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Catalytic Transformation of C_8 Aromatics over ZSM-5 Zeolites

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The catalytic transformation of C_8 aromatic hydrocarbons (present in a naphtha reformate) over H-ZSM-5, NiH-ZSM-5, PtH-ZSM-5, and PtNiH-ZSM-5 are reported. The influence of the SiO_2/Al_2O_3 ratio in the zeolite, the temperature of calcination and the reaction parameters of temperature, contact time, pressure, and space velocity have been investigated. The incorporation of nickel and platinum enhances the efficiency of the catalysts in producing *para*-xylene (by isomerization of the *meta* isomer and hydroisomerization of ethylbenzene). Simultaneously, these metals suppress the disproportionation and loss of xylenes to toluene and trimethylbenzenes. To elucidate the acidity of the active sites involved in the various reactions of the xylene isomerization process, selective poisoning with NH_3 was carried out. From the results it is concluded that relatively strong acid sites are needed for the disproportionation of xylenes and ethylbenzene, whereas relatively weak acid sites are sufficient for xylene isomerization. By selective suppression of the strong acid sites responsible for xylene disproportionation, it is feasible to enhance the net *para*-xylene production. © 1986 Academic Press, Inc.

INTRODUCTION

The C_8 aromatic fraction from a typical naphtha reformate contains around 20% each of ethylbenzene (EB), *ortho*-xylene (OX), and *para*-xylene (PX), the balance (around 40%) being *meta*-xylene (MX). The major demand is, however, for PX and, to some extent, OX. The C_8 aromatics fraction after the removal of OX and PX is isomerized to a composition closer to thermodynamic equilibrium and recycled to the separation stage.

Even though extensive reports are available on the reactions of individual C_8 isomers (*1–19*) over various catalysts, including ZSM-5 zeolites, there is no comprehensive report in the journal literature on the reactions occurring when all the isomers are simultaneously present in the feedstock, as in a commercial case. This paper presents the results of a detailed study of the catalytic transformations undergone by the C_8 aromatics present in a typical feed in a xylene isomerization plant over ZSM-5 zeolites. The influence of systematic variation in catalyst parameters and process conditions has been studied.

EXPERIMENTAL

Materials. ZSM-5 zeolite was prepared from solutions containing triethyl-*n*-propyl ammonium ions according to the procedure described elsewhere (*20*). The composition of the unit cell of the zeolite in the sodium form was $Na_{2.1}[(SiO_2)_{93.8}(AlO_2)2.2] \cdot 18H_2O$. The NH_4^+ form was obtained by ion exchange of the NaZSM-5 using NH_4Cl solution. The zeolite was analyzed by wet chemical analysis, atomic absorption, and flame photometry. The SiO_2/Al_2O_3 mole ratio of the NH_4ZSM-5 was 86 and the sodium content 0.05 wt%. The zeolite crystals were spherical in shape with a diameter of 1–3 μm. Most of the H-ZSM-5 samples were prepared by calcination of the NH_4ZSM-5 samples in static air for 8 h at 832 K. The temperature of the furnace was raised at a heating rate of 4 K min^{-1}. NiH-ZSM-5 was prepared by incorporation of nickel on NH_4ZSM-5 by ion exchange from 0.1 *M* nickel nitrate solution. The nickel

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content was 0.2 wt% of the catalyst (dry basis). PtH-ZSM-5 was similarly prepared by impregnation from a solution of chloroplatinic acid. The platinum content was 0.1 wt%. PtNiH-ZSM-5 was prepared by deposition of Pt on NiH-ZSM-5 from a solution of chloroplatinic acid. The Ni and Pt contents of PtNiH-ZSM-5 were 0.2 and 0.05 wt%, respectively. The samples were stored over saturated NH_4Cl solution. Before use in catalytic runs, the samples were calcined at 823 K for 8 h in a static air.

The feedstock for the isomerization reaction was obtained from a petrochemical complex. Its composition is given in Table 1, column 1.

