Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 125 (2007) 155–162
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Synthesis of ZSM-5 zeolite from expanded perlite and its catalytic performance in FCC gasoline aromatization

Ping Wang [a,b,c], Baojian Shen [a,b,c,*], Jinsen Gao [a,c,*]

[a] State Key Laboratory of Heavy Oil Processing, PR China
[b] The Key Laboratory of Catalysis of China National Petroleum Corporation (CNPC), PR China
[c] Faculty of Chemical Science and Engineering, China University of Petroleum, Beijing 102249, PR China

Abstract

A hydrothermal synthesis method for ZSM-5 preparation was investigated by using expanded perlite as the only alumina source. The effect of crystallization conditions on ZSM-5 zeolite formation, such as temperature, time, pH, chemical composition of the reaction mixture, were studied. The samples were characterized by XRD, IR, SEM, XRF and BET surface area measurements. The ZSM-5 zeolite from expanded perlite showed better catalytic activity for the FCC gasoline aromatization reaction compared to ZSM-5 prepared by the standard method.

Keywords: ZSM-5 zeolite; Expanded perlite; Synthesis; Aromatization

1. Introduction

China has the third largest in reserves of perlite in the world. Perlite is an acerbic, silicious, and volcanic glass lava containing crystal water, falling into the category of igneous rock. After calcination at high temperature, crystal water in the rocks evaporates, and the perlite may undergo a 15–20 times volume expansion with closed and open blowholes. The main component of expanded perlite is aluminosilicate.

The conversion of perlite to zeolitic materials under humid atmosphere and low to medium temperatures (75–250 °C) has been reported [1,2] and hence revealed a novel way to enhance the commercial value of the mineral. The attempts to prepare zeolites from perlite in laboratories have been successful leading to the formation of various types of zeolites, for example, epistilbite, gismondine, heulandite, tobermorite, zeolite-Pc, zeolite-V, phillipsite, sodalite octahydrate and faujasite [2–11]. There is no report on the synthesis of ZSM-5 from perlite.

ZSM-5 zeolite, which was developed in 1972 by Mobil, has a regular channel system, i.e. straight circular channels (5.4 Å × 5.6 Å) interconnecting with sinusoidal and elliptical channels (5.1 Å × 5.4 Å). ZSM-5 is typically produced via a hydrothermal synthesis from a mother liquid of alkaline silicate–aluminate using an organic cation as template. The properties that make ZSM-5 critical for industrial applications are its extremely high thermal and acid stability, high selectivity and high activity in certain catalytic conversions especially in the case of shape-selective catalysis. For example, it is widely used as a catalyst in the petrochemical industry for isomerization, alkylation and aromatization processes. This situation has created a huge demand for ZSM-5. Thus, research on the innovation of ZSM-5 preparation, to reduce cost and/or increase desired reactivity has received much attention.

This study is focused on the synthesis and characterization of ZSM-5 zeolite made from expanded perlite by using a hydrothermal preparation method. This is the first report to employ a cheap and widely available perlite as the only alumina source in the ZSM-5 synthesis. The catalytic activity of the ZSM-5 derived from perlite in FCC gasoline aromatization reaction, was also studied.

2. Experimental

2.1. Materials

The expanded perlite used in the present study was a commercially available product, and was sieved to <400 mesh

---

* Corresponding authors. Tel.: +86 10 89733369; fax: +86 10 89733369.
E-mail address: baojian@cup.edu.cn (B. Shen).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.03.010

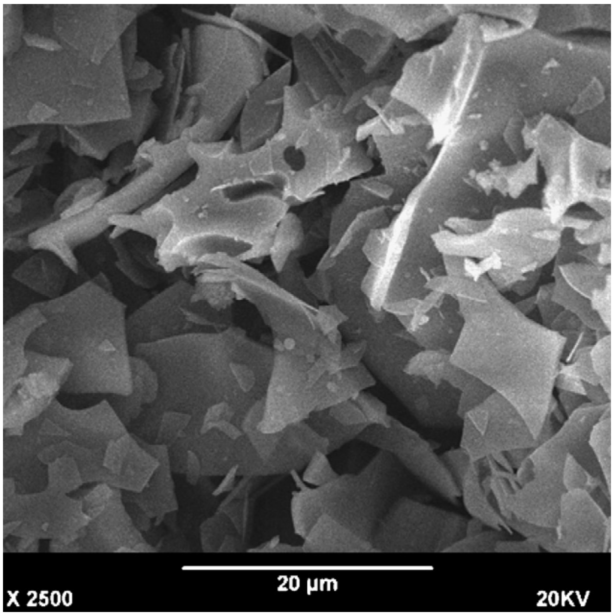

Fig. 1. SEM micrograph of expanded perlite.

before use. Fig. 1 shows the SEM micrograph of expanded perlite. The BET surface area of the expanded perlite was 5.86 $m^2 g^{-1}$ and its principal composition is SiO_2 69%, Al_2O_3 15% by weight. Sodium silicate was supplied by the Beijing Hongxing Sodium Silicate Company and its composition was SiO_2 20.9%, Na_2O 6.9% by weight. The seeding used was NaZSM-5 with relative crystallinity of 95%, and a SiO_2/Al_2O_3 ratio of 30.

