzag view.

were used for molecular dynamics simulations [55–57]. Since the COMPASS force field as an ab initio force field was suitable for simulation in most polymers, organic and inorganic small molecules, it was used for the dynamics simulations in this work [58]. Calculation of van der Waals potential energy by atom based technique and electrostatic potential energy by Ewald summation technique [54,56]. The cutoff distance was set to 9.5 Å, which was because the length of the cut-off radius was generally slightly less than half of the shortest length of the cell [56,57]. The buffer width and spline width were 0.50 and 1.00 Å, respectively.

The NVT ensemble was used in Forcite module, and in order to ensure a good energy conservation effect, the simulation time step should be small enough, so the simulation time step was 1.0 fs. The number of simulation steps were 1700 ps, the first 200 ps were number of balance steps, and the last 1500 ps were number of analysis steps. During the simulation, trajectories were saved every 1000 steps in preparation for further analysis. And Nosé-Hoover thermostat was used for temperature regulation in the simulations [59]. Sixteen independent MD simulations were performed for each calculation and the middle eight data were adopted to obtain better statistics.

The mean square displacement (MSD) of diffuser was recorded every 1000 steps. And the self-diffusion coefficient (D_s) was obtained by calculating these data using the Einstein equation:

$$D_s = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r(t) - r(0)|^2 \rangle \quad (3)$$

where D_s corresponded to the self-diffusion coefficient, $r(0)$ and $r(t)$ referred to the position vector of the molecules at time 0 and t , respectively [57].

3. Results and discussion

3.1. Intrinsic reaction of xylenes formation in BAS/Cu⁺-HZSM-5

3.1.1. Reaction mechanism of xylene formation in BAS/Cu⁺-HZSM-5

The introduction of Cu⁺ will form LAS sites in ZSM-5 zeolite, it has great influence on the reaction of toluene methylation reaction via methanol. We will explore the reaction mechanism of toluene methylation reaction via methanol over BAS/Cu⁺-HZSM-5 at first. As shown in Fig. 3, the first process is the dissociation of methanol. Methanol is adsorbed on acid site, and the C–O bond of methanol is broken, then the hydroxyl combines with H on zeolite to generate H₂O. The second process is the formation of xylenes. The methyl group closes to the *para*, *meta*, and *ortho* position of toluene gradually and reacts with them to form intermediate-C₈H₁₁⁺. Then this intermediate interacts with adjacent

framework O to form the new BAS and xylene after a deprotonation process. This process is similar to the formation of xylenes on HZSM-5 [4,60].

3.1.2. Dissociation of methanol on Cu⁺ modified HZSM-5

The dissociation process of methanol at acidic sites will be discussed in this section. The energy barrier diagrams and corresponding structures of reactant, transition state and product are illustrated in Fig. 4. In BAS/Cu⁺-HZSM-5, methanol prefers to adsorb at Cu⁺ of LAS by side-on model and be dissociated. In this process, the O atom of CH₃OH towards directly to Cu⁺, and then C–O bond in CH₃OH is broken leading to methyl and hydroxyl are adsorbed at Cu⁺. During this process, the distance between C atom in CH₃OH and Cu⁺ shortens from 2.901 Å in reactant via 2.126 Å in transition state to 1.947 Å in product, while the bond length of O–Cu⁺ shortens from 1.907 Å to 1.832 Å via 1.890 Å in TS1. The activation energy corresponding to this step is 109.7 kJ mol⁻¹, which is lower than that reported by Wen et al. [61] (145.0 kJ mol⁻¹) and Arstad et al. [62] (187.0 kJ mol⁻¹) for the dissociation of methanol on HZSM-5 zeolite. Meanwhile, the dissociation of methanol on HZSM-5 zeolite was investigated in our previous work [5]. During this process, methanol was adsorbed on the BAS of HZSM-5, and then dissociated to form methyl and H₂O molecule with an activation energy of 230.8 kJ mol⁻¹, which was much larger than that in BAS/Cu⁺-HZSM-5 (109.7 kJ mol⁻¹). And we also found that methanol was easier to dissociate on BAS/AlOH²⁺-HZSM-5 due to the lower dissociation activation energy of methanol (68.2 kJ mol⁻¹) compared with BAS/Cu⁺-HZSM-5. But the activation energy required for methanol dissociation on BAS/ZnOH⁺-HZSM-5 (113.9 kJ mol⁻¹) was similar to that on BAS/Cu⁺-HZSM-5. In addition, some relevant experimental studies have also shown that the introduction of Cu into HZSM-5 zeolite was beneficial to the dissociation of methanol. The HZSM-5 zeolite modified by CuO (CuO/HZSM-5) could increase the conversion rate of methanol from 38 to 97 wt% [23], and the CuZSM-5 could increase the conversion rate of methanol from 32.8 to 43.9 mol% by the research of Adebajo et al. [27]. Therefore, it can be concluded that methanol is more prone to dissociate on BAS/Cu⁺-HZSM-5, which is conducive to providing sufficient methyl groups for subsequent methylation reactions.

Besides, the existence of CuOCu²⁺ as active site has been confirmed from the experimental and theoretical perspectives [63,64], respectively. Therefore, the active site of CuOCu²⁺ will also be studied and analyzed here. The structure of BAS/CuOCu²⁺-HZSM-5 is shown in Fig. S3.

The energy barrier diagram of methanol dissociation on BAS/CuOCu²⁺-HZSM-5 and the corresponding structure diagrams of reactant, transition state and product are illustrated in Fig. S4. In BAS/CuOCu²⁺-HZSM-5, methanol prefers to adsorb at BAS by side-on model.

