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HYDRODENITROGENATION REACTION OF QUINOLINE WITH NASCENT HYDROGEN GENERATED FROM WATER GAS SHIFT REACTION

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Abstract– The HDN of quinoline was investigated for the purpose of utilizing the hydrogen which could be generated from the water gas shift reaction (WGSR). The optimum concentration of hydrogen were produced under 1.5 of water to carbon monoxide mole ratio and 6 hr^{-1} of space velocity at 390°C of temperature during WGSR over Co-Mo/γ-Al_2O_3 catalyst. The HDN reactions were compared by using the pure hydrogen and the nascent hydrogen which was produced by a WGSR. The pure hydrogen gave much higher activity in the overall HDN reaction than the nascent hydrogen. However, kinetic study on the hydrogenation, hydrogenolysis and cracking reaction steps showed that only at the cracking reaction step the nascent hydrogen gave the superiority to the pure hydrogen. This inferiority of the nascent hydrogen in overall HDN reaction could be resulted from the negative effect of water which should be accompanied during WGSR. The conversion of the HDN reaction was maximized at the water pressure of 150 kpa.

INTRODUCTION

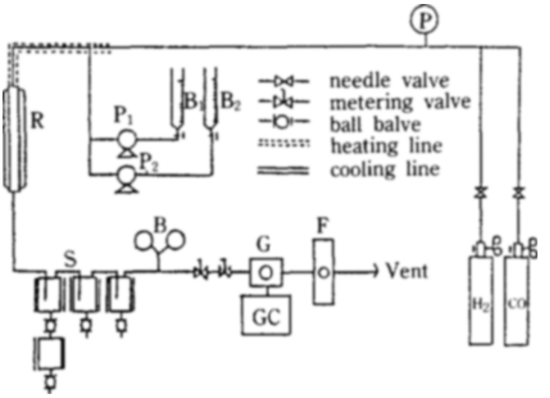
Various kinds of gases are generated as industrial by-products. Carbon monoxide is one of the gases to be produced in large quantity. The important industrial utilization of carbon monoxide is water gas shift reaction (WGSR) since the product, hydrogen, is more valuable raw material than carbon monoxide. That is why reduction reactions to utilize the hydrogen, which is obtained from WGSR, have been examined by numerous researchers [1-7]. Appell et al. [1] reported that a mixture of carbon monoxide and water is more powerful reducing agent than hydrogen in the liquefaction of coal. Hook and Akgermann [6] studied that hydrodesulfurization [HDS] reaction of thiophene and dibenzothiophene via WGSR.

In the petroleum industry, the hydrodenitrogenation (HDN) along with HDS is an essential refining process because nitrogen compounds can cause the deactivation of acidic catalysts in the cracking process. Several researchers [8-10] have investigated HDN reaction of quinoline as a model reaction of HDN with pure hydrogen. Satterfield and Smith [8] found that the efficiency of HDN of quinoline was increased by the addition of water and the formation of nonane was especially enhanced in the presence of hydrogen sulfide. Glütekin et al. [10] confirmed the positive effects of hydrogen sulfide, water and ammonia in the HDN reaction of quinoline.

In this study, we were trying to investigate the HDN reaction of quinoline by utilizing the hydrogen which was produced in the reaction of WGSR on a same catalyst. The purpose of this study is to understand the difference between HDN reaction with the pure hydrogen and in-situ HDN reaction with the nascent hydrogen produced by WGSR. Also, the role of water, which should be accompanied in the WGSR, was studied.

EXPERIMENTAL

The in-situ HDN reaction of quinoline by the hydrogen generated from WGSR was examined in a continuous fixed bed reactor as shown in Fig. 1. The reactor was made of stainless steel tube with a half inch of internal diameter. The top and bottom of the reactor were shielded with inert ceramic and glass wool to preheat and homogenize the reaction feed. A thermocouple was inserted in the middle of reactor to measure the reaction temperature which was regulated by a controller. Various high pressure condensers were installed at the exit of the reactor. The reaction



P: Pressure gauge
R: Reactor
G: Gas sampling pot
B_1B_2: Buret
P_1, P_2: High-pressure pump
S : High-pressure separator
F : Flowmeter
B : Back-pressure regulator

Fig. 1. Schematic diagram of in-situ HDN reaction apparatuses with the hydrogen generated from WGSR.

pressure was controlled with the back pressure regulator at 1000 psi. Carbon monoxide was directly fed in the reactor while regulating the pressure of gas by a metering valve. The catalyst used for the reaction was HR-306 Co-Mo/γ-Al_2O_3 having 188 m^2/g of surface area and 14-18 mesh of particle size. The catalyst was presulfied with the 10% H_2S/H_2 mixed gas (flow rate 40 ml/min) for 2 hours and reduced with hydrogen for 2 hours. Five grams of catalyst are loaded. The schematic diagram of HDN apparatuses was displayed in Fig. 1.

