Effect of Zeolite Crystallite Size on Pt/KL Catalysts Used for the Aromatization of n-Octane

SUPAK TRAKARNROEK,1 SOMLAK ITTISANRONNACHAI,1 SIRIPORN JONGPATIWUT,1 THIRASAK RIRKSOMBOON,1 SOMCHAI OSUWAN,1 AND DANIEL E. RESASCO2

1The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
2School of Chemical, Biological, and Materials Engineering, The University of Oklahoma, Norman, Oklahoma, USA

The effects of varying zeolite crystallite size in n-octane aromatization over Pt/KL have been studied on a series of catalysts. Various KL zeolites were synthesized via microwave-hydrothermal treatment, which allows for good control of crystallite morphology. Zeolites with different crystallite sizes were prepared by varying aging time (17–24 h), amount of barium (0–445 ppm), and seeding (0–8 wt%). The results showed that higher aging time resulted in smaller zeolite crystallite size, whereas the addition of barium resulted in larger crystallite size. Moreover, the addition of seeding reduced the crystallite size from 1.47 to 0.94 μm. Pt supported on different zeolite catalysts (Pt/KL) was prepared by vapor phase impregnation (VPI). The fresh catalysts were characterized by DRIFTS of adsorbed CO and volumetric hydrogen chemisorption. The results indicated that Pt clusters are well dispersed inside the zeolite channel in all the catalysts prepared. The aromatization of n-octane was tested on the different catalysts at 500°C and atmospheric pressure. It was found that the catalytic activity of all catalysts dropped rapidly after about 200 min on stream due to coke plugging inside the pore of the KL zeolite. It was also observed that less ethylbenzene (EB) and o-xylene (OX) were obtained as the conversion increased because both EB and OX are converted to smaller molecules such as benzene, toluene, etc., by secondary hydrogenolysis. Furthermore, the EB/OX ratio increases with zeolite crystallite size due to an enhanced preferential conversion of the larger OX molecules compared to the narrower EB as their path through the pores is restricted.

Keywords Microwave-hydrothermal treatment technique; n-Octane aromatization; Zeolite

Introduction

The aromatization of n-alkane is an important reaction used to obtain high-value-added products from a naphtha feedstock that is abundant in refinery operations. This reaction can be used in many industrial applications and can be carried out with...
either bifunctional (acid-metal) or monofunctional (only-metal) catalysts. The advantage of using monofunctional catalysts is that they are not active for isomerization paths, which typically occur on the bifunctional catalysts and result in lower selectivity to aromatics (Meriaudeau and Naccache, 1997). Platinum supported on alkaline LTL zeolite (Pt/KL) is an efficient catalyst for the dehydrocyclization of n-hexane into benzene (Bernard, 1980; Hunges et al., 1986; Tamm et al., 1988). However, for n-octane aromatization, Pt/KL catalysts are not as effective as for n-hexane aromatization. Although Pt/KL catalysts prepared by vapor phase impregnation (VPI) provide very high dispersion of Pt clusters that remain inside the channels of the zeolite (Jacobs et al., 1996, 2001), the selectivity for n-octane aromatization is still low and quickly drops after a few hours on stream (Jongpatiwu et al., 2003). The product distribution shows benzene and toluene as major aromatic products, with small quantities of ethylbenzene (EB) and o-xylene (OX), which are the only two expected products from a direct six-membered ring closure. The pore size of the KL zeolite is 0.71 nm, that is, larger than the critical diameter of EB but smaller than that of OX, thus OX diffuses through the zeolite crystal much more slowly than EB. As a result, OX is preferentially converted to benzene and toluene before escaping from the pore of zeolite. In our previous study (Jongpatiwu et al., 2003) it was proposed that the pore length of the zeolite should have a great impact on product distribution and catalyst life.