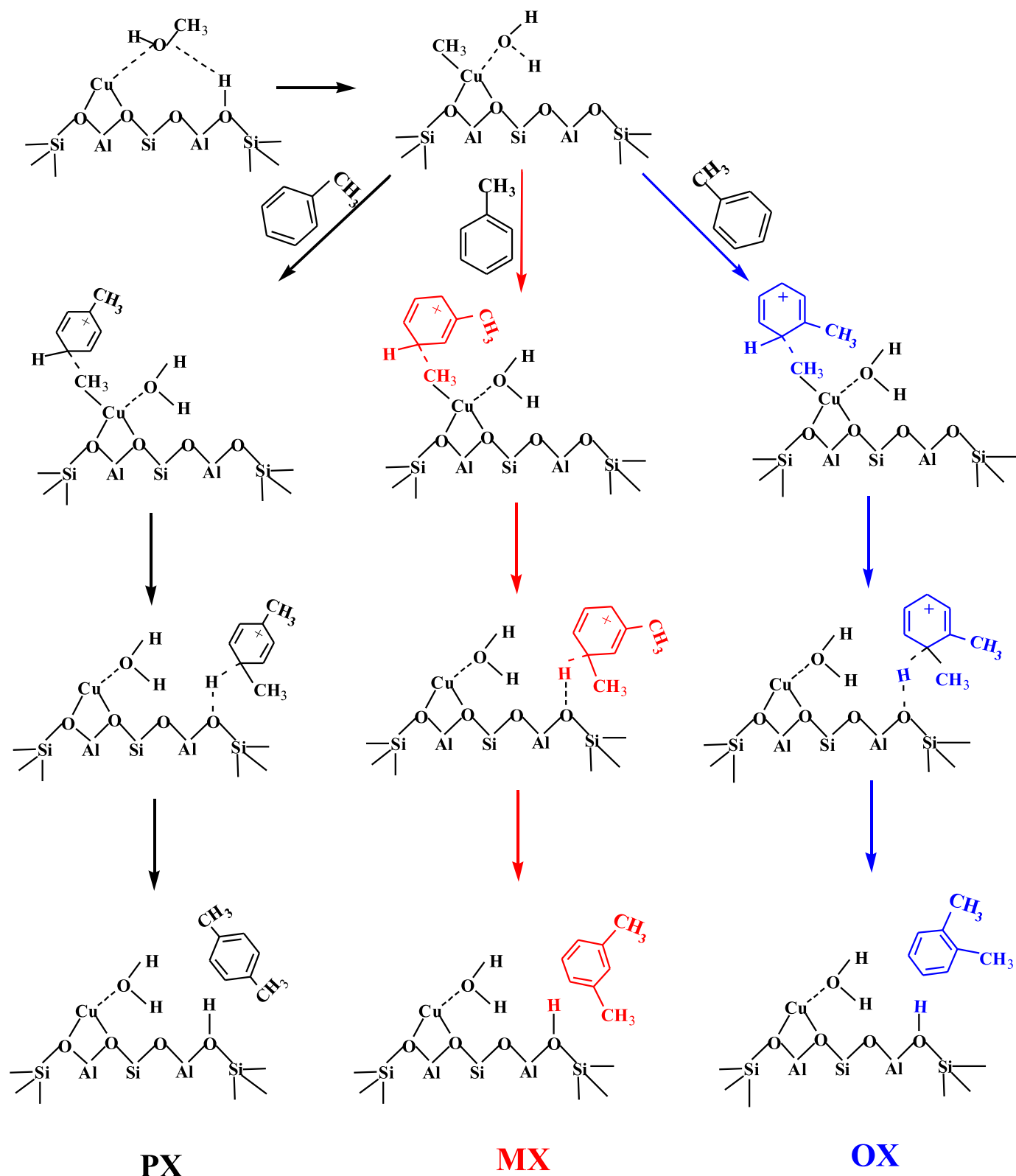


Fig. 3. The toluene methylation reaction via methanol over BAS/Cu⁺-HZSM-5.

And in this process, the O atom of CH₃OH is oriented towards to H atom on BAS directly. Then the C–O bond in CH₃OH is broken leading to the formation of methyl and hydroxyl, the C atom in methyl forms a bond with O atom in CuOCu²⁺. While the H atom in BAS forms a bond with O atom in hydroxyl to generate H₂O, which is adsorbed on Cu atom of the

CuOCu²⁺. During this process, the distance between C atom in CH₃OH and O atom in CuOCu²⁺ shortens from 2.949 Å in reactant via 2.269 Å in transition state to 1.437 Å in product. While the distance between O atom in CH₃OH and proton in BAS shortens from 1.544 Å to 1.028 Å via 1.232 Å in TS1. The activation energy corresponding to this step is

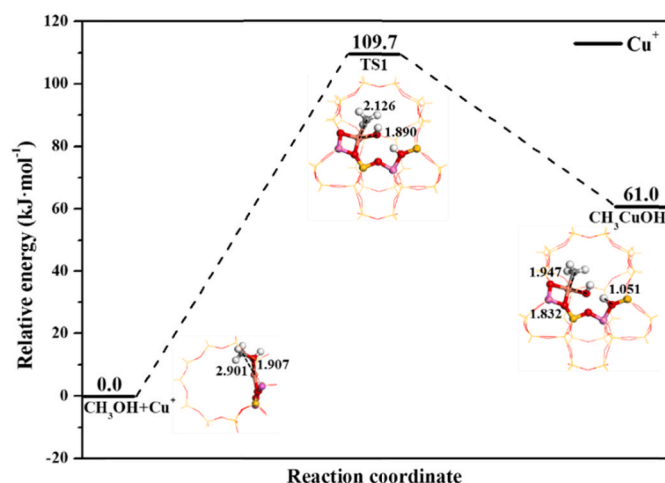


Fig. 4. The relative energy diagram and the reactant, transition state (TS) and product structures about the dissociation of methanol in BAS/Cu⁺-HZSM-5.

