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# 1. Introduction

Fischer–Tropsch synthesis which converts syngas (CO and  $H_2$ ) into liquid fuels provides a practical option to solve the increasing demand for oil resources and other chemicals.<sup>1</sup> Liquid fuels produced from the Fischer–Tropsch synthesis are generally of good quality to emit less nitrous and sulfur oxides. However, the high content of long chain olefins (C<sub>6</sub>– C<sub>10</sub>) in light-hydrocarbon distillates always causes the low knock rating of the oil products.<sup>2,3</sup> The conversion of olefins into aromatics over zeolite catalysts is a promising strategy to meet the expanding demand for platform chemicals, to increase the octane number of gasoline<sup>4</sup> and to produce important high-value alkyl-aromatics such as ethyltoluene, ethylbenzene and xylenes.<sup>5</sup>

Due to its unique pore structure and strong acidity, ZSM-5 zeolite has been widely investigated in the catalytic

Beijing, 101400, PR China. E-mail: liusuyao@synfuelschina.com.cn <sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, PR China



Liwei Zhang,<sup>ac</sup> Huaike Zhang,<sup>ab</sup> Zhiqiang Chen,<sup>ac</sup> Qiang Ning, <sup>10</sup><sup>ab</sup> Suyao Liu, <sup>10\*b</sup> Jie Ren,\*<sup>ab</sup> Xiaodong Wen <sup>10</sup><sup>ab</sup> and Yong-Wang Li<sup>ab</sup>

To correlate the relationship between the Al distribution and the catalytic performance of long-chain olefin aromatization, several ZSM-5 zeolites with different Al locations and proximities were prepared *via* adjusting the hydrothermal synthesis conditions. Characterization by XRD, SEM and N<sub>2</sub>-adsorption indicated that all the as-prepared ZSM-5 zeolites exhibited high crystallinities, uniform morphologies and open channels. However, a great difference in the framework Al (Al<sub>F</sub>) positions was observed by <sup>27</sup>Al MAS NMR and UV-vis-DRS of Co(II) ions, thus leading to the distinct acidity of various zeolites as determined by NH<sub>3</sub>-TPD and Py-IR. In 1-octene aromatization reaction, ZSM-5 catalysts exhibited significantly different catalytic performances and reaction pathways, which were closely related to the types and locations of the AlF atoms. The ZSM-5 zeolite catalyst with the most abundant single Al sites exhibited the lowest aromatics selectivity, while Al pairs in the framework were more favorable to the formation of aromatics. Moreover, the product distribution revealed that the Al pairs in the channel intersections of the ZSM-5 zeolite were responsible for the improved selectivity to heavy aromatics due to the fewer space restrictions; however, the Al pairs in the sinusoidal and straight channels with severe size restrictions suppressed the generation of bigger aromatics on the Al sites. This result provided a new potential method for precisely tailoring the catalytic selectivity in olefin conversion and upgrading the Fischer–Tropsch oil.

aromatization of short chain alkenes.<sup>6,7</sup> Although extensive research efforts focused on C<sub>3</sub> and/or C<sub>4</sub> olefin aromatization with ZSM-5 zeolite catalysts,8-10 less attention has been paid to the aromatization of longer chain olefins. It was reported that optimizing the acidity and the diffusion pathway of intermediates can enhance the catalytic performance, suggesting the close correlation between the acid sites and long chain alkene aromatization.<sup>11,12</sup> Moreover, as for the aluminosilicate zeolites which are assembled with the corneroxygen sharing of  $SiO_4$  and  $AlO_4$  tetrahedra, the cations (H<sup>+</sup>) as the acid sites are located near the AlO<sub>4</sub> structure within the zeolite framework to balance the electric charge and form catalytically active sites.13,14 It is therefore a reasonable assumption that the position and proximity of the Al atoms in the framework should be considered as crucial factors for the aromatization performance,15,16 due to the fact that the adsorption of reactant molecules, spatial constraints of the intermediates, and the diffusion behaviour of products are strongly influenced by the Al<sub>F</sub> positions.<sup>17,18</sup>

Recently, several studies about the distribution of the Al atoms in the framework of ZSM-5 zeolite materials have been performed. Liang and co-workers suggested that the  $Al_F$  locations and the Brønsted acid distribution in H-ZSM-5 zeolites strongly affected the reaction pathway and



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<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China. E-mail: renjie@sxicc.ac.cn <sup>b</sup> National Energy Research Center for Clean Fuels, Synfuels China Co., Ltd, Difference 101000, DB China, Description Comparison of Sciences, Statement of Sciences, Scie

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determined the catalytic performance in the methanol-toolefin (MTO) reaction.<sup>19</sup> Kim et al. prepared hierarchically structured ZSM-5 zeolites with various Al distributions and demonstrated that the Al atoms located in the straight channels promoted the reaction mechanism through an alkene-based cycle, leading to a high olefin selectivity.<sup>20</sup> Yokoi synthesized ZSM-5 zeolites with different locations of Al atoms by using various organic structure directing agents with or without Na cations. They found that the distribution of Al<sub>F</sub> affected the catalytic lifetime in the methylcyclohexane cracking reaction, and therefore the zeolite with Al atoms located at the intersection exhibited a shorter catalytic lifetime.21 The result of Sazama presented that the distribution of Al species in the framework of ZSM-5 zeolites obviously affected the product composition during the olefin cracking reactions. The enrichment of Al siting in the channel intersections was beneficial to the catalytic performance in 3-methylpentane cracking and aromatics disproportionation.<sup>22</sup> Janda reported that а high concentration of Al<sub>F</sub> distributed in the channel intersections of ZSM-5 zeolites could be obtained by increasing the Al content, which was beneficial for *n*-butane dehydrogenation.<sup>23</sup> Thus, it is of great importance to deeply research the impacts of the position and proximity of Al<sub>F</sub> in the ZSM-5 zeolite on the distribution and strength of the acid sites which strongly determine the reaction pathway and catalytic performance, providing a useful perspective for the design and synthesis of desired catalysts.

