

Influence of Silanol Defects of ZSM-5 Zeolites on Trioxane Synthesis from Formaldehyde

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Abstract

The silanol defects in ZSM-5 zeolite have been recognized as an important factor in catalytic activity. Here, ZSM-5 zeolites with different amounts of silanol defect sites were synthesized from synthetic gels containing fluoride medium and were applied as catalysts for trioxane synthesis. The results of XRD, SEM, NH₃-TPD, Py-IR, OH-IR, ²⁷Al MAS NMR, ¹H MAS NMR, and TG indicated that all ZSM-5 zeolites showed similar crystal size, relative crystallinity, porosity, and the number of Brønsted acid sites. However, the silanol defects reduced obviously and the number of Lewis acid sites reduced correspondingly when a little NH₄F was added in the synthesis gels and both of them decreased slightly with increase of F/Si ratio. Compared with ZSM-5 zeolite prepared in hydroxide medium, ZSM-5 zeolite prepared in fluoride medium displayed higher selectivity to trioxane and increased gradually with increase of F/Si ratio. Moreover, the lifetime of ZSM-5 zeolite prepared in fluoride medium was longer than that of prepared in hydroxide medium. Thus, ZSM-5 zeolite prepared in fluoride medium with contained the few silanol defects and low Lewis acid sites is an efficient catalyst for trioxane synthesis.

Graphic Abstract



A ZSM-5 zeolite prepared in hydroxide medium

B ZSM-5 zeolite prepared in fluoride medium

Keywords ZSM-5 zeolite · Fluoride · Silanol defects · Lewis acid · Trioxane synthesis

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1 Introduction

Trioxane (TOX), an important substitute for anhydrous formaldehyde, is mainly used for the synthesis of polyoxymethylene (POM) and poly(oxymethylene) dimethyl ethers (PODE) [1–5]. POM has been widely used as a traditional metal substitute due to its high mechanical strength, excellent abrasion resistance, fatigue resistance and moldability [6, 7]. The worldwide consumption of POM resins is more than 840 kt/a and continues to grow [8, 9]. PODE is considered as a promising diesel additive, which can significantly reduce emissions of hazardous exhaust gases such as CO_x , NO_x during diesel combustion [2]. Therefore, developing an efficient synthesis route of TOX has attracted much attention in recent years.

Commercial TOX is mainly produced by cyclization of about 60% aqueous formaldehyde with acid catalysts (Eq. 1) [10, 11]. Besides, several side reactions were also occurred. Methanol (MeOH) and formic acid (HCOOH) were formed via Cannizzaro reaction (Eq. 2); methyl formate (MF) came from esterification of MeOH and HCOOH (Eq. 3); dimethoxymethane (DMM) generated from the reaction of formal-dehyde and MeOH (Eq. 4) [10–13].

$$3CH_2O \rightleftharpoons^{H^+} (CH_2O)_3$$
 (1)

$$2CH_2O + H_2O \stackrel{Cat.}{\rightleftharpoons} CH_3OH + HCOOH$$
(2)

$$CH_{3}OH + HCOOH \stackrel{H^{+}}{\Rightarrow} HCOOCH_{3} + H_{2}O$$
(3)

$$CH_2O + 2CH_3OH \stackrel{H^+}{\Rightarrow} CH_3OCH_2OCH_3 + H_2O$$
(4)

Homogeneous catalysts such as sulfuric acid [11] and ionic liquid [14] are effective for TOX synthesis. However, the difficulty of homogeneous catalysts is to separate HCOOH from the mixture of feed and catalyst [15]. H-type zeolites are a good option to avoid the problems of homogeneous catalysts. In the previous study, ZSM-5, β and mordenite zeolites which had nanoparticle size and high SiO₂/Al₂O₃ ratio (\geq 45) showed comparable selectivity of TOX with sulfuric acid [16]. The effects of acid types of ZSM-5 zeolite on TOX synthesis were also investigated in our laboratory. It was found that ZSM-5 zeolite with the low concentration of Lewis acid sites exhibited a high selectivity to TOX. Some literature also reported that Cannizzaro reaction took place in the presence of Lewis acid catalysts [17–19]. Thus, to increase the selectivity of TOX catalyzed by zeolites, the Lewis acid sites should be controlled in a low concentration.

