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The effect of pre-coking and regeneration on the activity and stability of Zn/ZSM-5 in aromatization of 2-methyl-2-butene

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ABSTRACT

A new method to modify the acidity of zeolite was attempted to improve the activity and stability of Zn/ZSM-5 in aromatization of 2-methyl-2-butene. Pre-coking and regeneration in the presence of O_2 at 773 K generated a large exothermic heat in a short time, which resulted in the thermal dealumination of framework aluminum that acted as a Brønsted acid site. The treatment had a profound effect on the acid properties of the catalyst as probed by ^{27}Al MAS NMR, temperature-programmed desorption of ammonia, and pyridine FTIR. The results showed that the concentration of oxygen in regeneration step had critical effects on the acidity and stability of Zn/ZSM-5. Thus improvement of lifetime of Zn/ZSM-5 in aromatization of 2-methyl-2-butene was achieved without deteriorating activity and selectivity by the pre-coking and controlled regeneration by oxygen.

1. Introduction

In the era of high gasoline prices, the importance of fluid catalytic cracking (FCC) process that produces gasoline from vacuum gas oil and vacuum residue has increased last several decades. Accordingly, the generation of by-products which contain a large amount of olefins has also increased. Although olefins could be easily converted to paraffins by hydrogenation process, an excessive amount of hydrogen is consumed and the demand for the produced paraffins is limited. In addition, tightening regulations on olefin contents in reformulated gasoline in the near future requires new solutions. Aromatization could be one of the most effective and economical solutions to upgrade the low-value by-products obtained from FCC to higher value chemicals. Aromatization of propane has been already investigated for several decades and Zn/ZSM-5 has been found to be one of the most effective catalysts [1]. In aromatization of paraffins including propane, the rate determining step is dehydrogenation reaction which converts alkanes to corresponding alkenes of much higher reactivity [2,3]. Therefore, the olefin-rich FCC by-product gives us a new opportunity as a more effective feedstock of aromatization. Nevertheless, commercialization of olefin aromatization process still poses a great challenge because too high a reactivity of olefin in the feedstock deactivates the catalyst quickly by coke formation.

Various attempts have been made to overcome the limitation of this catalyst, *i.e.* short lifetime due to coke formation. Steam treatment, a well-known method to control the acidity of zeolites, was proved as an effective way to prolong the lifetime of catalyst in this reaction by several research groups. Thus, dealumination of H-ZSM-5 by steaming prolonged the lifetime of the catalyst in aromatization of acetone/n-butanol mixtures [4]. The alpha process was successfully developed and commercialized by Asahi/Sanyo with both hydrothermally treated Zn/ZSM-5 extruded with alumina as binder and a swing bed operation system [5]. The steam treatment made the Zn/ZSM-5 catalyst more stable, compared with K-loaded ZSM-5 in butene aromatization [6]. The improved stability was attributed to the altered distribution of acidity during hydrothermal process. An interesting method recently reported by Bauer et al. used pre-coking and post-modification procedures with hydrogen and alkanes to effectively passivate the acid sites on the external surface of ZSM-5 selectively, which resulted in the enhanced stability of catalyst as well as increased selectivity to para-xylene [7–9]. In aromatization, the effect of oxidative regeneration by air on the distribution of acidity was reported in detail by Tagliabue et al. [10]. Their FTIR results showed that the distribution of acid sites changed and their concentration decreased at the same time. In another report, oxidative regeneration also decreased the concentration of acid sites when applied to the low Si/Al zeolites [11].

Judging from these previous results, we conjectured that the lifetime of the Zn/ZSM-5 catalyst could be improved by careful control of the regeneration conditions. Thus in the present study,

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we modified the Zn/ZSM-5 catalyst by pre-coking and post treatment under oxidative conditions with various concentrations of O_2. Since usual FCC byproducts are made of branched hydrocarbons, we selected 2-methyl-2-butene as the model compound representing FCC olefins. The carefully modified catalyst exhibited enhanced stability in aromatization of 2-methyl-2-butene. The concentration of oxygen in the regeneration gas played a vital role in determining performance of the modified catalyst in this reaction. In addition, we attempted to elucidate the effect of oxidative regeneration on the acid property of the zeolite and its relationship with catalytic activity and stability of the Zn/ZSM-5 catalyst in the aromatization. The proposed new dealumination method is simpler and easier to control (by changing oxygen concentration only) in comparison with conventional methods such as steaming or acid treatment.

2. Experimental

2.1. Materials

NH_4-ZSM-5(HSZ-860NHA) obtained from Tosoh with Si/Al ratio of 34 was used as a parent catalyst. The catalyst was loaded with 2 wt% of Zn by incipient wetness impregnation by using a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich, 98%). The impregnated catalyst was dried at 353 K overnight and then calcined at 823 K in flowing air for 5 h under atmosphere pressure. The prepared catalyst was pelletized, crushed and sieved into 20/30 mesh for the reaction and regeneration under various conditions.

2.2. Pre-coking and oxidative regeneration

Pre-coking was carried out at 773 K and 0.5 MPa for 26 h using 2-methyl-2-butene (95%, Aldrich) as a coking agent at WHSV = 7 h^{-1} and high purity N_2 gas as a carrier gas. After the pre-coking, high purity N_2 gas was continuously flown for 1 h to flush out the residual pre-coking agents and some remained hydrocarbons inside the reactor. To elucidate the effect of O_2 concentration in the regeneration gas on the activity of the catalyst, the fully deactivated catalyst was regenerated under the flow of 10% O_2/N_2, 50% O_2/N_2 and 100% O_2 for 24 h, which were denoted as 10% O_2REG, 50% O_2REG and 100% O_2REG, respectively. The profile of temperature rise was recorded during this step. Finally, prior to the reaction, remained O_2 in the reactor was removed by flowing high purity N_2 for 1 h.

