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Steaming and washing effect of P/HZSM-5 in catalytic cracking of naphtha

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ABSTRACT

The influences of steaming or washing treatment on P-modified HZSM-5 catalyst were investigated systematically in order for getting deep insight into the role of P species in catalytic cracking. The impregnation of P leads to better hydrothermal stability and higher yields of light olefin (ethylene and propylene), but brings rapid decrease of acidity. During steaming, the impregnated P species become more condensed phase and the acidity and catalytic activity decreased further. However, the acidity and catalytic cracking activity recovered just by washing with water even for steamed samples, suggesting that the existence of condensed P species blocks the pores of zeolite reversibly and are responsible for the decrease of cracking activity of naphtha.

1. Introduction

ZSM-5 is one of the most efficient hydrocarbon cracking catalysts for the selective production of light olefins such as ethylene and propylene. To enhance light olefins selectivity and reduce coke formation, certain amount of steam has to be added together with hydrocarbon feedstock. Therefore, higher hydrothermal stability of ZSM-5 is required. Phosphorus has been known to be the most effective modifier to increase hydrothermal stability of ZSM-5 and has been interested in the past two decades [1]. Even though the phosphorus increases the cracking activity and selectivity of light olefins due to the prevention of dealumination from zeolite framework during steaming, it brings several negative effects: (a) reversible decrease in acidity and catalytic activity, (b) decrease in the micropore volume and partial blockage of the pore channel.

A lot of researches concerned about the modification of ZSM-5 with different P species and different loadings, and tried to interpret the interactions between P species and HZSM-5 using various experimental methods including XRD, FTIR, MAS NMR, and NH_3 TPD [1–11]. Different models have been proposed to show the interactions of phosphorus with zeolite Brönsted acid sites but some controversy still exists, as summarized by Ding et al. [2]. Therefore, the further details about the interaction of P and HZSM-5 and the nature of the acid sites induced by P are worthy of clarification.

According to Lischke et al. [3], Brönsted acid site can be restored reversibly by the elution of the orthophosphoric acid with water (80 °C). However, after calcining or steaming, irreversible decrease of Brönsted acidity occurs, which is caused by the reaction of P species with Brönsted acid sites of ZSM-5. Corma et al. [4] have reported the acidity of steamed P/HZSM-5 was partially restored by washing with NH_4Cl and NH_4F solution and the cracking activity of n-decane increased sharply. This result suggests that the P species interacted with Brönsted acid site and neutralized the acidity in a reversible way. However, it is not well described that what kind of particular P species is closely related to the catalytic activity.

In the present work, systematic studies were carried out to verify the behavior of P species during steaming or washing by water. That is, prepared P/HZSM-5 was sequentially treated with steaming and washing, and then their catalytic performances were evaluated in naphtha cracking. ^{27}Al- and ^{31}P-MAS NMR were performed in order to identify the formed Al and P species and their roles in the cracking.

2. Experimental

2.1. Catalyst preparation

The parent zeolite, HZSM-5 (Si/Al = 14.5), was obtained from Albemarle (named as Z). P-modified H-ZSM-5 catalysts were pre-

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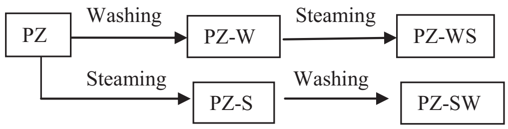

Fig. 1. Preparation of two series of P/HZSM-5 samples.

pared by impregnation method. H_3PO_4 solution corresponding to 3.2 wt% P based on H-ZSM-5 were prepared and impregnated on HZSM-5, dried overnight at 100 °C and then calcined at 650 °C for 6 h (named as PZ). For the prepared PZ, a series of steaming and water washing were carried out for sample PZ according to the procedure described in Fig. 1. Steaming (named as S) was carried out at 760 °C in 100% steam flow for 24 h, and then it was cooled down to room temperature with dry air. Washing with water (named as W) were carried out as follows: 300 g water was mixed with 10 g PZ series sample, and stirred overnight, then separated P/HZSM-5 catalyst sample by filtration, then rinsed it with 300 g H_2O, then finally dried overnight at 100 °C. In order to understand the effect of steaming and washing, two series of samples were prepared (see Fig. 1).