Procedures. The catalytic reactions at atmospheric pressure were carried out in a fixed-bed, down-flow integral reactor. The zeolite (2 g, 10–20 mesh) was first activated in dry air, usually at 823 K, for 2 h and then cooled to reaction temperature in a flow of dry nitrogen. The catalyst was then reduced in dry H_2 (IOL, Bombay) for 2 h. The isomer feedstock was fed by a metering pump (Model 352, Sage Instruments), vaporized in a preheater assembly and then passed through the catalyst. Experiments at high pressures were carried out in a Catatest Unit (Model B, Geomecanique, France). Fifteen grams of catalyst was used in these experiments. The products were analyzed by gas chromatography (Shimadzu Model GC-R 1A) using 5% diisodecyl phthalate and 5% Bentone-34 on Chromosorb W column (2 m). The reproducibility of the data was about ±0.3%.

TABLE 1

The Influence of the Temperature of Calcination of HZSM5

	Feed	Calcination temperature (K)		
		823	933	1123
Composition (wt %)				
C_8^- aliphatics	5.6	5.2	4.7	5.0
Benzene	0.9	2.0	2.2	1.0
Toluene	1.5	2.4	2.1	1.1
Ethylbenzene	19.2	15.1	15.5	18.5
p-Xylene	13.5	17.1	17.0	16.0
m-Xylene	55.0	42.6	44.9	48.7
o-Xylene	4.3	13.1	10.9	9.0
$C_9 + C_{10}$ aromatics	—	1.9	1.6	0.2
Δ Xylenes (wt %)	—	0	0	+0.9
C_8 aromatics loss (wt %)	—	4.1	3.7	+0.2
EB conversion (%)	—	19.1	15.7	3.5
PATE (%)	—	100	92.8	61.2

Note. Catalyst H-ZSM-5, reaction temperature = 623 K, pressure = 1 bar, molar ratio H_2/oil = 2.3, WHSV = 8 h^{-1}.

RESULTS AND DISCUSSION

The composition of one typical feedstock to a xylene isomerization plant is shown in Table 1, column 1. In addition to the C_8 aromatics, the feed contains a small amount of benzene, toluene, and C_7–C_9 aliphatics (mostly paraffins). A number of reactions occur when these constituents are reacted over ZSM-5 zeolites: (1) interconversion among the isomeric xylenes by the 1,2-alkyl shift mechanism; (2) disproportionation/transalkylation of xylenes and EB, the products including toluene, trimethylbenzenes (TMB), ethyltoluenes, and diethylbenzene. When a hydrogenation component such as platinum is also present on the catalyst, three additional reactions occur, one desirable and the others undesirable, namely (3) hydroisomerization of EB to OX, (4) hydrocracking, and (5) hydrogenation/hydrogenolysis of C_8 aromatics to aliphatic hydrocarbons, respectively. Reactions leading to the formation of "coke" belong to a sixth category which is mainly responsible for the slow deactivation of the catalysts. Catalysts for the xylene isomerization process are assessed with regard to their ability:

(1) To enhance the concentration of *p*-xylene in the product to a value close to the thermodynamic equilibrium value. The equilibrium distribution of the three isomers of xylenes at 700 K, for example,

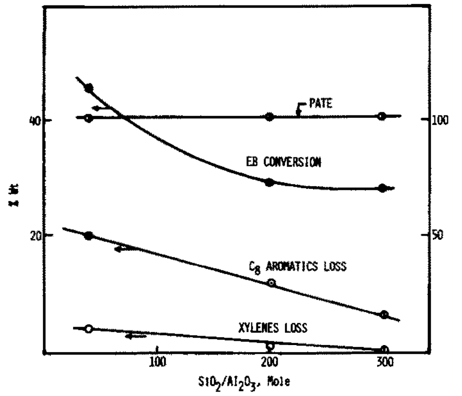

FIG. 1. The influence of the SiO_2/Al_2O_3 ratio in H-ZSM-5 zeolite on catalytic performance. Conditions: Temp. 653 K, pressure 13 bar, molar ratio H_2/oil 8, WHSV 5 h^{-1}. See Table 2 for composition of feed.

are *o*-xylene : *m*-xylene : *p*-xylene = 24.5 : 51.0 : 24.5. The *p*-xylene approach to equilibrium (PATE) is expressed as

$$\text{PATE (\%)} = \frac{(\%\ \text{PX in product}) - (\%\ \text{PX in feed})}{(\%\ \text{PX in equilibrium}) - (\%\ \text{PX in feed})} \times 100$$

Values of % PX in product in the above equation are obtained by normalizing the concentration of total xylenes in the reactor hydrocarbon effluent to 100 (% wt) and then calculating the percentage of the *para* isomer.

