

# ZEOLITE-CATALYZED CONFORMATIONAL ISOMERIZATION OF *cis*-DECAHYDRONAPHTHALENE. REACTION PATHWAYS AND KINETICS.

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Keywords: Zeolites, isomerization, decahydronaphthalene, kinetics

## INTRODUCTION

It was shown in literature that decalin (DHN) may be one of the potential endothermic jet fuels that can serve as the primary heat sink to cool the hot surfaces and system components [Donath and Hess, 1960; Lander and Nixon, 1987; Taylor and Rubey, 1987]. Commercial decalin solvents from industrial hydrogenation processes consist of almost equimolar mixtures of *cis*- and *trans*-DHN. Although the physical properties of these two isomers are similar, their chemical properties are different. One example is their difference in thermal stability at high temperatures. We have previously shown that as jet fuel components, *trans*-DHN is superior to *cis*-DHN for high temperature application because the former is much more stable at high temperatures [Song et al., 1992]. The excellent thermal stability at high temperatures is desirable for future high Mach aircraft. Besides, *trans*-DHN has the desirable ability of inhibiting the solid deposit formation from jet fuels and their components at high temperatures [Song et al., 1994a]. For example, adding 50 vol% *trans*-DHN to a JP-8P fuel, *n*-tetradecane, and *n*-butylbenzene thermally stressed at 723 K for 4 h significantly reduced the deposit formation from 3.1 to 0.1 wt%, from 3.0 to 0.1 wt%, and from 5.6 to 0.0 wt%, respectively. Although *cis*-DHN also has some potential industrial applications, it is desirable to convert *cis*-DHN to *trans*-DHN for fuel stability consideration at high temperatures.

There has been much research on the catalytic hydrocracking or dehydrogenation of decalin under high pressures and at temperatures generally in excess of 673 K [Ritchie and Nixon, 1967; Shabtai et al., 1979; Constant et al., 1986; Mostad et al., 1990a,b; Nimz, 1990; Sousa-Aguiar et al., 1994]. However, relatively little information about the conformational isomerization of *cis*-DHN into *trans*-DHN at lower temperatures is available. Petrov et al. (1977) reported the isomerization of *cis*- and *trans*-DHN on a nickel catalyst in the temperature range of 393-453 K. They claimed that the isomerization took place only in the presence of hydrogen. Our earlier exploratory work has shown that some mordenites and chemically modified zeolites may promote the isomerization of *cis*-DHN into *trans*-DHN at 523 K for 2 h under N<sub>2</sub> environment [Song and Moffatt, 1993, 1994]. This work extended previous exploratory studies on the catalytic isomerization of *cis*-DHN to *trans*-DHN. The objective of this work is to examine the effects of reaction conditions as well as catalyst properties on the catalytic reaction. An overall kinetic model for the catalytic reaction was proposed and empirical equations were presented to predict the selectivity.

## EXPERIMENTAL

The chemicals, *cis*-DHN, *trans*-DHN, and DHN (an almost equimolar mixture of *cis*- and *trans*-DHN) were obtained from Aldrich Chemical Company and were used as received. Their purities (>99%) were analyzed in our laboratory using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The six catalysts used in the catalytic isomerization reactions include: a hydrogen Y zeolite (HY), a metal ion-exchanged Y zeolite (LaHY), a hydrogen mordenite (HM30A), and three noble metal loaded mordenites (Pt/HM30A, Pd/HM30A, and Pt/HM20A). The noble metal loaded mordenites were prepared by dispersing the salt of platinum or palladium into the mordenites by incipient wetness impregnation method. The noble metal loading on the support was kept at nominally 6 wt%. The details of the preparation and properties of the catalysts are described elsewhere [Song and Moffatt, 1994; Schmitz et al., 1994].

Catalytic isomerization reactions were carried out in 28-mL horizontal type stainless steel tubing bomb reactors, which were charged with 1 g of *cis*-DHN, *trans*-DHN, or DHN (7.23 mmol) and 0.2 g of catalyst, at 473-548 K for 0.15-8 h under an initial pressure of 0.79 MPa UHP N<sub>2</sub> or H<sub>2</sub>. The reactor was agitated vertically at 240 cycles/min to ensure the uniformity of concentration and temperature inside the reactor. After the reaction, the gas products were collected in a gas bag and were quantitatively analyzed using a Perkin-Elmer Autosystem GC equipped with two detectors, a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid products were recovered by washing with acetone and were analyzed on an HP 5890II GC coupled with an HP 5971A Mass Selective Detector (MSD) and quantified by a Perkin-Elmer GC 8500 equipped with an FID. The catalyst was recovered and stored in a vial for thermogravimetric analysis performed later. More analytical details may be found elsewhere [Song et al., 1994b].

