Control of acidity on the external surface of zeolite Y for *m*-xylene isomerization using a mechanochemical neutralization method

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Abstract−To improve the ortho- or para-xylene selectivity via the isomerization of meta-xylene, the acid sites located on the external surface of zeolite Y crystals were neutralized by using the intrinsic mechanochemical method, which resulted in reduced coke formation. Zeolite Y crystals were mixed in an agate mortar with alkaline earth metal oxides supported on micro spherical non-porous silica. The catalytic performances into *o*- or *p*-xylene from the *m*-xylene isomerization reaction were enhanced, especially with either the CaO- or MgO-neutralized catalyst, as verified by adsorption of bipyridine, which could not access the pore channel due to its bulky molecular size. These consistent changes in the reaction performance could be ascribed to the decrease in the number of acid sites on the external surfaces.

Key words: Mechanochemical Neutralization Method, Alkaline Earth Metal Oxides, *m*-Xylene Isomerization, Coke Formation, Adsorption of Bi-pyridine

INTRODUCTION

Xylenes are important starting materials for many industrial processes, such as the production of synthetic fibers, plasticizers and resins. However, naphtha and gasoline, which are major sources of xylenes, have a higher ratio of low valued *m*-xylene. Therefore, an alternative route is required for the syntheses of high value *o*- and *p*-xylenes from *m*-xylene [1-6]. Studies on the syntheses of *o*- and *p*-xylenes using Y-type zeolites, which have the homologous structure of FAU (fauzasite), have been reported by several research groups [7,8], partly due to their increased chemical and thermal stability. Zeolite-Y is made ultra stable by the removal of aluminum from its framework. However, FAU has large cavities inside its crystal channel structure, which can lead to the risk of rapid coke formation [7] when the intrinsic strength and concentration of the acid sites inside the cavity are too great. Coke formation particularly occurred at the external surface of the crystals, as there is little to restrict the growth of fused-ring aromatics, i.e., the precursors of aromatic coke. Many investigations have been performed to overcome this problem, but it still remains to be resolved. Inui et al. [9-11] reported that the acid sites located on the external surface of Ga-incorporated MFI-type metallosilicate were reduced by Pt-ion exchange, with successive heat treatment resulting in a marked reduction of coke deposits due to hydrogen spillover through the Pt particles at the portholes. They extended their work using selective neutralization of the acid sites located on the outer surface of H-ZSM-5 and H-Ga silicate, which confirmed its neutralization effect on the methylation reaction of methylnaphthalene [12]. However, we have to realize that general impregnation methods which directly load alkaline earth metals onto the external surfaces of porous catalyst, have some risks. Entering alkali earth metal ions to internal pores of catalysts resulted in neutralizing internal surface acidic sites and in blocking the internal pores or making the internal pore sizes to the small

in catalysts. As a result, the diffusion rates of reactants in internal pores were reduced, and the total conversion and selectivity was also decreased. In our previous paper [13], the amount of coke deposited was shown to sensitively depend on the density of the acid sites of the external surface of Ni-SAPO-34 crystals in the methanol to light olefin conversion reaction. Also, the acid sites on the external surface decreased the selectivity to ethylene from methanol owing to the non-restricted oligomerization at the solid surfaces. Additionally, a mechanochemical neutralization method was adopted to neutralize the acid sites on the external surface of Ni-SAPO-34 crystal, with the intention of reducing the coke formation and increasing the shape selectivity for methanol conversion.

In this study, the only acid sites located on the external surface of zeolite Y crystals were neutralized by using the intrinsic mechanochemical method with alkaline earth metal oxides supported on micro spherical non-porous silica; expecting depress the coking formations and byproducts on the external acidic sites resulted in improvement of selectivity for *o*- or *p*-xylene from *m*-xylene. The neutralization of the external surface has been identified by using the adsorption of bipyridine. In particular, the relationship between the acidic sites on the external surfaces and catalytic performance in *m*-xylene isomerization was reconfirmed in this study.

