Comparative Study of the Hydrogenation of Tetralin on Supported Ni, Pt, and Pd Catalysts

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Abstract

Environmental legislation on diesel fuels is increasingly focusing on reduction of sulfur and aromatics content as well as maximum cetane number (CN). Hydrogenation of aromatics alone may not be sufficient to attain the high CN that has been projected for future legislation and further reactions such as selective ring opening of the hydrogenated compounds may be necessary. It has been shown that the two products of the hydrogenation of tetralin, i.e. cis- and trans-decalin have different reactivities for the subsequent ring-contraction and ring-opening reactions. Trans-decalin is the more stable isomer of the two, but at the same time is much less reactive than cis-decalin. In previous studies, we found that while cis decalin resulted in substantial selectivity to indanes and alkyl-cyclohexanes over HY catalysts, trans-decalin only converted at high temperatures with low selectivity to C10 products. As a result, we have investigated the gas-phase hydrogenation of tetralin over different catalysts to determine the evolution of the trans-to-cis ratio as a function of conversion. In this study alumina-supported Pt, Pd and Ni catalysts were prepared by incipient wetness impregnation and tested in a fixed-bed continuous flow reactor at a total pressure of 300 psi and 275°C. The catalytic activity tests revealed that the relative rates of hydrogenation to cis- and trans-decalin, 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 that obtained on Pt as the conversion approached zero. By contrast, the trans/cis ratio on Pd catalysts 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 to each isomer and the isomerization reaction. However, in order to get isomerized, the cis-decalin needs to compete for adsorption sites with tetralin. As a result, the isomerization is a strong function of conversion and the type of catalyst used.

Keywords: cis-decalin, trans-decalin, tetralin, hydrogenation, site competition, isomerization

Introduction

Environmentally friendly transportation is a major driving force for the development of stringent regulation in the near future around the world. The legislations in diesel fuel are mainly focused on decrease in sulfur and aromatic contents, and increase in cetane number as well (Stanislaus and Cooper, 1994; Kaufmann et al., 2000; Cooper and Donnis, 1996). Concern for the removal of aromatics hydrocarbon has received a considerable attention because they are related to the improvement of combustion efficiency, lower particulate and NOx emission (Cooper and Donnis, 1996). In addition, the decrease in aromatics contents is also closely related to the increase in cetane number. Typically, the increase in cetane number can be achieved by using several methods. Firstly, the addition of cetane boosters, e.g. alkyl nitrates, is introduced but it may cause hazardous and degrade the storage stability of the fuel. Second 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 with FT. The other alternative is deep hydrotreating process that is carried out by a two-stage process, conventional hydrotreating catalyst (CoMo, NiMo, and NiW on Al_2O_3) are used at the first stage and noble metal catalyst (Pt, Pd, Ni) with high hydrogenation activity are used in the second stage (Cooper and Donnis, 1996). However, the increase in cetane number is strongly depended on the nature of crude and refinery blending strategies. Recently, more Light Cycle Oil (LCO) was added in the diesel pool. Due to its high content of aromatic and low cetane number (typically between 20 and 30), the incorporated of LCO has a negative impact on cetane number of the diesel fuel. Although, most of aromatics in LCO are saturated in deep hydrogenation process, cetane number is still lower than the specification of diesel fuel in the future.