The idea of short-channel KL zeolite has been previously discussed by Treacy (1999) to minimize the problem of Pt entombment due to metal agglomeration and coking. Furthermore, zeolites with small crystallite size provide advantages over zeolites with large crystallite size by enhancing the ratio of surface area to mass. These advantages are higher diffusion rates and a lower rate of deactivation by pore plugging (Verduijn et al., 2001). Many researchers have focused on synthesis of KL zeolites by conventional hydrothermal treatment (Break and Nancy, 1965; Wortel, 1985; Verduijn, 1987, 1991; Koetsier and Verduijn, 1991). However, in the hydrothermal treatment, the heat transfer by both convection and conduction results in a slow temperature increase, which lengthens the crystallization time. The use of microwave radiation has been found to be advantageous in the production of microporous crystalline materials in comparison to the conventional method. The volumetric heat generated by microwaves results in a more homogeneous nucleation process and yields crystalline materials in shorter times than the conventional method (Chu et al., 1998). Furthermore, it is a clean and economical heating system (Park and Komarneni, 1998; Romero et al., 2004). To reduce the crystallite size of zeolite, crystallization conditions and composition-dependent parameters were investigated (Renzo, 1998). It was found that the aging process can reduce the size of zeolite crystals in the final product (Gontier and Tuel, 1996; Qinghua et al., 2001). Incorporation of colloidal L zeolite seeds into the gel before crystallization can also reduce the crystallite size (Break and Nancy, 1965).

In this contribution, we attempt to evaluate the effects of varying the zeolite crystallite size on the n-octane aromatization over Pt/KL catalysts. First, several KL zeolites were synthesized by using microwave hydrothermal treatment. The effects of synthesis conditions including aging time, amount of barium, and seeding on crystallite size of zeolite KL were investigated. The synthesized KL zeolites were characterized using X-ray diffraction (XRD), nitrogen adsorption (BET), scanning electron microscopy (SEM), X-ray fluorescence (XRF), Fourier transform-infrared spectroscopy (FT-IR), and dynamic light scattering spectrometry (DLS). Pt supported
on the synthesized KL zeolites was prepared by vapor phase impregnation (VPI) and tested for activity and selectivity of n-octane aromatization at 500°C and atmospheric pressure. This impregnation method has been shown to be the most effective to maximize selectivity to benzene from n-hexane (Jacobs et al., 1999, 2001; Jongpatiwut et al., 2003). The fresh catalysts were characterized by means of FT-IR of adsorbed CO, which provides information about the location of the Pt particles and hydrogen chemisorption that quantifies the metal dispersion. Temperature programmed oxidation (TPO) was used to analyze the amount and nature of coke deposited on the catalysts.

**Experimental Section**

**Materials**

n-Octane (C₈H₁₈) of minimum 99% purity was obtained from Merck. The commercial K-LTL zeolite (HSZ-500, SiO₂/Al₂O₃ = 6, surface area = 280 m²/g) was obtained from Tosoh, Japan. Platinum (II) acetylacetonate ([CH₃COCH=CO(CH₃)]₂Pt) was obtained from Alfa Aesar. Colloidal silica (40 wt% suspension) was obtained from Aldrich. Potassium hydroxide (KOH) and barium hydroxide (Ba(OH)₂) were supplied by Carlo Erba. Aluminium hydroxide (Al(OH)₃) of 99.8% purity was acquired from Merck.