2.3. Characterization

Temperature profiles were recorded by using Handycam of Sony during the regeneration. The temperature reading of the temperature controller was recorded as video and the values of every second were plotted manually. XRD patterns were recorded in the beamline 8C2 HRPD at Pohang Accelerator Laboratory (PAL), Pohang, Korea. The incident X-rays were vertically collimated by a mirror, and monochromatized to the wavelength of 1.54960 Å by a double-crystal Si(1 1 1) monochromator. A data set was collected from 5° to 50° with a step size of 0.01°. The unit cell dimensions of each sample were calculated. The ^{27}Al MAS NMR experiments were carried out to elucidate the effect of regeneration on dealumination by using a Varian Unity Inova 600 (14.1T) with a 2.5 mm zirconia rotor at 20 kHz of spinning rate. The same amount of each sample was employed.

Temperature-programmed desorption (TPD) of ammonia was carried out to probe the distribution of acidity in the catalyst. The experimental procedure for TPD is as follows: at first, the temperature of each catalyst (0.1 g) loaded on the U-shape quartz reactor was increased from room temperature to 823 K at a rate of 10 K/min, and maintained for 1 h to remove the physisorbed water. And then, the temperature was lowered to 393 K and subsequently 1%NH_3/He gas was introduced into the reactor for adsorption of NH_3 for 12 h. Since ammonia does not physisorb at 393 K, all adsorbed ammonia is chemisorbed one. Finally, TPD of NH_3 proceeded by increasing the temperature to 1073 K at 10 K/min and mass number (m/e^-) of 16(NH_2) was recorded by a mass spectrometer HP5973MSD. The amount of acid sites was estimated by absorption of desorped NH_3 in diluted H_2SO_4 solution and then back titration with a NaOH solution.

The FTIR analysis was performed by using Perkin Elmer Spectrum 2000 Explorer to estimate the concentration of Brønsted and Lewis acid sites. For the analysis, each sample of 15 mg was used to prepare self-supporting zeolite disks of 13 mm in diameter. Each disk was evacuated at 823 K for 2 h under 3.3×10^{-5} Torr and then cooled to 423 K to record baseline. Pyridine was introduced to the IR cell equipped with KBr windows for 1 min. Prior to FTIR measurement, the pyridine-adsorbed sample was evacuated at 473 K for 1 h and then cooled down to 423 K to rule out the temperature effect on the intensity and the half-width of the IR maxima [12]. The spectrum was recorded with 64 scans at a resolution of 4 cm^{-1} from 4000 to 1300 cm^{-1}. This procedure was repeated at 573, 673 and 773 K to estimate the distribution of acidity for each sample. For quantitative analysis, Beer–Lambert law was used [13]. The HSZ-860NHA and the fresh samples were used as standards. The absorption coefficients for Brønsted and Lewis acid sites (ε_B and ε_L) were estimated to be 0.59 and 1.44 cm μmol^{-1}, respectively. The acid strength distribution was calculated by difference in peak areas between a higher temperature spectrum and a lower temperature spectrum as follows: weak = $A_{473} - A_{573}$, medium = $A_{573} - A_{673}$, strong = $A_{673} - A_{773}$ and very strong = A_{773}.

2.4. Catalytic reaction

The 2 wt%Zn/NH_4-ZSM-5 catalyst (0.5 g) was loaded into the stainless steel reactor with an inside diameter of 1.1 cm equipped with a thermowell to measure and control the temperature at the center of catalyst bed. Aromatization of 2-methyl-2-butene was performed at 773 K, WHSV = 7 h^{-1}, and 0.5 MPa. The 2-methyl-2-butene (Aldrich, 95% purity reagent) feed was supplied by a double plunge HPLC pump (Waters 1525). All the products were analyzed by an on-line gas chromatograph (HP6890 GC) equipped with an FID detector and HP PONA (50 m × 0.2 mm × 0.5μm) capillary column every 100 min automatically. The effluent lines were maintained at 473 K to prevent condensation of the products.

3. Results

3.1. Physical characterization of catalysts

In the present study, we modified the Zn/ZSM-5 catalyst by precoking and post oxidative regeneration treatment to improve its stability. It was found that the concentration of oxygen in the regeneration gas played a vital role in determining performance of the modified catalyst in this reaction. To understand what happened during the regeneration process, the temperature profile of the reactor was recorded at different O_2 concentrations. Since the combustion of the coke is an exothermic reaction, reactor temperature increases with time by the generated heat. As shown in Fig. 1, the concentration of O_2 had a great effect on the temperature change. In the case of 100% O_2 regeneration, the maximum temperature of 987.3 K was recorded in 21 s while with 10% O_2/N_2, the temperature of catalyst bed increased slowly for 100 s to 810.2 K. It took 26 s to reach 949.0 K when 50% O_2/N_2 was used as a regeneration gas. Thus, the higher concentration of O_2 provides more heat and is expected to have more serious impact on the catalyst.

Table 1
The unit cell dimensions of fresh and three regenerated samples.