Recently, numerous present works have proposed that opening of at least one of the naphthenic ring is a promising reaction to attain high CN that have been projected for future legislation (Arribas and Mart´ýnez, 2002; Kubiˇcka et al., 2004). In order to achieve ring opening product, aromatic is firstly hydrogenated to napthenic molecule then C6 member ring is necessary isomerized to C5 member ring which facilitate the ring opening of a cyclic hydrocarbon ring (McVicker et al., 2002). Therefore, in the presence of BrØnsted acid site is essential for the accomplishment of both isomerization and ring opening. Unfortunately, high quantity of cracking and isoparaffins (branch chain) products which cause dramatically drop of cetane number are also obtained from acid-catalyzed reaction (Arribas and Mart´ýnez, 2002; Kubiˇcka et al., 2004). Therefore, the proper catalysts are very necessary to maximize selective ring opening (SRO) products while minimize cracking and branch chain products. Recent investigation has shown that ring opening of tetralin (TL) on HY catalyst occur much lower rate than that of decalin (Santikunaporn et al., 2004). In addition it was found that the two products of TL hydrogenation, i.e. cis- and trans-decalin (DL) have different reactivity for the subsequent ring-contraction and ring-opening reactions. Since cis-DL is less stable and more reactive than that of trans- isomer. Therefore, cis-DL resulted in substantial selectivity to indanes and alkyl-cyclohexanes over HY catalysts whereas trans-DL only converted at high temperatures with low selectivity to C10 products (undesired products). Therefore, cis-DL isomer should be maximized to favour ring opening products in subsequent process. However, the study of TL hydrogenation is still rarely reported. Previous work studied the TL hydrogenation in liquid phase on Ni/Al_2O_3 catalyst (Rautanen et al., 2001). It was found that TL was firstly hydrogenated via $\Delta^{9,10}$-octalin and $\Delta^{1,9}$-octalin. Then, these intermediate products were further hydrogenated to cis- and trans-DL products. Recent study of TL hydrogenation on Pt and Pd/Al_2O_3 has shown the interesting relationship between trans/cis-DL ratio (t/c ratio) and TL conversion. It reported the effect of site competition and cis-trans isomerization on product selectivity (Jongpatiwut et al., 2004). At low TL conversion, intrinsic relative rates to each isomer depend on the metal used, i.e. the t/c ratio is around 3 for Pd and PtPd, and around 1 for Pt catalysts. Since readsorption of cis-DL to isomerize to trans-DL isomer strongly inhibited by significant present of TL on catalyst surface. In contrast, at high TL conversion, t/c ratio greatly increases due to cis-trans isomerization because trans-DL is the thermodynamically favoured form of decalin. Unfortunately, these results have a negative impact to subsequent ring opening products because both high TL conversion and maximize cis-DL product are required to achieve an effective ring opening reaction. Therefore, selected catalyst is very important to maintain the high conversion level while to avoid and extensive cis- to trans- isomerization.

The aim of this contribution is to compare product selectivity from TL hydrogenation in gas phase reaction among Ni, Pt, and Pd metal catalysts supported on conventional gamma alumina.

Catalyst preparation

Commercial gamma-alumina support (γ-Al_2O_3, Saint-Gobian NorPro Corp, surface area 252 m^2/g) was ground and sieved to avoid internal mass transfer limitation. Pt, Pd and Ni metals were loaded on gamma-alumina using conventional incipient wetness impregnation technique with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ (Aldrich), $Pd(NO_3)_2.xH_2O$ (Aldrich) and $Ni(NO_3)_2.6H_2O$ (AnalaR), respectively. The concentration of the precursor solution was adjusted to the desired metal loading. In this study, 1 wt.%Pt and Pd, and 5 wt.% Ni loading catalysts were prepared. After the impregnation the sample was kept at ambient temperature for 4 h, then dried at 110 ºC overnight, and finally calcined in an oven for 2 h at 300 ºC for Pt and Pd samples and calcined at 400 ºC for Ni sample.

Catalytic activity testing

The catalytic activity measurements were carried out in a 3/4” O.D. continuous fixed bed stainless steel reactor equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The catalytic activity was conducted at 275˚C, pressure of 300 psig, and H_2/HC molar ratio of 25. Space velocities were systematically varied by changing either the catalyst amount or the hydrocarbon feed rate. The catalyst was first reduced under flowing H_2 at 300 psig for 1.5 h. The reduction temperatures were set of 300˚C for Pt and Pd and 450˚C for Ni catalyst. After the pretreatment, the reactor was cooled down in flowing H_2 to 275˚C. Then, liquid reactant was introduced to the reactor using a high-pressure pump. Two different hydrocarbon compounds, 1,2,3,4-tetrahydro-naphthalene (tetralin, TL, Fluka, 97+%) and decahydronapthalene (decalin, DL, Fluka, 99%, a mixture of trans- and cis- ratio 60/40) were used in this work. In these case of mixed feed utilized the mixture was prepared by blending 20 wt.% TL and 80 wt.% DL. The products were online analyzed by an HP6890 gas chromatograph with an FID detector equipped with using HP-5 column.

Results and discussion

The hydrogenation of TL was carried out on Ni, Pt and Pd catalysts. As illustrated in Fig.1, the interesting trend was observed on each catalyst. The t/c ratio remains constant at all conversion levels on Pd catalyst. In contrast, on Ni and Pt catalysts, the t/c ratio was strongly depended on catalyst type and TL conversion. The t/c ratio was classified into two regions, according with the previous study (Jongpatiwut et al., 2004). Firstly, at low TL conversion, t/c ratio remained unchanged as TL conversion increased because the ratio was not governed by cis-trans isomerization. Typically, stereoisomerization was known as a reversible reaction. However, the isomerization from trans- to cis-DL is not accounted because the forward cis- to trans-DL is much faster than the backward reaction (Lai and Song, 1996). Therefore, the isomerization of cis- to trans-DL could be treated as irreversible reaction (Huang and Kang, 1995). The adsorption of cis-DL in order to isomerize to trans-DL was greatly affected by the site competition of DL with TL. Therefore, intrinsic properties of each metal were revealed at TL conversion approach zero. The ratio observed from Pd catalyst was almost 2.5 times higher than that of Ni and Pt catalysts. Accordingly, Pd is more selective in hydrogenation toward trans-DL product than Pt and Ni catalysts. Secondly, at high TL conversion increasing of TL

