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Effects of steam and TEOS modification on HZSM-5 zeolite for 2,6-dimethylnaphthalene synthesis by methylation of 2-methylnaphthalene with methanol

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ABSTRACT

Shape-selective methylation of 2-methylnaphthalene (2-MN) over HZSM-5 catalysts modified by steam and tetraethoxysilane (TEOS) treatments was carried out in a fixed-bed reactor. Catalysts were characterized by XRD, NH_3-TPD, BET, FT-IR spectra of pyridine adsorbed, and by adsorption of hexane and cyclohexane. The results show that the TEOS treatment can effectively passivate external active site and narrow pore mouth of catalyst, but it has less effect on the internal surface than steam modification. Hydrothermal treatment can effectively reduce both external and internal acid sites, and adjust channel of catalyst. Steam treatment can effectively increase the ratio of 2,6/2,7-DMN, but the ratio has no increasing trend on TEOS modified catalyst. So adjusting acidity property is more useful to increase the selectivity to 2,6-DMN and the ratio of 2,6/2,7-DMN than narrowing catalyst pore mouth. Tailoring acidic characteristics is more important than spatial control for distinguishing between 2,6-DMN and 2,7-DMN.

1. Introduction

Shape-selective alkylation of polycyclic hydrocarbons for preparation of symmetric intermediates such as 2,6-dialkylnaphthalene (2,6-DAN) and 4,4-dialkylbiphenyl (4,4-DABP), the important precursors for advanced polymer materials [1–5], has been the focus on many recent studies [5–13]. Among 2,6-DANs, 2,6-dimethylnaphthalene (DMN) is regarded as the most desirable intermediate which can be oxidized with high selectivity into 2,6-naphthalenedicarboxylic acid (2,6-NDCA), a monomer for aromatic polyester materials [14,15]. Therefore, effective synthesis of 2,6-DMN has become an important subject.

2,6-DMN, 2,7-DMN, and 2,3-DMN are the β,β-DMN isomers among the 10 isomers of DMN, so shape selective processing can be used for synthesis of the slimmer isomer 2,6-DMN [15–19]. This selective procedure is helpful to prevent reactants from producing large amount of byproducts. However, it is difficult to increase the selectivity of 2,6-DMN among β,β-DMN and the ratio of 2,6/2,7-DMN. Therefore, we need to further modify catalyst by adjusting acidity and channel of the catalyst.

In the case of synthesis of 2,6-DMN, the most difficult issue is how to increase the ratio of 2,6/2,7-DMN. Because the boiling points of 2,6-DMN and 2,7-DMN are very similar (only 0.3 °C difference), it is very difficult to separate them from each other, and so several studies attempted to increase the ratio of 2,6-/2,7-DMN [20–22]. Good agreement has been obtained between quantum chemical calculation showing that C-6 position is relatively more active than C-7 on 2-MN due to different electronic density, and the experiments showing lowering acidic strength of catalysts favored 2,6-DMN selectivity [20,22]. But, there is still disagreement about the origin of selectivities to 2,6- and 2,7-DMN.

Another factor is external acid sites on catalyst particle surface. Tetraethylorthosilicate (TEOS, with molecular diameter of about 0.96 nm [23]) is commonly used as modification reagent for passivating external surface acidic sites and narrowing pore mouth without changing intrapore surface, because it is too large to enter the channel of the HZSM-5 type catalysts. Steaming treatment techniques have been developed for zeolites and are now widely used to remove part of aluminum species in zeolite frameworks with the aim of decreasing the acidity and adjusting channel of the resulting catalysts [24].

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In this work, we studied the effects of steam and TEOS modification on the selectivity and activity of HZSM-5 for the methylation of 2-MN with methanol, and identified the promising direction for modification towards increasing the ratio of 2,6/2,7-DMN.

2. Experiment

2.1. Samples of catalyst

HZSM-5 [CBV8014 ($SiO_2/Al_2O_3 = 80$)] sample in powder form was obtained from Zeolyst Corp. The sample was supplied in proton-form, and was activated before the catalytic test. Certain amount of TEOS was added to the suspension of 2 g of the HZSM-5 in 50 ml of cyclohexane, and then refluxed for 24 h under room temperature (25 °C). The modified sample was calcined at 550 °C (heating rate: 2 °C/min) for 5 h in air. The calcined catalyst is denoted as SiO_2–HZSM-5. The hydrothermally treated zeolites were obtained by steaming HZSM-5 at 500 °C for 6 h, followed by calcination at 540 °C (heating rate: 2 °C/min) for 5 h in air. The calcined catalyst is referred to as HT–HZSM-5.

