Transfer Hydrocracking of Diphenylpropane with Tetralin
## on Active Carbon Catalysts

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A nickel supported on active carbon catalyst was found to exhibit an excellent activity for transfer hydrocracking of diphenylpropane with tetralin at 400 °C. It is demonstrated that the catalytic transfer hydrogenation is effected by the reverse spillover of hydrogen atom over the active carbon.

Development of the technology for upgrading heavy oils such as petroleum residue, oil-sand bitumen or coal liquid to high quality distillates with low or no hydrogen consumption is strongly desired. The present authors have proposed a new process termed as transfer hydrocracking of heavy oils.[1] In the process, a heavy oil is cracked thermally in liquid phase in the presence of a metal-supported active carbon and slightly pressurized hydrogen. On the active carbon surface, polycyclic aromatic hydrocarbons are adsorbed to be cracked and dehydrogenated. Hydrogen atom thus liberated by the above dehydrogenation is supposed to be transferred to effect the hydrogenation of the cracked product. Thus, the consumption of hydrogen gas is minimized.

In order to make clear the reaction mechanism, a study using model compounds was carried out. Namely, diphenylpropane (DPP) was used in this experiment as a hydrogen acceptor, because it represents one of the typical chemical structure of heavy oil, and its C-C bond cracks at temperature above 350 °C through a radical chain mechanism which is presumed as follows;[2]
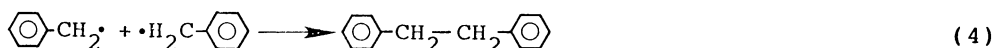
Initiation

(1)

Propagation


(2)

(3)

Termination

(4)
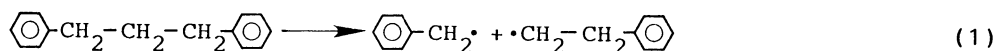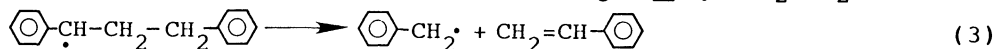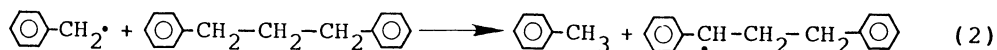
Thus, the products should be substantially an equimolar mixture of toluene and styrene. However, styrene is so reactive under reaction conditions that it polymerizes quickly to higher hydrocarbons and coke. If styrene is hydrogenated effectively, one can obtain the products composed of an equimolar amount of toluene and ethylbenzene.

Catalysts employed in this study were a 5 wt% Ni on commercially available active carbon (A.C.) (Takeda HGS616, charcoal made, specific surface area : 1500 $m^2 g^{-1}$) and a commercially available Raney Ni. Ni/A.C. was activated by calcining in N_2 at 450 °C for 3 h, reducing with H_2 at 450 °C for 1 h, and then sulfiding with H_2-H_2S mixture (4:1) at 400 °C for 1 h. Reactions were conducted in a conventional shaking autoclave with an inner volume of 75 cm^3. Standard reaction conditions were : temperature ; 400 °C, reaction time ; 1 h, initial hydrogen pressure ; 0-2.0 MPa(at room temperature), diphenylpropane (DPP) ; 3.00 g, tetralin (THN) as hydrogen donor; 4.04 g, catalyst ; 0.60 g. Both gaseous and liquid products were analyzed by gaschromatographs.

In table 1 are shown the experimental results of DPP cracking with THN. The conversion of DPP was 74% in the uncatalyzed reaction and usually higher than those in the catalyzed reactions. The non catalyzed dehydrogenation of THN was quite slow while it was accelerated to some extent by added DPP suggesting that homogeneous hydrogen transfer between DPP and THN proceeded. Only toluene, ethylbenzene, benzene, THN and naphthalene were found by gaschromatograph in the non catalyzed DPP/THN system, probably because styrene was polymerized to form higher boiling products. On the other hand, ethylbenzene/toluene ratio for the catalyzed reactions especially in Ni/A.C. system approached to 1 and ethylbenzene yield was close to DPP conversion. Especially, the reaction at 380 °C and under pressurized hydrogen (1.0 MPa) gave the ethylbenzen/toluene ratio of 1.0 and the product yield just corresponded to DPP conversion. The facts mean that free

Table 1. Transfer hydrocarcking of DPP with THN
Reaction conditions : temperature 400 °C, time 1 h, DPP 15.3 mmol, THN 30.6 mmol

