

Continuous Process for the Production of Aromatic Hydrocarbons from *n*-Hexane and C₅₊ Natural Gas Liquid over Pd-Loaded ZSM-5 Zeolite

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Abstract:

A continuous process for the production of aromatic hydrocarbons from *n*-hexane and C₅₊ natural gas liquid (C₅₊ NGL) over Pd-loaded ZSM-5 zeolite in a tubular reactor was developed. The optimal conditions for continuous aromatization of *n*-hexane and C₅₊ NGL were found at 400 °C reaction temperature and 0.4 cm³/min reactant feeding rate, employing ZSM-5 (0.5% Pd content) as a catalyst; under these conditions, *n*-hexane conversion and aromatic contents in reaction product were found to be 99.7% and 92.3%, respectively. GC and GC/MS analysis revealed that this continuous process for *n*-hexane aromatization yielded both benzene derivatives and naphthalene derivatives, including benzene (5.7%), toluene (23.6%), xylenes (25.0%), 4-ethyltoluene (3.5%), 1,3,5-trimethylbenzene (4.9%), 1-methylnaphthalene (4.3%), and 1,5-dimethylnaphthalene (3.6%). Under the same reaction conditions, C₅₊ NGL gave 94.3% conversion and 92.6% aromatic contents in reaction product. The composition of product included benzene (8.1%), toluene (23.3%), xylenes (22.8%), 4-ethyltoluene (4.3%), 1,3,5-trimethylbenzene (3.7%), 1-methylnaphthalene (4.1%), and 1,5-dimethylnaphthalene (2.9%).

Introduction

The transformation of alkanes into aromatic hydrocarbons is an area of great industrial relevance and also of academic interest for the production of benzene, toluene, xylene (BTX), and naphthalene derivatives. Aromatic hydrocarbons are important feedstock in chemical industries; for example, benzene is an important feedstock for the production of polystyrene (PS), toluene is used as feedstock for polyurethane (PU) production, *p*-xylene is employed in poly(ethylene terephthalate) (PET) production process, and naphthalene is a substrate for the production of phthalic anhydride, an intermediate for dyestuff manufacture.¹ In general, naphtha-reforming catalysts (Pt/Al₂O₃) have been used to convert heavy naphtha (C₇–C₁₀) into aromatic hydrocarbons, but lower alkanes (C₂–C₆) are hardly transformed over these catalysts.² Chen and co-workers³ first found the ability of

ZSM-5 zeolite to convert light hydrocarbons to BTX; however, these catalysts are poor for paraffin conversion because of excessive methane and ethane formation with low selectivity to aromatics. Consequently, there have been numerous reports on various ZSM-5-based catalysts for the conversion of light paraffins into aromatics. Due to low paraffin conversion, various types of activating agents (e.g., gallium, copper, zinc, and platinum) have been added to zeolite. Several systematic studies have been described.^{4–11} However, already a few researchers have studied *n*-hexane aromatization. Popova et al.¹² reported the batch transformation of *n*-hexane over Cu/ZSM-5 with 82% conversion and 14% aromatic selectivity. Bhattacharya et al.¹³ found that the aromatization of *n*-hexane over H-ZSM-5 zeolite in batch mode was enhanced by the promoters ZnO and Ga₂O₃, while Fe₂O₃ and Cr₂O₃ decreased its aromatization activity. Bhattacharya et al.¹⁴ also reported that ZSM-5 gave the highest aromatization activity compared to those of ZSM-22 and EU-1. Moreover, Rojasova and co-workers¹⁵ studied the role of zinc in Zn/ZSM-5 zeolite in a batch aromatization of *n*-hexane, of which the conversion of 47.6% with 50.2% aromatic selectivity was obtained.

Surprisingly, although there have been several studies using Pd/ZSM-5 on alkanes combustion,^{16–20} none has reported on the ability of Pd/ZSM-5 toward the aromatization, and this present work is the first aromatization reaction upon Pd/ZSM-5.