2.2. Characterization

X-ray powder diffraction patterns of the samples were recorded on a Rigaku D/max-2400 using Cu Kα1 radiation. The surface area and pore volume measurements of the catalysts were conducted on a volumetric adsorption apparatus (Micromeritics ASAP 2020) at 77 K using liquid N_2. NH_3-TPD experiments were performed on a conventional set-up equipped with a thermal conductivity detector (CHEMBET 3000). FT-IR (EQUINOX 55) coupled with pyridine adsorption was used to measure the acidic nature. Adsorption experiments with hexane and cyclohexane were carried out on a home-made instrument. The catalyst was activated at 350 °C in a glass tube for 1 h for dehydration, and then 50 ml/min of N_2 carrier with adsorbate passed over the catalyst at room temperature. After the desired time the catalyst was weighed using an electronic balance.

2.3. Catalytic reaction

Catalytic experiments were carried out in a fixed-bed flow reactor. The powder catalyst samples were pressed and ground to 20–40 mesh pellets. About 0.3 g of the pellets was loaded into the reactor for the test at atmospheric pressure. Before the reactant was introduced, the catalyst was activated in situ by heating at 450 °C for 1 h in a dry nitrogen flow. After lowering the temperature to 360 °C, a liquid mixture of 2-MN: methanol:mesitylene = 1:5:5 (molar ratio) was pumped into the reactor with a metering pump for the evaluation test. Nitrogen was used as a carrier gas with a flow-rate of 20 ml/min. Analysis of the products was performed by a gas chromatography with a Beta DEX 120 (60 m × 0.25 mm) capillary column. The detector and injector were both kept at 300 °C. The oven temperature was initially kept at 150 °C for 37 min, increased to 180 °C at a rate of 6 °C/min and held at the final temperature for 27 min. The conversion of 2-MN was calculated on the basis of the 2-MN concentration change, and the selectivity for 2,6-DMN was defined as the molar ratio of 2,6-DMN to all DMN isomers.

3. Results and discussion

3.1. Effect of different modification conditions on methylation of 2-MN

Fig. 1 shows the effect of different steaming temperatures on conversion of 2-MN and selectivity to 2,6-DMN. Lower steaming temperature at 400 °C did not change conversion or selectivity. With increasing steaming temperature to 500 and 600 °C, the conversion of 2-MN decreased sharply, but the selectivity of 2,6-DMN increased. Further steaming temperature from 600 to 700 °C decreased conversion but exhibited no further improvement in 2,6-DMN selectivity.

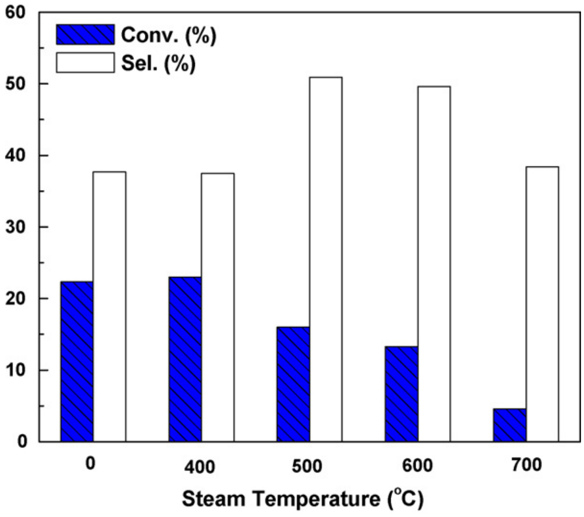

Fig. 1. 2-MN conversion and 2,6-DMN selectivity over the HZSM-5 treated under various steaming temperatures.

Fig. 2 shows the effects of TEOS treatment for coating SiO_2 over HZSM-5 on the conversion of 2-MN and the selectivity to 2,6-DMN. With increasing amount of SiO_2 coating up to 4 wt%, the conversion of 2-MN decreased, but the selectivity of 2,6-DMN increased, further increasing the amount of SiO_2 beyond 4% showed no significant impacts on 2-MN conversion and 2,6-DMN selectivity.