## RESULTS AND DISCUSSION

**Calculated composition of equilibria.** The equilibrium compositions of *trans*-DHN and *cis*-DHN at several temperatures were calculated to establish the theoretical upper limit of the catalytic conversion. The equilibrium constant (K) is related to the Gibbs energy change ( $\Delta G^0$ ) by Eq. (1)

$$\ln K = -\frac{\Delta G^0}{RT} \quad (1)$$

Using the data in Reid et al. (1987) for a binary mixture system of *cis*-DHN and *trans*-DHN, we have determined the general expression for the equilibrium constant as a function of temperature as shown in Eq. (2)

$$R \ln K = \frac{15370}{T} + 14.83 \ln T - 0.0365 T + 1.885 \times 10^{-5} T^2 - 4.49 \times 10^{-9} T^3 - 85.2 \quad (2)$$

where R is the gas constant (8.314 J/mol-K) and T is the temperature in K. The computed heat of reaction, equilibrium constant, and composition are shown in Table 1. It should be noticed that because of the exponential nature of Equation 1, the calculated results highly depend on the thermodynamic parameters used. For example, if the Gibbs energy was off by just 5-10%, the estimation error for the equilibrium constant at 473 K may be as large as 16-35%. The calculated mixture compositions will be compared with experimental data following the presentation of experimental results.

**Effectiveness of zeolitic catalysts.** Table 2 shows the products distribution from catalyzed isomerization of *cis*-DHN using 1-g commercial DHN (an almost equimolar mixture of *cis*- and *trans*-isomers) as starting reactant at 473 or 523 K under an initial pressure of 0.79 MPa UHP H<sub>2</sub> or N<sub>2</sub>. Pt- and Pd-loaded mordenites, i.e., Pt/HM30A, Pt/HM20A, and Pd/HM30A, are very effective catalysts under H<sub>2</sub> atmosphere for the conformational isomerization of *cis*-DHN to *trans*-DHN even at low temperature, 473 K. The conversion selectivity towards *trans*-DHN reached nearly 100%; in other words, there were almost no side-products accompanying the isomerization. Take Pt/HM30A as an example. The experimental final product composition of 92.3% *trans*-DHN and 7.3% *cis*-DHN at 473 K as shown in Table 2 is very close to the calculated equilibrium composition (95.3% *trans*-DHN, 4.7% *cis*-DHN), which is shown in Table 1. Although Pt- and Pd-loaded mordenites were effective catalysts under H<sub>2</sub> atmosphere, they became less effective under N<sub>2</sub> atmosphere (see Table 2). Pt/HM30A is a better catalyst than Pd/HM30A at 473 K under N<sub>2</sub> atmosphere in terms of conversion and *trans*-DHN selectivity although they are almost equally effective under H<sub>2</sub>. It is interesting to look at the yield change of tetralin, which initially existed as an impurity (0.7 wt%), under different gas environment. Tetralin was completely hydrogenated into decalin under H<sub>2</sub> environment because of the hydrogenation ability of Pt and Pd. On the other hand, the noble metals under N<sub>2</sub> served to dehydrogenate the decalin to tetralin and thus increased the yield of tetralin.

For the other three catalysts studied, HY, LaHY, and HM30A, they are much less effective than Pt- and Pd-loaded mordenites, and do not react at all at 473 K. It is also interesting to note that although the effectiveness of Pt- and Pd-loaded mordenites depends on the gas environment (H<sub>2</sub> or N<sub>2</sub>), H<sub>2</sub> has no impact on the performance of LaHY. The data in Table 3 seems to show that the hydrogen Y zeolite (HY) performed about as well as the metal ion-exchanged Y zeolite (LaHY), and HM30A is the least effective one among the catalysts studied.