Sample	Cell volume V (Å^3)	Cell dimensions a (Å)	b (Å)	c (Å)
Fresh	5376.08	20.117(5)	19.925(1)	13.411(9)
10% O_2REG	5364.95	20.110(0)	19.911(7)	13.398(2)
50% O_2REG	5358.98	20.107(2)	19.899(4)	13.393(4)
100% O_2REG	5352.33	20.102(1)	19.894(8)	13.383(3)

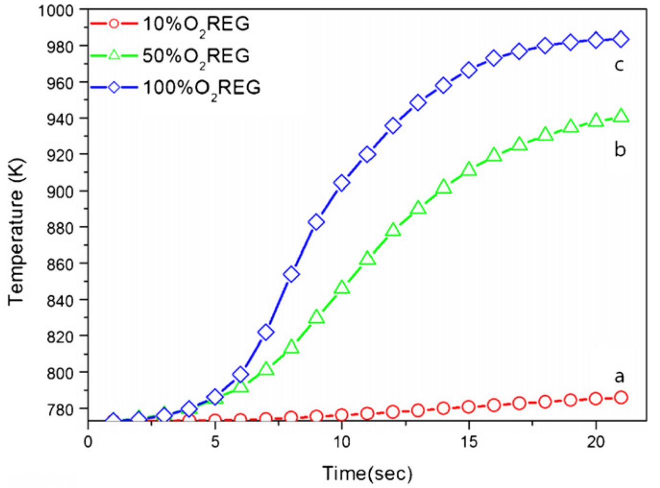


Fig. 1. Temperature profiles of the catalyst bed during oxidative regeneration with various concentrations of O_2, where: (a) – 10%O_2 REG, (b) – 50%O_2 REG, and (c)–100%O_2 REG.

The crystal structure of the catalysts remained unchanged during the regeneration process as shown in Fig. 2, where the XRD peaks representing the MFI structure of ZSM-5 were preserved. Yet, the peak intensities were reduced and peak positions were slightly changed. Table 1 shows decrease in the unit cell volume of the samples treated with the regeneration gas of various oxygen concentrations. The order of unit cell volume was as follows: Fresh > 10% O_2REG > 50% O_2REG > 100% O_2REG. This change could be rationalized by loss of framework aluminum from the zeolite by heat generated from burning the coke in the catalysts. The length of Al–O bond is longer than that of Si–O bond, so the unit cell should also contract depending on the degree of dealumination. This was also confirmed by ^{27}Al MAS NMR discussed below.

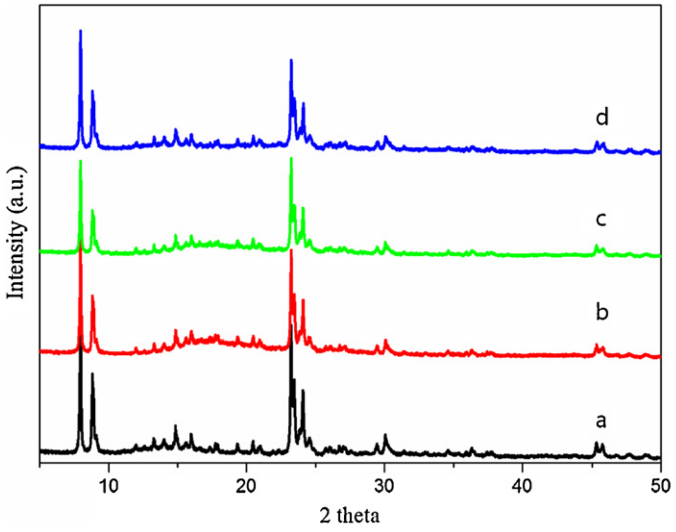


Fig. 2. X-ray powder diffraction patterns of fresh and regenerated samples, where: (a) – fresh, (b) – 10% O_2REG, (c) – 50% O_2REG, and (d) – 100% O_2REG.

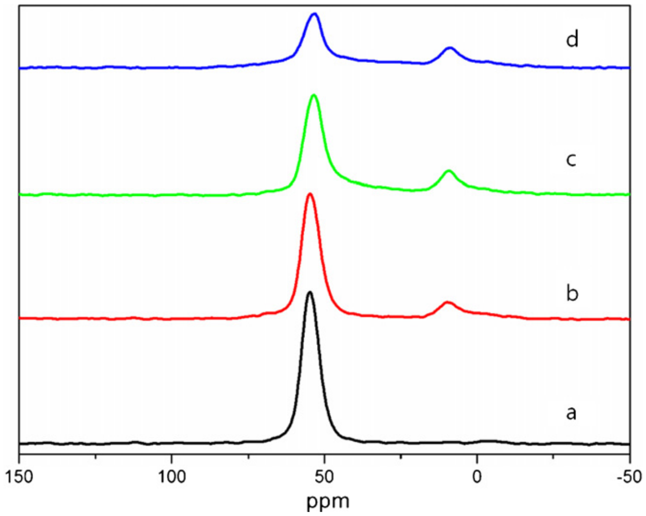


Fig. 3. ^{27}Al MAS NMR spectra of fresh and regenerated samples, where: (a) – fresh, (b) – 10% O_2REG, (c) – 50% O_2REG, and (d) – 100% O_2REG.

The ^{27}Al MAS NMR spectra in Fig. 3 show that all Al in the fresh sample is tetrahedrally coordinated, but all regenerated samples show a new peak around 0 ppm due to octahedrally coordinated Al. Thus, heat of combustion during regeneration results in extraction of the framework Al to generate octahedrally coordinated Al species out of the zeolite framework. Again, the concentration of oxygen in the regeneration gas had great effects on the state of aluminum species. In the case of 10% O_2REG, the peak intensity at around 54 ppm decreased and the new peak at 0 ppm appeared. Under the more severe regeneration condition of 50% O_2REG, the intensity of 54 ppm was further reduced and the peak shape also became asymmetrical, implying the presence of five-coordinated AlO_5 units. Finally, regeneration with pure oxygen resulted in the further removal of the framework Al. Our ^{27}Al MAS NMR results are well consistent with FTIR data reported earlier [10].

