Catalysis Letters 24 (1994) 123–132

Two sources of synergism in the reforming of *n*-hexane, methylcyclopentane, methylcyclohexane mixtures over composites of basic and acidic zeolites

Eli Ruckenstein [1] and Panagiotis G. Smirniotis

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260, USA

Received 9 August 1993; accepted 11 October 1993

Pt supported on composites of the basic L zeolite with either H/β or H/USY acidic zeolite are employed in the reforming of *n*-hexane, methylcyclopentane, methylcyclohexane and their mixtures. It was found that when mixtures of the above three compounds are used as feeds, the composites provide decreased benzene selectivity and increased conversion and aromatic selectivity in comparison with the conversion and selectivity calculated by weighting those of the individual compounds with their molar fractions in the feed. The synergism caused by the components of the composite in combination with the synergism due to the cooperative reactions of the components of the feed are suggested to be responsible for this behavior. A detailed explanation of the latter synergism is proposed. The balancing of the L zeolite with one of the above two acidic zeolites can provide a selective route to $C_{>7}$ aromatics from hydrocarbon feeds containing $C_{\geqslant 6}$ paraffins.

Keywords: Reforming; L zeolite; β zeolite; USY; composite zeolites; hydrocarbon mixtures

1. Introduction

The upgrading of naphthas through reforming has been one of the most important petroleum processes over the years. Chlorided or fluorided Al_2O_3 supported Pt, Pt–Re or Pt–Ir combinations are often employed as catalysts [1]. Recently, zeolites have been increasingly investigated. Twelve-ring pore acidic zeolites, such as β, Y, USY, ZSM-3 and ZSM-20 supported Pt, have been employed in the reforming of long chain *n*-paraffins. Bernard observed that Pt supported on the basic KL zeolite possesses a high aromatization capability for *n*-hexane [2]. The reforming of naphthenes over zeolites has been also investigated [3,4]. It was found that their pore structure and acidity stimulate bimolecular alkylation reactions which enhance the generation of $C_{>6}$ aromatics. It was also noted that composites made

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[1] To whom correspondence should be addressed.

of Pt/γ-Al_2O_3 and Pt/β zeolite exhibit a beneficial behavior in the reforming of methylcyclopentane [5].

In the present study we examine the performance of L–β and L–USY zeolite composites (both containing Pt) in the reforming of mixtures of *n*-hexane, methylcyclopentane and methylcyclohexane. In these novel bifunctional catalysts Pt supported on L zeolite provides the metallic function of the composites, since as shown below the Pt dispersion is high over this zeolite. The acidic zeolites supported Pt provide mainly the acidic function of the composites and to a smaller degree than the former zeolite the metallic function. For comparison purposes the catalytic reactions of the individual hydrocarbons were also carried out. It was found that the conversions and the aromatic selectivities over the composites for different hydrocarbon mixtures are higher than those calculated by weighting the conversions and selectivities of the individual compounds with their molar fraction in the feed stream. This behavior can be attributed, as demonstrated later in the paper, to two synergisms: one is due to components of the composite catalyst while the other to the components of the mixture.

2. Experimental

Zeolite β has been prepared hydrothermally from an aluminosilicate gel with a nominal molar composition of 30 SiO_2 : Al_2O_3 : 0.9 Na_2O : 3 TEAOH : 250 H_2O containing tetraethylammonium hydroxide (TEAOH) as template. The USY zeolite was donated to us by W.R. Grace (SMR 6-2811-0992). Elemental analysis has shown that the above two zeolites have a SiO_2/Al_2O_3 molar ratio of 28 and 5, respectively. Calcination of the β zeolite at 510°C for 5 h in ultra high purity O_2 was employed to burn the template. This was followed by its grinding and sieving (150 mesh size sieve). Both zeolites were cation exchanged under reflux with 4 M NH_4Cl at 95°C for 3 h. The zeolites were transformed to their acidic form by calcination at 450°C for 1 h in O_2. X-ray diffraction ensured that the zeolite crystal structure was not altered by the ion exchange and calcination. The Pt supported zeolites were prepared by wet impregnation with H_2PtCl_6 to obtain a metal loading of 0.5 wt%. The KL zeolite was provided by UOP (Lot No. 13923-02) and had a SiO_2/Al_2O_3 molar ratio of 6. The latter zeolite was ion exchanged with 0.3 M $Ba(NO_3)_2$ for 3 h at 95°C, followed by calcination at 600°C for 16 h in air. Wet impregnation with an aqueous solution of platinum(II) tetraamine nitrate (Alfa No. 88960) was employed to achieve a Pt loading of 0.5 wt%. In all cation exchanges 2 g of zeolite were employed in 1 ℓ solution. After impregnation all zeolites were dried overnight at 130°C, followed by grinding and sieving. In the preparation of L–β and L–USY composites, individual zeolites were mixed for 2 h with a shaker mixer. The weight fraction of the acidic component in the composites is denoted by ε. Details regarding the characterization of the zeolites supported Pt with TEM, Cl^- concentration and H_2-chemisorption will be published elsewhere.

