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Short communication

Effect of steam during catalytic cracking of *n*-hexane using P-ZSM-5 catalyst

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ABSTRACT

Phosphorus-modified ZSM-5 (P-ZSM-5) catalyst was active for steam cracking of *n*-hexane to produce propylene and ethylene; however, the P-ZSM-5 catalyst deactivated because of both dealumination and coke deposition, which were strongly influenced by the steam to *n*-hexane ratio in the reactant flow. The amount of coke deposition increased with decreasing the steam to *n*-hexane ratio from the TG-DTA measurement. The steam could reduce the reactions of the light olefins to BTX and coke and enhance the yield of the light olefins; however, the excess steam deactivated the ZSM-5 catalysts irreversibly via dealumination.

1. Introduction

Recently, huge energy is currently consumed in petrochemical industry to produce light olefins from naphtha by thermal steam cracking without catalysts at more than 1073 K [1] and worldwide propylene is produced from the steam cracking of naphtha (ca. 70%). Development of a catalysis technology to produce the light olefins from naphtha is required for the decrease of reaction temperature (873–973 K). ZSM-5 catalysts have been reported to be effective for naphtha cracking to provide high yields of light olefins [2–11]; however, the deactivation of ZSM-5 catalysts is an issue that is of greatest concern in commercial olefin production from naphtha. The deactivation of ZSM-5 catalysts is mainly caused by dealumination of ZSM-5 and coke deposition [12, 13]. The naphtha is usually carried with diluent gas on a commercial scale to inhibit coke deposition. Using an inactive gas other than steam such as nitrogen gas costs too much; thus, the steam should be used as a diluent for naphtha cracking and can reduce the coke deposition effectively. In the case of catalytic cracking without steam flow, the deactivation of ZSM-5 catalysts is mainly caused by the coke deposition [8–11]. The deactivated catalyst due to the coke deposition can be regenerated by calcination in a fluid catalytic cracking process; however, the coke deposition causes pressure drop and collapse of catalyst pellets in a fixed bed reactor as well as the catalyst deactivation. Thus, the steam is used as an inexpensive diluent of naphtha during the catalytic cracking for the decrease of coke deposition [14]; however, the catalysts are also deactivated by the dealumination of ZSM-5 in the case of catalytic steam cracking [15–17]. The phosphorus modification could especially enhance the resistance against the dealumination of ZSM-5 [16, 18–20]. We previously found that both the amount of phosphorus loading and the calcination temperature influenced the catalyst durability [21] and that 80% of initial activity was maintained over the phosphorus-modified ZSM-5 (P-ZSM-5) catalyst calcined at 1073 K for steam cracking for 30 h.

Understanding the effect of steam–hexane ratio on the deactivation of P-ZSM-5 and product distribution should be critical to evaluate the steam cracking of naphtha using ZSM-5 catalysts; however, surprisingly few attempts have so far been made at demonstrating the effect of steam–hexane ratio. In this manuscript, we investigated the effect of steam–hexane ratio during the catalytic steam cracking of *n*-hexane using the P-ZSM-5 catalyst, where *n*-hexane was a model compound of the naphtha.

2. Experimental

2.1. Catalyst

H-ZSM-5 powder ($SiO_2/Al_2O_3 = 60$) used in this work was purchased from JGC Catalysts and Chemicals Ltd. The phosphorus-modified H-ZSM-5 catalyst (P-ZSM-5) was prepared by an impregnation method of

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H-ZSM-5 and an aqueous solution of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 0.12 mol dm^{-3}, Nacalai Tesque, Inc.) as follows [21]. The slurry of H-ZSM-5 and aqueous solution of $(NH_4)_2HPO_4$ was stirred for 1 h at 313 K and evaporated to dryness at 323 K under reduced pressure by a rotary evaporator. Then, the sample was dried at 393 K for 10 h in an oven and calcined at 873 K (heating rate 0.167 K s^{-1}) for 5 h in flowing dry air. The amount of phosphorus was 1 wt.% of the catalyst.