The reactant, 0.5 wt% nitrogen containing quinoline in heptane was added to the reactor at the steady state of WGSR. The water used in WGSR was deionized by passing through 4-Module mili-Q. Carbon monoxide was purchased from Air Products, U.S.A. Quinoline and heptane were used without further purification.

RESULTS AND DISCUSSION

1. Water Gas Shift Reaction (WGSR)

To study the in-situ HDN reaction with WGSR, the optimum conditions in the WGSR was established. The optimum mole ratio of the H_2O/CO was examined at 390℃. Maximum conversion was obtained at the mole ratio of 1.5 as shown in Fig. 2. The conversion of WGSR was calculated from the following equation.

$$\text{Conversion } (\%) = \frac{S_0 - S_1}{S_0}$$

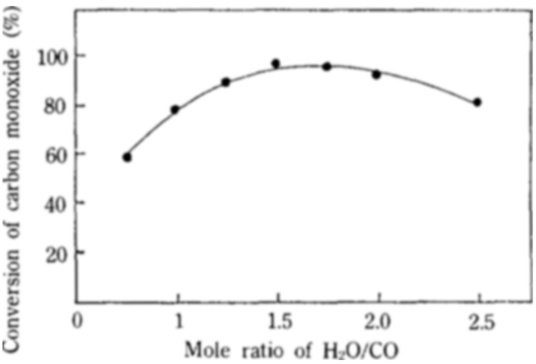


Fig. 2. The effect of mole ratio (H_2O/CO) on water gas shift reaction at 390°C.

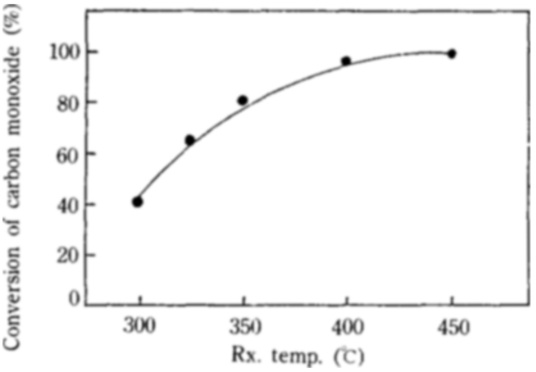


Fig. 3. The effect of reaction temperature on water gas shift reaction at the 1.5 mole ratio (H_2O/CO).

Where S_0=g mole of fed carbon monoxide, S_1=g mole of unreacted carbon monoxide

This result seemed to be very similar to that of Hou et al. [11]. The reaction temperature was also examined as shown in Fig. 3. The conversion in the WGSR was almost constant at the higher temperature than 390℃.

2. Quinoline Hydrodenitrogenation via WGSR

2-1. Effect of Reaction Temperature

The hydrodenitrogenation of quinoline was carried out at the above optimum conditions in the WGSR. The reaction mixtures were analyzed. These are unreacted quinoline, such as 1,2,3,4-tetra hydroquinoline (PY-TH quinoline), and 5,6,7,8-tetra hydroquinoline (BZ-TH quinoline) and cracked products e.g. n-propylcyclohexane, n-propylbenzene, n-propylcyclohexene and n-ethylcyclohexane. Fig. 4 depicted the composition profile of products as a function of the reaction temperature. The formation of PY-TH quinoline declined at higher than 300℃. However, the production of BZ-TH quinoline and cracked products increased with the increase in reaction temperature. The dimin-

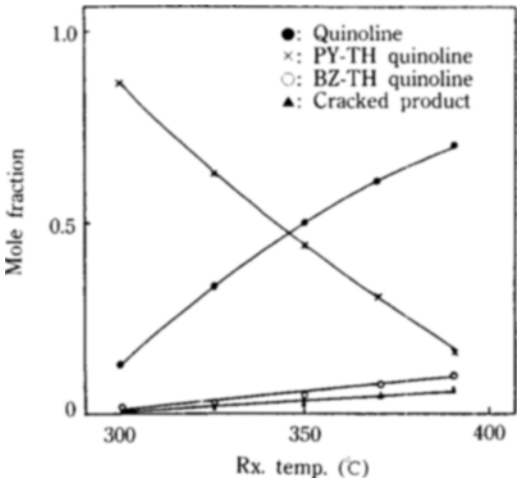


Fig. 4. Composition profile of nitrogen compounds depending on the reaction temperatures in HDN of quinoline by WGSR at 40 kg/cm^2, 3 hr^{-1} LHSV.

