Comparative study of the hydrogenation of tetralin on supported Ni, Pt, and Pd catalysts

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Abstract

The hydrogenation of tetralin in the vapor phase 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 concentration of each isomer in the product may be important in subsequent ring opening steps if cetane number improvement is desired. The *cis*-decalin isomer is preferred to open the naphthenic ring in a selective way instead of multiple cracking. However, thermodynamically, this isomer is the least favored; so, kinetic control is the only solution. By selecting the proper catalyst and operating conditions, one could keep the *trans/cis*-decalin ratio low. In this study, we have prepared a series of supported metal catalysts and tested them in a flow reactor at 3540 kPa and 548 K. Kinetic parameters for the hydrogenation of tetralin and the *cis*-to-*trans*-decalin isomerization over the various catalysts investigated were obtained by fitting the data with a generalized Langmuir–Hinshelwood model.

The kinetic analysis revealed that the relative rates of tetralin hydrogenation, as well as the *cis*-to-*trans* isomerization are greatly affected by adsorption site competition of decalin and tetralin, which in turn has different magnitudes over the different catalysts. At tetralin conversions above 30%, the Ni catalyst yields the lowest *trans/cis*-decalin ratio. In contrast, the *trans/cis* ratio on Pd catalyst remains constant at all conversion levels and is highest at low tetralin conversion. It is concluded that the *trans/cis* ratio is a combination of the intrinsic selectivity of each isomer and the isomerization reaction.
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Keywords: Cis-decalin; Trans-decalin; Tetralin; Hydrogenation; Site competition; Isomerization

1. 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 matters and NO$_x$ emissions [1–3]. 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 number can be carried out in two-stages. In the first stage a conventional hydrotreating catalyst (CoMo, NiMo, and NiW on Al$_2$O$_3$) can be employed while a noble metal catalyst (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 aromatics 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

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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 molecule to allow the cleavage of the C6 membered 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 [6–9]. 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 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 and co-workers 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 is significantly higher than that 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 aromatics ring in monoaromatic compounds as well as competition for adsorption sites, in which the compound 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/Al_2O_3 catalysts [3]. The role of site competition was illustrated in a quantitative form for the case of tetralin hydrogenation [20]. The kinetics parameters obtained from a combination of modeling 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 nonlinearity 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 *trans/cis* ratios obtained on Ni, Pt, and Pd metal catalysts as a function of tetralin conversion during the hydrogenation reaction. From kinetic 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 the most suitable as a deep hydrogenation catalyst to accompany a subsequent ring opening step.

2. Experimental

2.1. Catalyst preparation and characterization

The commercial gamma-alumina support (γ-Al_2O_3, Saint-Gobian NorPro Corp., surface area 252 m^2/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 $Ni(NO_3)_2 \cdot 6H_2O$ (AnalaR), $Pt(NH_3)_4(NO_3)_2$ (Aldrich), and $Pd(NO_3)_2 \cdot xH_2O$ (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

Table 1
Metal loading (wt.%) and CO:metal atomic ratio

Catalyst	Metal loading (%)	T_r (K)	CO:metal
Ni/Al$_2$O$_3$	5	723	0.05
Pd/Al$_2$O$_3$	1	573	0.33
Pt/Al$_2$O$_3$	1	573	0.88

T_r is the reduction temperature.

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 1 summarizes the metal dispersions obtained with each catalyst. As typically observed when alumina is used as a support, the Ni catalyst required higher reduction temperatures than the corresponding Pt and Pd catalysts, and consequently, its dispersion was significantly lower. We compensated this lower dispersion with a higher metal loading [27].

2.2. 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 H$_2$/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 firstly reduced under flowing H$_2$ 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 H$_2$ 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 decahydronapthalene (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 run. Under the conditions used in this study no catalyst deactivation was observed.

3. Results and discussion

3.1. Kinetics 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 2. In agreement with previous studies, Pt exhibited 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 as previously observed by Rahaman and Vanice for one-ring aromatics [11].

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 Eqs. (1) and (2), respectively.