In the present work, several ZSM-5 zeolites were prepared using hydrothermal synthesis and characterized systematically. All ZSM-5 samples exhibited similar SiO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub> ratios, high crystallinity, and uniform morphology. Moreover, various measurements including UV-vis-DRS of Co(II) ions and MAS NMR spectroscopy were used to differentiate the Al siting in the straight and sinusoidal channels and the channel intersections within the ZSM-5 framework, which is closely related to the acidity properties determined by NH<sub>3</sub>-TPD and Py-IR. Then, the 1-octene aromatization performance over ZSM-5 zeolites with various Al distributions was evaluated, and a correlation between the product selectivity and acid site distribution of the ZSM-5 zeolites was built. Furthermore, the alkylation of benzene with 1-octene was also used to investigate the formation pathway of the heavy aromatics. This work provides useful perspectives and better understanding for the selective conversion of olefins originating from the Fischer-Tropsch synthesis.

# 2. Experimental

#### 2.1 Materials

All chemicals were purchased from commercial suppliers and used without further purification. Tetrapropylammonium bromide (TPABr, 99%) was purchased from Tianjin Guangfu Chemical Co., Ltd. Tetrapropylammonium hydroxide (TPAOH, 25% solution in water), tetraethyl orthosilicate (TEOS, SiO<sub>2</sub> = 28 wt%), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>, 99%), aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O, 99%), aluminium nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99%), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%), sodium nitrate (NaNO<sub>3</sub>, 99%) and urea (99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH, 99%) and ammonium chloride (NH<sub>4</sub>Cl, 99%) were purchased from Beijing Chemical Co., Ltd. Silica sol (SiO<sub>2</sub>  $\geq$  30 wt%) was obtained from Qingdao Haiyang Chemical Co., Ltd. Benzene (99%) and 1-octene (98%) were obtained from Aladdin Reagent Co., Ltd.

#### 2.2 Preparation of various ZSM-5 zeolites

ZSM-5 zeolite with a spherical morphology was prepared using silica sol and  $Al_2(SO_4)_3 \cdot 18H_2O$  as silica and aluminium sources, respectively. TPAOH was used as an organic structure-directing agent (OSDA). The initial gel was obtained by adding a solution of TPAOH, silica gel, and Na<sub>2</sub>SO<sub>4</sub> to a solution of aluminium sulphate under stirring, successively. The molar composition for the spherical ZSM-5 zeolites was  $100SiO_2: 1.0Al_2O_3: 40TPAOH: 15Na_2O: 6400H_2O$ . Then, the resulting gel was transferred into a stainless-steel autoclave and hydrothermally crystallized at 180 °C for 36 h with autogenous pressure.

ZSM-5 zeolite with a hexagonal morphology was synthesized using TPABr and TPAOH as OSDAs. The gel for this sample synthesis was prepared by adding TPAOH and silica gel successively to a mixed solution of  $Al_2(SO_4)_3$ , urea, NaOH, and TPABr under stirring. A typical mixture had a molar composition of  $100SiO_2: 1Al_2O_3: 7.5TPABr: 6TPAOH:$ 2.5Na<sub>2</sub>O:16urea: 3000H<sub>2</sub>O. After being stirred for 1 h at room temperature, the mixture was placed in a stainless-steel autoclave and heated at 170 °C for 36 h in a furnace at autogenous pressure under stirring.

To obtain nano-ZSM-5 zeolite with a cylindrical morphology, an aqueous solution of TEOS and TPAOH was stirred at 80 °C for 24 h in a stainless-steel autoclave. Then, a solution of NaOH and  $Al(NO_3)_3$ ·9H<sub>2</sub>O was added into this mixture, successively. The starting molar composition was  $100SiO_2: 1Al_2O_3: 25TPAOH: 5Na_2O: 5000H_2O$ . The synthesis gels were heated to 175 °C and finally crystallized for 24 h.

After crystallization, various zeolites were filtered and washed with deionized water to neutral, and then dried at 120 °C overnight. The as-synthesized samples were calcined at 550 °C (ramping rate: 1 °C min<sup>-1</sup>) for 8 h under an air atmosphere to remove OSDAs. The calcined samples were ion-exchanged with a 0.5 M NH<sub>4</sub>Cl aqueous solution at 80 °C for 8 h to form NH<sub>4</sub>-ZSM-5 samples, followed by washing, drying and calcination steps at 550 °C for 4 h to obtain protonic form zeolites. The ion-exchange and calcination processes were repeated twice. The final products with spherical, hexagonal and cylindrical morphologies are denoted as ZSM-5-S, ZSM-5-H, and ZSM-5-C, respectively.

To determine the Al pairs and single Al atoms, Co ionexchanged ZSM-5 zeolites were prepared by following the method introduced by Dědeček.<sup>24,25</sup> Firstly, the as-prepared

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ZSM-5 zeolites were ion-exchanged with a 1.0 M NaNO<sub>3</sub> aqueous solution at 80 °C for 7 h to obtain Na-ZSM-5 samples. Then, the Na-ZSM-5 samples were ion-exchanged with an aqueous solution of cobalt nitrate (0.05 mol  $L^{-1}$ ) at 80 °C for 7 h. Finally, the resulting samples were washed with deionized water several times and dried at 120 °C overnight. The ion-exchange and drying steps were performed three times to obtain Co-ZSM-5.

#### 2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the various ZSM-5 zeolites were recorded on a D8 Advance diffractometer (Bruker, Germany) with Cu K $\alpha$ , operated at 40 kV and 40 mA.

 $N_2$  adsorption–desorption isotherms were measured with an ASAP 2020 instrument (Micromeritics, USA) at –196 °C. Prior to the adsorption–desorption test, all zeolites were degassed under  $5 \times 10^{-3}$  Torr at 350 °C for 8 h. The micropore surface area and volume were determined using the  $\tau$ -plot method.

The bulk  $SiO_2/Al_2O_3$  ratios of the various samples were determined by X-ray fluorescence (XRF) on a ZSX Primus II spectrometer (Rigaku, Japan).

Scanning electron microscopy (SEM) images of the ZSM-5 samples were taken with a QUANTA 400 (FEI, USA) operating at an electron acceleration voltage of 10 kV.

