Catal Lett (2007) 119:332–338
DOI 10.1007/s10562-007-9240-4

Benzene Alkylation with Propane over Mo Modified HZSM-5

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Received: 24 April 2007 / Accepted: 7 August 2007 / Published online: 7 September 2007

Abstract Benzene alkylation with propane has been studied over HZSM-5 loading 3.1–15.4 wt% Mo in continuous-flow microreactor under 350 °C and atmospheric pressure with the highest activity obtained at 6.7 wt% Mo loading. C_{7-9} aromatics were obtained as main products while the total amount of benzene rings kept unchanged. *i*-Propylbenzene and *n*-propylbenzene are formed primarily, while toluene, ethylbenzene, and ethyl-toluene are formed secondly from the propylbenzenes. Catalytic performance of 6.7 wt% Mo/HZSM-5(38) partially poisoned by NH_3 shows that the strong acid sites play a crucial role in the alkylation. Low SiO_2/Al_2O_3 ratio of HZSM-5 in the Mo modified catalysts gives high propane conversion. Two hydrothermal treatment methods were applied to the 6.7 wt% Mo/HZSM-5(38) catalyst, caused decrease of propane conversion but result in different product distribution. A possible reaction mechanism concerning bifunctional active centers resulted from combination of loaded Mo species and strong acid centers on HZSM-5 is proposed.

Keywords Benzene · Propane · ZSM-5 · Alkylation · Acidity

1 Introduction

Light alkanes such as methane, ethane, propane, and butane are among the most abundant and inexpensive hydrocarbons available today. There has been no efficient commercial process for light alkanes functionalization up to now. One possible way to upgrade light alkanes is to involve them in reactions with other molecules, for example, carbonylation [1] and alkylation of aromatic hydrocarbons.

The catalytic synthesis of alkyl aromatics from alkanes and benzene was first reported by Schmerling and Vesely [2] for the Friedel-Crafts catalyst systems and then studied by Olah et al. [3] in superacidic media. The above catalysts showed high catalytic activity and selectivity to products resulted from direct alkane addition to aromatics. However, these catalysts suffered from numerous, mainly environmental and corrosion drawbacks.

These drawbacks can be overcome by using solid catalysts. Over the past decade, metal-containing zeolites were reported to be potential catalysts for production of alkylbenzenes from benzene and propane. The attention was mainly focused on HZSM-5 zeolite usually modified by metal species such as Ga or Pt [4–14]. Over Pt/HZSM-5, the major products observed include C_1–C_4 gases, toluene (T), ethylbenzene (EB), *iso*propylbenzene (*i*PB), *n*-propylbenzene (*n*PB), and other products (in smaller amounts involving alkyl- and polyalkylbenzenes, naphthalene, and its derivatives) [6]. Ga-modified HZSM-5 zeolites have shown that toluene and ethylbenzene together with methane and ethane are formed as major products and *iso*propylbenzene and *n*-propylbenzene are also produced at low reaction temperatures in small amounts [10]. The reaction pathway leading to alkyl aromatics in the presence of these catalysts was found to be much more complicated

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than in the case of conventional acids. Evidently, the interaction between zeolite acids and loaded metal species was important.

Molybdenum-modified ZSM-5 catalysts have been found to be effective for propane activation including transformation to aromatics and dehydrogenation to propylene. But it has not been applied in the alkylation of benzene with light alkanes up to now to our knowledge. Considering that Mo is much cheaper than Pt or Ga, it is meaningful to apply Mo in alkylation of benzene with light alkane instead of Pt and Ga.

In this paper, we report on alkylation of benzene with propane over Mo modified HZSM-5.

2 Experimental

2.1 Preparation of Catalysts

NH_4ZSM-5 containing template with SiO_2/Al_2O_3 ratio of 25, 38, and 66 was provided by NanKai University of China. NH_4ZSM-5 powder was calcined in a muffle furnace at 550 °C for 5 h to obtain HZSM-5. SiO_2 (20–40 mesh) and γ-Al_2O_3 powder were also calcined in a muffle furnace at 550 °C for 5 h.