The catalytic experiments were performed in a vertical plug flow reactor of 1/8 in. o.d. and 40 cm length at 440–480°C under atmospheric total pressure. In each experiment 100 ± 2 mg of fresh catalyst were loaded in the reactor. The catalysts were activated in situ by oxidation at 300°C for 1 h in ultra high purity oxygen (99.999%), followed by purging with He (99.995%) for 15 min and reduction with high purity H_2 (99.999%) at 500°C for 1 h. Under the present activation conditions the Pt dispersion over β, USY and BaKL zeolites measured by hydrogen chemisorption was 0.15, 0.14 and 0.67, respectively. The reactants were *n*-hexane (Aldrich, 99+ wt%), methylcyclopentane (Aldrich, 99 wt%), methylcyclohexane (Aldrich, 99 wt%) and their mixtures. Three mixtures have been employed: mixture M1 with a molar ratio of *n*-hex : MCP : MCH = 60 : 20 : 20; mixture M2 with equal molar percentages of *n*-hex : MCP : MCH = 1 : 1 : 1; and mixture M3 with a molar ratio of *n*-hex : MCP : MCH = 20 : 40 : 40. The feed hydrocarbons were cofed into the reactor with H_2 through a heated line. A gas chromatograph (HP 5890 series II) equipped with a mass spectrometer (HP 5971 series) has been employed for the on-line analysis of the reaction products. The GC was equipped with a fused silica PoraPLOT wide bore capillary column, a molecular sieve packed column (5A) and a high performance capillary column (HP-1). A PC was attached to the GC/MS unit for data manipulation.

3. Results and discussion

The hydrocarbons employed in the present study are typical representatives of the compounds employed in reforming. For comparison purposes, the performance of the composites with the individual hydrocarbons was also determined. The conversion X and the selectivities S_i of the lumped species are defined as follows:

$$X = \left(1 - \frac{\text{moles of the reactant hydrocarbons in the products}}{\text{moles of the reactant hydrocarbons fed into the reactor}}\right) \times 100,$$

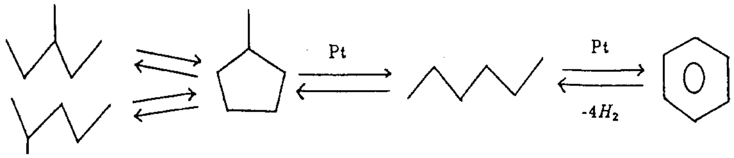
$$S_i = \left(\frac{\text{moles of } i \text{ species produced}}{\text{moles of all products}}\right) \times 100.$$

Since the reactions investigated are very complex, particularly when mixtures of hydrocarbons are employed as feed, the experiments were carried out at 5 min on stream in order to avoid the complexities generated by deactivation. Experiments were also performed at various times on stream. They indicated that the selectivities obtained at 5 min can be considered as the initial ones.

3.1. INDIVIDUAL HYDROCARBONS AS FEEDS

For a better understanding of the performance of composites with feed mixtures, the behavior of the individual components of the mixture over the different zeolites composites has to be examined.

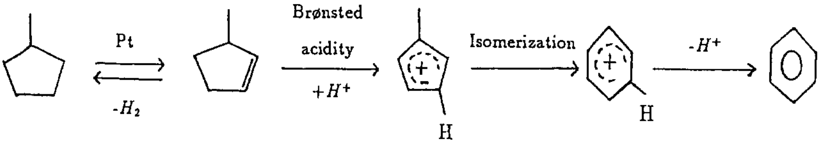
It was established earlier [6] than n-hexane is transformed to benzene very selectively over L zeolite supported Pt. Since BaKL zeolite lacks acidic sites, n-hexane is not cracked to light hydrocarbons. Regarding methylcyclopentane, the ring opening at the secondary–tertiary and secondary–secondary carbon atoms over the metal sites of the L zeolite generates n-hexane and C_6 isomers, respectively. The only possible pathway for the aromatization of methylcyclopentane over L zeolite is via n-hexane formation after the opening of the ring and the subsequent cyclization of n-hexane to benzene. The above steps in the reactions of hexane and methylcyclopentane over Pt supported on L zeolite are summarized as



(I)

We found that with methylcyclohexane as feed, the L zeolite provides the almost complete dehydrogenation to toluene.