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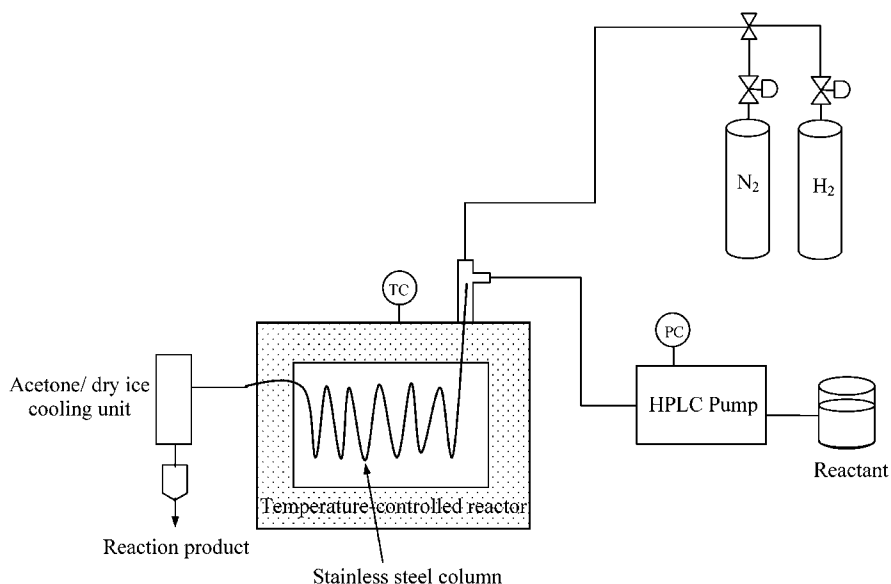


Figure 1. Reactor for continuous aromatization of *n*-hexane and C_{5+} natural gas liquid.

Aromatization is of industrial interest since it could be employed for the conversion of petrochemical byproduct that contains alkane (e.g., natural gas liquid (NGL) and light naphtha) into other useful products for other chemical industries. The C_{5+} NGL is a natural gas byproduct, comprising branched-chain alkanes (77%), cycloalkanes (16%), and other products (e.g. alkenes and aromatics, 7%).²¹ The present work is aimed at developing a continuous process for the production of benzene and naphthalene derivatives from C_{5+} NGL using *n*-hexane as a model compound and Pd-loaded ZSM-5 as catalyst.

Results and Discussion

Continuous Process for the Production of Aromatic Hydrocarbons from *n*-Hexane. Effect of Pd Contents in ZSM-5 Zeolite. The experiments were carried out in a home-built tubular reactor (Figure 1). The effects of Pd contents (0–0.5%) in ZSM-5 zeolite on both conversion and aromatic contents in reaction product of *n*-hexane were investigated at 400 °C reaction temperature and 0.4 cm³/min *n*-hexane feeding rate. *n*-Hexane conversion and aromatic contents in the reaction product of all catalysts increased when Pd contents in ZSM-5 zeolite increased (Figure 2). Although the *n*-hexane conversion at 0% Pd content in ZSM-5 zeolite was relatively high (50.2%), the aromatic contents in reaction product was considerably low (1.2%, Figure 2). This might be because *n*-hexane was cracked and converted to other products, e.g., small hydrocarbon molecules, without oligomerization and aromatization. It can further be noticed that *n*-hexane conversion (99.7%) and aromatic contents in reaction product (92.3%) attained their corresponding maximum when using 0.5% Pd in ZSM-5 zeolite.

Effect of Reaction Temperature and Reactant Feeding Rate. The effects of reactant feeding rate on both conversion and aromatic contents in reaction product of *n*-hexane over different temperatures were studied (Figure 3). It was found

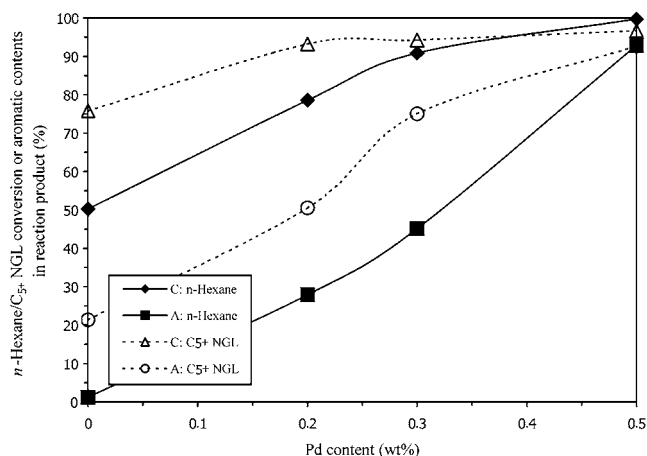


Figure 2. Effect of Pd contents in ZSM-5 zeolite on conversion and aromatic contents in reaction product of *n*-hexane and C_{5+} natural gas liquid. Conditions: reaction temperature, 400 °C; feeding rate, 0.4 cm³/min (C and A represent conversion and aromatic contents in reaction product, respectively).

