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Kinetics of heptane reforming on Pt / L zeolite

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The kinetics of heptane reforming over 0.64% Pt/KBaL have been measured over a wide range of conditions from 390 to 475°C, 0.05 to 1.00 atm heptane, and 0.2 to 25.0 atm hydrogen. Below about 6 atm H_2, the catalyst deactivates due to carbon fouling of the platinum particles. The reaction rate increases with hydrogen pressure under these conditions, presumably because this accelerates the rate of carbon hydrogenation off the metal surface. Above 6 atm H_2, no deactivation occurs. The activation energies and reaction orders in heptane and hydrogen at high H_2 pressure are: 39 kcal/mol, 0.7 and −1.9 for hydrogenolysis; 60 kcal/mol, 0.6 and −2.8 for isomerization; and 58 kcal/mol, 0.4 and −2.7 for dehydrocyclization. These kinetics are the same as those observed over platinum on nonacidic supports, and indicate that the reaction mechanism on Pt/KBaL is no different from that on monofunctional Pt catalysts.

Keywords: Kinetics; heptane reforming; Pt / BaL zeolite catalysts

1. Introduction

Hydrocarbon reforming over platinum in L zeolite is an attractive, high-yield process for converting light straight-run naphtha into aromatics [1–3]. Many studies have been conducted to find out why this catalyst is so active and selective for alkane dehydrocyclization [4–13]. However, relatively few studies have examined the reaction kinetics [9]. It has been shown that Pt/L is a monofunctional catalyst with the reforming reactions taking place only on the platinum particles [1,2,9,12]. Therefore, this system provides a unique opportunity to examine the kinetics of Pt-catalyzed reforming reactions. These results should provide a valuable comparison to the reaction kinetics observed for bifunctional catalysis over platinum on acidic alumina [14]. Below we report on our study of the kinetics of heptane reforming over Pt / KBaL zeolite.

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2. Experimental

A Pt/KBaL catalyst was prepared according to the method described in our previous paper [15]. Briefly, barium was exchanged into the zeolite at 25°C, and the zeolite calcined at 590°C to move the barium to the A and B sites inside the double six-membered rings and the ε-cages [16]. After this treatment, potassium was exchanged into the sample, and the sample dried at 120°C. The platinum was added by incipient wetness impregnation of $Pt(NH_3)_4Cl_2$, followed by heating the sample in air from 25 to 350°C over 11 h, and holding it an additional 3 h at 350°C. The composition of the catalyst was analyzed by inductively coupled plasma emission spectroscopy at Amoco Research Center in Naperville, IL. It contained 0.64 wt% platinum and exhibited a cation to aluminum mole ratio of 1.01. The cation distribution in the zeolite was 6.36 K^+ and 1.37 Ba^{2+} per unit cell [15].

The kinetics of heptane reforming were determined in a fixed-bed microreactor. Catalyst pellets, weighing 0.19 g and between 32 and 60 mesh size, were placed in a stainless steel tube of 6.35 mm o.d. A thermocouple was mounted just upstream of the catalyst bed. The tube was connected to the flow manifold and inserted in a clam-shell heater. After the system had been purged with helium, the catalyst was heated in 100 cm^3/min H_2 to 500°C over 1 h and reduced at this temperature for 2 h. Then the sample was cooled to the reaction temperature, and the reaction begun by switching to a mixture of heptane, hydrogen and helium. Two sets of reaction conditions were used: *low hydrogen pressure* – 450°C, 0.16 atm heptane, 0.95 atm H_2, 6.7 atm He, and 240 cm^3/min flow rate; and *high hydrogen pressure* – 430°C, 0.16 atm heptane, 12.0 atm H_2, 12.8 atm He, and 240 cm^3/min flow rate. This flow rate yielded a residence time of 5.5×10^{-5} h at 25°C and 1 atm pressure, based on the total volume of the catalyst bed.

