KINETIC STUDIES ON LIQUID-PHASE HYDROGENATION OF 1-METHYLNAPHTHALENE USING AN IMPROVED BASKET REACTOR

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An improved basket reactor, equipped with a specially designed catalyst basket assembly to determine the exact starting time of reaction in batchwise experiments, was developed. The reactor was proved to be useful in experiments even under high temperature and pressure. Using this reactor, kinetic studies of liquid-phase hydrogenation of 1-methylnaphthalene were carried out as a model reaction of regeneration of hydrogen donor solvent for coal liquefaction and hydrotreating of polyaromatic sources of gas oil, in the range of 583-643K temperature and 3.1-7.7 MPa hydrogen partial pressure over a commercial Co-Mo/γ-Al$_2$O$_3$ catalyst. To establish kinetic equations, the reaction equilibrium for conversion of 1-methylnaphthalene to methyltetralins was measured. Langmuir-Hinshelwood type kinetic equations, based on surface reaction between dual adsorption sites of hydrogen and reactants, fairly represented the effects of temperature and hydrogen partial pressure on the yields.

Introduction

Hydrogenation of polyaromatics is important in several processes such as coal liquefaction[6] and heavy oil upgrading[2, 15]. In these processes, partly hydrogenated polyaromatics such as tetralin have been effectively utilized as hydrogen donor solvents. The aromatics which are returned to the original aromatics after donation of hydrogen must be again hydrogenated for reuse. The degree of hydrogenation of the recycled donor solvent strongly affects product yields[2, 6].

In addition, highly polyaromatic oil like light cycle oil, which is a by-product of the fluid catalytic cracking process, has become an important source of gas oil to meet increasing demand for diesel fuel[3, 17]. Aromatics content in this oil should be reduced by hydrotreatment, both for improvement of its cetane number and for environmental protection.

For each application of hydrogenation of aromatics mentioned above, the degree of hydrogenation has to be carefully controlled by a suitable choice of reaction conditions, such as temperature, pressure and space velocity. Kinetic information is basic to the design of the hydrogenation reactors.

In commercial reactors, hydrogenation of polyaromatics principally proceeds in gas-liquid-solid three phase with gaseous hydrogen, liquid-phase aromatics and solid catalysts. The kinetics of liquid-phase hydrogenation for two- or three-ring aromatics have been

studied for naphthalene[5, 12-13, 18], 1-methylnaphthalene[10], 2-methylnaphthalene[7], biphenyl[14] and anthracene[12, 19]. In most of these publications, a pseudo-first order rate equation with respect to aromatics concentration has been reported. Insufficient quantitative information is available on the effect of the reaction conditions, except for the hydrogenation of biphenyl[14].

A stirred basket-type reactor has been successfully utilized to investigate the kinetics in gas-liquid-solid three-phase reactors[11]. In the case of batchwise experiments using the basket reactor at high pressure and temperature, one faces the problem of how to decide the timing when the reaction actually starts. To resolve this problem, Ohta et al.[9] enclosed a reactant in an ampoule prior to the reaction, then introduced the reactant into the liquid, followed by breaking the ampoule through rigorous agitation after reaction conditions were accomplished. However, uniform temperature in the liquid may not be achieved by this method due to there being no agitation during the heating-up period. Alternatively, Kawakami et al.[8] have employed a method in which feed gas was quickly charged to start reaction. This procedure is called the "gas-switching method" in this paper.

The purposes of the present work are (1) to improve the basket reactor for the determination of the exact starting time of reaction even at high temperature and pressure, and (2) to establish kinetic equations including the effect of temperature and hydrogen partial
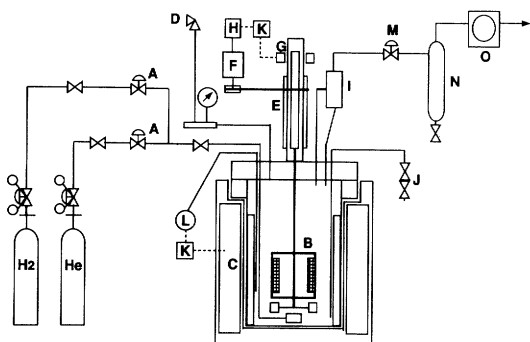
Fig. 1 Experimental apparatus: A, Mass flow controller; B, Catalystbasketassembly;C,Heater;D,Safetyvalve;E, Magnetic stirrer; F, Motor; G, Speed sensor; H, Invertor; I, Condenser; J, Sampler; K, Controller; L, Thermocouple; M, Back ressure regulator; N, Separator; O, Gas meter

Fig. 2 Detail of catalyst basket assembly.
(a) Before dropping
(b) After dropping

pressure on liquid-phase hydrogenation of 1-methyl-naphthalene.