**Synthesis of KL Zeolites**

The KL zeolites were synthesized from a mixture of silicate and potassium aluminate solutions to attain the following composition: 2.65K₂O: 0.0032BaO:0.5Al₂O₃: 10SiO₂: 159H₂O. The potassium aluminate solution was prepared by dissolving 2.64 g of Al(OH)₃ in 8.15 M of KOH solution. The silicate solution was prepared by mixing colloidal silica with 2.8 mM of Ba(OH)₂ solution and stirring for 15 min. The silicate and aluminate solutions were then mixed and stirred vigorously by a mechanical stirrer for different periods of aging time at ambient temperature. After that, the gel mixture was transferred to a microwave vessel and heated using a MARS5 microwave machine up to 170°C within 2 min and maintained at that temperature for 15–50 h. As a comparison sample, an L zeolite synthesized in a conventional manner was aged for 24 h and transferred to a 250 mL Teflon-lined autoclave that was then placed in an oven at 170°C and held at that temperature for 96 h. Moreover, the effects of adding barium (0–445 ppm) and seeding (0–8 wt%) were studied. The resultant material was washed with deionized water until a pH of 10 was reached. Then, it was centrifuged to separate the solid phase from the solution. The solid product was dried in an oven at 110°C overnight and then calcined at 500°C in flowing air. The synthesized zeolites are named by their synthesized conditions and compositions as listed in Table I.

**Characterization of the Synthesized KL Zeolites**

The structures of synthesized KL zeolites were evaluated using a Rigaku X-ray diffractometer, with Cu-K line as incident radiation, and a filter at a scanning rate of 5°/min. The Si/Al ratio was measured using an SRS 3400 Bruker X-ray fluorescence spectroscope, with 99.8% boric acid as binder. The crystal morphology
<table>
<thead>
<tr>
<th>Zeolite*</th>
<th>Ageing time (h)</th>
<th>Cryst. time (h)</th>
<th>Amount of Ba (ppm)</th>
<th>Amount of seeding (wt%)</th>
<th>Crystallite size (µm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Si/Al ratio</th>
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<tr>
<td>Commercial KL</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.53</td>
<td>302</td>
<td>0.206</td>
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<td>n/a</td>
<td>n/a</td>
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<tr>
<td>A24/C96/B1**</td>
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<td>0.112</td>
<td>3.20</td>
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</table>

*Ax represents aging time of xx h, Cxx represents crystallization time of h, Bx represents the amount of barium with 115, 230, and 345 ppm, where x = 1, 2, and 3, respectively, and Sx represents the seeding used of x wt%.

**Synthesized by using conventional hydrothermal treatment.
was investigated using a JEOL 5200-2AE scanning electron microscope. A Malvern 4700 DLS spectrophotometer equipped with Ar-ion laser as a light source was used to determine the average particle size. The detector was fixed at 60° with respect to incident beam direction. The photomultiplier aperture used was 150 μm. Nitrogen adsorption was employed to analyze the surface area and pore volume of synthesized KL zeolites. The adsorption isotherms were collected at 77 K using a Thermo Finnigan sorptomatic model 1100 series.

**Catalyst Preparation**

The various Pt/KL catalysts investigated were prepared by vapor phase impregnation (VPI) of the different L zeolites. Prior to impregnation, the zeolite support was dried in an oven at 110°C overnight and calcined at 500°C in flowing dry air of 100 cm³/min-g for 5 h. The Pt/KL catalysts were prepared by physically mixing a weighed amount of platinum (II) acetylacetonate (Pt(acac)₂) with a proper amount of dry zeolite support under nitrogen atmosphere. The mixture was then loaded in a tubular reactor before being subjected to a helium flow of 5 cm³/min-g. The reactor was gradually ramped to 40°C and held for 3 h, and ramped again to 60°C and held for 1 h. After that, it was further ramped to 115°C at which the mixture was held for 1 h to sublime the Pt(acac)₂. After being cooled down to room temperature, it was ramped to 350°C in flowing air and held for 2 h to decompose the platinum precursor. The actual metal content was analyzed by a Varian model SpectraA-300 atomic absorption spectroscope.

**n-Octane Aromatization Activity of the Catalysts**

The catalytic activity studies were conducted at atmospheric pressure in a 0.5-inch glass tube inserted with an internal K-type thermocouple for temperature measurement and control. The reactor was a single-pass and continuous-flow type. Two hundred milligrams of the catalysts were used in each run. Prior to reaction, the catalyst was slowly ramped in flowing H₂ for 2 h up to 500°C and reduced in situ at that temperature for 1 h. n-Octane was introduced to the system using a syringe pump. In all experiments, the hydrogen-to-n-octane molar ratio was maintained at 6:1. The products were analyzed using a Shimadzu GC-17A equipped with an HP-PLOT/Al₂O₃ “S” deactivated capillary column. The gas chromatography (GC) column temperature was programmed to obtain an adequate separation of the products. The GC oven temperature was first kept constant at 40°C for 10 min and then it was linearly ramped at a heating rate of 5°C/min to 195°C and held for 30 min.

