



CHAPTER IV

COMPARATIVE STUDY OF HYDROGENATION OF TETRALIN ON SUPPORTED Ni, Pt, AND Pd CATALYSTS*

4.1 Abstract

The gas phase tetralin hydrogenation has been investigated over Ni, Pt, and Pd catalysts to determine the evolution of the trans- and cis-decalin products as a function of conversion over the different catalysts. The study of tetralin conversion toward each isomer may be important for fuel improvement. The cis-decalin isomer is preferred to open the naphthenic rings in a selective way. However, thermodynamically, this isomer is the least favored. Therefore, one needs to control the trans/cis ratio kinetically, i.e., by selecting the proper catalyst and the proper operating conditions. In this study, we have prepared different supported metal catalysts and tested them in a fixed bed continuous flow reactor at 3540 kPa and 548 K. The kinetic parameters for tetralin hydrogenation, cis-trans decalin isomerization of catalysts prepared were obtained by fitting the data with a generalized Langmuir-Hinshelwood model. The catalytic activity tests revealed that the relative rates of tetralin hydrogenation, as well as the cis-trans isomerization were greatly affected by the site competition of decalin with tetralin, which in turn had different significance over the different catalysts. At conversions above 30%, Ni catalyst yielded the lowest trans/cis decalin ratio, but this ratio converged to about the same value as the one that was obtained on Pt as the conversion approached zero. By contrast, the trans/cis ratio on Pd catalyst remains constant at all conversion levels and is highest at low tetralin conversion. It is postulated that the trans/cis ratio is a combination of the intrinsic selectivity of each isomer and the isomerization reaction.

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4.2 Introduction

Environmental regulations keep compelling petroleum refiners to raise cetane number and to limit aromatics in diesel fuel in order to improve combustion efficiency and reduce particulate matter and NO_x emissions [1, 2, 3]. Consequently, the removal of aromatic hydrocarbons from diesel has received considerable attention. Addition of cetane boosters, e.g. alkyl nitrates, can result in improvement of cetane number. However, this improvement is limited to a rather narrow range and the use of these boosters may negatively affect the storability and handling of the fuel. Another alternative is blending with Fischer-Tropsch (FT) gas-to-liquid diesel fuel; however, this option may not be economically viable solution in case of extensive blend. A deep hydrotreating process to increase cetane can be carried out in two-stages. In the first stage a conventional hydrotreating catalyst (CoMo, NiMo, and NiW on Al₂O₃) can be employed while a noble metal catalyst (e.g. Pt, Pd) with high hydrogenation activity can be used in the second stage [2].

In this case, the increase in cetane number may strongly depend on the nature of the crude used as well as blending strategies used by the refiners. For example, in recent years, a greater fraction of the so-called light cycle oil (LCO) is incorporated in the diesel pool. Due to its high aromatic content and its low cetane number (typically between 20 and 30), the incorporation of LCO may have a negative impact on the cetane number of the diesel [4]. While an important fraction of the aromatics present in LCO can be saturated in a deep hydrogenation process, the cetane number may still be lower than the target values specified in future diesel legislations. Therefore, the opening of at least one of the naphthenic rings is a promising reaction to attain high cetane number [5, 6]. However, as we have recently shown not every ring opening path results in an increase in cetane number [7]. It is important to fully evaluate the catalysts and type of molecules involved in the reaction before one can determine whether the ring opening would cause an increase in cetane number.

In order to achieve the ring opening, aromatics must be first hydrogenated to the corresponding naphthenic molecules to allow the cleavage of the C6 member ring either on an acid or a metal catalyst [8]. The downside of ring opening is the

potential loss of hydrocarbons in the cetane range due to cracking and isomerization to branched hydrocarbons [6, 7, 8, 9]. Therefore, the proper catalysts are necessary to maximize selective ring opening (SRO) products while minimizing cracking and branched products. However, not only the catalyst but also the nature of the naphthenic molecules that are fed to the ring opening step may have an impact on the resulting cetane number. In this contribution, we investigate how the ratio of naphthenic isomers changes under the hydrogenation conditions.

In a previous work, we have shown that the two products of the hydrogenation of tetralin, i.e. cis- and trans-decalin have different reactivity in the subsequent ring-contraction and ring opening reactions [10]. Specifically, while trans-decalin is thermodynamically more stable it is much less active than cis-decalin towards ring-opening. It was shown that the conversion of pure cis-decalin at moderate temperatures resulted in substantial selectivity to indanes and alkyl-cyclohexanes over HY catalysts, but trans-decalin was converted only at high temperatures with low selectivity to C₁₀ products. Therefore, to maximize cetane number one would prefer having a high fraction of cis-decalin in the feed to the ring opening step. Unfortunately, trans-decalin is the preferential isomer at equilibrium. Therefore, it is important to study how the ratio of the two decalin isomers varies during the hydrogenation of tetralin that precedes the ring opening.