EXPERIMENTAL

1. Catalyst Preparation

Fig. 1 shows the mechanochemical neutralization method introduced in this study. Commercial zeolite Y (particle size; 5 µm, Aldrich) was used as a starting catalytic material. The zeolite Y was thermal treated in air at 600 ℃ for 3 h to remove the absorbed impurities prior to neutralization. The acid sites on the external surface were neutralized as follows: 70 wt% portion of zeolite Y crystalline particles were manually milled in an agate mortar for 30 min with 3 wt% of alkali earth metal oxide, such as MgO, CaO, BaO or SrO, supported on 27 wt% micro spherical non-porous silica particles 0.5-1.5 µm in diameter (PS-3, Onoda Cement). Here, we had

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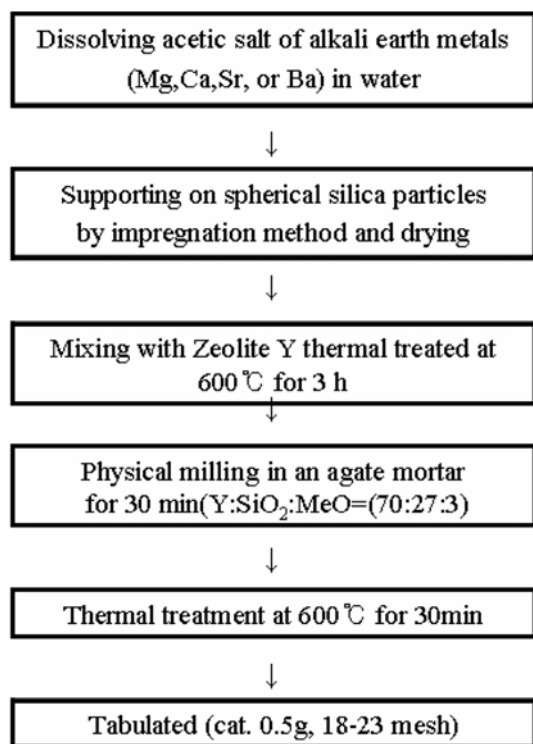E-mail: mskang@ynu.ac.kr

Fig. 1. The mechanochemical neutralization method for *m*-xylene isomerization.

to remove the risk that when alkali earth metal ions are directly loaded on zeolite Y, the alkali earth metal ions enter to internal pores of zeolite Y resulting in neutralizing internal surface acidic sites and in blocking the internal pores in catalysts. These samples were then tabulated and thermal treated in air at 600 °C for 30 minutes, followed by crushing and sieving to 18-23 mesh size to provide the

reaction. Five different samples were designated as catalysts.

2. Characteristics

The zeolite Y catalysts neutralized by the alkali earth metal oxides were subjected to XRD (model PW 1830; Philips, Amsterdam, The Netherlands), with nickel-filtered Cu$K\alpha$ radiation (30 kV, 30 mA) at 2θ angles, from 5 to 80°, with a scan speed and time constant of 10° min^{-1} and 1 second, respectively. The Brunauer, Emmett and Teller (BET) surface areas of the catalysts were measured by nitrogen gas adsorption using a continuous flow method. A mixture of nitrogen and helium was used as the carrier gas. The sample was treated at 350 °C for 30 min prior to nitrogen adsorption. The acidic properties of the catalysts were measured by the temperature-programmed desorption (TPD) of pre-adsorbed NH$_3$, *m*-xylene and bipyridine, using a Rigaku micro thermogravimetric analyzer Thermoflex TG 8110, equipped with a thermal analysis station TAS 100. TPD profiles were obtained from the differential of the integral curve of weight loss from 80 to 600 °C, at a constant heating rate of 10 °C/ min, in a 50 ml/min N$_2$ flow. The bipyridine adsorption was identified by using FT-IR spectra. The amount of coke deposited on the catalyst after the reaction was measured by temperature-programmed oxidation (TPO) using a Shimadzu DT-40 thermo-gravimeter. 20 mg sample was placed in a sample pan and heated from 50 to 800 °C, at a constant heating rate of 10 °C/min, in a 40 ml/min air flow. The profiles were obtained in the same manner as described for the TPD, with the coke contents calculated from the weight loss in the temperature range from 50 to 800 °C. The α-alumina (20 mg) was used as the reference.

