ORIGINAL ARTICLE

Alkylation of benzene with methanol to toluene over Na^3-H-Y: analysis of four aspects for obtaining reaction mechanism

Peng Dong[1] · **Jiale Meng**[1] · **Hongfei Yun**[1] · **Guixian Li**[1]

Abstract

Alkylation reactions was a promising technology for the preparation of chemical products such as toluene. However, the mechanism of such reactions yet remains as an unclear problem. Therefore, based on theoretical analysis, thermodynamics calculation, laboratory testing and density functional theory method analysis, the possible mechanism of catalytic reaction was proposed to clarify the alkylation of benzene with methanol over the Na^3-H-Y catalyst.

Keywords Benzene/methanol reaction · Toluene · Reaction mechanism · Thermodynamic calculation · Density functional method

Introduction

In the 1960s, Y zeolite was synthesized by artificially as solid acid catalyst and used widely as a substitute for amorphous silica-alumina catalyst in oil refining. The activity of cracking catalyst was increased by nearly 6 orders of magnitude, which triggered a refining revolution and that had led to the development of modern petroleum further processing industry. Hitherto, Y zeolite was still the main component of catalyst in fluidized bed for the process of oil refining. The performance improvements of Y zeolite would save a lot of petroleum resources and contribute to the efficient use of petrochemical energy around the world [1–3].

Y zeolite owns the advantages of high surface area, hydrothermal stability, resistance to carbon deposition and metal pollution etc., which would create just what it's worth-is used in catalysis, sorption and ionexchange [1, 4]. The catalytic activity of Y zeolite was not only related to acidity, but also Si/Al ratio and metal ions of zeolite [4]. Protons in zeolite was generally isolated and highly dispersed, and coexisted in the crystal system [1]. Compared with amorphous aluminosilicate, the acid strength of Y zeolite was comparable to that of sulfuric acid. Compared with liquid inorganic acids or organic acids, Y zeolite acid catalysts had some technological merit, such as poisonless and harmless, not corrosion to equipment and easy to separate and recycle from the reaction system [5–7]. Therefore, it was more value in industrial application that solid-acid catalysts substitute for liquid inorganic acids or organic acid catalysts.

According to the literature, the reactions catalyzed by acidic zeolites was highly important in the cracking of C_5–C_6 to C_2–C_4 olefins [8], benzene alkylation with methanol, toluene alkylation with methanol reactions, the isomerization and aromatization of 1-$C_6^=$ [9], methanol to olefins (MTO) [7, 10], methanol to propylene (MTP) [11] methanol to hydrocarbons (MTH) [12, 13], methanol to gasoline (MTG) [14], as well as methanol to aromatization (MTA) [15]. Such as HZSM-5 [16] and HZSM-11 [17], was particularly suited to the transformations of BTX (benzene, toluene and xylene) because the structure of HZSM-5 or HZSM-11 could control the structures of transition-state to enhance the selectivity of target products. For a detailed study of the difference of catalytic process between Y and HZSM-5 zeolites, density functional theory (DFT) analysis would be adopted to reveal the essence of catalytic mechanisms, by which the possible Na$^+$ substituted locations of H$^+$ and the accurate content of Na$^+$ could be proposed. However, there was no literature had investigated successfully into the possible catalytic mechanisms of benzene/methanol to toluene(B/MTT) over Na-H-Y zeolite by using DFT method.

✉ Peng Dong
  dongpeng06190318@126.com

✉ Guixian Li
  lgxwyf@163.com

1 College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, People's Republic of China

Based on the theoretical and experimental researches, two different mechanisms were proposed for the alkylation of benzene with methanol: concerted and stepwise mechanisms [17]. The concerted pathway of methanol molecule and benzene molecule were adsorbed simultaneously on the acid site by bridge oxygen bond in the zeolites, forming $C_7H_9^+$ and H_2O. $C_7H_9^+$ would deprotonate rapidly, generating toluene and regenerating the acid sites of the zeolites. Thus, the catalytic cycle was completed. Compared with the concerted pathway, the stepwise pathway involved an intermediate-methoxy group and then methoxy group with benzene would further react, forming $C_7H_9^+$ and H_2O and so on.

However, no conclusive evidence could be employed to attest which routes was suitable during alkylation reactions. The surface-methoxy group had been captured in situ by testing instrument where would prove the rationalisation of stepwise mechanisms [18, 19]. Mynsbrugge et al. [13] found that the concerted pathway was suitable for the methylation of benzene with methanol over HZSM-5 and H-beta catalysts. However, the comprehensive survey was not reported for explaining benzene alkylation with methanol over Na-H-Y catalyst.

In this investigation and summary, base on thermodynamics calculation, we had tested the optimum catalytic performance of Na-H-Y by B/MTT reaction in a continuous-flow jet bubbling reactor with a glass tube (8 mm i.d.) under certain conditions [3]. At the same, explored the concerted and stepwise pathways for the alkylation of benzene with methanol over Na-H-Y catalyst by employing density functional theory method.

Computational methods

The density functional theory (DFT) calculations were done by VASP software with a periodic slab. The Perdew–Burke–Ernzerhof (PBE) functional with the generalized gradient approximation (GGA) was used to describe the electronic structures, and the projector augmented wave method was applied to calculate the interaction between electrons and atomic cores. All the calculations used a cutoff energy of 400 eV with the force threshold of 0.05 eV $Å^{-1}$. The lattice parameters of FAU primitive cell were firstly optimized and the Brillouin zone was described by $3\times3\times1$ k-points. The optimized lattice parameter of the FAU primitive cell is 17.72 Å, consistent with the experimental value 17.70 Å. For the calculations of intermediates and transition states, we used a $1\times1\times1$ supercell of FAU based on the optimized lattice parameters. One Na atom is added into the FAU zeolite and the Na^+ was located in a small cage, as depicted in Fig. 1. The Brillouin zone of the FAU supercell was described with a $1\times1\times1$ k-point grid. All of the atoms in FAU framework were relaxed in both structural optimization and transition state structures, and the transition
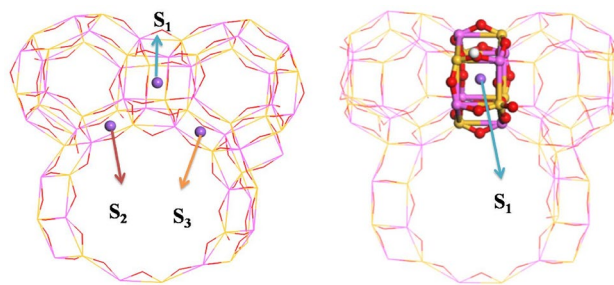

Fig. 1 Schematic representation of the Y zeolite with Na^+ (Na^+ is caged in the Y zeolite framework)

states were located by Climbing image nudged elastic band (CI-NEB) method. The energies of gas species considered in this work, e.g. benzene, toluene, CH_3OH, H_2O and CH_4, were calculated in a 10 Å$\times$10 Å$\times$10 Å cubic lattice and k-points used $1\times1\times1$.