**Catalyst Characterization**

**DRIFTS of Adsorbed CO**

The fresh Pt/commercial KL and Pt/synthesized KL catalysts were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using CO as a probe in a Bruker Equinox 55 spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. Experiments were performed in a diffuse reflectance cell from Harrick Scientific, type HVC-DR2, with ZnSe windows. For each IR spectrum, a background was collected on the sample reduced in situ under a flow of H₂ at 300°C for 1 h and purged in He for 30 min at ambient temperature. Then, a flow
of 5% CO in He was passed through the sample for 30 min, followed by a purge in He flow for 30 min. After such a treatment, the spectrum of adsorbed CO was collected.

**Hydrogen Chemisorption**

Hydrogen uptake and degree of dispersion were determined using a pulse technique (Thermo Finnigan model TPDRO 1100). Prior to pulse chemisorption, the sample was reduced in H₂ atmosphere at 500°C for 1 h. Then it was purged with N₂ at 500°C for 30 min and cooled down to 50°C in flowing N₂. H₂ pulses (purged H₂, 0.4 mL) were injected onto the sample at 50°C until saturation was observed.

**TPD of Isopropylamine**

The acidity of the prepared catalyst was tested by the amine temperature programmed desorption (TPD) technique developed by Gorte and coworkers (Parrillo et al., 1990). The test was conducted in a 1/4-inch quartz reactor. First, 30 mg of sample was pretreated at 500°C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to room temperature and then 30 μL of isopropylamine was injected over the sample. After removing the excess of isopropylamine by flowing He overnight, the sample was linearly heated to 700°C at a heating rate of 10°C/min. Masses 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propene, and ammonia, respectively. The amount of desorbed propene was calibrated with 5 mL pulses of 2% propene in He.

**Temperature Programmed Oxidation (TPO)**

Temperature programmed oxidation (TPO) was employed to analyze the amount and characteristics of coke formation on the spent catalysts. TPO of the spent catalysts was performed in a continuous flow gas of 2% O₂ in He, and the temperature was linearly increased with a heating rate of 12°C/min. The oxidation reaction was conducted in a 1/4-inch quartz fixed-bed reactor. The spent catalyst was dried at 110°C overnight. Thirty milligrams of dried sample were placed in between the layers of quartz wool. The sample was flushed by flowing 2% O₂ in He for 30 min before the TPO was performed. CO₂ produced by the oxidation of coke species was further converted to methane using a methanizer filled with 15% Ni/Al₂O₃ and operated at 400°C. The methane was analyzed as a function of temperature using a flame ionization detector (FID).

**Results and Discussion**

**Synthesis of KL Zeolites**

**Effect of Aging and Crystallization Times**

For the controlled synthesis of KL zeolites by the microwave-hydrothermal treatment technique (MH), aging times and crystallization times were systematically varied. In this way, the optimum conditions to produce crystalline KL zeolites were determined. The aging times and crystallization times were varied in the range of 0–30 h and 20–50 h, respectively. XRD patterns of selected synthesized zeolites are shown in Figure 1. Their crystallinity as a function of aging and crystallization times is presented in Figure 2. It was found that when the gel was not aged, amorphous phase was observed even though the crystallization time was increased. This is because with no aging processes, the solution does not have enough nucleation
centers to induce the crystal growth (Slangen et al., 1997). Furthermore, if the gel was aged for less than 17 h, a mixture of KL zeolites, amorphous phase as well as other crystal phases, was observed. The appearance of pure crystalline KL was detected only at aging times longer than 17 h and crystallization time of 30 h. Crystalline KL mixed with amorphous material was obtained when the crystallization times were shorter than 30 h. In contrast, other crystal phases were formed when the crystallization time was longer than 30 h, as shown in Figure 3. In addition, it was found that to synthesize zeolite by conventional hydrothermal treatment (CH), much longer crystallization times (96 h) were needed, compared with much shorter times for microwave treatment (see Figure 1).