2.2. *Characterization of P/HZSM-5*

NH_3-TPD experiments were conducted on AutoChem II 2920 instrument. 100 mg of a dried sample was placed in a quartz sample tube supported with quartz wool. The sample was pretreated in He flow at 200 °C for 2 h. Then, the temperature was decreased to 100 °C and treated with anhydrous NH_3. The sample was flushed with 50 mL/min He for 100 min and then NH_3-TPD was carried out from 100 to 800 °C.

The ^{27}Al MAS NMR spectra were obtained on a Bruker AVANCE 500 spectrometer at a ^{27}Al frequency 130.325 MHz in 4 mm rotors at a spinning rate 12.0 kHz. The spectra were obtained with an acquisition of ca. 3000 pulse transient, which were reported with a $\pi/4$ rad pulse length of 5.00 μs and a recycle delay of 1.0 s. The ^{27}Al chemical shifts were referenced to $Al(H_2O)_6^{3+}$ solution. The ^{31}P MAS NMR spectra at a spinning rate of 11.0 kHz were recorded on the same spectrometer at a ^{31}P frequency of 202.450 MHz. The spectra were obtained with an acquisition of about 100 pulse transients, which were repeated with a $\pi/2$ rad pulse length of 5.0 μs and a recycle delay of 30 s. The ^{31}P chemical shifts were referenced to H_3PO_4 solution.

2.3. *Reaction conditions*

Naphtha cracking reactions were performed at 720 °C and WHSV = 64 h^{-1} in micro-activity test unit, which was based on ASTM D-3907. As a feed, a heavy naphtha containing 22.0 wt% n-paraffins, 33.2 wt% i-paraffins, 19.8 wt% naphthenes, 11.5 wt% olefins, and 13.6 wt% aromatics and average molecular weight of about 106 g/mol was used.

3. Results and discussion

3.1. *Catalyst characterization*

3.1.1. *Pore analysis*

Textural properties including surface area, pore volume, micropore volume, micropore area, external surface area, and pore size for prepared samples are presented in Table 1. The adsorption isotherms of all samples (not shown here) were typically type I. The steaming treatment of parent zeolite HZSM-5 resulted in a decrease of both micropore volumes and surface areas, however, an increase of pore size, total pore volume and external surface area. This is mainly caused by dealumination from the zeolite framework and partial damages in pore structure. BET surface area (m^2/g), pore volume (cm^3/g) and pore size (Å) of H-ZSM-5 decreased after P modification, suggesting the formation of polymeric phosphates species, which located inside and blocks the zeolite channel. A new large pore at around 7.5–7.9 Å generated after steaming, probably due to the dealumination. The subsequent washing treatment of the steamed sample lead to an increase of the pore size newly formed. This may be caused by the removal of soluble P species which is formed by hydrolysis of condensed P species.

3.1.2. *NH_3-TPD*

Parent HZSM-5 (sample Z) has two desorption peaks at 312 and 490 °C corresponding to weak and strong acid sites, respectively. If the parent HZSM-5 was steamed at 760 °C for 24 h almost all of the acid sites were destroyed and only weak desorption peak at 219 °C was found (Fig. 2(A)). The impregnation of P also led to a sharp decrease in acidity, and two peaks at 200 and 387 °C was observed, suggesting that the strong acid sites, i.e., the Brönsted acid sites of zeolite, disappear completely by P modification and a new peak with medium acid strength contributed by the P–OH group appears. If the P/HZSM-5 was steamed further decrease of acidity was observed (Fig. 2(B), PZ-S). However, after removing soluble P species by washing, some of the acid sites were recovered together with generation of a new acid site at 564 °C stronger than the original Brönsted acid of HZSM-5 (PZ-SW). This result suggests that some of acid sites are preserved by the impregnation of P even though the quantity is quite low compared with pure HZSM-5.

3.1.3. *Solid-state MAS NMR*

Fig. 3 shows ^{27}Al MAS NMR spectra of P-free and P-modified H-ZSM-5 catalysts and ^{31}P MAS NMR spectra of P modified catalysts. The ^{27}Al MAS NMR of the H-ZSM-5 sample shows two peaks at 53 ppm and at −1.5 ppm. The peak at 53 ppm is attributed to tetrahedrally coordinated Al in zeolite framework, while the peak at −1.5 ppm to octahedrally coordinated extra framework Al species

Table 1
Textual properties of P-free and P-modified HZSM-5 catalysts.

