Accepted Manuscript

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PII:	S1566-7367(18)30560-0
DOI:	doi:10.1016/j.catcom.2018.10.029
Reference:	CATCOM 5540
To appear in:	Catalysis Communications
Received date:	4 August 2018
Revised date:	22 October 2018
Accepted date:	29 October 2018

Please cite this article as: Ting Xu, Huikang Liu, Qianyi Zhao, Shiyu Cen, Lifang Du, Qinghu Tang, Conversion of chloromethane to propylene over fluoride-treated H-ZSM-35 zeolite catalysts. Catcom (2018), doi:10.1016/j.catcom.2018.10.029

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Conversion of Chloromethane to Propylene over Fluoride-treated H-ZSM-35 Zeolite Catalysts

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Abstract

H-ZSM-35 with 2D channel intersections has been first found to be an effective catalyst over chloromethane transformation into propylene. Fluoride treatment is further introduced to improve the catalytic performance. With a proper concentration of fluoride treatment, the selectivity and yield of propylene can be enhanced significantly while a high propylene/ethylene ratio is achieved. Detailed characterizations demonstrate that dealumination caused by fluoride treatment results in a reduction in acidic sites, which is responsible for the improvement of catalytic performance.

Keywords

Propylene, Chloromethane, H-ZSM-35, Fluoride treatment, Structural properties, Acidity

1. Introduction

Propylene is an important and widely used raw material. The existing propylene production routes suffer from energy consuming, high cost and low efficiency. Therefore, it is imperative to develop new nonpetroleum and economically feasible pathways to produce propylene. As a low cost and energy-efficient path, the conversion of methyl halide to hydrocarbons has attracted much attention [1].

The production of light olefins including ethylene, propylene and butylene from methyl halide has been well studied over SAPO-34 and ZSM-5 catalysts [2-10]. However, little attention was paid on the selectivity of propylene which is more demanded compared with other light olefins. As far as we know, there is only one example reported by Wang et al. concerning on the selective production of propylene from methyl halides [11]. Fluoride-treated H-ZSM-5 was employed as the catalyst over which high propylene yield and propylene/ethylene ratio (P/E ratio) was obtained.

In a comparative study, Haw et al. found that H-Ferrierite with 2D channels (FER topology, Scheme 1Sa) were more preferable to produce light olefins than H-ZSM-5 with 3D channels (MFI topology, Scheme 1Sb) in the methanol-to-olefins (MTO) reaction [12]. Because of the resemblance of MTO and methyl halide-to-olefins (MeXTO) reaction [13], the zeolites with FER topology may exhibit better catalytic performance in the MeXTO reaction compared with H-ZSM-5. Previously, only one FER zeolite catalyst (H-ZSM-35) was preliminarily attempted by Liu et al. in the MeXTO reaction under high partial pressure of chloromethane [14]. Without any further regulation, H-ZSM-35 showed low activity. However, it is still reasonable to believe that zeolites with FER topology might demonstrate excellent performance in the MeXTO reaction with moderate modification and reaction condition.

In this paper, we employ H-ZSM-35 zeolite as the catalyst for the selective conversion of chloromethane to propylene. Modification of H-ZSM-35 by impregnation with NH_4F aqueous solution is introduced to improve the catalytic activity. The influence of fluoride treatment on the structure, acidity and catalytic performance of H-ZSM-35 is investigated in detail. Key factors determining the catalytic behaviors and the roles of fluoride treatment are also discussed.

2. Experimental

2.1 Catalyst preparation

Na-ZSM-35 was prepared via the static hydrothermal method reported by Hu et al. using pyrrolidine as a structure directing agent (SDA) [15]. The molar composition of the starting gel is $1.56Na_2O$: Al_2O_3 : $25SiO_2$: $600.73H_2O$: 18.96SDA. In a typical synthesis, 2 g of sodium hydroxide and predetermined amount of sodium aluminate were dissolved in 85.5 mL of distilled water to form a clear solution. Subsequently, 37.45 g of colloidal silica (40wt% in aqueous solution) was added dropwise under vigorous stirring. After stirring for 2 h, 15.8 mL of pyrrolidine was added. Followed by stirring of 1 h, the suspension was transferred into a Teflon-lined stainless-steel autoclave and heated at 170 °C for 48 h. After crystallization, the resultant mixture was filtered, washed and dried at 100 °C overnight to yield a white solid. Finally, the obtained solid was calcined at 550 °C in air for 10 h. To prepare the proton form, Na-ZSM-35 was impregnated with 1 M NH₄NO₃ solution (1 g sample vs 20 mL solution) at 80 °C for 4 h followed by filtering, washing, drying and calcination at 550 °C for 6 h. The obtained sample is denoted as H-ZSM-35.