For zeolites [20], the Brønsted acid sites originated from the presence of protons balancing the negative charge which induced by the framework Al atoms in tetrahedral sites; the Lewis acid sites came from the presence of extra-framework Al and/or framework perturbed Al species. The extra-framework Al Lewis acid sites formed at the expenses of adjacent Brønsted acid sites, however, such extra-framework Al species were in very small quantity in the HZSM-5 zeolites with high SiO_2/Al_2O_3 ratio of 20 [21]. The formation of framework Al Lewis acid sites came from the dehydroxylation of Brønsted acid sites which originated from perturbed framework Al atoms [22, 23]. By using a DFT calculation, it was confirmed that the defects coming from the dehydroxylation of vicinal silanol defect sites and Brønsted acid sites were the primary candidate for the framework Lewis acid sites in zeolites [24]. So the relative concentration of the vicinal silanol defect sites next to Brønsted acid sites would determine the formation of framework Lewis acid sites.

As reported, zeolites synthesized in fluoride medium exhibited low concentration of silanol defect sites compared with that of synthesized in hydroxide medium [25-28]. For example, ZSM-5 zeolite with a high SiO₂/Al₂O₃ ratio of 90 which synthesized in fluoride medium showed both few structural defects and Lewis acid sites [29]. However, little attention has been paid to the effects of silanol defects on TOX formation. In order to increase selectivity to TOX, the effects of silanol defects in ZSM-5 zeolites on TOX formation from formaldehyde were investigated in this study. Thus, ZSM-5 zeolites with different amounts of silanol defect sites and Lewis acid sites were synthesized in hydroxide and fluoride medium with different F/Si ratio. The catalytic performances for the reaction of formaldehyde to TOX and the stability of the synthesized ZSM-5 zeolites were investigated.

2 Experimental

2.1 Materials

Formaldehyde (60 wt%) was prepared by concentrating a 37 wt% industrial formaldehyde solution supplied by Chengdu (China) Weite Plastic Co. Tetraethyl orthosilicate (TEOS, 98%), aluminum nitrate (Al(NO₃)₃·9H₂O, 99%), ammonium fluoride (NH₄F, 98%) and hydrochloric acid (HCl, 37%) were supplied by Chron Chemical Industrial Corporation (Chengdu, China). Tetrapropylammonium hydroxide (TPAOH, 20% aqueous solution) and chromatographically pure 1,4-dioxane (99.99%) were supplied by Aladdin Industrial Corporation (Shanghai, China).

2.2 Catalyst Preparation

The synthesis of ZSM-5 zeolites was performed from a gel with the composition: 1.0SiO₂:0.01Al₂O₃:0.377TPAOH:

(0–0.15)NH₄F:27H₂O. First, TEOS was added slowly into the TPAOH aqueous solution and the resultant mixture was kept for 3 h to hydrolyze TEOS. The aluminum nitrate solution was added under vigorously stirring. NH₄F was added before the aluminum nitrate solution. The mother gels were stirred at room temperature for 2 h and then hydrothermally treated at 170 °C for 7 days. After filtration and washing with deionized water to neutral, all of the as-synthesized ZSM-5 zeolites were dried overnight at 110 °C, and calcined for 4 h in an oven at 550 °C to remove the template. Then H-types zeolites were obtained directly. The samples synthesized in hydroxide medium and in fluoride medium were designated as ZSM-5-OH and ZSM-5-F-x respectively, where x represents the F/Si mole ratio.

2.3 Catalyst Characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D8 ADVANCE X-ray diffractometer with Cu Ka radiation in the 2θ range from 5 to 50° at a scanning rate of 3° min⁻¹. The actual SiO₂/Al₂O₃ ratio was analyzed by X-ray fluorescence (XRF, S4 Explorer, Bruker AXS). N2 adsorption/desorption measurements were performed with a Kubo X-1000 (Bjbuilder). Specific surface areas (SSA_{BET}) were determined from the BET equation. The total volume was calculated from nitrogen adsorbed volume at $P/P_0 = 0.99$ and the external surface areas (SSA_{ext.}) was calculated from isotherms by t-plot method. Electron micrographs were taken on an FEI Inspect F50 (FSEM) scanning electron microscope (SEM) equipped with a field emission gun. Thermogravimetric measurements (TG) was carried out on TGA apparatus (Pyris Diamond, Perkin-Eimer, heating rate 10 °C/ min, helium flow 30 ml/min).