For subsequent comparison of the above two modification methods, we choose the catalyst with steaming modification at 500 °C (HT–HZSM-5) and the catalyst with 4% SiO_2 (SiO_2–HZSM-5) with similar 2-MN conversion for further research.

3.2. Characterization of the modified HZSM-5 catalysts

Fig. 3 shows the XRD patterns of the samples before and after the modification. As shown in Fig. 3, the structure did not change

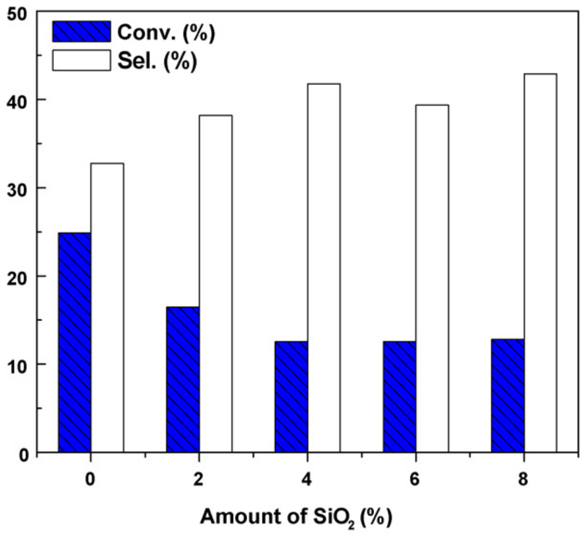

Fig. 2. 2-MN conversion and 2,6-DMN selectivity over the HZSM-5 with different SiO_2 amounts by TEOS treatment.

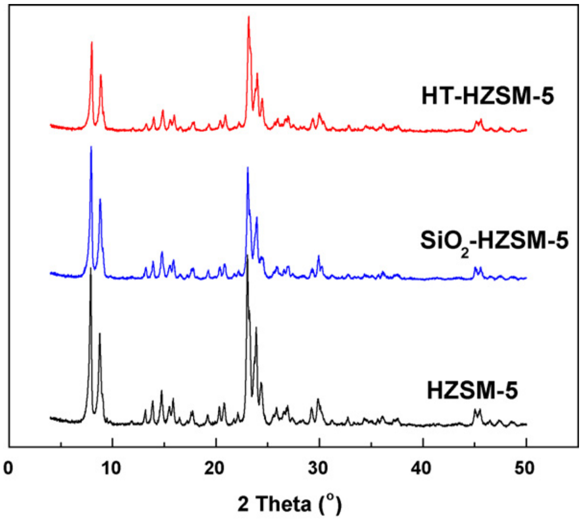

Fig. 3. XRD patterns of original HZSM-5, HT–HZSM-5 and SiO_2–HZSM-5 catalysts.

after the modification; the crystal structure of HZSM-5 was maintained after the modifications.

Table 1 shows the change of physical and chemical properties of catalyst before and after modification. Because the size of mesitylene is much bigger than catalyst pore size, it is difficult to enter the channel of HZSM-5. We conducted isomerization reaction of mesitylene (TMB) to evaluate the change of external surface acidity. As can be seen from Table 1, mesitylene isomerization activity decreased significantly after both modifications. On the parent HZSM-5, the conversion of TMB can reach 41.5%, while on the HT–HZSM-5 and SiO_2–HZSM-5 mesitylene conversion decreased to 28.4% and 15.2%, respectively. These results indicate that TEOS can more effectively passivate external surface acidic sites. Furthermore, from the variation of the BET surface areas and the pore volumes of HZSM-5 and modified catalysts, as shown in Table 1, it can be seen that the micropore surface area of the HZSM-5 catalyst decreased sharply from 345 m^2/g of the fresh sample to 243 m^2/g after steam modification, however, the extent of the decrease in the micropore surface area of SiO_2–HZSM-5 was much smaller than that of HT–HZSM-5 (321.9 m^2/g). The variation of micropore volume of catalysts shows the same trend. This implies that some pore channel blockage occurred on the HT–HZSM-5 because of the dealumination. Owing to its large size, TEOS treatment has less effect on the pore channel of HZSM-5. The relative crystallinity was determined by the intensity of the characteristic peaks in the 2θ range of 22.5–25°. The XRD peak intensity of HT–HZSM-5 decreased more than that of SiO_2–HZSM-5 due to dealumination with the former. The results show that the relative crystallinity was lower with HT–HZSM-5 than with SiO_2–HZSM-5.