180.9 kJ mol⁻¹. It can be concluded that methanol is more prone to dissociation on BAS/Cu⁺-HZSM-5 (109.7 kJ mol⁻¹) compared with BAS/CuOCu²⁺-HZSM-5. Therefore, we did not consider BAS/CuOCu²⁺-HZSM-5 in the subsequent reaction process due to the higher activation energy of methanol dissociation.

3.1.3. Formation of xylene products

Toluene molecule enters the channel of BAS/Cu⁺-HZSM-5 zeolite, and different positions of carbon atoms in toluene towards to the methyl group on Cu⁺ will lead to the formation of different products. H atom on BAS bonds with the hydroxyl group on Cu⁺ will form water molecule, as shown in Fig. 5. In this figure, 'MB' represents the toluene. 'X' and 'ZOH' represent the xylene and the BAS/Cu⁺-HZSM-5 with H atom, respectively. In the *p*-ads structure, the distance between C atom in *para* position of toluene and C atom in methyl is 2.998 Å, and then the intermediate *p*-C₈H₁₁⁺ is formed when methyl attacks the *para* position of toluene. The corresponding bond length of C-C shortens to 1.591 Å in intermediate via 2.355 Å in *p*-TS2, and the activation energy is 12.7 kJ mol⁻¹. Similarly, intermediates *m*-C₈H₁₁⁺ and *o*-C₈H₁₁⁺ are formed when methyl groups attack the *meta* and *ortho* position of toluene, respectively. Calculations indicate that the corresponding activation energies are only 5.5 and 1.9 kJ mol⁻¹, respectively. They are significantly lower than the activation energies previously accounted by Wen et al. [61] (127.0, 105.0 and 106.0 kJ mol⁻¹) for these processes in HZSM-5 zeolite. During the formation of *m*-C₈H₁₁⁺, the distance between C atom in *meta* position of toluene and C atom in methyl shortens from 3.107 Å in *m*-ads via 2.549 Å in *m*-TS2 to 1.587 Å in *m*-C₈H₁₁⁺. And the C-C bond is also shortened to 1.583 Å during the formation of *o*-C₈H₁₁⁺. Meanwhile, H atom at BAS bonds with the hydroxyl group on the Cu⁺, leading to the formation of water.

Subsequently, the C₈H₁₁⁺ intermediate is rotated in order to the deprotonation process of C₈H₁₁⁺ intermediate and the H restoring to the framework oxygen of ZSM-5. The corresponding rotation energies are -55.6, -32.6, and 9.6 kJ mol⁻¹, respectively, indicating that rotation of *o*-C₈H₁₁⁺ is an endothermic process. The deprotonation energy of *p*-C₈H₁₁⁺ is only 1.5 kJ mol⁻¹, as well as 11.8 and 14.2 kJ mol⁻¹ for the deprotonation of *m*-C₈H₁₁⁺ and *o*-C₈H₁₁⁺. And the distance between H in C₈H₁₁⁺ and O in framework gradually shortens from intermediate via TS3 to product.

It can be seen that the activation energies of PX, MX and OX formation are 12.7, 11.8, and 14.2 kJ mol⁻¹ in BAS/Cu⁺-HZSM-5 via methyl groups attacking different sites of toluene. In addition, in our previous work [5], it was found that the formation of the C₈H₁₁⁺ intermediate and the production of xylene were carried out on BAS in HZSM-5 zeolite. And the corresponding activation energies of PX, MX

and OX formation were greatly up to 66.2, 81.5, and 90.9 kJ mol⁻¹, respectively. Meanwhile, we found that the activation energies for the formation of xylenes on BAS/AlOH²⁺-HZSM-5 were as high as 129.2, 153.1 and 140.5 kJ mol⁻¹ compared with BAS/Cu⁺-HZSM-5. While although the activation energies of xylenes formation (92.9, 133.6 and 109.4 kJ mol⁻¹) in BAS/ZnOH⁺-HZSM-5 were higher than BAS/Cu⁺-HZSM-5, but BAS/ZnOH⁺-HZSM-5 have higher selectivity to PX due to the relatively low activation energy of PX formation. And it is reported by Wen et al. [61] that the activation energies of xylenes formation were 127.0, 105.0, and 106.0 kJ mol⁻¹ in HZSM-5, respectively. These results indicate that xylenes are more likely to be produced in BAS/Cu⁺-HZSM-5. However, the energy required to form PX is only 0.9 kJ mol⁻¹ higher than MX, and 1.5 kJ mol⁻¹ lower than OX. This result indicates that generation of three xylenes in BAS/Cu⁺-HZSM-5 is a strongly competitive reaction, and the selectivity of PX is very poor.