2.2. Synthesis of ZSM-5 zeolite

In ZSM-5 zeolite synthesis, the expanded perlite was used as the only alumina source, sodium silicate was used as supplementary silica source, and H_2SO_4 or NaOH aqueous solution was employed to adjust the pH of the reaction mixture and the Na_2O/SiO_2 ratio. A small quantity of seeding NaZSM-5 zeolite was added into the reaction mixture with good mixing. The composition of the mother liquor was SiO_2/Al_2O_3 ratio 15–61, H_2O/SiO_2 ratio 20–34, Na_2O/SiO_2 ratio 0.18–0.26. Reaction temperature and time varied between 140 and 190 °C and 3–30 h. A series of experiments were performed in a 1 l teflon-lined stainless steel autoclave. After completion of the reaction, the synthesized product was cooled to room temperature, rinsed with distilled water, and dried at 120 °C.

2.3. Characterization

Synthesized ZSM-5 zeolite products were characterized by X-ray diffraction (XRD; Shimadzu 6000) using Cu Kα radiation operated at 40 kV and 30 mA with a 2θ scanning speed of 6 ° min^{-1}. Diffraction lines of 2θ between 5° and 50° were taken to confirm the phase of zeolite.

A NaZSM-5 zeolite sample which had very good crystallinity was used as the reference for crystallinity comparison. Herein, the degree of crystallinity of ZSM-5 zeolite was defined utilizing the main X-ray diffraction peak ($2\theta = 22.5–25.0°$) using the following equation:

$$\text{crystallinity}\ (\%) = \frac{\text{peak area of product}}{\text{peak area of reference sample}}$$

Fourier transform infrared (FT-IR) analysis of the products were performed with a MAGNA-IR 560 FT-IR instrument using KBr discs, in the range 400–4000 cm^{-1}. The powder morphology as well as the microstructure formed in the samples were determined by scanning electron microscope (Cambridge S-360). The porous properties were determined from N_2 gas adsorption and desorption isotherms measured at −196 °C using Quantachrome-autosorb-1 instrument. The surface areas were calculated using the conventional BET method. The ZSM-5 product was analyzed for Na_2O, SiO_2 and Al_2O_3 by XRF (ZSX-100e).

2.4. Catalyst preparation and catalytic activity evaluation

For sodium removal, NaZSM-5(P), which was synthesized by using expanded perlite, was treated with an aqueous solution of $(NH_4)_2SO_4$ at 90 °C for 2 h and then calcined at 540 °C for 3 h. The Na content of the product HZSM-5 was determined to be below 0.1 wt.% by XRF. The incipient wetness impregnation method was used to incorporate zinc into the HZSM-5, where the samples were impregnated with aqueous $Zn(NO_3)_2$ solutions, dried at 120 °C over night, and then calcined at 540 °C for 4 h in air. After this process, zinc salt can be converted to ZnO and the samples are denoted as Zn-ZSM-5(P). Two zeolites were prepared and denoted Zn-ZSM-5(P1), Zn-ZSM-5(P2), respectively, each with different crystallinity.

In order to investigate differences in the FCC gasoline aromatization activities of the ZSM-5 zeolite derived from expanded perlite and ordinary ZSM-5, the ordinary ZSM-5 ($SiO_2/Al_2O_3 = 30$, produced by seeding using sodium silicate as the silica source and $Al_2(SO_4)_3$ as the alumina source) were used to prepare Zn-ZSM-5 catalysts by the same procedure as Zn-ZSM-5(P).

The final catalyst sample composition was as follows: oven-dried slurry of 35 wt.% zeolite, 50 wt.% kaolin and 15 wt.% alumina binder. The catalysts were shaped by spray drying and then were further steam-deactivated (750 °C/6 h/100% steam) before use.

The FCC gasoline aromatization catalytic activity of the catalysts was measured at reaction temperature of 550 °C in a fluidized bed reactor. A feed rate of (weight hourly space velocity, WHSV) 8 h^{-1} and a catalyst/oil ratio of 7 were used.

The products obtained were analyzed as follows: hydrocarbon composition and octane number of liquid were analyzed by gas chromatography (SP-3420) and the components were identified in a PIONA-library and classified as paraffins, *i*-paraffins, olefins, naphthenes and aromatics. An HP6890 gas chromatograph with Chem Station software was used to measure the volume percentage of cracked gas components. (Here, two capillary columns, two packed columns and one porous polymeric column were used. A TCD was used to measure hydrogen, methane, carbon oxide and carbon dioxide at 250 °C, and a FID was utilized to measure other components in cracked gas at 250 °C.) The equation of state for ideal gases converts these data to mass percentage. The weight percentage of coke on catalyst was measured with a coke analyzer.

3. Results and discussion

3.1. Effect of reaction time on the synthesis of ZSM-5

ZSM-5 zeolites were prepared by varying the reaction time from 3 to 30 h with the composition of $13Na_2O{\cdot}Al_2O_3{\cdot}51SiO_2{\cdot}1592H_2O$ at 180 °C. The pH value of reaction mixture was adjusted to 10.25 and the seeds/SiO_2 ratio was set at 7%. The formation of NaZSM-5 and its degree of crystallinity are confirmed by comparing to the pattern of the reference NaZSM-5 sample.

Fig. 2 shows the relative crystallinity of samples at various reaction times. The crystallinity of ZSM-5 increased with time within the first 24 h. However, the crystallinity did not increase any more after 24 h crystallization. This phenomenon indicated that ZSM-5 zeolite was well formed in 24 h.