Mo/HZSM-5 catalysts were prepared by impregnation of HZSM-5 with aqueous solution of $(NH_4)_6Mo_7O_{24}$, followed by drying and calcination in a muffle furnace at 550 °C for 5 h. The powder was pressed into pellets, then crushed and sieved into 20–40 mesh particles for catalytic test. The loading amount of molybdenum was calculated as Mo: HZSM-5. SiO_2/Al_2O_3 ratio of ZSM-5 is indicated in parentheses such as 6.7 wt% Mo/HZSM-5(38) denoting the catalyst loading 6.7 wt% Mo on HZSM-5 with SiO_2/Al_2O_3 ratio of 38. Mo/SiO_2 and Mo/Al_2O_3 catalysts were prepared in the same way except that pelleting, crushing, and sieving was ignored for Mo/SiO_2.

Hydrothermal treatment was performed in a muffle furnace at definite temperatures for 6 h. The temperature was increased at a rate of 5 °C/min to required value, and a water steam of 80 mL/h was introduced into the furnace to carry out the hydrothermal treatment. This procedure was carried out before or after the impregnation.

2.2 Catalytic Tests

Benzene alkylation with propane was performed in a down-flow fixed-bed stainless tubular microreactor (8 mm i.d.) equipped with an axial thermowell (4 mm o.d.) under atmospheric pressure. In order to prevent condensation of the products before analyzation, all product lines were heated. One gram of catalyst was loaded into the reactor and purged in H_2 flow (purity >99.999%, 30 mL/min) at 450 °C for 3 h before introduction of reactants at 350 °C.

For catalysts adsorbed by NH_3, 1 g of the sample was purged in H_2 flow (purity >99.999%, 30 mL/min) at 450 °C for 3 h in a 15 mm i.d. quartz tube to avoid NH_3 pollution to the reactor. As the catalyst was cooled to 350 or 400 °C, 80 mL NH_3 (purity >99.999%) was slowly injected into the quartz tube during 5 min. Purged for 4 h in H_2 flow with the temperature unchanged to remove excess ammonia, the sample was quickly transferred into the reactor. Then the catalyst was purged in H_2 flow at 350 °C for about 10 min before introduction of reactants.

The reaction mixture was analyzed on line by a gas chromatography equipped with a 50 m PONA capillary column connected to a flame ionization detector.

The data showed that the carbon atom proportion of benzene-ring in reaction mixture was identical with the feed, which meant benzene ring was not formed or broken during the reaction.

2.3 Characterization Techniques

Chemical composition of the catalysts was determined with a Philips Magix X-Ray Fluorescence spectrometer.

XRD patterns were obtained on a Rigaku D/max-rB X-ray powder diffractometer under graphite monochromatized Cu Kα radiation (λ = 1.54178 Å), 40 kV, and 50 mA, with scanning rate 5 min^{-1}.

NH_3-TPD (NH_3-temperature-programmed desorption) was performed on two apparatuses denoted by NH_3-TPD-MS (mass spectrometer as detector) and NH_3-TPD respectively. NH_3-TPD-MS was performed on Micromeritics AutoChem 2910 connected to an Ominister MS detector. About 0.14 g of the sample was placed in a reactor, flushed with H_2 (30 mL/min) at 450 °C for 1 h, then cooled to desired temperature (100, 350, and 400 °C) and saturated with NH_3 until equilibrium was reached after H_2 was replaced by He (20 mL/min). When the baseline was stable, NH_3-TPD-MS was conducted from 100 to 650 °C at 20 °C/min. The NH_3-TPD was measured on a conventional TPD apparatus with TCD detector. About 0.1 g of sample was placed in a reactor, flushed with H_2 (30 mL/min) at 450 °C for 1 h, then cooled to 100 °C. After H_2 was replaced by He (40 mL/min), the sample was saturated with ammonia until equilibrium was reached. When the baseline was stable, NH_3-TPD was carried out from 100 to 650 °C at 20 °C/min.