3. Reaction Method

The *m*-xylene isomerization was carried out in an ordinary fixed flow-type apparatus, as shown in Fig. 2. Zeolite Y of 0.5 g neutralized by the alkali earth metal oxides was packed into a quartz tubular reactor with an inner diameter of 5.0 mm, with a reaction gas composed of 10 mol% *m*-xylene and 90 mol% N$_2$ allowed to flow
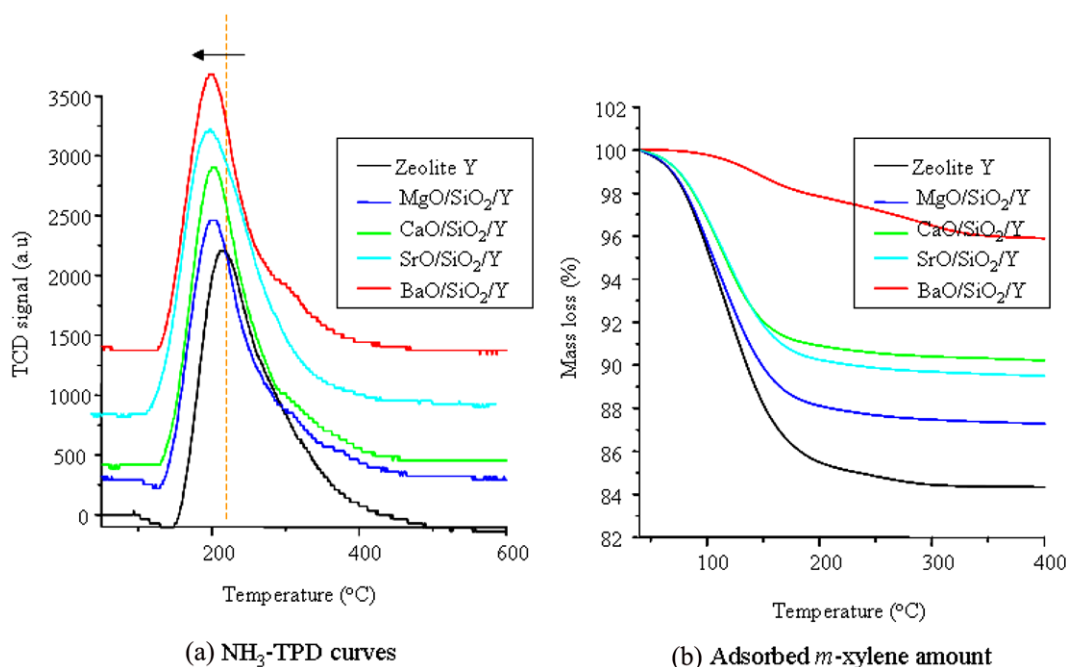

(a) NH$_3$-TPD curves

(b) Adsorbed *m*-xylene amount

Fig. 2. The NH$_3$-TPD curves and amount of *m*-xylene adsorbed for the Zeolite Y catalysts neutralized by MgO, CaO, SrO or BaO.

at a gaseous hourly-space velocity (GHSV) of 1,200 h^{-1} and temperature range from 300 to 550 °C for 1-34 h on stream. The products were analyzed by three FID-type gas chromatographs (Donam Korea, DS6200).