Fig. 3 presents FT-IR spectra of ZSM-5 zeolites formed with different crystallization times. For reaction times of 6 and 12 h, the absorption bands near 546 cm^{-1} appeared which indicate the formation of D_5R (double five ring) by tetrahedral SiO_4 and AlO_4 units [12]; however, bands near 1229 cm^{-1} which signify the formation of crystalline ZSM-5 are nearly nonexistent. Therefore, only partial formation of ZSM-5 zeolite crystals exists at this point. The IR spectra of products obtained after 18 h include not only the 1229 cm^{-1} band specifying the existence of pores with 3D channels, but also bands at 447, 546, and 798 cm^{-1} indicating the complete crystalline structure of ZSM-5 zeolites. This result is similar to synthesis of ZSM-5 from serpentine [13].

Fig. 4 shows the SEM micrographs of the products obtained at different crystallization times. At 3 h, there is no observation of the crystal of ZSM-5. Spherical and cubic shapes are simultaneously observed after 6 h, and increased amount of cubic forms of the ZSM-5 crystals appeared after 12 h of crystallization. After 24 h, well developed ZSM-5 crystals are distinctly observed.

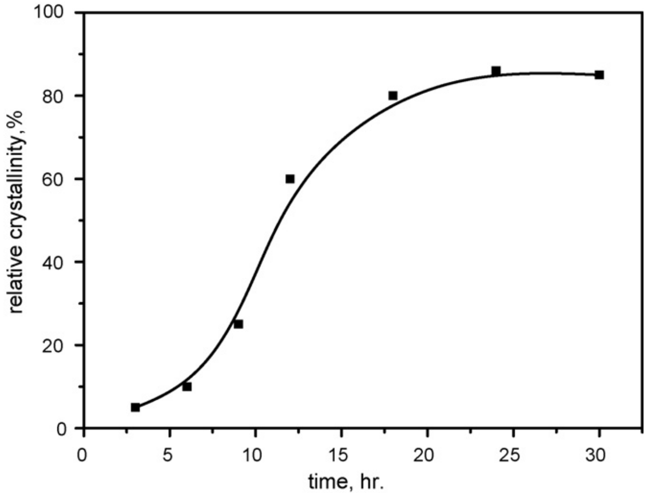

Fig. 2. The relative crystallinity of samples obtained at different reaction times.

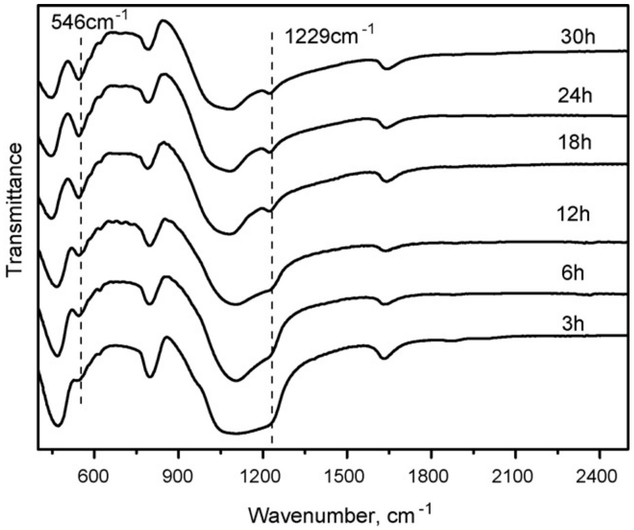

Fig. 3. FT-IR spectra of products obtained at different reaction times.

3.2. Effect of reaction temperature on the formation of ZSM-5

The effect of reaction temperature on the synthesis of ZSM-5 zeolites was studied in the range 140–190 °C at an interval of 10 °C, with a composition of $9Na_2O{\cdot}Al_2O_3{\cdot}38SiO_2{\cdot}1187H_2O$ and reaction time of 24 h. The pH values of reaction mixture were adjusted at 10.25 and a seeds/SiO_2 ratio of 7%. Fig. 5 shows the relative crystallinity of the synthesized ZSM-5 at different reaction temperatures. The maximum peak intensity is found at 180 °C, but it actually drops at 190 °C.

Fig. 6 displays FT-IR spectra of ZSM-5 zeolites prepared between 140 and 190 °C. The differences in the spectra are noticeable. The 447 and 798 cm^{-1} absorption band is observed at 140 °C and 150 °C, but the 546 and 1229 cm^{-1} bands are not seen. In other words, the zeolites prepared at 150 °C and lower, do not have a complete crystalline structure of ZSM-5. At temperatures of 160 °C and higher, the absorption bands characterizing the ZSM-5 zeolite (447, 546, 798, and 1229 cm^{-1}) appear. The absorption band near 1229 cm^{-1}, which reliably indicates the formation of ZSM-5 with 3D channel morphology, is most distinctive at 180 °C.

3.3. Effect of the reaction mixture pH value on the formation of ZSM-5

The effect of the reaction mixture pH value on the synthesis of ZSM-5 zeolites was studied in the range of 9.5–10.8 with a composition of $13Na_2O{\cdot}Al_2O_3{\cdot}51SiO_2{\cdot}1592H_2O$ at 180 °C. The reaction time was 24 h and the seeds/SiO_2 ratio was 7%. The effect of the reaction mixture pH value on the crystallinity is evidenced as shown in Fig. 7. The characteristic maximum peaks of the zeolites clearly appear at pH value 10.25.