3 Results and Discussion

3.1 Effect of Mo Loading Amount on Alkylation of Benzene with Propane over Mo/HZSM-5(38)

Catalysts loading 3.1–15.4 wt% Mo on HZSM-5(38) were prepared. XRD patterns showed that addition of Mo does not induce any obvious change in crystal structure or crystallinity of the zeolite ZSM-5. An obvious feature was that no crystal phase of molybdenum oxides appeared which meant that the Mo oxide was well dispersed on the surface of ZSM-5. Catalytic performance of Mo/HZSM-5(38) and HZSM-5(38) is listed in Table 1.

Alkylation of benzene with propane over HZSM-5(38) produced non-aromatics and C_{10+} aromatics in large amount besides C_{7-9} aromatics. Addition of 3.1–15.4 wt% Mo to HZSM-5(38) decreased non-aromatics and C_{10+} aromatics to such an extent that they were beyond detection limit under most cases. The activity was obviously depressed by Mo addition, but the catalyst loading 6.7 wt% Mo exhibited much higher activity than other Mo/HZSM-5(38) catalysts.

NH_3-TPD profiles of Mo/HZSM-5(38) are shown in Fig. 1. The profile of HZSM-5(38) shows two NH_3 desorption peaks at about 200 and 430 °C. We refer to the acid sites corresponding the low/high temperature NH_3 desorption peak as the weak/strong acid sites. Loading of Mo decreased concentrations of the acid sites especially the strong acid sites. The strength of the strong acid sites is weakened while the high temperature peak of NH_3-desorption shifts to lower temperature becoming tailing part of the low temperature peak. On the catalyst loading as high as 15.4 wt% Mo, the concentration of weak acid sites decreases sharply due to covering of zeolite surface by Mo.

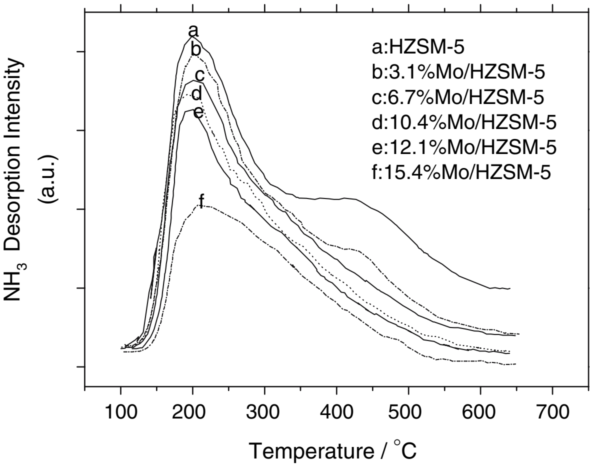

Fig. 1 NH_3-TPD profiles of Mo/HZSM-5(38)

So, it can be concluded that there exists an interaction between loaded Mo and acid centers of HZSM-5 resulting in new bifunctional surface species being responsible for the selective alkylation of benzene with propane producing C_{7-9} aromatics. An intermediate loading amount of Mo around 6.7 wt% on HZSM-5(38) will produce most such bifunctional surface species.

3.2 Effect of Contact Time on Product Distribution over 6.7 wt% Mo/HZSM-5(38)

In order to illuminate if transformation between the C_{7-9} aromatics products occurred over Mo/HZSM-5, the alkylation was carried out at different WHSV over 6.7 wt% Mo/HZSM-5(38). The relation between conversion of propane and product distribution is shown in Fig. 2. It is observed that *i*-propylbenzene (*i*PB) and *n*-propylbenzene (*n*PB) are formed primarily, while toluene (T), ethylbenzene (EB) and ethyl-toluene (ET) are formed secondly from *i*-propylbenzene and *n*-propylbenzene.