The hydrogenation of aromatics has been extensively studied in the past. Outstandingly, in a large number of articles, Vannice *et al.* have provided a comprehensive comparison of the kinetics of the hydrogenation of monoaromatic molecules (benzene, toluene, and xylene) over Pt and Pd catalysts [11-17]. The studies show that while the turnover frequency TOF for aromatic hydrogenation reactions on Pt are significantly higher than on Pd, the kinetic behavior of these reactions over the two metals is very similar [16]. Also, their studies compared different aromatics on a given catalyst. For example, they found that the TOF for hydrogenation on Pd decreased in the following order: benzene > toluene > p-xylene > m-xylene > o-xylene [11]. To explain this trend, the role of the electron density in the aromatic ring was considered. Also, steric hindrance was proposed as responsible for the low rate exhibited by molecules such as o-xylene. Vannice interpreted the kinetics in terms of a reaction mechanism involving the sequential

addition of H atoms to the benzene ring. The model also included a reversible dehydrogenation reaction and formation of carbonaceous species, which inhibited the reaction rate. Recently, the hydrogenation of the last ring in di-, and poly-aromatic compounds has received considerable attention. It is experimentally verified that the hydrogenation of the first ring in polynuclear aromatics is easier to attain compared to the hydrogenation of the final ring. This difference has been ascribed to both, the stabilization of aromatic rings in monoaromatic compounds as well as competition for adsorption sites in which the compounds with the larger number of aromatic rings prevail [18, 19]. This competition was clearly shown in the case of phenanthrene, naphthalene, and tetralin hydrogenation over Pt/Al₂O₃ catalysts [3]. The role site competition was illustrated in a quantitative form for the case of tetralin hydrogenation [20]. The kinetic parameters obtained from a combination of modelling and experimental adsorption constants were consistent with a Langmuir Hinshelwood model of competing adsorption, in agreement with Vannice's results with monoaromatic compounds on Pt and Pd [14, 16].

Tetrahydronaphthalene (tetralin) has been frequently used to represent aromatics in diesel fuels in hydrogenation reactions [21-25]. The most widely accepted hydrogenation pathway includes $\Delta^{1,9}$ -octalin (octahydronaphthalene) as an intermediate that is further hydrogenated to the cis- or trans-decalin product.

In a previous study, we found an interesting evolution of the trans/cis ratio as a function of tetralin conversion [26]. We found that until a very high percentage of tetralin was converted, the trans/cis ratio in the decalin product remained constant. Only at high tetralin conversions, the trans/cis ratio greatly increased approaching the high equilibrium value (about 11 at the reaction temperature employed in the study). We explained this non-linearity in terms of a strong competition for adsorption sites in which the cis-to-trans isomerization was blocked by adsorbed tetralin.

In this work, we compare cis/trans ratios obtained on Ni, Pt, and Pd metal catalysts as a function of tetralin conversion during the hydrogenation reaction. From kinetics analysis of the simultaneous hydrogenation and isomerization reactions we attempt to evaluate the effect of site competition on the various catalysts and determine which one would be most suitable as a deep hydrogenation catalyst to accompany a subsequent ring opening step.

4.3 Experimental

4.3.1 Catalyst Preparation and Characterization

The commercial gamma-alumina support ($\gamma\text{-Al}_2\text{O}_3$, Saint-Gobian NorPro Corp, surface area $252\text{ m}^2/\text{g}$) used in this study was ground and sieved to mesh 20-40 before impregnating the metals, Ni, Pt, and Pd. The metal incorporation was accomplished through conventional incipient wetness impregnation technique with aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{ H}_2\text{O}$ (AnalaR), $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Aldrich), and $\text{Pd}(\text{NO}_3)_2 \cdot x\text{ H}_2\text{O}$ (Aldrich), respectively. The concentration of the precursor solutions was adjusted to the desired metal loading in each catalyst, i.e., 1.0 wt. % for Pt and Pd, and 5.0 wt.% for Ni. After impregnation, the sample was kept at ambient temperature for 4 h, then dried at 383 K overnight, and finally calcined in an oven for 2 h at 573 K for the Pt and Pd samples and calcined at 673 K in the case of the Ni sample.