$r_{1(\text{hydrogenation})}$

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

$r_{2(\text{isomerization})}$

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

Under the conditions of this study, the hydrogenation of tetralin can be considered as irreversible whereas cis–trans isomerization should be considered reversible. The equilibrium constant K_{CD-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

Table 2
Tetralin hydrogenation activity on different catalysts

Catalyst	Specific reaction rate		TOF (s^{-1} × 10^3)[a]
	μmol TL/s gcat	mmol TL/s gmetal	
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

Reaction conditions: 3540 kPa, 548 K, H$_2$/HC = 25, TOS = 6 h.
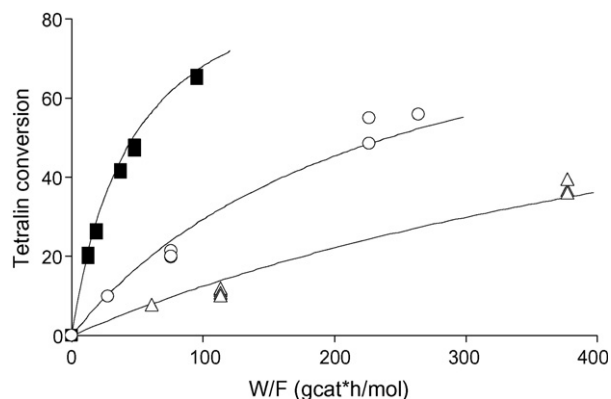[a] Based on CO/M chemisorption uptakes. TL conversion range: 10–20%.

Fig. 1. Tetralin conversion to decalin as a function of space time during hydrogenation in a flow reactor at 3540 kPa and 548 K H₂/HC = 25, TOS = 6 h. (■) Pt/Al₂O₃; (○) Ni/Al₂O₃; (Δ) Pd/Al₂O₃. Solid lines are the results of the kinetic model.

Table 3
Kinetics parameters for the hydrogenation of tetralin ($r_{1(hydrogenation)}$, as shown below) and *cis*-to-*trans*-decalin isomerization ($r_{2(isomerization)}$, as shown below) at 3540 kPa and 548 K, H₂/HC = 25, TOS = 6 h

	Ni	Pd	Pt
k_1 (h^{-1})	8.0 ± 0.5	1.8 ± 0.5	12.8 ± 0.5
k_2 (h^{-1})	9.0 ± 0.5	2.0 ± 0.5	30.2 ± 3.0
K_{H_2}	0.3 ± 0.05	0.40 ± 0.05	0.60 ± 0.1
K_{TL}	0.11 ± 0.03	0.25 ± 0.03	0.23 ± 0.03
K_{cis}	0.01 ± 0.005	0.01 ± 0.005	0.060 ± 0.01
K_{trans}	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.01

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

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

hydrogenation had the highest rate constants on Pt, followed by Ni, while Pd showed the lowest activity.

3.2. Trans/cis-decalin ratio

The evolution of the *trans*/*cis* ratio as a function of tetralin conversion during the hydrogenation reaction is compared in Fig. 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 reports [19,26,33,38]. 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.

the reaction order for TL (n_1) were chosen in agreement 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.

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 Eqs. (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 Fig. 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 in Fig. 2. 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_{CD}) and *trans*-decalin (K_{TD}). The resulting values obtained in the fit for these parameters are shown in Table 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
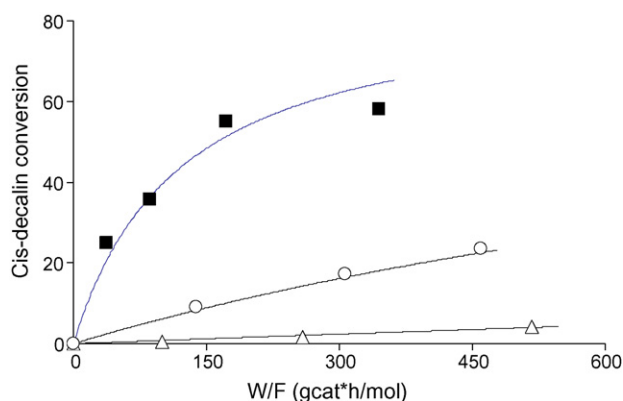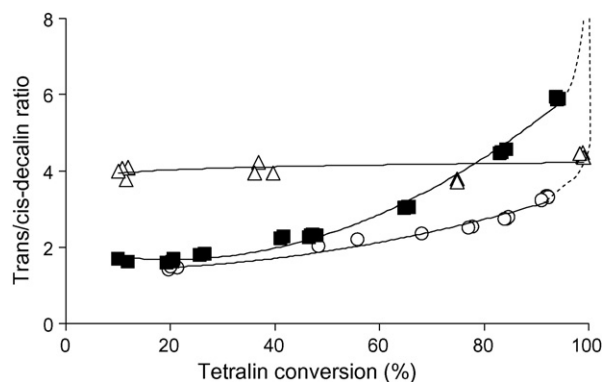

Fig. 2. *Cis*-to-*trans*-decalin isomerization in pure decalin feed (*trans*:*cis* feed ratio is 60:40). Reaction conditions: 3540 kPa and 548 K, H₂/HC = 25, TOS = 3 h. (■) Pt/Al₂O₃; (○) Ni/Al₂O₃; (Δ) Pd/Al₂O₃. Solid lines are the results of the kinetic model.