The acidic zeolites enhance the cyclization over the acidic sites of the olefinic intermediates (generated by the dehydrogenation of n-hexane over the Pt sites) to benzene [7]. With methylcyclopentane as feed, the isomerization of methylcyclopentenes (generated from methylcyclopentane over the Pt sites) over the Brønsted sites via a carbenium ion mechanism, leads to the enlargement of the C_5 ring to a C_6 ring, and further via dehydrogenation to benzene [8],



(II)

Methylcyclohexane is transformed to toluene over the Pt sites and toluene is transalkylated over the acidic sites to benzene and xylenes.

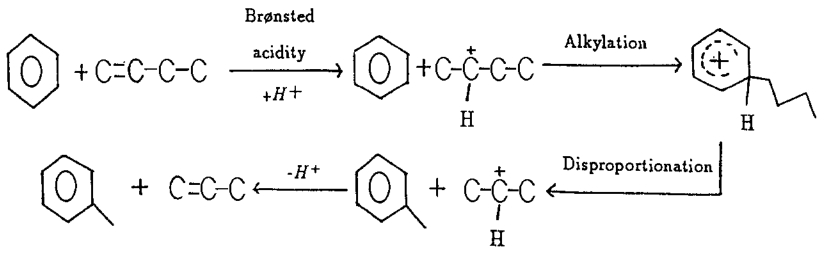
The product distributions for the reaction of individual hydrocarbons over L–β and L–USY composites with equal weights of L and acidic zeolites are presented in table 1. With n-hexane as feed relatively large amounts of propane are formed by the "center" cracking of the feed hydrocarbon due to the acidic component of the composite. The fact that the selectivities for C_1 and C_2 hydrocarbons are small indicates that hydrogenolysis and hydrocracking occur to small extents only. C_6 isomers are detected in very small amounts, especially with the β zeolite composites. Relatively high benzene selectivities stimulated by the L zeolite, which are however smaller than those obtained with L zeolite alone, and high $C_{>6}$ aromatic selectiv-

Table 1
Product distribution and conversion for *n*-hexane (WHSV = 2.00 h^{-1}, H_2/oil = 4.2), methylcyclopentane (WHSV = 1.79 h^{-1}, H_2/oil = 4.8) and methylcyclohexane (WHSV = 0.70 h^{-1}, H_2/oil = 16.2) over L–β zeolite and L–USY zeolite composites at T = 480°C (5 min on stream, 0.5 wt% Pt loading)[a]

Products (mol%)	*n*-hexane		Methylcyclopentane		Methylcyclohexane	
	Pt/β	Pt/USY	Pt/β	Pt/ USY	Pt/β	Pt/USY
methane	0.6	0.4	0.8	1.3	1.2	0.7
ethene	–	–	0.7	1.3	–	–
ethane	2.5	1.6	0.7	0.8	0.2	0.3
propene	2.2	2.8	0.8	0.5	–	–
propane	35.4	28.3	3.7	1.6	0.3	1.0
i-butane	8.4	7.4	2.5	0.5	0.1	0.4
2-butene	1.9	1.8	0.8	0.5	–	–
n-butane	9.5	3.2	2.0	0.8	0.6	0.3
i-pentane	1.9	5.3	2.2	0.8	0.4	–
n-pentane	1.3	1.8	1.2	1.0	1.1	0.1
2-pentene	–	–	0.7	0.3	–	–
2-methylpentane	–	5.2	–	–	–	–
3-methylpentane	–	3.4	–	–	–	–
methylcyclopentenes	–	–	9.8	18.4	–	–
benzene	15.1	21.6	37.6	47.0	22.5	25.2
cyclohexane	–	–	1.9	1.0	–	–
toluene	11.7	23.6	16.6	7.0	45.5	42.4
ethylbenzene	–	–	1.5	1.0	3.7	2.3
o-xylene	1.9	2.6	2.7	2.4	7.8	10.8
m-xylene	2.2	2.8	2.9	2.1	4.9	9.6
p-xylene	4.5	5.5	6.4	5.0	10.1	14.6
1-ethyl-4-methylbenzene	0.3	0.4	1.2	1.6	1.5	0.8
1-ethyl-3-methylbenzene	–	–	0.3	1.0	–	–
1,3,5-trimethylbenzene	0.6	1.2	2.6	1.0	2.9	1.5
conversion (mol%)	100.0	81.9	59.0	38.1	100.0	100.0

[a] The composites contain equal weights of L zeolite with each of the acidic zeolites.

ities due to bimolecular alkylation reactions (reaction scheme III), which are higher than those obtained with pure acidic zeolites since the latter generate less benzene, are observed over the composites.