Chemisorption of CO at room temperature was used to estimate the metal dispersion of the catalysts. The CO uptake measurements were conducted in a 1/4" flow reactor made of quartz, containing 0.01 g catalyst. Before exposing to CO gas, the samples were reduced in-situ under 50 ml/min of H_2 at the specified reduction temperature (573 K for Pt and Pd, 723 K for Ni) during 1 h, purged in flowing He for 30 min, and then cooled down to room temperature. The stream was continuously monitored online by a mass spectrometer. Calibrated pulses of 250 μl of 5 % CO in He were sent over the catalyst every 5 min, until the areas of the $m/e=28$ peak stopped increasing, which indicated that the saturation adsorption capacity had been reached. The total amount of CO taken up by the sample was calculated by quantifying the area of the peak with the total number of CO moles present in the 250 μl calibration loop, filled with 5%CO in He.

Table 4.1 summarizes the metal dispersions obtained with each catalyst. As typically observed on alumina, the Ni catalyst, had to be reduced at higher temperatures than those of Pt and Pd to get completely reduced, had a metal dispersion significantly lower. We compensated this lower dispersion with a higher metal loading [27].

Table 4.1 Characterization of the catalysts investigated

Catalyst	Metal loading (%)	T _r (K)	CO: metal
Ni/Al ₂ O ₃	5.0	723	0.05
Pd/Al ₂ O ₃	1.0	573	0.33
Pt/Al ₂ O ₃	1.0	573	0.88

4.3.2 Catalytic Activity Tests

The catalytic activity measurements were carried out in a continuous fixed bed stainless steel 3/4" O.D. reactor, equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The reaction was conducted in the gas phase at 548 K and 3540 kPa; the H₂/HC molar ratio was kept at 25. Space velocities were systematically varied by independently changing the catalyst amount or the hydrocarbon flow rate. The catalyst was first reduced under flowing H₂ at 3540 kPa for 1.5 h at 573 K for Pt and Pd, and 723 K for Ni. After this reduction treatment, the reactor was cooled down in flowing H₂ to 548 K. Then, the liquid reactant was introduced to the reactor using a high-pressure pump at a rate of 3.6 ml/h. Two different hydrocarbon compounds, 1,2,3,4-tetrahydro-naphthalene (tetralin, Fluka, 97+%) and decahydronaphthalene (decalin, Fluka, 99%, a mixture of trans- and cis-decalin at a 60/40 molar ratio) were used as pure feeds. When a mixed feed was used, tetralin was mixed with decalin, keeping a 20/80 ratio. The products were analyzed online in a HP6890 gas chromatograph, equipped with an FID detector and an HP-5 column. Different amounts of catalyst were tested to obtain the evolution of products as a function of space time, expressed as W/F, where W is the mass of catalysts (g) and F is the flow rate of hydrocarbon feed (mol/h). In all cases, the product distribution was compared after 6 h on stream (TOS = 6 h), using a fresh catalyst sample in each individual run. Under the conditions used in this study no catalyst deactivation was observed.

4.4 Results and Discussion

4.4.1 Kinetic Study

The products of tetralin hydrogenation were cis- and trans-decalin. Only trace amounts of naphthalene and $\Delta^{1,9}$ -octalin were detected under the conditions of this study. The turnover frequencies (TOF) based on CO chemisorptions for each catalyst at a total pressure of 3540 kPa, 548 K, $H_2/HC=25$ and after 6 h on stream are summarized in Table 4.2. In agreement with previous studies, Pt exhibited a significantly higher specific activity than those of Ni and Pd [28]. The activity for tetralin hydrogenation followed the trend $Pt > Ni > Pd$, which is the same trend previously observed by Vanice *et al.* for one-ring aromatics [11].

Table 4.2 Tetralin hydrogenation activity on different catalysts. Reaction conditions: 3540 kPa, 548K, $H_2/HC=25$, TOS=6 h

Catalyst	Specific Reaction Rate in		TOF ($s^{-1} \times 10^3$) ^a
	$\mu\text{mol TL/s.cat}$	m mol TL/s/ g metal	
Ni/Al ₂ O ₃	71.5	1.4	28.6
Pd/Al ₂ O ₃	26.2	2.6	7.9
Pt/Al ₂ O ₃	428.8	42.9	48.7

^a based on CO/M chemisorption uptakes. Tetralin (TL) conversion range: 10-20%

As in our previous study a generalized Langmuir-Hinshelwood equation was chosen as the basis for the kinetic analysis [20]. In this equation, competitive adsorption of products and reactants on the same type of sites is assumed [11, 20]. Two simplified reactions are taken into account in the analysis; they are the tetralin hydrogenation to both trans- and cis-decalin and the cis-to-trans isomerization. The rate expressions for hydrogenation and isomerization are described by equations (1) and (2), respectively.