Table 1 Benzene alkylation with propane over Mo/HZSM-5(38) and HZSM-5(38)

Mo loading (wt%)	0	3.1	6.7	10.4	12.1	15.4
Propane conversion (%)	7.8	1.1	6.4	3.5	3.1	2.2
Product distribution* (mol%)						
Non-aromatics	23.3	~0	~0	~0	~0	~0
Toluene	4.7	9.9	2.9	6.4	10.0	10.5
C_8 aromatics	8.4	20.8	39.9	24.6	26.3	28.0
C_9 aromatics	27.5	64.1	57.2	69.0	59.2	61.5
i-Propylbenzene	5.4	22.4	26.1	30.4	21.8	22.6
n-Propylbenzene	22.1	39.2	31.1	38.7	37.4	38.9
Ethyl-toluene	~0	2.6	~0	~0	~0	~0
C_{10+} aromatics	36.2	5.2	~0	~0	4.4	~0

Reaction conditions: WHSV = 2 h^{-1}, T = 350 °C, benzene/propane molar ratio = 0.8, TOS = 0.5 h

*Non-aromatics including methane, ethane, C_4–C_5. C_8 aromatics are mainly ethylbenzene

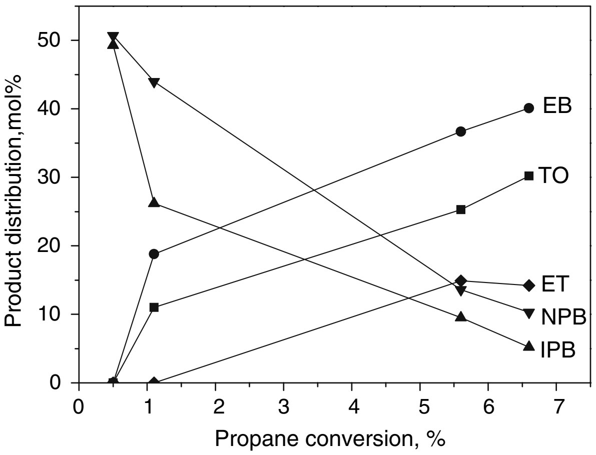

Fig. 2 Product distribution versus propane conversion over 6.7 wt% Mo/HZSM-5(38) catalyst. T = 350 °C, benzene/propane = 1.1 mol/mol, TOS= 0.5 h, no xylem detected

3.3 Catalytic Behavior of Mo/HZSM-5 with Different Si/Al_2 Ratios

Figure 3 shows the NH_3-TPD-MS profiles of catalysts loading 6.7 wt% Mo on HZSM-5 with different SiO_2/Al_2O_3 ratios (Si/Al_2). As the SiO_2/Al_2O_3 ratio of HZSM-5 increases from 25 to 66, the density of both weak and strong acid sites decreases, and propane conversion decreases from 7.0 to 2.4% (see Table 2). With propane conversion increase, selectivity for C_9 aromatics decreases, and selectivity for C_7 and C_8 aromatics increase due to transformation of C_9 aromatics. This indicates that high acid density of HZSM-5 helps to lift the activity of benzene alkylation with propane at definite Mo loading amount. Taking results of Sect. 3.1 into consideration, there may exists different optimal Mo loading amount for HZSM-5 with different SiO_2/Al_2O_3 ratio.