(III)

The Brønsted acidity of the zeolite stimulates the formation of lower hydrocarbons (including olefins) and the bimolecular alkylation of benzene with olefins which leads to alkylbenzenium ions. The disproportionation of the latter intermediate molecules results in the enrichment of the initial aromatic molecule in carbon atoms [9,10]. The lighter olefin generated after disproportionation can be used subsequently in other alkylation reactions.

With methylcyclopentane the lumped C_1–C_6 paraffinic plus olefinic selectivity remains at a low level. The benzene selectivity, which is a result of the isomerization-enlargement over the Brønsted acid sites of the composite (reaction scheme II) of the C_5 cyclic olefinic intermediates formed over the Pt sites, is high but smaller than over pure acidic zeolites. An increased $C_{>6}$ aromatic selectivity is observed as a result of bimolecular alkylation reactions.

With methylcyclohexane as feed, complete conversion is achieved and the lumped C_1–C_6 paraffinic plus olefinic selectivity remains at low levels. Its dehydrogenation to toluene over Pt sites of the composite is responsible for the relatively large amount of toluene generated especially at small values of ε. The relatively large concentrations of benzene and C_8 aromatics detected in the products when the amount of acidic zeolite is increased indicates that the toluene generated over the Pt sites is partially transalkylated to the above compounds over the acidic sites. Both β and USY containing composites behave in a similar way.

3.2. REACTIONS OF HYDROCARBON MIXTURES OVER COMPOSITES

The performance of L–β and L–USY composites with a mixture containing equal molar amounts of *n*-hexane, methylcyclopentane and methylcyclohexane is presented in figs. 1 and 2, respectively. For comparison purpose, the conversion and the selectivities of aromatics and of lumped C_1–C_6 paraffins plus olefins are (open symbols) calculated by weighting those of the individual feed hydrocarbons with their molar fractions in the feed mixture. One can observe that with both types of composites the conversions and aromatic selectivities of the hydrocarbon mixture are higher than those calculated, and that the benzene (see table 2) and the lumped C_1–C_6 paraffinic plus olefinic selectivities are lower. With all mixtures, the L zeolite alone provides a higher benzene selectivity, smaller conversion and $C_{>7}$ aromatic selectivity than the composites which contain an acidic zeolite. The toluene selectivity over the acidic zeolites is lower than that over L zeolite.

The above observations regarding the increased conversion and aromatic selectivity and decreased benzene selectivity for the mixtures reveal that synergisms among the components of the composites and those of the mixture exist. When Pt is supported on the L zeolite, the catalyst transforms *n*-hexane almost completely to benzene. The inclusion of an acidic zeolite in the catalyst decreases the selectivity to benzene for two reasons: (1) the cracking of a fraction of hexane to lighter paraffins and olefins, and (2) the bimolecular alkylation reaction of benzene with olefins (scheme III) followed by disproportionation to $C_{\geqslant 7}$ aromatics and lighter olefins.