Sample	Sample treatment	Surface area (m^2/g)	Micropore area (m^2/g)	External surface areas (m^2/g)	Pore volume (cm^3/g)		Pore size distribution (Å)
					Micropore (*t*-plot)	Total (P/P_0 = 0.995)	
Z	Parent HZSM-5	447	432	15.3	0.153	0.17	5.4
ZS	Sample Z steamed at 760 °C, 24 h	408	379	29.1	0.135	0.18	5.6
PZ	P/ZSM-5 calcined at 650 °C, 6 h	271	268	3.36	0.095	0.12	5.1
PZ-W	Sample PZ washed with water	307	299	7.53	0.109	0.12	5.1
PZ-WS	Sample PZ-W steamed at 760 °C, 24 h	383	379	4.70	0.133	0.15	5.1, 7.5
PZ-S	Sample PZ steamed at 760 °C, 24 h	357	357	0.05	0.125	0.13	5.1, 7.5
PZ-SW	Sample PZ-S washed with water	345	338.7	6.24	0.120	0.13	5.1, 7.9

Surface area and pore volume were derived from BET and BJH methods. Micropore volume, micropore area, and external surface areas were derived from the *t* method. Pore size distribution was derived from the Horvath–Kawazoe method.

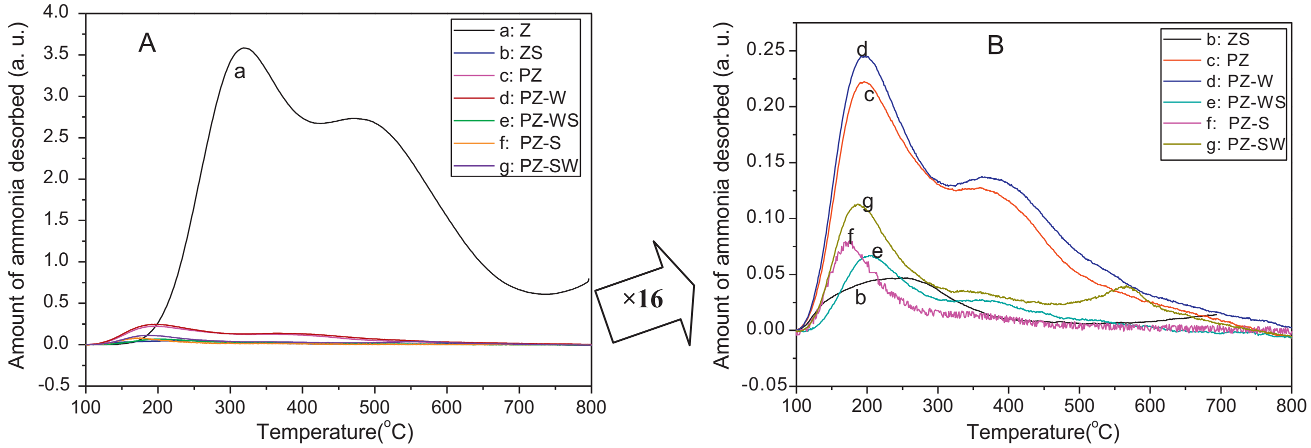

Fig. 2. NH_3-TPD of all P-free and P-modified HZSM-5 catalysts (A); enlarged NH_3-TPD of P-modified and steamed P-free HZSM-5catalyst.

(Fig. 3(A)). If it was steamed (ZS), the peak at 53 ppm deceased due to the dealumination, and a broad peak at ca. 36 ppm attributed to tetrahedral aluminum in a distorted environment at either framework or non-framework positions appeared. If the HZSM-5 was modified with P (PZ), the peak intensity of tetrahedral Al at 55 ppm decreased and the peak at −1.5 ppm disappeared completely, while a new peak at −11 ppm assigned to octahedral Al species attached to phosphorus appeared. This suggests that both the octahedral and some of tetrahedral Al species interact with orthophosphoric acid during calcination and $AlPO_4$ is formed. However, if the P modified HZSM-5 is steamed quite different species were observed. A new peak at 40 ppm attributed to distort tetrahedral Al in the framework or extra framework, or pentacoordinated Al species was observed over the all of the PZ series samples treated with steam [1,6,12]. No obvious changes in Al environment were observed for the calcined P/HZSM-5 after washing (PZ-W vs. PZ), while the peak at 53 ppm partially reappears for the steamed PZ samples after washing (PZ-S vs. PZ-SW). However, it is difficult to conclude that the appearance of strongest acid site at ca. 550 °C in NH_3-TPD for the steamed P/ZSM-5 after washing is due to this recovered tetrahedral framework Al.