1. Experimental

1.1 Catalyst

The catalyst used was a commercial supported Co-Mo/γ-Al$_2$O$_3$ catalyst (CDS-D21, manufactured by Catalysts and Chemicals Ind. Co., Japan) supplied as extrudate of 1.6 mm diameter and 4.0 mm length. Fresh catalyst, weighed and packed in a catalyst basket, was sulfided with a mixture of 3 mol% hydrogen sulfide and 97 mol% hydrogen at a gas hourly space velocity of 1000 h^{-1} and 603 K for 12 hours under atmospheric pressure.
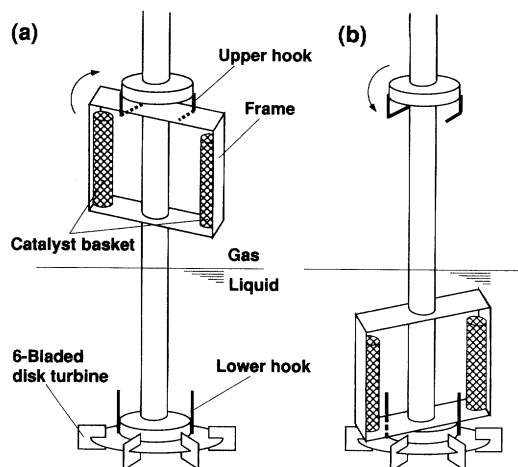
1.2 Feed liquid

The feed liquid contained 10 wt% 1-methylnaphthalene and 90 wt% solvent (Normal Paraffin-H supplied by Katayama Chemical Ind. Co., Japan), consisting of 20.3 wt% n-tetradecane, 68.8 wt% n-pentadecane and 10.9 wt% n-hexadecane. Carbon disulfide was added into the feed liquid to a level of 0.3 wt% to maintain the catalyst in the sulfided form.

1.3 Apparatus and procedure

A schematic drawing of the apparatus is shown in **Fig. 1**. The reactor was a stainless steel autoclave of 80.0 mm inner diameter and 200.0 mm height, equipped with four evenly spaced baffle plates. Hydrogen and/or helium could be introduced into the reactor through mass flow controllers.

The catalyst basket assembly as illustrated in **Fig. 2**, was equipped with a rotating shaft, a frame with two catalyst baskets and a stirrer, and was magnetically driven via invertor control. The cylindrical baskets, made of stainless steel screen were 8.0 mm in diameter and 45.0 mm in height.

As shown in Fig.2(a), the frame was held by upper hooks above the liquid level until the hydrogen gas flow-rate, temperature and pressure attained the specified reaction conditions. After these conditions was established, the frame was automatically dropped into liquid-

phase with the baskets by inverting the direction of agitation. Then the frame was put between lower hooks on the stirrer and rotated without slipping, as shown in Fig. 2(b). At this point, the reaction started. This procedure is called the "basket-dropping method" in this paper.

Initial loadings of catalyst and liquid for each run were 3.0 g and 3.5 × 10^{-4} m^3 respectively. Stirring speed was fixed at 500 rpm where external mass transfer resistance was considered negligible from preliminary experiments. The gas flowrate was 4.2 × 10^{-6} m^3/s in the normal state. These conditions were fixed if not particularly described elsewhere.

1.4 Product analysis and determination of liquid-phase concentrations

Periodically, 5 × 10^{-7} m^3 liquid was sampled and analyzed by a gas chromatograph equipped with a frame ionization detector and a capillary column (PONA Column, manufactured by Hewlett Packard Co.). Identification of the products was carried out by a gas mass spectrometer.