3.2. Molecular dynamics simulations of xylenes diffusion in BAS/Cu⁺-HZSM-5

Results of DFT calculations found that PX selectivity is poor in the toluene methylation reaction via methanol in BAS/Cu⁺-HZSM-5. Aiming at studying the xylenes selectivity in BAS/Cu⁺-HZSM-5, more importantly, to investigate the selectivity to PX, the diffusion properties of xylenes in the zeolite will be studied through molecular dynamics simulations, and the channel shape selectivity of BAS/Cu⁺-HZSM-5 to PX will be discussed.

3.2.1. Diffusion at different temperatures

The diffusions of three types of xylenes in the case of six xylene molecules loaded in BAS/Cu⁺-HZSM-5 are studied at different temperatures, and the effect of channel shape selectivity of zeolite in the separation process of mixed xylenes will be discussed.

As given in Fig. 6, we obtain the anisotropic MSD of these xylenes in BAS/Cu⁺-HZSM-5 at different temperatures. It can be found that the anisotropic self-diffusion coefficients of three types of xylenes along the Y direction are the largest. The similar phenomenon was also observed in pure silicon ZSM-5, in where the ethanol and water have the largest anisotropic self-diffusion coefficients in the Y axis direction [56]. The reason is that the straight channel of ZSM-5 zeolite is more prone to diffusion, which is parallel to the Y axis direction. While the zigzag channel, located in the *xz*-plane, is more difficult for the diffusion of xylenes than the straight channel.

The self-diffusion coefficients are shown in Fig. 7 and Table 1. It can be found that the self-diffusion coefficient of PX increases drastically, from 9.75×10^{-12} to 162.96×10^{-12} m² s⁻¹, when the temperature increases from 400 to 800 K. In addition, although the self-diffusion coefficients of MX and OX have not changed significantly, they also tend to increase. The self-diffusion coefficient of MX rises from 3.56×10^{-12} m² s⁻¹ at 400 K to 3.59×10^{-12} m² s⁻¹ at 800 K, corresponding that of OX from 1.88×10^{-12} to 3.18×10^{-12} m² s⁻¹. This phenomenon shows that the diffusions of all three types of xylenes will be promoted with the increasing of temperature. Moreover, it can be found that in all cases, the diffusion rate of PX is greater than that of MX and OX. This is owing to the critical diameters of MX and OX are closer to the maximum channel diameter of BAS/Cu⁺-HZSM-5, while the critical diameter of PX is smaller than that of MX and OX. It makes PX easier to move from one position to the other in the channels of zeolite, this is similar to the description of Bu et al. [54] for the diffusion processes of xylenes in HZSM-5 zeolite.

3.2.2. Diffusion at different concentrations

The diffusion rate of xylene is closely related to the temperature, and the movement of xylene molecules is also related to the interaction between channel walls of the zeolite and xylene molecules. In addition, the number of diffusion molecules also affects the diffusion behavior. As the concentration of the diffusate changes, the self-diffusion coefficients