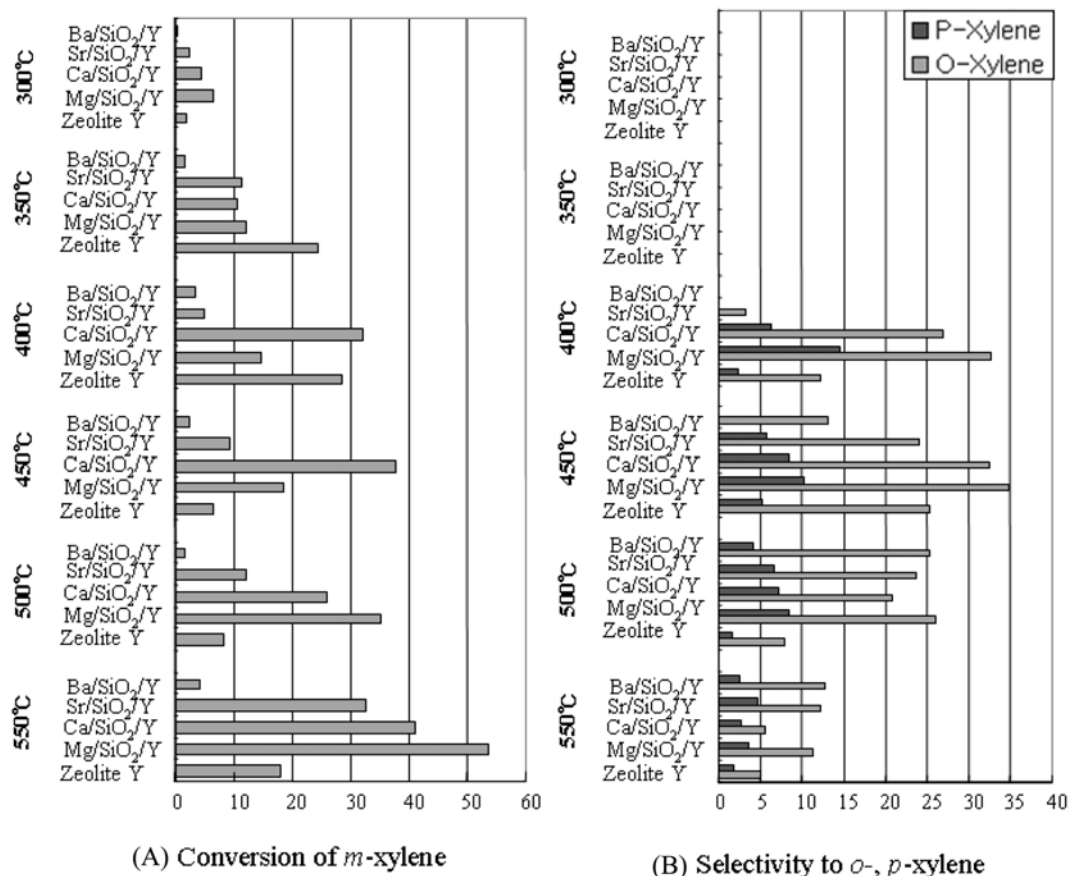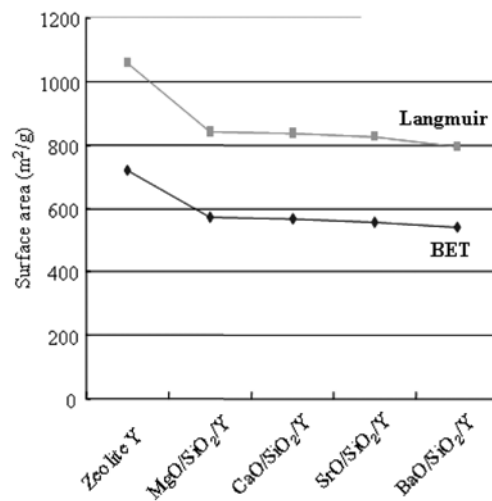## RESULTS AND DISCUSSION

1. Physical Properties of the Zeolite Y Catalysts Neutralized by Alkali Earth Metals

The neutralized catalysts are identified by X-ray diffraction, the peaks for the modified and unmodified catalysts almost coincided with one another. However, the total peak intensities decreased slightly with increasing basic property of the support alkali metal. A peak

Table 1. The atomic compositions, as analyzed by EDAX and BET surface areas, of the Zeolite Y catalysts neutralized by MgO, CaO, SrO or BaO

Catalyst/Elements	Atomic ratio (%)					
	O	Na	Si	Al	Metal	Al/Si
Zeolite Y	54.7	7.96	28.15	9.45		0.336
MgO/SiO$_2$/Y	59.11	6.05	27.53	7.01	0.28	0.255
CaO/SiO$_2$/Y	62.02	5.24	25.44	5.68	1.62	0.223
SrO/SiO$_2$/Y	55.64	6.85	28.70	7.32	1.50	0.255
BaO/SiO$_2$/Y	61.52	5.84	24.97	6.19	1.50	0.248

(A) Conversion of *m*-xylene   (B) Selectivity to *o*-, *p*-xylene

Fig. 3. The changes in the conversion and selectivity of m-xylene to *o*-, *p*-xylene with increasing temperature over the Zeolite Y catalysts neutralized by MgO or CaO.