The fluoride treatment reported by Wang et al. [11] was performed on H-ZSM-35. Typically, 2 g H-ZSM-35 was immersed into 50 mL NH₄F aqueous solution. The concentration of NH₄F solution varied from 0.02 to 0.06 M. The mixture was stirred at room temperature for 6 h. Afterwards, the suspension was vapored at 80 °C until dryness. The yielded solid was calcined at 600 °C for 6 h to produce the catalyst which is denoted as H-ZSM-35-*x*M where *x* represent the concentration of NH₄F solution used for fluoride treatment.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were gained on D8 ADVANCE diffractometer using Cu Kα radiation under 40 kV, 40 mA. Scanning electron microscope (SEM) images were collected on a Hitachi SU8000 operated at 15 kV. X-ray fluorescence (XRF) spectroscopy were performed on SPECTROS COUT spectrometer. The pore structure was explored with argon physisorption on Micromeritics ASAP2020 apparatus. Ammonia temperature-programmed desorption (NH₃-TPD) were measured on a Micromeritics AutoChem II 2920 apparatus. Pyridine-adsorbed Fourier-transform infrared spectra (Py-IR) was employed to analyze the species of acidic sites on a Nicolet Avatar instrument equipped with an MCT detector at a resolution of 4 cm⁻¹. ²⁷Al and ²⁹Si magic-angle spinning nuclear magnetic resonance (²⁷Al MAS NMR and ²⁹Si MAS NMR) were both recorded on Bruker Avance III 500 NMR spectrometer. For ²⁷Al MAS NMR, it was operated with frequency at 104.26 MHz and spinning rate of 6 kHz; For ²⁹Si MAS NMR, it was operated with frequency at 79.5 MHz and spinning rate of 4 kHz. The ²⁷Al and ²⁹Si chemical shifts were referenced to Al(NO₃)₃ aqueous solution (1 M, 0 ppm) and TMS (0 ppm), respectively.

2.3 Catalyst reaction

The performance of catalysts on chloromethane conversion was conducted on a self-made apparatus operated at atmospheric pressure. The continuous flow of CH_3Cl and N_2 both controlled by a mass flow controller were mixed together followed by passing through the catalyst placed in a quartz reactor to carry out the reaction. At the exit of reactor, an aqueous sodium hydroxide solution collector kept at 0 °C was installed to trap the produced hydrogen chloride and higher hydrocarbons. The flow out from the trap was analyzed online with two GCs: one was equipped with a RT-Q-BOND capillary column and FID detector, the other was equipped with a 5A packed column and TCD detector.

3. Results and discussion

3.1 Catalytic performance

Table 1

The catalytic performance of parent and fluoride treated H-ZSM-35 is shown in Table 1. The CH₃Cl conversion was enhanced significantly just by treating with a low concentration (0.02 M) of NH₄F solution. When the concentration of NH₄F solution was continuously increased to 0.06 M, the conversion of CH₃Cl was reduced gradually from 88.4% to 54.9%. The selectivity of propylene was increased with the enhancement of NH₄F concentration while selectivity of ethylene and paraffins were decreased. The highest propylene yield of 32.0% was obtained on the H-ZSM-35-0.03M catalyst. At the same time, the P/E ratio of 3.7 was gained. With the increasement of NH₄F concentration. Furthermore, the P/E ratio was also enhanced significantly with the increasement of NH₄F concentration. During 10 h on steam, the H-ZSM-35 catalyst kept steady while a slight deactivation was observed over H-ZSM-35-0.03M (Figure 1S).

NH ₄ F	Conv.	Selectivity (%) ^b						C ₃ H ₆ vield	
conc. (M)	(%)	CH ₄	C_2H_4	C ₃ H ₆	C_4H_8	$C_2^{\ 0}-C_4^{\ 0}$	others	(%)	P/E
0	76.1	1.4	14.8	24.7	17.8	13.0	28.4	18.8	1.7
0.02	88.4	1.0	12.1	33.0	18.9	7.6	27.3	29.1	2.7
0.03	85.1	1.4	11.0	37.7	18.1	7.0	24.9	32.0	3.7
0.04	75.4	1.1	8.9	41.4	17.8	6.4	24.4	31.2	4.7
0.05	68.2	1.3	5.4	45.3	17.2	5.5	25.2	30.9	8.4
0.06	54.9	1.4	2.9	46.7	15.2	8.2	25.6	25.7	16.1

Catalytic performance of catalysts on the conversion of CH₃Cl^a.

^a Reaction conditions: T = 420 °C, $p(CH_3Cl) : p(N_2) = 1 : 9$, w = 1 g, F = 30 mL/min, time on stream = 1 h.

^b $C_2^{\ 0}$ - $C_4^{\ 0}$ denotes the C_2 - C_4 paraffins; others are products trapped in the collector which mainly consists of higher hydrocarbons.