FT-IR is another technique that can be used to verify the crystallinity of the synthesized zeolites. Spectra of the synthesized zeolites prepared with different aging times and compositions are compared in Figure 4 to those of commercial KL zeolite. As previously reported (Joshi et al., 1990), an absorption band centered at 620 cm$^{-1}$.

**Figure 1.** XRD patterns of synthesized KL zeolites obtained with different aging times at crystallization temperature of 170°C and crystallization time 30 h.

**Figure 2.** Characteristics of products obtained with various aging and crystallization times.
is characteristic of crystalline KL, and such results are in good agreement with those obtained by XRD (Figure 1).

The Si/Al ratio, particle size, surface area, and pore volume of all the synthesized and commercial KL zeolites were determined by XRF, DLS, and BET, respectively. The results are given in Table I. It was found that under the same conditions, the zeolites obtained with 24 h aging time resulted in smaller crystallite size (1.47 μm) than those obtained with 17 h aging time (1.81 μm). This result is in good agreement with a previous study done by Ertl et al. (1997). They reported that the zeolite prepared with longer aging time resulted in smaller crystal size because at longer aging time, the concentration of nuclei was enhanced. However, aging times longer than 30 h did not result in further reduction of crystallite size. The crystallite sizes of synthesized zeolites are still larger than those of the commercial KL by a factor of three. Also, the surface area and pore volume of the synthesized KL zeolites are

**Figure 3.** XRD patterns of synthesized KL zeolite obtained with different crystallization times at crystallization temperature of 170°C and ageing time of 17 h.

**Figure 4.** FT-IT spectra of synthesized KL zeolite obtained with different aging times and different crystallization times compared to commercial KL zeolite.
much lower than those of the commercial KL. XRF results showed that the Si/Al ratios for all synthesized KL zeolites are between 3.2 and 3.5 while that of the commercial KL is 3.0. SEM images of the synthesized and commercial KL zeolites are shown in Figure 5. It is clearly seen that the synthesized KL zeolites have a flat-cylindrical shape whereas the commercial KL has an irregular spherical shape.

Effect of Barium
It has been reported that the formation of KL zeolite can be promoted by addition of Ba (Verduijn, 1987, 1991). In this report, the effect of barium on the formation of KL zeolite was investigated by varying the amount of barium from 0 to 445 ppm. The synthesis gel was aged for 24 h and heated to 170°C for 30 h for the crystallization process. All synthesized KL zeolites were characterized by FT-IR. The results given in Figure 6 show that, without Ba, the characteristic band of KL zeolite at 620 cm⁻¹ was not observed. That is, the product was amorphous aluminosilicate.

Figure 5. SEM images of synthesized KL zeolite crystal obtained with (a) commercial KL zeolite and (b) aging time of 24 h and crystallization time of 30 h (A24/C30/B1).

Figure 6. FT-IT spectra of synthesized KL zeolites obtained with different amounts of barium at aging time of 24 h and crystallization time of 30 h.
However, when small amounts of barium were added, crystalline KL was obtained. In addition, it was found that a higher amount of barium resulted in a larger crystallite size, as shown in Table I. The crystallite size increased from 1.47 to 2.07 μm when the amount of barium was increased from 115 to 445 ppm. However, the surface area, pore volume, and Si/Al ratio were not significantly different among the various zeolites prepared with different amounts of Ba.