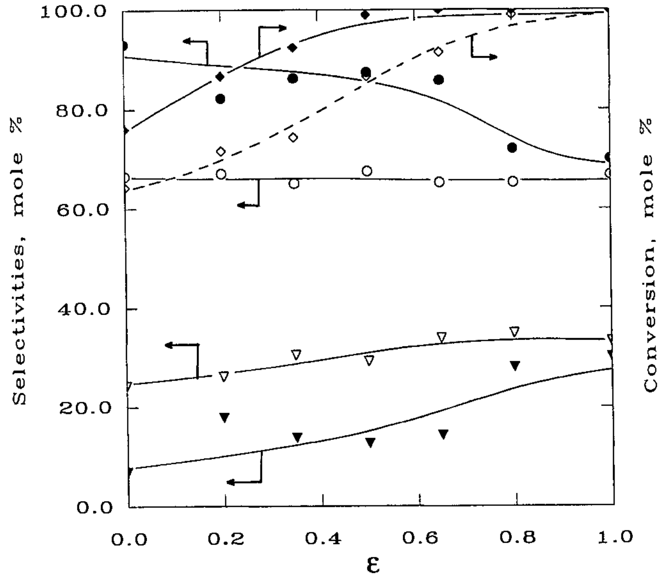


Fig. 1. Selectivities for C_1–C_6 paraffins plus olefins (▼) and aromatics (●) for M2 over L–β zeolite composites. The open symbols stand for the selectivities calculated from the single hydrocarbon selectivities. The continuous line stands for the conversion of M2 and the dashed line stands for the calculated conversion (WHSV = 2.00 h^{-1}, H_2/oil = 4.5, 5 min on stream, 0.5 wt% Pt).

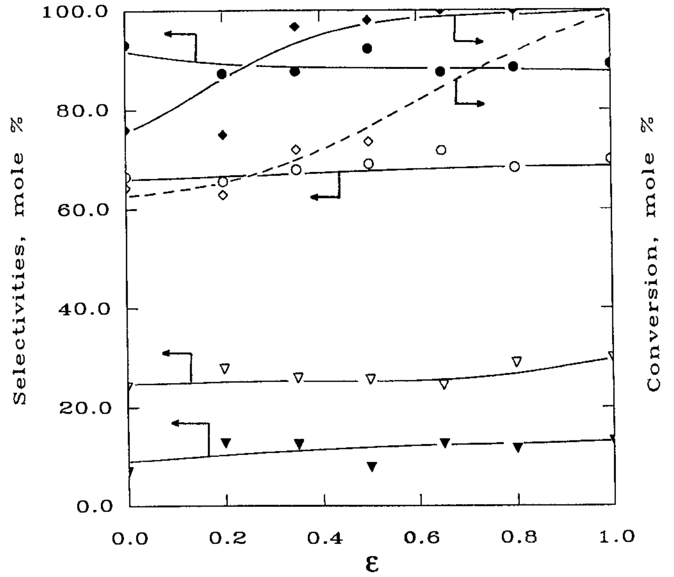


Fig. 2. Selectivities for C_1–C_6 paraffins plus olefins (▼) and aromatics (●) for M2 over L–USY zeolite composites. The open symbols stand for the selectivities calculated from the single hydrocarbon selectivities. The continuous line stands for the conversion of M2 and the dashed line stands for the calculated conversion (WHSV = 2.00 h^{-1}, H_2/oil = 4.5, 5 min on stream, 0.5 wt% Pt).

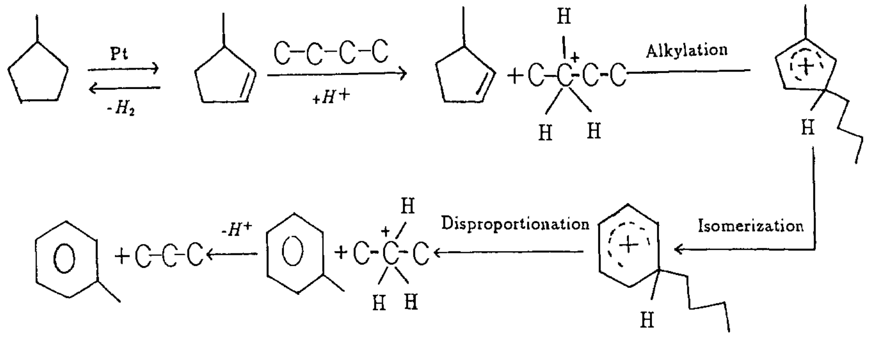
Table 2
Product distribution and conversion for mixtures over L–β zeolite and L–USY zeolite composites at $T = 480°C$ (5 min on stream, 0.5 wt% Pt loading, WHSV = 2.00 h^{-1}, H_2/oil = 4.5)[a]