3.2 Structural properties

The influences of different concentrations of NH₄F solution on the crystalline structure and crystallinity of H-ZSM-35 were studied by XRD techniques. As shown in Figure 1, peaks occurred at $2\theta = 9.4^{\circ}$, 12.6° , 22.3° , 25.6° and 26.4° were assigned to the feature peaks of ZSM-35 [15]. The crystallinity of the catalysts

was calculated using sum of the intensity of the more important peaks at $2\theta = 9.4^{\circ}$, 25.6°, and 26.4°. Compared with the standard pattern, the diffraction lines were almost fully matched. This implied that all the catalysts were ZSM-35 without impure phases and fluoride treatment did not alter the crystalline of H-ZSM-35. Furthermore, the intensity of diffraction peaks became stronger with the increasing concentration of NH₄F solution up to 0.03 M. When the concentration of NH₄F solution was further enhanced, the peak intensity was weakened slightly. This result indicated that the crystallinity could be raised if H-ZSM-35 was treated with proper concentration of NH₄F solution while decreased under high concentration. The enhancement of crystallinity might be resulted from elimination of the few amorphous species [11]. The calculated lattice parameters and unit volume (Table 2S) also support these conclusions.



Fig. 1. XRD patterns of the catalysts

Changes of morphology after fluoride treatment were observed by SEM. The images of catalysts are shown in Figure 2. The non-treated H-ZSM-35 was sheet-like at the size of \sim 5 µm which is the typical morphology of zeolites with 2D topology. After treatment with low concentration (0.02 M or 0.03 M) of NH₄F solution, the morphology of catalysts remained sheet-like but the size became smaller to \sim 2 µm. When the NH₄F concentration was raised to 0.04 M, the ZSM-35 sheets started to crush. Further, the sheets of ZSM-35 were broken down to small particles with the continuous increasement of NH₄F concentration. The rupture of ZSM-35 sheets might be responsible for the decreasing of crystallinity at high NH₄F concentration.



Fig. 2. SEM images of H-ZSM-35 treated with different concentration of NH₄F solution

Pore structures were studied through argon physisorption. Table 2 demonstrates the textural properties including surface area and micropore volume. With the increasement of NH_4F concentration, the volume and surface area of micropores were reduced while the external surface area was increased. Furthermore, the total surface area was decreased a little after fluoride treatment. The adsorption isotherms (Figure 2S) indicated that no mesopores were produced in all samples.

Table 2

NH ₄ F Conc. (M)	Micropore volume (cm $^{3}/g$)	BET surface area (m^2/g)				
		Micropore	External	Total		
0	0.079	181.8	37.1	218.9		
0.02	0.076	172.6	41.7	214.3		
0.03	0.074	169.8	43.9	213.7		
0.04	0.071	166.6	41.5	208.1		
0.05	0.072	158.0	47.4	205.4		
0.06	0.066	153.5	51.6	205.0		

Textural properties of the catalysts.

In order to clarify the influence of fluoride treatment on the distribution of Al species, ²⁷Al MAS NMR technique was employed. The results are shown in Figure 3. For the non-treated H-ZSM-35, a main peak appeared at 54 ppm which was assigned to the tetrahedral framework Al (FAI) while a small peak of the octahedral extra-framework Al (EFAI) was detected at 0 ppm [16]. This indicated that the parent H-ZSM-35 had good crystallinity, in agreement with the XRD results shown in Figure 1. After treatment with 0.02 M of NH₄F solution, the peak at 54 ppm became broader, which should be related to the distortion of FAI species [17, 18]. Meanwhile, the peak area at 54 ppm was reduced and the peak at 0 ppm was enlarged. This result illuminated that a part of FAI was transformed into EFAI during the fluoride treatment at low concentration.

When the concentration of NH_4F solution was raised to 0.03 M, a new peak of the fluorinated hexacoordinated EFAl species was occurred at -14 ppm [19]. Further, with the enhancement of NH_4F concentration, the signal of FAl was weakened, and the signal of EFAl species became stronger correspondingly. This observation implied that more Al atoms migrated from the framework of H-ZSM-35 to form extra-framework Al species at the surface. The results were also supported by chemical composition (XRF, Table 1S) and ²⁹Si MAS NMR (Figure 3S) measurements.



Fig. 3. ²⁷Al MAS NMR spectra of H-ZSM-35 treated with different NH_4F concentration of (a) 0, (b) 0.02 M, (c) 0.03 M, (d) 0.04 M, (e) 0.05 M, (f) 0.06 M.