Table 1
Physical and chemical properties of catalysts.

Sample	X_{TMB} (%)	Surface area (m^2/g)		Pore volume (ml/g)		Relative crystallinity (%)
		Total	Micropore	Total	Micropore	
HZSM-5	41.5	486.2	345.0	0.39	0.14	100
HT–HZSM-5	28.4	402.0	243.2	0.43	0.11	80
SiO_2–HZSM-5	15.2	429.8	321.9	0.30	0.13	91

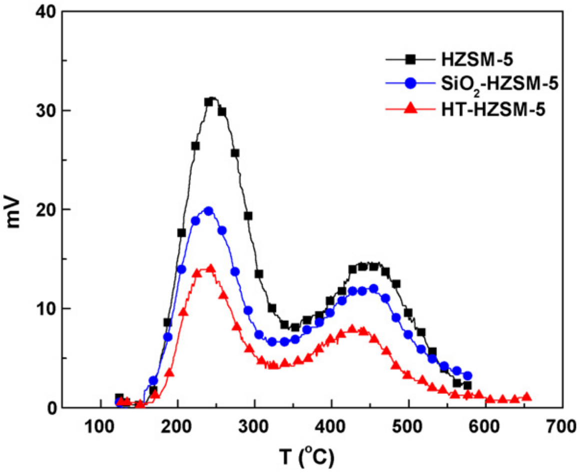

Fig. 4. NH_3-TPD profiles of the original and modified HZSM-5 catalysts.

The effects of the steam and TEOS modification on acidity and acidic strength distribution of the resulting catalysts were studied by the NH_3-TPD technique and the results are shown in Fig. 4. It can be seen that each curve in the figure has two desorption peaks appearing at high and low temperatures, respectively, with the former assigned to strong acid sites and the later to weak acid sites. Acid strengths were decreased by the modification, and the peak temperature moved to lower temperature in TPD profiles, especially HT–HZSM-5. Acidity (amount of acid sites) was also decreased by these two modification methods. But after SiO_2 modification, the acid amount remains higher than that after steam modification. As previous analysis about mesitylene isomerization, SiO_2–HZSM-5 has less external surface acid sites, and in NH_3-TPD case, HT–HZSM-5 shows lower amount of total acid sites. Therefore, it can be concluded that TEOS does not enter the pore channel so the SiO_2 modification does not affect the acidity of the internal pore surfaces in the channel of HZSM-5 catalyst. On the other hand, steaming modification can effectively adjust (decrease) both of external and internal surface acidity.

Fig. 5 shows the FT-IR spectra of pyridine adsorbed on HZSM-5 and modified HZSM-5 catalysts after desorption at 300 °C. The relatively strong peak around 1545 cm^{-1} is attributed to pyridine bound on Brönsted acid (proton) sites; the peak around 1490 cm^{-1} is attributed to pyridine associated with both Brönsted and Lewis acid sites; a weak peak around 1455 cm^{-1} is due to pyridine bound on Lewis acid sites (e.g., adsorption of pyridine at an exposed

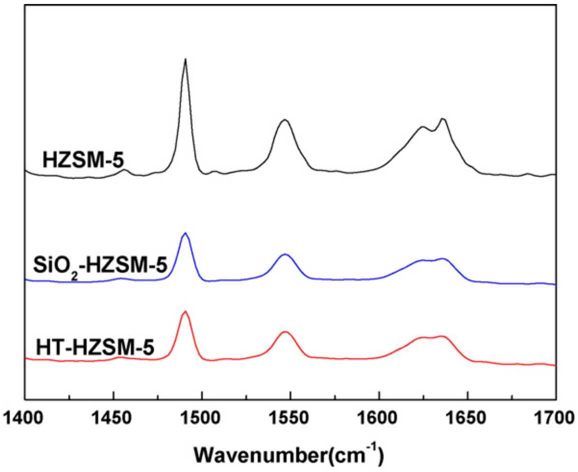

Fig. 5. FT-IR spectra of pyridine adsorbed on the HZSM-5 catalysts after desorption at 300 °C.

Table 2
Ratio of Brönsted to Lewis acidity (B/L ratio) of the catalysts.