2.2. Catalytic activity test

Catalytic steam cracking of *n*-hexane was carried out in a packed-bed reactor. The catalysts (0.2 g, pellet diameter of 0.5–1.0 mm, without using a binder) were placed within a quartz tube (10 mm diameter) with a K-type thermocouple enclosed in a quartz sheath in contact with the catalyst bed [13,21]. Water and *n*-hexane were introduced using syringe pumps into the reactant stream by vaporizing into a stainless line kept at 423 K. All transfer lines from the injection point to the gas chromatograph were kept above 423 K to avoid condensation. Dinitrogen gas (3.0 cm^{-3} min^{-1}) as an internal standard for gas chromatography analysis was metered by an electronic flow controller. The reaction conditions were the following: reaction temperature of 923 K, and WHSV(hexane) 11 h^{-1}, W/F 8.0 g-cat h/mol-hexane. The flow rate of *n*-hexane was 9.7 sccm (standard cubic centimeters per minute at 298 K) (3.1 liquid-cm^{-3} h^{-1} at ambient condition) and that of steam was 0, 4.6, 9.2, 22.9, and 45.9 sccm (0, 0.2, 0.4, 1.0, and 2.0 liquid-cm^{-3} h^{-1} at ambient condition, respectively) where steam–hexane (S/nC6) ratios were 0, 0.1, 0.2, 0.5, and 1.0 (wt/wt), respectively. The concentrations of reactant and products were measured by on-line gas chromatography using a MolecularSieve 13X column (for