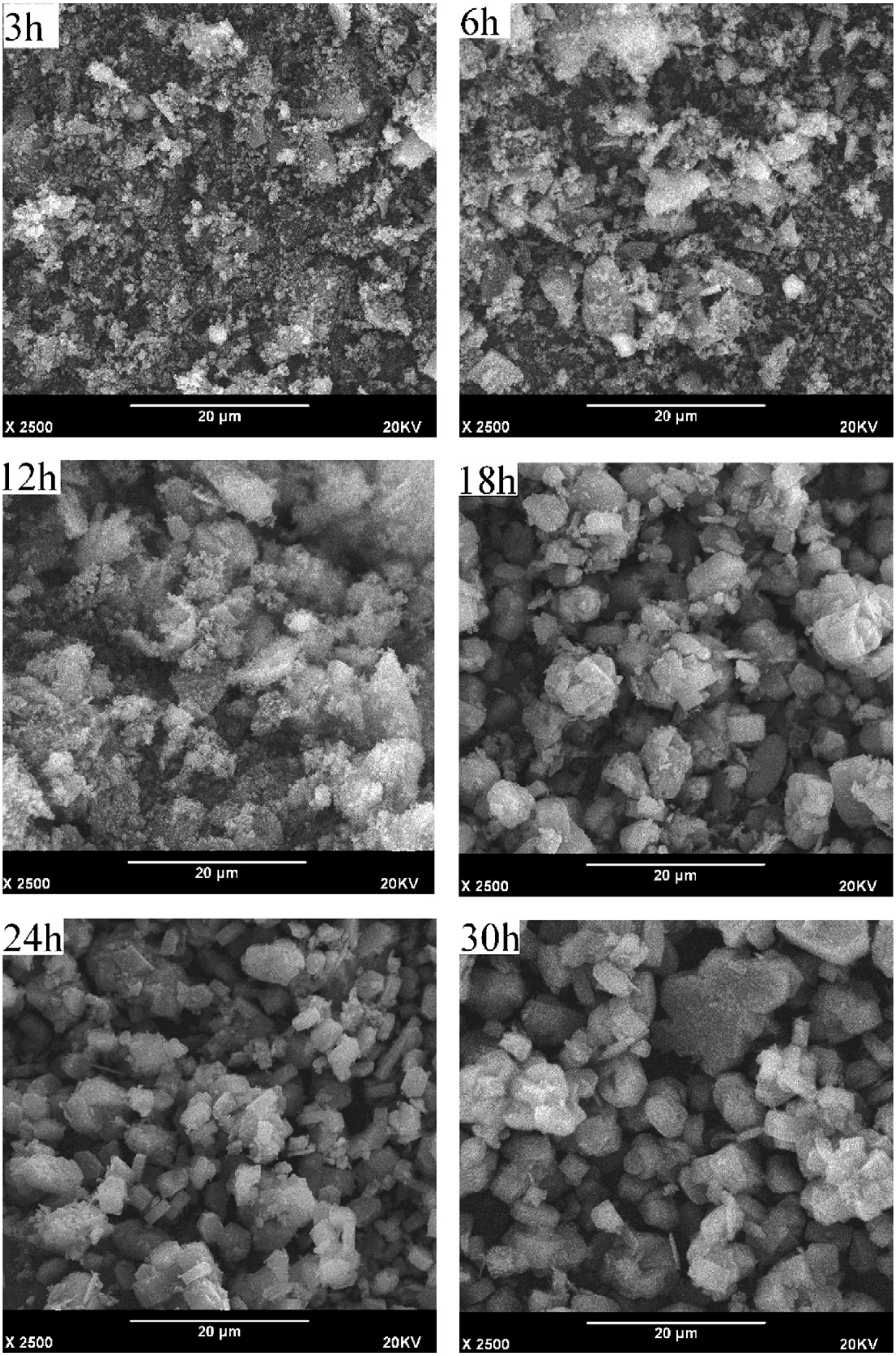

Fig. 4. SEM micrographs of products obtained at different reaction times.

3.4. Effect of composition on the formation of ZSM-5

The crystallinity of ZSM-5 zeolite has the same sensitivity to composition as to synthesizing conditions. The crystallization degree of ZSM-5 zeolite depends greatly on molar ratios such as SiO_2/Al_2O_3, Na_2O/SiO_2, H_2O/SiO_2 and the quality of seeds. In the present work, the physical characteristics of the synthesized zeolites were studied by varying the

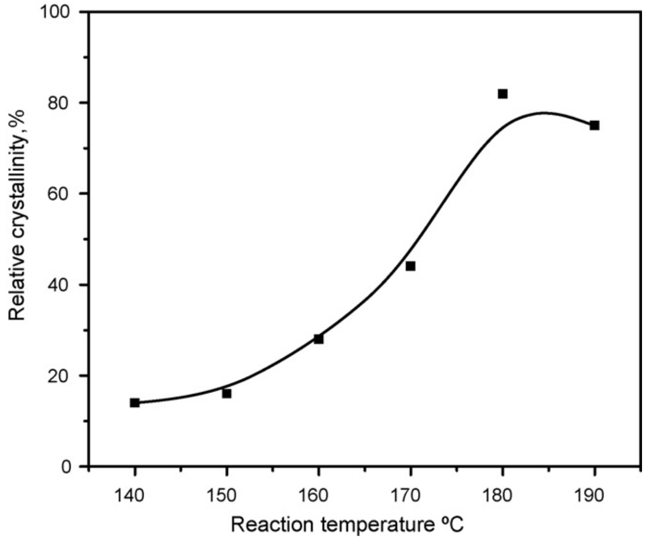

Fig. 5. The crystallinity of products obtained at different reaction temperature.

compositions of SiO_2/Al_2O_3, Na_2O/SiO_2, H_2O/SiO_2 and the quality of seeds.

