ELSEVIER

Catalysis Today 31 (1996) 171–181

CATALYSIS TODAY

Conformational isomerization of *cis*-decahydronaphthalene over zeolite catalysts

Wei-Chuan Lai, Chunshan Song *

Fuel Science Program, 209 Academic Projects Building, The Pennsylvania State University, University Park, PA 16802, USA

Abstract

This paper presents our exploratory studies on zeolite-catalyzed conformational isomerization of *cis*-decahydronaphthalene (*cis*-DeHN, or *cis*-decalin) to *trans*-DeHN at relatively low temperatures. The catalytic reactions were mainly conducted at 473–573 K for 0.15–8 h under an initial pressure of 0.79 MPa N_2 or H_2 using six catalysts: a hydrogen Y zeolite, a lanthanum ion-exchanged Y zeolite, a hydrogen mordenite, and three noble metal loaded mordenites. Pt- and Pd-loaded mordenites displayed the highest selectivity towards *trans*-DeHN (nearly 100%), with a *trans*-DeHN/*cis*-DeHN ratio of about 13 under H_2 at 473 K; however, they are less effective under N_2. Pre-reduction of Pt/HM30A could improve its catalytic effectiveness in N_2 atmosphere. These results reveal a molecular H_2-promoted isomerization reaction. HY, LaHY, and HM30A are not as effective as Pt- and Pd-loaded mordenites, and the catalyst with the lowest acidity (HM30A) displayed the lowest activity as well as selectivity to *trans*-DeHN. The activity for *cis*-DeHN conversion decreases in the following order: Pt/HM30A ≈ Pd/HM30A ≈ Pt/HM20A > HY > LaHY > HM30A. An overall kinetic model for the catalytic reaction was proposed and empirical equations capable of predicting reaction conversion and product yield were presented. The theoretical equilibrium compositions of *trans*-DeHN and *cis*-DeHN at several temperatures were calculated and corroborated well with the experimental results over effective catalysts such as Pt- and Pd-loaded mordenites. In addition, a lower reaction temperature is found to be thermodynamically favorable.

Keywords: Zeolite; Catalyst; Isomerization; Decahydronaphthalene; Kinetics

1. Introduction

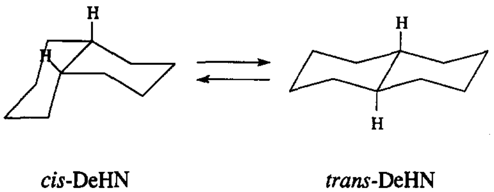
There has been much research on cracking, hydrocracking and dehydrogenation of decalin (decahydronaphthalene, abbreviated as DeHN) at temperatures generally in excess of 673 K under elevated pressures [1–7]. However, little information is available about the conformational isomerization of *cis*-DeHN into *trans*-DeHN at lower temperatures. Our earlier exploratory work [8,9] has shown that some zeolites can promote the isomerization of *cis*-DeHN into *trans*-DeHN, as shown in Scheme 1, at 523 K for 2 h under N_2 environment.

Commercial decalin solvents from industrial hydrogenation processes consist of almost equimolar mixtures of *cis*- and *trans*-DeHN. Although the physical properties of these two

---

* Corresponding author. Fax. (+1-814) 8653075; e-mail: csong@psu.edu

PII S0920-5861(96)00034-X



Scheme 1. Conformational isomerization of *cis*-decalin to *trans*-decalin.

isomers are similar, their chemical reactivities are different. One example is their difference in thermal stability at high temperatures. We have previously shown that as jet fuel components, *trans*-DeHN is superior to *cis*-DeHN because the former is much more stable at high temperatures [10]. The excellent thermal stability at high temperatures is desirable for use as fuel for future high Mach aircraft [11]. It was reported in the literature that decalin may be one of the potential endothermic jet fuels that also serve as the primary heat sink to cool the hot surfaces and system components of aircraft [12–14]. In addition, *trans*-DeHN has the desirable ability of inhibiting the solid deposit formation from jet fuels and their components at high temperatures [15]. For example, adding 50 vol% *trans*-DeHN to a JP-8P fuel, *n*-tetradecane, or *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 wt%, respectively. Although *cis*-DeHN also has some potential industrial applications, it is desirable to convert *cis*-DeHN to *trans*-DeHN for enhancing fuel stability at high temperatures.

This work is a continuation of our exploratory studies on the zeolite-catalyzed conformational isomerization of *cis*-DeHN into *trans*-DeHN. The objectives of this work are to examine the effects of catalyst type, reaction temperature, noble metals and gas atmosphere on the catalytic reaction, and to develop an overall kinetic model for the catalytic reaction and empirical equations to predict the product yields.