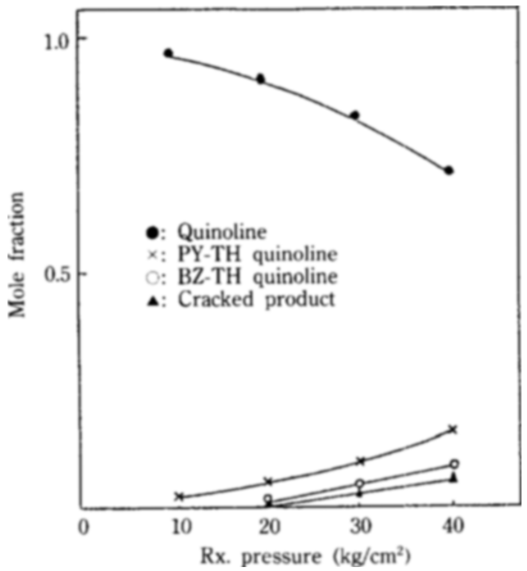


Fig. 5. Composition profile of nitrogen compounds depending on the CO pressure in HDN of quinoline by WGSR at 390°C, 3 hr^{-1} LHSV.

ished amounts of PY-TH quinoline was almost same as the increments of unreacted quinoline. In other words, the equilibrium between quinoline and PY-TH quinoline was shifted into quinoline at higher temperature (see kinetic study). These results showed the same aspects as the results published by Aboul Gheit et al. [12] and Yan et al. [9].

2-2. Effect of Reaction Pressure

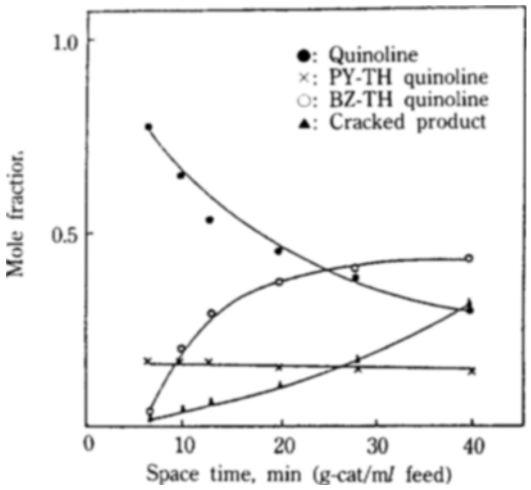


Fig. 6. Composition profile of nitrogen compounds depending on the space times in the HDN reaction of quinoline with pure H_2 stream (390°C, 20 kg/cm^2 H_2 pressure).

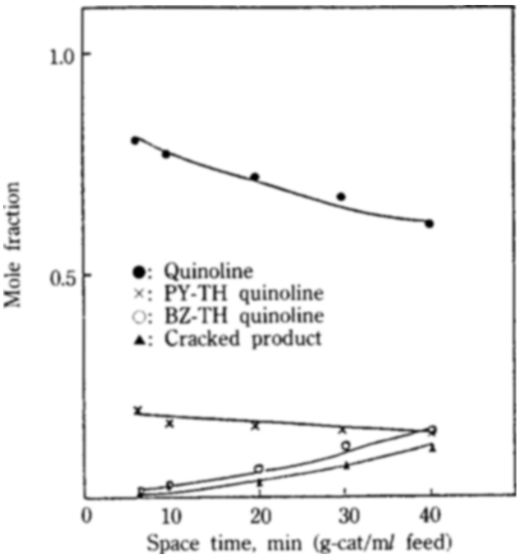
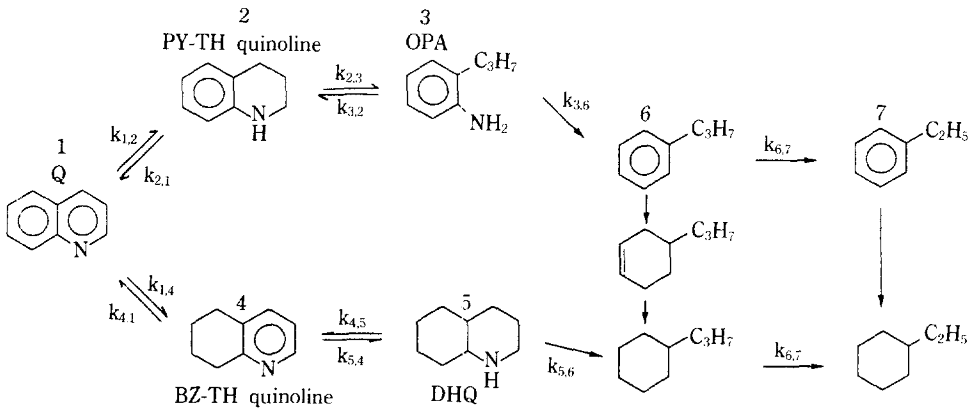