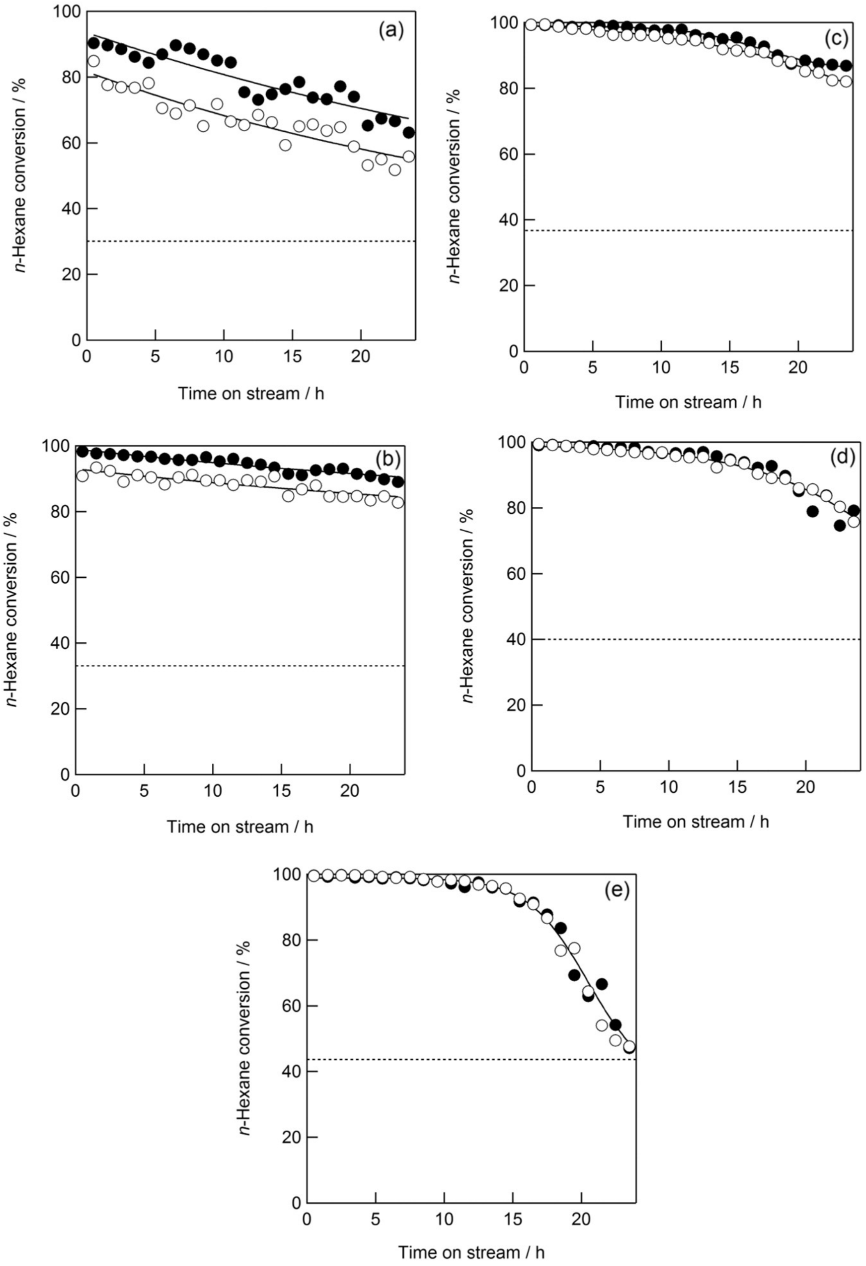

Fig. 1. Conversion of *n*-hexane during steam cracking at 923 K with different steam–hexane ratios over P-ZSM-5. The P-ZSM-5 catalyst was treated under O_2(20%)/He(80%) flow at 893 K for 5 h after 24 h of time on stream (1st run, filled circles) and used again for 24 h of time on stream (2nd run, unfilled circle). The reaction conditions were the following: reaction temperature of 923 K, WHSV(hexane) 11 h^{-1}, W/F 8.0 g-cat h/mol-hexane, and the steam–hexane ratios (wt/wt): (a) 1.0, (b) 0.5, (c) 0.2, (d) 0.1, and (e) 0. Dottted line indicates *n*-hexane conversion during thermal cracking without the P-ZSM-5 catalysts.

dinitrogen, carbon monoxide, and methane) and a PorapakTypeQ column (for carbon dioxide, methane, ethane, and ethylene) with a thermal conductivity detector and using a SP1700 column (for methane, propane, propylene, *n*-butane, *i*-butane, *n*-pentane, and *n*-hexane) and a Gaskuropack54 column (for methane, *n*-heptane, benzene, toluene, and xylene) with a flame ionization detector. Conversion of *n*-hexane and product yield based on carbon were defined as given below.

$$\text{Conversion }(\%) = \left(1 - \frac{\text{mol of unreacted } n\text{−hexane in products}}{\text{mol of reactant } n\text{−hexane}}\right) \times 100 \qquad (1)$$

$$\text{Yield based on carbon }(\text{C }\%) = \left(\frac{\text{mol of carbon atom in product}}{\text{mol of carbon atom in reactant } n\text{−hexane}}\right) \times 100 \qquad (2)$$

Catalytic steam cracking of *n*-hexane was carried out for 24 h of time on stream (1st run). Then, the P-ZSM-5 catalyst was calcined under O_2(20%)/He(80%) flow at 893 K for 5 h to remove the coke deposition and the calcined catalyst was used for the *n*-hexane cracking again for 24 h of time on stream (2nd run).

2.3. Characterization

Thermogravimetric and differential thermal analysis (TG-DTA) was carried out for the catalysts after the reaction of 2nd run on a TG-DTA2100SA thermal analyzer (Bruker AXS, Japan) at a heating rate of 10 K min^{-1} in flowing dry air.

3. Results and discussion

Fig. 1 shows the *n*-hexane conversion during the catalytic cracking with different S/nC6 ratios at 923 K over the P-ZSM-5 catalyst. The conversion of *n*-hexane with 1.0 of S/nC6 ratio over the P-ZSM-5 catalyst decreased from 90 to 60% for 24 h of time on stream (Fig. 1(a)), consistent with the previous paper [21]. The P-ZSM-5 catalyst was calcined under O_2(20%)/He(80%) flow at 893 K for 5 h to remove the coke deposition after the 1st run of 24 h and the calcined catalyst was used for the *n*-hexane cracking again. Most of deposited coke could be burned by the catalyst calcination at 893 K, which was higher than the reported temperature (ca. 773–823 K) of the calcination for the regeneration of the coke-deposited ZSM-5 catalysts [22–24]. The initial conversion of the 2nd run with 1.0 of S/nC6 ratio was 84%, which was higher than the conversion measured at the last of the 1st run (60%) and was lower than the initial conversion of the 1st run (90%), indicating that the P-ZSM-5 catalyst deactivated because of both the coke deposition and the dealumination of ZSM-5. We previously reported that the deactivation caused by the coke deposition could be recovered by the calcination at 893 K and that the irreversible deactivation was caused by the dealumination [13]. In the case of 0.5 of S/nC6 ratio (Fig. 1(b)), the conversion of *n*-hexane over the P-ZSM-5 catalyst decreased from 98 to 89% for 24 h of time on stream (Fig. 1(b)), where the slope of deactivation was smaller than that in the case of 1.0 of S/nC6 ratio. The initial conversion of the 2nd run with 0.5 of S/nC6 ratio was 91%, which was a little higher than the conversion measured at the last of the 1st run (89%) and was lower than the initial conversion of the 1st run (98%), indicating that the deactivation was also caused by both the coke deposition and the dealumination of ZSM-5. On the other hand, the initial conversions of both the 1st and the 2nd runs were 100% in the cases of 0.2, 0.1, and 0 of S/nC6 ratios (Fig. 1 (c, d, and e)), indicating that the deactivation was reversible under these conditions. The P-ZSM-5 catalyst was not seriously deactivated by the dealumination irreversibly and mainly deactivated reversibly by the coke deposition. Interestingly, among the conditions for 0.2, 0.1, and 0 of S/nC6 ratios, the final conversions with less steam showed lower value.