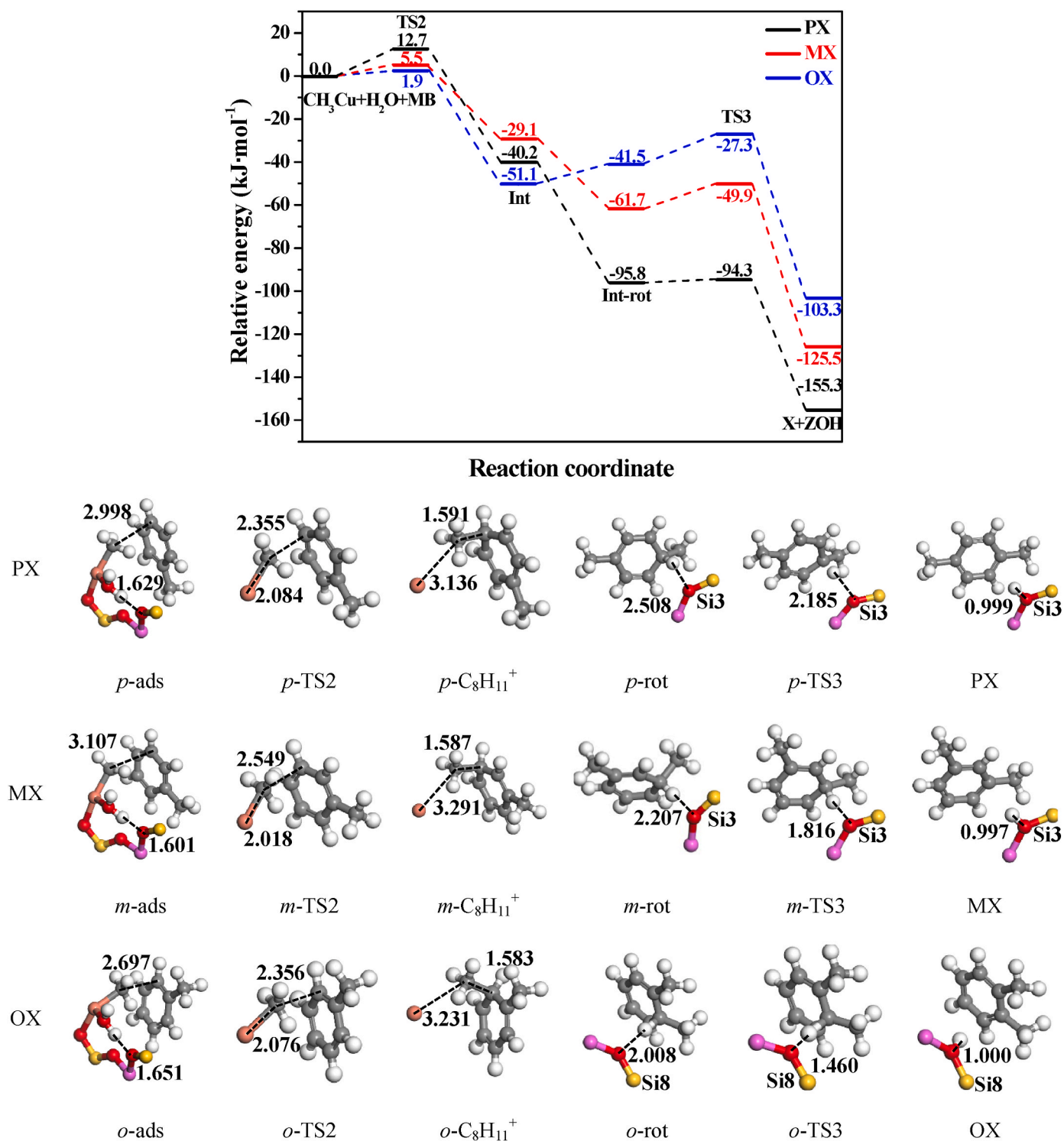


Fig. 5. The relative energy diagrams and reactants, transition states (TS) and products structures (Å) about the formation of PX, MX and OX in BAS/Cu⁺-HZSM-5.

at different concentrations will be various. Aiming at more comprehensively exploring the influence of concentration on the movement behavior of the diffusate, we investigate the diffusion behavior of xylenes with 2 and 4 molecules, as well as comparing with that of 6 molecules of PX, MX and OX, respectively.

The diffusion of 2, 4 and 6 xylene molecules in BAS/Cu⁺-HZSM-5 channel at the temperatures of 400, 600 and 800 K are studied. Table 2 shows the self-diffusion coefficients of xylene with different concentrations in BAS/Cu⁺-HZSM-5 at different temperatures, respectively. When

the temperature reaches 800 K, the self-diffusion coefficient of xylene is greatly affected by the concentration. The lower the concentration, the easier it is to diffuse. When the concentration goes from 6 to 2 molecules, the self-diffusion coefficients of PX, MX and OX vary from 162.96×10^{-12} , 3.59×10^{-12} and $3.18 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ to 376.64×10^{-12} , 7.04×10^{-12} and $7.34 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively, which indicates that the diffusion behavior of PX is more susceptible to concentration.

As also shown in Table 2 and Fig. 8, when the concentration of PX increases, its self-diffusion coefficient decreases rapidly, while the