Fig. 7. Composition profile of nitrogen compounds depending on the space times in HDN reaction of quinoline with H_2 generated in-situ from WGSR (390 °C, 20 kg/cm^2 H_2 pressure).

The HDN reaction of quinoline is strongly dependent on the pressure of hydrogen. However, it is well known that WGSR does not rely on pressure. The hydrogen pressure is directly controlled by the pressure of carbon monoxide. Thus, pressure effect was examined by controlling the reaction pressures. Product profile as a function of pressure is shown in Fig. 5. The yields of products (PY-TH quinoline, BZ-TH



Scheme 1. The revised mechanism of HDN reaction of quinoline.

quinoline and cracked product) were increased with the increase of reaction pressure.

3. The Comparison between the Activities of Commercial Pure Hydrogen and Hydrogen Generated from WGSR in the HDN Reaction of Quinoline

The HDN reaction of quinoline with pure hydrogen produced almost the same products as in the in situ HDN reaction with WGSR as following: BZ-TH quinoline, PY-TH quinoline, decahydroquinoline, n-propylaniline, 1-methyl-2-propylcyclopentane, n-propylcyclohexane, n-propylcyclohexene and n-propylbenzene. To compare the reactivities of pure hydrogen and the nascent hydrogen from WGSR in the HDN reaction of quinoline, we studied the composition of products as a function of the space time of feeding material at the same reaction conditions: hydrogen partial pressure of 20 kg/cm^2 and reaction temperature of 390℃. The composition profiles of products are shown in Fig. 6 and 7, respectively. The efficiency of HDN reaction by ordinary hydrogen was shown to be greater than that in the in-situ HDN reaction with WGSR.

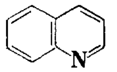
4. Reaction Mechanism

To understand low conversion of the in situ HDN reaction with WGSR, we took into considerations on the reaction mechanisms of HDN reaction studied by a number of investigators, with pure hydrogen [13-15]. And a revised mechanism as Scheme 1 is suggested for the explanation of low activity in the in situ HDN with WGSR. The mechanism of quinoline HDN reaction is consisted of three steps: hydrogenation of quinoline, PY-TH quinoline and BZ-TH quinoline ($k_{1,2}$; $k_{2,3}$; $k_{1,4}$ and $k_{4,5}$), hydrogenolysis of o-propylaniline and decahydroquinoline ($k_{3,6}$; $k_{5,6}$) and cracking of n-propylbenzene and n-propyl cyclohexane ($k_{6,7}$). The rate constant of each step was examined under the pseudo-first order reaction condition with authentic reaction intermediates such as PY-TH quinoline, BZ-TH quinoline, o-propylaniline, decahydroquinoline, n-propylbenzene and n-propyl cyclohexane. The kinetic studies on the both HDN reaction with the pure hydrogen and the hydrogen generated in the in-situ from WGSR were comparatively carried out at the same reactions. The rate constants are summarized in Table 1. Several conclusions could be derived from Table 1. The reaction rate with pure hydrogen showed much faster than with the nascent hydrogen at the steps of hydrogenation and hydrogenolysis. However, in the cracking step it was totally opposite from the hydrogenation and hydrogenolysis step. In other words, the activity of HDN using the nascent hydrogen was larger than using the pure hydrogen at the cracking step. Because, the nascent hydrogen showed poor activities at the steps of hydrogenation and hydrogenolysis. So the effect of water at the HDN reaction of quinoline was considered.

5. Effect of Water in HDN Reaction of Quinoline

Satterfield et al. [8] and Glütekin et al. [10] already examined the effect of water on HDN reaction of quinoline with pure hydrogen and reported that the presence of water increased the conversion of the HDN reaction. This is entirely opposite to our speculation. The water effect on the HDN was reexamined through the kinetic study with pure hydrogen by adding the water.