Effect of Seeding
Seeding is a technique of adding small amounts of small particles of material to help crystallization of the synthesis gel; this is typically done just before the crystallization step to direct the crystallization process towards a desired zeolite structure. Seeding can increase the crystallization rate, resulting in shorter crystallization time, and also helps control the size of the final crystals (Ertl et al., 1997). If zeolite is formed at a lower temperature and shorter crystallization time, the crystallite size obtained should be smaller (Hincapie et al., 2004). Therefore, crystallization time is an additional parameter that we have adjusted in this work to control the crystallite size. Here, we have used commercial KL zeolite as a seed. The amount of seed added to the mixture was varied from 0 to 8 wt%. The crystallization time was reduced from 30 to 25 h when seed was added. From Table I, it can be seen that the amount of seed when ranging from 2 to 8 wt% resulted in smaller crystals than other synthesized zeolites; compared to zeolites without seeding at crystallization time of 30 h, the addition of seed resulted in the reduction of crystal size from 1.47 to 0.94 μm, as shown in Figure 7.

Characterization of the Fresh Catalysts
To study the effect of crystallite size on catalytic activity and selectivity for n-octane aromatization, a number of synthesized zeolites with different crystallite sizes were selected for preparing Pt/KL catalysts and compared with Pt/KL catalysts prepared with commercial KL zeolite (0.53 μm). As summarized in Table I, the zeolite samples used to prepare catalysts were A24/C25/B1/S5 (0.94 μm), A24/C30/B1 (1.47 μm), A17/C30/B1 (1.81 μm), and A24/C30/B3 (2.07 μm), where Axx stands for aging

![Figure 7. SEM images of synthesized KL zeolite obtained with (a) 0 wt% seeding at aging time of 24 h and crystallization time of 30 h and (b) 5 wt% seeding at aging time of 24 h and crystallization time of 25 h.](image-url)
time in h; Cx for crystallization time in h; Bx for the amount of Ba with 115, 230, and 345 ppm where x = 1, 2, and 3, respectively; and Sx for the seeding used of x wt% the number in parentheses is the crystallite size. For the sake of simplicity, in the rest of the text the catalysts are identified only by the average crystallite size, i.e., Pt/KL-0.94, Pt/KL-1.47, Pt/KL-1.81, Pt/KL-2.07, and Pt/KL-0.53, respectively.

All Pt/KL catalysts were analyzed by diffuse reflectance FT-IR of adsorbed CO (DRIFTS) and pulse hydrogen chemisorption techniques. As in previous studies by our group, DRIFTS has been employed to investigate the size and location of the Pt clusters in the KL zeolite (Bernard, 1980; Hunges et al., 1986; Jongpatiwut et al., 2003). A typical FT-IR spectrum of CO adsorbed on Pt/KL exhibits bands in the region 2150–1900 cm⁻¹. The band below 2050 cm⁻¹ represents Pt clusters located inside the channels of the L zeolite, whereas the band between 2050 and 2075 cm⁻¹ corresponds to larger Pt clusters located at the pore mouth of the L zeolite, and the bands above 2075 cm⁻¹ represent Pt clusters located outside the L zeolite pores. DRIFTS spectra for different Pt/KL catalysts are shown in Figure 8. The strong absorption bands at the lower frequencies for all the catalysts in series indicate that, even though the crystallite sizes are different, all of the catalysts present a large fraction of small Pt clusters inside the channels of KL zeolite and a small fraction of Pt clusters located at the pore mouth and outside of the zeolite pores.

Hydrogen chemisorption was used to determine the Pt dispersion of the fresh catalysts, after reduction at 500°C. The Pt dispersions expressed in terms of the H/Pt ratio are reported in Table II. Most of the catalysts yielded H/Pt ratios higher than unity, indicating a very high state of dispersion, consistent with the formation of small Pt clusters that have a particle size diameter of less than 1 nm (Davis, 1994).