	150 °C	300 °C	450 °C
HZSM-5	13.29	13.70	11.73
SiO_2–HZSM-5	13.08	12.26	11.01
HT–HZSM-5	11.06	9.26	8.14

aluminum cation). It can be seen from Fig. 5 that both Brönsted and Lewis acidic sites coexist but there are more Brönsted sites on the modified and the original HZSM-5 catalysts.

Table 2 shows the changes of the ratio of Brönsted to Lewis acid sites (B/L ratio). After the modification, B/L ratio for both modified catalyst decreased, but HT–HZSM-5 showed more significant decrease than that for SiO_2–HZSM-5. This trend is most likely the results of dealumination and the creation of Lewis acidic external framework aluminum during treatment. These IR results are in good agreement with those of NH_3-TPD analysis.

Figs. 6 and 7 show hexane and cyclohexane adsorption, respectively, on modified and unmodified HZSM-5 zeolites. The change of total amount of hexane adsorbed reflects on changes in pore volume. The adsorption of hexane was influenced by the steam modification, the amount and the rate of adsorption decreased significantly upon the steam modification. However, the rate of adsorption on TEOS modified HZSM-5 zeolite was almost at the same level as that for unmodified HZSM-5. This change is in agreement with the BET analysis.

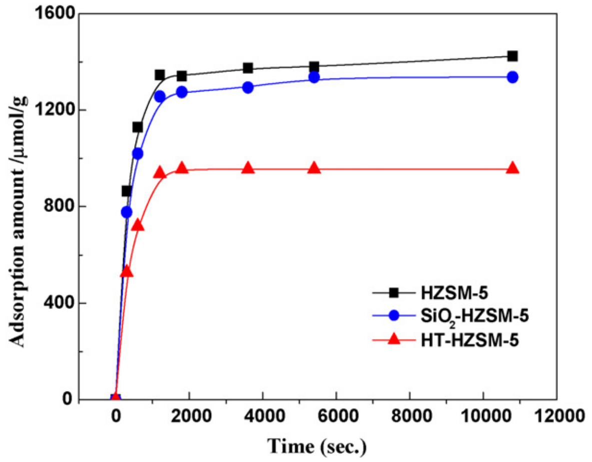

Fig. 6. Adsorption curves of hexane on original HZSM-5, HT–HZSM-5 and SiO_2–HZSM-5 catalysts.

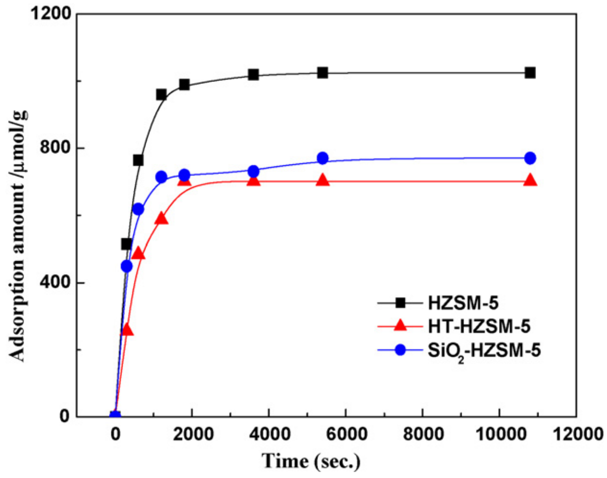

Fig. 7. Adsorption curves of cyclohexane on original HZSM-5, HT–HZSM-5 and SiO_2–HZSM-5 catalysts.

The changes in adsorption of cyclohexane relative to that of hexane provide a qualitative measurement on the changes in pore mouth of catalysts. Both modified catalysts exhibit similar cyclohexane adsorption level. After the modification adsorption of cyclohexane decreases sharply, but the change of cyclohexane adsorption on HT–HZSM-5 is similar to that of hexane. On the basis of this comparative examination, it appears that there is no significant change in the size of pore mouth of HT–HZSM-5.

From these two series of adsorption experiments, it can be concluded that TEOS treatment mainly serves to cover the external particle surface with SiO_2 which can also slightly narrow the pore mouth of catalyst without causing changes inside pore channel surface of the catalyst. On the other hand, steam modification results in changes inside pore channel of catalyst by dealumination and also adjust pore mouth size.

