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# Influence of calcination temperature on the stability of fluorinated nanosized HZSM-5 in the methylation of biphenyl

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A series of fluorinated nanosized HZSM-5 catalysts were prepared by impregnating the zeolite with $NH_4F$ solution. The samples were characterized by XRD, XRF, FTIR-Py, TPD, $^{27}Al$ and $^{29}Si$ MAS-NMR. The effect of calcination temperature on the structure and acidity was studied in the range of 400–500 °C. When the calcination temperature increases, more framework aluminum atoms are removed due to the fluorination. As a result, the number of acid sites and the acid strength decrease, but the ratio of the total Brönsted acid sites to the total Lewis acid sites ($B_T/L_T$) increases. The fluorinated nanosized HZSM-5 catalysts exhibit better stability in the methylation of biphenyl (BP) with methanol. Moreover, the stability increases with the increase of the calcination temperature. When the fluorinated nanosized HZSM-5 is calcined at 500 °C, the conversion of BP can keep at about 10% for 50 h. The enhancement of stability may be due to the decrease of the acid strength and the increase of the ratio of $B_T/L_T$.

**KEY WORDS:** nanosized HZSM-5; stability; fluorination; calcination temperature; dealuminum; methylation; biphenyl.

## 1. Introduction

Linear polynuclear aromatic hydrocarbons, such as 4-alkylbiphenyl and 4,4′-dialkylbiphenyl or $\beta$-alkyl and $\beta,\beta'$-dialkylnaphthalene, have attracted great attention because they can be used as promising precursors for advanced polymer materials [1–4]. The alkylation of biphenyl (BP) to 4,4′-dialkylbiphenyl with large alkylating agents over shape-selective catalysts has been studied for many years and good results have been obtained [5,6]. However, it is difficult to synthesize 4,4′-dimethylbiphenyl by the methylation of BP with methanol by one-step. Up to now, only a few groups focused on the methylation of 4-methylbiphenyl (4-MBP) with methanol into 4,4′-dimethylbiphenyl [7–9]. The methylation of BP to 4-MBP has seldom been studied because of the low selectivity of 4-MBP, the low conversion of BP and the poor stability of the catalyst. Dubuis *et al.* reported that the conversion of BP was less than 20% over the microsized HZSM-5 and the catalyst deactivated sharply [10].

For the industrial application, it is necessary for the catalysts to have good stability and coke resisting ability. In order to improve the stability of the catalysts, many modification methods have been proposed. Among them, the dealumination of zeolite is one of the effective methods [11]. The fluorination reportedly can provoke dealuminum of the lattice, which has been found in many zeolite catalysts, such as Y, ZSM-5 and HM [12–17]. This kind of modification often decreased the total Brönsted acid sites ($B_T$) and total Lewis acid sites ($L_T$), but increased the strength of the remaining framework Brönsted sites. Furthermore, the catalytic activity increased apparently on the fluorinated zeolites with optimum fluorine content in some reactions [12–15]. However, it was rarely reported that the dealumination by fluorination can bring about the enhancement of stability.

Nanosized zeolites have exhibited higher activity, stronger ability of resisting coke, and longer lifetime than conventional microsized zeolites in some catalytic reactions [18,19]. In this paper, nanosized HZSM-5 was modified with $NH_4F$ to investigate the effect of fluorination at different calcination temperature on the catalytic properties and the stability of the catalyst in the methylation of BP with methanol.

## 2. Experimental

### 2.1. Sample preparation

Nanosized NaZSM-5 (70–100 nm) zeolite was prepared in our laboratory according to a procedure in our previous patent [20]. Its ammonium-form was obtained by repeated exchange of NaZSM-5 with 0.4 mol/L $NH_4NO_3$ solution at 80 °C for 2 h with stirring. After each treatment, the product was filtered, washed with

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distilled water and then dried at 100 °C. The obtained ammonium-form ZSM-5 was calcined at 540 °C for 6 h in air to form the HZSM-5.

The fluorinated samples were obtained by impregnating 5 g nanosized HZSM-5 (nano-HZSM-5) zeolite with the 25 ml $NH_4F$ solution (0.01 g/ml). The samples were kept at room temperature for 10 h, dried at 100 °C overnight, and calcined for 5 h at four different temperatures 400, 450, 475 and 500 °C, respectively. They are abbreviated as HZSM-5-F400, HZSM-5-F450, HZSM-5-F475 and HZSM-5-F500.