Thermodynamics analysis

The process of alkylation reaction of benzene/methanol was studied thermodynamically based on functional group contribution method of Benson, and Gibbs energy change ΔG_T and equilibrium constant K_p of major and minor reactions were calculated. The thermodynamic properties of the material involved were derived from data manual [20].

The Gibbs energy change ΔG_T and equilibrium constant K_p were calculated from below.

$$C_p^0 = a + bT + cT^2 + dT^3 \tag{1}$$

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3 \tag{2}$$

$$\Delta H_T = \Delta H_{298}^\theta + \int_{298}^T \Delta C_p dT \tag{3}$$

$$\Delta S_T = \Delta S_{298}^\theta + \int_{298}^T \frac{\Delta C_p}{T} dT \tag{4}$$

$$\Delta G_T = \Delta H_T - T\Delta S_T \tag{5}$$

$$K_p = \exp\left(-\Delta G_T/RT\right) \tag{6}$$

$$R = 8.314\, J/(mol\, K)$$

The optimum catalytic performance of Na³-H-Y

The activity of various catalysts was evaluated and the results are shown in Fig. 2. It can be seen that the catalytic performance of Na-Y was inactive due to the catalyst did not own acid [3]. Be surprised to discover that the catalytic performance of H-Y was also worse due to the temperature activated of H-Y catalyst was as high as 550–600 °C [21]. However, when Na^+ was introduced, the activity of the catalyst would change dramatically. And the mass fraction of Na^+ was 2.136%, the conversion of benzene and the selectivity of toluene over Na³-H-Y was just 43.9% and 87.7%, respectively. Hence, the presence of Na^+ played an important role in the activity of the catalysts.
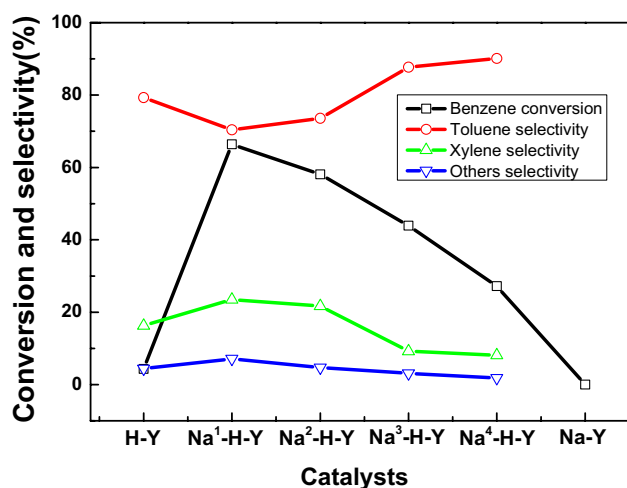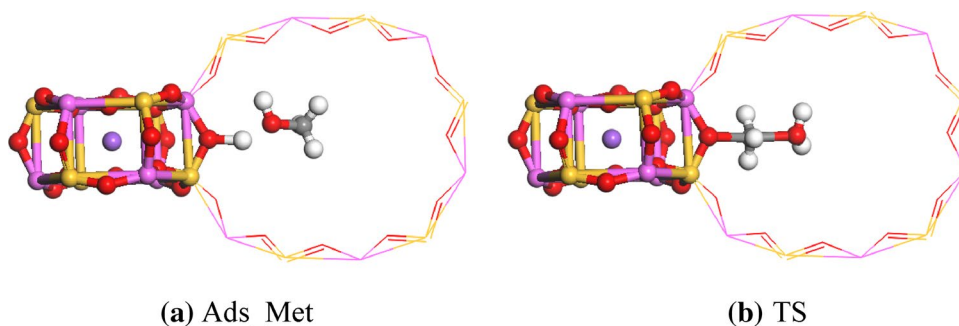
Location of Na^+ in Na-Y and Na³-H-Y

Zeolite Y was a synthetic material with 56 Na^+ in the unit cell and Si/Al ratio greater than 1.5 [22]. There were 3 different locations about Na^+ in NaY zeolite (seen Fig. 1), namely S_1, S_2 and S_3. Thereinto, Na^+ of S_2 and S_3 positions was easy to exchange by ion exchange method. However, Na^+ of S_I position(16 Na^+) in the center of hexagon prism cage was hard to get swapped [21]. Therefore, when Na^+ of S_2 and S_3 positions was completely displaced by ion exchange method, exchange degree of Na^+ was 71.4%. While the amount of residual Na^+ was 30.5% (2.136/6.993) from experimental results (using ICP). It was noteworthy that the theoretical and experimental values was added up to approximately 100%. From the above, Na^+ of S_2 and S_3 positions was completely displaced and one Na^+ was added into the FAU zeolite and the Na^+ was located in a small cage, as depicted in Fig. 1.

Results and discussion

The stepwise pathway of B/MTT reaction

According to the literature and the results from research works [17], the stepwise pathway included that methanol was dehydrated to form methoxy group and benzene was attacked by methoxy group to form alkylation products. The optimized geometries of methanol to methoxy group was displayed in Fig. 3, which was initiated by the adsorption of methanol on acid site of Na³-H-Y catalyst. The energy diagram of methanol to methoxy group was manifested in Fig. 4, which was calculated as being −71 kJ/mol about the adsorption energy of methanol over Na³-H-Y.