$$r_{1(\text{hydrogenation})} = \frac{k_1 K_{TL} P_{TL}^{n_1} K_{H_2} P_{H_2}^{n_2}}{(1 + K_{cis} P_{cis} + K_{trans} P_{trans} + K_{TL} P_{TL} + \sqrt{K_{H_2} P_{H_2}})^z} \quad (1)$$

$$r_{2(\text{isomerization})} = \frac{k_2 K_{cis} (P_{cis} - \frac{P_{trans}}{K_{CD-TD}})}{(1 + K_{cis} P_{cis} + K_{trans} P_{trans} + K_{TL} P_{TL} + \sqrt{K_{H_2} P_{H_2}})^z} \quad (2)$$

where k_1 is the rate constants for tetralin hydrogenation;
 k_2 is the rate constants for cis- to trans- isomerization;
 K_{H_2} is the apparent adsorption constants for hydrogen;
 K_{TL} is the apparent adsorption constants for tetralin;
 K_{cis} is the apparent adsorption constants for cis-decalin; and
 K_{trans} is the apparent adsorption constants for trans-decalin.

Under the conditions of this study, the hydrogenation of tetralin can be considered as irreversible whereas cis-trans isomerization must considered reversible. The equilibrium constant KCD-TD for the reversible reaction, determined by using the software HSC-Chemistry-5.0, matched well with the previously reported values [29]. The adsorption exponent z and the reaction order for tetralin (n_1) were chosen according with previous reports as 2 and 1, respectively [1, 30-32]. The reaction order with respect to hydrogen was not used as an adjustable parameter but assumed to be zero due to the high excess of hydrogen kept throughout the catalyst bed in all runs.

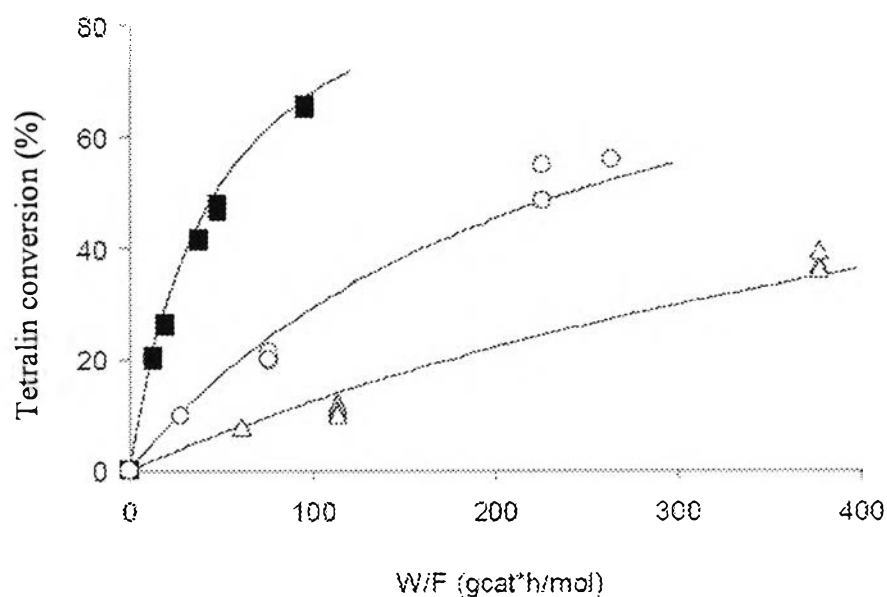


Figure 4.1 Tetralin conversion to decalin as a function of space time during hydrogenation in a flow reactor at 3540 kPa and 548 K $H_2/HC=25$, TOS = 6 h. ■, Pt/Al₂O₃; ○, Ni/Al₂O₃; △, Pd/Al₂O₃. Solid lines are the results of the kinetic model.

The hydrogenation and isomerization reaction data obtained as a function of W/F on the three catalysts (alumina-supported Ni, Pt, and Pd) were fitted with equations 1 and 2, respectively. The best fits of the hydrogenation conversion data in the form of total tetralin conversion as a function of W/F at 548 K are shown in Figure 4.1 for the three catalysts. Similarly, the isomerization conversion data obtained with a decalin feed under the same reaction conditions are shown together with the fitted curves on Figure 4.2.