### 2.2. Catalyst characterization

The crystal size and the habit of catalysts were determined on a JEOL JSM-6700F Field Emission Scanning Electron Microscope. X-ray diffraction patterns were obtained on a Rigaku D/max-2400 diffractometer using Cu K$\alpha$1 radiation, an operating voltage of 40 kV, an electron current of 100 mA, and a scanning speed of 4° 2$\theta$/min. The $SiO_2$ and $Al_2O_3$ contents were measured with Bruker SRS-3400 Sequential X-ray fluorescence spectrometer.

The $NH_3$ sorption and temperature programmed desorption ($NH_3$TPD) was performed on a Chembet 3000 chemical adsorber from Quantachrom Co. Prior to adsorption experiments, the samples (0.2 g) were first pre-treated at 540 °C for 1 h in a quartz U-tube in a He stream. Then, they were cooled down at 120 °C and saturated with ammonia. Finally, the desorption was carried out from 100 °C to 500 °C at a heating rate of 10 °C per min in a He stream. The FTIR spectra were recorded using Bruker EQUINOX55 infrared spectrometer in the range of 400–4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ on thin wafers of KBr in which zeolite was dispersed. The pyridine was used as a probe. The wafers were calcined under vacuo at 450 °C (ca. $10^{-4}$ torr) for 3 h, followed by the adsorption of pyridine vapor at room temperature for 30 min. IR spectra were recorded after subsequent evacuation at 150, 300, and 450 °C for 1 h

NMR spectra were obtained on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO2 rotors. $^{29}$Si MAS-NMR spectra were acquired at 79.5 MHz using a 0.8 $\mu$s $\pi/8$ pulse with a 4 s recycle delay and 2000 scans. The chemical shifts were referred to 4,4-dimethyl-4-silapentane sulfonate sodium (DSS).$^{27}$Al MAS-NMR spectra were collected at 104.3 MHz using a 0.75 $\mu$s $\pi/12$ pulse with a 3 s recycle delay and 600 scans. The chemical shift reference was 1% aqueous $Al(H_2O)_6^{3+}$.

### 2.3. Catalyst testing

The methylation of BP was carried out in a fixed-bed, down-flow stainless steel reactor. The catalyst (1 g) was placed in the middle of the tube reactor and activated at 450 °C for 1 h prior to reaction. Mesitylene was used as the solvent. The typical reaction conditions are as follows: feed biphenyl: methanol: mesitylene = 1:5:5 (molar ratio), reaction temperature 450 °C, $N_2$ flow 20 ml/min. Analysis of the products was performed on GC with a column of BETA DEX 120 (60 m×0.25 mm). The detector and injector were both kept at 300 °C. The oven temperature was initially kept at 170 °C for 20 min, increased to 190 °C at a rate of 4 °C/min and held at the final temperature for 35 min. The conversion of BP was calculated on the basis of reacted BP, and the selectivity of mono-MBP was defined as the ratio of mono-MBP to all MBP isomers.

## 3. Results and discussion

Recently, the fluorination has often been used to improve the catalytic properties of the zeolite catalysts. Fluorinating agent and fluorine content have been widely studied and found to have an important impact on the activity of the fluorinated catalysts [12–17]. In fact, fluorination conditions, especially the calcination temperature, can also affect the properties of the zeolite catalysts greatly. It is very essential to take it into account when fluorination is carried out. Here, we focus on the effect of calcination temperature on the structure and acidity of fluorinated zeolites.

### 3.1. Characterization of catalysts

Figure 1 shows the SEM photographs of nano-HZSM-5 and HZSM-5-F475. Obviously, the crystal size of HZSM-5-F475 is similar to that of nano-HZSM-5. This indicates that the fluorination does not lead to the decrease of the crystal size.

The results of chemical analysis for the nano-HZSM-5 and fluorinated nano-HZSM-5 are shown in table 1. It can be seen that the Si/Al molar ratio (from XRF measurement) keeps constant after the fluorination at different calcination temperatures. However, the Si/FAl molar ratio (from NMR measurement) increases gradually with the increase of calcination temperature. These results imply that the Al species removed from the framework still remain in ZSM-5 catalysts.

Figure 2 shows the XRD patterns of the samples before and after $NH_4F$ treatment. Obviously, $NH_4F$-modified samples keep their crystalline structures, and the fluorinated species are not found. The relative crystallinity was determined by the intensity of the characteristic peaks in the 2$\theta$ range of 22.5–25°. As shown in table 1, it has no apparent change after the nano-HZSM-5 catalysts are fluorinated.