Elemental analysis was carried out to determine the Co contents using inductively coupled plasma-optical emission spectroscopy (ICP-OES) with an Optima 2100DV (Perkin-Elmer, USA).

Ultraviolet-visible light-diffuse reflectance spectroscopy (UVvis-DRS) was performed using a UH4150 spectrophotometer (Hitachi, Japan) equipped with a photodiode array detector and a diffuse reflectance attachment. The scan speed was set at 600 nm min<sup>-1</sup>. Prior to the test, all the samples were dehydrated at 400 °C for 6 h. The concentrations of single Al and Al pairs were calculated by:

where  $[Al_{total}]$  and  $[Co_{max}]$  are the Al and Co contents in the ion-exchanged Co-ZSM-5 zeolites, respectively, and both of these were determined by ICP-OES analysis.

Solid state <sup>27</sup>Al magic angle spinning nuclear magnetic resonance (<sup>27</sup>Al MAS NMR) spectroscopy was performed on an Advance 600 NMR spectrometer (Bruker, Germany). <sup>27</sup>Al MAS NMR spectra were recorded using a 4 mm ZrO<sub>2</sub> rotor and spin at a spinning frequency of 12 kHz with a pulse angle of  $\pi/12$  and a recycle delay of 1 s. The chemical shifts were given relative to a 1 M aqueous solution of aluminium nitrate.

The acidity of the ZSM-5 zeolites was determined by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) using an Autochem II 2920 instrument (Micromeritics, USA). Firstly, the ZSM-5 zeolite samples were pre-treated at 550 °C in a He flow (50 mL min<sup>-1</sup>) for 1 h, and then saturated with  $NH_3$  (balance He, flow rate: 50 mL min<sup>-1</sup>) for 10 min at 100 °C. Subsequently, the physically adsorbed ammonia was removed by flowing He (50 mL min<sup>-1</sup>) for 60 min. Finally, the  $NH_3$  desorption was performed by heating the samples to 600 °C at a ramping rate of 10 °C min<sup>-1</sup> under a flow of pure helium (50 mL min<sup>-1</sup>). The temperature and  $NH_3$  concentration were monitored continuously with a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (Omnistar Pfeiffer, Germany), simultaneously.

Pvridine-adsorbed Fourier-transform infrared (Pv-FTIR) spectra of the various ZSM-5 zeolites were collected using an in situ cell on an EOUINOX 70 (Bruker, Germany). A selfsupporting wafer with about 15 mg of the sample was placed in an *in situ* cell equipped with a CaF<sub>2</sub> window and a vacuum system. The powder zeolite was activated at 400 °C for 4 h under vacuum and then pyridine vapor was introduced into the cell. Afterward, prior to the collection of the IR spectra, the sample was evacuated at 200 °C and 350 °C to remove the weakly bound pyridine, respectively. The adsorption amount of pyridine degassed at 200 °C was ascribed to the total acid amount, whereas the adsorption amount of pyridine, degassed at a relatively high temperature of 350 °C, corresponded with the amount of strong acidity. The difference in the adsorption amounts between 200 °C and 350 °C was attributed to the weak acid sites. The quantities of Brønsted and Lewis acid sites were estimated from the bands at 1545 cm<sup>-1</sup> and 1455 cm<sup>-1</sup> of the Pv-FTIR spectra, according to the Lambert-Beer law<sup>26</sup> and the molar absorption coefficients of  $\varepsilon_{\rm B}$  = 1.13 cm  $\mu {\rm mol}^{-1}$  and  $\varepsilon_{\rm L}$  = 1.28 cm  $\mu$ mol<sup>-1</sup>,<sup>27</sup> respectively.

#### 2.4 Catalytic performance

1-octene aromatization was carried out in a continuous flowing fixed-bed stainless-steel reactor. In a typical experiment, 5.0 mL of sieved zeolite catalyst (20-40 mesh) was loaded into the centre of the reactor and pre-treated at 450 °C under a N<sub>2</sub> flow for 2 h. The activated sample was cooled down to the target temperature (340 °C, 360 °C, and 380 °C) in the flow of N<sub>2</sub>. Subsequently, the feedstock of 1-octene was fed to the reactor using a microscale pump at a certain flow rate, and the reaction was carried out at 1.0 MPa. The volume ratio of N<sub>2</sub>/feed was 300, and the liquid hourly space velocity (LHSV) of each catalyst was set at 2.0 h<sup>-1</sup>. The products were separated at the outlet of the reactor, leading to the liquid products being collected, while the gaseous products were evacuated. The gas products were analysed using an on-line gas chromatograph (Agilent 7890A, equipped with a flame ionization detector and a capillary column,  $Al_2O_3$  30 m × 0.32 mm × 0.25 µm). The liquid products were analysed using an off-line gas chromatograph (Agilent 7890A, equipped with a flame ionization detector and a capillary column, DB-PONA 50 m × 0.20 mm × 0.55 μm). The liquid products were identified using an Agilent/HP 6890 gas chromatograph equipped with a 5973 mass selective detector (GC-MS). In each experiment, the carbon balance

was maintained above 95%. The calculation methods of conversion and selectivity are shown as follows:

Conversion of 1-octene (%) = 
$$\frac{w_0 - w}{w_0} \times 100$$
  
Product Selectivity (%) =  $\frac{w_i}{w_0 - w} \times 100$ 

where  $w_0$  and  $w_1$  represent the weights of 1-octene in the feed and product, respectively, and  $w_i$  denotes the weight of the products to which the reactant was converted.

## 3. Results and discussion

#### 3.1 Structure and morphology

The bulk  $SiO_2/Al_2O_3$  molar ratios of the various ZSM-5 zeolites were analysed using XRF. As summarized in Table 1, the  $SiO_2/Al_2O_3$  ratios of all the zeolite samples are almost the same regardless of the initial compositions.