Intrinsic energy barriers of methanol dehydration to form methoxy group was 141 kJ/mol over Na³-H-Y, which was consistent with others obtained in HZSM-5 (149 kJ/mol) and mordenite (150 kJ/mol) [17], are deduced to form methoxy group from methanol dehydration over Na³-H-Y. The presence of methoxy group had been proved to be a very
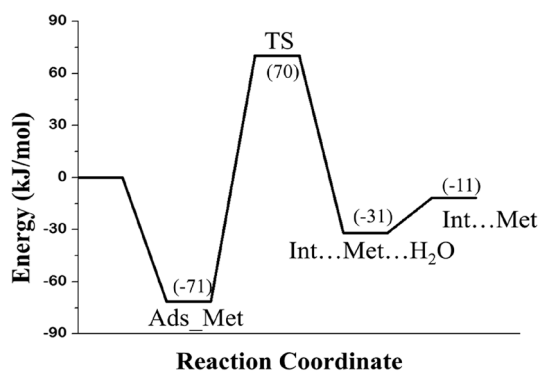
Fig. 2 Products content of benzene alkylation with methanol over the different catalysts. Reaction Condition: Catalyst = 0.5 g; T = 400 °C; Reaction time = 3 h; Pressure = the atmospheric, Feed (Benzene/Methanol) ratio = 1:1. Type of catalyst: Na-Y (6.993%); Na¹-H-Y (0.078%); Na²-H-Y (1.542%); Na³-H-Y (2.136%); Na⁴-H-Y (3.506%); the numbers in parentheses refer to mass fraction of Na

Fig. 3 Optimized geometries involved in methanol dehydration over Na³-H-Y **a** Methanol adsorption; **b** Transition state

(a) Ads_Met

(b) TS

Fig. 4 Relative energy of each state involved in methanol dehydration

important conclusion by FTIR and NMR experiments, which had provided the basis for the rationality of the stepwise pathway [18, 19].

When benzene molecule entered into the channel of Na^3-H-Y and then was attracted by a methoxy group. As shown in Fig. 5a, due to the size of benzene molecule was about that of the Y zeolite pore, which was adsorbed in the center of the Y zeolite pore. Moreover, the calculations

showed that the adsorption energy of methoxy group vis benzene molecule over Na^3-H-Y (Fig. 6) was − 51 kJ/mol. And the transition state geometry was portrayed in Fig. 5b. It was observed that the spatial pattern of methyl group was almost parallel to that of benzene molecule. Happen to find that the obtained energy barrier to form toluene was 141 kJ/mol over Na^3-H-Y, which was equal to that of formation of the methoxy group.

Furthermore, the C–C bond between benzene ring and the methyl group might be broke in Fig. 5e, where would generate methane in benzene alkylation with methanol and $C_6H_5^+$. Methane was easy to escape from the pores of Na^3-H-Y because methane was not easily adsorbed. Once methane was formed, $C_6H_5^+$ was remained resulting in the absence of protons. In other words, $C_6H_5^+$ could no longer supply a proton to the bridging oxygen. It might connect with the bridging oxygen to compensate the negative charge in the acid sites (recorded as C_6H_5-Z in Fig. 5e), which would pile up and become also a possible reason for the activity reduced of the catalyst.

As can be seen in Fig. 6, the predicted energy barrier to form methane over Na^3-H-Y was − 33 kJ/mol, which was much less than that of HZSM-5. So it also illustrated the

Fig. 5 Optimized geometries of benzene methylation over Na^3-H-Y: **a** Benzene adsorbed in methoxy group; **b** Transition state of forming toluene; **c** Intermediate; **d** Toluene adsorbed; **e** Transition state of methane formation
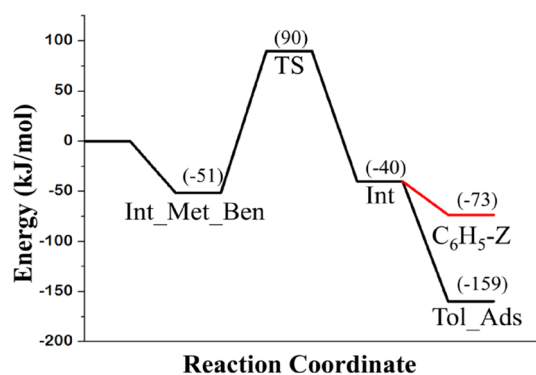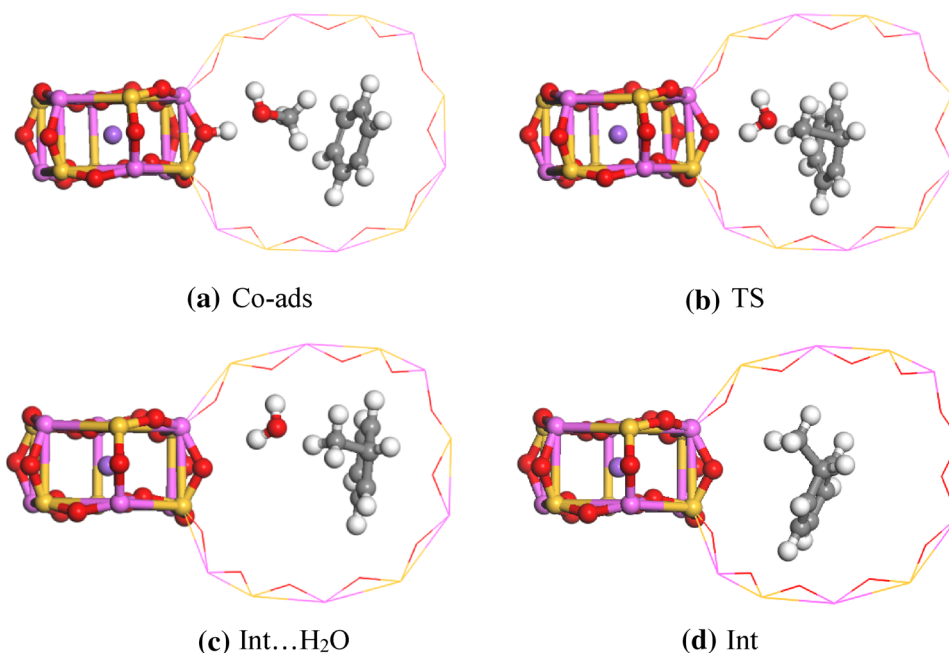