2. Experimental

2.1. Reactants and catalysts

The chemicals, *cis*-DeHN, *trans*-DeHN, and DeHN (an almost equimolar mixture of *cis*- and *trans*-DeHN) were obtained from Aldrich Chemical Company and were used as received. Their purities (> 99%) were analyzed 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 Y zeolites (HY and LaHY) were prepared according to the procedures described elsewhere [16]. The HM30A mordenite was prepared by heat treatment of a commercial ammonium mordenite sample [17] and has a SiO_2 to Al_2O_3 mole ratio of 38. 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 zeolites was kept at 6 wt%. The details of the preparation and properties of the catalysts are described elsewhere [9,18].

2.2. Reaction procedure and product analysis

Catalytic isomerization reactions were carried out in 28-ml horizontal type stainless steel tubing bomb reactors, which were generally charged with 1 g of *cis*-DeHN, *trans*-DeHN, or DeHN (7.23 mmol) and 0.2 g of catalyst, at 473–573 K for 0.15–8 h under an initial pressure of 0.79 MPa UHP N_2 or H_2. The reactor was agitated vertically at 240 cycles/min. 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. More analytical details may be found elsewhere [19].

3. Results and discussion

3.1. Effect of catalyst type and reaction conditions

Table 1 shows the products distribution from catalyzed isomerization of *cis*-DeHN over three catalysts (LaHY, HY, and HM30A) at 473–573 K for 0.5–8 h under an initial pressure of 0.79 MPa UHP N_2 or H_2 using 1 g commercial DeHN as reactant. The purity analysis of the starting material is also presented in Table 1. The as-received reactant contains about 48.3% of *trans*-DeHN, 50.6% of *cis*-DeHN, 0.7% of tetralin, and 0.34% of *n*-decane impurity. Fig. 1 presents an expanded retention time window of three GC profiles for the liquid products over

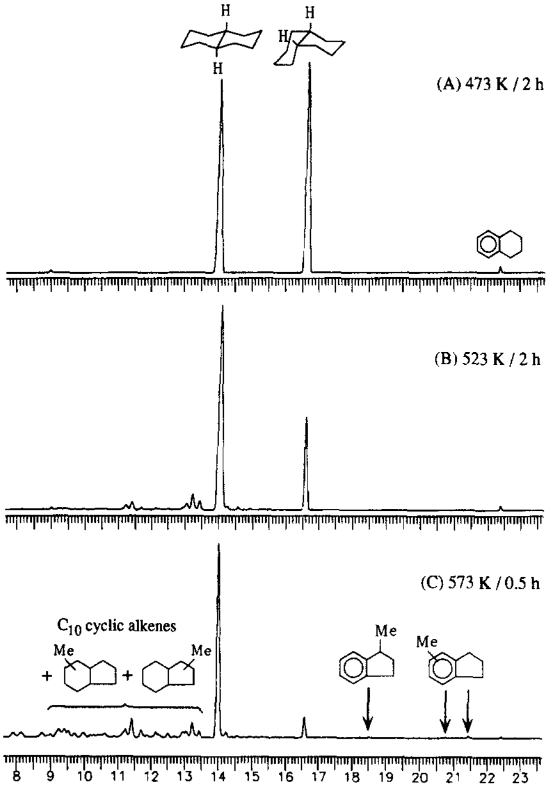


Fig. 1. Expanded retention time window of GC profiles for three liquid products from decalin over LaHY: (A) 473 K/2 h; (B) 523 K/2 h; (C) 573 K/0.5 h.

Table 1

Catalyzed isomerization of *cis*-decalin under an initial pressure of 0.79 MPa UHP N_2 or H_2 using commercial decalin as reactant

Catalyst type	Temperature (K)	Time (h)	Gas	Product (wt% of feed)				*trans* / *cis* ratio	X [c] (%)	Sel. [d]
				trans-DeHN	*cis*-DeHN	Tetralin	Others [b]			
		[a]		48.34	50.62	0.70	0.34			
LaHY	473	2.0	N_2	48.29	50.73	0.68	0.30	0.95	0	
LaHY	508	8.0	N_2	59.67	32.32	0.62	7.07	1.85	18.3	0.62
LaHY	523	0.5	N_2	57.36	36.25	0.67	5.35	1.58	14.4	0.63
LaHY	523	2.0	N_2	65.15	18.82	0.61	15.42	3.5	31.8	0.53
LaHY	523	2.0	H_2	65.79	16.73	0.59	16.89	3.9	33.9	0.52
LaHY	573	0.5	N_2	47.83	4.48	0.36	46.55	10.68	46.1	
HY	508	8.0	N_2	64.76	25.26	0.59	9.06	2.56	25.4	0.65
HY	523	0.5	N_2	52.38	44.68	0.64	1.97	1.17	5.9	0.68
HY	523	2.0	N_2	65.92	19.04	0.60	14.44	3.5	31.6	0.56
HY	548	0.5	N_2	62.18	7.36	0.43	29.49	8.45	43.3	0.32
HY	573	0.5	N_2	45.60	3.74	0.33	49.34	12.19	46.9	
HM30A	523	2.0	N_2	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 (wt% of feed).