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out on a chemisorption apparatus (Micromeritics, AutoChem II 2920). First, the samples were activated at 550 °C for 30 min, then cooled to 100 °C to absorb NH₃ for 30 min. After purging with helium gas for 1 h to remove physisorbed ammonia, NH₃-TPD profiles were acquired by heating samples at 10 °C min⁻¹ from 100 to 550 °C.

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet FTIR 6700 spectrometer in accordance with a previously reported procedure [30]. Zeolite samples were directly pressed into self-supporting wafers and evacuated under vacuum at 450 °C for 3 h. OH-IR spectra were recorded at room temperature and 150 °C. Then, the samples were saturated with pyridine for 1 h at room temperature. After evacuated for 1 h to remove the physically adsorbed pyridine, the Py-IR spectra were recorded at 150 °C. The amounts of Brønsted and Lewis acid sites were determined by using an integrated area of a given band with the molar extinction coefficients: $1.88 \text{ cm } \mu \text{mol}^{-1}$ and $1.42 \text{ cm } \mu \text{mol}^{-1}$ for Brønsted and Lewis acid sites respectively.

Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of ²⁷Al and ¹H were performed on a Bruker AVANCE III NMR spectrometer at a magnetic field of 14.1 T. The ²⁷Al MAS NMR spectra were recorded at a resonance frequency of 600 MHz, spinning rate of 14 kHz, and flip angle of 15°. The pulse width was 0.65 μ s, which corresponded to $\pi/12$, and the recycle delay was 1 s. The samples for ¹H MAS NMR spectra were dehydrated at 350 °C for 4 h under vacuum. The ¹H MAS NMR measurements were performed at 400 MHz with a $\pi/2$ pulse of 3.5 μ s, spinning rate of 14 kHz and a recycle delay of 2 s. Aqueous solutions of Al(NO₃)₃ and tetramethylsilane (TMS) were used as standard references for chemical shifts of ²⁷Al and ¹H, respectively.

2.4 Catalytic Reaction

TOX was prepared from formaldehyde via reaction distillation, which involved a 250 ml glass reactor and a distillation column. A condenser, which was added to the top cover of the packer tower to collect the reaction gas mixture, was heated with warm water at 50 °C to avoid the vapor phase precipitated on the inner face. The reaction mixture composed of formaldehyde (100.0 g) and solid catalyst (5.0 g) was introduced into the reactor and heated in an oil bath with continuous stirring. A Pt/100 monitoring temperature sensor was inserted into the reactor to control the reaction temperature with an uncertainty of ± 0.1 °C. After the reaction time was recorded when the temperature reached ca. 100 °C, the formaldehyde was continuously fed to the reactor and the feed rate of the formaldehyde was adjusted to keep a constant level of the reaction mixture. The continuous reaction proceeded for 3 h to compare catalytic performances of different zeolite. For the stability test of the ZSM-5-OH and ZSM-5-F-0.15 zeolites, the distillate was analyzed every 8 h and the continuous experiment was finished until the conversion decreased by 10%. The distillate was analyzed by gas chromatography with a thermal conductivity detector, using 1, 4-dioxane as internal standard material. The formaldehyde conversion and selectivity of products were calculated by carbon molar quantity in feed using Eqs. 5, 6:

$$Conversion_{HCHO}(\%) = \frac{all products carbon molar quantity in feed}{HCHO molar quantity in feed} \times 100\%$$
(5)

$$Selectivity_{product}(\%) = \frac{product \, carbon \, molar \, quantity}{all \, products \, carbon \, molar \, quantity \, infeed} \times 100\%$$
(6)

3 Results and Discussion

3.1 General Characterization of ZSM-5 Zeolites

XRD patterns of zeolites prepared in hydroxide and fluoride medium showed that all samples were identified as MFI structure with a high crystallinity (Fig. 1, Table 1). The SiO₂/Al₂O₃ ratio of the ZSM-5-OH zeolite was 102, which was close to the initial gel SiO_2/Al_2O_3 ratio of 100. For the ZSM-5-F zeolites, the SiO₂/Al₂O₃ ratios were little higher than the initial gels and slightly increased from 110 to 114 with the increase of F/Si ratio from 0.02 to 0.15. This was consistent with the results of previous studies [31, 32], since the presence of fluoride ions in the gel could complex aluminum atoms to inhibit the incorporation of aluminum in ZSM-5 zeolite framework [33]. SEM micrographs showed that ZSM-5-OH zeolite was round particles and ZSM-5-F zeolites exhibited hexagonal particles, but the diameters of all samples were about 230-260 nm (Fig. 2, Table 1). Similar specific surface areas, external surface areas and



Fig. 1 XRD patterns of ZSM-5-OH and ZSM-5-F with different F/Si ratio

total pore volume in all samples were also identified by N_2 adsorption/desorption measurements (Table 1). Thus, the presence of NH_4F in the gel had little influence on the particle size and porosity properties.