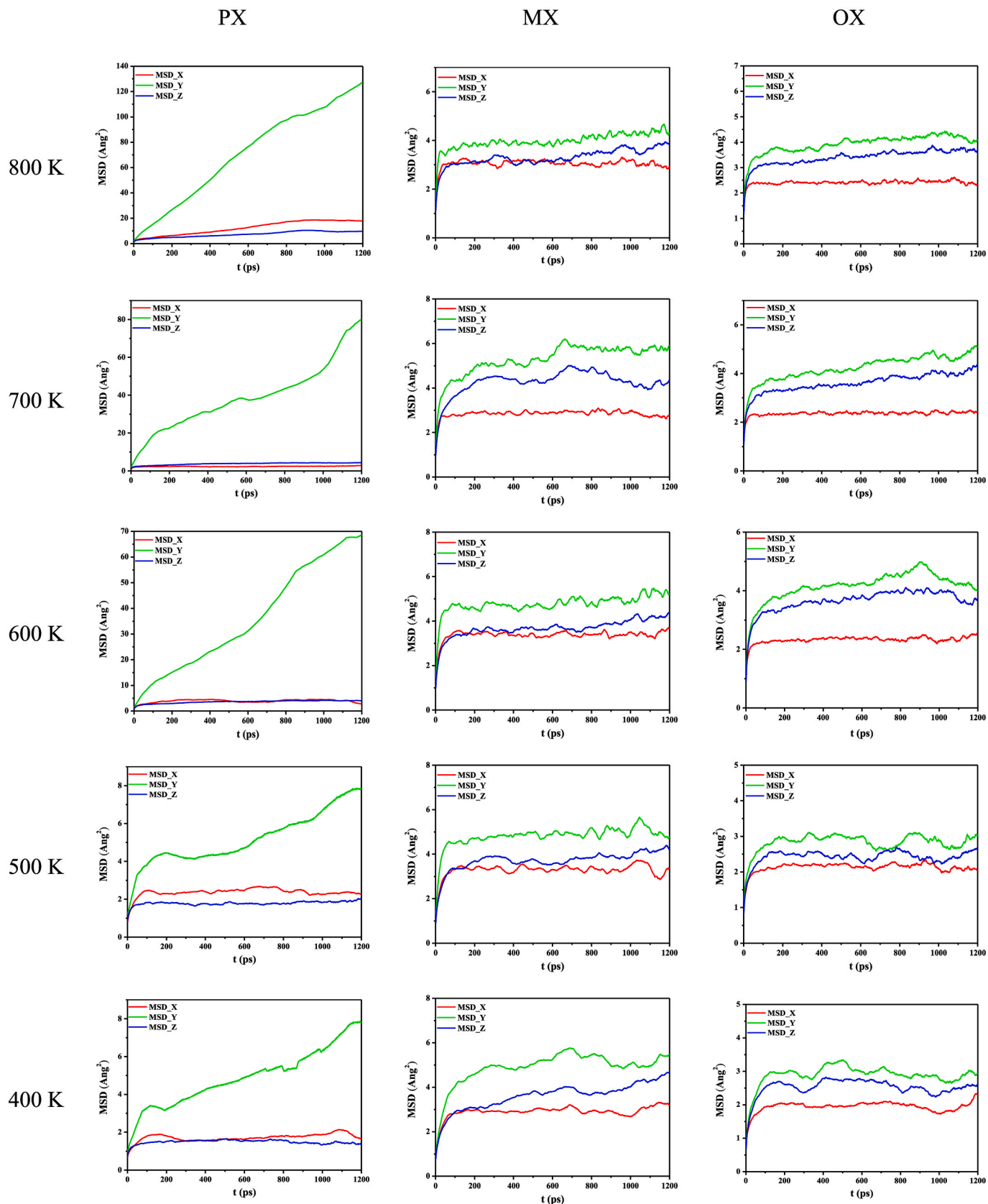


Fig. 6. MSD of anisotropic self-diffusivities of high concentration xylenes in BAS/Cu⁺-HZSM-5 at 400–800 K.

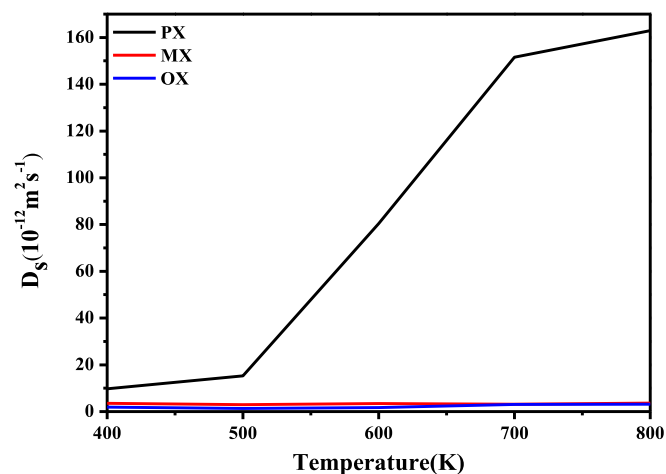


Fig. 7. The self-diffusion coefficients of high concentration xylenes in BAS/Cu⁺-HZSM-5 at 400–800 K.

Table 1

The calculated D_s of three types of xylenes in BAS/Cu⁺-HZSM-5 from 400 to 800 K.

Molecular species	$D_s/(10^{-12} \text{ m}^2 \text{ s}^{-1})$				
	400 K	500 K	600 K	700 K	800 K
PX	9.75	15.30	80.42	151.61	162.96
MX	3.56	3.00	3.45	3.13	3.59
OX	1.88	1.30	1.70	3.03	3.18

Table 2

The self-diffusion coefficients of xylenes with different concentration in BAS/Cu⁺-HZSM-5 at 400, 600 and 800 K.

Molecular species	Concentration/(unit cell)	$D_s/(10^{-12} \text{ m}^2 \text{ s}^{-1})$		
		400 K	600 K	800 K
PX	2	4.18	137.68	376.64
	4	20.49	139.87	210.94
	6	9.75	80.42	162.96
MX	2	5.18	5.62	7.04
	4	4.00	3.37	5.21
	6	3.56	3.45	3.59
OX	2	2.67	2.90	7.34
	4	2.73	1.60	4.21
	6	1.88	1.70	3.18

values of self-diffusion coefficients of MX and OX fluctuate or decrease slightly. However, the self-diffusion coefficient of PX shows an abnormal change at 400 K: the value first increasing and then decreasing obviously with the increase of PX concentration. The reason is that the strong interaction between channel wall and PX when the concentration of PX is low, and the steric hindrance of the channel caused by the occupation of Cu⁺ hinders the diffusion. When the PX concentration increases gradually, there will be some free PX molecules in the channels. It leads to that the self-diffusion coefficient of PX increases slightly with increasing concentration. But continue to increase the content of PX, the collision between PX and the channel wall will increase greatly, which will cause the diffusion of PX decrease significantly. However, because the critical diameters of MX and OX are larger than PX and close to the maximum channel diameter, these properties make them difficult to diffuse in the channel [54]. Therefore, it can be concluded that the change of factors such as concentration has a very weak effect on their diffusion rate. In addition, the self-diffusion coefficient of PX is greater than that of the other two xylenes in most cases. It means that the diffusion of PX is faster in BAS/Cu⁺-HZSM-5 and which is easier to diffuse compared with MX and OX.