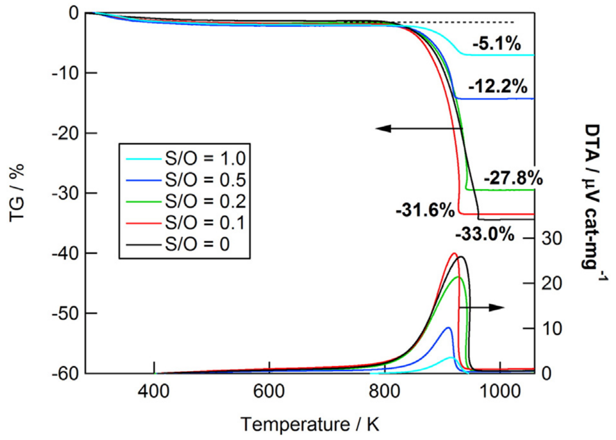

Fig. 2. TG-DTA of P-ZSM-5 catalysts after the 2nd run (24 h of time on stream) of *n*-hexane cracking at 923 K. The reaction and calcination conditions are the same as Fig. 1.

To understand the effect of S/nC6 ratio on the coke deposition, we carried out TG-DTA measurement for the P-ZSM-5 catalysts after the 2nd run of *n*-hexane cracking with different S/nC6 ratios (Fig. 2). The exothermic peak around 880 K and the weight loss was observed, which were attributed to the combustion of coke deposited on the P-ZSM-5 catalysts during the 2nd run of *n*-hexane cracking for 24 h [13]. The amount of coke deposition increased with decreasing the S/nC6 ratio (Fig. 3), which was consistent with the results that the catalyst deactivated by the coke deposition at the low S/nC6 ratios. In the case of thermal cracking of naphtha, the coking decreases with increasing the steam ratio to naphtha from simulation results [25] and experimental results [26]. On the other hand, in the case of catalytic cracking, the effect of steam ratio to naphtha on the amount of coke has not been investigated. The effect of steam treatment on sweeping of the deposited coke was investigated on H-ZSM-5 [27]. The amount of deposited coke was reduced by the steam treatment at 823 K and the temperature for the combustion of the coke which remained on H-ZSM-5 was raised after the steam treatment, indicating that the coke with low H/C ratio remained [27]. In this study, the amount of the deposited coke with the high S/nC6 ratio was smaller and the coke combustion started from a little higher temperature (Fig. 2), which was consistent with the sweeping effect of steam [27]. The mechanism of coke formation on H-ZSM-5 catalysts during the catalytic cracking of naphtha has been reported. At first, light olefins such as propylene are formed from naphtha and the sequential reactions of the light olefins produce BTX

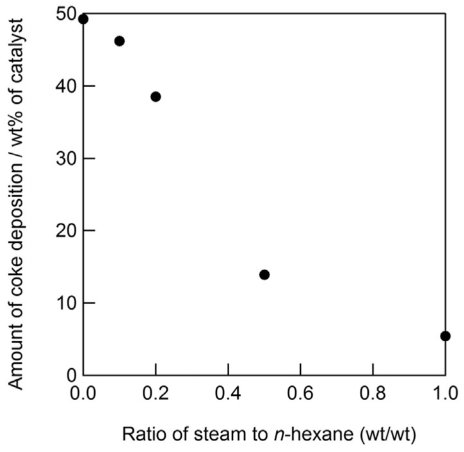

Fig. 3. Amount of coke deposition over the P-ZSM-5 catalysts after the 2nd run (24 h of time on stream) of *n*-hexane cracking at 923 K. The reaction and calcination conditions are the same as Fig. 1.