The $^{29}$Si MAS-NMR spectra of the parent and modified nano-HZSM-5 zeolites consist of four signals at ca. −103, −107, −114 and −117 ppm (figure 3). The signals at −114 and −117 ppm that overlap with each other are caused by $Si(OSi)_4$ sites in the framework of ZSM-5 structure, while the shoulders at −107


Figure 1. The SEM photographs of nano-HZSM-5 and HZSM-5-F475.

and −103 ppm are due to $AlOSi(OSi)_3$ sites and $HOSi(OSi)_3$ sites, respectively. With the increase of the calcination temperature, the signal at −107 ppm decreases and the line width of the $Si(OSi)_4$ sites at −114 ppm narrows, which indicate that more framework aluminum atoms are removed at the higher calcination temperature.

It is well-known that the nature and concentration of Al species in aluminosilicate materials are closely related to the acidity which is crucial for the catalytic performance of the catalysts. Solid-state[27] Al MAS-NMR is a sensitive tool commonly used for determining the coordination of Al. For HZSM-5 zeolites, the resonances at chemical shifts of 54 ppm and −1 ppm (figure 4) can be assigned to tetrahedral (4-coordinated) framework Al and octahedral (6-coordinated) nonframework Al species, respectively. Another peak at 30 ppm is attributed to penta-coordinated aluminum by some research groups, but it is assigned to the distorted tetrahedral coordinated aluminum in extraframework Al or the distorted framework Al by others [17]. The signal at 54 ppm for framework Al apparently decreases after $NH_4F$ modification and continuously decreases with the increase of calcination temperature. The results indicate the aluminum atoms are dislodged from their tetrahedral sites. A new hexa-coordinated Al resonance at −16 ppm arising from the fluorinated species [12] is found in the fluorinated nano-HZSM-5. This band becomes broad because more penta-coordinated aluminum or distorted tetrahedral coordinated aluminum species are formed with the increase of the calcination temperature. So, it can be concluded that the calcination temperature has a great effect on the fluorinated nano-HZSM-5. The higher the calcination temperature is, the more framework aluminum is removed and the more nonframework aluminum is generated.

The dealuminum often results in the change of acidity which is important to explain the catalytic properties of the catalysts. The density and nature of surface acid sites were determined by chemical adsorption of pyridine. Figure 5 shows IR spectra of pyridine adsorbed on the parent and fluorinated nano-HZSM-5. Three bands at 1547, 1448 and 1491 $cm^{-1}$ are attributed to the pyridine adsorbed on Brönsted acid sites (B), Lewis acid sites (L) and on both acid sites (B, L), respectively. The total Lewis acid sites ($L_T$) decrease with the increase of calcination temperature, although $NH_4F$ modification leads to more framework Al atoms removed from their tetrahedral sites. This means that not all the nonframework Al can promote the generation of Lewis acid sites. The total Brönsted acid sites ($B_T$) decrease obviously only when the calcination temperature is up to 500 °C.

In figure 5, a new Brönsted acid site appears around 1535 $cm^{-1}$ in HZSM-5-F400 and HZSM-5-F450. This

Table 1
Element analysis and relative crystallinity of the fluorinated nano-HZSM-5 catalysts

| Sample | $SiO_2$wt% | $Al_2O_3$wt% | Si/Al(molar ratio) | Si/FAl(molar ratio) | Relative Crystallinity, % |
|---|---|---|---|---|---|
| Nano-HZSM-5 | 92.71 | 5.538 | 14.22 | 23.4 | 100 |
| HZSM-5-F400 | 92.37 | 5.383 | 14.58 | 26.1 | 99 |
| HZSM-5-F450 | 91.87 | 5.377 | 14.52 | – | 94 |
| HZSM-5-F475 | 92.45 | 5.259 | 14.94 | 34.2 | 94 |
| HZSM-5-F500 | 91.97 | 5.302 | 14.74 | 36.3 | 94 |