3.2. Acid properties of modified catalysts

To probe the acid properties of the Zn/ZSM-5 catalyst, the catalyst itself was first analyzed by FTIR. Silanol group of Si–OH is distinguished from the acidic OH group of Si–OH–Al. As shown in Fig. 4, silanol group and acidic Si–OH–Al appeared in all

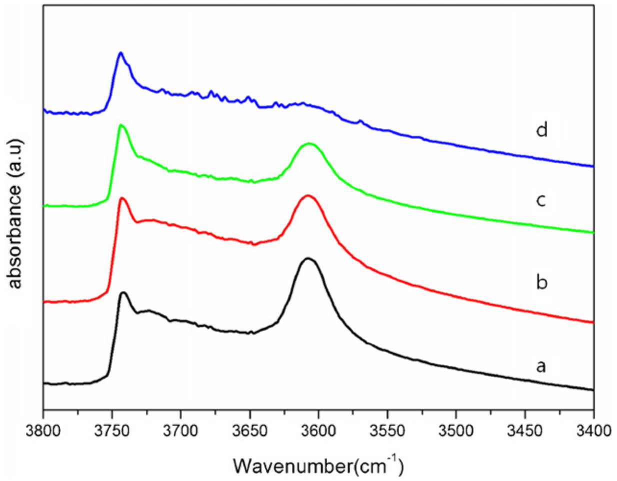


Fig. 4. FTIR spectra of OH region recorded at 473 K, where: (a) – fresh, (b) – 10% O_2REG, (c) – 50% O_2REG, and (d) – 100% O_2REG.

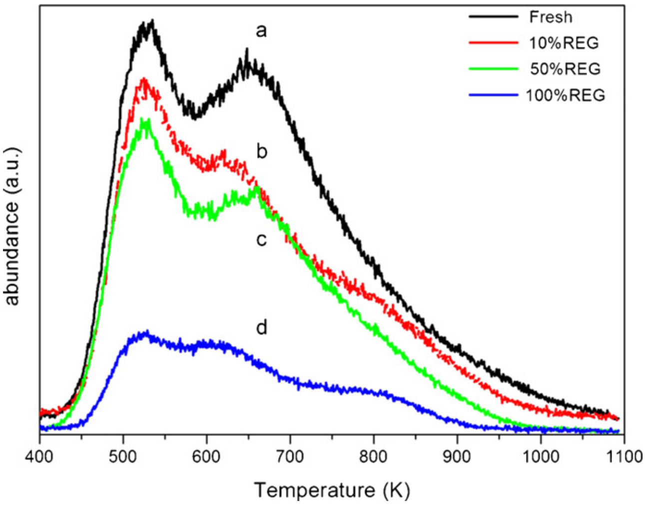


Fig. 5. TPD spectra of ammonia, where: (a) – fresh, (b) – 10% O_2REG, (c) – 50% O_2REG, and (d) – 100% O_2REG.

samples at 3744 and 3607 cm^{-1}, respectively [14]. The fresh sample showed a well developed peak at 3607 cm^{-1} and a relatively small peak of 3744 cm^{-1}, whereas regenerated samples showed that the peak intensity of acidic Si–OH–Al at 3607 cm^{-1} was reduced while the silanol peak at 3744 cm^{-1} became relatively more pronounced. As the concentration of O_2 increased, this tendency became more pronounced and eventually only a little peak of acidic OH group was observed in the 100% O_2 REG sample. Because a tetrahedrally coordinated framework Al in the zeolite can generate a maximum of 4 silanol groups by dislodgement of Al–O bonding, the increase of Si–OH bond indicates decreased concentration of Brønsted acid sites.

The TPD of ammonia is most common and simplest technique to investigate the general acid properties of solid acids. The results of ammonia TPD in Fig. 5 and Table 2 indicate that regeneration process dramatically change the acid properties of the Zn/ZSM-5 catalysts. The fresh catalyst showed two peaks at 522 K and 657 K. In 10% O_2REG sample, the TPD peak area representing total number of acidic sites was reduced by about 11% and the intensity of high temperature peak at 573–773 K was relatively more affected. In 50% O_2REG sample, the amount of acid sites was further decreased by around 17% and especially the very high temperature peak in the region of 723–1073 K was lowered to a greater degree. Finally, the majority of acid sites was removed upon 100% O_2 regeneration.

Pyridine FTIR experiment exhibited similar results as shown in Fig. 6. All the samples showed characteristic three peaks at 1545,

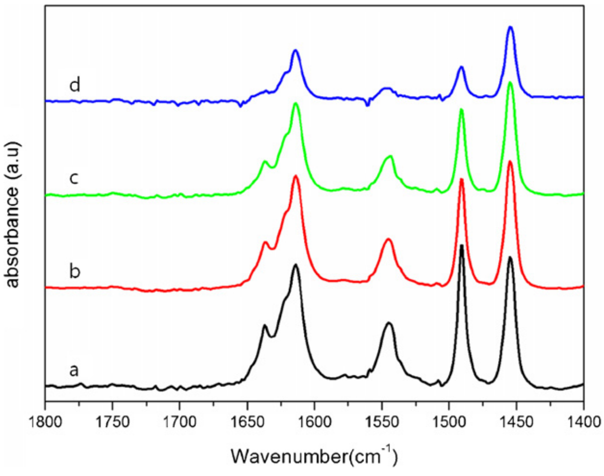


Fig. 6. FTIR spectra of pyridine FTIR spectra recorded at 473 K, where: (a) – fresh, (b) – 10% O_2REG, (c) – 50% O_2REG, and (d) – 100% O_2REG.