(benzene, toluene, and xylene). Finally, the coke is formed via reactions of BTX [12,28,29]. From this coke formation mechanism, coke would be preferentially deposited on the last part of the catalyst bed [30]; however, we cannot measure the coke profile along the catalyst bed because the catalyst bed is only a few centimeter in this study. Urata et al. reported that the coke was formed on the external surface of H-ZSM-5 and the catalyst was deactivated by the channel blocking by the external coke [31]. The amount of coke deposition increased with decreasing the steam ratio to *n*-hexane (Fig. 3), which could explain the results that larger reversible deactivation could be observed at the lower S/nC6 ratios (Fig. 1).

Fig. 4 shows product distributions from the *n*-hexane cracking at 923 K with different steam–hexane ratios over P-ZSM-5. In the case of high steam ratio to *n*-hexane (S/nC6 = 1.0 and 0.5, Fig. 4 (a and b)), the high propylene yields in the range of 22–28 C% could be observed; however, the BTX yields were not high (at most 7.7 C%). The initial BTX yields clearly increased with decreasing the S/nC6 ratios and the initial BTX yield at the S/nC6 ratio = 0 (Fig. 4(e)) was 29 C%. On the other hand, the propylene yields at the low S/nC6 ratios were lower than those at the high S/nC6 ratios. Especially, the propylene yields were low when the high BTX yield was observed, which was consistent with the coke formation mechanism that the sequential reactions of the