Fig. 3. *Trans*/*cis*-decalin ratio during tetralin hydrogenation as a function of tetralin conversion. Reaction conditions: 3540 kPa and 548 K, H₂/HC = 25, TOS = 6 h. (■) Pt/Al₂O₃; (○) Ni/Al₂O₃; (Δ) 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 case 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 are the cases 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 Fig. 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 Eq. (2)). In fact, as shown in Table 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 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 3, k_2 for Pd is more than an order of magnitude lower than that for Pt.

3.3. Isomerization of cis-to-trans-decalin in the presence of tetralin on Pt and Ni catalysts

As shown in Fig. 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:

(a) The isomerization activity (i.e., rate constant k_2) is much lower on Ni than on Pt catalyst.
(b) 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 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
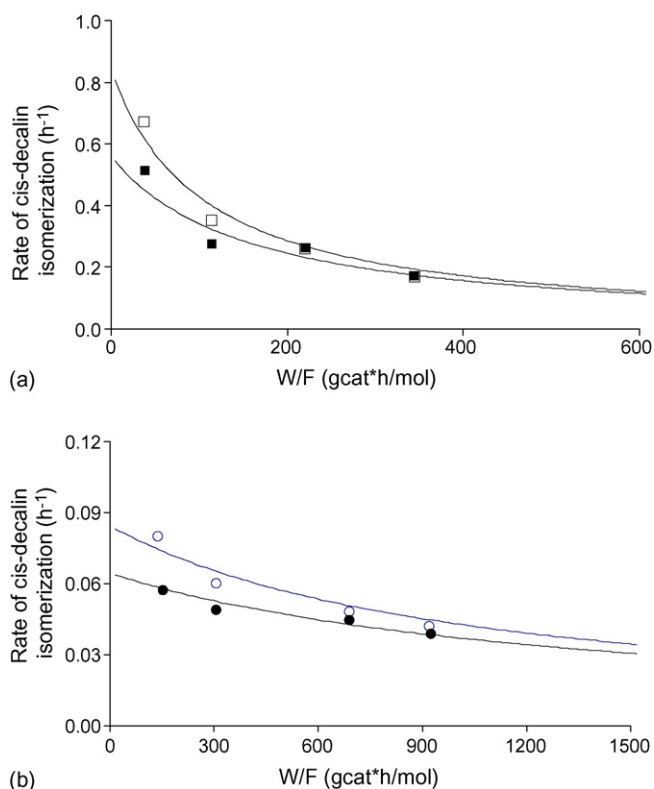

(a)

(b)

Fig. 4. (a) Rate of *cis*-to-*trans* isomerization in a mixed feed (■) (tetralin:*cis*-decalin:*trans*-decalin, 20:32:48) compared to the isomerization rate obtained in a *pure decalin feed* (□) (*cis*:*trans*, 40:60) on Pt/Al$_2$O$_3$ as a function of *W/F*. Reaction conditions: 3540 kPa and 548 K, H$_2$/HC = 25, TOS = 6 h. Solid lines are the results of the kinetic model. (b) 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/Al$_2$O$_3$ as a function of *W/F*. Reaction conditions: 3540 kPa and 548 K, H$_2$/HC = 25, TOS = 6 h. Solid lines are the results of the kinetic model.

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 investigate the effects of controlled amounts of tetralin on the rate of the *cis*-to-*trans* isomerization reaction over Pt and 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 obtained using the mixed feed was compared to the rate obtained with the pure feed on Ni and Pt catalysts under the same conditions as those described in the previous section. The comparison for the two catalysts is made in Fig. 4a and b, respectively. The experimental data were fitted very well with the selected model, using the kinetic parameters summarized in Table 3. The results from the fitting are shown as solid lines in Fig. 4a and b. In this fitting, the concentration of tetralin was estimated to drop according to the rate of hydrogenation as calculated from Eq. (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. Conclusion

In summary, it can be concluded that the selectivity of *trans*- 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*-decalin is inhibited. Therefore, only at low tetralin conversions, the product selectivity is the result of the intrinsic relative rate of production of each isomer, which is different on different metals. Accordingly, it can be concluded that the intrinsic selectivity for each isomer is about the same on Ni and Pt, while the *trans*-form is favored on Pd. In all cases, the intrinsic *trans/cis* ratio is much lower than the equilibrium. At high tetralin conversions, 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 over the entire tetralin conversion range due to the low isomerization activity of Pd compared to those of Ni and Pt.

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