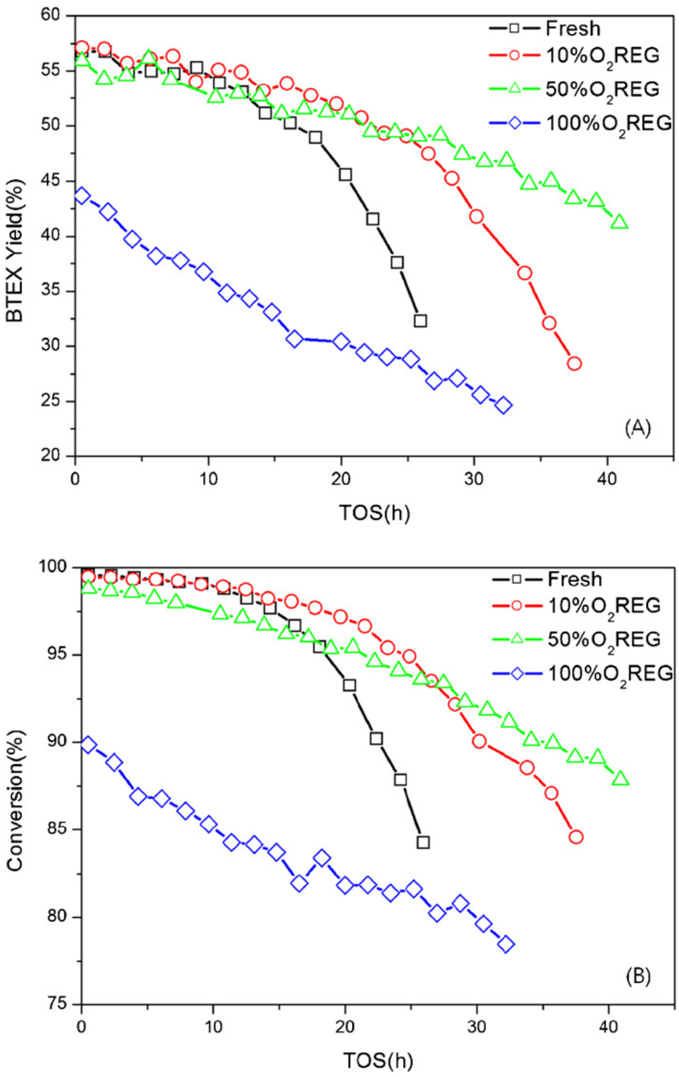


Fig. 7. BTEX yield (a) and conversion of 2-metheyl-2-butene (b) with time on stream (TOS).

Table 2
Distribution of acidity from ammonia TPD and pyridine FTIR.

	Samples Fresh	10% O_2REG	50% O_2REG	100% O_2REG
B weak[a]	0.028	0.021	0.013	0.009
B medium[a]	0.020	0.018	0.014	0.009
B strong[a]	0.050	0.045	0.024	0.002
B very strong[a]	0.104	0.072	0.073	0.022
L weak[b]	0.093	0.055	0.052	0.033
L medium[b]	0.020	0.057	0.052	0.043
L strong[b]	0.057	0.060	0.075	0.047
L very strong[b]	0.167	0.163	0.141	0.086
L/B[c]	1.66	2.15	2.58	4.90
Acid sites[d]	0.54	0.48	0.41	0.19

[a] Brønsted acid sites (mmol/g) detected by pyridine FTIR.
[b] Lewis acid sites (mmol/g) detected by pyridine FTIR.
[c] Measured by pyridine FTIR at 423 K.
[d] Measured by back titration (mmol/g).

Table 3
Initial products composition at 30 min of time on stream.

	Fresh	10% O_2REG	50% O_2REG	100% O_2REG
C1	6.14%	6.16%	5.17%	2.78%
C2	11.28%	10.22%	9.43%	5.54%
C3	14.34%	14.64%	14.79%	14.10%
C4	5.72%	6.75%	10.04%	18.80%
C5	0.45%	0.56%	1.33%	9.53%
C6	0.00%	0.00%	0.00%	1.30%
Benzene	10.12%	10.16%	9.72%	5.58%
Toluene	27.34%	27.79%	26.88%	21.25%
Ethylbenzene	0.48%	0.49%	0.89%	2.14%
m-Xylene	10.11%	10.01%	9.87%	7.36%
p-Xylene	4.24%	4.18%	4.18%	4.32%
o-Xylene	4.52%	4.47%	4.40%	3.02%
BTEX	56.80%	57.10%	55.94%	43.67%
n-Propyl benzene	0.00%	0.00%	0.00%	0.19%
1-Ethyl-3-methyl benzene	0.41%	0.42%	0.77%	1.60%
1-Ethyl-4-methyl benzene	0.18%	0.18%	0.33%	0.97%
1,3,5-Trimethyl benzene	0.33%	0.28%	0.16%	0.00%
1-Ethyl-2-methyl benzene	0.18%	0.21%	0.23%	0.00%
1,2,4-Trimethyl benzene	1.42%	1.43%	1.44%	1.11%
C9 unknown	0.19%	0.18%	0.00%	0.00%
C9 total	2.73%	2.71%	2.92%	3.86%
C10 total	0.85%	0.69%	0.22%	0.31%
C11 total	1.47%	1.19%	0.16%	0.12%
C12 total	0.22%	0.00%	0.00%	0.00%

1454 and 1491 cm^{-1} attributed to Brønsted (B) acid sites, Lewis (L) acid sites and both B and L acid sites, respectively [15]. Fresh catalyst had the most acid sites composed mainly of ‘strong’ and ‘very strong’ Brønsted and Lewis acid sites. After regeneration, the strength of all Brønsted acid sites was reduced and in particular, strong and very strong Brønsted acid sites disappeared. Simultaneously, the number of Lewis acid sites and L/B ratio increased with increasing O_2 concentration, suggesting that the newly generated octahedrally coordinated Al species detected by ^{27}Al MAS NMR played a role of Lewis acid sites of medium to strong strength as listed in Table 3 and Fig. 6. Similar to these results, Occelli et al. also reported decrease in the acidity of FCC catalyst after regeneration by using ammonia and pyridine as probe molecules with the microcalorimetry technique [16]. Judging from our pyridine FTIR results, we can conclude that Brønsted acid sites are more affected than Lewis acid sites by the regeneration process.