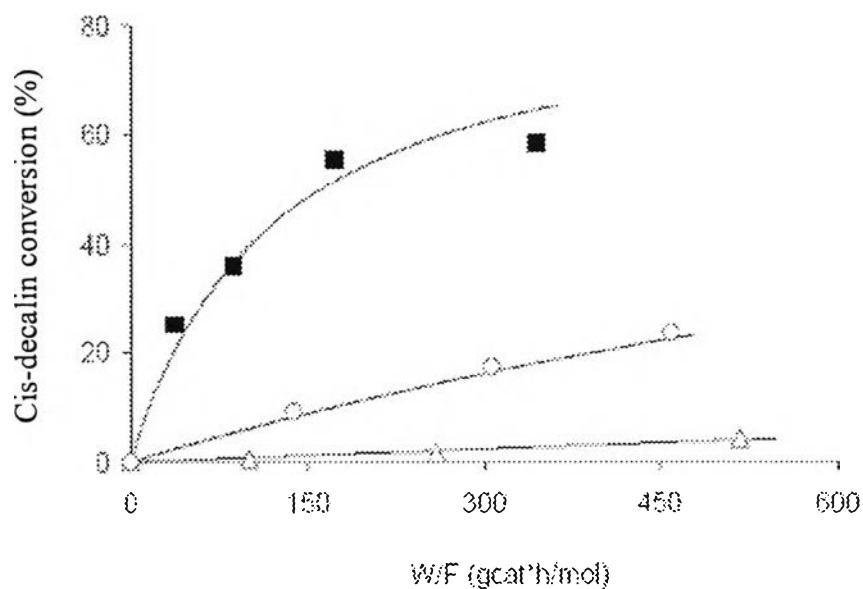


Figure 4.2 Cis-to-Trans decalin isomerization in pure decalin feed (trans :cis feed ratio is 60:40). Reaction conditions: 3540 kPa and 548 K, $H_2/HC=25$, TOS = 3 h. ■, Pt/ Al_2O_3 ; ○, Ni/ Al_2O_3 ; △, Pd/ Al_2O_3 . Solid lines are the results of the kinetic model.

The same adsorption parameters were used for the two reactions; they are the apparent adsorption constants for hydrogen (K_{H_2}), tetralin (K_{TL}), cis-decalin (K_{cis}) and trans-decalin (K_{trans}). The resulting values obtained in the fit for these parameters are shown in Table 4.3, together with the rate constants for tetralin hydrogenation (k_1) and cis-to-trans isomerization (k_2). The same activity trend was obtained for the two reactions. Both, decalin isomerization and tetralin hydrogenation had the highest rate constants on Pt, followed by Ni, while Pd showed the lowest activity.

Table 4.3 Kinetics parameters for the hydrogenation of tetralin (r_1 , as shown below) and cis-to-trans decalin isomerization (r_2 , as shown below) at 3540 kPa and 548 K, $H_2/HC=25$, TOS = 6 h

Kin. Parameters	Ni	Pd	Pt
k_1 (h^{-1})	8.0 \pm 0.5	1.8 \pm 0.5	12.8 \pm 0.5
k_2 (h^{-1})	9.0 \pm 0.5	2.0 \pm 0.5	30.2 \pm 3.0
K_{H_2}	0.3 \pm 0.05	0.40 \pm 0.05	0.6 \pm 0.1
K_{TL}	0.11 \pm 0.03	0.25 \pm 0.03	0.23 \pm 0.03
K_{trans}	0.01 \pm 0.005	0.01 \pm 0.005	0.060 \pm 0.01
K_{cis}	0.05 \pm 0.01	0.05 \pm 0.01	0.06 \pm 0.01

$$r_{1(\text{hydrogenation})} = \frac{k_1 K_{TL} P_{TL}^2 K_H P_{H_2}^2}{(1 + K_{cis} P_{cis} + K_{trans} P_{trans} + K_{TL} P_{TL} + \sqrt{K_{H_2} P_{H_2}})^2}$$

$$r_{2(\text{isomerization})} = \frac{k_2 K_{cis} (P_{cis} - \frac{P_{trans}}{K_{CD-TD}})}{(1 + K_{cis} P_{cis} + K_{trans} P_{trans} + K_{TL} P_{TL} + \sqrt{K_{H_2} P_{H_2}})^2}$$

4.4.2 Trans/Cis Decalin Ratio

The evolution of the trans/cis ratio as a function of tetralin conversion during the hydrogenation reaction is compared in Figure 4.3 for the three different catalysts (Pt, Ni and Pd). First, we must indicate that the trans/cis ratio extrapolated to zero conversion corresponds to the ratio of primary decalin products directly formed from tetralin hydrogenation, before any cis-to-trans isomerization occurs. Therefore, it is interesting to note that this ratio strongly depends on the catalyst used, as previously pointed out [26, 33]. It is clearly seen that the original trans/cis ratio for Pt and Ni is about the same, near 1.5. This value is more than twice for the case of the Pd catalyst, but in both cases the value is much lower than the equilibrium trans/cis ratio, which at this temperature (548 K) is 11 [29]. High selectivities towards trans-decalin on Pd have been reported in previous work [19, 26, 33]. However, in most cases the intrinsic ratio produced from the primary

hydrogenation reaction can be masked by the subsequent isomerization. By analyzing the trans/cis ratio at zero conversion one can evaluate the intrinsic tendency of a given catalyst to produce one isomer or the other.