(2) To eliminate ethylbenzene from the feedstock (EB conversion);

(3) To achieve the above objectives with a minimum loss of total xylenes (in the form of disproportionation products) from the feed.

The influence of the SiO_2/Al_2O_3 ratio in HZSM5 zeolite on catalytic performance is shown in Fig. 1. The characteristics of surface acidity of these samples, as revealed by the temperature-programmed desorption of NH_3, had been published earlier (*21*). While PATE is not affected, both EB conversion and xylenes loss are suppressed at higher SiO_2/Al_2O_3 ratios. Since the major pathways for xylene loss are the disproportionation and transalkylation reactions of xylenes (with EB, for example), it is not surprising that a lower xylene loss is observed when the EB conversion is lower. The results in Fig. 1 indicate that the acid sites responsible for the formation of PX (from MX) by the 1,2-alkyl shift are different from those responsible for the disproportionation/transalkylation reactions. In earlier studies (*2, 21*) we have established that while strong acid sites at channel intersections are active in xylene isomerization, both strong and medium acid sites, the latter probably located on the external surface of the zeolite crystals, are active in the disproportionation reactions. Even though both the isomerization and disproportionation of xylenes decrease at higher SiO_2/Al_2O_3 ratios due to the lower concentration of strong acid sites, the latter reaction will be suppressed relatively more than the former. This is due to the fact that while xylene isomerization is a unimolecular reaction (*23*) and follows a single site reaction model (*24*) involving the adsorption of xylene on the protonic site and subsequent intramolecular isomerization, the disproportionation reaction involves two molecules of xylenes (or one molecule each of xylene and EB) adsorbed on two adjacent sites (*25*). Hence, any decrease in the strength and density of acid sites will selectively suppress the disproportionation activity of the zeolite.

The influence of the temperature of calcination of the zeolite on its catalytic activity is shown in Table 1. The XRD pattern, surface area, adsorption capacity for H_2O, argon and *o*-xylene, acid strength distribution, and catalytic activity in the isomerization of *o*-xylene of these samples have already been reported (*2*). There was no collapse of the crystalline lattice structure in any of the three samples. The sample calcined at 1123 K, however, had (1) a comparatively lower adsorption capacity for *o*-xylene, (2) a lower concentration of strong acid sites, and, consequently, (3) a lower catalytic activity (*2*). As the temperature of calcination is increased from 823 to 1123 K, three effects are seen: (1) the conversion of EB decreases (from 19.1 to 3.5

wt%), (2) the *p*-xylene approach to equilibrium (PATE) decreases from 100 to 61.2 wt%, and (3) the xylene gain increases from 0 to 0.9 wt%. We have shown earlier that both the isomerization (2) and disproportionation reactions (*21*) on zeolites are dependent on the presence of strong acid sites. Since the concentration of such sites decreases at high calcination temperatures and SiO_2/Al_2O_3 ratios the above result is in accord with expectations. The small increase in total xylenes (about 0.9 wt%) observed for the sample calcined at 1123 K is probably due to the aromatization of some C_8 aliphatics present in the feed.

The influence of temperature on the product distribution is shown in Table 2. Increasing the reaction temperature increases the ethylbenzene conversion as well as the xylene and C_8 aromatics losses; the PATE, however, is not influenced very much (Table 2). It may be mentioned here that the equilibrium concentration of the three xylene isomers does not vary significantly in this temperature range.

TABLE 2

The Influence of Temperature

	Feed	Reaction temperature (K)		
		623	653	683
Composition (wt %)				
C_8^- aliphatics	4.1	2.2	1.4	1.9
Benzene	1.9	5.9	9.0	11.0
Toluene	2.4	5.1	7.0	9.5
Ethylbenzene	27.6	15.9	11.7	8.3
p-Xylene	9.4	15.0	14.6	14.4
m-Xylene	48.2	32.0	31.0	30.1
o-Xylene	6.4	14.4	14.3	14.2
$C_9 + C_{10}$ aromatics	—	9.5	10.9	10.5
Δ Xylenes (wt %)	—	−2.6	−4.0	−5.2
C_8 aromatics (wt %)	—	14.3	19.9	24.5
EB conversion (%)	—	31.7	45.9	58.8
PATE (%)	—	100	100	100

Note. Catalyst H-ZSM-5, (SiO_2/Al_2O_3 = 36), pressure = 13 bar, molar ratio H_2/oil = 8, WHSV = 5 h^{-1}.