**Reaction pathways and kinetic data.** We further investigated the performance of LaHY and HY intending to get the kinetic data. These isomerization reactions were carried out using 1 g of *cis*-DHN instead of DHN mixture, and 0.2 g of catalyst, at 508-548 K for 0.15-8 h under an initial pressure of 0.79 MPa UHP N<sub>2</sub>. The experimental results are shown in Table 3. Isomerization is the dominant reaction under the conditions employed. The dominant products are two types of isomers: *trans*-DHN (from conformational isomerization) with as high as 81% selectivity (defined as the ratio of molar yield of the product to the conversion), and other decalin isomers from ring-opening or ring-contraction isomerization. Although cracking products are not shown in Table 3, they are in general small (less than 4% selectivity) except under severe conditions such as at 538-548 K for 1 h. There was no apparent dehydrogenation reaction from decalin to tetralin observed judging from the gradually decreasing yield of tetralin, which initially existed as an impurity in *cis*-DHN (0.27 wt%).

Figure 1 presents the *trans*-DHN selectivity vs *cis*-DHN conversion plots for LaHY and HY catalysts at four different temperatures. There are a few features that may be pointed out from examining Table 3 and Figure 1. First, the more complete data in Table 3 seem to indicate that HY performs slightly better than LaHY in terms of criteria such as activity and selectivity. This observation is somewhat different from what we said earlier that they perform equally well judging from the data in Table 2 where commercial decalin was used as the starting material. Second, selectivity towards *trans*-DHN decreases with increasing temperature. This is not unexpected since the isomerization from *cis*-DHN to *trans*-DHN is exothermic, 13212 J/mol (95 J/g or 3.16 kcal/mol) at 523 K (our calculation in Table 1). Third, the product (*trans*-DHN) selectivity decreases with increasing conversion level under isothermal condition, and displays a concave downward behavior, which could be empirically fitted by a second degree polynomial as demonstrated later. The trend of selectivity vs conversion in Figure 1 provided useful information about the reaction pathways. It implied that the reactions proceeded through a parallel-consecutive network [Bond, 1987].

Based on the previous observations, a simple reaction pathway model for the catalytic reaction of *cis*-DHN to products was proposed. It should be noted that readers interested in more detailed mechanisms from *cis* to *trans* isomers may refer to the review by Weitkamp (1968). The overall reaction is modeled as the parallel-consecutive kinetic scheme shown in Figure 2. The isomerization between *cis*- and *trans*-DHN was known to be a reversible process; thus the interconversion between them was also included in Figure 2. However, our experimental data using both *cis*- and *trans*-DHN have shown that the forward reaction from *cis*- to *trans*-DHN is much faster than the backward reaction, i.e.,  $k_1 \gg k_{-1}$ . In addition, for the reaction conditions studied, the reactions were taken to be approximately first order. With these assumptions, the rate equations may be written as the following:

$$\frac{dA}{dt} = -(k_1 + k_2) A \quad (3)$$

$$\frac{dB}{dt} = k_1 A - k_3 B \quad (4)$$

$$\frac{dC}{dt} = k_2 A + k_3 B \quad (5)$$

Equations 3-5 may be solved to give

$$A/A_0 = \exp [-(k_1+k_2) t] = \exp [-k t] \quad (6)$$

$$B/A_0 = [k_1/(k_1+k_2-k_3)] [\exp (-k_3 t) - \exp (-k t)] \quad (7)$$

$$C = A_0 - A - B \quad (8)$$

Because we are mainly interested in the yield of *trans*-DHN and only limited data are available in the current work, we did not intend to find all the kinetic parameters. Instead, we used the experimental data to find the lumped rate constant  $k$  (equal to  $k_1+k_2$  in Eq. 6) and then developed empirical equations to predict the product yield of *trans*-DHN. The procedures are described as follows. First, the rate constant  $k$  was determined by using Eq. (6) for all the experiments shown in Table 3. Then, the rate constant ( $k$ ) was correlated by the Arrhenius law as shown in Eq. (9)

$$k = A^* e^{-E_a/RT} \quad (9)$$

where  $A^*$  ( $\text{h}^{-1}$ ) is the frequency (or preexponential) factor,  $E_a$  is the apparent activation energy (kcal/mol), and  $R$  is the gas constant ( $\text{kcal mol}^{-1} \text{K}^{-1}$ ). The  $E_a$  and  $A^*$  values determined from Arrhenius plots are as follows:

$$\text{for HY} \quad E_a = 49.9 \text{ kcal/mol} \quad \text{and} \quad A^* = 6.03 \times 10^{20} \text{ h}^{-1} \quad (10)$$

$$\text{for LaHY} \quad E_a = 54.6 \text{ kcal/mol} \quad \text{and} \quad A^* = 3.36 \times 10^{22} \text{ h}^{-1} \quad (11)$$