3.4.1. *SiO_2/Al_2O_3 ratio*

The ZSM-5 zeolites were obtained with a composition of H_2O/SiO_2 ratio of 32 and Na_2O/SiO_2 ratio of 0.26 at 180 °C for 24 h. The SiO_2/Al_2O_3 ratio varied between 15 and 61 following the change of quantity of expanded perlite. The pH values of reaction mixture were adjusted to 10.5 and the seeds/SiO_2 ratio was 7%.

As shown in Fig. 8, the zeolites only have 33% crystallinity at SiO_2/Al_2O_3 molar ratios 15. The crystallinity increased along with SiO_2/Al_2O_3 molar ratio, however, after a 90% crystallinity was achieved at SiO_2/Al_2O_3 molar ratio 31, the crystallinity of the ZSM-5 decreased at higher SiO_2/Al_2O_3 molar ratios. Hence the SiO_2/Al_2O_3 molar ratio of 31 is the best in this composition range. The properties of ZSM-5 were presented in Table 1, and the products with high crystallinity also have a reasonable BET surface area and large pore volume.

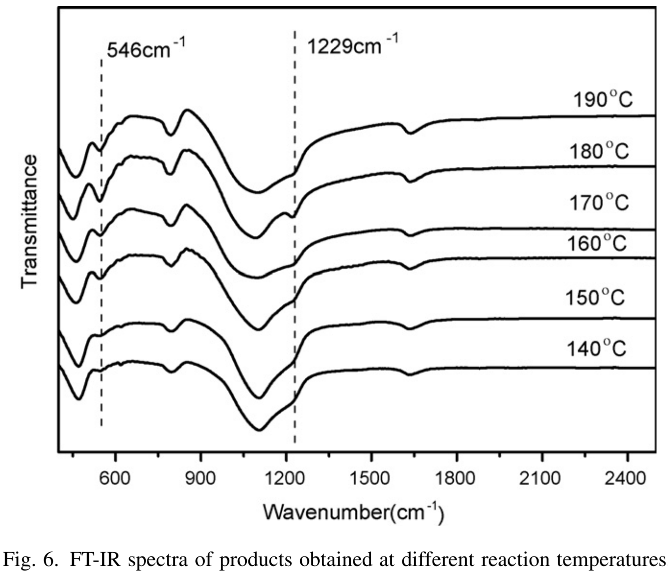

Fig. 6. FT-IR spectra of products obtained at different reaction temperatures.

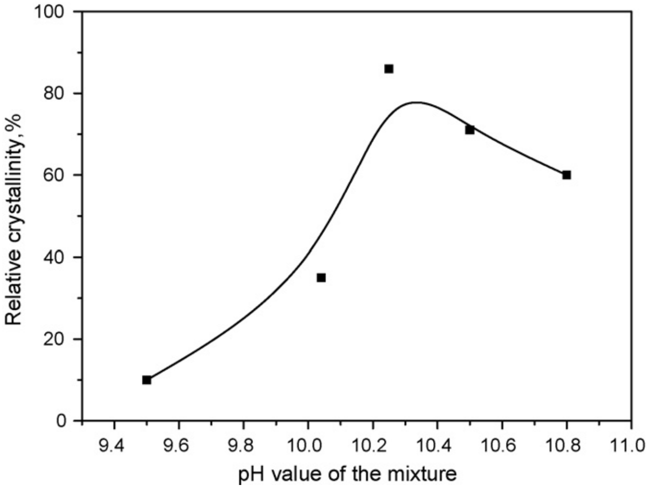

Fig. 7. The relative crystallinity of products at different pH value of the reaction mixture.

3.4.2. *Na_2O/SiO_2 ratio*

The ZSM-5 zeolites were obtained with a composition of H_2O/SiO_2 ratio of 31 and a SiO_2/Al_2O_3 ratio of 35 at 180 °C for 24 h. The Na_2O/SiO_2 ratio varied between 0.24 and 0.40 following the quantity of NaOH. The pH values of reaction mixture were adjusted to 10.5 and the seeds/SiO_2 ratio was 7%. Fig. 9 shows the zeolite were well developed at a Na_2O/SiO_2 ratio of about 0.26 in this composition.

3.4.3. *H_2O/SiO_2 ratio*

The ZSM-5 zeolites were obtained with a composition of SiO_2/Al_2O_3 ratio of 35 and Na_2O/SiO_2 ratio of 0.24 at 180 °C for 24 h. The H_2O/SiO_2 ratio varied between 21 and 35. The pH values of reaction mixture were adjusted to 10.22 and the seeds/SiO_2 ratio was 7%.