Table 2 Effect of Si/Al_2 ratio of HZSM-5 on benzene alkylation with propane over 6.7 wt %Mo/HZSM-5

SiO_2/Al_2O_3 ratio (mol/mol)	25	38	66
Propane conversion (%)	7.0	5.6	2.4
Product distribution (mol%)			
Toluene	31.9	25.3	23.3
C_8 aromatics*	46.4	36.7	35.3
Ethylbenzene	40.6	36.7	35.3
p-Xylene	5.8	~0	~0
C_9 aromatics	21.6	38.0	41.4
i-Propylbenzene	10.3	9.5	15.6
n-Propylbenzene	11.3	13.6	25.8
Ethyl-toluene	~0	14.9	~0

Reaction conditions: WHSV = 2.3 h^{-1}, T = 350 °C, benzene/propane molar ratio = 1.1, TOS = 0.5 h

**m*, *o*-Xylene not detected

3.4 Catalytic Behavior of Mo/HZSM-5(38) Partially Poisoned by NH_3

Figure 4 shows the NH_3-TPD-MS profiles of 6.7 wt% Mo/HZSM-5(38) catalyst at different NH_3 adsorption temperatures. The profile adsorbing NH_3 at 100 °C shows two NH_3 desorption peaks at about 200 and 380 °C, corresponding to the situation in which all the acid sites are occupied by NH_3. When NH_3 was adsorbed at 350 or 400 °C, all the weak acid sites and most strong acid sites were free of NH_3 while a small part of the strong acid sites were occupied by NH_3. The high temperature NH_3 desorption peaks of the profiles adsorbing NH_3 at 350 or 400 °C shift to higher temperature zone indicates that the adsorbed NH_3 occupies the stronger part of the strong acid sites for the strength of acid sites on solid acid catalyst surface is not uniform.

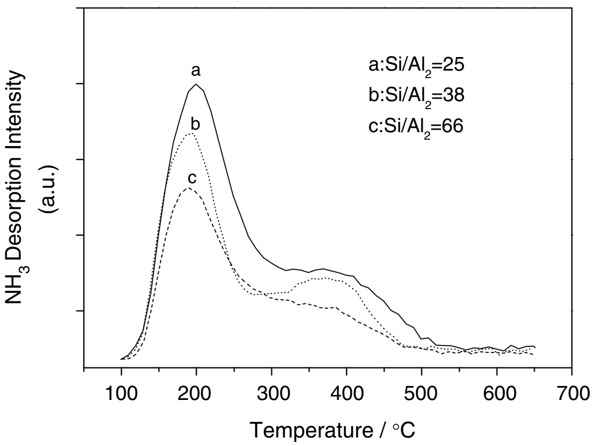

Fig. 3 NH_3-TPD-MS profiles of 6.7 wt% Mo/HZSM-5 catalysts with different Si/Al_2 ratios

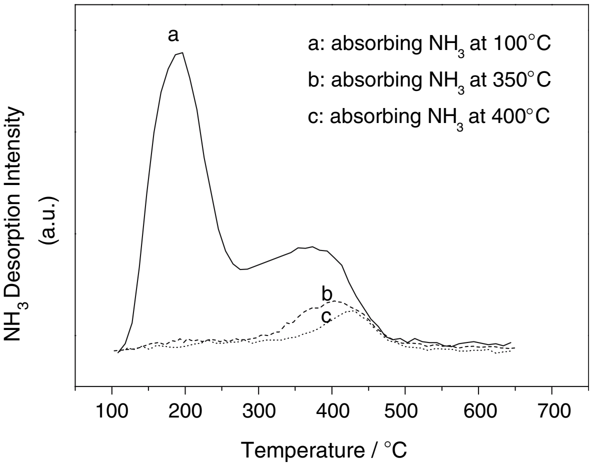

Fig. 4 NH_3-TPD-MS profiles of 6.7 wt% Mo/HZSM-5(38) at different NH_3 adsorption temperatures

Table 3 Benzene alkylation with propane over 6.7 wt% Mo/HZSM-5(38) at different NH_3 adsorption temperatures

NH_3 adsorption temperature (°C)	Adsorbing no NH_3	400	350
Propane conversion (%)	5.6	1.6	0.9
Product distribution (mol%)			
Toluene	25.3	12.2	11.9
C_8 aromatics*	36.7	31.5	27.0
C_9 aromatics	38.0	56.3	61.1
i-Propylbenzene	9.5	21.7	29.0
n-Propylbenzene	13.6	34.6	32.1
Ethyl-toluene	14.9	~0	~0

Reaction conditions: WHSV = 2.3 h^{-1}, T = 350 °C, benzene/propane molar ratio = 1.2, TOS = 0.5 h

*C_8 aromatics are mainly ethylbenzene

So, information about the role of acid sites with different strength in benzene alkylation with propane can be got by comparison of catalytic performance of the catalysts adsorbing NH_3 at 350 and 400 °C with the catalyst adsorbing no NH_3 which is shown in Table 3.