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

LaHY at 473, 523, and 573 K. The window covers DeHN and its major products.

No apparent reaction was observed when the experiment was carried out at 473 K for 2 h without a catalyst or with a LaHY catalyst. However, reactions proceed over LaHY when the temperature was raised to 523 K, as shown in Fig. 1. Isomerization is the dominant reaction under the conditions employed. The major products from *cis*-DeHN are *trans*-DeHN (from conformational isomerization), which dominated at 523 K with higher selectivity (defined as the ratio of molar yield of the product to the conversion), and other products from ring-opening or ring-contraction isomerization, which prevailed at 573 K. Cracking products are, in general, of little significance and are not shown in Table 1. Trace amounts of hydrocarbon gases, mainly C_1–C_3 gases, were detected but their total yields were negligible. There was no apparent dehydrogenation reaction from decalin to tetralin, judging from the gradually decreasing yield of tetralin, which initially existed as an impurity (0.7 wt%). It was experimentally observed in this work that LaHY at 573 K also enhances the isomerization of tetralin to form 1-methylindane, with a selectivity of about 0.3.

Table 1 shows that the hydrogen Y zeolite (HY) performed about as well as the metal ion-exchanged Y zeolite (LaHY), and the catalyst with the lowest acidity (HM30A) is the least effective one, displaying the lowest activity as well as selectivity to *trans*-DeHN, among the three catalysts. Reaction conditions at 548–573 K for 0.5 h seem too severe for the isomerization reaction of *cis*-DeHN to form *trans*-DeHN judging from the low selectivity towards *trans*-DeHN. Enhanced competitive side reactions or secondary reactions including ring-opening, ring-contraction, and cracking reactions contributed to the low selectivity of *trans*-DeHN at severe conditions. Petrov et al. [20] reported the isomerization of *cis*- and *trans*-DeHN on a nickel catalyst in the temperature range of 393–453 K. They reported that the isomerization took place only in the presence of hydrogen. However, the present results clearly showed that the isomerization of *cis*-DeHN into *trans*-DeHN could occur over HY, LaHY, and HM30A even under N_2. It is also interesting to note that gas environment (N_2 or H_2) has no impact on the performance of LaHY as shown in Table 1.

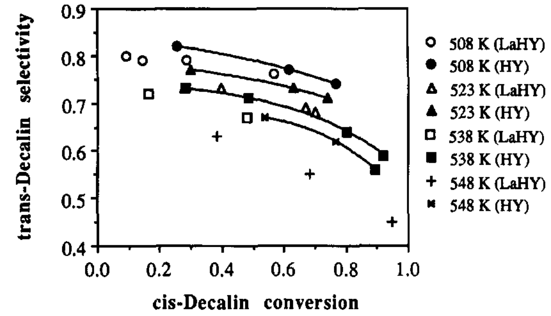


Fig. 2. *trans*-Decalin selectivity vs. *cis*-decalin conversion plots for LaHY and HY catalysts at four different temperatures.

3.2. Reaction pathways and kinetic data

We further investigated the performance of LaHY and HY, with an intention to obtain relevant kinetic data. These isomerization reactions were carried out using pure *cis*-DeHN instead of DeHN 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_2. The experimental results are shown in Table 2. Fig. 2 presents the *trans*-DeHN selectivity versus *cis*-DeHN conversion plots for LaHY and HY catalysts at four different temperatures.

There are several features that can be seen from examining Table 2 and Fig. 2. First, HY performs slightly better than LaHY in terms of activity and selectivity. This observation for runs using pure *cis*-DeHN is slightly different from the trend observed for runs with commercial DeHN mixture, where the two catalysts performed equally well (Table 1). Second, selectivity towards *trans*-DeHN decreases with increasing temperature. This is not unexpected since the isomerization from *cis*-DeHN to *trans*-DeHN is exothermic, 13212 J/mol (95

Table 2
Catalyzed isomerization of pure *cis*-decalin under an initial pressure of 0.79 MPa UHP N_2

	Catalyst: 0.2 g of LaHY													
Temperature (K)	508	508	508	508	523	523	523	523	538	538	538	548	548	548
Residence time [a] (min)	60	120	240	480	30	60	120	120	9	18	60	9	18	60
Reaction time [b] (min)	54	114	234	474	25	55	115	115	4	13	55	5	14	56
Product yield [c] (wt %)														
trans-DeHN	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
cis-DeHN	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
trans-/cis-DeHN 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
cis-DeHN conversion [c]	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^{-1})	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
trans-DeHN 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
Residence time [a] (min)		120	240	480	30	60	120	9	18	30	60	9	18	30
Reaction time [b] (min)		114	234	474	25	55	115	4	13	25	55	5	14	26
Product yield [c] (wt %)														
trans-DeHN		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
cis-DeHN		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
trans-/cis-DeHN 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
cis-DeHN conversion [c]		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^{-1})		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
trans-DeHN 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 experimentally measured heat-up time).