(a) Int_Met_Ben

(b) TS

(c) Int
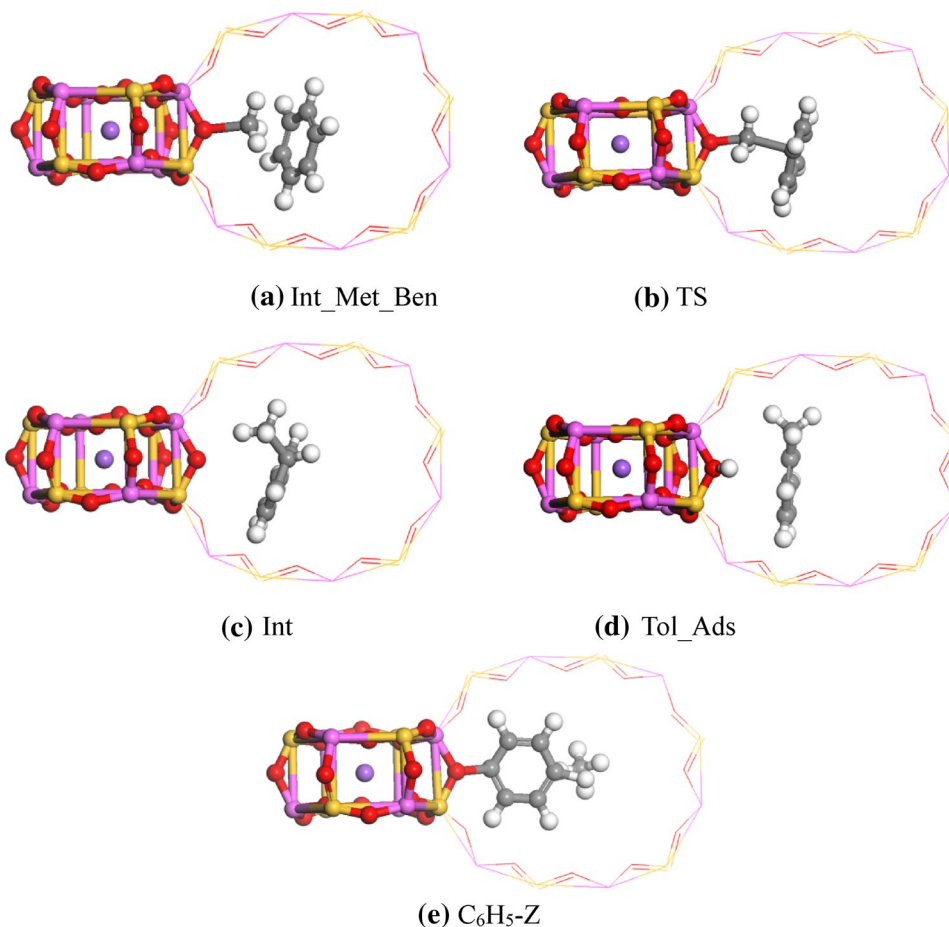
(d) Tol_Ads

(e) C_6H_5-Z

Fig. 6 Relative energy of each state involved in benzene methylation step

likelihood that this step would occur. However, the predicted energy barrier to form C_6H_5-Z over Na^3-H-Y was much higher than that of Tol_Ads, which would decide that the production of toluene was the preferred step.

The concerted pathway of B/MTT reaction

The co-adsorption geometries of benzene and methanol over Na^3-H-Y for B/MTT reaction were shown in Fig. 7. Due to methanol molecule was relatively small (in Fig. 8) and the characteristic of methanol molecule (–OH), which was adsorbed on the acid site by bridge oxygen bond in Y zeolite, forming hydrogen bonds between the oxygens of the deprotonated acid site and the hydrogens on protonated methanol. This conclusion was in good agreement with other theoretical studies reported in the literatures [17]. However,

due to the size of benzene molecule was about that of the Y zeolite pore, which was adsorbed in the center of the Y zeolite pore. Figure 9 provided the relative energy variations of concerted pathway. The co-adsorption energy of benzene/methanol was − 124 kJ/mol over Na^3-H-Y catalyst. The energy barrier to form toluene over Na^3-H-Y catalyst in concerted pathway was 143 kJ/mol, showing a lower energy barrier over Na^3-H-Y for benzene alkylation compared with HZSM-5 (149 kJ/mol) [17]. The carbon atom of benzene ring would be attacked the carbon atom of the methyl group to form intermediates in Fig. 7b–d. During this process, the permittivity of water molecules must effectively shield the cationic field (namely solvent effect), so the water molecule would be taken into account. Finally, the reason for the fast deprotonation of $C_7H_9^+$ was that the deprotonation of $C_7H_9^+$ was virtually barrierless (5–15 kJ/mol) [23], generating C_7H_8 and regenerating the acid sites of Na^3-H-Y. Ultimately, the catalyst would return to its original state.

B/MTT reaction mechanism and discussion

During the benzene alkylation, CH_4, C_2H_4, C_3H_6 and other gaseous products, Toluene(T), Xylene(X), Ethyl-benzene (EB), propylbenzene (PB), tri-methylbenzene (TMB), tetra-methyl-benzene (TTMB), etc. were measured using GC7900 and coke deposition was observed. Meanwhile, all the reactions were exothermic except for the coke deposition reaction in B/MTT reaction. There might be many reactions in the process of benzene and methanol alkylation. The main reaction & possible secondary reaction was as follows [24].
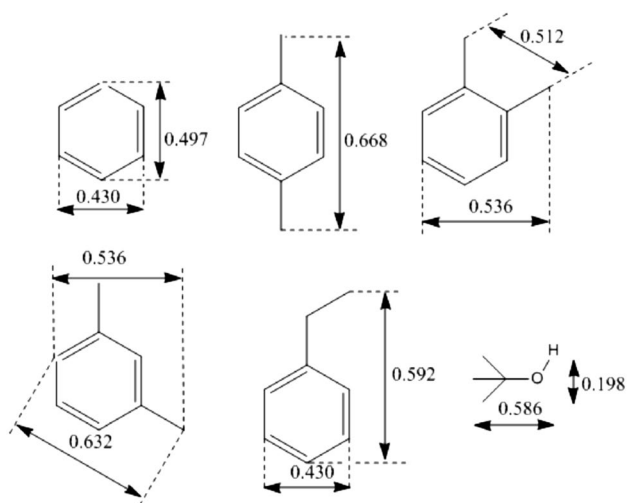
Fig. 7 Optimized geometries involved in concerted pathway over Na^3-H-Y **a** Co-adsorption of benzene and methanol; **b** Transition state; **c** Intermediate H_2O; **d** Intermediate