Third, empirical equations were developed to predict the product yield of *trans*-DHN. Based on the results in Figure 1, we proposed that the selectivity of *trans*-DHN could be presented by a second degree polynomial as shown in Eq. (12)

$$\text{Selectivity of } \textit{trans}\text{-DHN} = a_1 + a_2 X + a_3 X^2 + a_4 T + a_5 X T \quad (12)$$

where  $X$  is the *cis*-DHN conversion,  $T$  is the temperature in K, and  $a_i$  ( $i=1,\dots,5$ ) are the empirical parameters to be found. Using the data in Table 3, we have determined the parameters  $a_i$  as follows:

$$\text{for HY} \quad \text{Sel.} = 1.938 + 0.779 X - 0.285 X^2 - 0.00228 T - 0.0012 X T \quad (13)$$

$$\text{for LaHY} \quad \text{Sel.} = 1.534 + 2.745 X - 0.082 X^2 - 0.00146 T - 0.0054 X T \quad (14)$$

In order to check the reliability of these equations in predicting the conversion and selectivity, predictions based on equations 6, 10, 11, 13, and 14 are compared with experimental results. Figures 3 and 4, respectively compare the experimental selectivity and yield of *trans*-DHN to the values predicted from the empirical equations for both catalysts. The line corresponding to exact agreement is drawn as a diagonal. It is clear from Figures 3 and 4 that the predicted values are generally in good agreement with experimental values over a wide range of conversion.

## SUMMARY

This work presented some exploratory studies on the effects of reaction conditions as well as catalyst properties on the catalytic isomerization of *cis*-DHN to *trans*-DHN. The theoretical equilibrium compositions of *trans*-DHN and *cis*-DHN at several temperatures were calculated and compared with experimental data. The catalytic reactions were studied under  $\text{N}_2$  or  $\text{H}_2$  environment using HY, LaHY, HM30A, Pt/HM30A, Pd/HM30A, and Pt/HM20A. Pt- and Pd-loaded mordenites are very effective catalysts under  $\text{H}_2$  atmosphere for the conformational isomerization of *cis*-DHN to *trans*-DHN at 473 K; however, they are less effective under  $\text{N}_2$  atmosphere. Pt/HM30A is a better catalyst than Pd/HM30A at 473 K under  $\text{N}_2$  atmosphere in terms of conversion and *trans*-DHN selectivity although they are almost equally effective under  $\text{H}_2$ . HY, LaHY, and HM30A are much less effective than Pt- and Pd-loaded mordenites, and their performance was not affected by  $\text{H}_2$ . Besides, they do not react at all at 473 K. HY performs slightly better than LaHY, and HM30A is the least effective one among the catalysts studied. Selectivity towards *trans*-DHN decreases with both increasing temperature and increasing conversion level (under isothermal condition). A simple reaction pathways model containing parallel-consecutive kinetic scheme was proposed. The  $E_a$  and  $A^*$  values for the *cis*-DHN conversion were determined from Arrhenius plots. Empirical equations capable of predicting product yields were also developed. In short, equations 6, 10, 11, 13, and 14 may be used to predict reaction conversion and major products.

## ACKNOWLEDGMENTS

We are grateful to Prof. H. H. Schobert and Prof. P. B. Weisz for their encouragement and support, and to Ms. Cindy Chan of PSU for carrying out many of the catalytic experiments. Funding was provided by U.S. Department of Energy and U.S. Air Force. We wish to thank Mr. W. E. Harrison III of USAF and Dr. S. Rogers of DOE for their support.

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Table 1. Calculated heat of reaction, equilibrium constant and composition for a binary mixture system of *cis*-decalin and *trans*-decalin

Temperature (K)	Heat of reaction $\Delta H$ (J/mol)	Equilibrium constant <sup>a</sup>	Composition (wt %)	
			<i>cis</i> -DHN	<i>trans</i> -DHN
473	-13205.8	20.5	4.65%	95.35%
508	-13210.1	16.3	5.79%	94.21%
523	-13212.0	14.9	6.30%	93.70%
538	-13213.7	13.7	6.82%	93.18%
548	-13214.6	12.9	7.17%	92.83%
573	-13215.7	11.4	8.06%	91.94%
623	-13210.6	9.1	9.87%	90.13%
673	-13192.9	7.6	11.69%	88.31%
723	-13160.2	6.4	13.48%	86.52%

a) Equilibrium constant for the reaction: *cis*-DHN  $\leftrightarrow$  *trans*-DHN

$$K = \frac{[\textit{trans}\text{-DHN}]}{[\textit{cis}\text{-DHN}]}$$

Table 2. Catalyzed isomerization of *cis*-decalin (starting reactant is 1-g commercial decalin) under an initial pressure of 0.79 MPa UHP H<sub>2</sub> or N<sub>2</sub>