Propane conversion of 5.6% is obtained over clean 6.7 wt% Mo/HZSM-5(38). With a small (around one fourth) part of the strong acid sites is poisoned by NH_3 (the catalyst adsorbing NH_3 at 400 °C), propane conversion drops sharply to 1.6% (70% activity lost). When more strong acid sites are poisoned (the catalyst adsorbing NH_3 at 350 °C), propane conversion drops to only 0.9% which means only 16% activity left though more than half of the strong acid sites is free of NH_3. This strongly implies that the strong acid sites are concerned in the alkylation while the contribution of the weak acid sites is minor and the stronger the acid sites, the higher the activity. Loading of Mo may change the proportion of Brönsted and Lewis acid sites. The effect needs further investigation. The relation between product distribution and propane conversion is consistent with the results of Sect. 3.2.

3.5 Effect of Hydrothermal Treatment

Hydrothermal treatment is a usual method to modify acidity of zeolites. Due to the importance of zeolite acidity demonstrated by the above results, the effect of hydrothermal treatment was investigated. The hydrothermal treatment was carried in two modes. One is treating the 6.7 wt% Mo/HZSM-5(38) directly, and the other is treating the zeolite HZSM-5(38) followed by Mo loading.

Table 4 shows the catalytic performance of 6.7 wt% Mo/HZSM-5(38) undergoing hydrothermal treatment at 400–600 °C.

Figure 5 shows the NH_3-TPD-MS profiles of the catalysts treated in two modes. With the temperature of hydrothermal treatment increased, both amount of weak and strong acid sites decrease drastically, especially for the strong acid sites.

No matter in which mode the hydrothermal treatment was carried out, conversions of propane over the treated catalysts are all lower than untreated 6.7 wt% Mo/HZSM-5(38) and decrease with the temperature of hydrothermal treatment increasing, in line with decrease of amount of strong acid sites due to dealumination of the zeolite which can be seen from Fig. 5. This is in agreement with the conclusion that the strong acid sites are concerned in the alkylation while the contribution of the weak acid sites is minor.

The product distribution of 6.7 wt% Mo/HZSM-5(38) undergone hydrothermal treatment differs from expectation based on Fig. 2. C_9 aromatics contents are obviously lower over the treated catalysts. For example, it is 62.0 and

Table 4 Benzene alkylation with propane over 6.7 wt% Mo/HZSM-5(38) undergoing hydrothermal treatment

	No treatment	Loading Mo first			Hydrothermal treatment first		
Treatment temperature (°C)	–	400	500	600	400	500	600
Propane conversion (%)	5.6	2.1	1.8	1.1	2.4	1.1	0.7
Product distribution (mol%)							
Toluene	25.3	18.5	11.7	9.9	24.9	13.7	14.0
C_8 aromatics*	36.7	30.9	37.2	28.1	47.2	36.8	13.0
Ethylbenzene	36.7	30.9	37.2	28.1	47.2	18.2	13.0
p-Xylene	~0	~0	~0	~0	~0	18.5	~0
C_9 aromatics	38.0	50.6	51.1	62.0	27.9	49.5	72.8
i-Propylbenzene	9.5	24.6	26.2	31.0	14.3	24.0	38.4
n-Propylbenzene	13.6	26.0	24.9	31.0	13.6	25.5	34.4
Ethyl-toluene	14.9	~0	~0	~0	~0	~0	~0