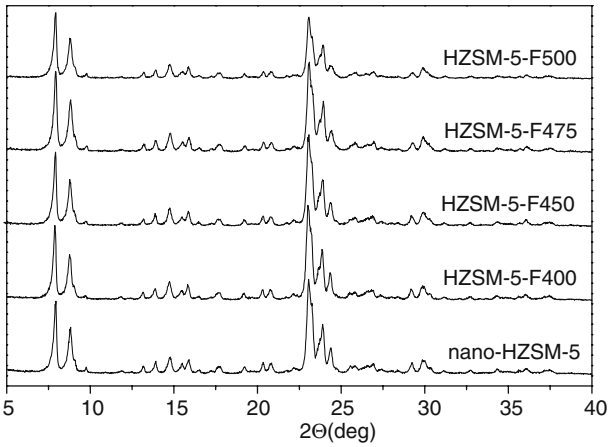


Figure 2. XRD patterns of nano-HZSM-5 and fluorinated nano-HZSM-5 catalysts.

phenomenon can be explained by a mechanism proposed by Mao *et al.* [16]. They suggested that the $NH_4F$ was decomposed when calcined at 300 °C, and new hydroxyl groups formed at 400 °C by the reaction of zeolite surface with the protons of the remaining ($H^+...F^-$) ion pairs. So, it can be inferred that the new

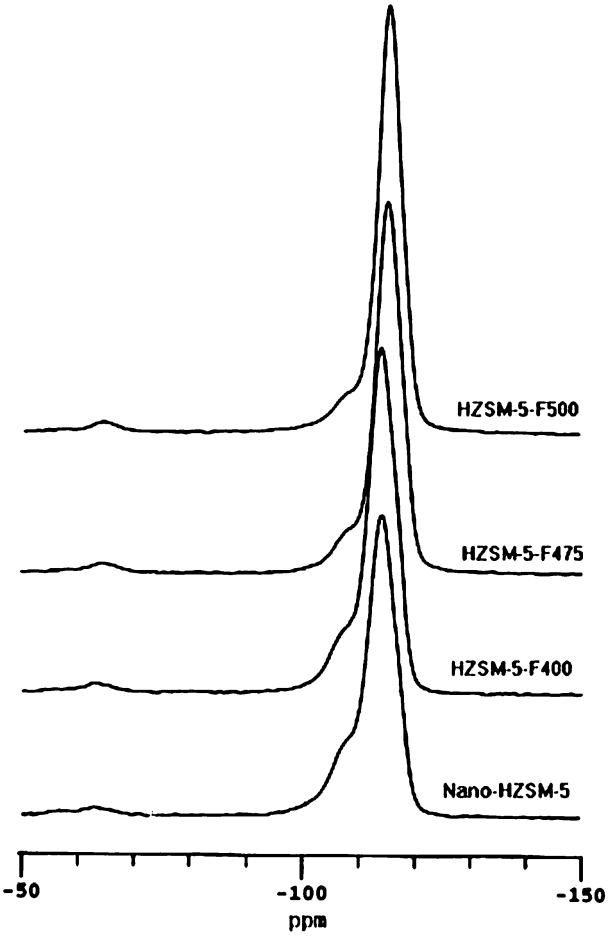


Figure 3. $^{29}Si$ MAS-NMR spectra of fluorinated nano-HZSM-5 catalysts.

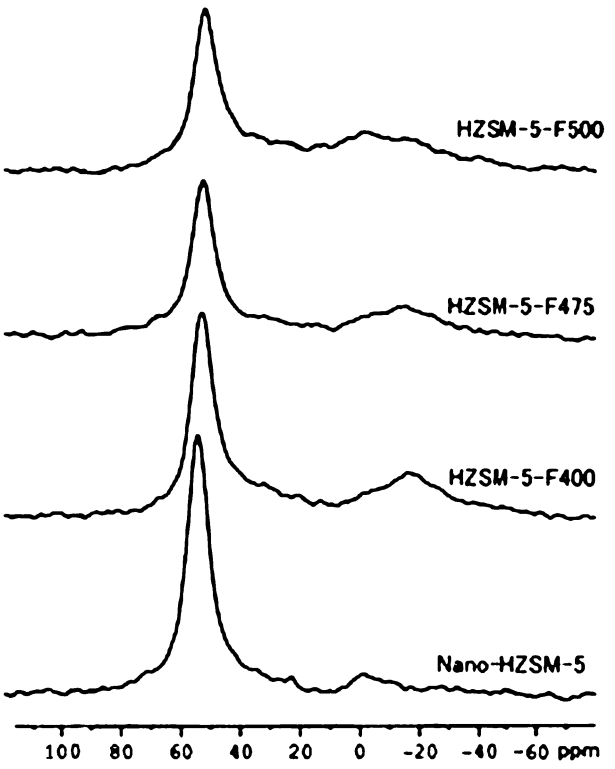


Figure 4. $^{27}Al$ MAS-NMR spectra of fluorinated nano-HZSM-5 catalysts.