Catalyst type	Temp. (K)	Time (h)	Gas	Product (wt % of feed)				<i>trans/cis</i> ratio	X <sup>c</sup> (%)	Sel. <sup>d</sup>
				<i>trans</i> -DHN	<i>cis</i> -DHN	Tetralin	Others <sup>b</sup>			
		0.0 <sup>a</sup>		48.34	50.62	0.70	0.34			
Pt/HM30A	473	2.0	H <sub>2</sub>	92.34	7.25	0	0.41	12.7	43.4	1.00
Pd/HM30A	473	2.0	H <sub>2</sub>	92.31	7.23	0	0.46	12.8	43.4	1.00
Pt/HM20A	473	8.0	H <sub>2</sub>	91.50	7.95	0	0.55	11.5	42.7	1.00
Pt/HM30A	473	2.0	N <sub>2</sub>	62.40	33.46	2.26	1.88	1.9	17.2	0.82
Pd/HM30A	473	2.0	N <sub>2</sub>	54.50	42.43	1.84	1.23	1.3	8.2	0.75
LaHY	473	2.0	N <sub>2</sub>	48.29	50.73	0.68	0.30	0.95	0	-
LaHY	523	2.0	N <sub>2</sub>	65.92	19.04	0.60	14.44	3.5	31.6	0.56
LaHY	523	2.0	N <sub>2</sub>	65.15	18.82	0.61	15.42	3.5	31.8	0.53
LaHY	523	2.0	H <sub>2</sub>	65.79	16.73	0.59	16.89	3.9	33.9	0.52
HM30A	523	2.0	N <sub>2</sub>	53.02	31.60	0.38	15.00	1.7	19.0	0.25

a) This row presents the purity of as-received commercial decalin including 0.34% *n*-decane.

b) Unreacted *n*-decane plus products of ring-contraction and ring-opening reactions.

c) Conversion of *cis*-decalin (weight % of feed).

d) Selectivity to *trans*-decalin, defined as a fraction of *cis*-decalin conversion.

Table 3. Catalyzed isomerization of *cis*-decalin (starting reactant is 1-g *cis*-decalin) under an initial pressure of 0.79 MPa UHP N<sub>2</sub>

Catalyst: 0.2 g of LaHY														
temperature (K)	508	508	508	508	523	523	523	523	538	538	538	548	548	548
residence time <sup>a</sup> (min)	60	120	240	480	30	60	120	120	9	18	60	9	18	60
reaction time <sup>b</sup> (min)	54	114	234	474	25	55	115	115	4	13	55	5	14	56
product yield <sup>c</sup> (wt %)														
<i>trans</i> -DHN	7.4	11.5	22.7	43.0	20.4	29.0	47.7	46.3	11.7	32.7	50.4	24.2	37.9	42.5
<i>cis</i> -DHN	90.5	85.2	70.8	42.8	72.0	60.1	29.4	32.5	83.5	51.4	10.2	61.2	31.2	4.7
<i>trans</i> -/ <i>cis</i> -DHN ratio	0.08	0.13	0.32	1.00	0.28	0.48	1.62	1.42	0.14	0.64	4.94	0.40	1.21	9.08
<i>cis</i> -DHN conversion <sup>c</sup>	9.1	14.4	28.8	56.8	27.6	39.5	70.2	67.1	16.1	48.2	89.4	38.4	68.4	94.9
rate constant, k (h <sup>-1</sup> )	0.11	0.08	0.09	0.11	0.78	0.55	0.63	0.58	2.62	3.02	2.45	5.83	4.92	3.19
<i>trans</i> -DHN selectivity	0.80	0.79	0.79	0.76	0.73	0.73	0.68	0.69	0.72	0.68	0.56	0.63	0.55	0.45