assigned to SiO$_2$, used as a support, showed at 2 theta=26° in all the catalysts. However, no other peaks assigned to the loaded metal oxides were seen in all the samples, suggesting that the alkali metals are highly dispersed on the external surface of zeolite Y. Table 1 summarizes the physical properties of the neutralized catalysts. From the energy dispersive analysis of X-rays (EDAX), the true loaded alkali metals were less than 3.0 wt%. The true atomic ratios of Al/Si in the Zeolite Y catalysts neutralized by alkali earth metal oxides appear to decrease to 0.255, 0.223, 0.255 and 0.248, respectively, compared to 0.336 for pure zeolite Y, because of the added silica amount in a step of mechanochemical neutralized method. Generally, the surface area is strongly related to the particle size; when the particle size decreases, the surface area increases. However, this was not the case in our results. The surface areas decreased with increase of basic ability of the loaded alkali metals, because the surfaces and pores of zeolite Y were partially covered by bigger alkali metal oxides. The NH$_3$-TPD profiles for the neutralized zeolite Y and the un-neutralized zeolite Y catalyst are shown in Fig. 2. Generally, the NH$_3$-TPD profiles consisted of two peaks: one appearing at a low-temperature range, around 150-200 °C, with the other at a high-temperature range, around 350-450 °C. The low- and high-temperature peaks corresponded to the weak and strong acid sites,

respectively. However, the zeolite Y having an FAU structure showed a broad band at around 120-450 °C. The band intensities and areas did not change in the neutralized compared with the un-neutralized catalysts; however, most bands shifted to a slightly lower temperature, correspondent to the basic abilities of the loaded alkali metals. This was ascribed to the acid sites on the zeolite Y surfaces being partly neutralized. Conversely, there were varying amounts of *m*-xylene adsorption, with the amount adsorbed onto the crystals largely reduced in the zeolite Y catalysts neutralized by alkali earth metals; these decreased in the order of zeolite Y>>the neutralized by MgO>SrO>CaO>>BaO, regardless of the NH$_3$-TPD result. Here, it is important that the catalytic activities are particularly strongly related to the initial adsorbed reactants. To confirm the neutralization on the external surface of zeolite Y, bipyridine adsorption was performed using FT-IR spectra Vibrations for the adsorbed bipyridine were found at around 1,650, 1,540 and 1,460 cm^{-1}. The adsorption of bipyridine molecules onto Brönsted acid sites gave the characteristic adsorption bands at close to 1,650 and 1,540 cm^{-1}. The adsorptions of bipyridine onto Lewis acid sites, tri-coordinated aluminum ions, occurred via a coordinate bond, which gave rise to a band close to 1,460 cm^{-1} [14]; however, this band was not found in this study. The band at 1,650 cm^{-1} remained after neutralization, shifted to slight-
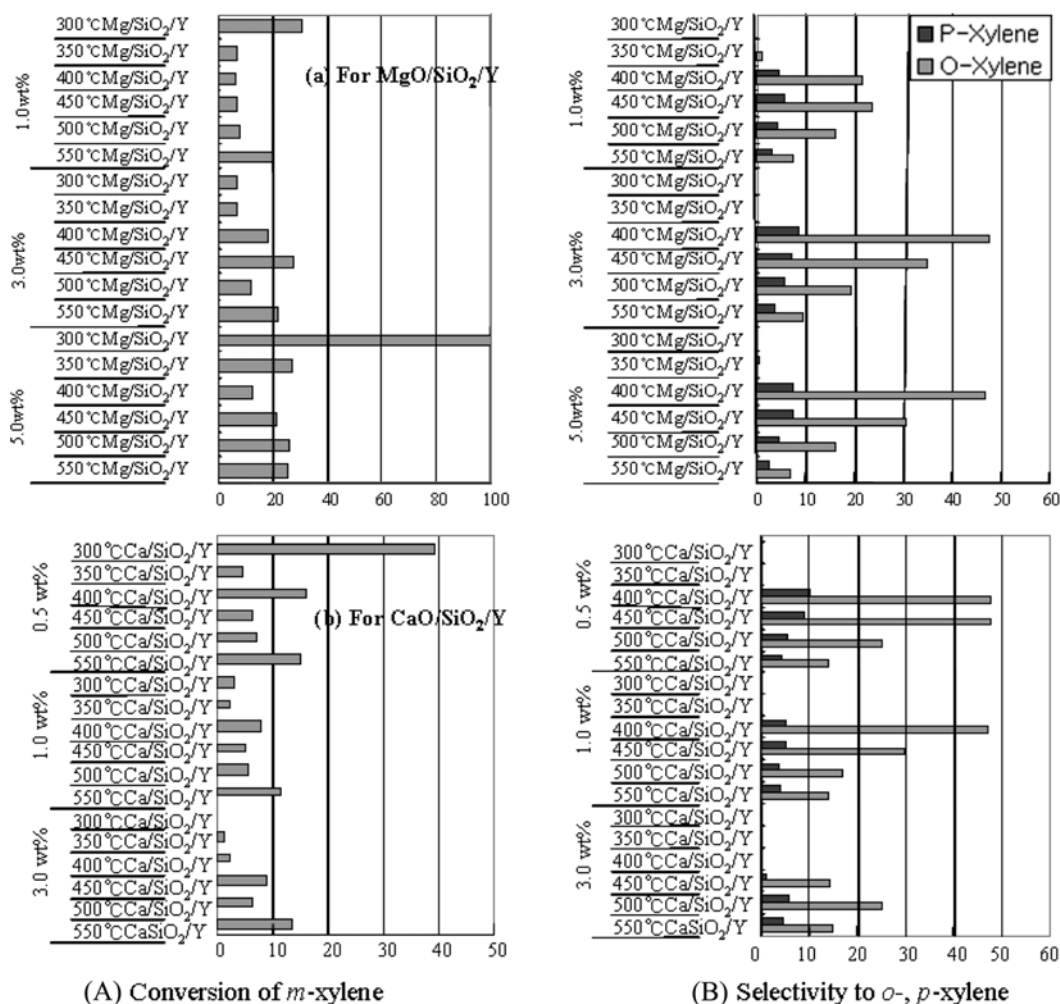