(a) Co-ads

(b) TS

(c) Int…H_2O

(d) Int

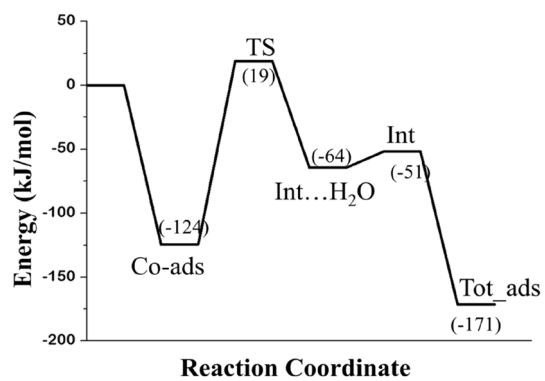**Fig. 8** Size of main organic molecules

Fig. 9 Relative energy of each state involved in concerted pathway
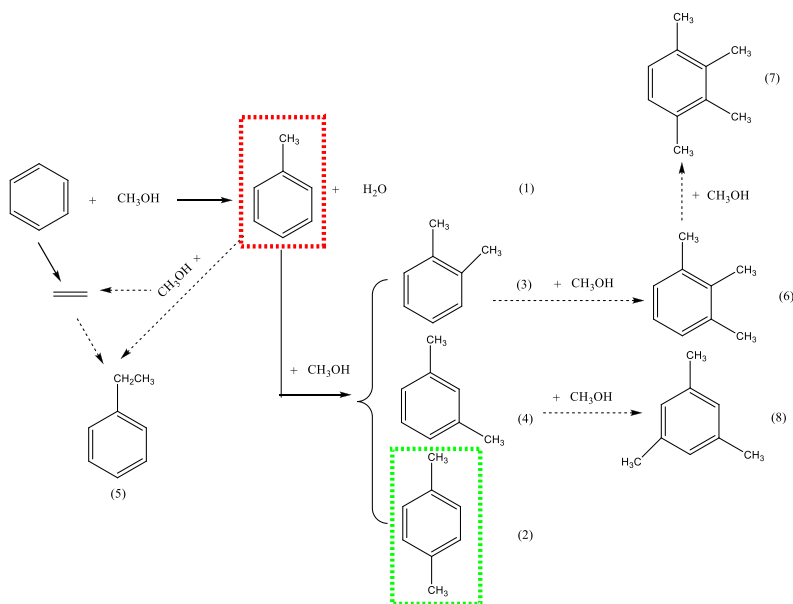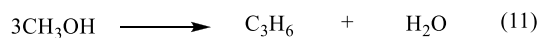
(1) Main alkylation reaction:

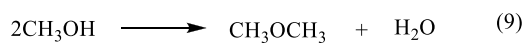**Table 1** The Gibbs energy change ΔG_T and equilibrium constant K_p

Thermodynamic data	T	No.						
		1	2	3	4	5	6~7	8
ΔG_T (kJ mol^{-1})	623~723 K	$-79~-85$	$-68~-73$	$-67~-70$	$-62.5~-63$	$-60~-62$	$-40~-21$	$-41~-20$
InK_p	623~723 K	15.5~14	13~12	13~11.5	12~10	11.5~10	7.1~4.5	8~3
Thermodynamic data	T	No.						
		9	10		11	12	13~15	16
ΔG_T (kJ mol^{-1})	623~723 K	-12.7	$-90~-120$		$-25~-14$	11~38	$-9~7$	<-43
InK_p	623~723 K	2	17~20		5~2	<2	1.5~-1.5	3~10.5

(2) Methanol self reaction:

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad (9)$$

$$2CH_3OH \longrightarrow C_2H_4 + H_2O \qquad (10)$$

$$3CH_3OH \longrightarrow C_3H_6 + H_2O \qquad (11)$$
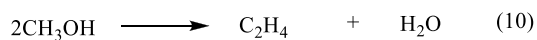
(3) Other alkylation reactions:
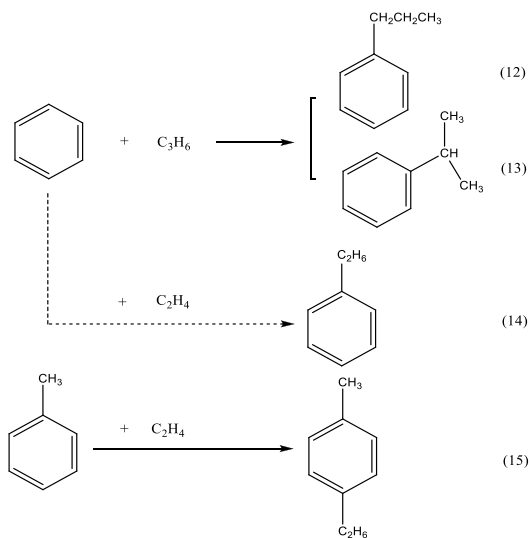
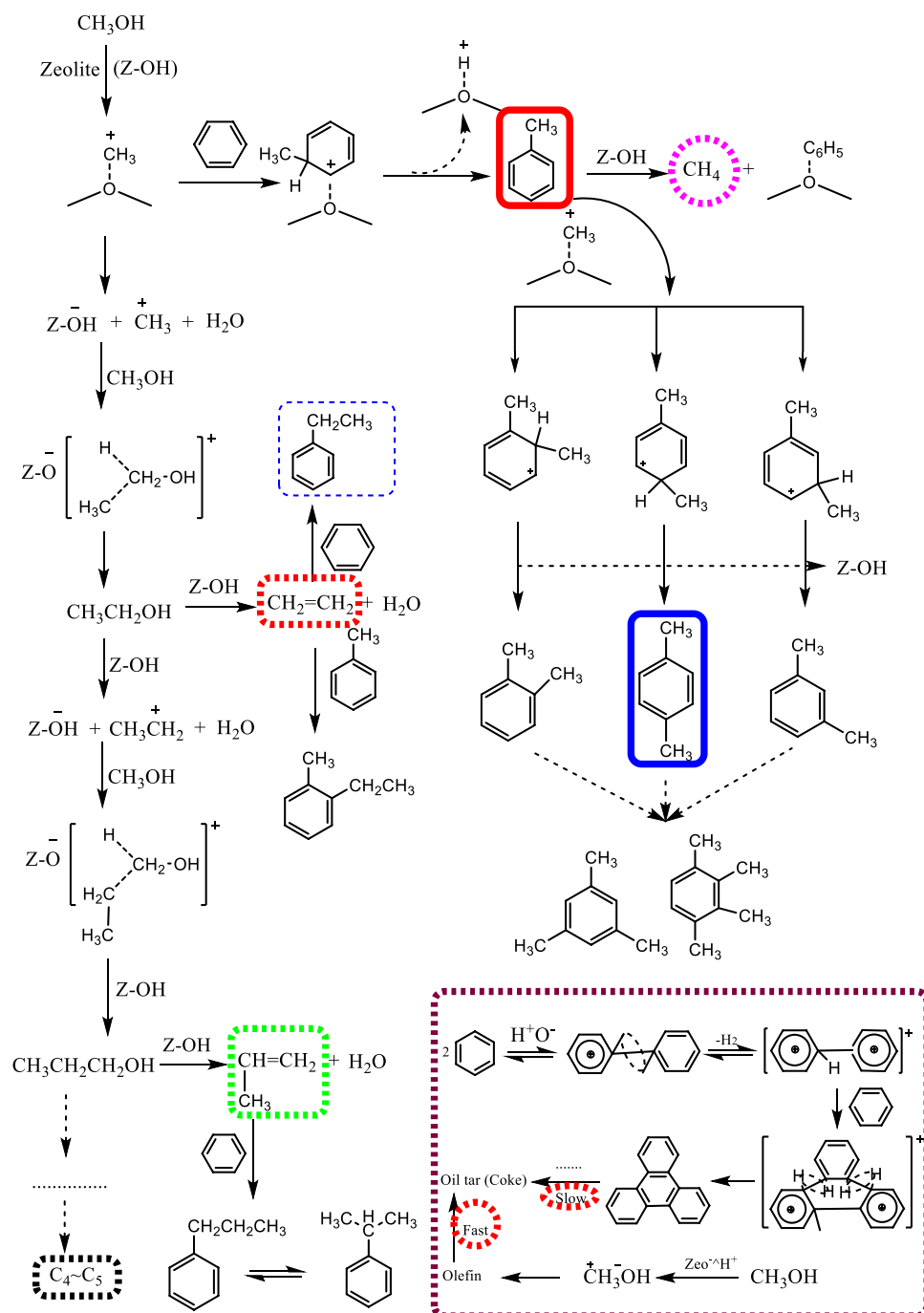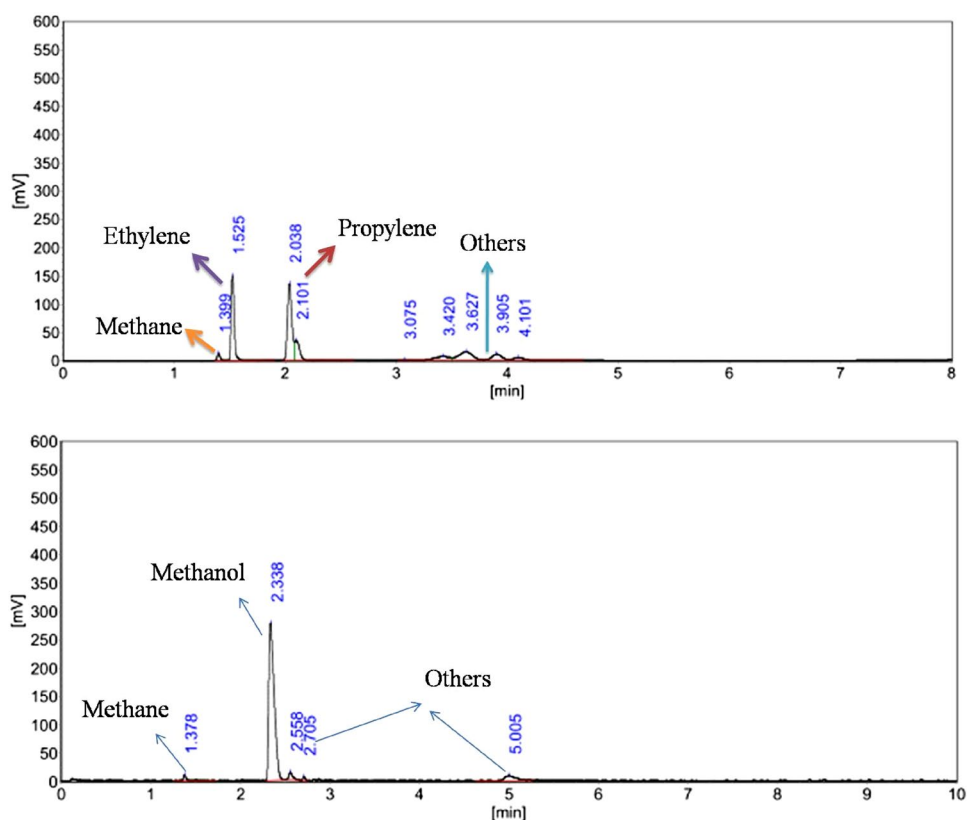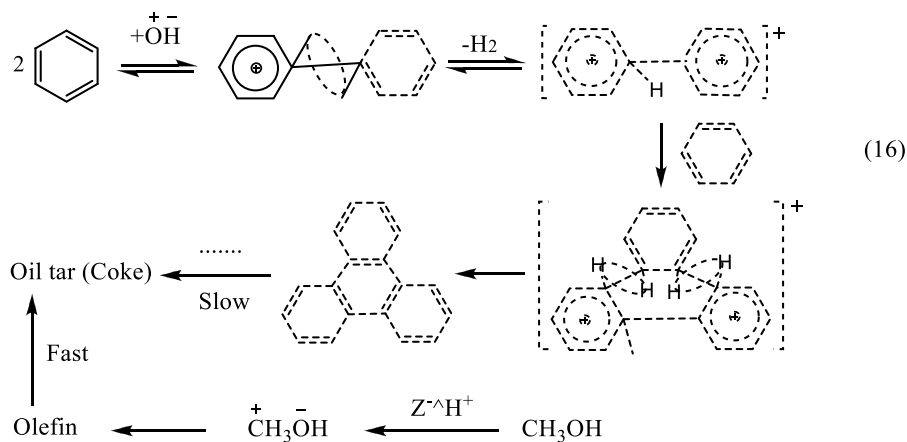**Scheme 1** Possible mechanism for benzene alkylation with methanol