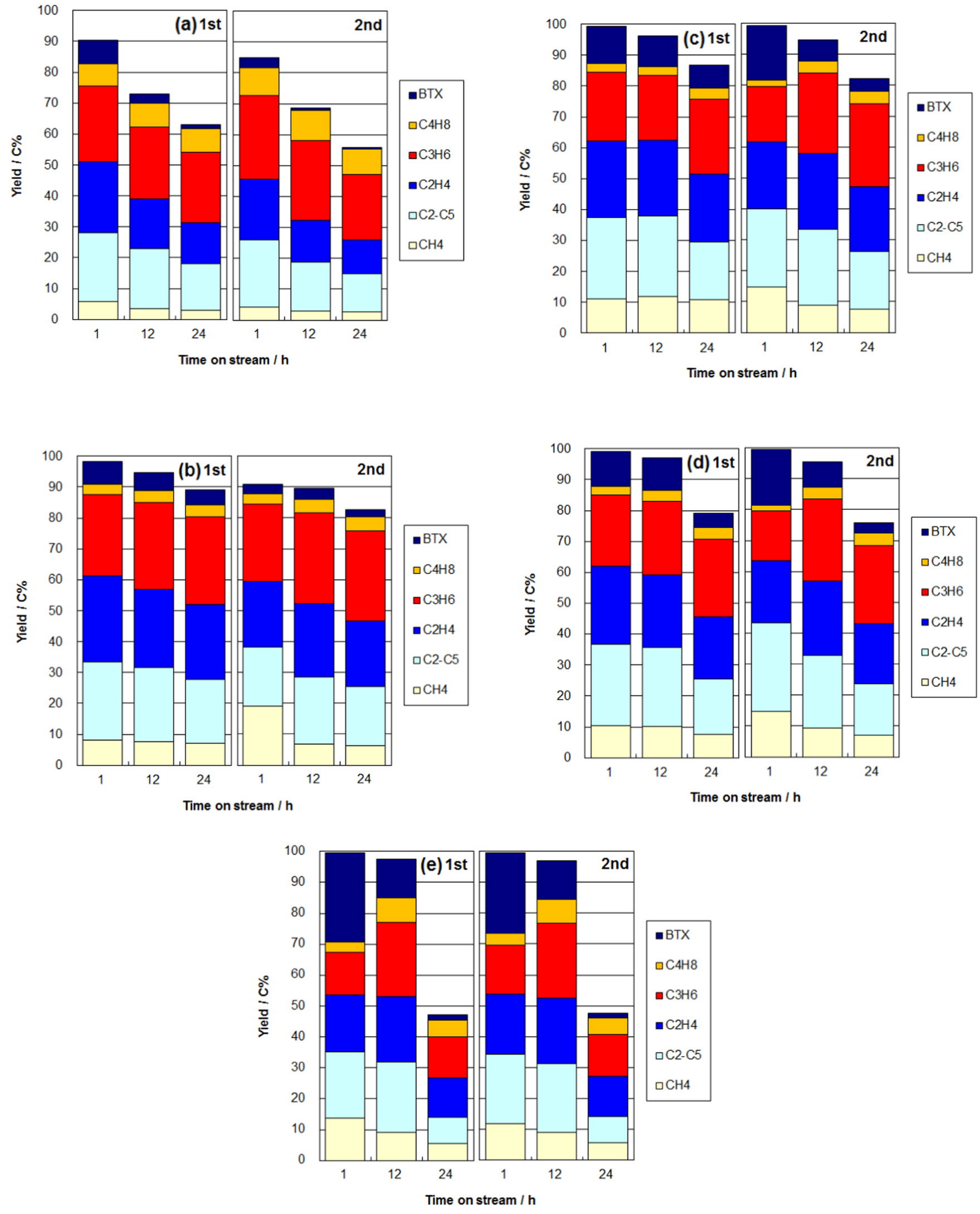

Fig. 4. Product distribution from *n*-hexane cracking at 923 K with different steam–hexane ratios over P-ZSM-5. The P-ZSM-5 catalyst was treated under O_2(20%)/He(80%) flow at 893 K for 5 h after 24 h of time on stream (1st run) and used again for 24 h of time on stream (2nd run). The reaction conditions were the following: reaction temperature of 923 K, WHSV(hexane) 11 h^{-1}, W/F 8.0 g-cat h/mol-hexane, and the steam–hexane ratios (wt/wt): (a) 1.0, (b) 0.5, (c) 0.2, (d) 0.1, and (e) 0. BTX indicates total amounts of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene, and C2–C5 indicates paraffin hydrocarbon with from two to five carbon atoms.

light olefins produce BTX and that the coke was formed via reactions of BTX [12,28,29]. Actually, the amount of coke increased with increasing the BTX yields. These results indicated that the steam could reduce the reactions of the light olefins to BTX and coke and that the steam enhanced the yield of the light olefins; however, the excess steam deactivated the ZSM-5 catalysts irreversibly via the dealumination.

Finally, we weigh the advantages and disadvantages of the steam during the catalytic cracking of *n*-hexane using the P-ZSM-5 catalyst. The advantages of steam are (i) lower coke deposition and (ii) higher propylene yields; however, the disadvantages are (iii) dealumination of ZSM-5 and (iv) energy requirement for heating water up to 923 K. The coke deposition causes not only the catalyst deactivation but also the pressure drop and collapse of catalyst pellets on a commercial scale; thus, the steam is effective to reduce the coke deposition. On the other hand, the dealumination of ZSM-5 is caused by the steam irreversibly, leading to the deactivation of the catalyst. The S/nC6 ratios of 0.2 and 0.1 would be suitable by considering a balance between the advantages and disadvantages.

4. Conclusions

When the S/nC6 ratios were more than or equal to 0.5, the P-ZSM-5 catalyst was deactivated not only by the coke deposition but also by the dealumination of ZSM-5. In the cases of 0.2, 0.1, and 0 of S/nC6 ratios, the P-ZSM-5 catalyst was deactivated mainly by the coke deposition and could be regenerated after the reaction for 24 h by the calcination at 893 K. The amount of coke deposition increased with decreasing the S/nC6 ratio from the TG-DTA measurement. The higher propylene yields and lower BTX yields could be obtained with higher S/nC6 ratios. The steam could reduce the reactions of the light olefins to BTX and coke and enhance the yield of the light olefins; however, the excess steam deactivated the ZSM-5 catalysts irreversibly via dealumination.

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