Table 1. Contact time between reactants (*n*-hexane and C_{5+} NGL) and catalyst at different reactant feeding rates²²

reactant feeding rate (cm ³ /min)	contact time (min)
0.4	79.25
0.6	52.83
0.8	39.63
1.0	31.70

that when the reaction temperature increased, both conversion and aromatic contents in reaction product proportionally increased (Figure 3). However, the aromatic contents in reaction product at 450 °C was lower than that at 400 °C (Figure 3), and this might be due to the degradation of aromatic products to small hydrocarbon molecules. Decreasing trends in their conversion and aromatic contents in reaction product, at all reaction temperatures, were observed when the feeding rate increased (Figure 3). These results indicated that both conversion and aromatic contents in

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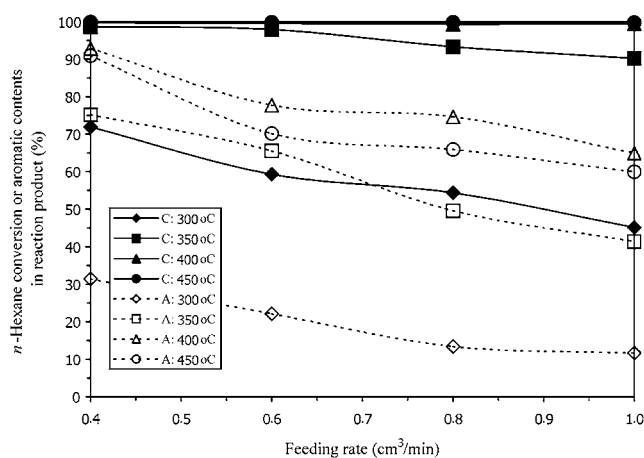


Figure 3. Effect of the feeding rate on *n*-hexane conversion and aromatic contents in reaction product over 0.5% Pd in ZSM-5 zeolite at different temperatures (C and A represent conversion and aromatic contents in reaction product, respectively).

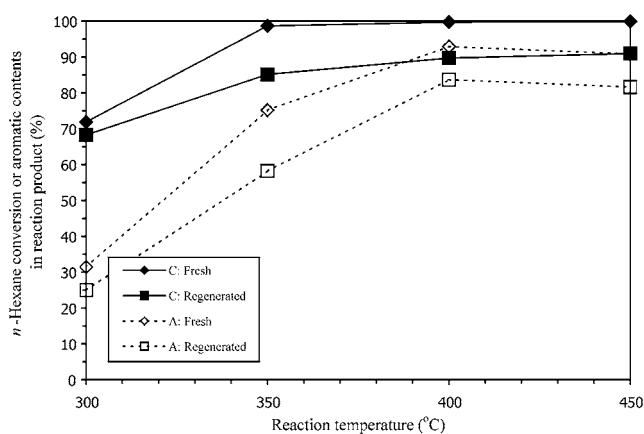


Figure 4. Activity comparison between fresh and regenerated catalysts on *n*-hexane conversion and aromatic contents in reaction product at different temperatures. Conditions: feeding rate, 0.4 cm³/min; catalyst, 0.5% Pd in ZSM-5 zeolite (C and A represent conversion and aromatic contents in reaction product, respectively).

reaction product were affected by the contact time between *n*-hexane and catalyst (Table 1). The feeding rate of 0.4 cm³/min at the reaction temperature of 400 °C provided the highest *n*-hexane conversion (also highest contact time) and aromatic contents in reaction product as compared to other conditions.