Rate measurements at different temperatures and reactant pressures were taken between 3 and 11 h of reaction. The flow rate was varied during these measurements to keep the conversion constant and below 8%. Periodically, the rate was recorded at the standard reaction conditions in order to account for catalyst deactivation. The heptane used in these experiments was VWR Scientific Omnisolv grade of 99.9% purity which contained less than 5 ppb sulfur. The hydrogen and helium were 99.95 and 99.995% pure, and were passed through Alltech oxygen adsorbent and 13X molecular sieves held at −78°C. The reaction products were analyzed by gas chromatography, using a J&W Scientific Megabore capillary column (DB-1 active phase, 30 m in length) and a flame ionization detector. The products were initially identified by GC-MS. Standards were injected to calibrate the GC peak areas.

Before and after each run, the platinum dispersion was measured in situ by hydrogen titration of adsorbed oxygen. It was found to remain constant at 62 ± 5%.

3. Results

3.1. LOW HYDROGEN PRESSURE

The dependence of the heptane conversion on time for reaction at 450°C, 0.16 atm heptane, 0.95 atm H_2, and 6.7 atm He is shown in fig. 1. The rate falls rapidly over the first 50 min, then decays slowly from 50 to 500 min on stream. The solid line in fig. 1 is the best fit of the data to a power-law dependence of the rate on time. The equation of this line is $r = 0.017 \times t^{-0.22}$ (mol C_7/h g).

Presented in table 1 is the product distribution obtained after 3 h of heptane reforming at these conditions. The products are listed in terms of the amount of heptane converted. For example, the ppms of heptane converted into propane equals 3/7s the ppms of propane in the reactor exit stream. The main hydrocarbon products are methane and ethane, benzene, heptene, ethylcyclopentane, and toluene. The gas chromatograph did not separate methane and ethane so they are listed together in table 1. If the heptene and C_7 isomers are excluded from the products, the selectivity to aromatics is 72.3%. The preference for terminal cracking can be evaluated by comparing the selectivity to C_6 hydrocarbons relative to C_5 and C_4 hydrocarbons: $C_6/(C_5 + C_4) = 1.2$. At the beginning of the run, this ratio is 1.4.

Shown in table 2 are the activation energies and reaction orders measured for heptane conversion to the main products at low hydrogen pressure. Reaction rates were measured between 3 and 8 h on stream, and were corrected to account for any deactivation that occurred over this period. The kinetic parameters were

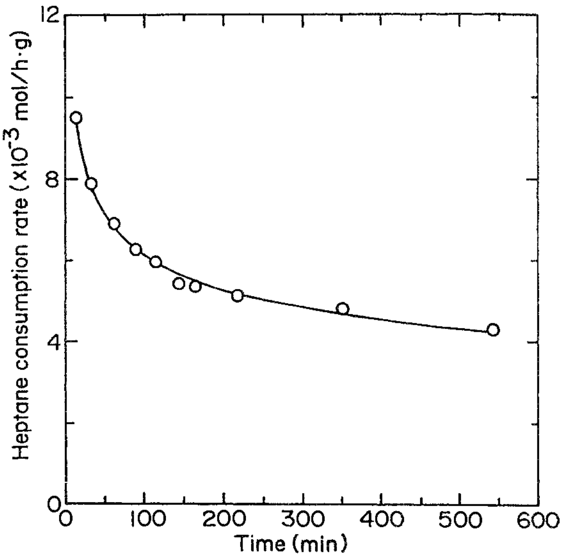

Fig. 1. The dependence of the heptane consumption rate on time for reaction at 450°C, 0.16 atm heptane, 0.95 atm H_2, and 6.7 atm He.