TPD of isopropylamine was performed on selected catalysts, i.e., Pt/KL-0.53, Pt/KL-1.81, and Pt/KL-2.07. The result illustrates that the prepared catalysts have no residual acidity as no peak of m/e = 41, 17 was found during the course of increasing temperature. In addition, there is high fraction of peak of m/e = 44, which corresponds to the unreacted isopropylamine, as shown in Figure 9.

Figure 8. DRIFTS spectra of CO adsorbed on different crystallite sizes of Pt/KL catalysts.
Catalytic Activity Measurements

The prepared Pt/KL catalysts with different zeolite crystallite sizes were tested for their catalytic activity and selectivity of n-octane aromatization. The conversion and selectivity to total aromatics are shown in Figures 10(a) and 10(b), respectively. After 10 min on stream, the n-octane conversions are almost 100% for all catalysts. However, these catalysts deactivated quickly during the first few hours on stream due to coke deposition that plugs the pores of the KL zeolite (Treacy, 1999). Regardless of their crystallite size, all catalysts exhibited similar selectivity towards the total aromatics. Moreover, all catalysts resulted in low C8 aromatics selectivity (ethylbenzene (EB), o-xylene (OX), m-xylene (MX), and p-xylene (PX)) when compared to the selectivity for total aromatics; see Table III. The major aromatics products were benzene and toluene, which are the secondary products from hydrogenolysis of EB and OX over the Pt clusters, as has been reported in our previous work (Jongpatiwut et al., 2003).

The EB/OX ratio is a good indicator of the importance of diffusional effects in the reaction (Jongpatiwut et al., 2003). The ratio of the primary products EB/OX is about unity from the direct aromatization on Pt surfaces, free of diffusional effects. In fact, a ratio of unity is observed over nonmicroporous Pt/SiO₂ catalysts (Jongpatiwut et al., 2003). On the other hand, the EB/OX ratio becomes greater than 1 when there is pore restriction, and it gets greater as the diffusional effects become more

### Table II. Analysis of fresh and spent catalysts

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<tr>
<th>Catalysts</th>
<th>Zeolite support</th>
<th>Pt content (wt%)</th>
<th>H/Pt after reduction at 500°C</th>
<th>Coke deposited after rxn with n-C8 for 550 min (wt%)</th>
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**Figure 9.** Mass spectra of TPD of isopropylamine of (a) Pt/KL-0.53 and (b) Pt/KL-2.07.
pronounced, for example, by carbon deposition. Since the critical size of the OX molecule is larger than that of EB, the diffusion of OX is slower than that of EB and it is easily converted to smaller molecules such as benzene, toluene, and methane by secondary hydrogenolysis. Figure 11 shows the evolution of EB/OX ratio as a function of zeolite crystallite size. It can be observed that the ratio rapidly increased with increasing crystallite size. It is clear that the difference in rate of diffusion out of the zeolite of EB and OX after being formed makes the slower molecule (OX) more

Table III. Properties of various catalysts tested for n-octane aromatization after 550 min