[c] Based on the initial amount of *cis*-DeHN.

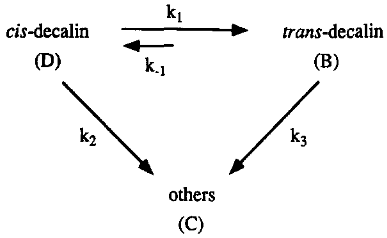


Fig. 3. Overall reaction pathways for the catalytic reaction of cis-decalin. The dehydrogenation, ring-contraction, and cracking products are grouped as the 'others'.

J/g or 3.16 kcal/mol) at 523 K (from thermodynamic calculation to be discussed later). Third, the product (*trans*-DeHN) 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 versus conversion in Fig. 2 provided useful information about the reaction pathways. It implied that the reactions proceeded through a parallel-consecutive network [21].

Based on the previous observations, a simple reaction pathway model for the catalytic reaction of *cis*-DeHN to products was proposed. The overall reaction is modeled as the parallel-consecutive kinetic scheme shown in Fig. 3. The isomerization between *cis*- and *trans*-DeHN was known to be a reversible process; thus the inter conversion between them was also included in Fig. 3. However, our experimental data using both *cis*- and *trans*-DeHN have shown that the forward reaction from *cis*- to *trans*-DeHN 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:

$$\frac{\mathrm{d}D}{\mathrm{d}t} = -(k_1 + k_2)D \tag{1}$$

$$\frac{\mathrm{d}B}{\mathrm{d}t} = k_1 D - k_3 B \tag{2}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_2 D + k_3 B \tag{3}$$

where D and B are *cis*-DeHN and *trans*-DeHN, respectively, and C, denoted as the 'others' in Fig. 3, represents the grouped products from dehydrogenation, ring-contraction, and cracking reactions. Eqs. (1)–(3) can be solved to give

$$D/D_0 = \exp[-(k_1 + k_2)t] = \exp[-kt] \tag{4}$$

$$B/D_0 = [k_1/(k_1 + k_2 - k_3)] \times [\exp(-k_3 t) - \exp(-kt)] \tag{5}$$

$$C = D_0 - D - B \tag{6}$$

Because we are mainly interested in the yield of *trans*-DeHN 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. (4)) and then developed empirical equations to predict the product yield of *trans*-DeHN. The procedures are described as follows. First, the rate constant k was determined by using Eq. (4) for all the experiments shown in Table 2. Then, the rate constant (k) was correlated by the Arrhenius law as shown in Eq. (7)

$$k = A\mathrm{e}^{-E_a/RT} \tag{7}$$

where A (h^{-1}) is the frequency (or pre-exponential) factor, E_a is the apparent activation energy (kcal/mol), and R is the gas constant (kcal mol^{-1} K^{-1}). The apparent E_a and A values determined from Arrhenius plots (as shown in Fig. 4) are as follows:

$$\text{for HY } E_a = 49.9 \pm 2.6\,\text{kcal/mol and } A = 6.03 \times 10^{20}\,\mathrm{h}^{-1} \tag{8}$$

$$\text{for LaHY } E_a = 54.6 \pm 2.6\,\text{kcal/mol and } A = 3.36 \times 10^{22}\,\mathrm{h}^{-1} \tag{9}$$

Thirdly, empirical equations were developed to predict the product yield of *trans*-DeHN. Based on the results in Fig. 2, we found that the selectivity of *trans*-DeHN can be presented by a second degree polynomial as shown in Eq. (10)

$$\text{Selectivity of } trans - \text{DeHN} = a_1 + a_2 X + a_3 X^2 + a_4 T + a_5 XT \tag{10}$$

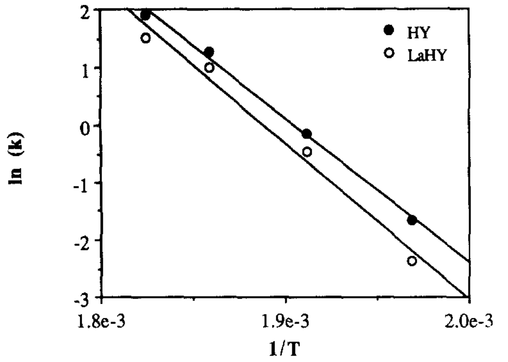


Fig. 4. Arrhenius plots for LaHY and HY catalysts at temperatures 508–548 K.