The XRD patterns of the as-synthesized zeolites are shown in Fig. 1, and the calculated crystallinities are listed in Table 1. All the samples exhibit characteristic peaks of the MFI-type structure at  $2\theta = 7.9^{\circ}$ ,  $8.8^{\circ}$ ,  $22.3^{\circ}$ ,  $23.1^{\circ}$ , and  $23.8^{\circ}$ .<sup>28</sup> Apparently, the ZSM-5-C sample exhibits much broader diffraction peaks in comparison to the other zeolites, because the optimized pre-aging step before the crystallization produces a large number of nuclei particles in the initial synthesis gel and finally leads to the formation of ZSM-5 zeolites with small particles.<sup>29</sup> Compared to the ZSM-5-C and ZSM-5-S samples, the ZSM-5-H zeolite exhibits a higher intensity of the diffraction peak at  $2\theta = 8.76^{\circ}$  which can be assigned to the (020) crystal plane that is perpendicular to the *b*-axis of the MFI crystal structure.<sup>30,31</sup> The relative crystallinity of the as-synthesized ZSM-5 zeolite is defined as the percentage of the diffraction peak intensity at  $2\theta = 22.3^{\circ}$ based on that of sample ZSM-5-H at this angle.<sup>32</sup> As shown in Table 1, all the samples exhibit high relative crystallinity, suggesting negligible impurity phases. Taking the crystallinity of the ZSM-5-H sample as 100%, the relative crystallinities of the ZSM-5-S and ZSM-5-C zeolites are 93% and 89%, respectively.

The morphology of the various ZSM-5 samples was evaluated by SEM observations (Fig. 2). Obviously, all the samples exhibit a uniform size and shape, and amorphous aluminosilicates cannot be observed, confirming their high crystallinity consistent with the XRD result. The ZSM-5-S



Fig. 1 XRD patterns of various ZSM-5 zeolites.

zeolite presents a uniformly spherical morphology with an average diameter of 5.0  $\mu$ m (Fig. 2a). Moreover, a clear and regular aggregation structure of small flake-like particles is observed within the particles of the ZSM-5-S sample as shown in Fig. 2b. The SEM images of the ZSM-5-H sample (Fig. 2c and d) shows coffin-shaped particles with a uniform size of about 5.0  $\mu$ m, which is a typical morphology of ZSM-5 single crystals. For the ZSM-5-C sample, the SEM images (Fig. 2e and f) provide the visual indication that this material consists of cylindrical-like particles with an average crystallite size of 250 nm.

The N<sub>2</sub> adsorption-desorption isotherms and the corresponding textural properties of the various zeolites are shown in Fig. 3 and Table 1. All the ZSM-5 zeolites exhibit high uptake at a relatively low pressure  $(P/P_0 = 0.01)$ , illustrating the established microporous structure in all the samples. However, the distinct hysteresis loops in the range of  $P/P_0 = 0.4-1.0$  indicate the different types of pore properties. An obvious hysteresis loop is observed in the isotherm of the ZSM-5-S sample at relatively intermediate pressure  $(P/P_0 = 0.4-0.8)$  due to N<sub>2</sub> adsorption on the layer accumulation of the small particles.<sup>33</sup> However, no hysteresis loop in the isotherm of the ZSM-5-H sample is observed, suggesting that no intercrystalline mesoporosity is present.<sup>34</sup> As for the ZSM-5-C sample, the hysteresis loop (H4 type) at high pressure demonstrates the generation of mesomacropores which probably arise from the inter-crystal voids caused by the stacking of the small zeolite crystals. As shown in Table 1, the BET surface areas are found to be 364.8, 367.0, and 395.0 m<sup>2</sup> g<sup>-1</sup> for the ZSM-5-S, ZSM-5-H, and ZSM-5-C samples, respectively. Similarly, the external surface area of the various samples increases with the decrease of crystal size. The micropore surface areas, which are defined as the

Table 1	Crystallinit	y and te	extural pro	perties of	f various	ZSM-5	zeolites
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		Crystallinity <sup>b</sup>	Textural properties <sup>c</sup>					
Samples	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	(%)	BET surface area $(m^2 g^{-1})$	Micropore area $(m^2 g^{-1})$	External area $(m^2 g^{-1})$	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )		
ZSM-5-S	82.4	93	364.8	301.9	62.9	0.14		
ZSM-5-H	84.2	100	367.0	309.4	57.6	0.14		
ZSM-5-C	81.8	89	395.0	331.8	63.2	0.15		

<sup>*a*</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios measured by XRF. <sup>*b*</sup> Calculated from the XRD patterns by comparing the intensity of the diffraction peak at  $2\theta = 22.3^{\circ}$ . <sup>*c*</sup> Determined by N<sub>2</sub>-adsorption.

Paper



Fig. 2 SEM images of the ZSM-5-S (a and b), ZSM-5-H (c and d), and ZSM-5-C (e and f) samples.



Fig. 3 Nitrogen adsorption/desorption isotherms of various ZSM-5 zeolites.

difference between the  $S_{\text{BET}}$  and  $S_{\text{EXT}}$ , are above 300.0 m<sup>2</sup> g<sup>-1</sup> for all the samples. In addition, all the samples exhibit similar micropore volumes (~0.14 cm<sup>3</sup> g<sup>-1</sup>).

#### 3.2 Framework structure

The location and content of the aluminum species in the framework determine the several properties of zeolites including the acidity and catalytic performance. Thus, it is necessary to investigate and compare the Al distributions in the various ZSM-5 zeolites.