Table 1
Product distribution for heptane reforming over Pt/KBaL after 3 h of reaction at 450°C and 0.95 atm of H_2

Product[a]	Heptane converted (ppm)	Selectivity (%)
methane and ethane	109	6.8
propane	25	1.6
butane	23	1.4
butene	1	0.1
pentane	45	2.8
pentene	4	0.3
cyclopentane	19	1.2
3-methylpentane	9	0.6
hexane	47	2.9
hexene	15	0.9
methylcyclopentane	30	1.9
methylcyclopentene (cyclohexene)	7	0.4
benzene	190	11.8
3-ethylpentane (2,3-dimethylpentane)	12	0.7
3-methylhexane (2-methylhexane)	23	1.4
heptene	173	10.8
ethylcyclopentane (1,2-dimethylcyclopentane)	187	11.6
toluene	687	42.8

[a] Products in parentheses were not distinguished from their isomers.

obtained by varying the conditions from 425 to 475°C, 0.05 to 0.4 atm heptane, 0.2 to 2.0 atm H_2, and 3 to 10 atm total pressure. At these low hydrogen pressures, the rates of hydrogenolysis, isomerization and dehydrocyclization exhibit positive, fractional order dependencies on the heptane and hydrogen pressures. The order in hydrogen is highest for ethylcyclopentane and lowest for methane and ethane. The apparent activation energies for these reactions vary over a wide range, from 0 kcal/mol for ethylcyclopentane to 55 kcal/mol for methane and ethane.

Table 2
Kinetic constants for heptane reforming over Pt/KBaL at low hydrogen pressure

Product	Activation energy (kcal/mol)[a]	Reaction orders in		
		heptane	hydrogen	total pressure[b]
methane and ethane	55	0.5	0.2	0.7
ethylcyclopentane	0	0.7	0.8	1.3
benzene	37	0.0	0.3	0.4
toluene	27	0.3	0.6	0.6

[a] 1 kcal = 4.184 kJ.
[b] For $H_2/C_7 = 6.0$.

3.2. HIGH HYDROGEN PRESSURE

When the hydrogen pressure is increased to 12 atm, the catalyst no longer deactivates during the reaction. Instead the reforming rate increases by about 50% over the first 30 min of the run, and remains constant thereafter. The product distribution obtained after 3 h of reaction at 430°C, 0.16 atm heptane, 12 atm H_2, and 12.8 atm He is shown in table 3. No benzene or olefins are made under these conditions. In addition, the rates of hydrogenolysis and isomerization have increased relative to the rate of dehydrocyclization. Excluding the C_7 isomers from the product, the selectivity to toluene is 26.7%. The preference for terminal cracking is: $C_6/(C_5 + C_4) = 0.61$. This ratio is lower than that observed at low hydrogen pressure.

Shown in table 4 are the apparent activation energies and reaction orders measured for heptane conversion to the different products at high hydrogen pressure. In table 5, these parameters are lumped into the three main reactions, hydrogenolysis, isomerization and dehydrocyclization. The kinetic parameters were obtained by varying the conditions from 390 to 440°C, 0.16 to 1.0 atm heptane, and 6 to 25 atm H_2. At high hydrogen pressures, the rates of hydrogenolysis, isomerization and dehydrocyclization exhibit positive, fractional order dependencies on the heptane pressure, and large, negative-order dependencies on the hydrogen pressure. The reaction orders for hydrogen are close to −2 for hydrogenolysis and −3 for isomerization and dehydrocyclization. At high hydrogen pressure, the activation energy for hydrogenolysis is significantly lower than the activation energies for isomerization and dehydrocyclization, i.e. 39 compared to 60 and 58 kcal/mol.

Table 3
Product distribution for heptane reforming over Pt/KBaL after 3 h of reaction at 430°C and 12 atm of H_2

Product[a]	Heptane converted (ppm)	Selectivity (%)
methane and ethane	8	5.7
propane	13	9.3
butane	14	10.0
pentane	9	6.4
hexane	14	10.0
3-ethylpentane (2,3-dimethylpentane)	9	6.4
3-methylhexane (2-methylhexane)	14	10.0
ethylcyclopentane (1,2-dimethylcyclopentane)	38	27.1
toluene	21	15.0

[a] Products in parentheses were not distinguished from their isomers.