where X is the *cis*-DeHN conversion, T is the temperature in K, and a_i $(i = 1,\ldots,5)$ are the empirical parameters to be found. Using the data in Table 2, we have determined the parameters a_i as follows:

$$\text{for HY Selectivity} = 1.938 + 0.779X - 0.285X^2 - 0.00228T - 0.0012XT \tag{11}$$

$$\text{for LaHY Selectivity} = 1.534 + 2.745X - 0.082X^2 - 0.00146T - 0.0054XT \tag{12}$$

In order to check the reliability of these equations in predicting the conversion and selectivity, predictions based on Eqs. (4), (8), (9), (11), and (12) are compared with experimental results. Fig. 5 compares the experimental selectivity of *trans*-DeHN 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 that the predicted values are generally in good agreement with experimental values over a wide range of conversion. Similarly, Fig. 6 compares the predicted and measured *trans*-DeHN yield, which is the product of conversion and selectivity. Again, there is good general agreement. These examples demonstrated the reliability and potential usefulness of the aforementioned equations in predicting conversion and product yield.

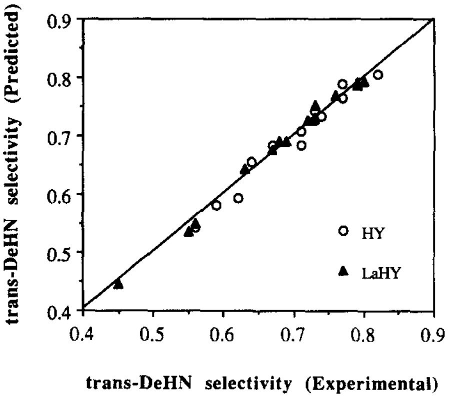


Fig. 5. Predicted vs. measured values of *trans*-decalin selectivity for the catalytic isomerization of *cis*-decalin using HY and LaHY at 508–548 K for 9–480 min.

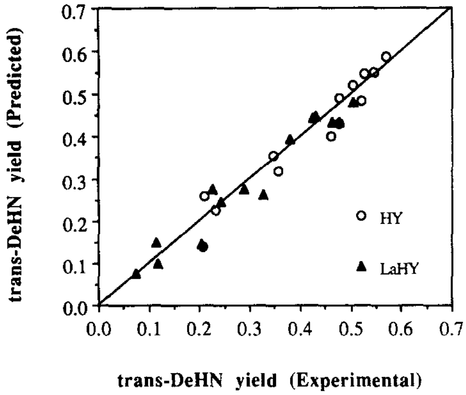
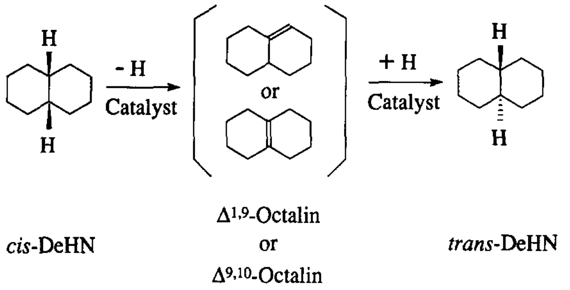


Fig. 6. Predicted vs. measured values of *trans*-decalin yield for the catalytic isomerization of *cis*-decalin using HY and LaHY at 508–548 K for 9–480 min.

3.3. Effect of noble metals

Recall that the experimentally determined activation energies for HY and LaHY, as shown in Eqs. (8) and (9), are unusually high for catalytic reactions. There are two possible explanations for this. First, the first-order reaction was assumed to simplify the calculation of rate constant, but the isomerization of *cis*-DeHN into *trans*-DeHN may not be a real first-order reaction and can involve several reaction steps. Second, these two catalysts are not effective in some of the key reaction steps; thus the apparent activation energy values are higher than expected.

In considering the possible reaction mechanisms, it occurred to us that this isomerization



Scheme 2. Proposed reaction pathway for isomerization of *cis*-DeHN into *trans*-DeHN.

may proceed through a two-step process involving dehydrogenation of *cis*-DeHN to form an olefinic intermediate (possibly $\Delta^{1,9}$-octalin, or $\Delta^{9,10}$-octalin, or both) followed by addition of hydrogen to this olefinic intermediate to give *trans*-DeHN, as illustrated in Scheme 2. It should be noted that *trans*-DeHN can be formed by hydrogen addition to either $\Delta^{1,9}$-octalin, or $\Delta^{9,10}$-octalin [22,23]. If this two-step process is the case, then the high values of apparent activation energy with HY and LaHY catalysts suggest that either the dehydrogenation or the subsequent hydrogenation or both are relatively difficult over HY and LaHY under the conditions used. These considerations prompted us to examine the effect of noble metals, because they are known to be good catalysts for both dehydrogenation and hydrogenation. We then tested Pt- and Pd-loaded mordenites for this reaction.