<sup>27</sup>Al MAS NMR was used to determine the coordination environments of Al species of the different samples. As shown in Fig. 4, all the samples exhibit two peaks at 54.5 and 0 ppm corresponding to the tetrahedral Al species in the framework and the octahedral coordination of the extra-framework Al



Fig. 4  $^{27}$ Al MAS NMR spectra (a) of different ZSM-5 samples and simulated spectra of ZSM-5-S (b), ZSM-5-H (c), and ZSM-5-C (d).

species, respectively.<sup>35</sup> The relative concentrations of framework and extra-framework Al species, which are determined by integrating the <sup>27</sup>Al MAS NMR signal, are listed in Table 2. Apparently, the Al<sub>F</sub> sites are dominant in all the samples. The Al concentrations in the extra-framework of the various samples follow the order ZSM-5-C > ZSM-5-S > ZSM-5-H, which is consistent with the crystallinity shown in Table 1. Moreover, the peak assigned to the Al<sub>F</sub> species can be deconvoluted into five peaks, centered at 52, 53, 54, 56, and 58 ppm.<sup>36</sup> Generally, the peak at 54 ppm is associated with the Al species located in the intersection of the straight and sinusoidal channels, while the peak at 56 ppm can be assigned to the Al sites in the straight and/or sinusoidal

Table 2 Al distributions of various ZSM-5 zeolites determined from  $^{\rm 27}Al$  MAS NMR spectra

			$Al_F$ distribution (%)		
Samples	$\mathrm{Al_{FW}}^a$	$\mathrm{Al_{EFW}}^b$	$\overline{\mathrm{Al}_{(54)}}^{c}$	Al <sub>(56)</sub> <sup>c</sup>	
ZSM-5-S	94.8	5.2	12.6	36.2	
ZSM-5-H	97.5	2.5	37.4	26.9	
ZSM-5-C	93.3	6.7	26.0	31.5	

<sup>*a*</sup> The relative concentration of  $Al_F$ , which is determined by integrating the <sup>27</sup>Al MAS NMR signal between the chemical shifts at 20 and 85 ppm. <sup>*b*</sup> The relative concentration of extra-framework aluminium, which is determined by integrating the <sup>27</sup>Al MAS NMR signal between –10 and 10 ppm. <sup>*c*</sup> Determined by deconvolution of the <sup>27</sup>Al MAS NMR spectra. channels.<sup>37</sup> The concentration of these sites, calculated from the area of these individual peaks, is given in Table 2. The concentrations of Al sites located at the intersection follow the order ZSM-5-H > ZSM-5-C > ZSM-5-S, while the Al concentrations in the independent channels decrease in the order ZSM-5-S > ZSM-5-C > ZSM-5-H, suggesting that the Al sites at the channel intersections can be suppressed by the accumulation of these nanocrystals.

Kim and Sazama suggested that the tetrahedral Al sites can be separated as a single Al atom or Al pairs, according to the number of (Si-O) groups between two Al sites in the zeolite framework. When the number of (Si-O) groups between two tetrahedral Al sites exceeds two, the Al sites are named single Al atoms owing to the long distance between them. Moreover, only the Al-O-(Si-O)<sub>2</sub>-Al groups can be formed, which are denoted as Al pairs.<sup>22</sup> According to the ICP-OES result of Co ion-exchanged ZSM-5 zeolites, the fractions of single Al atoms and Al pairs are obtained and summarized in Table 3. Almost all of the Al atoms in the ZSM-5-H sample exist in the form of single Al atoms. However, as for the ZSM-5-S sample, 78.1% of the Al sites exist as Al pairs which are slightly more prevalent than those in the ZSM-5-C sample. To further investigate the difference in the location of Al<sub>F</sub> sites in the ZSM-5-S and ZSM-5-C samples, more detailed locations of the Al pairs were determined by UV-vis-DRS of the Co-exchanged ZSM-5 samples.

As shown in Fig. 5, the spectra of the Co-exchanged ZSM-5-S and ZSM-5-C samples exhibit a broad band ranging from 13 000 to 24 000 cm<sup>-1</sup>, corresponding to the d-d transitions of bare  $Co(\pi)$  cations in several cationic sites. The amount of these sites is obtained by deconvolution of the UV-vis-DRS spectra in Fig. 5 using Gaussian functions. The  $\alpha$ -type cationic sites in the straight channels are identified by the single peak at about 15100 cm<sup>-1</sup>, and the peaks at 16000, 17 150, 18 600, and 21 200 cm<sup>-1</sup> are assigned to the sites ( $\beta$ type) at the intersections between the straight and sinusoidal channels. The  $\gamma$ -type sites in the sinusoidal channels are defined by peaks at about 20100 and 22000 cm<sup>-1.19</sup> The contents of these sites in the ZSM-5-S and ZSM-5-C samples are listed in Table 3. Due to the low Co content as determined by ICP-OES analysis, it is difficult to distinguish the location of the Al pairs in the ZSM-5-H sample. Obviously, the fraction of the Al pairs as the  $\alpha$ -type and  $\gamma$ -type sites in the ZSM-5-S sample is more than that of the ZSM-5-C sample, suggesting that the Al pairs of the ZSM-5-S zeolite prefer to

Table 3 Framework Al distributions of different ZSM-5 samples

	Al content	<sup>a</sup> (%)	Al pair distribution <sup><math>b</math></sup> (%)			
Samples	Al pairs	Single Al	α	β	γ	
ZSM-5-S	78.1	21.9	22.1	59.5	18.4	
ZSM-5-H	7.8	92.2			_	
ZSM-5-C	76.2	23.8	14.9	70.3	14.8	

<sup>*a*</sup> Calculated from the ICP-OES analysis of Co-exchanged ZSM-5 samples. <sup>*b*</sup> Determined from the fitting peaks of the UV-vis-DRS spectra of Co-exchanged ZSM-5 samples.



Fig. 5 UV-vis-DRS spectra of Co-exchanged ZSM-5-S (a) and ZSM-5-C (b) zeolites. The fractions of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -type Al pairs are also shown.

locate at both the straight and sinusoidal channels. In contrast, the ZSM-5-C zeolite holds more Al pairs ( $\beta$ -type) in the channel intersections (70.3%) than the ZSM-5-S sample (59.5%) due to the dissimilarity of silica sources used in the zeolite synthesis procedure.<sup>25,38</sup>

In summary, by combining the  ${}^{27}$ Al MAS NMR results, XRF data, ICP-OES analysis, and UV-vis-DRS spectra, it can be concluded that the coordination environments of Al<sub>F</sub> can be quite different for various zeolites with similar bulk SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. Furthermore, 92.2% of Al atoms in ZSM-5-H exist in the form of the single Al. However, the Al atoms prefer to locate in channel intersections of the ZSM-5-C zeolite as Al pairs, while the ZSM-5-S zeolite has more Al pairs in the straight and sinusoidal channels.