Different from ^{27}Al NMR, more detail information could be derived from ^{31}P NMR depending on the steaming and washing (Fig. 3(B)). Many kinds of peaks at 0.9, −6, −16, −25, −32, and −39 ppm were observed from the calcined samples regardless of washing (PZ and PZ-W). However, from the steamed samples different peaks observed; peaks at −6, −32, −39 and −46 ppm from PZ-S and PZ-WS and only peaks at −32 and −39 ppm from PZ-SW. One important finding for the samples after steaming is that the peaks above −16 ppm disappears and the peaks in the region of −32 to −46 ppm assigned to poly phosphates become dominant, clearly indicating that P species become more condensed phase after steaming. The phosphorus species having chemical shift of −46 ppm, known for branching groups of P in the compound like P_4O_{10}, were formed during steaming and removed by washing. This suggests that the branched polyphosphate species is more easily formed during steaming and would undergo hydrolysis reaction quickly after washing. The signal at ca. −32 ppm, assigned to amorphous aluminum phosphate [13], were found in all the samples regardless steaming and washing, which means that the dealumination of framework Al and the formation of insoluble aluminum phosphate occur simultaneously just by calcining. The signal at −39 ppm, assigned to highly condensed polyphosphate or polyphosphoric species [4,7], decreased partially after washing (PZ-S to PZ-SW), which suggests that the polyphosphate formed during steaming becomes soluble by hydrolysis under acidic environment and then removed by the subsequent rinsing procedure. According to the result of Corma et al. [4], the optimum loading of P in HZSM-5 is around 0.6–0.7 P/$Al_{framework}$. Because the P/HZSM-5 prepared in this study contains excess P loading (1.0 P/$Al_{framework}$), the peak at −6 ppm, assigned to pyrophosphoric acid species or the terminal phosphorus atoms not attached to Al, was found in the calcined sample (PZ) due to the excess P loading. These species are quite soluble and could be removed by washing (PZ-W) and the peak intensity decreased obviously after washing. According to the work of Munson [14], the ion concentrations of $H_4PO_4^+$, $H_2PO_4^-$, and $H_2P_2O_7^{2-}$ are 5.4%, 0.26, 0.28 in the 100% H_3PO_4 solution, respectively. So the pyrophosphoric acid will be the most abundant soluble P species presented in the calcined sample (PZ). Quite small peaks at −16 and −25 ppm assigned to the middle phosphorus atoms in polyphosphates or some specially polymerized short-chain polyphosphates attached or not to Al [4] were formed after calcining but disappeared after steaming (PZ-W).

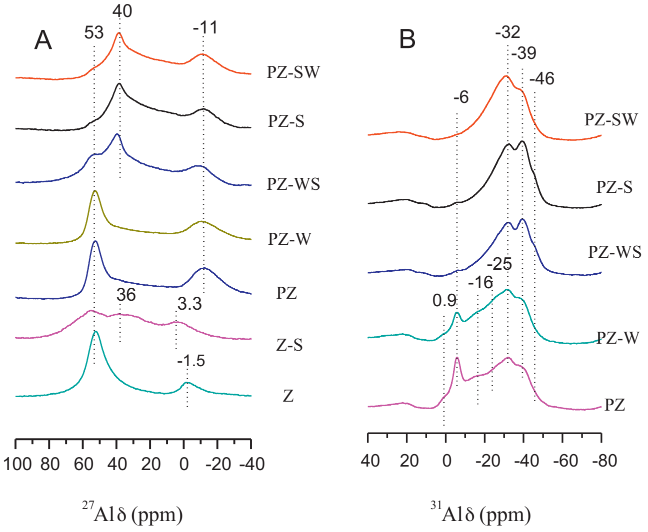

Fig. 3. (A) ^{27}Al MAS NMR spectra and (B) ^{31}P MAS NMR spectra of P-free and P-modified HZSM-5 catalysts.