3.2 Acidic Properties of ZSM-5 Zeolites

The total acid amounts of HZSM-5-OH and ZHSM-5-F with different F/Si ratios were measured by NH₃-TPD (Fig. 3a, Table 2). There were two desorption peaks at 200–240 °C and 350-420 °C, which were ascribed to weak and strong acid sites, respectively [34]. The total acid amounts decreased slightly with increase of F/Si ratio. This trend was consistent with the results of the SiO₂/Al₂O₃ ratios of zeolites. There were two absorption peaks located at 1540 and 1450 cm⁻¹ in the Py-IR spectra (Fig. 3b), which attributing to Brønsted acid sites and Lewis acid sites respectively [30, 35, 36]. The amounts of Brønsted acid sites and Lewis acid sites were also quantitatively calculated and listed in Table 2. The amount of Brønsted acid sites of different samples was very similar. Thus, the amounts of Brønsted acid had been little affected by adding NH₄F in the gel. Compared with ZSM-5-OH, however, the amount of Lewis acid sites decreased obviously in the samples of ZSM-5-F and it was decreased gradually with increase of F/Si ratio. This illustrated that the amount of Lewis acid sites could be reduced by synthesizing in fluoride medium, which was consistent with previous reports [27, 29].

Since the major difference in acidity between ZSM-5-OH and ZSM-5-F with different F/Si ratio was the amount of Lewis acid sites, the reason for the decrease of the amount of Lewis acid sites in the presence of fluoride ions was of particular importance. Lewis acid sites came from extra-framework Al and/or framework Al in zeolites, therefore, the ²⁷Al MAS NMR spectra were used to analysis the complex environments of Al in the synthesized zeolites (Fig. 4). The peak at ca. 56 ppm was contributed to tetrahedrally coordinated framework Al. Another one at ca. 0 ppm corresponded to hexacoordinated extra-framework Al. All samples had a sharp peak at ca. 56 ppm but the peak at ca. 0 ppm was

Catalyst	Relative crystallinity (%)	SiO ₂ /Al ₂ O ₃	Particle size (nm)	$SSA_{BET} (m^2/g)^a$	$SSA_{ext} \cdot (m^2/g)^b$	V _{total} (cm ³ /g) ^c
ZSM-5-OH	98.5	102	230	480	217	0.367
ZSM-5-F-0.02	94.0	110	234	459	216	0.357
ZSM-5-F-0.08	96.6	113	255	458	216	0.357
ZSM-5-F-0.15	100	114	260	450	210	0.351

^aBET method

^bt-plot method

^cVolume absorbed at $p/p^0 = 0.99$

ZSM-5 zeolites

Table 1 Relative crystallinity, SiO_2/Al_2O_3 ratio, particle size, and porosity of the studied



Fig. 2 SEM micrographs of ZSM-5-OH and ZSM-5-F with different F/Si ratio: a ZSM-5-OH; b ZSM-5-F-0.02; c ZSM-5-F-0.08; d ZSM-5-F-0.15



Fig. 3 a NH₃-TPD profiles of ZSM-5-OH and ZSM-5-F with different F/Si ratio; b Py-IR spectra of ZSM-5-OH and ZSM-5-F with different F/Si ratio

 Table 2
 Catalytic acidity of ZSM-5-OH and ZSM-5-F with different

 F/Si ratio
 F/Si ratio

Catalyst	Total acid amounts (mmol/g) ^a	Acid amou	Acid amounts (mmol/g) ^b			
		Brønsted	Lewis	L/B		
ZSM-5-OH	0.305	0.161	0.062	0.385		
ZSM-5-F-0.02	0.301	0.163	0.040	0.245		
ZSM-5-F-0.08	0.290	0.164	0.035	0.213		
ZSM-5-F-0.15	0.286	0.159	0.033	0.208		

^aDetermined by NH₃-TPD

^bDetermined by Py-IR



Fig. 4 $\,^{27}\text{Al}$ MAS NMR spectra of ZSM-5-OH and ZSM-5-F with different F/Si ratio

nearly unobserved, meaning that almost all Al was inserted in the framework and there was very little extra-framework Al in the synthesized ZSM-5 zeolites. This was mainly because the SiO_2/Al_2O_3 ratios of the synthesized ZSM-5 zeolites were much higher than 20 [21]. Thus, combined with the results of Py-IR above, the Lewis acid sites were mainly originated from framework Al in this study.