#### 3.3 Acidity

The acidic characteristics of the as-prepared ZSM-5 samples were determined by NH<sub>3</sub>-TPD and Py-IR. The NH<sub>3</sub>-TPD curves of the different zeolites are shown in Fig. 6. All spectra of the ZSM-5 zeolites exhibit two desorption peaks at about 195 °C and 370 °C, which can be attributed to NH<sub>3</sub> adsorbed on weak and strong acid sites, respectively.<sup>39</sup> The amounts of various acid sites are fitted for the quantitative analysis using Gaussian deconvolution (as shown in Table 4). The amounts of weak acid sites on the different samples follow the order ZSM-5-S > ZSM-5-H > ZSM-5-C, while the amounts of strong acid sites decrease in the order ZSM-5-S ≈ ZSM-5-C.

The type and concentration of Brønsted (B) and Lewis (L) acid sites for the various samples are determined by Py-IR as



Fig. 6 NH<sub>3</sub>-TPD spectra of various ZSM-5 zeolites.

 $+L)^{\alpha}$ 

Catalysis Science & Technology

Table 4 Acidity properties of various ZSM-5 zeolites measured by NH3-TPD and Py-IR									
Samples	Acidity <sup><i>a</i></sup> (µmol $g^{-1}$ )		Acidity/ $(\mu mol_{Py} g^{-1})^b$						
	Weak	Strong	Brønsted		Lewis		I./(P		
			200 °C	350 °C	200 °C	350 °C	(%)		
ZSM-5-S	105.8	164.6	124.5	112.2	8.0	8.0	6.3		
ZSM-5-H	91.1	163.6	155.4	119.4	7.1	5.5	4.4		
ZSM-5-C	82.0	128.2	77.5	70.9	8.1	6.9	9.2		

<sup>*a*</sup> The quantitative results of weak and strong acid sites determined by  $NH_3$ -TPD were measured by monitoring the desorbed ammonia at 195 and 370 °C, respectively. <sup>*b*</sup> The quantitative results of Brønsted and Lewis acid sites were calculated from the Py-IR spectra. <sup>*c*</sup> This ratio was calculated using the number of Lewis acid sites over the number of all acid sites determined from the Py-IR spectra.

shown in Fig. 7 and the quantitative results are summarized in Table 4. Apparently, all the samples exhibit small amounts of L acid sites, whereas the ZSM-5-H and ZSM-5-S zeolites have many more B acid sites than the ZSM-5-C sample. It should be noted that the L/(B + L) ratios over the different samples follow the order ZSM-5-H (4.4) < ZSM-5-S (6.3) <ZSM-5-C (9.2), regardless of the pyridine desorption temperature. This result is consistent with the content of exframework Al species in the different samples determined by <sup>27</sup>Al MAS NMR (as shown in Table 2), suggesting that the L acid sites might mainly originate from the ex-framework Al species. It is generally accepted that the B acid sites are derived from the framework aluminium.40,41 Therefore, the amounts of B acid sites over the different samples follow the order ZSM-5-H > ZSM-5-S > ZSM-5-C, showing a correlation with the contents of ex-framework and framework Al obtained from the <sup>27</sup>Al MAS NMR results, respectively. It is worth noting that a slight difference between the quantitative results of NH<sub>3</sub>-TPD and Py-IR for the ZSM-5-S and ZSM-5-H samples is observed. This phenomenon is probably due to the readsorption of ammonia<sup>42,43</sup> on the ZSM-5-S zeolite with layer accumulation and higher diffusion resistance compared to the ZSM-5-H zeolite with a more *b*-axis structure.

Table 3 indicates that the most of the  $Al_F$  atoms exist as the single Al type in the ZSM-5-H sample. Borade *et al.* reported that the percentage of strong acid sites increased with the increase of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.<sup>44</sup> The larger the distance between two Al atoms, the stronger the acidity strength of zeolite.<sup>45</sup> Thus, the ZSM-5-H sample shows a larger amount of strong B acid sites in comparison to other

 $(\mathbf{r}_{i}) = (\mathbf{r}_{i}) = (\mathbf{$ 

Fig. 7 Pyridine adsorbed FT-IR spectra of various ZSM-5 zeolites at 200  $^{\circ}\text{C}$  (a) and 350  $^{\circ}\text{C}$  (b).

zeolites due to it having the largest amount of single Al in the zeolite framework.

#### 3.4 Catalytic performance

To test the effect of the reaction temperature on the catalytic activity and product selectivity, the 1-octene aromatization performance was investigated at 340 °C, 360 °C and 380 °C, as shown in Fig. S1 in the ESI.† At different reaction temperatures, the conversion of the various catalysts is above 99%, suggesting that 1-octene can be totally converted. Apparently, the selectivity to total aromatics and BTEX (benzene, toluene, ethylbenzene, and xylene) increases with the increase of the reaction temperature. This result indicates that the increase of the reaction temperature in this range is beneficial for the formation of aromatics, due to the aromatization activity of olefins being favourable with high temperature. However, high temperature always leads to the cracking reaction, thus resulting in the decrease of  $C_9^+$ aromatics selectivity. The distribution of aromatics and cracked products over the different catalysts at a higher temperature (380 °C) is further classified and analysed to reveal the impact of Al distributions on the catalytic performance for 1-octene aromatization.

The catalytic performance and product distribution of the various ZSM-5 zeolites for 1-octene aromatization obtained with time-on-stream of 6.0 h at 380 °C are summarized in Fig. 8, and the detailed product selectivity is listed in Table S1 of the ESL† The conversions of the 1-octene feed over all the catalysts are almost 100%. Great differences in the product behavior are observed between these catalysts. Apparently, the selectivity to BTEX over the various catalysts follows the order ZSM-5-S (27.0%) > ZSM-5-C (21.2%) > ZSM-5-H (18.8%), and the total aromatics selectivity exhibits the same trend under the same reaction conditions. As for the heavy aromatics ( $C_{10}^+$ ), the highest selectivity is observed on the ZSM-5-C catalyst (13.0%), and the selectivities on the ZSM-5-S and ZSM-5-H catalysts are 10.7% and 8.7%, respectively.