Liquid-phase concentration of hydrogen and products was determined by prediction of vapor-liquid equilibria using the Soave-Redlich-Kwong (SRK) equation of state[16] and by calculated liquid density in accordance with the method of the American Petroleum Institute[1]. Binary interaction parameters in the SRK equation (K_{ij}) were determined from the binary data for hydrogen and n-hexadecane and for hydrogen and 1-methylnaphthalene in the literature[20]. The value of K_{ij} for n-hexadecane was applied for other normal paraffins. Liquid-phase hydrogen concentration and liquid density were assumed to be constant during the reaction.

The calculated results of liquid-phase hydrogen concentration and liquid density for the experimental conditions set in this work are summarized in **Table 1**.

Table 1. Calculated results of C_H and liquid density

T [K]	P [MPa]	P_H [MPa]	C_H [mol/m³]	Liquid density [kg/m³]
583	5.0	4.7	324	558
	6.5	6.2	422	558
	8.0	7.7	519	559
603	6.2	3.1**	227	517
	5.0	4.5	330	533
	6.5	6.0	430	533
	8.0	7.5	531	536
623	5.0	4.3	334	505
	6.5	5.8	446	515
	8.0	7.3	572	537
643	5.0	4.1	351	491
	6.5	5.6	486	517
	8.0	7.1	623	539

** Helium was used as dilution gas.

2. Results and Discussion

2.1 Comparison of reaction starting procedures

Figure 3 shows the change of product concentration in hydrogenation of 1-methylnaphthalene (1-MN) at 603 K and total pressure of 8.0 MPa with the basket-dropping method (abbreviated as BDM) and the gas-switching method (abbreviated as GSM).

In the case of BDM, although hydrogenated products were observed owing to vapor-phase reaction before dropping the baskets, these amounts were negligibly small. The reactant was rapidly consumed after dropping baskets. Therefore, the starting time of reaction could be determined exactly.

In the case of GSM, helium was fed into the reactor to prevent the reaction. At the specified reaction conditions, the helium was quickly switched to hydrogen to start the reaction. The reactant was gradually consumed during more than one hour after switching gas. This time lag may be explained by the high solubility of hydrogen, resulting in slow replacement of hydrogen in the liquid-phase. From the data of GSM, it would be difficult to determine kinetic parameters because of ambiguity in the reaction starting time.

Therefore, the basket-dropping method (BDM) was proved to be useful in obtaining kinetic data in batchwise experiments at high temperature and pressure. The following experiments were performed using BDM.
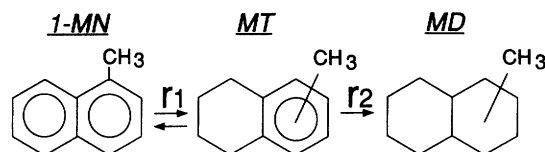
2.2 Reaction path

During the course of the reaction as shown in Fig. 3, 1-methylnaphthalene (1-MN) was consecutively hydrogenated to all isomers of methyltetralins (MT) and methyldecalins (MD). For example, the product liquid produced by BDM after 18 hours in Fig. 3 contained 2.0 wt% 1-MT, 4.1 wt% 5-MT, 0.15 wt% 2-MT, 0.69 wt% 6-MT, 2.0 wt% 1-MD and 1.7 wt% 2-MD.

Small fractions of 1-MN remained nearly constant after 10 hours. Therefore, the reverse reaction should be considered for conversion of 1-MN to MT. **Figure 4** shows a plausible reaction path from our results above. Patzer et al.[10] found dealkylation of 1-MN to naphtha-
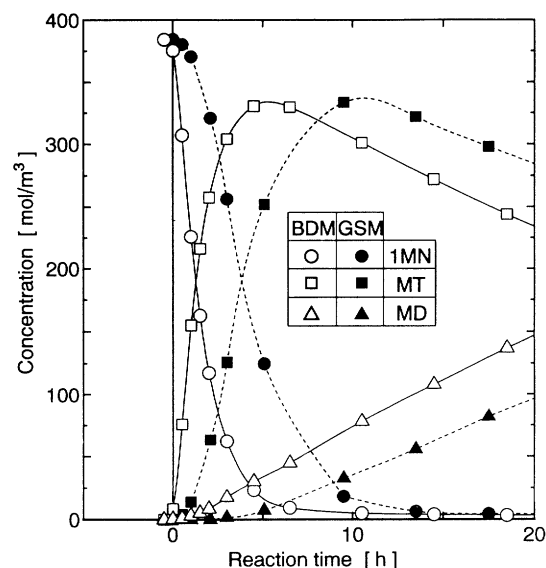
Fig. 3 Change of product concentration in hydrogenation of 1-methylnaphthalene with basket-dropping method (BDM) and gas-switching method (GSM).
T = 603 K; P = 8.0 MPa