Fig. 4. The changes in the conversion and selectivity m-xylene to *o*-, *p*-xylene with increasing Mg or Ca concentration.

ly higher wave numbers with increasing basicity. In addition, a band at 1,540 cm^{-1} completely disappeared with neutralization. From this result, the acid sites on the external surfaces of the zeolite Y catalysts were assumed to be well neutralized, with the coke formation throughout *m*-xylene isomerization on the external surfaces of the zeolite Y consequently depressed.

2. m-Xylene Isomerization over the Zeolite Y Catalysts Neutralized by Alkali Earth Metals

Fig. 3 shows the changes in the conversion of m-xylene and the selectivity to *o*- and *p*-xylene as a function of the reaction temperature for a reaction time of 1 h on the catalysts neutralized with different alkali metal oxides. Here, propane, benzene, toluene and trimethylbenzene were also found as byproducts, as reported by Inui et al. [7]; however, their selectivities were disregarded as there were no target compounds in this study. The neutralized catalysts exhibited higher *m*-xylene conversions than the un-neutralized, as shown in A). In particular, the conversion increased at mild temperatures between 400 (32%) and 450 °C (38%) on Ca/SiO$_2$/Y neutralized by CaO; however, the best conversion was obtained on MgO/SiO$_2$/Y at higher temperatures between 500 (35%) and 550 °C (54%). The selectivity to *o*- and *p*-xylene was also enhanced on the neutral-