Brönsted acid site might be due to the formation of these new hydroxyl groups. When the catalyst is calcined at higher temperature than 450 °C, a significant loss of the F–Al...OH occurs, which results in the disappearance of new formed hydroxyl groups.

The ratios (B/L) of Brönsted acid sites (around 1547 and 1535 $cm^{-1}$) to Lewis acid sites (around 1448 $cm^{-1}$) are shown in table 2. At three different desorption temperatures, the B/L ratio of any fluorinated catalyst is higher than its parent. Significantly, the B/L ratio increases with the increasing of calcination temperature at the desorption temperature of 150 °. In other words, the ratio of $B_T/L_T$ increases when the calcination temperature increases.

The $NH_3$-TPD (figure 6) shows the changes of the intensity and the number of total acid sites. The low temperature peak is mainly due to the desorption of adsorbed ammonia from the weak acid sites or nonacid sites, whereas the high temperature peak is related to the desorption of ammonia from the strong acid sites. It can be found that the acid strength and acid concentration decrease at higher calcination temperature. Based on such decrease of acidity, the improvement of the stability can be expected on the fluorinated catalysts.

### 3.2. Catalytic properties

In order to investigate the catalytic properties of the fluorinated nano-HZSM-5 catalysts, the methylation of

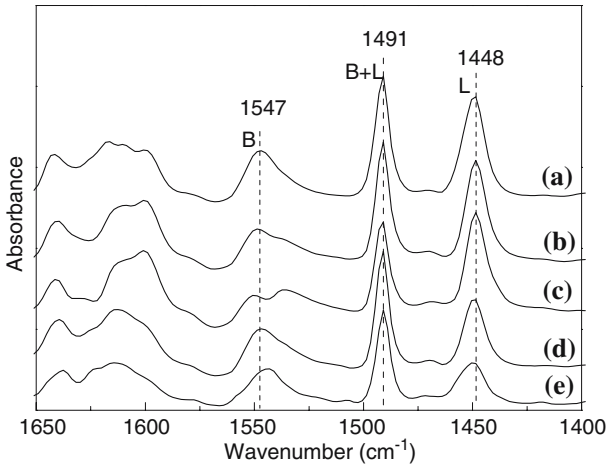


Figure 5. FTIR spectra of pyridine adsorbed on nano-HZSM-5 and fluorinated nano-HZSM-5 catalysts after evacuated at 150 °C. (a)nano-HZSM-5, (b) HZSM-5-F400, (c) HZSM-5-F450, (d) HZSM-5-F475, (e) HZSM-5-F500.

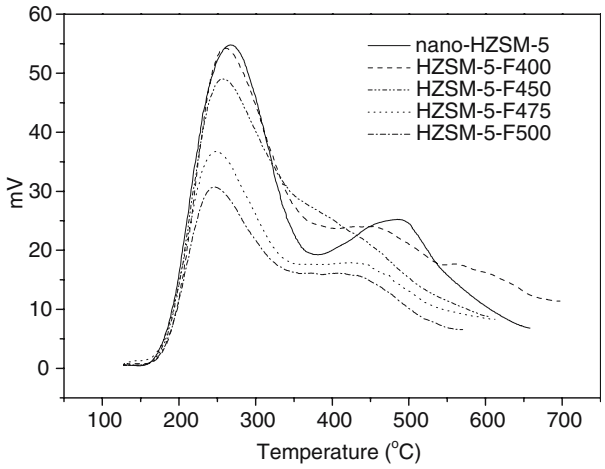


Figure 6. TPD curves of fluorinated nano-HZSM-5 catalysts.

BP with methanol is employed as a test reaction. For this reaction, the stability is one of the crucial problems. But few catalysts were found to exhibit good stability. Dubuis *et al*. reported that the conversion of BP sharply decreased from 19% to 13% in 3 h on microsized HZSM-5 (Zeocat PZ-2/50), which is unfavorable for industrial application.

Figure 7 shows the comparison of the stability of the parent and fluorinated catalysts calcined at different temperatures. The stability of parent catalyst is observed to be similar to that of microsized catalyst mentioned above. The conversion of BP decreases from 34% to 1% in 20 h. Significantly, it is found that the $NH_4F$ modification can dramatically improve the stability of the catalyst. Moreover, the stability of the fluorinated catalysts increases with the increase of calcination temperature. The conversion of BP keeps at about 10% for 50 h on HZSM-5-F500. The result is much better than any other catalysts for the methylation of polynuclear aromatic hydrocarbons.