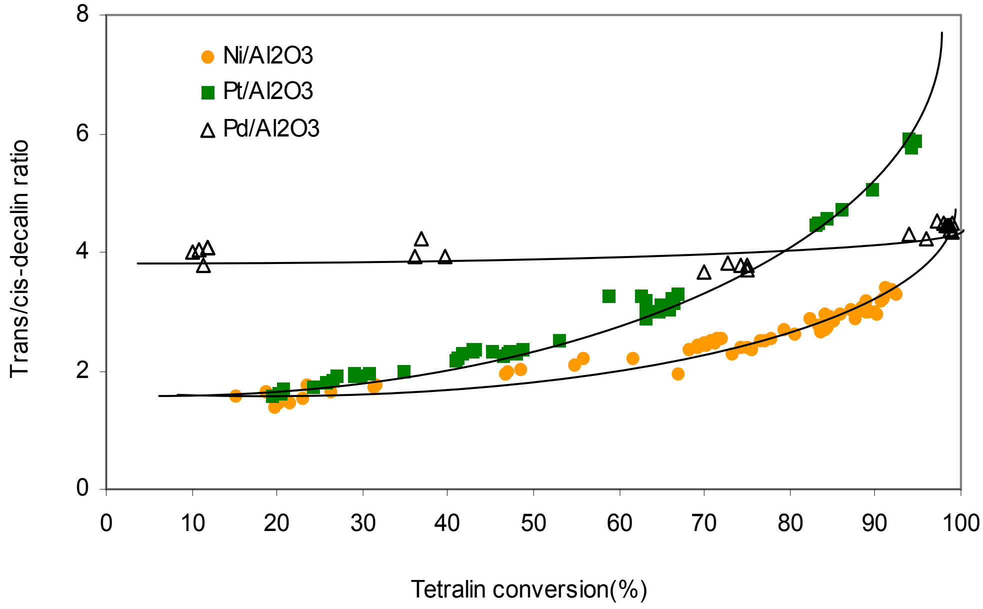

Figure 1. Trans/cis-DL ratio of TL hydrogenation over Pd, Pt, and Ni catalyst as a function of TL conversion. Reaction condition: Feed: tetralin, 300 psig., 275ºC, H_2/HC=25, TOS = 6 h.

conversion resulted an increasing of t/c ratio on Pt and Ni but remain constant on Pd catalyst. The result on Pt and Ni catalyst is not unexpected, since at low TL concentration present on the surface, cis-DL molecule is allowed to re-adsorb. Then, cis-trans isomerization is obtained. However, the unchanged of t/c ratio on Pd catalyst will be discussed later.

TL hydrogenation pathway was proposed that TL molecule was firstly hydrogenated to $\Delta^{9,10}$-octalin and $\Delta^{1,9}$-octalin intermediate (Weitkamp, 1968). Then, $\Delta^{9,10}$-octalin was slowly hydrogenated to cis-DL product. By contrast, $\Delta^{1,9}$-octalin obtain either trans- or cis-isomer depending on the configuration of intermediate that located on the surface. Cis-DL was obtained when the adsorption of the hydrogen atom in position 10 was facing to the surface, then the addition of hydrogen atom was preceded on the same side of the molecule. Since the adsorption of hydrogen atom was facing away from the surface, then hydrogen undergo on different side, trans-DL was obtained. Alternatively, desorption of $\Delta^{1,9}$-octalin may not be necessary for the formation of trans if it is considered that $\Delta^{1,9}$-octalin may roll over of the surface then hydrogenated on the opposite site (Weitkamp, 1968).