3.3. 2-MN methylation over the modified HZSM-5

As can be seen from Table 3, after the modification, 2-MN conversion decrease on both modified catalyst, but on HT–HZSM-5, the conversion of 2-MN is 15.8% which is higher than that on SiO_2–HZSM-5 (12.6%), this trend is contrary to the change of NH_3-TPD. This phenomenon should be attributed to that TEOS narrowed pore mouth, and the reactant encountered more diffusion barrier in entering into the pore channel of catalyst resulting in less opportunity to contact active sites on internal surface of catalyst.

Selectivity of DMNs in the alkylation products was enhanced significantly after the modification. On the HT–HZSM-5 the selectivity to DMN increased to 64.7% (vs. 44.6% on original HZSM-5), and over SiO_2–HZSM-5 it increased to 54.2%. At the same time, poly-alkylation was restrained with the modification; TMN selectivity decreased on both modified catalysts. Furthermore, HT–HZSM-5 possesses the high conversion, resulting in a high 2,6-DMN yield of 4.9%. So steam modification is better than TEOS for this reaction. Based on the results of adsorption of hexane and cyclohexane, NH_3-TPD and PY-IR, the increase of DMN selectivity should be attributed to the facts that pore size of catalyst is narrowed and external surface activity sites are reduced by hydrothermal (steam) treatment and TEOS modification methods, which limits isomerization of 2-MN and further alkylation of DMN once it is formed.

After the modification, SiO_2–HZSM-5 shows improvement in the selectivity to 2,6-DMN at 41.8%, but 2,6/2,7-DMN is only 1.2 which is lower than that of parent catalyst. It shows that TEOS deposition can retard isomerization of desirable product but has no

Table 3
Comparison of experimental results over different catalysts.

	HZSM-5	HT–HZSM-5	SiO_2–HZSM-5
Conversion (%)	24.9	15.8	12.6
Sel. (%)			
NA	1.0	0.6	1.4
DMN	44.6	64.7	54.2
Poly-MN	15.7	13.8	14.1
DMN distribution (%)			
2,6-DMN	32.8	48.2	41.8
2,7-DMN	23.9	32.4	34.5
1,6-DMN	17.8	9.6	8.8
1,7-DMN	13.1	6.7	7.0
Other DMN	12.4	3.1	7.9
2,6-/2,7-DMN	1.3	1.6	1.2
2,6-DMN yield (%)	3.6	4.9	2.9

Reaction temperature: 360 °C, WHSV: 6 h^{-1}, reaction time: 2 h, and carrier gas flow-rate: 20 ml/min.

pronounced impact on distinguishing 2,6-DMN from 2,7-DMN. In distinct contrast, much higher selectivity of 2,6-DMN (48.2%) and ratio of 2,6/2,7-DMN (1.6) were achieved with HT–HZSM-5. Several previous reports [25–27] have shown that, in the isopropylation or methylation of naphthalene, the dealumination of HM could enhance the selectivity of 2,6-isomer. Here also, the positive impact of dealumination in HZSM-5 on the selectivity for 2,6-DMN is observed. This may be attributed to a decrease of the unit cell volume of HZSM-5 upon dealumination [28,29]. The slight decrease in channel size of the micropores could improve the shape-selective catalysis in the methylation of 2-MN. On the other hand, based on the computational analysis using MOPAC, Song et al. [5,6,20] put forward a hypothesis, known as the restricted electronic transition state selectivity effected by the frontier electron density, and their quantum chemical calculations [6,20] demonstrate that the carbon at position 6 of 2-isopropylnaphthalene and 2-methylnaphthalene has the higher frontier electron density than that of position 7 and thus has higher reactivity towards electrophilic substitution. This hypothesis suggests that the formation of 2,6-DMN is more electronically favored than that of 2,7-DMN. Therefore, if we can passivate strong acid sites and keep weak acid site at a certain extent, we could get higher ratio of 2,6/2,7-DMN. After the steam treatment for HZSM-5, the 2,6-/2,7-DMN ratio increases from 1.3 to 1.6. Based on the ratio of 2,6/2,7-DMN and selectivity of 2,6-DMN and 2,7-DMN over modified and unmodified catalysts, it can be concluded that narrowing pore size can effectively enhance selectivity 2,6-DMN and 2,7-DMN simultaneously, hence, adjusting acidity is more effective than adjusting the size of pore entrance for increasing this ratio. Since the dimension of 2,6-DMN is similar to that of 2,7-DMN, spatial restriction has less effect than acidic property on distinguishing between them. Meanwhile it is worth noting that the selectivity of 1,6-DMN on modified catalyst is much lower than that of HZSM-5, literatures [28,30] show the main isomerization product of 2,6-DAN is 1,6-DAN without steric restriction and only β-substituted of 2-methylnaphthalenes can take place within the HZSM-5 micropores, reactions leading to α-substituted methylnaphthalenes must occur on external surface catalyst sites. Therefore, combined with the above results of NH_3-TPD and isomerization reaction of TMB, it reveals that the enhancement of 2,6-DMN selectivity is attributed to that these two modification methods can effectively reduce the density of external surface activity sites.