Catalyst	Non.[a]	Non.	Raney Ni	A.C.	Ni/A.C.	Ni/A.C.[b]
Atmosphere	H_2	H_2	N_2	N_2	N_2	H_2
Initial pressure/MPa	1.0	1.0	3.6	3.6	3.6	1.0
DPP conversion/%	–	74.2	75.4	66.7	59.0	21.2
◯-C_2H_5/◯-CH_3/mole ratio	–	0.21	0.27	0.54	0.89	1.0
H_2 to gas phase/mmol	1.5	2.3	5.0	1.9	13.0	9.8
Product yield/mol%						
◯ [c]	–	0.6	tr.	0.4	1.0	tr.
◯-CH_3[c]	–	91.2	78.0	79.0	64.6	20.6
◯-C_2H_5[c]	–	19.2	21.4	42.6	57.4	20.6
Naphthalene[d]	1.0	6.7	8.7	16.9	35.1	25.2

a) Without tetralin. b) Reaction temperature 380 °C. c) Based on DPP.
d) Based on THN.

radicals and styrene were effectively stabilized by hydrogenation over the catalyst. Active carbon itself showed catalytic activity to some extent for dehydrogenation of THN to form naphthalene. Ni/A.C. catalyst showed synergistic effects of Ni catalyst and carbon catalyst, it gave 35% of naphthalene yield, while the cracking of DPP was the lowest. Figure 1 shows the relationship between the degrees of hydrogenation of products or DPP conversion and the degree of dehydrogenation of THN which expressed by naphthalene yield. The degree of hydrogenation was defined by ethylbenzene/toluene ratio. It is clear from the figure that the ethylbenzene/toluene ratio increases, whereas DPP conversion decreases, with increasing THN dehydrogenatoin, respectively. The former should be attributed to the hydrogenation of styrene to ethylbenzene and the latter should be attributed to the stabilization of benzyl radical, which is the chain carrier of DPP cracking, by hydrogenation to toluene.

Figure 2 shows how the initial pressure of hydrogen affects cracking of DPP and dehydrogenation of THN. The conversion of DPP decreased slightly and the dehydrogenation of THN decreased markedly with the increase in hydrogen pressure up to 2.1 MPa. It is also clear that the amount of hydrogen recovered after reaction was not largely affected by the amount of hydrogen charged which corresponded to the initial hydrogen pressure, except 0 MPa.
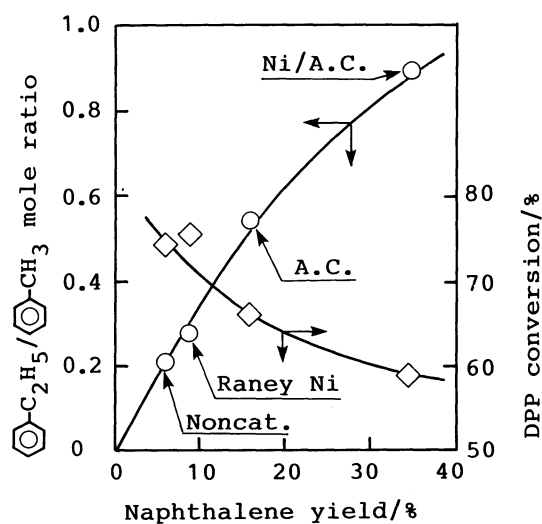
Destination of hydrogen supplied

Fig. 1. Transfer hydrocracking of DPP with THN. Reaction conditions ; 400 °C, 1 h
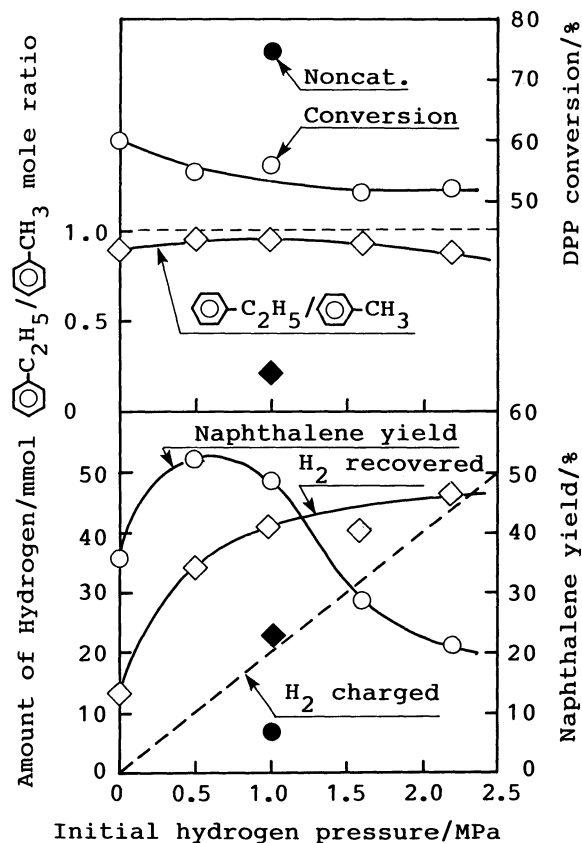