ized catalysts, as shown in B). Total production of *o*-xylene was much greater than that of *p*-xylene with all catalysts. Especially, this effect was largest when MgO was used as the modifier; the total selectivity was most improved on MgO/SiO$_2$/Y at almost all temperatures ranging from 400 to 550 °C. Conversely, both the conversion and selectivity were rather decreased in the catalysts neutralized by stronger alkali components, SrO and BaO. From this result, it was supposed that a too strong alkali metal can cover the internal as well as external acidic sites. Consequently, an appropriate alkali component, such as CaO and MgO, would be needed as the neutralizer to improve the catalytic activity as a result of the depressed coke formation. Fig. 4 expresses the changes in the conversion of *m*-xylene and the selectivity to *o*- and *p*-xylene as a function of the alkali metal concentration on the MgO/SiO$_2$/Y and CaO/SiO$_2$/Y, and they showed excellent performance. For MgO/SiO$_2$/Y, the *m*-xylene conversion was enhanced with a greater Mg ion concentration, and the selectivity to *o*- and *p*-xylene was best, 56% at 400 °C, when neutralized by 3.0 wt% MgO. Otherwise, the conversion of *m*-xylene was somewhat enhanced when a lower concentration of CaO, in particular 0.5 wt%, was used to neutralize the zeolite Y. The total selectivity to *o*- and *p*-xylene reached 59% at a reaction temperature of
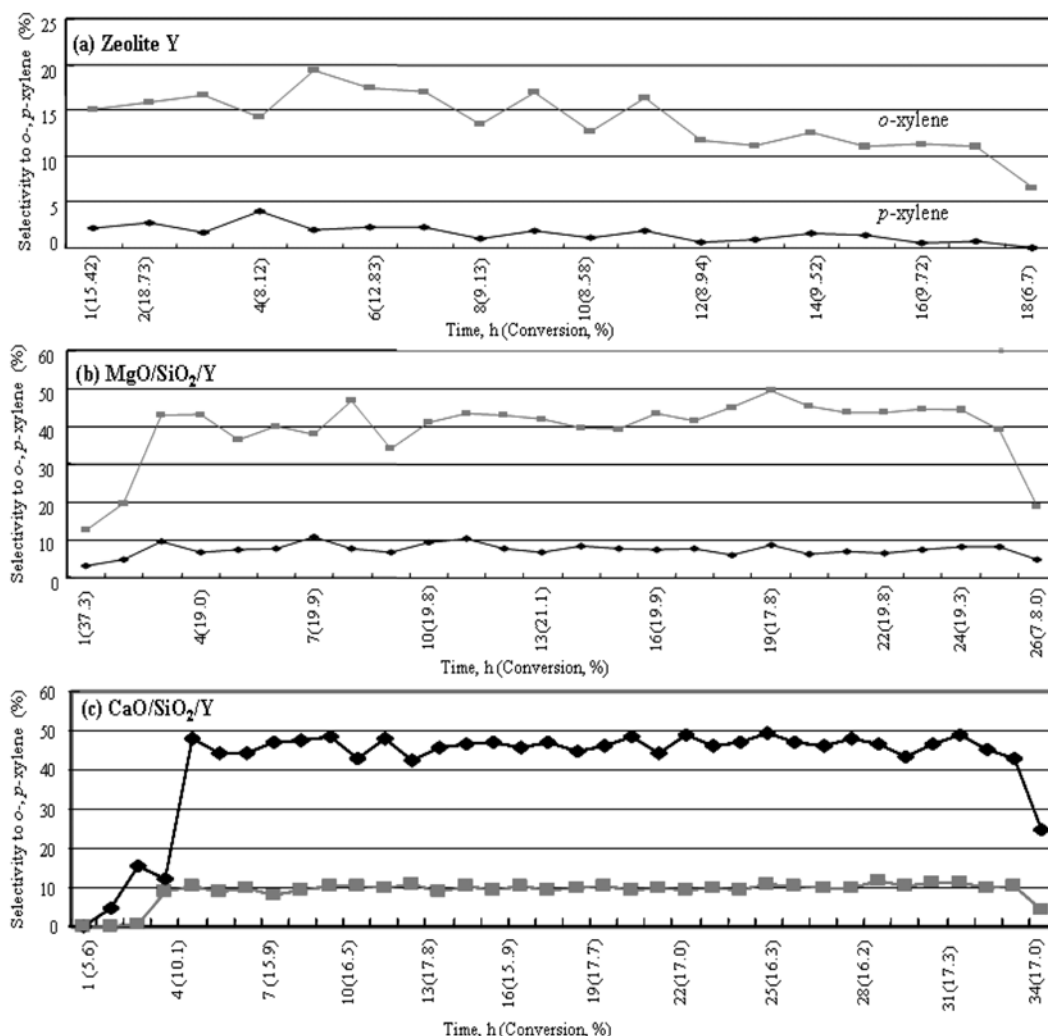

Fig. 5. The catalytic life times for 3.0 wt% MgO/SiO₂/Y and MgO/SiO₂/Y at a reaction temperature of 450 °C.