Reaction conditions: WHSV = 2.3 h^{-1}, T = 350 °C, benzene/propane molar ratio = 1.2, TOS = 0.5 h

**m*, *o*-Xylene not detected

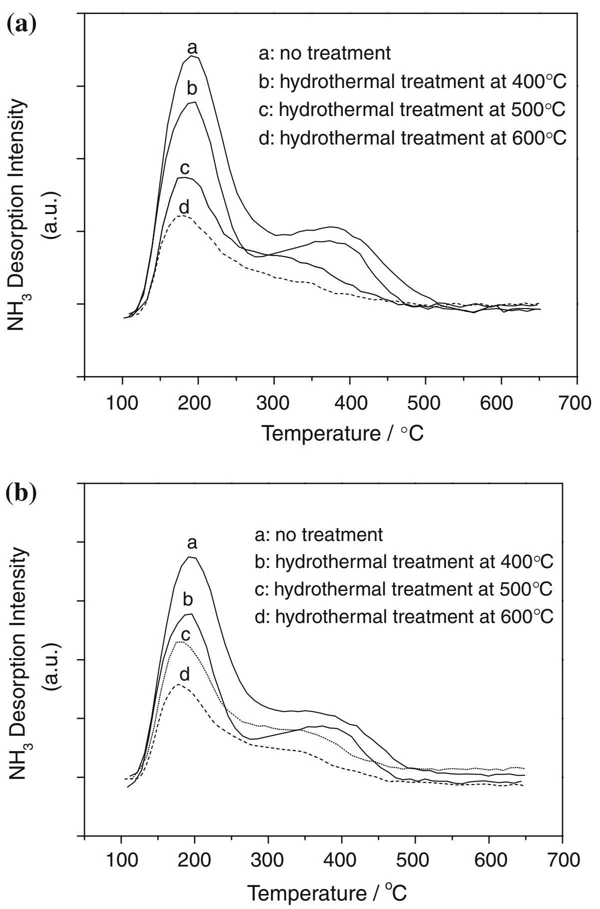

Fig. 5 NH_3-TPD-MS profiles of 6.7 wt% Mo/HZSM-5(38) catalyst undergoing hydrothermal treatment. (**a**) Hydrothermal treatment before loading Mo to HZSM-5. (**b**) Hydrothermal treatment after loading Mo to HZSM-5

49.5 mol% in Table 4 while it reaches 70 mol% in Fig. 2 at the same propane conversion of 1.1%. This shows that hydrothermal treatment has different effects on the activity for primary alkylation forming C_9 aromatics and secondary transformation of C_9 aromatics forming $C_{7–8}$ aromatics. And the effects are different under the two treating mode.

3.6 Reaction Mechanism of Benzene Alkylation with Propane on Mo/HZSM-5

In situ ^{13}C MAS NMR studies investigating benzene alkylation with propane over Ga-modified HZSM-5 catalysts have shown that the reaction mechanism is bifunctional with toluene and ethylbenzene as the major primary products [4, 15]. Propane adsorbs on a bifunctional active site leading to pseudo-protonated cyclopropane (PPCP) intermediate. The PPCP intermediate can decompose in various ways resulting in the formation of CH_4 and $C_2H_5^+$ or C_2H_6 and CH_3^+ or H_2 and $C_3H_7^+$. These carbenium ions can lead to the corresponding alkylbenzenes: toluene, ethylbenzene, *i*-propylbenzene and *n*-propylbenzene. Reverse reaction of unstable *i*-propylbenzene and *n*-propylbenzene to propane and benzene is followed by alkylation leading to more stable toluene and ethylbenzene.

Bifunctional mechanism is also recommended for Pt/HZSM-5 catalytic system with *i*- and *n*-propylbenzene as the major primary products [6]. Propane dehydrogenation and protonation may take place on a metal-acidic center, which results in direct benzene alkylation. The propylbenzenes can undergo dealkylation and dismutation reactions leading to benzene and propylene or toluene and ethylbenzene respectively. Large amount of CH_4, C_2H_6, and $C_{4–5}$ are also formed secondly.