3.3. *Aromatization of 2-methyl-2-butene*

In Fig. 7, the conversion of 2-methyl-2-butene and the yields of benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are displayed against time on stream (TOS). The conversion on the fresh catalyst decreased slowly during the first 12 h of TOS, the catalyst deactivated rapidly after then, and most of the activity was lost after 26 h of TOS. The sample prepared by pre-coking and regeneration with 10% O_2/N_2 showed substantially improved stability and the rapid deactivation started only after 26 h of TOS. The highest stability was observed for 50% O_2/N_2REG catalyst showing no sudden rapid deactivation. The 100% O_2REG catalyst showed low activity from the beginning of the reaction. The BTEX yield also showed the similar trend to 2-methyl-2-butene conversion. Thus,

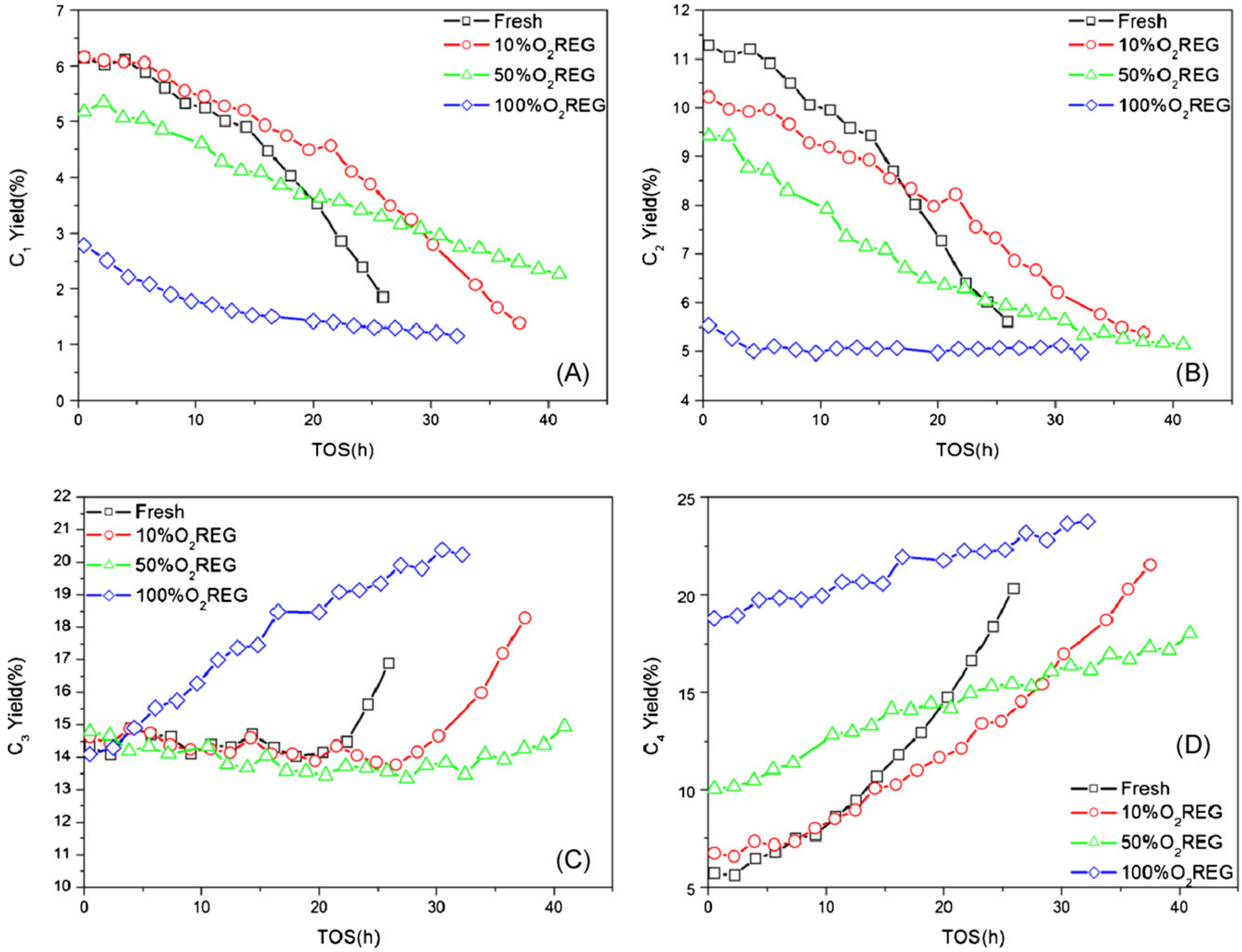


Fig. 8. C_1–C_4 yield, where: (a) – C_1 yield, (b) – C_2 yield, (c) – C_3 yield, and (d) – C4 yield.