As shown in Fig. 10, the relative crystallinity of the product varied marginally from H_2O/SiO_2 ratio of 21–35. The sample in H_2O/SiO_2 ratio value 35 has maximum crystallinity.

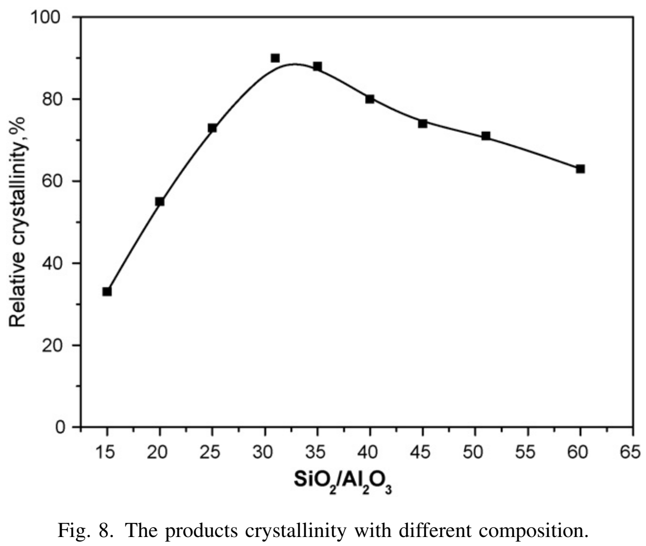

Fig. 8. The products crystallinity with different composition.

Table 1
Properties of the ZSM-5 and its synthesis composition

Composition in gel			Crystallinity (%)	ZSM-5 SiO_2/Al_2O_3 ratio[a]	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
SiO_2/Al_2O_3 ratio[b]	H_2O/SiO_2 ratio[b]	Na_2O/SiO_2 ratio[b]				
15	32	0.26	33	14	135	0.11
20	32	0.26	55	17	218	0.14
31	32	0.26	90	30	313	0.19
40	32	0.26	80	38	281	0.18

[a] Measured by XRF.

[b] Determined based on reactant stoichiometry.

3.4.4. The seed/SiO_2 ratio

The ZSM-5 zeolites were obtained with a composition of $13Na_2O\cdot Al_2O_3\cdot 51SiO_2\cdot 1592H_2O$ at 180 °C for 24 h. The pH of the reaction mixture was adjusted to 10.25 and the seeds/SiO_2 ratio varied between 1 and 9%. As shown in Fig. 11, adding the seeds were helpful for the synthesis of ZSM-5, and about 7% seeds/SiO_2 was optimum value in this test.

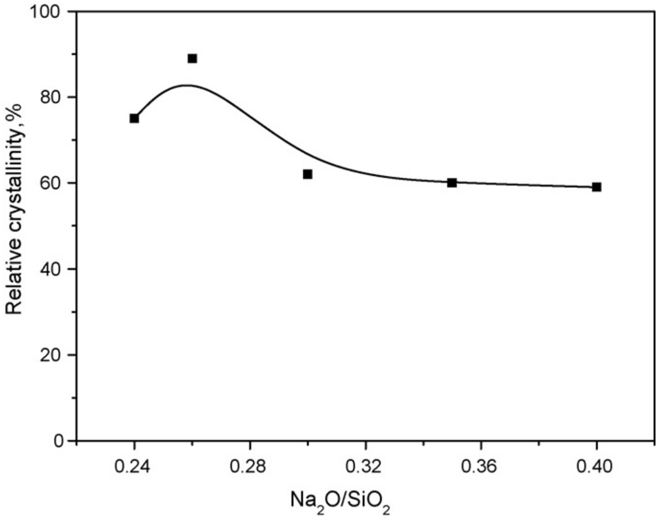

Fig. 9. The crystallinity of products obtained at different Na_2O/SiO_2 ratio.

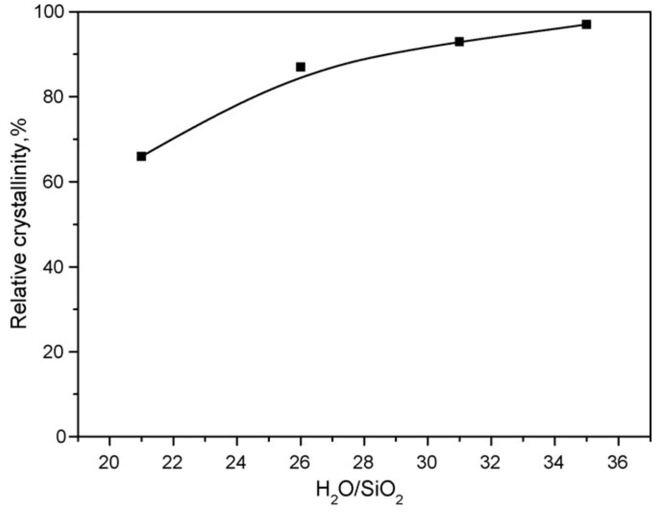

Fig. 10. The crystallinity of products obtained at different H_2O/SiO_2 ratio.