The FT-IR spectra in the region of OH stretching vibrations were recorded in Fig. 5. There were several bands in the OH-stretch vibrations region. The first one at 3500 cm⁻¹ correspond to silanol groups, the second one at 3720 cm⁻¹ was attributed to internal silanol sites, the third band at 3736 cm⁻¹ was assigned to external silanol sites, and two shoulder bands at 3610 cm⁻¹ and 3667 cm⁻¹ were associated to strongly acidic bridging Si(OH)Al groups (Brønsted acid sites) and low acidity perturbed Al–OH groups respectively [37, 38]. The weak intensity of two bands at 3610 cm⁻¹ and 3667 cm⁻¹ were similar in all samples, since the low Al content in the zeolite with high SiO₂/Al₂O₃ molar ratio. It should be noted that the bands at 3720 cm⁻¹ and 3736 cm⁻¹



Fig. 5 Infrared spectra of ZSM-5-OH and ZSM-5-F with different F/ Si ratio

were intense and broad in the sample of ZSM-5-OH. However, these two bands became sharpen and shifted back to higher wavenumbers in the samples of ZSM-5-F but did not change significantly as the F/Si ratio increased. The band at 3500 cm⁻¹ in the samples of ZSM-5-F also became less intense than that of ZSM-5-OH. Thus, the amounts of the silanol groups including internal silanol sites and external silanol sites in the samples of ZSM-5-F were generally higher than that of ZSM-5-OH but increased slightly as the F/Si ratio increased. This result was in accord with the amounts of Lewis acid sites of HZSM-5-OH and ZHSM-5-F with different F/Si ratios. Therefore, the amount of framework Al Lewis acid sites, which originating from the perturbation of tetrahedrally coordinated framework Al, was related to silanol defects [22, 24, 39, 40].

¹H MAS NMR was performed to further examine the silanol sites information of the ZSM-5 zeolite samples (Fig. 6). The assignments and relative distributions of ${}^{1}\text{H}$ MAS NMR resonances were also achieved by simulation using the Gaussian Deconvolution method (Fig. 6, Table 3). There were five distinct resonance peaks in the profiles, locating at 1.7, 2.0, 2.5, 4.0 and 5.0 ppm respectively. The peak at 1.7 ppm was assigned to external silanol groups (SiOH_{ext}), the one at 2.0 ppm was ascribed to silanol groups in defect sites (SiOH_{def.}), the peak at around 2.5 ppm belonged to extra-framework Al-OH [37, 41]. The rather broadband at around 3.2-6 ppm, which was decomposed into two peaks at 4.0 and 5.0 ppm, corresponded to bridging Si(OH)Al groups [41]. As seen from Table 3, the relative peak area of bridging Si(OH)Al groups in two samples kept constant. Compared with ZSM-5-OH, however, ZSM-5-F-0.15 showed that the relative peak area of silanol groups in defect sites was reduced significantly. This result was consistent with the FT-IR analysis above. It also further



Fig. 6 ¹H MAS NMR spectra of ZSM-5-OH and ZSM-5-F-0.15

Table 3 Relative peak area and assignments of OH groups in ${}^1\!\mathrm{H}$ MAS NMR spectra

Catalyst	Relative peak area (%)					
	SiOH _{ext.}	SiOH _{def.}	Al–OH	Si(OH)Al		
ZSM-5-OH	16.64	27.72	12.16	43.48		
ZSM-5-F-0.15	28.89	18.51	8.82	43.78		

confirmed that the amount of framework Al Lewis acid sites was related to silanol groups in defect sites.