It is widely accepted that the olefin aromatization has several reaction steps including olefin cracking, isomerization, oligomerization, cyclization and hydrogen transfer reactions,<sup>46</sup> in which almost all steps occur on the B acid sites. Thus, it can be inferred that the B acid sites



**Fig. 8** Catalytic performance and the detailed product distribution over the different ZSM-5 catalysts for 1-octene aromatization ( $C_i^{=}$  and  $C_i^{0}$  mean the alkene and alkane hydrocarbons with *i* carbon atoms, respectively; reaction conditions: time on stream = 6.0 h, pressure = 1.0 MPa, temperature = 380 °C, N<sub>2</sub>/1-octene = 300, LHSV = 2.0 h<sup>-1</sup>).

derived from the  $Al_F$  with different positions and proximities can significantly influence the aromatization performance. As listed above, the  $Al_F$  atoms in the ZSM-5-H catalyst are enriched in the intersections between the straight and sinusoidal channels as single Al atoms, while the Al pairs in the ZSM-5-C catalyst are concentrated in the channel intersections and those in the ZSM-5-S catalyst prefer to locate in the straight and sinusoidal channels.

Therefore, for the 1-octene aromatization reaction, the single Al species with corresponding strong acid sites in the ZSM-5-H catalyst are responsible for the highest selectivity to cracking products and the lowest aromatics selectivity, leading to more C<sub>4</sub> paraffins and C<sub>5</sub> hydrocarbons, suggesting that the independent Al atoms in the framework are probably not favorable to the aromatization. Furthermore, the ZSM-5-S and ZSM-5-C catalysts with more Al pairs exhibit higher aromatics selectivity because the Al pairs are more favourable for the hydrogen transfer reactions, thus leading to the formation of the aromatics.<sup>5</sup> Compared with the ZSM-5-C catalyst, the more B acid sites and the corresponding higher hydrogen transfer of the ZSM-5-S catalyst guarantee the easier aromatization to form BTEX. This result indicates the increasing occurrence of the oligomerization and hydrogen transfer reactions with higher concentration of acid sites, favoring the formation of aromatics. However, the difference in the distribution of Al pairs in the framework and the crystal sizes also results in different BTEX and total aromatics selectivities, especially for the  $C_{10}^{+}$  aromatics. The ZSM-5-C catalyst with a small crystal size exhibits the highest

selectivity to the heavy aromatics  $(C_{10}^{+})$  among all the catalysts probably due to its less diffusion resistance and more external acid sites, leading to the further transformation of the BTEX to form  $C_{10}^{+}$  aromatics. The higher concentrations of the Al pairs in the intersections of two types of 10-membered channels in the ZSM-5-C catalyst also provide a more suitable space with fewer space limitations for the formation of C110 aromatics mainly including 1,3,4,5-tetramethylbenzene and 1,2,4,5tetramethylbenzene as the biggest products, which can only be formed in the channel intersections of the ZSM-5 zeolite.47,48 However, the shape selectivity of the straight and sinusoidal channels of the ZSM-5 zeolite suppresses the formation and the diffusion of much bigger aromatics, which can only be formed on the acid sites at the external surface by isomerization and/or alkylation.49 Thus, the ZSM-5-S catalyst exhibits a lower selectivity to the C<sub>11</sub><sup>+</sup> aromatics mainly including dimethylindane and naphthalene with its derivatives than the ZSM-5-C catalyst, due to the larger amount of B acid sites of the ZSM-5-S sample as determined by NH<sub>3</sub>-TPD and Py-IR which may lead to the further cracking and dealkylation reaction.

In addition, the distribution of cracking products can reflect the structural features of these catalysts and the initial step of the 1-octene aromatization.<sup>50</sup> As shown in Fig. 8,  $C_3$  hydrocarbons (mainly  $C_3$  paraffins) are the primary small cracked molecule products, followed by the  $C_4$ ,  $C_5$ , and  $C_6$  components for the ZSM-5-S and ZSM-5-C catalysts. However, for the ZSM-5-H catalyst, the most abundant cracked product is  $C_4$  hydrocarbon followed by the  $C_3$ ,  $C_5$ , and  $C_6$  components, further suggesting the different cracking pathways among the various zeolites. It is important to mention that the  $C_3^-$  favors the formation of toluene precursors.<sup>51</sup> Therefore, compared to the ZSM-5-C catalyst, the ZSM-5-S catalyst shows less  $C_3$  and higher selectivity to  $C_9$  aromatics.

The TGA profiles of the spent ZSM-5 catalysts after 24 h on stream for 1-octene aromatization are shown in Fig. 9. The different temperatures of the sharp weight loss can reflect the crystal size of the spent ZSM-5 catalysts suggesting that the carbonaceous deposits can be burnt more easily in



Fig. 9 TGA profiles for the spent ZSM-5 catalysts after 1-octene aromatization for 24 h (reaction conditions: time on stream = 24 h, pressure = 1.0 MPa, temperature = 380 °C, N<sub>2</sub>/1-octene = 300, LHSV =  $2.0 \text{ h}^{-1}$ ).

the small crystals. Quantitative analysis by TGA indicates that the coke content of the spent catalysts increases in the order ZSM-5-S (10.8%) < ZSM-5-H (12.0%) < ZSM-5-C (13.2%), which is correlated with the Al<sub>F</sub> properties of the different ZSM-5 catalysts. It is clear that the largest amount of coke is formed during the 1-octene aromatization over the ZSM-5-C catalyst because Al<sub>F</sub> sites as Al pairs prefer to locate in the intersections providing a broad space for the formation of big aromatics which will eventually lead to coking. However, the formation of heavy aromatics is strongly suppressed on the Al<sub>F</sub> sites located in the 10-membered ring channels of the ZSM-5-S catalyst, leading to less carbonaceous deposits compared to the ZSM-5-C catalyst. As for the ZSM-5-H catalyst, single Al sites are responsible for the serious cracking reaction (as shown in Fig. 8), thus resulting in the formation of light products; on the other hand, the large amount of Al sites in the intersections (Table 2) is favorable for the formation of heavy products.