Activity of Regenerated Catalyst. The activities of fresh and regenerated catalysts on *n*-hexane aromatization were studied (Figure 4). The catalysts were regenerated when their activity was ca. 80% of fresh catalyst (after feeding 3024 cm³ of *n*-hexane for 86 h). It was found that all catalysts showed similar increasing trends in their *n*-hexane conversion and aromatic contents in reaction product (Figure 4). Fresh catalyst generally provided higher *n*-hexane conversion and aromatic contents in reaction product than did regenerated catalysts (Figure 4). The margin 10% activity lost was observed between fresh and regenerated catalyst. The regenerated catalyst might have some carbon deposits that covered the catalyst surface, thus reducing the catalyst activity.^{22,23}

Aromatic Contents in Reaction Product and Product Distributions. The aromatic contents in reaction product and product distributions of *n*-hexane aromatization were explored at the optimal conditions (reaction temperature, 400 °C; reactant feeding rate, 0.4 cm³/min; catalyst, 0.5% Pd in ZSM-5), and the results are shown in Table 2. GC and GC/MS analysis revealed that this continuous process for *n*-hexane aromatization yielded not only benzene and its derivatives but also naphthalene derivatives. The product distributions were benzene (5.7%), toluene (23.6%), xylenes (25.0%), 4-ethyltoluene (3.5%), 1,3,5-trimethylbenzene (4.9%), 1-methylnaphthalene (4.3%), and 1,5-dimethylnaphthalene (3.6%). Among these aromatics, xylenes were obtained as the highest percentage (25.0%). When comparing among three isomers of xylene, the percentage of *p*-xylene was higher than that of *m*- and *o*-isomers (Table 2). This can be explained theoretically by comparing pore aperture of ZSM-5 zeolite (0.54 nm × 0.56 nm and 0.51 nm × 0.55 nm) with kinetic molecular diameters of *m*-, *o*-, and *p*-isomers of xylene, which are 0.63, 0.64, and 0.57 nm, respectively.⁸ On the basis of these data, only *p*-xylene possesses a certain size that could easily exit from the pore system. In addition, the slimmer shape of the molecule of *p*-xylene, which exhibits a rate of diffusion faster by a factor of 10⁴ than the other two isomers, also explains the favored formation of *p*-xylene.²⁴

On the basis of the products formed from *n*-hexane aromatization, the main reaction pathways converting *n*-hexane to aromatics may be explained as follows. Due to the bifunctional property of the Pd-loaded ZSM-5, in the presence of metal and acidity, *n*-hexane is cracked to small hydrocarbon molecules and then oligomerized on the acid sites in the zeolite channels. The oligomerized products can undergo either cracking to light hydrocarbons (C₂–C₄) or dehydrocyclization to aromatics via the Pd-function.^{8,10} At higher conversion levels (high temperature), naphthalene derivatives were formed because mononuclear aromatics might condense into polynuclear aromatics, especially naphthalene and its derivatives.⁸

Under the optimal conditions (reaction temperature, 400 °C; reactant feeding rate, 0.4 cm³/min; catalyst, 0.5% Pd in ZSM-5), *n*-hexane aromatization gave higher conversion (99.7%) and aromatic contents in reaction product (92.3%) than those previously reported by Rojasova et al.,¹⁵ from which the conversion of 47.6% with 50.2% aromatic contents in reaction product was obtained in a batch aromatization of *n*-hexane using Zn/ZSM-5 zeolite as a catalyst. Previous works on the aromatization of alkanes was conducted in a batch system,^{4–15} and this present work is the first aromatization carried out using a continuous mode. Concerning the catalyst performance (under our optimal conditions), we found that 2.28 and 2.23 g of the total products formed per g of catalyst per h for the aromatization of *n*-hexane and

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Table 2. Product distributions from continuous aromatization of *n*-hexane and C₅₊ NGL at their optimal conditions^a compared to their corresponding reactant compositions and commercial mixture of benzene, toluene, and xylene