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<th>Properties</th>
<th>Pt/KL-0.53</th>
<th>Pt/KL-0.94</th>
<th>Pt/KL-1.47</th>
<th>Pt/KL-1.81</th>
<th>Pt/KL-2.07</th>
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<tr>
<td>Conversion (%)</td>
<td>23.3</td>
<td>21.8</td>
<td>25.2</td>
<td>18.2</td>
<td>29.2</td>
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<tr>
<td>Product distribution (%)</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>C1–C5</td>
<td>19.7</td>
<td>22.5</td>
<td>21.8</td>
<td>21.6</td>
<td>24.6</td>
</tr>
<tr>
<td>Total enes (C6–C8enes)</td>
<td>12.4</td>
<td>9.7</td>
<td>5.5</td>
<td>8.1</td>
<td>5.5</td>
</tr>
<tr>
<td>Total aromatics</td>
<td>67.9</td>
<td>67.8</td>
<td>72.7</td>
<td>70.2</td>
<td>69.9</td>
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<tr>
<td>Aromatics selectivity (%)</td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td>19.0</td>
<td>17.9</td>
<td>21.3</td>
<td>18.2</td>
<td>23.9</td>
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<tr>
<td>Toluene</td>
<td>27.6</td>
<td>31.7</td>
<td>34.3</td>
<td>32.4</td>
<td>28.3</td>
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<tr>
<td>EB</td>
<td>13.9</td>
<td>12.7</td>
<td>12.4</td>
<td>14.9</td>
<td>15.2</td>
</tr>
<tr>
<td>m-, p-Xylene</td>
<td>1.8</td>
<td>1.6</td>
<td>1.6</td>
<td>1.7</td>
<td>0.0</td>
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<tr>
<td>o-Xylene</td>
<td>5.5</td>
<td>3.9</td>
<td>3.0</td>
<td>3.0</td>
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<tr>
<td>EB/OX ratio</td>
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<td>3.3</td>
<td>4.2</td>
<td>4.9</td>
<td>6.3</td>
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<tr>
<td>TOF (s⁻¹)*100</td>
<td>3.66</td>
<td>4.2</td>
<td>5.24</td>
<td>3.75</td>
<td>6.82</td>
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susceptible to secondary conversion as the crystallite size increases than the faster molecule (EB).

**Characterization of Spent Catalysts**

The spent catalysts were analyzed by a temperature programmed oxidation (TPO) technique to determine the amount of coke deposited after n-octane aromatization.

**Figure 11.** Variation of EB/OX ratio obtained from different Pt/KL catalysts at 460 min time on stream as a function of zeolite crystallite size. Reaction conditions: temperature = 500°C, WHSV = 5 h⁻¹, and H₂/HC = 6.

**Figure 12.** TPO profiles of coke deposits left over the different catalysts after 550 min on stream during n-octane aromatization. Reaction conditions: temperature = 500°C, WHSV = 5 h⁻¹, and H₂/HC = 6.
reaction for 550 min. The results are summarized in Table II. The results show that significantly smaller amounts of coke were deposited on the Pt/synthesized KL zeolites than on the Pt/commercial KL. Moreover, the TPO profiles shown in Figure 12 indicate that a large fraction of the excess carbon deposited on the Pt/commercial KL was oxidized only at high temperatures. Such a high temperature band is thought to be due to carbon blocking zeolite pores (Jongpatiwut et al., 2005). The significant differences shown in TPO and in the EB/OX ratio suggest that the catalysts prepared with smaller zeolite crystallites should behave better in terms of selectivity and resistance to deactivation. It is postulated that the rate of deactivation should be much less pronounced at higher pressures, under conditions in which the presence of high partial pressures of hydrogen can help remove the coke precursors. It is possible that under such conditions, the effect of crystallite size will be more pronounced than that presented in this work.

Conclusions

It has been shown that during the synthesis of KL zeolite by the microwave thermal method, parameters such as aging time, amount of Ba, and amount of seeding have an important effect on the resulting zeolite crystallite size. It was found that small crystallites can be obtained using long aging times and larger amounts of seeding material. The degree of zeolite crystallinity is greatly improved by the addition of Ba, but at the same time the size of the zeolite crystallite increases with increasing amounts of Ba.

Regarding the catalytic performance, it was found that the crystal size had a great effect on the observed EB/OX ratio. The larger crystallite size gave the higher EB/OX ratio due to an enhanced restriction to the diffusion of OX through the zeolite channels. In order to maximize C8-aromatics by avoiding secondary hydrogenolysis, zeolites with shorter pore length are required.

Acknowledgments

This work was supported by the Thailand Research Fund (TRF), the Petroleum and Petrochemical Technology Consortium (PPT) through CU-PPC of the Petroleum and Petrochemical College, Chulalongkorn University, and Ratchadapiseksomphon Endowment Fund of Chulalongkorn University. We gratefully acknowledge the Oklahoma Center for Advancement of Science and Technology (OCAST) for providing financial support of the work accomplished at the University of Oklahoma.

References