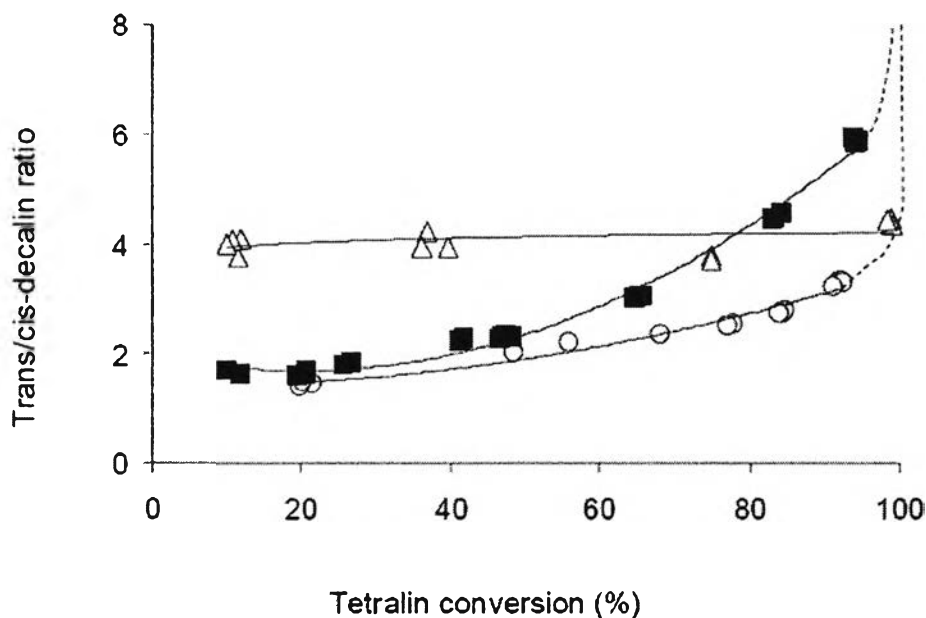


Figure 4.3 Trans/cis-decalin ratio of tetralin hydrogenation as a function of tetralin conversion. Reaction conditions: 3540 kPa and 548 K, $H_2/HC=25$, TOS = 3 h. ■, Pt/Al₂O₃; ○, Ni/Al₂O₃; △, Pd/Al₂O₃.

Almost 40 years ago, Weitkamp proposed that tetralin is firstly hydrogenated to $\Delta^{9,10}$ -octalin and $\Delta^{1,9}$ -octalin intermediates [19]. The former has the double bond in the bridging position and would yield only cis-decalin because the addition of the two hydrogen atoms occurs from the same side. However, the rate of hydrogenation of the latter is apparently much higher and both isomers are typically produced. Depending on how the $\Delta^{1,9}$ -octalin intermediate is oriented on the surface one can obtain each of the two isomers because the hydrogen addition to a double bond is always syn (i.e., both H atoms are added on the same side). When the hydrogen atom in position 10 is facing towards the surface, the addition of the two hydrogen atoms to positions 1 and 9 also occurs on the same side that faces the surface and the cis isomer is produced. On the other hand, if the hydrogen atom in

position 10 faces away from the surface, the hydrogen incorporation occurs on the opposite side and, consequently, trans-decalin is obtained.

One may speculate that in the cases in which the hydrogen incorporation is fast, soon after the $\Delta^{1,9}$ -octalin hits the surface it is hydrogenated. Therefore one may expect a trans/cis ratio near unity, as is the case for Pt and Ni, which have high intrinsic hydrogenation activity. When the catalyst is much less active, as in the case of Pd, one may expect that $\Delta^{1,9}$ -octalin may have time to accommodate and roll over on the surface before being hydrogenated. In that case, it is plausible that the preferred orientation would be one with the H atom facing away from the surface, which would explain that the preferred hydrogenation product on Pd is trans-decalin in a ratio of 4:1. Therefore, it may be generalized that the intrinsic trans/cis ratio is inversely related to the hydrogenation activity; the more active the catalyst, the closer the trans/cis ratio to unity (at low conversions).