**Fig. 4** Reaction path for hydrogenation of 1-methylnaphthalene

lene took place over Ni-Co-Mo/γ-Al$_2$O$_3$. In addition, Bouchy et al.[3] reported isomerization of 1-MN to 2-methylnaphthalene (2-MN) in gas-phase hydrogenation of 1-MN over Ni-Mo-P/γ-Al$_2$O$_3$. However, neither naphthalene nor 2-MN could be detected in our experiments. This result is consistent with the result of 2-MN hydrogenation over Ni-Mo/γ-Al$_2$O$_3$ reported by Ho et al.[7] The dealkylation is undesirable from an economical point of view because it may result in increase of hydrogen consumption and light gas yield. Extensive studies on the relationship between characteristics of catalyst and activity of dealkylation may be required.

2.3 Effect of reaction conditions

To investigate the effects of temperature and hydrogen partial pressure on the yield of products, experiments were performed at temperatures of 583, 603, 623 and 643 K, and at total pressures of 5.0, 6.5 and 8.0 MPa.

1) Effect of hydrogen partial pressure **Figure 5** shows the effect of hydrogen partial pressure (P_H) on the concentration of products at 603 K. The reaction at a P_H of 3.1 MPa was also performed at a total pressure of 6.2 MPa using helium as dilution gas to prevent significant loss of the feed liquid. As the hydrogen partial pressure increased, the rate of hydrogenation was obviously accelerated. The maximum yield of MT was approximately independent of hydrogen partial pressure.
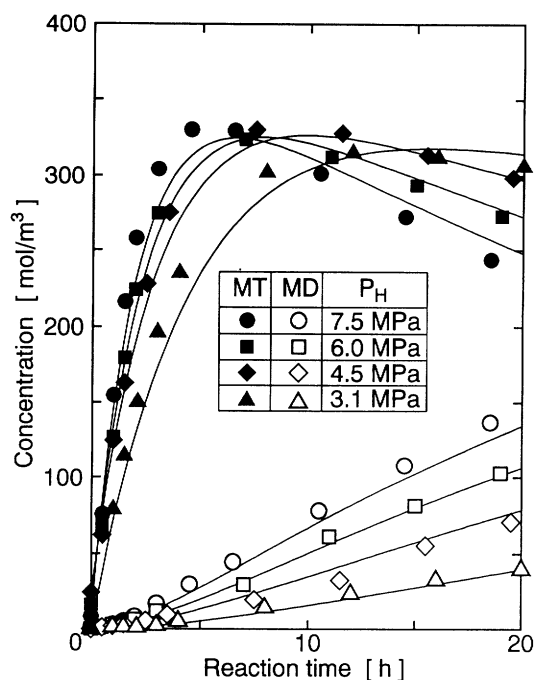
Fig. 5 Effect of hydrogen partial pressure on concentration of methyltetralins (MT) and methyldecalins (MD).
Solid lines: calculated using Eqs. (2)-(7). $T = 603$ K

Fig. 6 Effect of temperature on concentration of methyltetralins (MT) and methyldecalins (MD).
Solid lines: calculated using Eqs. (2)-(7). $P = 6.5$ MPa