The HDN reaction of quinoline can be simplified as the following, because the nitrogen atom was removed from quinoline.



$\longrightarrow$ cracked products (1)

The rate equation of the above reaction has been pro-

Table 1. Rate constants in the HDN reaction of quinoline in the cases using pure hydrogen and hydrogen generated from WGSR as reductant

Hydrogen source	Rate constant(min^{-1})					
	$k_{1,2}$	$k_{2,1}$	$k_{2,3}$	$k_{3,2}$	$k_{3,6}$	$k_{6,7}$
Pure	0.0073	0.032	0.017	0	0.037	0.0038
WGSR	0.0085	0.047	0.0070	0.015	0.019	0.0084

Hydrogen source	Rate constant(min^{-1})					
	$k_{1,4}$	$k_{4,1}$	$k_{4,5}$	$k_{5,4}$	$k_{5,6}$	$k_{6,7}$
Pure	0.023	0.015	0.018	0.042	0.029	0.0038
WGSR	0.0076	0.042	0.0071	0.026	0.011	0.0084

Table 2. The pseudo-first order rate constants depending on the water partial pressure

Water partial pressure (kg/cm^2)	Rate constants, k(min^{-1})
0	0.0115
0.0007	0.0138
0.0015	0.0155
0.005	0.0136
0.009	0.0116
0.018	0.00782
0.036	0.00265
0.054	0.00207

posed as showing first order kinetics by a number of investigators [16-18]. This rate equation can be expressed as equation (2), in the case of isotherm gas reaction.

$$-\frac{d[Q]}{dt}=k[P_{H_2}]^n[P_Q] \qquad (2)$$

where $[P_{H_2}]$ and $[P_Q]$ were the partial pressures of hydrogen and quinoline, respectively. When hydrogen existed in excess, the rate equation could be represented as pseudo-first order kinetics with respect to pressures of quinoline.

The pseudo-first order rate constants depending on the pressures of water are listed in Table 2. The $k_{H_2+H_2O}/k_{H_2}$ versus water partial pressure was plotted in Fig. 8. The terms of $k_{H_2+H_2O}$ and k_{H_2} represent the rate constants in the presence and absence of water, respectively. As shown in the Fig. 8, the maximum conversion was found at the water pressure of 0.0015 kg/cm^2 and the conversions increased to the maximum point, but decreased above the point.

Satterfield et al. [8] and Glütekin et al. [10] studied only in the low pressure range of water. Consequently, water might be partly attributable to slow the hydrogenolysis and hydrogenation steps of in-situ HDN reaction with WGSR, because the large quantity of water could deactivate the catalyst. Small amounts of water at lower pressure than 0.0015 kg/cm^2 transformed the catalyst to a active form such as Brönsted acid by interaction with catalyst to accelerate the HDN reaction.

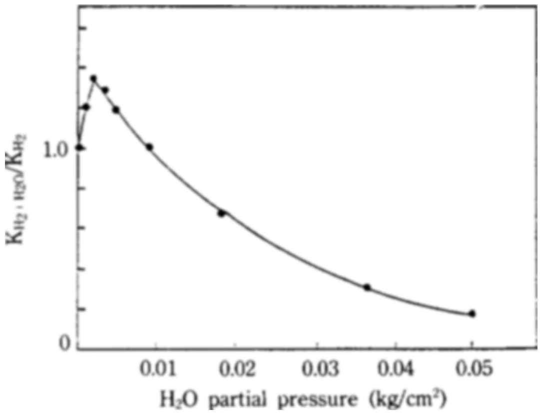


Fig. 8. Effect of water partial pressures on HDN reaction of quinoline with pure hydrogen (390°C, 20 kg/cm^2 H_2 pressure).

Further studies are in progress, concerning the reasons why hydrogenolysis and hydrogenation step are entirely opposite in the case of using the nascent hydrogen.

CONCLUSION

The efficiency in the HDN reaction when the pure hydrogen was used showed much higher than using the nascent hydrogen, which was produced by the in-situ HDN reaction with WGSR. However, the rate in the cracking step during in-situ HDN reaction was faster than that HDN by using pure hydrogen, hydrogenation and hydrogenolysis steps were entirely reversed. Water was one of the causes to retard the rate in the hydrogenation and hydrogenolysis steps of in-situ HDN. To rationalize the phenomena of in-situ HDN reaction, further investigation is in progress.

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