As mention earlier, t/c ratio observed from Pd was almost 2.5 times higher than that of Pt and Ni catalysts. It may be postulated that hydrogen atom in position 10 of $\Delta^{1,9}$-octalin intermediate prefers to adsorb facing away on Pd surface than that on Pt and Ni surface. Recently, cis- to trans-DL isomerization pathway was proposed that cis-DL was converted to octalin products via dehydrogenation and consequently hydrogenated to trans-DL product (Lai and Song, 1996). Although both $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin olefin intermediate were proposed to yield trans-DL product, the main reaction was proposed to proceed through $\Delta^{1,9}$-octalin intermediate. Since hydrogenation rate of $\Delta^{1,9}$-octalin is much faster than that of $\Delta^{9,10}$-octalin (Weitkamp, 1968). It is expected that, at high TL conversion t/c ratio obtained on Pd catalyst should be highest among catalysts employed. Since the intrinsic properties of the Pd catalyst prefer hydrogen atom in position 10 of $\Delta^{1,9}$-octalin intermediate adsorb facing away from its surface that could drive $\Delta^{1,9}$-octalin olefin intermediate to be further hydrogenated to trans-DL. However, at high TL conversion, the unchanged of t/c ratio on Pd compare to the significant increase of the ratio on Pt and Ni catalyst was observed (Fig.1). As a result, it may conclude that unchanged of t/c ratio at high TL conversion of Pd due to its low dehydrogenation activity.

Interestingly, at TL conversions above 30 %, Ni catalyst yielded the lower t/c ratio, but this ratio converged to about the same value as that obtained on Pt as the conversion approached zero. At high TL conversion, the subsequence cis- to trans- DL isomerization reaction on Ni seems to be slower than that on Pt catalyst. Since product selectivity was governed by the effect of site competition and isomerization. There are two possible explanations:

a) The site competition is more pronounced on Ni catalyst than that of Pt catalyst. Therefore, at the same TL concentration present on the surface, cis-trans isomerization is more difficult on Ni than that of Pt catalyst.

b) Cis-trans isomerization activity on Ni is lower than that on Pt catalyst even in the absence of TL molecule.

To elucidate which one is the case, a set of experiment was done by using mixed feed (a mixture of TL, trans- and cis-DL ratio, 20/48/32) and pure DL feed (a mixture of trans- and cis-DL, ratio 60/40) were used to compare the cis isomerization activity of Ni and Pt catalysts. Mixed TL and DL feed was introduced to obtain the space time of each catalyst to achieve the same (or similar) TL conversion. Then, these specific space times of each catalyst will be compared for cis-trans isomerization activity by using pure DL feed.

Hydrogenation of mixed feed was carried out on Ni and Pt catalysts. TL and cis-DL conversions as a function of space time on Ni and Pt catalyst were illustrated in Fig. 2(a), and 2(b), respectively.

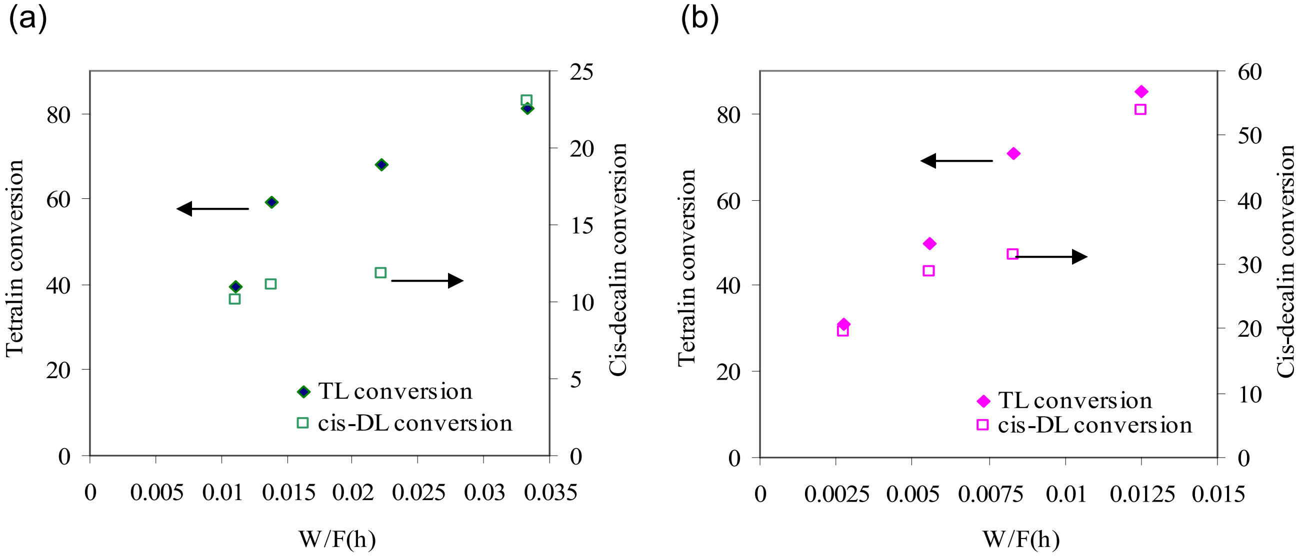

Figure 2. Conversion of tetralin and cis-decalin as a function of space time (W/F, h) on (a) Ni and (b) Pt catalysts. Reaction condition: Mixed feed (a mixture of TL, trans- and cis-DL ratio, 20/48/32), 300 psig, 275°C, H_2/HC=25, TOS = 6 h.