3.3 Acidic properties

The acidic properties of zeolites affect their catalytic performance in MeXTO reaction significantly [20]. NH_3 -TPD results (Figure 4S) showed that both acidic sites were remarkably reduced after fluoride treatment. It was notable that the strong acidic sites almost vanished even at low NH_4F concentration. The amount of Brønsted acidic sites (BAS) and Lewis acidic sites (LAS) were measured by Py-IR. Figure 4 shows the IR spectra of catalysts. The bands at ~1540 cm⁻¹ and ~1450 cm⁻¹ belonged to BAS and LAS, respectively, while the band at ~1485 cm⁻¹ could stem from both BAS and LAS [21]. All the catalysts exhibited weak bands at ~1450 cm⁻¹ which implied the deficiency of LAS. The BAS were dominant acid sites which were reduced with the increasement of NH_4F concentration and almost disappeared after fluoride treatment at high concentration (quantitative results are shown in Table 3S). These results indicated that the strong acidic sites showed Brønsted acidity was reduced after fluoride treatment.



Fig. 4. Py-IR spectra of H-ZSM-35 treated with different NH_4F concentration of (a) 0, (b) 0.02 M, (c) 0.03 M, (d) 0.04 M, (e) 0.05 M, (f) 0.06 M.

3.4 The role of fluoride treatment

Based on the results, we proposed the role of fluoride treatment in CH_3Cl conversion over ZSM-35 catalysts as shown in Scheme1: During the impregnation stage, some fluoride ions could be combined with framework Si or Al atoms. The bridged Si–(OH)–Al bonds that contributed to the Brønsted acidic sites were broken to form extra-framework fluorinated aluminum species and internal silanols at the calcination stage. At high concentration of NH₄F, the fluorinated silicon species (SiF_x) might be removed to the gas phase.



Scheme 1. Schematic model of fluoride treatment on H-ZSM-35.

The decreasing Brønsted acidic sites led to an enhancement of propylene selectivity and reduction in the selectivity of ethylene, paraffins and higher hydrocarbons. The change of product distribution was due to the suppression of cracking and hydrogen-transfer reactions by weakening the Brønsted acidic sites [22, 23]. An obvious reduction of chloromethane conversion observed at high fluoride treatment concentration was related to the over reduced Brønsted acidic sites. On the other hand, the desilication and dealumination caused by fluoride treatment also brought damage to the structure of zeolite. Some micropores were blocked while the sheets of H-ZSM-35 were broken down. These induced instabilities were responsible for the more rapid deactivation of fluoride-treated H-ZSM-35 compared with parent ones. The postulated mechanism about transformation of chloromethane to propylene and by-products is shown in Scheme 2S.

4. Conclusions

H-ZSM-35 was first found to be an effective catalyst for the conversion from chloromethane to propylene. The fluoride treatment by impregnation with NH₄F solution at moderate concentration followed by calcination could enhance not only the selectivity and yield of propylene but also the P/E ratio significantly. Detailed characterizations indicated that fluoride treatment could cause the migration of framework Al which led to the reduction of strong Brønsted acidic sites. The decrease of acidic sites induced the enhancement of the selectivity of propylene by suppressing the hydrogen-transfer and cracking reactions. On the other hand, extra-framework Al species were generated from dealumination caused by fluoride treatment. They could block micropores in the zeolite and break down the ZSM-35 sheet as well, resulting in the instability and slight deactivation of the fluoride-treated catalysts.

Acknowledgements

This work is supported by the Natural Science Foundation of China (21503070, 21501048), the Key Scientific Project of Universities from Education Department of Henan Province (14B150041) and the Key Science and Technology Project of Henan Province (182102210377).

Appendix A. Supplementary data

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0.02	88.4	1.0	12.1	33.0	18.9	7.6	27.3	29.1	2.7
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0.04	75.4	1.1	8.9	41.4	17.8	6.4	24.4	31.2	4.7
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0.06	54.9	1.4	2.9	46.7	15.2	8.2	25.6	25.7	16.1

Table 1
Catalytic performance of catalysts on the conversion of CH ₃ Cl ^a

^a Reaction conditions: T = 420 °C, $p(CH_3Cl) : p(N_2) = 1 : 9$, w = 1 g, F = 30 mL/min, time on stream = 1 h.

^b C_2^{0} - C_4^{0} denotes the C_2 - C_4 paraffins; others are products trapped in the collector which mainly consists of higher hydrocarbons.

Textural properties of the catalysts.

NH E Cong. (M)	Mianan ana ana hanna (am ³ /a)	BET surface area (m ² /g)			
NH_4F Conc. (M)	where $\frac{1}{g} = \frac{1}{g}$	Micropore	External	Total	
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0.05	0.072	158.0	47.4	205.4	
0.06	0.066	153.5	51.6	205.0	

Highlights:

- H-ZSM-35 is an effective catalyst for the conversion of chloromethane to propylene.
- Fluoride treatment can enhance the catalytic performance of H-ZSM-35 significantly.
- Fluoride treatment result in desilication and dealuminization to the framework.
- The strong Brønsted acidic sites are reduced by the fluoride treatment.
- Catalytic activity is improved by the suppression of hydrogen-transfer reactions.

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