Fig.10 Gas phase composition of Na^3-H-Y and other catalyst

(4) Carbon deposition reaction

$$(16)$$

The four primary reactions could occur spontaneously in the range of 623–723 K because Gibbs energy change $\Delta G_T < 0$. EB, TMB, TTMB could also occur spontaneously in Table 1. And the formation reaction of propyl-benzene, isopropyl benzene and ethyl-4-methylbenzene couldn't be proceeded spontaneously at this temperature because Gibbs energy change $\Delta G_T > 0$.

According to the relationship between Gibbs energy change ΔG_T and equilibrium constant K_p, the K_p value of the reactions (1–4) was very large and close, indicating that the main reaction was considered to be irreversible. Olefin especially ethylene (10) was more likely to happen than main reactions because K_p value was one of the biggest. Therefore, MTO was mainly competing reaction. EB, TMB and TTMB had a lower degree of reaction than the main

reaction. The equilibrium constant of propyl-benzene, iso-propyl-benzene and ethyl-4-methyl-benzene was less than 1.5 or even 0, indicating that high temperature could inhibit their generation. The equilibrium constant K_p of EB was more than 10. The equilibrium constant K_p of TMB, TTMB was less than 10, but was large relatively compared with others reaction. Results showed that TMB, EB, TTMB were the main byproducts in benzene/methanol alkylation. The equilibrium constant K_p of ethylene constant from self-methanol reaction was much larger than 0, indicating that methanol could spontaneously generate alkene. Other researchers [25, 26] reported that ethylene was the key reactant for the formation of EB and ethylene content decreased was a possible way to solve the problem of EB.

In conclusion, the selectivity of T and PX were enhanced, the critical point lied in the fact that:

(1) MTO was mainly competing reaction and must be suppressed.
(2) The temperature couldn't be too high.

Therefore, through theoretical analysis, thermodynamic calculation, laboratory testing and density functional theory (DFT) analysis, a possible mechanism of catalytic reaction for clarifying the benzene alkylation with methanol over the Na^3-H-Y catalyst was depicted in Scheme 1.

Among the product of the benzene alkylation, CH_4, C_2H_4, C_3H_6 and other gaseous products were formed through the reaction of the methanol itself, eventually triggering the formation of EB and PB. Furthermore, the C–C bond between benzene ring and the methyl group might be broke, where would generate an obbligato gaseous product (methane) in benzene alkylation with methanol and $C_6H_5^+$ carbocation by DFT analysis. $C_6H_5^+$ could no longer supply a proton to the bridging oxygen. It might connect with the bridging oxygen to compensate the negative charge in the acid sites, which would pile up and become also a possible reason for the reduced activity of the catalyst.

Whether it was a synergistic mechanism or a step by step mechanism, the data obtained about B/MTT reaction over Na^3-H-Y catalyst by DFT was very useful. Although B/MTT reaction excited over Na^3-H-Y catalyst needed more energy than using HZSM-5 catalyst, the energy barrier to form toluene over Na^3-H-Y catalyst in concerted pathway showed a lower energy barrier over Na^3-H-Y for benzene alkylation compared with HZSM-5. As a consequence, Na^3-H-Y catalyst showed great potential for the preparation of toluene.

Coke deposition was mainly caused by the side effects of self-methanol. This conclusion could be evaluated by testing with only methanol or only benzene as raw material. The coke rate of only methanol as a reactant was much higher than that of only benzene. But the MTO reaction could be inhibited. For example, our research group

have found that the amount of ethylene and propylene were plentiful over Na^3-H-Y catalyst. By contrast, the amount of ethylene and propylene were almost none over other catalyst in Fig. 10. Therefore, the stability of the alkylation catalyst was enhanced by preparing the appropriate catalyst.

From the above, Na^3-H-Y catalyst was the most potential and first choice for the preparation of toluene in B/MTT reaction.

Conclusions

Alkylation of benzene with methanol was one of the important reactions in organic chemistry for the preparation of toluene. But in order to use resources more efficiently, it was important to understand the mechanism of B/MTT reaction. In this contribution, the activity of various catalysts was evaluated and when the mass fraction of Na^+ was 2.136%, the benzene conversion and selectivity of desired toluene over Na^3-H-Y was just 43.9% and 87.7%, respectively. Hence, the presence of Na^+ played an important role in the activity of the catalyst. During the benzene alkylation, CH_4, C_2H_4, C_3H_6 and other gaseous products, T, X, EB, PB, TMB, TTMB, etc. were measured using GC7900 and by thermodynamic calculation. Whether it was a synergistic mechanism or a step by step mechanism, B/MTT reaction excited over Na^3-H-Y catalyst need more energy than using HZSM-5 catalyst, the energy barrier to form toluene over Na^3-H-Y catalyst in concerted pathway showed a lower energy barrier over Na^3-H-Y for benzene alkylation compared with HZSM-5. As a consequence, based on through theoretical analysis, thermodynamic calculation, laboratory testing and DFT analysis, a possible mechanism of catalytic reaction was proposed to clarify the alkylation of benzene with methanol over the Na^3-H-Y catalyst. At the same time showed that Na^3-H-Y catalyst was great potential for the preparation of toluene.