Products (mol%)	Mixture 1		Mixture 2		Mixture 3	
	Pt/β	Pt/USY	Pt/β	Pt/USY	Pt/β	Pt/USY
methane	2.1	2.4	2.1	1.4	2.6	2.6
ethane	2.5	2.4	2.4	1.4	1.3	1.7
propane	6.5	3.7	2.4	2.0	3.3	1.1
i-butane	2.8	2.4	2.3	0.9	0.6	1.0
2-butene	0.4	0.2	0.2	–	–	0.1
n-butane	3.3	1.0	1.4	1.0	1.3	1.0
i-pentane	1.2	1.8	1.1	0.3	0.2	0.4
n-pentane	0.8	0.4	0.8	0.1	0.3	0.3
2-methylpentane	0.6	2.1	0.5	0.7	0.1	0.4
3-methylpentane	0.4	0.8	0.3	–	–	–
benzene	15.0	18.1	16.5	18.4	19.8	20.7
toluene	36.8	39.6	34.9	39.7	43.6	43.3
o-xylene	8.9	6.2	6.8	6.0	4.5	5.5
m-xylene	3.4	2.9	3.9	3.7	3.3	4.1
p-xylene	10.9	7.2	9.1	9.0	6.5	6.1
ethylbenzene	0.2	0.3	1.1	1.5	2.1	2.5
1-ethyl-4-methylbenzene	1.6	3.3	6.1	7.2	5.4	4.9
1,3,5-trimethylbenzene	2.2	6.8	7.0	6.0	4.9	4.6
conversion (mol%)	98.7	95.2	99.2	98.1	95.6	89.7

[a] The composites contain equal weights of L zeolite with each of the acidic zeolites.

If besides hexane, naphthenes are also present, benzene is generated by a number of reactions: (1) The dehydroisomerization of methylcyclopentane over the metal and acidic sites of the composite; (2) the *n*-hexane cyclization over the L zeolite (reaction scheme (I)); (3) the transalkylation of toluene (generated over Pt sites by the dehydrogenation of methylcyclohexane) over the acidic sites. The benzene thus generated is alkylated with olefins and the resulting alkylbenzenium intermediates are disproportionated to higher aromatics and lighter olefins (the latter molecules may participate in subsequent alkylation reactions). These reactions consume the benzene and the olefins generated.

Another type of alkylation reaction occurs between methylcyclopentenes (formed via dehydrogenation of methylcyclopentane over the metallic sites) with carbonium ions formed by the protonation of paraffins and by the ring opening of the methylcyclopentane over the Brønsted sites of the catalyst which decreases significantly the amount of paraffins generated. This is followed by the disproportionation of the generated intermediates to a $C_{\geq 7}$ aromatic and to a lighter paraffin [3]. This reaction can provide additional C_4, C_5 paraffins.



(IV)

Moreover, the consumption of benzene by alkylation reactions shifts the cyclization of *n*-hexane over the L zeolite to benzene thus decreasing the fraction of *n*-hexane which is transformed to C_1–C_6 paraffins and olefins. As an overall result of the above cooperative reactions, the benzene and the lumped C_1–C_6 paraffinic plus olefinic selectivities are decreased while the aromatic selectivity is increased. One can observe in both figures that for the L zeolite alone, the aromatic selectivity for the mixture is significantly higher than that calculated. A possible explanation is that the ring opening of methylcyclopentane to hexane is accelerated. This probably occurs because the transformation of *n*-hexane to benzene is faster than the transformation of methylcyclopentane to *n*-hexane by ring opening. This shifts the transformation of methylcyclopentane in the direction of *n*-hexane.

The product distributions of a more paraffinic mixture of hydrocarbons (M1) and a more naphthenic mixture (M3) over composites containing equal weights of L and acidic zeolite are also included in table 2. With M1 the product distribution is shifted to lighter hydrocarbons than with the other two mixtures, because of its more paraffinic character.

While the study of a catalyst with individual hydrocarbons can provide insight in its catalytic performance it cannot give detailed information regarding its behavior with a complex feed.

4. Conclusions

Two types of synergisms are present in the reforming of hydrocarbon mixtures over Pt supported on L–β and L–USY composite zeolites. One is due to the components of the composite catalyst, and the other is a result of the cooperative reactions among the components of the mixture. The L zeolite alone transforms *n*-hexane in benzene; if an acidic zeolite is also present, a fraction of *n*-hexane is cracked to lower paraffins and olefins. The latter molecules participate in alkylation reactions with methylcyclopentane and benzene, respectively, and the intermediates formed are disproportionated to higher aromatics and lighter paraffins or olefins. The alkylation of benzene accelerates the *n*-hexane cyclization over L zeolite to benzene. Methylcyclohexane is dehydrogenated to toluene which in turn, because acidic sites are present, is transalkylated to benzene and C_8 aromatics. For these reasons the performance of some catalysts with a mixture of hydrocarbons can be significantly different from that predicted by weighting the performances of the individual compounds with their molar fractions in the feed.

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