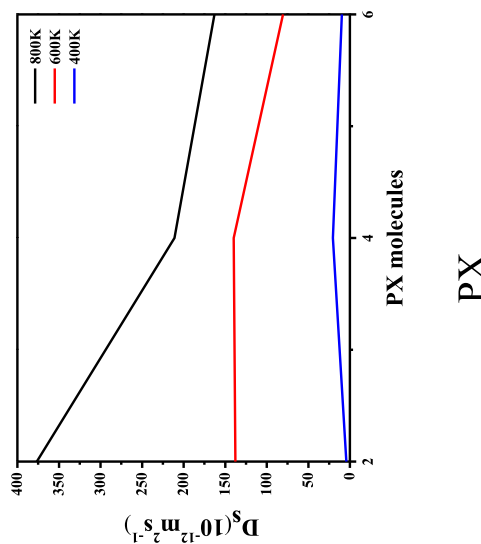
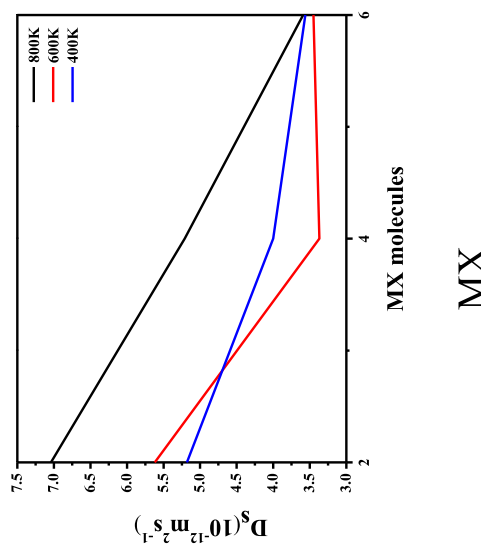
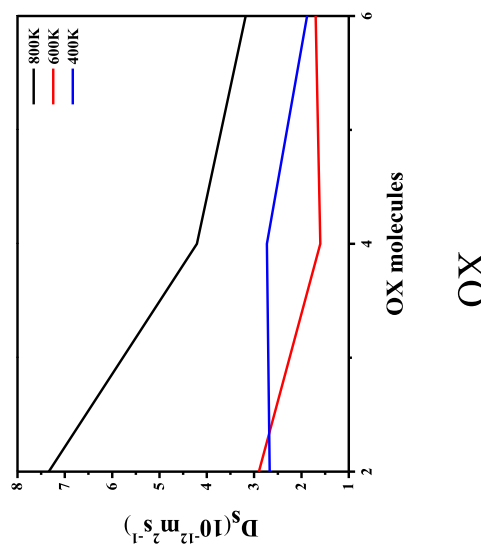


Fig. 8. Variation of the self-diffusion coefficients of xylenes with increasing concentration at different temperatures.

In summary, temperature and concentration will affect the diffusion behavior of three xylenes in BAS/Cu⁺-HZSM-5, especially the diffusion behavior of PX. Increasing the temperature and decreasing the concentration can effectively increase the self-diffusion coefficient of PX. And MX and OX will have greater steric hindrance compared with PX, which indicates that MX and OX will be difficult to diffuse in BAS/Cu⁺-HZSM-5.

3.3. Effect of Cu⁺ modification on HZSM-5 on intrinsic reaction and molecular diffusion

3.3.1. Effect on activity for toluene methylation reaction

The modification of Cu⁺ has great effect on dissociation process of methanol. As shown in Fig. 9, when Cu⁺ as the LAS, the methanol will be adsorbed on Cu⁺, methyl and hydroxyl groups produced from methanol dissociation will also be adsorbed on Cu⁺. Therefore, when both Cu⁺ and BAS are present, Cu⁺ plays a key role in the methanol dissociation process.

We further analyze the distance (Å) between the C atom in methanol and the Cu⁺ in the transition state structure of methanol dissociation via a microscopic point of view, and labeled it as $D_{C-O(Cu)}$. As listed in Table 3, the $D_{C-O(Cu)}$ values corresponding to BAS/Cu⁺-HZSM-5 and HZSM-5 are 2.126 and 2.266 Å, respectively [62]. It can be found that the $D_{C-O(Cu)}$ of BAS/Cu⁺-HZSM-5 is shorter, and the energy required for methanol dissociation is 109.7 kJ mol⁻¹. Meanwhile the energy required for methanol dissociation in HZSM-5 is higher than that in BAS/Cu⁺-HZSM-5, reaching 187.0 kJ mol⁻¹ [62], indicating that Cu⁺ modified HZSM-5 is able to significantly decrease the energy required for methanol dissociation. From the subsequent xylenes production reaction, it can be seen that the energies required for the formation of PX, MX and OX in BAS/Cu⁺-HZSM-5 are 12.7, 11.8 and 14.2 kJ mol⁻¹, respectively, which are very low compared to the corresponding activation energies in HZSM-5, indicating that these three types of xylenes are easier to generate in BAS/Cu⁺-HZSM-5.

According to these microscopic intrinsic reactions, we can find that Cu⁺ modification of HZSM-5 will significantly reduce the activation energy barrier of methanol dissociation and increase the activity of xylene formation. However, although the activation energy barriers of three kinds of xylene are very low, the difference in activation energy of these xylenes is relatively small, and we cannot control the selectivity of PX formation in BAS/Cu⁺-HZSM-5.

3.3.2. Effect on the diffusion of xylene and selectivity to PX

Controllable diffusivity is considered as the critical factor to the selectivity of PX. As mentioned above, the introduction of Cu⁺ improves the activity of the toluene methylation reaction via methanol. In the other hand, the introduction of modified species such as Cu⁺ into the zeolite will not only improve the catalytic performance of the zeolite, but also partially block the channels of zeolite. This phenomenon results in a reduction in the degree of opening of the channels and in the diffusion rate of the diffusate in zeolite, which can cause carbon deposits to deactivate the zeolite. Aiming at investigating the influence of the introduction of Cu⁺ on the diffusion of xylene molecules and compare with BAS/Cu⁺-HZSM-5, the diffusion of xylene molecules in HZSM-5

Table 3

The activation energies (kJ·mol⁻¹) and the bond distances (Å) for dissociation of methanol in BAS/Cu⁺-HZSM-5 and HZSM-5.