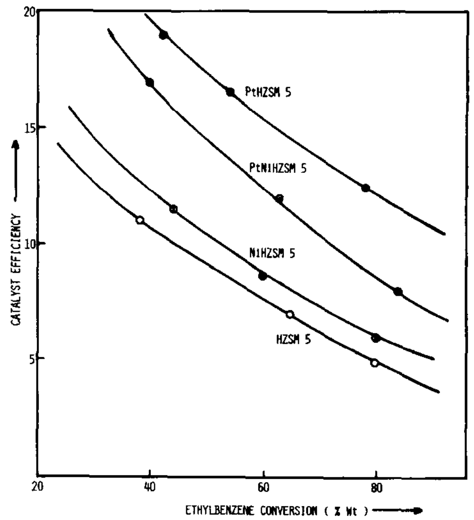

FIG. 2. Comparative evaluation of H-ZSM-5, NiH-ZSM-5, PtH-ZSM-5, and PtNiH-ZSM-5 catalysts at different levels of ethylbenzene conversion. See text for definition of catalyst efficiency.

The influence of the incorporation of Ni or/and Pt on the isomerization activity of H-ZSM-5 zeolites is illustrated in Table 3. As mentioned earlier, catalysts for the xylene isomerization process are evaluated for their ability to produce the maximum amount of PX (PATE) with a minimum loss of xylenes or xylene-precursors (C_8 aromatics) at a high conversion of EB. To enable at least a semiquantitative comparison of the four catalysts shown in Table 3 to be made, a parameter called catalyst efficiency is defined as

$$\text{Catalyst efficiency} = \frac{\text{PATE}}{C_8 \text{ aromatics loss } (\%)}.$$

The values of "Catalyst Efficiency" for the four catalysts of Table 3 at various values of EB conversion are shown in Fig. 2. PtH-ZSM-5 has a high efficiency factor combining high EB conversion with high PATE and minimum loss of C_8 aromatics (Table 3). This is probably due to the hydroisomerization of EB to xylenes which can occur on PtH-ZSM-5 but not on H-ZSM-5 or NiH-ZSM-5 catalysts. Apparently, part of the platinum in PtH-ZSM-5 (and to a less

TABLE 3

Xylene Isomerization over H-ZSM-5, NiH-ZSM-5, PtH-ZSM-5, and PtNiH-ZSM-5

	Feed	Catalyst			
		H-ZSM-5	NiH-ZSM-5	PtH-ZSM-5	PtNiH-ZSM-5
Composition (wt %)					
C_8^- aliphatics	3.5	2.3	2.1	1.5	3.3
Benzene	1.2	4.3	8.8	10.5	7.8
Toluene	3.2	5.0	8.2	3.8	5.1
Ethylbenzene	20.8	11.6	6.1	4.4	6.7
p-Xylene	12.5	16.7	17.2	18.4	18.0
m-Xylene	54.1	40.2	38.0	44.4	40.4
o-Xylene	3.8	14.6	17.0	15.8	17.3
$C_9 + C_{10}$ aromatics	—	4.6	3.3	1.1	2.2
Δ Xylenes (wt %)	—	+1.0	+1.1	+8.2	+5.0
C_8 aromatics loss (wt %)	—	8.2	13.0	7.8	9.1
EB conversion (%)	—	38.6	61.1	78.8	64.1
PATE (%)		96.3	100	97.2	100

Note. Temp. = 673 K, pressure = 1 bar, molar ratio H_2/oil = 2, WHSV 5 h^{-1}.

extent in PtNiH-ZSM-5) is in a metallic state and can hence hydrogenate EB to ethylcyclohexane. The latter can isomerize to dimethylcyclohexane with subsequent dehydrogenation to xylenes (*6*). This bifunctional route for converting EB to xylenes is not available on H-ZSM-5 which functions as a purely acidic catalyst.