Over Mo/SiO_2 or Mo/Al_2O_3 catalysts, neither alkylation of benzene with propane nor propane dehydrogenation was detected under the reaction conditions of Table 1. And the product distribution of Mo/HZSM-5 is quite different from HZSM-5. These imply that the alkylation mechanism over Mo/HZSM-5 is bifunctional as Pt or Ga modified HZSM-5. But essential absence of methane, ethane, and propane over Mo/HZSM-5 catalysts suggests that the alkylation occurs in a way different from Ga/HZSM-5 and Pt/HZSM-5. Based on the above results, a possible bifunctional reaction mechanism is proposed as described in Scheme 1.

Propane adsorbs on a bifunctional active site leading to PPCP intermediate (Eq. 1). The bifunctional active sites are resulted from combination of Mo species and strong acid sites of HZSM-5. The PPCP intermediate mainly decomposes to H_2 and $C_3H_7^+$ (Eq. 2) resulting in the formation of *i*-propylbenzene and *n*-propylbenzene (Eqs. 3, 4). For toluene and ethylbenzene did not appear as primary products, they can only be formed from propylbenzenes and not from the PPCP intermediate as over Ga/HZSM-5. The adsorbed propylbenzene species can decompose in two ways resulting in the formation of toluene and $C_2H_5^+$

$$C_3H_8 + H^+S^- \longleftrightarrow C_3H_9^+S^- \text{ (PPCP)} \qquad (1)$$

$$C_3H_9^+S^- \rightarrow C_3H_7^+S^- + H_2 \qquad (2)$$

$$C_3H_7^+S^- + C_6H_6 \rightarrow C_3H_7C_6H_6^+S^- \qquad (3)$$

$$C_3H_7C_6H_6^+S^- \rightarrow C_3H_7C_6H_5 + H^+S^- \qquad (4)$$

$$C_3H_7C_6H_6^+S^- \rightarrow C_2H_5^+S^- + CH_3C_6H_5 \qquad (5)$$

$$C_2H_5^+S^- + C_6H_6 \rightarrow C_2H_5C_6H_5 + H^+S^- \qquad (6)$$

$$C_3H_7C_6H_6^+S^- \rightarrow CH_3^+S^- + C_2H_5C_6H_5 \qquad (7)$$

$$CH_3^+S^- + C_6H_6 \rightarrow CH_3C_6H_5 + H^+S^- \qquad (8)$$

$$2\ CH_3^+S^- \rightarrow C_2H_5^+S^- + H^+S^- \qquad (9)$$

Scheme 1 Proposed mechanism for benzene alkylation with propane over Mo/HZSM-5 (H^+S^- denotes the bifunctional active center of Mo/HZSM-5 catalyst)

(Eq. 5) or ethylbenzene and CH_3^+ (Eq. 7). These carbenium ions can lead to the corresponding alkylbenzenes (Eqs. 6 and 8).

4 Conclusion

With Mo/HZSM-5 as catalyst, C_{7-9} aromatics can be produced selectively in benzene alkylation with propane while amount of benzene rings keep unchanged. *i*-Propylbenzene and *n*-propylbenzene are formed primarily, while toluene, ethylbenzene, and ethyl-toluene are formed secondly from the propylbenzenes.

Low SiO_2/Al_2O_3 ratio of HZSM-5 in the Mo modified catalysts give high propane conversion. Two hydrothermal treatment modes applied to the 6.7 wt% Mo/HZSM-5(38) catalyst both decrease propane conversion but result in different product distribution.

Essential absence of C_1–C_4 hydrocarbon in the products suggests that the alkylation occurs in a way quite different from Ga/HZSM-5 and Pt/HZSM-5. A bifunctional reaction mechanism is proposed.

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