Table 4
Kinetic constants for heptane reforming over Pt / KBaL at high hydrogen pressure

Product	Activation energy (kcal/mol)	Reaction orders in	
		heptane	hydrogen
methane and ethane	33 ± 6	0.8 ± 0.1	−1.7 ± 0.2
propane	41 ± 5	0.8 ± 0.1	−1.9 ± 0.2
butane	44 ± 5	0.7 ± 0.1	−1.9 ± 0.2
pentane	37 ± 6	0.7 ± 0.1	−1.9 ± 0.2
hexane	46 ± 3	0.4 ± 0.1	−1.9 ± 0.2
ethylpentane	57 ± 5	0.5 ± 0.1	−2.6 ± 0.1
methylhexane	50 ± 4	0.5 ± 0.1	−2.4 ± 0.1
ethylcyclopentane	68 ± 11	0.7 ± 0.2	−3.2 ± 0.4
toluene	58 ± 8	0.4 ± 0.1	−2.7 ± 0.5

These results may be contrasted to those obtained at low hydrogen pressure. In the latter case, the activation energy for hydrogenolysis is greater than those for isomerization and dehydrocyclization, and the dependence on hydrogen pressure is positive in all cases. This change in the kinetics is also evident in fig. 2. Below 6 atm H_2, the reaction rates are not sensitive to the hydrogen pressure, whereas above this point, the rates decrease rapidly with hydrogen pressure.

4. Discussion

The effect of hydrogen on the rate of heptane reforming over Pt/ KBaL is similar to that observed for hydrocarbon reforming over platinum on alumina. Sinfelt [14,17] reported that the rate of heptane dehydrocyclization over Pt/Al_2O_3 increases with hydrogen pressure from 0 to 6 atm H_2, then falls as the hydrogen pressure increases further. This trend is also observed for pentane isomerization over Pt/Al_2O_3 [14]. Sinfelt attributed these kinetics to the influence of coke formation on the catalyst activity. Below 6 atm H_2, the platinum surface is covered with carbon residues which block the reforming reaction. This carbon can be hydrogenated off the surface, thereby freeing up sites for catalysis. Increasing the hydrogen pressure, increases the rate of carbon removal, and in turn, the rate of reforming.

Table 5
Kinetic constants for heptane hydrogenolysis, isomerization and dehydrocyclization over Pt /KBaL at high hydrogen pressure

Reaction	Activation energy (kcal/mol)	Reaction orders in	
		heptane	hydrogen
hydrogenolysis	39	0.7	−1.9
isomerization	60	0.6	−2.8
dehydrocyclization	58	0.4	−2.7

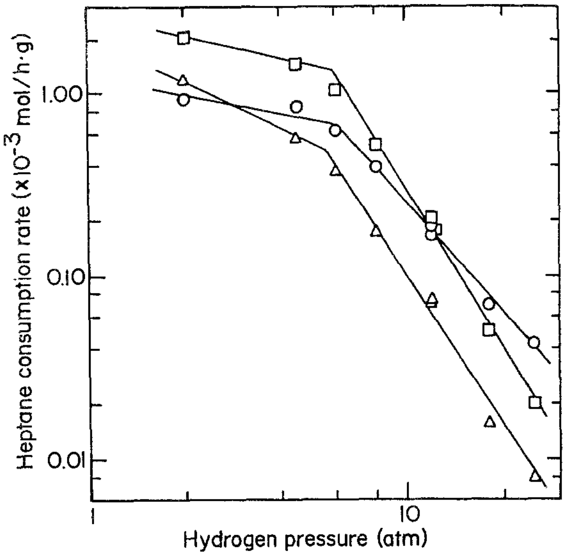

Fig. 2. The effect of the hydrogen pressure on the rates of hydrogenolysis (○), isomerization (□) and dehydrocyclization (△) at 430°C, 0.16 atm heptane, 25 atm total pressure, and 3–11 h on stream.