TABLE 4

The Influence of Total Pressure

	Feed	Pressure (bar)			
		4	10	20	30
Composition (wt %)					
C_8^- aliphatics	—	—	—	1.2	3.6
Benzene	2.8	5.8	6.2	7.3	7.8
Toluene	2.9	3.9	4.5	5.6	6.6
Ethylbenzene	20.0	11.8	11.0	9.8	8.8
p-Xylene	13.7	18.1	17.7	17.2	17.2
m-Xylene	55.8	41.4	40.3	37.8	38.0
o-Xylene	4.7	14.7	15.1	15.4	15.7
$C_9 + C_{10}$ aromatics	—	4.2	5.2	5.5	4.5
Δ Xylenes (wt %)	—	—	−1.1	−3.8	−3.3
C_8 aromatics loss (wt %)	—	8.2	10.2	14.0	14.5
EB conversion (%)	—	41	45	51	56
PATE (%)	—	100	100	100	100

Note. Catalyst NiH-ZSM-5, Temp. = 633 K, molar ratio H_2/oil = 8, WHSV =4 h^{-1}.

The influence of pressure on xylene isomerization over NiH-ZSM-5 is shown in Table 4. While both the conversion of EB and the loss of xylenes increases at higher pressures, the PATE decreases mainly due to the preponderance of bimolecular disproportionation reactions at higher pressures.

The influence of contact time on the isomerization process is shown in Table 5. Contact time here is defined as

$$\text{Contact time (s)} = \frac{\text{Volume of catalyst bed (cm}^3\text{)}}{\text{Volumetric flow of gas (cm}^3\text{NTP/s)}}.$$

A significant feature of Table 5 is that while the isomerization reaction (as indicated by PATE) is not affected by an increase in the contact time (at least in the range studied), the disproportionation reactions of EB and xylenes [producing benzene, toluene, and ($C_9 + C_{10}$) aromatics] are enhanced at high contact times. Hence, industrial feedstock containing little or no EB can be processed

TABLE 5

The Influence of Contact Time

	Feed	Contact time (s)			
		0.5	1.2	1.8	3.5
Composition (wt %)					
C_8^- aliphatics	4.4	1.2	1.5	1.3	1.1
Benzene	1.5	5.7	5.4	6.8	7.3
Toluene	3.6	3.6	4.5	6.5	8.3
Ethylbenzene	20.0	12.1	7.5	4.2	1.1
p-Xylene	11.3	18.4	19.3	19.0	19.1
m-Xylene	55.7	44.1	43.3	41.8	41.9
o-Xylene	3.5	14.3	16.2	16.9	17.1
$C_9 + C_{10}$ aromatics	—	0.4	2.6	3.7	4.1
Δ Xylenes (wt %)	—	+6.3	+8.2	+7.1	+7.7
C_8 aromatics loss (wt %)	—	1.6	4.2	8.6	11.3
EB conversion (%)	—	38.3	60.6	76.6	93.7
PATE (%)	—	100	100	100	100

Note. Catalyst NiH-ZSM-5, Temp. = 623 K, pressure = 1 bar, molar ratio H_2/oil = 8.

at a much higher space velocity than those with a large content of EB. In the latter case, the need to eliminate EB from the isomer loop will necessitate the use of lower space velocities.

In a petrochemical complex the hydrogen used in the xylene isomerization process is usually obtained from the naphtha reformer and is likely to be contaminated with sulfur or chlorine impurities. The influence of S and Cl on product distribution is shown in Table 6. The data refer to a time-on-stream (for each feedstock) of 20 h. Under the reaction conditions, CCl_4 is converted into methane and HCl. Chlorine does not affect the product distribution. On the other hand, thiophene (which is converted into butane/butene and H_2S) decreases the gain of xylenes. It is probable that H_2S reacts with the zeolite surface generating strong acidic sites which enhance the disproportionation reactions which lead to the loss of xylenes.