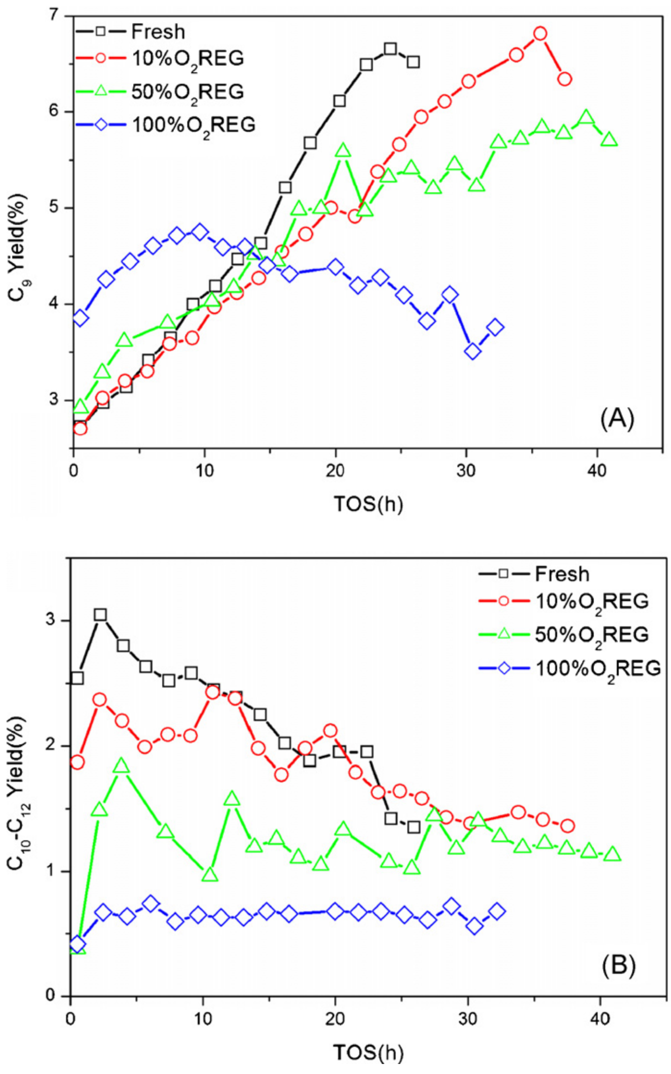


Fig. 9. C_9 yield (a) and C_{10}–C_{12} yield (b).

50% O_2REG catalyst maintained the high initial 2-methyl-2-butene conversion (∼98%) and BTEX selectivity (∼57%), but 100% O_2REG showed greatly reduced initial BTEX yield of ∼44% and initial conversion of ∼90%.

The initial product composition measured after 30 min of reaction is listed in Table 3. Yields of C_1, C_2, BTEX, and C_{10}–C_{12} aromatics decreased but C_4 isomers and C_9 aromatics increased as O_2 concentration increased (Figs. 7–9). The C_{10} aromatics were composed mainly of naphthalene and a little amount of alkylbenzene derivatives, and 1-methyl naphthalene and 2-methyl naphthalene were the major products of C_{11} aromatics. The C_{12} products were made up of dimethylnaphthalene isomers. These hydrocarbons were identified by GC/MS (HP5973MSD). The yields of each product were plotted with TOS in Fig. 9. Although concentration of naphthalene derivatives in C_{10}–C_{12} was so small that the data showed some fluctuations, the yield was typically decreased with TOS. However, the yield of C_9 aromatics increased with TOS and reached a maximum point, which indicated that the C_9 aromatics were intermediate of C_{10}–C_{12} aromatics. The reduced concentration of acid sites by the pre-coking and regeneration treatment suppressed the conversion of C_9 to C_{10}–C_{12} which could act as coke precursor. As a result, the improved stability was achieved through the treatment.

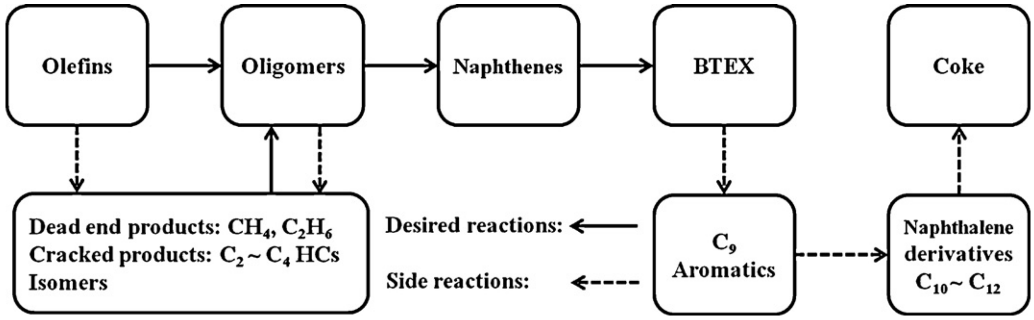
4. Discussion

In the present study, we modified the Zn/ZSM-5 catalyst by pre-coking and post treatment under oxidative conditions to improve its stability in aromatization of 2-methyl-2-butene. The concentration of oxygen in the regeneration gas played a vital role in determining performance of the modified catalyst in this reaction. The oxidative regeneration caused dealumination from the zeolite framework and tuned its acid property, which in turn modified activity and stability of the Zn/ZSM-5 catalyst in the aromatization.

The changes in structure and acid properties during the regeneration treatment have been confirmed. Thus, the contraction of unit cell volume from 5376.08 Å^3 to 5364.95, 5358.98 and 5352.33 Å^3 was revealed with synchrotron XRD. In ^{27}Al MAS NMR, the decrease in the peak intensity at 54 ppm and concomitant generation of a new peak at about 0 ppm indicated that the tetrahedrally coordinated framework Al was transformed to penta-coordinated nonframework Al or octahedrally coordinated extraframework Al. The FTIR analysis showed increase in silanol peak at 3744 cm^{-1} and decrease in acidic Si–OH–Al peak at 3607 cm^{-1}. All these results indicate thermal dealumination during the oxidative regeneration, the degree of which depended critically on the concentration of O_2. As a result, the distribution of acidity of catalyst is modified, which changes the initial composition of products as well as the lifetime of catalyst.

In catalysis by zeolites, their acidity plays the key role in all reactions of hydrocarbons. Aromatization has also been extensively studied [2,17–19], and the current understanding on its reaction pathway could be summarized as in Scheme 1. Oligomerization and cyclization take place on Brønsted acid sites while Lewis acid sites promote dehydrogenation of generated naphthenes. Because the coke, responsible for deactivation, is mainly deposited on Brønsted acid sites, their role is most important.