Above 6 atm H_2, the platinum surface is kept clear of carbon, so that now hydrogenation of adsorbed hydrocarbon intermediates limits the rate of reaction. In this case, increasing the hydrogen pressure, raises the surface coverage of hydrogen, and suppresses the dehydrogenation rate.

The deactivation of the Pt/KBaL catalyst at low hydrogen pressure provides additional evidence that carbon accumulates on the platinum under these conditions. The activity of the catalyst falls at a rate proportional to the -0.22 power of time. This power-law dependence is the same as that observed by Pacheco and Petersen [18] for carbon fouling of Pt/Al_2O_3 during dehydrogenation of methylcyclopentane. They found that carbon deposition on the platinum causes its activity to decay with the -0.2 power of time.

We have characterized the distribution of platinum in the Pt/KBaL catalyst by transmission electron microscopy, chemisorption, and infrared spectroscopy of adsorbed carbon monoxide [15]. The L zeolite contains a bimodal distribution of platinum, consisting of a few large crystallites outside the pores and many small clusters inside the pores. The heptane reforming activity of the catalyst is essentially due to the small clusters, since they account for more than 90% of the exposed metal. Based on this information, we can suggest two possible mechanisms for carbon fouling of the Pt/KBaL catalyst: (1) Heptane decomposes to coke on the surfaces of the clusters and the crystallites and deactivates them for reforming. (2) Heptane decomposes to coke only on the crystallites. Then this coke spreads out over the zeolite surface and blocks the pores so that heptane cannot reach the platinum clusters. Unfortunately, we did not examine the deactivated catalyst by electron microscopy, and do not know whether coke had spread out over the zeolite surfaces.

Recently, Iglesia and Baumgartner [13] have studied the carbon fouling of Pt/KL and Pt/SiO_2 during heptane reforming. They found that these two catalysts exhibit the same activity and selectivity for heptane dehydrocyclization at the start of the reaction. However, after several hours on stream, the performance of Pt/KL has not changed, while the Pt/SiO_2 has become much less active and selective for dehydrocyclization. The latter catalyst deactivates as a result of the carbon deposition on the metal particles. These authors concluded that the L zeolite pores inhibit coke formation so that platinum inside the pores remains free of carbon residues. In the study by Iglesia and Baumgartner, the heptane forming reaction was carried out in 6.7 atm of hydrogen. At this hydrogen pressure, we did not observe any deactivation of 0.64% Pt/KBaL, even though this sample contains large platinum crystallites outside the pores. These results suggest the following question: Does a Pt/L catalyst with no platinum inside the pores deactivate during heptane reforming in 1 atm of hydrogen?

Shown in table 6 are the activation energies and reaction orders reported in the literature for hydrogenolysis and isomerization of linear alkanes at hydrogen pressures above 5 atm. The kinetics observed in other studies are in good agreement with the results we obtained on Pt/KBaL provided that the supports are nonacidic. For example, Kikuchi et al. [19] examined pentane hydrogenolysis over Pt/SiO_2 and Pt/carbon and obtained activation energies of 28–34 kcal/mol and reaction orders for pentane and hydrogen of 0.8 and −1.4. We find that for heptane hydrogenolysis over Pt/KBaL, the activation energy is 39 kcal/mol and the reaction orders for heptane and hydrogen are 0.7 and −1.9. On the other hand, the isomerization

Table 6
Comparison of reported reaction kinetics for alkane reforming at high hydrogen pressure

Reactant	Catalyst	Activation energy (kcal/mol)	Reaction orders in		Ref.
			alkane	hydrogen	
hydrogenolysis					
n-pentane	Pt/SiO_2	28	0.7	−1.4	[19]
n-pentane	Pt/carbon	34	0.8	−1.4	[19]
n-pentane	Pt/Al_2O_3	35–45	–	−0.6–1.7	[20]
n-heptane	Pt/KBaL	39	0.7	−1.9	this work
isomerization					
n-pentane	Pt/Al_2O_3	55	–	−1.8	[20]
n-pentane	Pt/Al_2O_3^{a}	–	0.5	−0.5	[21]
n-hexane	Pt/HMor^{b}	29–34	0.8	−0.8	[22]
n-heptane	Pt/KBaL	60	0.6	−2.8	this work

[a] Acidic chlorided alumina.