It was found that increasing cis-DL conversion corresponds to the increasing in TL conversion. The result was clearly shown that in order to isomerize to trans-, the adsorption of DL has to compete with TL molecule. As a result, the lower concentration of TL present on catalyst surface, the higher cis-trans isomerization. Conversion of cis-DL is an important calculation for the activity comparison. In this set of experiment, total cis-DL was combined cis-DL presented in feed (32wt.%) and cis-DL product from TL hydrogenation. From Fig.1, cis- and trans-DL from TL hydrogenation were obtained from intrinsic properties of the metal, i.e. at TL conversion approach zero t/c ratio is 1.6:1 on Pt and Ni catalysts. For example, basis feed is 100 moles, and at 81.05% TL conversion in mixed feed (a mixture of TL, trans- and cis-DL ratio, 20/48/32), cis-DL product obtained from the hydrogenation is 6.2 moles. Then, total cis-DL is 38.2 moles. Since, cis-DL from products analysis is 29.4 moles. Therefore, cis-DL conversion from isomerization is 23.1%.

The cis-trans isomerization in mixed feed from 2(a) and 2(b) were taken to compare with the isomerization in the absent of TL (pure DL feed). Therefore, the space time to reach TL conversion at high TL conversion (81.1% for Ni and 85.1% for Pt catalysts) and moderate TL conversion (67.9% for Ni and 49.6% for Pt catalysts) were selected to study the cis-trans isomerization activity in the presence and absence of TL as shown on Table 1.

Conversion of cis-DL in mixed feed and pure DL feed was illustrated in Table 1. It was observed that, at high TL conversion (>80%), there was no significant difference in the cis-DL conversion between mixed and pure feeds. In contrast, at lower TL conversion, the cis-DL conversion in mixed feed was significant lower than that on pure feed. These trends were obtained on both Ni and Pt catalyst.

Table 1. Conversion of tetralin and cis-decalin in mixed feed and pure decalin feed over Ni and Pt catalysts

Catalyst	W/F(h)	mixed feed		Pure feed
		TL conversion	cis-DL conversion	cis-DL conversion
Ni	0.0330	81.1	23.1	23.5
	0.0220	67.9	11.8	17.3
Pt	0.0125	85.1	53.8	55.2
	0.0005	49.6	28.9	34.7

Reaction condition: mixed feed: tetralin: trans-decalin: cis-decalin = 20:48:32, pure feed: decalin (trans/cis ratio is 60/40), 300 psig, 275°C, H_2/HC=25, TOS = 6 h.

The results indicated that the presence of TL molecule on the surface inhibits the cis- to trans-DL isomerization. Interestingly, at higher TL conversion (>80%), which is less effect of site competition on product, conversion obtained from Pt was 2 times higher than that on Ni catalyst. It was indicated that the lower t/c ratio observed on Ni at high TL conversion from Fig. 1 was due to the lower isomerization activity on Ni catalyst. However, quantitative study of each metal (Pd, Pt, and Ni) should be further investigated in order to explain complicated phenomena on catalyst surface unquestionably.

Conclusion

Trans- and cis-DL products selectivity from TL hydrogenation was strongly depended on site competition and cis- to trans- isomerization, which in turn depend on intrinsic properties of each metal. At low TL convertion, product selectivity only resulted from intrinsic relative rates to each isomer of each metal, since site competition of DL with TL inhibited cis-trans isomerization. By contrast, at high TL conversion, the products selectivity was governed by cis- to trans- isomerization. The observation of t/c ratio on Pd is almost 2.5 times higher than that of Pt and Ni catalysts. Therefore, Pd is more selective to trans- product than that of Pt and Ni catalysts. However, Pd is also exhibited the low cis-trans isomerization that may be due to its low dehydrogenation activity.

Interestingly, at low TL conversion, t/c ratio of Pt and Ni catalysts are similar while the ratio obtained on Pt catalyst is more greatly increased at high TL conversion. The result on Pt catalyst has a negative impact to ring opening products in subsequent process since yield of cis-DL isomer is also significantly decreased at high TL conversion. In contrast, Ni catalyst shown slightly increase in t/c ratio because of its low cis-trans isomerization activity.

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