Desired reactions of oligomerization and cyclization as well as undesired reactions of cracking, alkylation of produced aromatics and coke formation are all catalyzed by Brønsted acid sites but each reaction has its own favorable strength of Brønsted acid sites [20]. It is well established that coke formation generally takes place



Scheme 1. Summary of reaction pathways of aromatization.

on strong Brønsted acid sites while oligomerization and cyclization occurs on weaker Brønsted acid sites [21]. Thus, for successful aromatization with high stability and high yield of BTEX, appropriate modification of the distribution of Brønsted acid sites is most important. In the fresh catalyst, there were too many ‘strong’ and ‘very strong’ Brønsted acid sites of 0.154 mmol/g. It was reduced to 0.117, 0.097 and 0.024 mmol/g after 10% O_2REG, 50% O_2REG and 100% O_2REG, respectively, which resulted in suppressing the generation of monomolecular cracking products such as C_1 and C_2 and the conversion of C_9 to C_{10}–C_{12}, which are coke precursors. Although the number of weak and medium Brønsted acid sites was also reduced greatly after regeneration, the results showed that 0.027 mmol/g in 50% O_2REG was enough to produce oligomers and cyclic hydrocarbons. Therefore, elimination of unnecessary excess ‘strong’ and ‘very strong’ Brønsted acid sites can suppress the side reactions and the rate of coke formation, which results in the increase in the catalyst lifetime.

It is also well known that too high density of Brønsted acid sites makes the catalyst deactivation fast [22]. In Fig. 7, the fresh catalyst showed the fastest rate of deactivation for this reason. The total concentration of Brønsted acid sites decreased from 0.23 mmol/g to 0.156, 0.124 and 0.043 mmol/g as listed in Table 2 upon oxidative regeneration. The 50% O_2REG catalyst showed the best stability maintaining the same high activity although the density of Brønsted acid sites was reduced by about half. However, this concentration of Brønsted acid sites seems enough to catalyze this reaction. In the case of 100% O_2REG, the density of Brønsted acid sites was decreased by 80%, which is too small to promote the reaction. Thus, the density of Brønsted acid sites could be controlled by adjusting O_2 concentration during the regeneration treatment so that the catalyst lifetime is prolonged without sacrifice in its activity and selectivity.

5. Conclusions

As a new method to control acidity of zeolite catalyst, pre-coking and oxidative regeneration have been demonstrated. Thermal dealumination preferentially modified the distribution and density of the Brønsted acid sites. The concentration of O_2 in regeneration gas was found as the key factor. Partial removal of strong Brønsted acid sites reduced the undesired side reactions leading to coke formation. Thus, the lifetime of catalysts was improved without deteriorating activity and selectivity in the aromatization of 2-methyl-2-butene. The proposed new dealumination method is simpler and easier to control (just by changing oxygen concentration) in comparison with conventional methods such as steaming or acid treatment.

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References

[1] T. Mole, J.R. Anderson, G. Creer, Appl. Catal. 17 (1985) 141.
[2] N. Viswanadham, A.R. Pradhan, N. Ray, S.C. Vishnoi, U. Shanker, T.S.R. Prasada Rao, Appl. Catal. A 137 (1996) 225.
[3] D. Seddon, Catal. Today 6 (1990) 351.
[4] A. de Lucas, P. Canizares, A. Durán, A. Carrero, Appl. Catal. A 154 (1997) 221.
[5] Y. Nagamori, M. Kawase, Micropor. Mesopor. Mater. 21 (1998) 439.
[6] Y. Song, H. Li, Z. Guo, X. Zhu, S. Liu, X. Niu, L. Xu, Appl. Catal. A 292 (2005) 162.
[7] F. Bauer, W.-H. Chen, Q. Zhao, A. Freyer, S.-B. Liu, Micropor. Mesopor. Mater. 47 (2001) 67.
[8] F. Bauer, W.-H. Chen, H. Ernst, S.-J. Huang, A. Freyer, S.-B. Liu, Micropor. Mesopor. Mater. 72 (2004) 81.
[9] F. Bauer, E. Bilz, A. Freyer, Appl. Catal. A 289 (2005) 2.
[10] M. Tagliabue, A. Carati, C. Flego, R. Millini, C. Perego, P. Pollesel, B. Stocchi, G. Terzoni, Appl. Catal. A 265 (2004) 23.
[11] G. Caeiro, R.H. Carvalho, X. Wang, M.A.N.D.A. Lemos, F. Lemos, M. Guisnet, F. Ramôa Ribeiro, J. Mol. Catal. A: Chem. 255 (2006) 131.
[12] B. Gil, L. Mokrzycki, B. Sulikowski, Z. Olejniczak, S. Walas, Catal. Today 152 (2010) 24.
[13] F. Thibault-Starzyk, B. Gil, S. Aiello, T. Chevreau, J.-P. Gilson, Micropor. Mesopor. Mater. 67 (2004) 107.
[14] H.G. Karge, V. Dondur, J. Phys. Chem. 94 (1990) 765.
[15] E.P. Parry, J. Catal. 2 (1963) 371.
[16] M.L. Occelli, M. Kalwei, A. Wölker, H. Eckert, A. Auroux, S.A.C. Gould, J. Catal. 196 (2000) 134.
[17] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro, M. Guisnet, Appl. Catal. 35 (1987) 93.
[18] M. Guisnet, N.S. Gnep, F. Alario, Appl. Catal. A 89 (1992) 1.
[19] S. Bhatia, J. Beltramini, D.D. Do, Catal. Rev. 31 (1989) 431.
[20] J.A. Lercher, A. Jentys, A. Brait, Mol. Sieves 6 (2008) 153.
[21] H. Lechert, C. Dimitrov, C. Bezuhanova, V. Nenova, J. Catal. 80 (1983) 457.
[22] F. Bauer, H.G. Karge, Mol. Sieves 5 (2007) 249.