[b] Acidic H-mordenite.

kinetics change significantly when the reaction is catalyzed by platinum on acidic supports instead of nonacidic ones. This may be seen by comparing the data for Pt/HMor and Pt/KBaL. On the former sample, the activation energy is much lower and the reaction order in hydrogen is less negative.

A characteristic of alkane isomerization over platinum on acidic supports is that the dependence of the rate on hydrogen pressure is inverse to the dependence of the rate on alkane pressure [21],

$$r = k([\mathrm{HC}]/[\mathrm{H_2}])^n. \tag{1}$$

Sinfelt [14] has proposed that the rate-limiting step on these catalysts is alkene isomerization on the acid site. The alkene is assumed to be in equilibrium with the alkane and hydrogen due to the rapid dehydrogenation of the alkane on platinum. Substitution of the equilibrium relationship for the alkene into a Langmuir–Hinshelwood expression for its reaction on the acid site yields eq. (1). Conversely, when alkane isomerization is catalyzed by the platinum alone, such as on Pt/KBaL, the rate-limiting step involves the reaction of a dehydrogenated hydrocarbon intermediate on the platinum surface. The formation of this intermediate is inhibited by hydrogen, and yields a large, negative-order dependence on the hydrogen pressure.

The similarity of the heptane and hydrogen pressure dependencies for hydrogenolysis, isomerization and dehydrocyclization over Pt/KBaL, table 5, suggests that these reactions have similar mechanisms. In each case, the rate-limiting step most likely involves the transformation of a dehydrogenated, adsorbed hydrocarbon species. Sinfelt [14] and more recently Dumesic [23] have interpreted the magnitude of the exponent in hydrogen as a measure of the extent of dehydrogenation of the adsorbed hydrocarbon: the more negative the exponent, the more H atoms that are stripped away from the molecule. A comparison of the values listed in table 5 reveals that hydrogenolysis proceeds through a less dehydrogenated intermediate than isomerization or dehydrocyclization.

The dehydrocyclization selectivity exhibited by Pt/KBaL is sensitive to the reaction conditions. The results obtained here indicate that the ratio of dehydrocyclization to the rate of hydrogenolysis equals

$$r_\mathrm{d}/r_\mathrm{h} = 1.2 \times 10^6 P_{\mathrm{C_7}}^{-0.3} P_{\mathrm{H_2}}^{-0.8} \exp(-19000/RT). \tag{2}$$

At the conditions used to test the catalyst, 430°C, 0.16 atm heptane, and 12 atm H_2, the ratio of the rates is 0.36, and the selectivity to toluene (excluding isomers) is 26.7%. However, at 500°C, 1 atm heptane and 6 atm H_2, the ratio of the rates is calculated to be 1.21, yielding a selectivity to toluene of 55%. Other researchers have reported higher selectivities to aromatics at these conditions [2,3,13]. The low value obtained by us may be attributed to the less than optimum distribution of platinum in the zeolite, and to carrying out the reaction at conversions below 5 mol% [9,12,13].

According to eq. (2), the maximum yield of aromatics is obtained by operating at as high a temperature and as low a hydrogen pressure as possible. The upper limit for temperature is 500°C, since above this temperature the platinum clusters in L zeolite agglomerate [2]. The lower limit for hydrogen pressure is 6 atm, because below this point carbon fouling occurs.

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