	<i>n</i> -hexane		C ₅₊ NGL		commercial mixture of benzene, toluene, and xylene ^b
	before aromatization ^b	after aromatization ^b	before aromatization ^b	after aromatization ^b	
conversion (%)	—	99.73 ± 0.0070	—	94.30 ± 0.0530	—
	Product Distributions (%)				
less than C ₆ hydrocarbons	2.19 ± 0.0446	6.83 ± 0.0084	—	5.32 ± 0.0131	—
hexane	-96.69 ± 0.0729	0.27 ± 0.0070	—	0.30 ± 0.0044	—
total aromatics	—	92.25 ± 0.0226	27.34 ± 0.0275	92.64 ± 0.0241	91.03 ± 0.0035
benzene	—	5.67 ± 0.0057	8.24 ± 0.0018	8.08 ± 0.0113	6.50 ± 0.0004
toluene	—	23.63 ± 0.0085	3.29 ± 0.0046	23.31 ± 0.0077	19.99 ± 0.0017
xylene	—	24.97 ± 0.1476	1.28 ± 0.0030	22.75 ± 0.0220	29.54 ± 0.0013
<i>m</i> -xylene	—	2.17 ± 0.0082	—	3.31 ± 0.0026	5.19 ± 0.0000
<i>o</i> -xylene	—	5.20 ± 0.0247	0.22 ± 0.0070	4.45 ± 0.0167	8.11 ± 0.0008
<i>p</i> -xylene	—	17.59 ± 0.1312	1.06 ± 0.0039	14.99 ± 0.0079	16.24 ± 0.0003
4-ethyltoluene	—	3.50 ± 0.0083	—	4.30 ± 0.0028	5.73 ± 0.0007
1,3,5-trimethylbenzene	—	4.86 ± 0.0072	—	3.65 ± 0.0034	7.75 ± 0.0003
1-methylnaphthalene	—	4.33 ± 0.0105	—	4.06 ± 0.0167	—
1,5-dimethylnaphthalene	—	3.57 ± 0.0071	—	2.87 ± 0.0230	—

^a Conditions: catalyst, 0.5% Pd in ZSM-5; reaction temperature, 400 °C; feeding rate, 0.4 cm³/min. ^b Average ± standard deviations, *n* = 2. ^c Compositions of less than C₆ hydrocarbons in C₅₊ NGL were 2-methylpropane (0.25%), *n*-butane (2.25%), 2,2-dimethylpropane (0.06%), 2-methylbutane (21.57%), *n*-pentane (20.07%), 2,2-dimethylbutane (0.82%), cyclopentane (1.50%), 2,3-dimethylbutane (1.99%), 2-methylpentane (8.64%), and 3-methylpentane (4.47%).

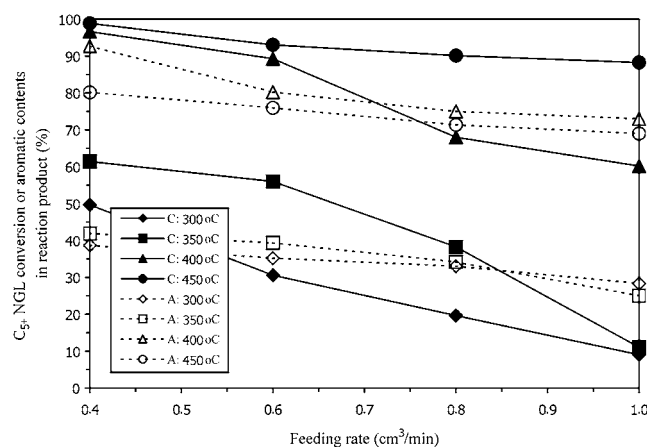


Figure 5. Effect of the feeding rate on C₅₊ natural gas liquid conversion and aromatic contents in reaction product over 0.5% Pd in ZSM-5 zeolite at different temperatures (C and A represent conversion and aromatic contents in reaction product, respectively).

C₅₊ NGL, respectively (or 455 and 446 g product formed per g Pd per h). This continuous aromatization process is expected to be employed for the conversion of petrochemical byproducts that contains alkane (e.g., NGL and light naphtha) into high-value-added products. The following experiments were performed using the continuous system for the aromatization of C₅₊ NGL, which is one of the major petrochemical byproducts from natural gas separation industry.

Continuous Process for the Production of Aromatic Hydrocarbons from C₅₊ NGL. The aromatization of C₅₊ NGL was conducted in the continuous system (Figure 1). It was found that the effect of Pd contents in ZSM-5 zeolite, reaction temperature and reactant feeding rate, and the activity of regenerated catalyst, on C₅₊ NGL aromatization were similar to that of *n*-hexane aromatization. The optimum conditions for C₅₊ NGL conversion (94.3%, calculation based on 21.57% of 2-methylbutane in C₅₊ NGL, Figure 5) and