From the results of characterization of the fluorinated catalysts, it can be presumed that there are two possible reasons for the improvement of stability. One is the decrease of the acid strength. As we have known, the strong acid sites can lead to the formation of by-products and the coke, and make the catalyst deactivate fast. This means that the lifetime of the catalysts depends on the acid strength. From figures 6 and 7, the lifetime of the catalyst is prolonged with the decrease of acidity. The HZSM-5-F500 catalyst has the weakest acid strength, but exhibits the best stability. The other reason for the better stability of fluorinated catalysts might be the increased ratio of $B_T/L_T$. From table 2 and figure 7, it can be seen that the change of ratio of $B_T/L_T$ is in good agreement with the increase of stability of the catalyst. The methylation of BP is a reaction catalyzed by the Brönsted acid sites. So, the increase of the ratio of $B_T/L_T$ may also be responsible for the improvement of the stability.

The initial conversion of BP decreases with the increase of calcination temperature because of the decrease of the number of acid sites. But, the fluorination

Table 2
The B/L ratios of fluorinated nano-HZSM-5 catalysts at three different desorption temperatures

| Catalysts | 150 °C | 300 °C | 450 °C |
|---|---|---|---|
| Nano-HZSM-5 | 1.23 | 2.12 | 2.19 |
| HZSM-5-F400 | 1.25 | 2.13 | 2.87 |
| HZSM-5-F450 | 1.32 | 2.31 | 2.97 |
| HZSM-5-F475 | 2.21 | 3.06 | 2.46 |
| HZSM-5-F500 | 2.30 | 2.57 | 2.43 |

$B/L = (\varepsilon_L/\varepsilon_B)(A_B/A_L)$ where $(A_B/A_L)$ is the absorbance ratio and $\varepsilon_L/\varepsilon_B$ is the molar absorption coefficient ratio which is taken as 1.5 for samples having Si/Al > 7.5 [21].

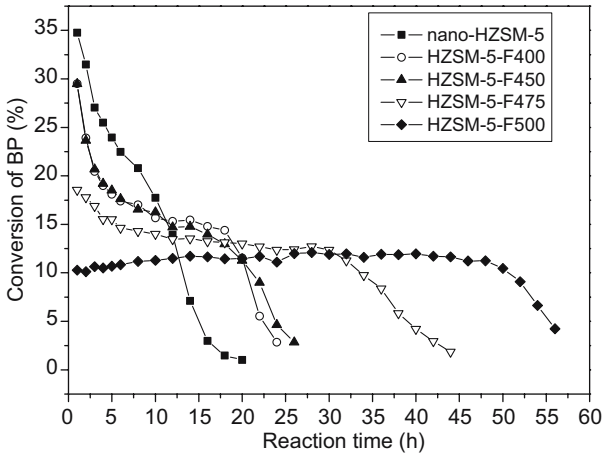


Figure 7. Variation in conversion of BP with reaction time over the parent and fluorinated catalysts calcined at different temperatures.

and calcination temperature does not exert obvious influence on the selectivity of 4-MBP. The highest selectivity of 4-MBP on the fluorinated catalyst can reach about 47% which is a bit higher than that on its parent. In this reaction, the selectivity is not improved obviously because the formed 4-MBP is easily isomerized to other isomers at external surface.

## 4. Conclusion

The fluorination of nano-HZSM-5 by $NH_4F$ solution results in dealumination of the zeolite. The higher calcination temperature leads to more Al atoms to be removed from framework positions. The total Brönsted acid sites and total Lewis acid sites decrease after fluorination, so does the acid strength. But, the ratio of $B_T/L_T$ increases with the increasing of calcination temperature. A new weak Brönsted acid site is found in the fluorinated catalysts calcined at 400 and 450 °C.

The methylation of BP with methanol is carried out on the fluorinated nano-HZSM-5 catalysts. The stability of catalyst is improved after fluorination, and it increases gradually with the increase of the calcination temperature, which can be ascribed to the decrease of the acid strength and the increase of the ratio $B_T/L_T$. When the fluorinated nano-HZSM-5 is calcined at 500 °C, the conversion of BP can keep at about 10% for 50 h. So far, the stability of this catalyst is the best for the methylation of polynuclear aromatic hydrocarbons.

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