Table 3 shows the products distribution from catalyzed isomerization of *cis*-DeHN using 0.2 g noble metal loaded catalysts and 1 g commercial DeHN as starting reactant at 473 K under an initial pressure of 0.79 MPa UHP H_2 or N_2. Pt- and Pd-loaded mordenites, i.e. Pt/HM30A, Pt/HM20A, and Pd/HM30A, are very effective catalysts under H_2 atmosphere for the conformational isomerization of *cis*-DeHN to *trans*-DeHN even at low temperature, 473 K. Their selectivity towards *trans*-DeHN reached nearly 100%; in other words, there were almost no side-reactions. Take Pt/HM30A as an example. The experimental product composition of 92.3% *trans*-DeHN and 7.3% *cis*-DeHN at 473 K (as shown in Table 3) is very close to calculated thermodynamic equilibrium composition (95.3% *trans*-DeHN, 4.7% *cis*-DeHN, in Table 5 to be discussed later).

Changing the gas environment from H_2 to N_2 significantly affects the effectiveness of noble metal loaded catalysts and therefore the final product distribution. Although Pt- and Pd-loaded mordenites are effective catalysts under H_2 atmosphere, they are much less effective under N_2 atmosphere (see Table 3). Pt/HM30A is a better catalyst than Pd/HM30A at 473 K under N_2 atmosphere in terms of conversion and *trans*-DeHN selectivity although they are almost equally effective under H_2. It is also interesting to note the yield change of tetralin, which initially existed as an impurity (0.7 wt%), under

Table 3
Catalyzed isomerization of *cis*-decalin under an initial pressure of 0.79 MPa UHP H_2 or N_2 using commercial decalin as reactant

Catalyst type	Temperature (K)	Time (h)	Gas	Product (wt% of feed)				*trans/cis* ratio	X [c] (%)	Sel. [d]
				trans-DeHN	*cis*-DeHN	Tetralin	Others [b]			
		[a]		48.34	50.62	0.70	0.34			
Pt/HM30A	473	2.0	N_2	62.40	33.46	2.26	1.88	1.9	17.2	0.82
Pd/HM30A	473	2.0	N_2	54.50	42.43	1.84	1.23	1.3	8.2	0.75
Pt/HM30A	473	2.0	H_2	92.34	7.25	0	0.41	12.7	43.4	1.00
Pd/HM30A	473	2.0	H_2	92.31	7.23	0	0.46	12.8	43.4	1.00
Pt/HM20A	473	8.0	H_2	91.50	7.95	0	0.55	11.5	42.7	1.00

[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 (wt% of feed).
[d] Selectivity to *trans*-decalin, defined as a fraction of *cis*-decalin conversion.

different gas environment. Table 3 shows that tetralin was completely hydrogenated into decalin under H_2 environment due to the good hydrogenation ability of Pt and Pd. On the other hand, the noble metals under N_2 served to dehydrogenate decalin to tetralin and thus increased the yield of tetralin.

To improve the effectiveness of noble metal loaded mordenites under N_2, we explored the possible effect of catalyst pre-reduction. Table 4 shows the results at 453 and 443 K over Pt/HM30A using *cis*-DeHN as the starting material. Three types of experiments were carried out. The first one was carried out in N_2 using catalyst without pre-reduction; the second was carried out in N_2 using pre-reduced catalyst, and the third was carried out in H_2 with the catalyst being reduced in situ. The catalyst performs the best in the presence of H_2, and the worst in N_2 atmosphere using catalyst without pre-reduction. The effectiveness of catalyst was apparently improved at 453 K when the catalyst was pre-reduced, judging from the higher *trans*-DeHN yield. Similar improvement was also observed for the reaction at 443 K. It is speculated that the isomerization of *cis*-DeHN to *trans*-DeHN starts with dehydrogenation occurring on the metal surface to form olefinic intermediates, for example, $\Delta^{1,9}$-octalin. The olefinic compounds later are hydrogenated to *trans*-DeHN. Since the dehydrogenation and hydrogenation steps occur on the metal and involve hydrogen, pre-reduction of the catalyst and the presence of H_2 could facilitate the isomerization reaction.

The above results present an interesting case of molecular H_2-promoted conformational isomerization of a bicyclic alkane. Combined analysis of the above results also suggests that the noble metals loaded on mordenites strongly promote the isomerization by catalyzing both the initial dehydrogenation of *cis*-DeHN to form the olefinic intermediates and the subsequent hydrogen addition to the olefinic intermediate to form *trans*-DeHN. This consideration is supported by the following facts: (1) these catalysts became much less effective for isomerization but enhanced dehydrogenation of *cis*-DeHN under N_2; (2) the pre-reduction improved the catalytic activity for isomerization under N_2; and (3) these catalysts can drive the reaction to equilibrium quickly and highly selectively under H_2 atmosphere.