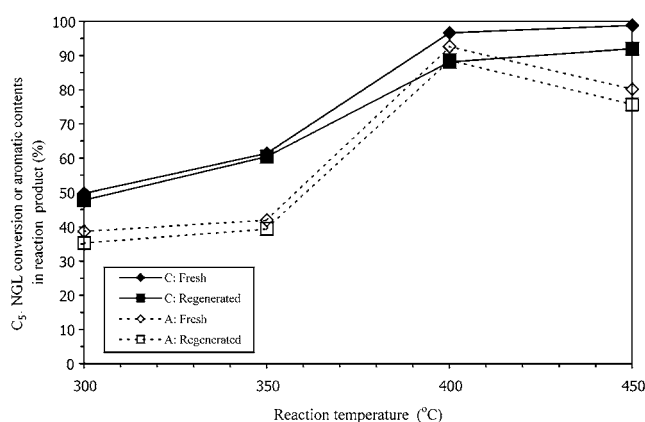


Figure 6. Activity comparison between fresh and regenerated catalysts on C₅₊ natural gas liquid conversion and aromatic contents in reaction product at different temperatures. Conditions: feeding rate, 0.4 cm³/min; catalyst, 0.5% Pd in ZSM-5 zeolite. (C and A represent conversion and aromatic contents in reaction product, respectively).

aromatic contents in reaction product (92.6%, Figure 5) were at 0.5% Pd content in ZSM-5 (Figure 2), 400 °C reaction temperature (Figure 5), and 0.4 cm³/min C₅₊ NGL feeding rate (Figure 5). GC and GC/MS analysis demonstrated that this continuous aromatization of C₅₊ NGL yielded benzene (8.1%), toluene (23.3%), xylenes (22.8%), 4-ethyltoluene (4.3%), 1,3,5-trimethylbenzene (3.7%), 1-methylnaphthalene (4.1%), and 1,5-dimethylnaphthalene (2.9%). However, similar to *n*-hexane aromatization, toluene and xylenes represented major percentage of products (23.3% and 22.8%, respectively) from the C₅₊ NGL reaction. The activity of fresh and regenerated catalysts on C₅₊ NGL aromatization was also studied, and it was found that 7% activity lost was observed between fresh and regenerated catalysts (Figure 6). Similarly to that of *n*-hexane, the regenerated catalyst might have some carbon deposits, thus reducing the catalyst activity. Additionally, sulfur present in C₅₊ NGL (0.0030

Table 3. Sulfur contents in reactants (*n*-hexane and C₅₊ NGL), fresh catalysts, and regenerated catalysts

	sulfur content (wt %) ^a
<i>n</i> -hexane	0.0019 ± 0.0001
C ₅₊ NGL	0.0030 ± 0.0003
fresh catalyst before <i>n</i> -hexane aromatization	0.0180 ± 0.0028
regenerated catalyst after <i>n</i> -hexane aromatization	0.0425 ± 0.0021
fresh catalyst before C ₅₊ NGL aromatization	0.0180 ± 0.0028
regenerated catalyst after C ₅₊ NGL aromatization	0.0625 ± 0.0035

^a Average ± standard deviations, *n* = 2.

wt %, Table 3) could also deactivate the catalyst. It is known that sulfur poisoning in catalysts leads to the deactivation of catalyst performance.²⁵ In our system, the amount (2160 cm³) of C₅₊ NGL (sulfur-containing substrate) that caused 20% reduction of the catalyst activity was less than that (3024 cm³) of *n*-hexane (AR grade reagent with a sulfur content less than 0.0020 wt %, Table 3), clearly demonstrating that the presence of sulfur gave a negative effect to the catalytic performance.

The above experiments provided the evidence that this continuous aromatization process may be applied for the conversion of petroleum byproduct into high value-added products.

Conclusions

The model process for the production of aromatic hydrocarbons using *n*-hexane as a model substrate was successfully performed over Pd-loaded ZSM-5 zeolite in a continuous mode. The optimal conditions were at 0.5% Pd content in ZSM-5, 400 °C reaction temperature, and 0.4 cm³/min reactant feeding rate, providing *n*-hexane conversion and aromatic contents in reaction product at 99.7% and 92.3%, respectively. GC and GC/MS analysis revealed that this *n*-hexane aromatization preferably yielded benzene and naphthalene derivatives, including benzene (5.7%), toluene (23.6%), xylenes (25.0%), 4-ethyltoluene (3.5%), 1,3,5-trimethylbenzene (4.9%), 1-methylnaphthalene (4.3%), and 1,5-dimethylnaphthalene (3.6%). Under the same reaction conditions, C₅₊ NGL gave 94.3% conversion and 92.6% aromatic contents in reaction product, and the aromatization products were benzene (8.1%), toluene (23.3%), xylenes (22.8%), 4-ethyltoluene (4.3%), 1,3,5-trimethylbenzene (3.7%), 1-methylnaphthalene (4.1%), and 1,5-dimethylnaphthalene (2.9%).