References

1. Huang, Z.T., Peng, F.: Design and Development of Industrial Catalysts. Chemical Industry Press, Beijing (2009)
2. Zhao, Y.Z., Li, Y.H., Li, L.F., Zhang, L.P.: Study on alkylation desulfurization of FCC gasoline by USY molecular sieve. J. Mol. Catal. (China) **23**, 17–21 (2008)
3. Dong, P., Li, Z.Y., Ji, D., Yun, H.F., Du, Z.S., Li, G.X.: Catalytic benzene mono-alkylation over three catalysts: improving

activity and selectivity with M-Y catalyst. J. Incl. Phenom. Macro **90**, 149–155 (2018)

4. Borgna, A., Sepúlveda, J., Magni, S.I., Apesteguía, C.R.: Active sites in the alkylation of toluene with methanol: a study by selective acid–base poisoning. Appl. Catal. A **276**, 207–215 (2004)

5. Chiu, J., Pine, D., Bishop, S., Chmelka, B.: Friedel-Crafts alkylation properties of aluminosilica SBA-15 meso/macroporous monoliths and mesoporous powders. J. Catal. **221**, 400–412 (2004)

6. Bachari, K., Millet, J., Benaïchouba, B., Cherifi, O., Figueras, F.: Benzylation of benzene by benzyl chloride over iron mesoporous molecular sieves materials. J. Catal. **221**, 55–62 (2004)

7. Dong, P., Li, Z.Y., Wang, X.R., Yun, H.F., Li, G.X.: The alkylation reaction of benzene with methanol to produce toluene: Y-C and Y-C$_{Cs}$ catalyst. Green Chem. Lett. Rev. **11**, 158–164 (2018)

8. Bortnovsky, O., Sazama, P., Wichterlova, B.: Cracking of pentenes to C2–C4 light olefins over zeolites and zeotypes: role of topology and acid site strength and concentration. Appl. Catal. A **287**, 203–213 (2005)

9. Zhang, L., Liu, H., Li, X., Xie, S., Wang, Y., Xin, W., Liu, S., Xu, L.: Differences between ZSM-5 and ZSM-11 zeolite catalysts in 1-hexene aromatization and isomerization. Fuel Process. Technol. **91**, 449–455 (2010)

10. Chen, J.Q., Bozzano, A., Glover, B., Fuglerud, T., Kvisle, S.: Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process. Catal. Today **106**, 103–107 (2005)

11. Koempel, H., Liebner, W.: Lurgi's methanol to propylene (MTP®) report on a successful commercialization. Stud. Surf. Sci. Catal. **167**, 261–267 (2007)

12. Bleken, F., Skistad, W., Barbera, K., Kustova, M., Bordiga, S., Beato, P., Lillerud, K.P., Svelle, S., Olsbye, U.: Conversion of methanol over 10-ring zeolites with differing volumes at channel intersections: comparison of TNU-9, IM-5, ZSM-11 and ZSM-5. Phys. Chem. Chem. Phys. **13**, 2539–2549 (2011)

13. Mynsbrugge, J.V., Visur, M., Olsbye, U., Beato, P., Bjørgen, M., Speybroeck, V.V., Svelle, S.: Methylation of benzene by methanol: single-site kinetics over H-ZSM-5 and H-beta zeolite catalysts. J. Catal. **292**, 201–212 (2012)

14. Svelle, S., Joensen, F., Nerlov, J., Olsbye, U., Lillerud, K., Kolboe, S., Bjørgen, M.: Conversion of methanol into hydrocarbons over zeolite H-ZSM-5: ethene formation is mechanistically separated from the formation of higher alkenes. J. Am. Chem. Soc. **128**, 14770–14771 (2006)

15. Barthos, R., Bansagi, T., Sulizakar, T.S., Solymosi, F.: Aromatization of methanol and methylation of benzene over Mo2C/ZSM-5 catalysts. J. Catal. **247**, 368–381 (2007)

16. Svelle, S., Rønning, P.O., Olsbye, U., Kolboe, S.: Kinetic studies of zeolite-catalyzed methylation reactions. Part 2. Co-reaction of [^{12}C]propene or [^{12}C]n-butene and [^{13}C]methanol. J. Catal. **234**, 385–400 (2005)

17. Wen, Z.H., Yang, D.Q., He, X., Li, Y.S., Zhu, X.D.: Methylation of benzene with methanol over HZSM-11 and HZSM-5: a density functional theory studys. J. Mol. Catal. A **424**, 351–357 (2016)

18. Svelle, S., Visur, M., Olsbye, U., Saepurahman, Bjørgen, M.: Mechanistic aspects of the zeolite catalyzed methylation of alkenes and aromatics with methanol: a review. Top. Catal. **54**, 897–906 (2011)

19. Saepurahman, Visur, M., Olsbye, U., Bjørgen, M., Svelle, S.: In situ FT-IR mechanistic investigations of the zeolite catalyzed methylation of benzene with methanol: H-ZSM-5 versus H-beta. Top. Catal. **54**, 1293–1301 (2011)

20. Ma, P.S.: The Experimental Data Manual of Organic Compound. Chemical Industry Press, Beijing (2006)

21. Venuto, P.B., Landis, P.S.: Organic Catalysis Over Crystalline Aluminosilieates. Petroleum Chemical Press, London (1968)

22. Chen, Y.Y., Wang, Q.: Scientific Fundamentals and Technologies. Chemical Industry Press, Beijing (2016)

23. Lesthaeghe, D., Van Der Mynsbrugge, J., Vichel, M., Waroquier, P.M.: full theoretical cycle for both ethene and propene formation during methanol-to-olefin conversion in H-ZSM-5. ChemCatChem **3**, 208–212 (2011)

24. Dong, P., Li, Z.Y., Wang, D.L., Wang, X.R., Guo, Y.Q., Li, G.X., Zhang, D.Q.: Alkylation of benzene by methanol: thermodynamics analysis for designing and designing for enhancing the selectivity of toluene and para-xylene. Catal. Lett. **149**, 248–258 (2019)

25. Hu, H.L., Zhang, Q.F., Cen, J., Li, X.N.: High suppression of the formation of ethylbenzene in benzene alkylation with methanol over ZSM-5 catalyst modified by platinum. Catal. Commun. **57**, 129–133 (2014)

26. Zhu, Z.R., Chen, Q.L., Xie, Z.K., Yang, W.M., Li, C.: The roles of acidity and structure of zeolite for catalyzing toluene alkylation with methanol to xylene. Microporous Mesoporous Mater. **88**, 16–21 (2006)