The feasibility of suppressing the loss of xylenes and enhancing the yield of PX by selectively poisoning (with NH_3) the strong acid sites responsible for the disproportionation reactions on NiH-ZSM-5 zeolites have been demonstrated by us earlier (*26*). To characterize in more detail the acid sites of different strength participating in the var-

TABLE 6

The Influence of Cl and S on Xylene Isomerization

	Feed	Reactants			
		Feed alone	Feed+ 2 ppm CCl_4	Feed+ 20 ppm CCl_4	Feed+ 2 ppm thiophene
Composition (wt %)					
C_8^- aliphatics	3.4	3.2	3.2	3.4	3.0
Benzene	1.3	4.9	4.9	5.0	4.3
Toluene	3.2	4.1	4.7	4.3	5.0
Ethylbenzene	20.1	12.9	12.9	12.8	13.0
p-Xylene	12.8	17.7	17.7	17.7	17.3
m-Xylene	54.5	40.3	40.4	39.9	39.9
o-Xylene	3.8	15.1	15.1	15.1	14.6
$C_9 + C_{10}$ aromatics	—	1.7	1.7	1.8	3.0
Δ Xylenes (wt %)	—	+2.0	+2.1	+1.6	+0.7
C_8 aromatics loss (wt %)	—	5.2	5.1	5.7	6.4
EB conversion (%)	—	32	32	31.5	30.5
PATE (%)	—	100.0	100.0	100.0	100.0

Note. Catalyst NiH-ZSM-5, temp. = 613 K, pressure = 8 bar, molar ratio H_2/oil = 10, WHSV = 3 h^{-1}.

TABLE 7

Regeneration of Active Sites after Total Poisoning with NH_3

	Feed	Time on stream (after injection of NH_3) (h)						
		1	2	3	4	5	6	50
Composition (wt %)								
C_8^- aliphatics	2.1	2.1	2.2	2.3	2.8	2.8	2.8	2.9
Benzene	1.4	1.4	1.5	1.4	1.4	2.1	2.3	3.6
Toluene	3.3	3.3	3.4	3.4	3.4	3.4	3.4	3.9
Ethyl benzene	24.9	24.9	24.9	25.0	23.2	21.6	21.0	18.1
p-Xylene	7.7	9.4	11.8	13.7	15.2	15.8	15.8	15.8
m-Xylene	53.9	50.5	46.8	43.4	41.1	39.5	39.4	38.0
o-Xylene	6.7	8.2	9.4	10.5	12.1	13.1	13.2	13.8
$C_9 + C_{10}$ aromatics	—	—	—	0.1	0.1	1.8	1.9	3.9
PX + OX (wt %)	14.4	17.6	21.2	24.3	27.4	28.9	29.0	29.16
Δ Xylenes (wt %)	—	−0.2	−0.3	−0.7	+0.1	+0.1	+0.1	−0.7
C_8 aromatics loss (wt %)	—	0.2	0.3	0.6	1.6	3.2	3.8	7.5
EB conversion (%)	—	—	—	—	6.8	13.2	15.7	27.3
PATE (%)	—	20.9	50.2	74.3	90.5	97.7	97.7	100

Note. Catalyst H-ZSM-5, temp. = 633 K, pressure = 16 bar, molar ratio H_2/oil = 6, WHSV = 3 h^{-1}.

ious reactions during the isomerization process (isomerization, disproportionation, aromatization of aliphatics, etc.) the following experiment was performed. The H-ZSM-5 catalyst was first completely poisoned by injection of NH_3 in H_2. The NH_3 flow was then stopped and the reaction was continued in H_2. The products were analyzed and the pick-up in catalytic activity was monitored continuously. The results are shown in Table 7. The regeneration of catalytic activity occurs in the following sequence. The isomerization of MX to OX and PX picks up first. This is followed by the disproportionation of EB to benzene and diethylbenzene. The activity for the disproportionation of xylenes to toluene and trimethylbenzene was the last to be restored and, hence, presumably, occurs on the strongest acid sites. Since it is expected that NH_3 desorption begins from weak acid sites and that the strongest acid sites are liberated only toward the end, we may classify the functional characteristics of the acid sites on H-ZSM-5 zeolites in the following order of increasing acidity: xylene isomerization < EB disproportionation < xylene disproportionation. Xylene isomerization activity is essential for maximizing PATE and EB disproportionation is desirable to eliminate EB from the isomerizer loop. On the other hand, the xylene disproportionation reaction leading to a loss of xylenes is undesirable. By selective suppression of the last reaction which requires the strongest acid sites (by attenuation of the surface acidity at the catalyst preparation stage, for example) it is feasible to enhance the net production of *p*-xylene.

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