Acidity of catalyst is closely related to the cracking activity. According to the result of NH_3-TPD, the strong acid site at 564 °C in NH_3-TPD profile appears for the steamed PZ samples after washing (PZ-SW). Even though data is not given, if secondary steaming is done for this washed PZ-SW sample, this strong acid site disappears (PZ-SWS) and reappears after washing (PZ-SWSW). Therefore, it can be concluded that this strong acid site is responsible for high cracking activity of washed samples. However, with the result of

Table 2
Yields of main products in naphtha cracking over P-free and P-modified HZSM-5 catalysts (wt%).

Catalyst	Z	ZS	PZ	PZ-W	PZ-WS	PZ-S	PZ-SW
CH_4	12.2	5.15	7.56	7.80	6.32	5.21	8.61
C_2H_6 and C_3H_8	13.2	3.57	7.23	10.4	5.77	3.98	10.6
C_4	6.69	8.51	9.25	10.0	8.86	8.20	8.37
C_5^+	15.0	26.9	21.7	20.1	23.6	23.9	20.7
Benzene	4.38	0.95	1.26	2.02	1.12	0.81	1.57
C_2H_4 and C_3H_6	27.2	17.6	29.2	32.0	26.7	20.5	29.0

^{27}Al and ^{31}P MAS NMR, it is difficult to explain why this kind of strong acid site is generated after washing. To prove this, further work is required.

3.2. Catalytic activity

Table 2 presents the yield distributions of main products in naphtha cracking depending on the catalyst treatments. The yield of light olefins (C_2H_4 and C_3H_6) of parent HZSM-5 (sample Z) having highest acidity is lower than that P modified HZSM-5 (27.2 wt% vs. 29.2 wt%). It is due to the over cracking of produced light olefins to saturated hydrocarbons such as methane, ethane and propane and the secondary reaction of aromatization to BTX (benzene, toluene and xylene). If the unmodified HZSM-5 was steamed, the cracking activity decreased sharply and only 17.6 wt% olefin yield was obtained (ZS). Different from pure HZSM-5, all the series of P modified HZSM-5s revealed higher olefin yields even after steaming, which clearly suggesting the enhancement of hydrothermal stability by the introduction of P. However, further decreased cracking activity was obtained after high temperature steaming and which can be contributed to the loss of acidity and the formation of condensed P species blocking the pore channels of zeolite (PZ vs. PZS and PZ-W vs. PZ-WS). Another important finding is that increased cracking activities were obtained after washing with water even for steamed PZ samples (PZ vs. PZ-W, PZ-S vs. PZ-SW). This can be explained by the reversible blocking of acid site by phosphorous. Because steaming condition is more severe than calcination, more condensed P species are formed during steaming than calcining and lower cracking activities are observed over the steamed samples. However, theses condensed P species could be removed by washing and cracking activity is recovered. The effect of washing is more pronounced on the steam-deactivated P/HZSM-5 and an increase of 8.5 wt% in olefin yield was obtained (PZ-S to PZ-SW). This can be explained by the unique properties of P species, i.e., the hydrolysis and condensation reactions of orthophosphoric acid can occur simultaneously under steaming. It is a clear evidence that the hydrolysis reaction of condensed P species in sample PZ-S would be dominant during washing towards the redistribution of P species and some of soluble P species formed by hydrolysis are removed by rinsing procedure and some new stronger acid sites recovered. From these results, it could be suggested that the hydrolysis of P species is important for removing condensed P species and recovering acidity of P/HZSM-5 samples.

4. Conclusions

The introduction of phosphorous in HZSM-5 will cause a sharp decrease in acidity but brings good hydrothermal stability. During calcination some of the Brönsted acid sites were neutralized by attaching P species and subsequent hydrothermal treatment of P/HZSM-5 converted the P species to more condensed phase which block pores of zeolite reversibly. When washing, the condensed P species formed by steaming transformed to less condensed P species by hydrolysis. Some of them become soluble and can be removed; new stronger acid sites appear which further lead to the increase of acidity and catalytic cracking activity. The condensed P species on HZSM-5 are responsible for the decrease of cracking activity, and the cracking activity could be recovered by hydrolysis of the condensed P species when washing.

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