However, as illustrated in Figure 4.3, the trans/cis ratio greatly changes as a function of tetralin conversion to eventually reach the equilibrium value (11 in this case). It is seen that in the case of Pt and Ni, the ratio increases very slowly with conversion until very high conversions. As we have explained in previous studies, the slow increase in trans/cis ratio on Pt (and now on Ni as well) is not due to a low intrinsic rate of isomerization, but rather to a strong site competition by tetralin (i.e., denominator in equation 2). In fact, as shown in table 4.3, although the rate constant (k_2) of the cis-to-trans isomerization reaction was higher than that of tetralin hydrogenation reaction (k_1) the cis-trans isomerization on Pt and Ni catalysts was taken place when the concentration of tetralin on the surface was decreased [20]. As discussed in our previous study, the high adsorption constant of tetralin compared to that of decalin may be ascribed to the parallel adsorption of a more rigid aromatic-containing molecule than a bent naphthenic molecule [34-36].

The case of Pd is more unusual. Unlike Ni and Pt, the ratio observed on Pd remained unchanged until maximum conversion that we could measure without increasing to the equilibrium value. In this case, it is not so much the site competition with unreacted tetralin what limits the isomerization, but rather the very low intrinsic isomerization activity exhibited by Pd under these conditions. As

shown in Table 4.3, k_2 for Pd is more than an order of magnitude lower than that for Pt.

4.4.3 Isomerization of Cis-to-Trans Decalin in the Presence of Tetralin on Pt and Ni Catalysts

As shown in Figure 4.3, the trans/cis decalin ratio at low conversions is the same for both catalysts, but as the conversion increases the curves split up with the ratio obtained on Pt consistently higher than that obtained on Ni. That is, while the intrinsic (primary product) trans/cis ratio is about the same on both catalysts, the subsequent cis- to-trans- isomerization is significantly lower on Ni than on Pt. There were two possible causes for this difference:

The isomerization activity (i.e. rate constant k_2) is much lower on Ni than on Pt catalyst. The decalin-tetralin adsorption competition is more pronounced on Ni than on Pt catalyst. Therefore, for a given tetralin concentration in the gas phase the cis-to-trans isomerization is more inhibited on Ni than on Pt.

The kinetic parameters shown in Table 4.3 indicate that it is the former rather than the latter the main responsible for the differences observed in the trans/cis ratio. To provide further evidence to support this conclusion a set of experiments was conducted using a mixed feed (tetralin: trans-decalin: cis-decalin, 20:48:32). These results were compared to those obtained with a feed of pure decalin (trans/cis ratio: 60/40). This comparison allowed us to study the effect of the presence of controlled amounts of tetralin in the cis-to-trans isomerization reaction on the Pt and the Ni catalysts.

Since Ni is significantly less active than Pt, different space time ranges were used for each catalyst in order to compare the cis-to-trans isomerization activity at the same tetralin concentration [37]. The W/F range used for Pt was 50-350 gcat*h/mol, while the range used for Ni was 150-950 gcat*h/mol.

The rate of cis-decalin isomerization in the mixed feed was compared to that of the pure feed on Ni and Pt catalysts under the same conditions as those described in the previous section. The comparison for over the two catalysts is made in Figs. 4.4a and 4.4b, respectively. The experimental data were fitted very well with

the selected model, using the kinetic parameters summarized in Table 4.3. The results from the fitting are shown as solid lines in Figs. 4.4a and 4.4b.