3.5. Character of modified zeolite and catalytic activity tests

The properties of four catalysts used for FCC gasoline aromatization were shown in Table 2. The XRD patterns (Fig. 12) show no crystal phase other than that for ZSM-5

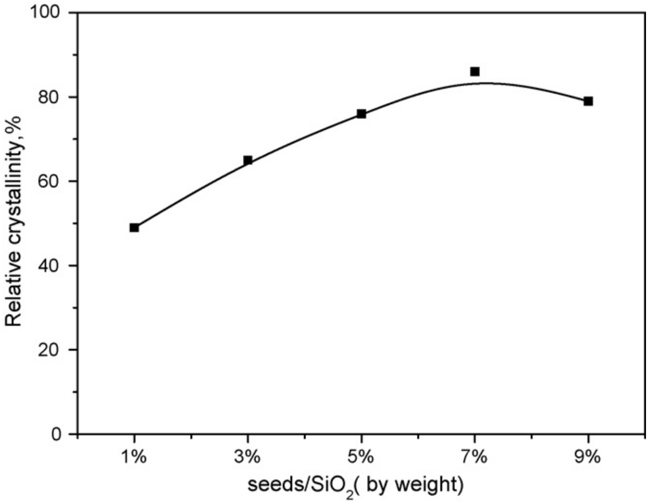

Fig. 11. The relative crystallinity of products obtained at different seed/SiO_2 ratio.

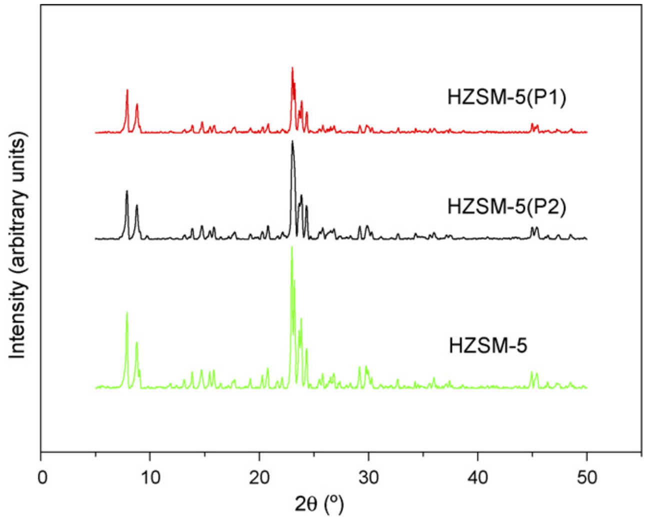

Fig. 12. XRD patterns of modified zeolites.

Table 2
The properties of modified zeolites

Samples	Crystallinity (% by XRD)	SiO_2/Al_2O_3 ratio by XRF	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	t-Method micro pore		BJH desorption cumulative data of pores	
					Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
HZSM-5	95	30	380	0.21	358	0.17	147	0.09
HZSM-5(P1)	52	30	195	0.29	127	0.06	95	0.23
HZSM-5(P2)	90	30	382	0.23	352	0.17	148	0.10

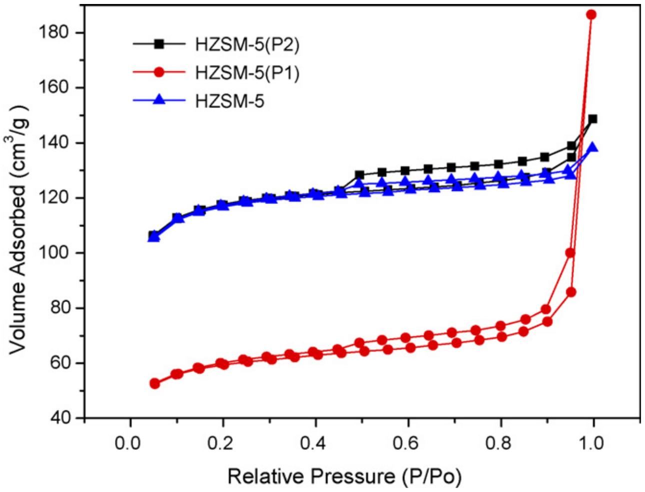

Fig. 13. Nitrogen adsorption–desorption isotherm of modified zeolites.

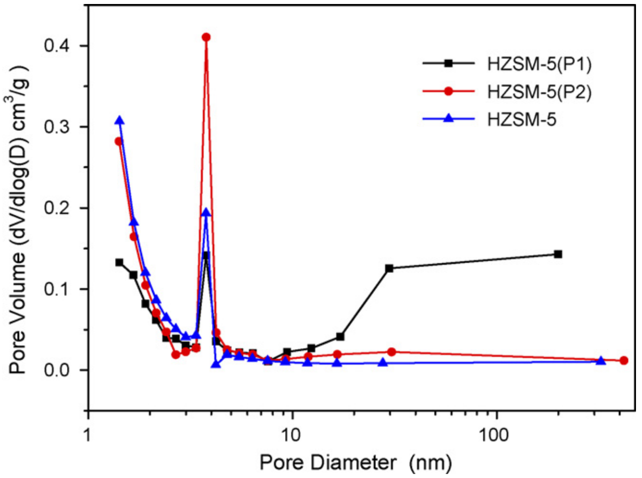

Fig. 14. BJH desorption pore distribution vs. pore diameter of modified zeolites.

appeared in the modified zeolites. Nitrogen adsorption-desorption isotherms and pore distribution curves of modified zeolites are shown in Figs. 13 and 14, respectively. The ZSM-5(P) from perlite, especially ZSM-5(P1), had a distinctive pore system with large pore volume and small crystal grain size.