The stability of the activity with time on stream and ratio of 2,6/2,7-DMN for the modified and original HZSM-5 catalysts were examined at 360 °C, and the results are illustrated in Fig. 8. The activity of untreated HZSM-5 is higher than that of modified catalysts. The initial conversion of 2-MN is 29% and decreases to 23% after 6 h reaction. The conversion on both modified catalysts decreases with time on stream. The catalyst deactivation is retarded on HT–HZSM-5 although at lower conversion with this modification. But the stability of SiO_2–HZSM-5 has not been improved. The steady conversion of HT–HZSM-5 may be associated closely with its weaker acidic strength and little changes in pore mouth. The poor stability of SiO_2–HZSM-5 should be related to the slightly reduced size of pore mouth such that coke can block the pore entrance more easily.

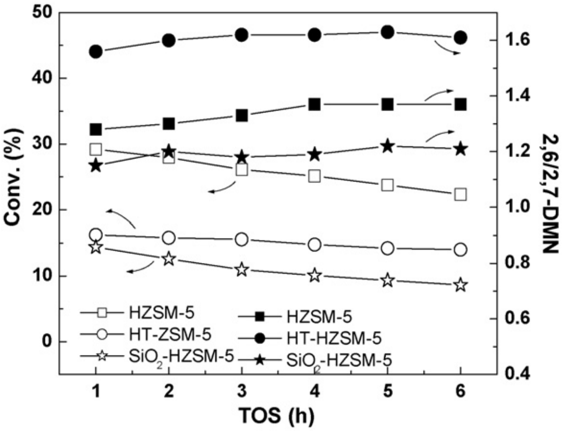

Fig. 8. The conversion of 2-MN and ratio of 2,6/2,7-DMN over modified and unmodified HZSM-5 vs. time on stream.

4. Conclusion

We have examined the effects of steam and TEOS modification of HZSM-5 zeolite on the physico-chemical properties, and catalytic selectivity and activity for synthesis of 2,6-DMN by methylation of 2-methylnaphthalene (2-MN) with methanol. The acidity was reduced by both modifications. The TEOS modification of HZSM-5 zeolites effectively deactivates the external acid sites and also appears to slightly narrow the size of pore entrance. But it has little impact on the pore surface inside the channel of HZSM-5. The hydrothermal (steam) treatment can reduce acid sites and acidic strength on both external and internal surface and may partially or locally narrow some parts of the channel of HZSM-5.

The selectivity of 2,6-DMN in the methylation of 2-MN increased while the conversion decreased by the steam and TEOS modification of HZSM-5 zeolite. The enhancement of the selectivity of 2,6-DMN on SiO_2–HZSM-5 is mainly due to the deactivation of external acid sites which minimizes non-selective methylation and retards the isomerization of 2,6-DMN product that could otherwise occur on external surface acid sites. However, the HT–HZSM-5 shows higher 2,6-DMN selectivity and higher 2,6/2,7-DMN ratio than those on SiO_2–HZSM-5. This is because that steam modification can reduce the acidic sites on the internal surface of catalyst and possibly also slightly narrow the pore channel of catalyst. Regarding the impact on the ratio of 2,6/2,7-DMN, these two modified catalysts have opposite results, on the HT–HZSM-5 the ratio increased to 1.6, but on the SiO_2–HZSM-5, the ratio did not increase.

Based on the characterization and reaction results, it can be concluded that adjusting the acidic property of HZSM-5 catalyst has more desirable impact on shape-selective methylation of 2-MN than optimizing pore channel and pore mouth of the catalyst. Tailoring acidic characteristics is more important than spatial control for distinguishing between 2,6-DMN and 2,7-DMN. Therefore, how to optimize acidic characteristics is a key factor for improving the ratio of 2,6-DMN to 2,7-DMN in methylation of 2-MN with methanol for the synthesis of 2,6-DMN.

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