	BAS/Cu ⁺ -HZSM-5	HZSM-5
E_a (kJ·mol ⁻¹)	109.7	187.0
$D_{C-O(Cu)}$ (Å)	2.126	2.266

will be simulated and analyzed in this section.

The self-diffusion coefficients of three types of xylenes in HZSM-5 zeolite at different temperatures and concentrations are listed in Table 4. Compared with HZSM-5 zeolite, the self-diffusion coefficient of PX in BAS/Cu⁺-HZSM-5 (Table 2) is reduced, which proves that the modification of Cu⁺ can reduce the channel space of zeolite and increase the steric hindrance of the channels in zeolite. However, there is a little influence on the diffusion rates of MX and OX comparing to PX. At the same time, although the self-diffusion coefficient of PX is reduced after Cu⁺ modification, which is still significantly larger than that of MX and OX.

It can be seen that modified Cu⁺ as the active site improves the catalytic activity of HZSM-5, and promotes the formation of PX, MX and OX via methyl attacking different ring C atoms of toluene, respectively. In addition, the special channel in BAS/Cu⁺-HZSM-5 results in high selectivity to PX, although the introduction of Cu⁺ causes the steric hindrance leading to the diffusion rate of PX is lower than that in HZSM-5, which is greatly larger than that of MX and OX. The synergistic effect of active sites and special channels in BAS/Cu⁺-HZSM-5 results in its excellent catalytic performance to PX. Si et al. [26] also found that the selectivity of PX could be improved by using CuO/HZSM-5 modified with 10% CuO in the toluene methylation reaction via methanol.

4. Conclusion

DFT calculations as well as molecular dynamics simulations are carried out to investigate the formation and diffusion of *para*-xylene (PX) on BAS/Cu⁺-HZSM-5 zeolite and the effect of Cu⁺ modification on HZSM-5 on the intrinsic reaction and molecular diffusion has also been obtained. The adsorption and dissociation of methanol preferentially occur on the Cu⁺ in the BAS/Cu⁺-HZSM-5 catalyst, but not on Brønsted

Table 4

The self-diffusion coefficients of xylenes with different concentration in HZSM-5 at 400, 600 and 800 K.

Molecular species	Concentration/(unit cell)	$D_s/(10^{-12} \text{ m}^2 \text{ s}^{-1})$		
		400 K	600 K	800 K
PX	2	209.72	487.06	750.87
	4	166.89	395.36	676.21
	6	126.87	235.75	339.26
MX	2	3.29	2.37	5.72
	4	2.81	3.09	2.98
	6	2.37	2.00	5.20
OX	2	2.39	1.77	5.64
	4	2.52	1.72	3.20
	6	2.25	1.87	5.44

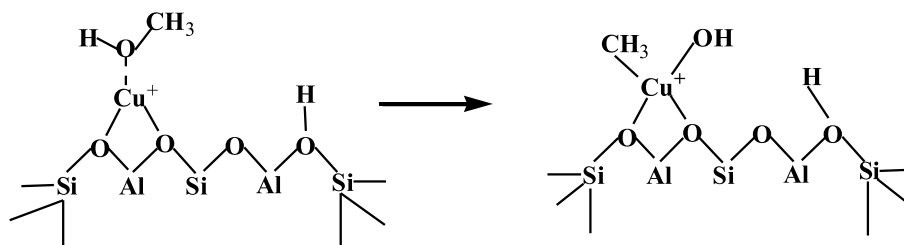


Fig. 9. The dissociation pathway of methanol in BAS/Cu⁺-HZSM-5.

acid site. Compared with HZSM-5, BAS/Cu⁺-HZSM-5 has lower methanol dissociation activation energy, implying that modified Cu⁺ as the active site facilitates the dissociation of methanol. In addition, modification of Cu⁺ also promotes the formation of xylenes with activation energies of 12.7, 11.8 and 14.2 kJ mol⁻¹ for PX, MX and OX via methyl attacking different ring C atoms of toluene, respectively. However, the similar activation energies show that the formation of three xylenes on BAS/Cu⁺-HZSM-5 is a competitive reaction, and the selectivity of PX is poor.

Additionally, the diffusion of three xylenes is further carried out, and it shows that temperature and the concentration of xylenes have a greatly impact on the diffusion behavior of PX. In most cases, self-diffusion coefficient of PX is greater than that of MX and OX, indicating that PX suffers less steric hindrance and the diffusion rate in BAS/Cu⁺-HZSM-5 is more rapidly than the others. It can be concluded that the synergistic effect of active sites and special channels in BAS/Cu⁺-HZSM-5 results in its excellent catalytic performance to PX. The intrinsic reaction results indicate the BAS/Cu⁺-HZSM-5 has higher catalytic performance and molecular diffusion simulations indicate the BAS/Cu⁺-HZSM-5 holds better channel shape selectivity to PX. The research results have guiding significance for the preparation of zeolite and process optimization in the future.

CRedit authorship contribution statement

Ning Li: Data curation, Investigation, Writing – original draft, Writing – review & editing. **Min Han:** Writing – original draft, Data curation. **Zhongzhong Xue:** Writing – review & editing. **Panyue Liu:** Writing – review & editing. **Lixia Ling:** Conceptualization, Formal analysis, Funding acquisition, Writing – review & editing. **Ping Liu:** Writing – review & editing, Conceptualization. **Riguang Zhang:** Funding acquisition, Writing – review & editing. **Baojun Wang:** Software, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2022.111910>.

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