Catalyst: 0.2 g of HY														
temperature (K)	508	508	508	523	523	523	538	538	538	538	548	548	548	548
residence time <sup>a</sup> (min)	120	240	480	30	60	120	9	18	30	60	9	18	30	36
reaction time <sup>b</sup> (min)	114	234	474	25	55	115	4	13	25	55	5	14	26	26
product yield <sup>c</sup> (wt %)														
<i>trans</i> -DHN	21.1	47.6	57.0	23.1	46.1	52.7	20.7	34.6	51.9	54.5	35.8	47.8	50.3	
<i>cis</i> -DHN	73.9	37.8	23.0	69.3	36.8	25.6	71.6	51.1	19.4	7.4	45.9	23.1	10.2	
<i>trans</i> -/ <i>cis</i> -DHN ratio	0.28	1.26	2.48	0.33	1.25	2.06	0.29	0.68	2.67	7.35	0.78	2.07	4.93	
<i>cis</i> -DHN conversion <sup>c</sup>	25.8	61.8	76.6	30.3	62.9	74.0	28.0	48.5	80.3	92.2	53.7	76.5	89.4	
rate constant, k (h <sup>-1</sup> )	0.16	0.25	0.18	0.87	1.08	0.70	4.91	3.06	3.89	2.78	9.16	6.19	5.17	
<i>trans</i> -DHN selectivity	0.81	0.77	0.74	0.76	0.73	0.71	0.73	0.71	0.64	0.59	0.67	0.62	0.56	

- a) Reactor residence time in sand bath preheated to reaction temperature.  
 b) Corrected reaction time (reactor residence time minus heat-up time).  
 c) Based on the initial amount of *cis*-DHN.

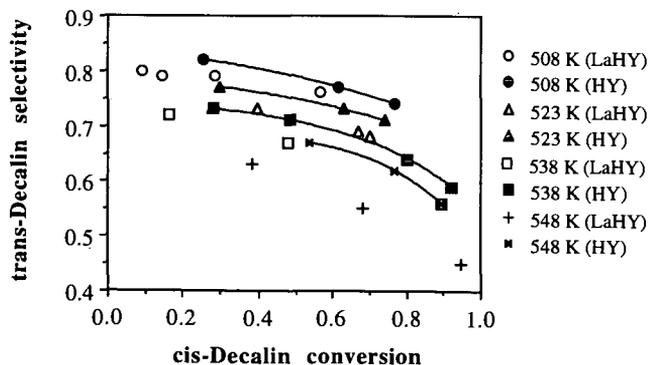


Figure 1. *trans*-Decalin selectivity vs *cis*-decalin conversion plots for LaHY and HY catalysts at four different temperatures.

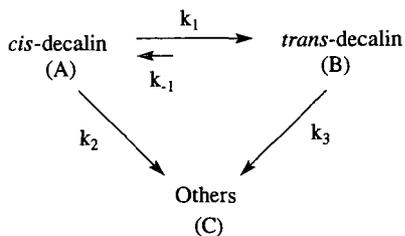


Figure 2. Proposed overall reaction pathways for the catalytic reaction of *cis*-decalin.

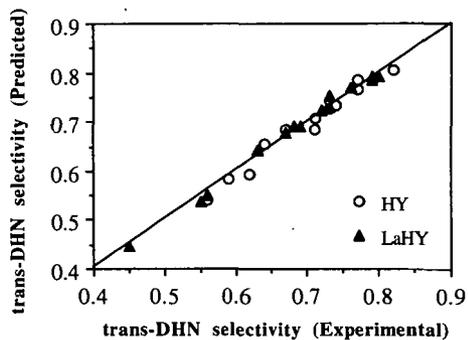


Figure 3. Predicted versus measured values of *trans*-decalin selectivity for the catalytic isomerization of *cis*-decalin using HY and LaHY at 508-548 K for 9-480 min.

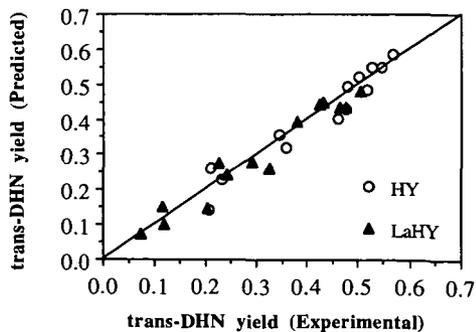


Figure 4. Predicted versus measured values of *trans*-decalin yield for the catalytic isomerization of *cis*-decalin using HY and LaHY at 508-548 K for 9-480 min.