400 °C. This result explains that a higher alkali metal concentration is required to improve *m*-xylene isomerization when weak (MgO) alkali metals are used as a neutralizer, which also gave very reliable results. Here, the catalytic life times of zeolite Y, MgO/SiO$_2$/Y, and CaO/SiO$_2$/Y were determined when using 3 wt% alkali metals for the neutralizations, with selectivity to *o*- and *p*-xylene as expressed in Fig. 5. Both neutralized catalysts had longer catalytic life times relative to the un-neutralized zeolite Y catalyst. The catalytic deactivation in pure zeolite Y is starting from 17 h with below 20% of *o*- and *p*-xylene selectivities and below 10% of conversion. Selectivity of about 55% to *o*- and *p*-xylene on MgO/SiO$_2$/Y, as shown in Fig. (b) was maintained with increasing time on stream up to 24 h, but markedly decreased thereafter; the conversion of *m*-xylene was within the range of 17-21%. Conversely, as shown in c), the catalytic life of CaO/SiO$_2$/Y was longer than that of MgO/SiO$_2$/Y; selectivity to *o*- and *p*-xylene was stably continued at about 60% with increasing time on stream up to 33 h, but the conversion of *m*-xylene was somewhat decreased compared to that on MgO/SiO$_2$/Y, which was within the range 15-17%. As a consequence, the catalytic deactivation was slightly more moderated on CaO/SiO$_2$/Y, as it included the stronger alkali metal compared to on MgO/SiO$_2$/Y, which included the weaker alkali metal. Here, it was supposed that the prolonged catalytic life of the modified catalysts indicated a decrease in the formation of coke on the external surface. The selectivity to *o*- and *p*-xylene over the neutralized catalysts was higher than that over the un-neutralized catalysts, as shown in Figs. 3-5. The *o*- and *p*-xylene were selectively produced on the internal acid sites, while non-selective reaction occurs on the external acid sites. Therefore, the neutralization of the external acid sites increased the *o*- and *p*-xylene selectivity. However, over both the neutralized and un-neutralized catalysts, the selectivities of conversions of *m*-xylene to *o*- and *p*-xylene were decreased with increasing time on stream. This was ascribed to the pore mouths of the crystal gradually becoming blocked by coke during *m*-xylene isomerization. Consequently, the amount of coke deposited was closely related to the number of acid sites on the external surface of the crystals. After 20 h of reaction,
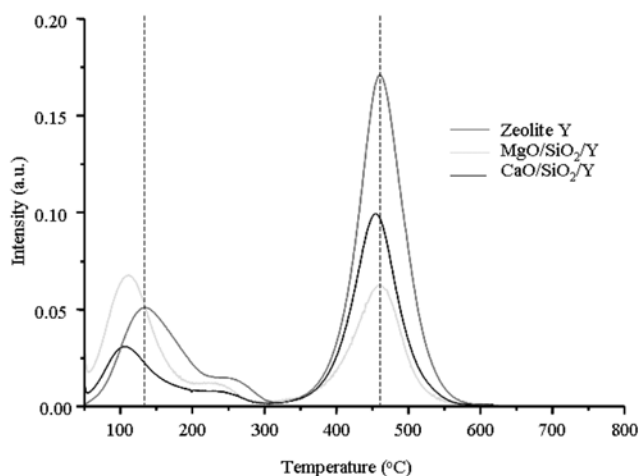
the amounts of coke deposited on the MgO and CaO neutralized and un-neutralized catalysts were analyzed by TPO, the profiles of which are shown in Fig. 6. Compared with the un-neutralized zeolite Y catalyst, the amount of coke deposited on the neutralized MgO/SiO$_2$/Y and CaO/SiO$_2$/Y catalysts decreased, indicating that the number of acid sites located on the external surface had decreased. Furthermore, on the catalysts modified by the stronger alkali compounds, such as CaO, the TPO band shifted to a lower temperature, indicative of shorter coke chains. These results suggest the acid sites on the external surface of zeolite Y crystals were significantly neutralized with the alkali ingredient via the mechanochemical method.

CONCLUSION

The acid sites on the external surface of Zeolite Y crystals could be selectively neutralized by using the mechanochemical method with alkali earth metal oxides supported on the micro spherical non-porous silica. For the *m*-xylene isomerization, the neutralized zeolite Y catalysts exhibited higher selectivities to *o*- and *p*-xylene and longer catalytic lives, particularly over MgO/SiO$_2$/Y and CaO/SiO$_2$/Y, than the un-neutralized catalyst, with a corresponding decrease in coke formation on the acid sites located on the external surface of the crystals. The bulkiest isomer *m*-xylene was selectively retained in the pores. Its higher effective residence time in the pores allowed conversion to *p*- and *o*-xylene. Xylene isomerization catalyzed by Brönsted acid sites not in the pore mouth of the zeolite also on the external surfaces were largely suppressed after neutralized.

ACKNOWLEGMENT

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Fig. 6. The TPO curves for 3.0 wt% MgO/SiO$_2$/Y and MgO/SiO$_2$/Y after *m*-xylene isomerization at a reaction temperature of 450 °C for 20 h.