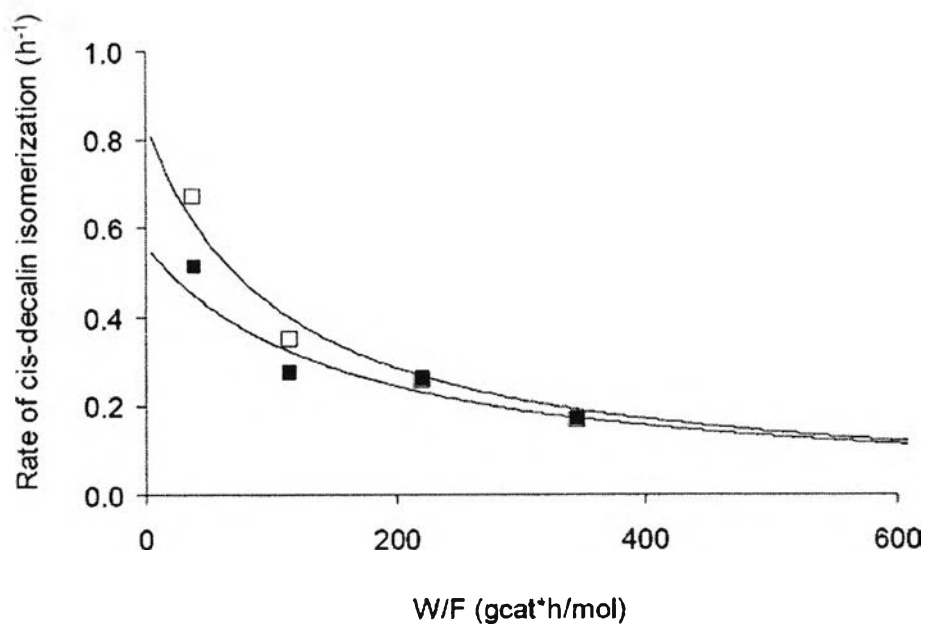


Figure 4.4a Rate of cis-to-trans isomerization in a combined feed (■) (tetralin:cis-decalin:transdecalin, 20:32:48) compared to the isomerization rate obtained in a pure decalin feed (□) (cis:trans, 40:60) on Pt/Al₂O₃ as a function of W/F. Solid lines are the results of the kinetic model.

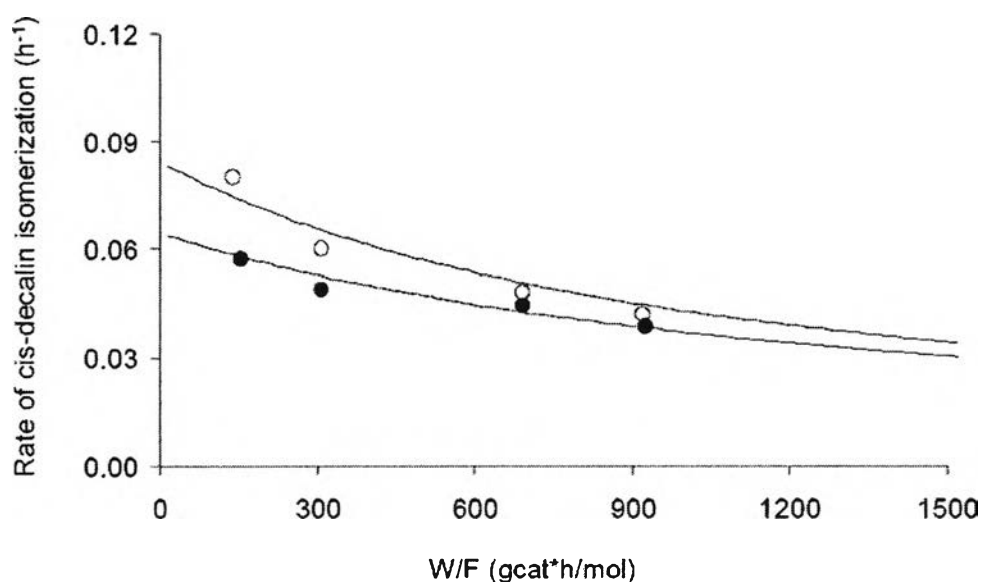


Figure 4.4b Rate of cis-trans isomeriation in mixed feed (●) (tetralin:cis-decalin:trans-decalin, 20:32:48) compared to rate of cis-trans isomerization in pure feed (○) (cis:trans, 40:60) on Ni/Al₂O₃ as a function of W/F. Solid lines are the Results of the kinetic model.

In this fitting, the concentration of tetralin was estimated to drop according to the rate of hydrogenation as calculated from equation 1. At low W/F, with significant presence of tetralin, the rate of isomerization in the mixture was slightly lower than that of the pure feed. At high W/F, the rate on both feeds converged to the same value due to the disappearance of tetralin by hydrogenation to decalin. A similar trend was observed for both Ni and Pt catalysts.

4.5 Conclusions

In summary, it can be concluded that the selectivity of trans-decalin and cis-decalin from tetralin hydrogenation is strongly dependent on both, the site competition between tetralin and decalin as well as the intrinsic rate of cis-to-trans isomerization. When a significant concentration of tetralin is present, the adsorption of cis-decalin to isomerize to trans- is inhibited. Therefore, at low tetralin conversion,

the product selectivity is mainly the result of the intrinsic relative rate of production of each isomer, which is different on different metals. It has been found that the intrinsic selectivity on Ni and Pt were about the same, while on Pd the trans-form is favored. In all cases, the trans/cis ratio is much lower than the equilibrium.

In addition, at high tetralin conversion, the trans/cis decalin ratio continuously increases with conversion over Ni and Pt catalysts due to increasing cis-to-trans isomerization. In contrast, over Pd catalyst the ratio remains unchanged at all tetralin conversion due to the low isomerization activity compared to that of Ni or Pt. The kinetic parameters were determined and fit well with hydrogenation and isomerization activity of catalysts prepared.

4.6 Acknowledgements

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