2) Effect of temperature **Figure 6** shows the influence of temperature on the concentration of products at a total pressure of 6.5 MPa. The yield of MT was greatly influenced by temperature; higher temperature resulted in lower yield of MT. Gradual deactivation of the catalyst was observed at 643 K due to coking on the catalyst surface or reduction of presulfided catalyst.
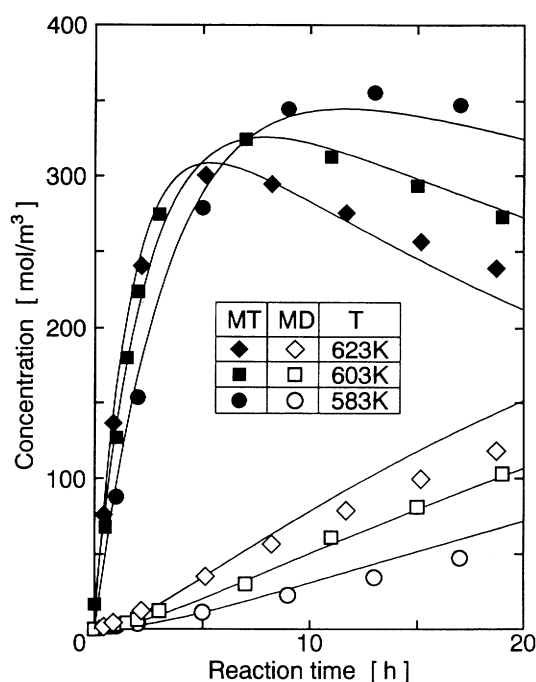
Figure 7 shows semilog plots of unconverted fraction of 1-MN (1-X_{MN}) vs. reaction time. At the lowest temperature of 583K, a straight line can be obtained, and therefore the rate of conversion of 1-MN to MT may be expressed with irreversible first-order kinetics with respect to 1-MN concentration. However, at the higher temperatures of 603 and 623K, deviation from the straight line is observed when reaction time increases. These results suggest that reaction equilibrium should be considered for the conversion of 1-MN to MT.

2.4 Reaction equilibrium

The results in the previous section show that quantitative analysis of reaction equilibrium is necessary to establish the kinetics; however, reaction equilibrium data for liquid-phase hydrogenation of 1-MN have not been available. To determine equilibrium constants in Eq. (1), the experiments were performed by increasing the amount of catalyst to 7.8 g to accelerate the rate of reaction.

$$K_{C1} = C_{MT} / \left(C_{MN} C_H^2 \right) \tag{1}$$

The reaction reached equilibrium at 603, 623 and 643 K after 40 hours. However, K_{C1} at 583 K could not be determined because no 1-MN was finally detected in the product within the accuracy of analysis. A Van't Hoff plot is shown in **Fig. 8**. K_{C1} can be expressed as follows:

$$K_{C1} = \exp(-34.19 + 16070 / T) \tag{2}$$

2.5 Kinetic studies

From least-squares estimation of the results except those at 643K where the catalyst was gradually deactivated, the following Langmuir-Hinshelwood type kinetic equations gave the best fit to our data.

$$r_1 = k_1 K_H^2 \left(C_{MN} C_H^2 - C_{MT} / K_{C1} \right) / \left(1 + K_H C_H \right)^2 \tag{3}$$

$$r_2 = k_2 K_H^3 C_{MT} C_H^3 / \left(1 + K_H C_H \right)^3 \tag{4}$$

The kinetic equations suggest that surface reaction between dual adsorption sites of hydrogen and aromatics may be rate-limiting.

This corresponds to the mechanism proposed for hydrogenation of biphenyl[14] and hydrogenolysis and hydrogenation of dibenzothiophene[4] over the same type of catalyst Co-Mo/γ-Al$_2$O$_3$.

Arrhenius plots are also shown in Fig. 8. Each parameter can be correlated by:

$$k_1 = \exp(4.04 - 8410 / T) \tag{5}$$

$$k_2 = \exp(4.91 - 10500 / T) \tag{6}$$

$$K_H = \exp(-9.09 + 2120 / T) \tag{7}$$

Activation energies for k_1 and k_2 were 69.8 kJ/mol and 87.1 kJ/mol respectively. Adsorption constant K_H, 3.8×10^{-3} m^3/mol at 603 K and heat of adsorption E_H, 18.0 kJ/mol obtained by Eq. (7) were comparable to the previously reported values over Co-Mo/γ-Al$_2$O$_3$: 2.9×10^{-3} of K_H at 598 K[4] and 20.9 kJ/mol of E_H[14].