Fig. 2. Effects of hydrogen pressure on tansfer hydrocracking of DPP with THN on Ni/A.C. catalyst. Reaction conditions; 400 °C, 1 h

by THN dehydrogenation is shown in Fig. 3. While the amount of hydrogen transferred to cracking products was almost independent on hydrogen pressure, the amount of hydrogen desorbed to gas phase decreased with an increase in hydrogen pressure. It can be concluded that desorption of hydrogen supplied by THN, from catalyst surface is suppressed by hydrogen in the gas phase. It is suggested that in the presence of Ni/A.C. catalyst, the hydrogen in the gas phase and in THN are exchangeable and reach an equilibrium during the reaction.

A reaction mechanism is illustrated in Fig. 4. THN is dehydrogenated on the carbon surface to form naphthalene and surface hydrogen atoms. The hydrogen atom migrates on the carbon surface to reach the sulfided metal particle loaded on it.[3] Some part of surface hydrogen react with free radicals formed by dissociation of DPP C-C bond, while the other part of hydrogen combines to form hydrogen molecules and then desorbs into gas phase. In the presence of pressurized hydrogen, the desorption of hydrogen gas is suppressed and thus consumed selectively to hydrogenate olefins or free radicals.

These results substantiate a new method for heavy oil upgrading termed as transfer hydrocracking which is composed of thermal cracking and in situ transfer hydrogenation.

; H_2 transferred to products.
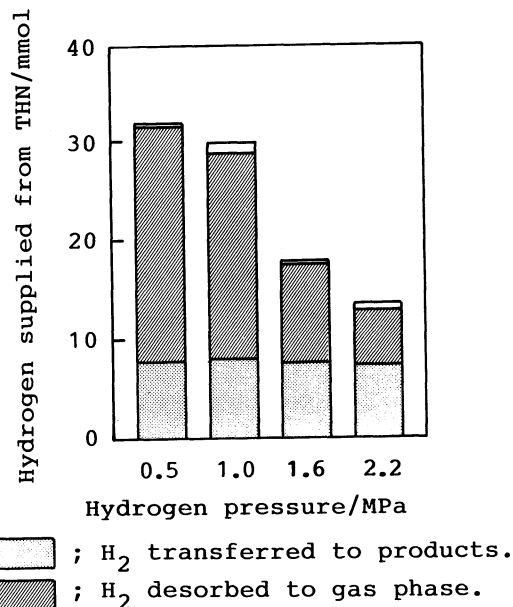
; H_2 desorbed to gas phase.

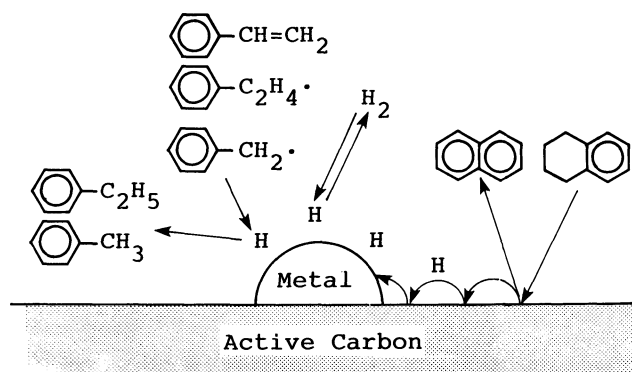Fig. 3. Hydrogen destination in transfer hydrocracking of DPP with THN on Ni/A.C. catalyst.

Fig. 4. Reaction model of transfer hydrocracking.

References

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3) S. Asaoka, K. Masamizu, K. Fujimoto, and T. Kunugi, Nippon Kagaku Kaishi, 1976, 388.