The aromatic tests results (shown in Tables 3 and 4) indicated that olefins in the FCC gasoline can be transformed to aromatics to a different degree on the three catalysts. For example, the aromatics content in the liquid product obtained on the Zn-ZSM-5(P1) catalyst reached 34.89%, an increment of 13.94%, in comparison to that of the feedstock FCC gasoline. The aromatics content in the liquid product obtained on the corresponding Zn-ZSM-5 catalyst was 33.11%. The lower content of gasoline aromatic from Zn-ZSM-5 catalyst than that from Zn-ZSM-5(P1) and Zn-ZSM-5(P2) catalyst indicated that the Zn-ZSM-5(P1) and Zn-ZSM-5(P2) catalysts have better aromatization activity for FCC gasoline upgrading. The possible reasons of this phenomenon can be explained by the fact that ZSM-5(P) was crystallized in situ from expanded perlite, which provided a distinctive pore system: a combination of the medium pores of ZSM-5 and the large pores of perlite where ZSM-5 was located. The gasoline obtained from Zn-ZSM-5(P2) catalyst showed a higher RON (97) than that from Zn-ZSM-5(P1) catalyst and Zn-ZSM-5 catalyst, since it showed both higher content in aromatic and in olefin (Table 4).

Table 3
Yields of products on different catalysts in FCC gasoline aromatization (wt.%)

Catalysts	Zn-ZSM-5(P1)	Zn-ZSM-5(P2)	Zn-ZSM-5
Dry gas	1.95	3.14	3.40
Liquefied petroleum gas	19.74	25.49	25.48
Liquid	78.24	71.29	71.03
Coke	0.07	0.08	0.09

Reaction conditions: WHSV = 8 h^{-1}; 550 °C; catalyst/oil ratio = 7 (wt./wt.).

Table 4
Composition of products on different catalysts in FCC gasoline aromatization

	Catalysts		
	Zn-ZSM-5(P1)	Zn-ZSM-5(P2)	Zn-ZSM-5
Composition in liquefied petroleum gas (wt.%)			
C_3H_8	1.03	1.74	2.90
C_3H_6	61.91	61.79	60.01
i-C_4H_{10}	0.99	1.45	2.43
n-C_4H_{10}	0.42	0.66	1.01
trans-2-Butene	7.29	7.13	6.54
n-Butene	6.13	5.94	5.82
i-Butene	17.10	16.30	16.65
cis-2-Butene	5.13	4.99	4.64

	Feedstock	Catalysts		
		Zn-ZSM-5(P1)	Zn-ZSM-5(P2)	Zn-ZSM-5
Group composition in liquid product (vol.%)				
n-Paraffin	7.48	16.23	8.59	8.06
i-Paraffin	15.58	13.28	14.90	20.12
Olefin	48.33	30.37	39.60	31.86
Naphthene	7.66	5.23	2.40	6.85
Aromatics	20.95	34.89	34.51	33.11
Calculated RON	90	94	97	94

Reaction conditions: WHSV = 8 h^{-1}; 550 °C; catalyst/oil ratio = 7 (wt./wt.).

4. Conclusions

A practical hydrothermal synthesis method for the preparation of well-crystallized ZSM-5 zeolite was successfully developed by using expanded perlite as the only alumina source. It was found that chemical reaction conditions (temperature, time, pH, chemical composition of the reaction mixture) were prominent factors in the synthesis of the ZSM-5. As for the distinctive pore system of ZSM-5(P), which was a combination of medium pore ZSM-5 and large pore perlite, Zn-ZSM-5(P) catalyst was a potentially good catalyst for FCC gasoline aromatization.

Acknowledgments

The authors gratefully acknowledge the funding of this project by PetroChina, MOST "973" Project of China (2004CB217806) and NSFC (ID 20276039).

References

[1] J.W. Noh, J.R. Boles, Clay Clay Miner. 37 (1989) 47.
[2] S. Khodabandeh, M.E. Davis, Micro. Mater. 9 (1997) 161.
[3] N. Moreno, X. Querol, C. Ayora, C. Fernandez-Pereira, M. Jansses-Jurkovicova, Environ. Sci. Technol. 35 (2001) 3526.
[4] H. Chang, W. Shih, Ind. Eng. Chem. Res. 37 (1998) 71.
[5] V. Berkgaut, A. Singer, Appl. Clay Sci. 10 (1996) 369.
[6] W.P. Ma, P.W. Brown, S. Komarneni, J. Mater. Res. 13 (1998) 3.
[7] H. Chang, W. Shih, Ind. Eng. Chem. Res. 39 (2000) 4185.
[8] W. Shih, H. Chang, J. Mater. Lett. 28 (1996) 263.
[9] A. Srinivasan, M.W. Grutzeck, Environ. Sci. Technol. 3 (1999) 1464.
[10] G.E. Christidis, I. Paspaliaris, I. Kontopoulos, Appl. Clay Sci. 15 (1999) 305.
[11] A. Rujiwatra, Mater. Lett. 58 (2004) 2012.
[12] W.B. Fan, R.F. Li, J.H. Ma, B.B. Fan, J.H. Cao, Micro. Mater. 4 (1995) 301.
[13] D.J. Kim, H.S. Chung, Appl. Clay Sci. 24 (2003) 69.