Concentration profiles for the conditions in Figs. 5 and 6 were calculated using Eqs. (2)-(7) and are shown with solid lines in the figures. The kinetic model fairly
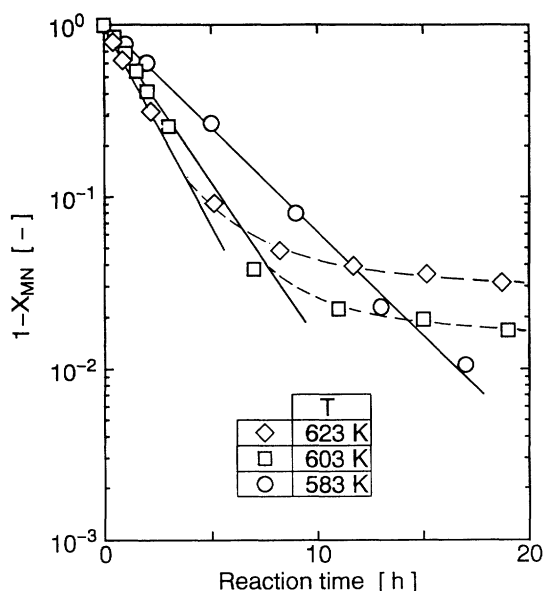
Fig. 7 Effect of temperature on unconverted 1-methylnaphthalene ($1-X_{MN}$). $P = 6.5$ MPa

Fig. 8 Van't Hoff plots and Arrhenius plots

represents the effects of hydrogen partial pressure and temperature on the yields.
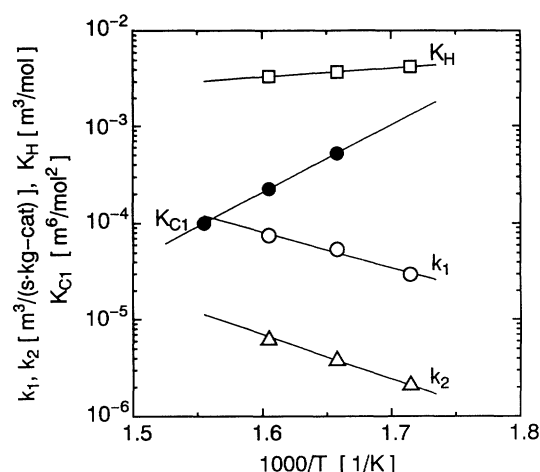
Conclusions

An improved basket reactor was developed to determine the exact starting time of reaction in batch-wise experiments. The reactor was experimentally proved to be useful in experiments even at high temperature and pressure. The maximum yield of intermediate products (methyltetralins) was greatly changed with temperature. Raising hydrogen partial pressure accelerated the rate of hydrogenation; however, that did not notably affect the maximum yield of methyltetralins at the same temperature.

Langmuir-Hinshewood type kinetic equations based on the surface reaction mechanism between dual adsorption sites of hydrogen and aromatics fairly well represented the effects of temperature and hydrogen partial pressure on the yields in the range of temperature of 583-623 K and hydrogen partial pressure of 3.1-7.7 MPa.

Nomenclature

C_i	=	concentration of component i	[mol/m^3]
E_H	=	heat of adsorption of hydrogen	[J/mol]
K_{C1}	=	equilibrium constant of the first reaction in Fig. 4	[m^6/mol^2]
K_H	=	adsorption constant for hydrogen	[m^3/mol]
P	=	total pressure	[Pa]
P_H	=	partial pressure of hydrogen	[Pa]
T	=	temperature	[K]
X_i	=	conversion of component i	[-]
k_i	=	reaction rate constant of i-th reaction in Fig. 4	[m^3/(s·kg-cat)]
r_i	=	reaction rate of i-th reaction in Fig. 4	[mol/(s·kg-cat)]

<Subscripts>

MN	=	1-methylnaphthalene
MT	=	methytetralins
MD	=	methyldecalins
H	=	hydrogen
1	=	the first reaction in Fig. 4
2	=	the second reaction in Fig. 4

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