Up to date, there have been only few applications in turning C₅₊ NGL into other useful products, besides burnt out as fuel. The present work implied that the continuous process for the aromatization of C₅₊ NGL may be another option for the conversion of C₅₊ NGL into high value-added products.

Experimental Section

Materials and General Methods. Zeolite NaZSM-5 (SiO₂/Al₂O₃ = 58) was obtained from Nissan Girdler Co.

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Ltd., Japan. The structure of zeolite was confirmed by a JEOL (model JDX-8030) X-ray powder diffractometer. All reagents were of analytical grade from Fluka. The Pd and S contents in each reactant and catalyst, as well as the SiO₂/Al₂O₃ ratio, were determined using a Phillips (model PW-2400) X-ray fluorescence spectrometer. C₅₊ NGL was obtained from the PTT Public Co. Ltd., Thailand, and was analyzed and quantified in the same manner as that for reaction products by GC/MS. The compositions of C₅₊ NGL are shown in Table 2. The reaction products were analyzed and quantified by two techniques: (A) a Hewlett-Packard (model 6890) gas chromatograph (GC) equipped with a HP-5 capillary column (30 m × 0.32 mm i.d.) and flame ionization detector (FID), and (B) a Fisons Instruments (model 8060) gas chromatograph (GC) equipped with a HP-5 capillary column (30 m × 0.32 mm i.d.) using a Fisons Instruments (model Trio 2000) mass spectrometer as a detector. All products were identified by comparison with their authentic compounds obtained from Fluka.

Preparation of Pd/ZSM-5. Pd/ZSM-5 catalysts with various amounts of Pd were prepared by an ion-exchange technique. Aqueous solutions (500 cm³) of palladium (II) chloride using 0, 0.2, 0.3, and 0.5 g of Pd (II) per 100 g of NaZSM-5, were vigorously stirred at 80 °C for 15 h. The cation-exchanged zeolite was filtered and washed with deionized water to remove chloride ions until it tested negative with an aqueous solution of silver nitrate. Then, the zeolite catalyst was dried at 110 °C, calcined at 550 °C for 4 h, and stored as powdered form in a desiccator. After this calcination, the SiO₂/Al₂O₃ ratio of the catalyst was changed from 58 to 63 due to partial dealumination. The Pd contents of the exchanged catalyst were found close to the expected values. Moreover, the structure of the calcined Pd/ZSM-5 catalyst was found to be the same as that of noncalcined ZSM-5 zeolite, as revealed by X-ray powder diffractometer.

Continuous Aromatization Reactor. All experiments were carried out in a home-built tubular reactor (Figure 1). The reactor was constructed from a stainless steel tubing of 120 cm long (105 cm long catalyst bed), 0.62 mm i.d., and 0.68 mm o.d. and was heated in an old GC oven. Each column was separately packed with 8.0 g of ZSM-5 catalyst with 0, 0.2, 0.3, or 0.5% of Pd. Prior to each experiment, the catalyst was reduced in situ at 450 °C for 5 h under constant flow of nitrogen and hydrogen mixed gas. Subsequently, both nitrogen and hydrogen streams were removed from the system, and the reactant was continuously introduced into the top of the column at various feeding rates using a Waters (model 510) HPLC pump. The reactor effluent was collected in an acetone/dry ice cooling unit and subsequently analyzed by GC (conditions: H₂ carrier gas; 30 m × 0.32 mm i.d. fused silica column coated with a 0.25-μm film of HP-5; flame ionization detector or mass spectrometer detector; linear temperature program from 45 to 180 °C with the heating rate of 5 °C/min).

Regeneration of Spent Catalyst. The catalyst was regenerated when its catalytic activity was reduced ca. 20%. The spent catalyst was taken out of a tubular column and

heated in a furnace at 650 °C for 10 h. The regenerated catalyst was repacked again in a column and reduced in situ as mentioned above, prior to each experiment.

Acknowledgment

S.S. is a Ph.D. student under the scholarship from the Royal Golden Jubilee Ph.D. Program, the Thailand Research

Fund. We thank Dr. P. Kittakoop for his comments and suggestion on the manuscript. Numerous comments and suggestions from the reviewers are gratefully acknowledged.

Received for review February 19, 2003.

OP030007B