3.4. Calculated equilibrium composition

The equilibrium compositions of *trans*-DeHN and *cis*-DeHN 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 (ΔG°) by Eq. (13)

$$\ln K = \frac{-\Delta G^\circ}{RT} \qquad (13)$$

Thermochemical data such as standard enthalpy of formation, standard Gibbs energy of formation, and isobaric heat capacity, are needed to establish the equilibrium constant as a function of temperature. Using the thermochemical data in Reid et al. [24] for *cis*-DeHN and

Table 4
Catalyzed isomerization of pure *cis*-decalin over Pt/HM30A

Temperature (K)	Time (h)	Catalyst H_2 treated?	Gas	Product (wt% of feed)		
				trans-DeHN	*cis*-DeHN	Tetralin
453	0.25	No	N_2	0.6	98.1	1.3
453	0.25	Yes	N_2	23.7	75.1	1.2
453	0.25	No	H_2	52.1	47.9	
443	0.25	No	N_2	0.6	97.9	1.5
443	0.25	Yes	N_2	9.6	88.3	2.1
443	0.25	No	H_2	69.3	30.7	

trans-DeHN, we have determined the general expression for the equilibrium constant as a function of temperature as shown in Eq. (14)

$$R \ln K = \frac{15370}{T} + 14.83 \ln T - 0.0365T + 1.885 \times 10^{-5}T^2 - 4.49 \times 10^{-9}T^3 - 85.2 \qquad (14)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K. The calculated heat of reaction, equilibrium constant, and composition are shown in Table 5. It should be noticed that because of the exponential nature of Eq. (13), the calculated results are highly dependent on the thermodynamic parameters used. For example, if the Gibbs energy was off by only 5–10%, the estimation error for the equilibrium constant at 473 K may be as large as 16–35%.

The theoretical calculation results show that the isomerization from *cis*-DeHN to *trans*-DeHN is exothermic (Table 5), and the equilibrium conversion of *cis*-DeHN decreases with increasing temperature. Therefore, a lower reaction temperature is thermodynamically favorable. The yield of *trans*-DeHN could reach over 90% for the temperature range studied (below 573 K). Comparing the calculated mixture compositions with experimental data for the six catalysts studied in this work, we could find that the optimal product yields, i.e., the theoretical equilibrium compositions, could be approached by using very effective catalysts (Pt- and Pd-loaded mordenites) under appropriate conditions (under H_2 atmosphere at 473 K). The data in Table 1 also showed that reactions at 573 K for 0.5 h over LaHY and HY seemed to have approached the equilibrium state for *trans*- and *cis*-isomers because the experimental ratios of *trans*- to *cis*- are very close to the theoretical value (11.4 at 573 K, as shown in Table 5). It is kinetically desirable to run the reaction under the condition that could quickly push the reaction to near equilibrium stage. However, some conditions (at 573 K for 0.5 h over LaHY and HY) may be too severe for the isomerization reaction of *cis*-DeHN to *trans*-DeHN because of the undesirable side reactions. In any case, the theoretically calculated equilibrium compositions (in Table 5) are useful and can be used as guidelines for the evaluation of reaction conditions and the effectiveness of catalysts.

4. Conclusions

Pt- and Pd-loaded mordenites are very effective catalysts under H_2 for the conformational isomerization of *cis*-DeHN to *trans*-DeHN at 473 K. The selectivity towards *trans*-DeHN with these catalysts is very high (nearly 100%) with a *trans*-DeHN/*cis*-DeHN ratio of near 13.

Table 5
Calculated heat of reaction, equilibrium constant and composition for a binary mixture system of *cis*-decalin and *trans*-decalin

Temperature (K)	Heat of reaction ΔH (J/mol) [a]	Equilibrium constant [b]	Composition (wt%)	
			cis-DeHN	*trans*-DeHN
473	−13206	20.5	4.65%	95.35%
508	−13210	16.3	5.79%	94.21%
523	−13212	14.9	6.30%	93.70%
538	−13214	13.7	6.82%	93.18%
548	−13215	12.9	7.17%	92.83%
573	−13216	11.4	8.06%	91.94%
623	−13211	9.1	9.87%	90.13%
673	−13193	7.6	11.69%	88.31%
723	−13160	6.4	13.48%	86.52%

[a] The values of standard enthalpy of formation for *cis*- and *trans*-DeHN at 298.2 K are -1.691×10^5 and -1.824×10^5 J/mol, respectively.

[b] Equilibrium constant for the reaction: *cis*-DeHN ↔ *trans*-DeHN $K = ([\textit{trans}\text{-DeHN}])/([\textit{cis}\text{-DeHN}])$.