#### 3.5 Aromatization mechanism of 1-octene

The above catalytic results demonstrate that the ZSM-5 zeolites with various properties of Al positions and proximity exhibit similar 1-octene conversions and apparently different product selectivities. Moreover, the selectivity and product distribution are significantly related to the location of acid sites and the siting of  $Al_F$  as well as the type of Al species, because the reaction pathway and process for 1-octene aromatization are affected by the properties of the B acid sites. The enrichment of single  $Al_F$  atoms in the channel intersections of ZSM-5 probably leads to the cracking reaction rather than aromatization, while the Al pairs are more favourable for the formation of BTEX, whereas the Al pairs in the interconnection channels enhance the  $C_{10}^{++}$ aromatics selectivity by providing a more suitable environment. Combining the above results and literature data, a detailed mechanism of 1-octene aromatization over the ZSM-5 catalysts with different Al distributions is proposed. As shown in Fig. 10, 1-octene can directly cyclize and hydrogen transfer (route 1) over the ZSM-5 zeolite, leading to the formation of ethylbenzene. However, the



Fig. 10 Simplified reaction pathway for 1-octene aromatization over ZSM-5 zeolites with different Al positions (reaction conditions: pressure = 1.0 MPa, temperature = 380 °C, N<sub>2</sub>/1-octene = 300, LHSV = 2.0 h<sup>-1</sup>).

selectivity to ethylbenzene over various catalysts is very low (<2.0%), indicating that the direct cyclization and hydrogen transfer are probably not the main pathways for the formation of aromatics. Meanwhile, the low selectivity to isooctene also suggests that the route of 1-octene isomerization (route 2) is difficult to occur. Therefore, the cracking reaction of 1-octene is dominant via  $\beta$  cleavage to produce light products, which is a typical result.<sup>52,53</sup> As shown in Fig. 8, it can be inferred that the single Al sites of ZSM-5-H are probably more favourable to the formation of  $C_4^{=}$  and i- $C_4^{=}$ through route 4, whereas the Al pairs of the ZSM-5-S and ZSM-5-C catalysts are more favourable to the generation of i-C<sub>5</sub><sup>=</sup> and C<sub>3</sub><sup>=</sup>. The BTEX products are formed via oligopolymerization, cyclization and hydrogen transfer over the ZSM-5 catalysts by coupling different cracked products (route 5). In addition, the coupling reaction of the 1-octene and cracked products (routes 6 and 7) and the alkylation reactions (routes 8 and 9) are probably responsible for the formation of heavy aromatics  $(C_{10}^{+})$ .

Fig. 8 shows the high fraction of  $C_{10}^{+}$  aromatics in the total aromatics, and therefore the formation pathway of these products should also be well considered because the formation mechanism of the heavy aromatics is still unclear. Thus, a typical alkylation reaction by using a mixture of benzene and 1-octene as reactants was performed over the ZSM-5-S catalyst under the same conditions as the 1-octene aromatization. The detailed experimental process and catalytic performance are shown in the ESI.† The 1-octene conversion over the ZSM-5-S catalyst is above 99% consistent with the 1-octene aromatization reaction, while the benzene conversion is 47.5%. Apparently, compared to the product distribution of 1-octene aromatization, different product selectivities over the ZSM-5-S catalyst for the alkylation of benzene with 1-octene are observed in Table S2 of the ESI,† whereas more TEX (35.1%) and heavy aromatics (17.1%) are formed. The alkylation reaction catalysed by acidic zeolites is commonly considered via the carbonium ion mechanism.<sup>54</sup> Under these reaction conditions, 1-octene is firstly cracked to light olefins (Fig. 10, routes 3 and 4). Then, the formed light alkenes are protonated by the B acid sites to form the intermediates.55 The latter can be further converted following two major routes: they can be coupled with benzene to produce  $C_9^+$  aromatics through alkylation or they can react with another cracked olefins producing toluene which can undergo further oligomerization, cracking, isomerization and alkylation, giving olefins and other alkylbenzenes. This result further provides solid evidence that the C<sub>10</sub><sup>+</sup> aromatics in the 1-octene aromatization can be formed through two main routes including the alkylation of the formed benzene with light olefins and the aromatization reaction between the 1-octene and formed light olefins.

### 4. Conclusions

Converting the long chain olefins in light-hydrocarbon distillates from the Fischer–Tropsch synthesis over ZSM-5

zeolite catalysts can not only increase the octane number of gasoline but can also produce heavy aromatics to improve the diesel quality, while the key properties and catalytic are determined bv the coordination performance environments of Al species in ZSM-5 zeolites. In the present work, ZSM-5 zeolites with different Al positions and proximities were obtained by tuning the synthesis conditions. Their phase, morphology, textural properties, acidity, Al siting, and catalytic performance in 1-octene aromatization were well investigated. Although all zeolites exhibit high crystallinity, uniform morphology, and open textural properties, an obvious difference in the Al<sub>F</sub> position and proximity was found via 27Al MAS NMR and UV-vis-DRS of Co(II) ions, thus resulting in the different acidities as determined by NH<sub>3</sub>-TPD and Py-IR. As a result, the catalytic performance of the ZSM-5 catalyst in 1-octene aromatization is found to be strongly related to the Al<sub>F</sub> positions and proximity. The product selectivity demonstrated that the single Al atoms in the ZSM-5 framework are responsible for the highest activity in the cracking reaction, leading to the lowest aromatics selectivity. However, the Al pairs in the framework were more favorable to the formation of aromatics. In addition, from the distribution of the aromatics and cracked products, the Al pairs in the channel intersections of the ZSM-5 zeolite resulted in the enhancement of the selectivity to heavy aromatics due to the fewer space restrictions, while the Al pairs in the sinusoidal and straight channels with severe shape selectivity suppressed the generation of bigger aromatics. Nevertheless, the alkylation of benzene with 1-octene provided solid evidence that heavy aromatics can be formed through both the alkylation reaction and the aromatization reaction. This finding here provides useful perspectives on developing aromatization catalysts for olefin conversion and quality upgradation of Fischer-Tropsch synthesis products.

## Conflicts of interest

There are no conflicts to declare.

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