3.3 Catalytic performance

The effects of ZSM-5-OH and ZSM-5-F with different F/Si ratio on the conversion of formaldehyde and selectivity of products in the formation of TOX are listed in Table 4. For ZSM-5-OH, the conversion of formaldehyde was 32.61%. For ZSM-5-F, the conversion of formaldehyde decreased from 32.26 to 29.58% with increase of F/Si ratio from 0.02 to 0.15. Compared with ZSM-5-OH, the conversion of

formaldehyde catalyzed by ZSM-5-F-0.15 only reduced by 3.03%. However, the selectivity of TOX increased obviously when catalyzed by ZSM-5-F zeolites. For ZSM-5-F-0.02 zeolite, the selectivity to TOX was 93.36%, which was higher than that of ZSM-5-OH by 5.76%; the selectivity to HCOOH, MeOH, MF, and DMM were 0.58%, 3.35%, 0.41%, and 2.30%, which were lower than that of ZSM-5-OH by 0.87%, 1.47%, 1.6%, and 1.82%, respectively. By continuing to increase the F/Si molar ratio, the selectivity to TOX increased slightly and selectivities to all byproducts also decreased gradually. Since the Lewis acid sites initiated the side reaction of Cannizzaro [17-19], HCOOH and MeOH were formed (Eq. 2). Then, the esterification (Eq. 3) [42] of HCOOH and MeOH and the acetalization (Eq. 4) [43, 44] of formaldehyde and MeOH took place with Brønsted acidic catalysts to generate MF and DMM. Without the byproducts of MeOH and HCOOH, the reactions of esterification of HCOOH and MeOH and the acetalization of formaldehyde and MeOH would not occur in this system. Thus, the increase of TOX selectivity and the decrease of byproducts selectivities were mainly ascribed to the less silanol defect sites and thus of the Lewis acid sites in ZSM-5-F zeolites.

Lifetime experiments were performed to examine the stability of the ZSM-5-OH and ZSM-5-F-0.15 zeolites on the reaction of formaldehyde to TOX (Fig. 7). Similarly as above, ZSM-5-F-0.15 showed higher selectivity of TOX but lower conversion of formaldehyde and lower selectivities of all byproducts including HCOOH, MeOH, MF, and DMM than ZSM-5-OH. Moreover, ZSM-5-F-0.15 exhibited a longer lifetime of 186 h, while ZSM-5-OH only had a lifetime of 146 h. Two zeolites after reaction were analyzed by TG to determine their coke deposition (Fig. 8). The weight loss of the ZSM-5-F-0.15 zeolite was ca. 10%, which was lower than that of ZSM-5-OH (ca. 13%). This suggested that the low concentration of silanol defect sites would prevent the coke formation, so had a long lifetime.

4 Conclusions

ZSM-5 zeolites which had similar crystal size, relative crystallinity and porosity porosities were synthesized in hydroxide medium and fluoride medium. The amounts of

Table 4Conversion of TOXand selectivities of TOX andbyproducts over ZSM-5-OHand ZSM-5-F with different F/Si ratio

Catalyst	Conversion (%)	Selectivity (%)					
		TOX	НСООН	МеОН	MF	DMM	
ZSM-5-OH	32.61	87.60	1.45	4.82	2.01	4.12	
ZSM-5-F-0.02	32.26	93.36	0.58	3.35	0.41	2.30	
ZSM-5-F-0.08	31.63	93.77	0.53	3.30	0.28	2.12	
ZSM-5-F-0.15	29.58	94.69	0.50	2.82	0.25	1.74	



Fig. 7 a Conversions of formaldehyde with ZSM-5-OH and ZSM-5-F-0.15; b selectivities of TOX and byproducts catalyzed by ZSM-5-OH; c selectivities of TOX and byproducts catalyzed by ZSM-5-F-0.15



Fig. 8 TG measurement of ZSM-5-OH and ZSM-5-F-0.15 after continuous reactions

Brønsted acid sites were nearly kept constant in the samples of ZSM-5-OH and ZSM-5-F zeolites. However, while adding NH₄F in the gels, the amounts of silanol defect sites and Lewis acid sites reduced obviously and both of them decreased slightly with increase of F/Si ratio. This results suggested that the formation of silanol defect sites contributed to the formation of framework Lewis acid sites and it could be inhibited by adding NH₄F in the synthetic gel. In the system of TOX synthesis from formaldehyde, the selectivity of TOX catalyzed by ZSM-5-F zeolite was higher than that of ZSM-5-OH and increased gradually with increase of F/Si ratio. Moreover, ZSM-5-F zeolite showed a longer lifetime than that of ZSM-5-OH.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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