On the other hand, they are less effective under a hydrogen-deficient environment such as under N_2. The isomerization of *cis*-DeHN to *trans*-DeHN is thought to involve dehydrogenation and hydrogenation on the metal surface. The effectiveness of Pt/HM30A in N_2 environment could be improved by pre-reduction in H_2. Pt/HM30A is a better catalyst than Pd/HM30A at 473 K under N_2 atmosphere, in terms of conversion and *trans*-DeHN selectivity, although they are almost equally effective under H_2. HY, LaHY, and HM30A are not as effective as Pt- and Pd-loaded mordenites, and their activities under N_2 and under H_2 are similar to each other. Among these three catalysts, HY performs slightly better than LaHY, and the catalyst with the lowest acidity (HM30A) displayed the lowest activity. The observed activity for *cis*-DeHN conversion is: Pt/HM30A ≈ Pd/HM30A ≈ Pt/HM20A > HY > LaHY > HM30A. Selectivity towards *trans*-DeHN decreases with both increasing temperature and increasing conversion level (under isothermal condition).

A simple reaction pathways model containing parallel-consecutive kinetic schemes was proposed. Empirical equations capable of predicting product yields were developed. The Eqs. (4), (8), (9), (11), and (12) may be used to predict reaction conversion and major products. The theoretical equilibrium compositions of *trans*-DeHN and *cis*-DeHN at several temperatures were calculated and compared with experimental data. The experimental results for very effective catalysts such as Pt- and Pd-loaded mordenites, corroborated well with theoretical calculations. The calculated equilibrium compositions are useful as guidelines for evaluating the effects of catalysts and reaction conditions.

Acknowledgements

We are grateful to Professor H.H. Schobert for his encouragement and support, and to Ms. C. Chan of PSU for conducting many of the isomerization experiments. Funding was provided by the US Department of Energy and US Air Force. We wish to thank Mr. W.E. Harrison III of USAF and Dr. S. Rogers of DOE for their support. We also thank Professor P.B. Weisz for his encouragement.

References

[1] A.W. Ritchie and A.C. Nixon, Prepr. Am. Chem. Soc., Div. Petrol. Chem., 12 (1967) 117.

[2] J. Shabtai, R. Ramakrishnan and A.G. Oblad, Adv. Chem. Ser., 183 (1979) 297.

[3] W.D. Constant, G.L. Price and E. McLaughlin, Fuel, 65 (1986) 8.

[4] H.B. Mostad, T.U. Riis and O.H. Ellestad, Appl. Catal., 58 (1990) 105.

[5] H.B. Mostad, T.U. Riis and O.H. Ellestad, Appl. Catal., 63 (1990) 345.

[6] M. Nimz, Zeolites, 10 (1990) 297.

[7] E.F. Sousa-Aguiar, M. Pinhel da Silva, M.L. Murta Valle and D. Forte da Silva, Prepr. Am. Chem. Soc., Div. Petrol. Chem., 39 (1994) 356.

[8] C. Song and K. Moffatt, Prepr. Am. Chem. Soc., Div. Petrol. Chem., 38 (1993) 779.

[9] C. Song and K. Moffatt, Microporous Mater., 2 (1994) 459.

[10] C. Song, W.-C. Lai and H.H. Schobert, Prepr. Am. Chem. Soc., Div. Fuel Chem., 37 (1992) 1655.

[11] C. Song, S. Eser, H.H. Schobert and P.G. Hatcher, Energy Fuels, 7 (1993) 234.

[12] E.E. Donath and M. Hess, Chem. Eng. Progr., 56 (1960) 68.

[13] H.R. Lander and A.C. Nixon, Prepr. Am. Chem. Soc., Div. Petrol. Chem., 32 (1987) 504.

[14] P.H. Taylor and W.A. Rubey, Prepr. Am. Chem. Soc., Div. Petrol. Chem., 32 (1987) 521.

[15] C. Song, W.-C. Lai and H.H. Schobert, Ind. Eng. Chem. Res., 33 (1994) 548.

[16] C. Song, H.H. Schobert and H. Matsui, Prepr. Am. Chem. Soc., Div. Fuel Chem., 36 (1991) 1892.

[17] C. Song and S. Kirby, Microporous Mater., 2 (1994) 467.

[18] A.D. Schmitz, G. Bowers and C. Song, Prepr. Am. Chem. Soc., Div. Fuel Chem., 40 (1995) 930.

[19] C. Song, W.-C. Lai and H.H. Schobert, Ind. Eng. Chem. Res., 33 (1994) 534.

[20] L. Petrov, L. Angelova and D. Shopov, Bokl. Bolg. Akad. Nauk, 30 (1977) 85.

[21] G.C. Bond, Heterogeneous Catalysis: Principles and Applications, 2nd ed., Oxford University Press, Oxford, 1987, pp. 52–53.

[22] A.W. Weitkamp, in D.D. Eley, H. Pines and P.B. Weisz (Editors), Advances in Catalysis and Related Subjects, Academic Press, New York, 1968, Vol. 18, pp. 1–110.

[23] J.F. Sauvage, R.H. Baker and A.S. Hussey, J. Am. Chem. Soc., 83 (1961) 3874.

[24] R.C. Reid, J.M. Prausnitz and B.E. Poling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.