Catalytic cracking of 4-(1-naphthylmethyl)bibenzyl in sub- and supercritical water

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Abstract: In order to investigate the catalytic cracking of coal derived liquids, 4-(1-naphthylmethyl)bibenzyl (NMBB) as a model compound with coal structures was hydrogenated with Ni/ active carbon catalyst in sub- and supercritical water. Water might act as a H donor. The NMBB conversion under subcritical water was much higher than that under supercritical water. Furthermore, in H_2 atmosphere NMBB conversion was higher than that of N_2 atmosphere, indicating that the process of in-situ H_2 formation from subcritical water was more easily. Therefore, the cracking of NMBB in subcritical water and H_2 could be regarded as a reasonable reaction conditions.

Keywords: NMBB, Catalytic cracking, Supercritical water.

1. Introduction

Coal and coal derived liquids is composed of aromatic moieties connecting with ether or aliphatic linkages and S and N moieties were also contained. Therefore, the upgrading and reforming of them are needed for the use of clean liquid fuels. In order to investigate the catalytic cracking of the coal-derived liquids, 4-(1-naphthylmethyl)bibenzyl (NMBB) has been employed as a model compound of coal and coal-derived liquids, since it has an intriguing feature of the presence of five different potential cleavage sites C-C bonds and several aromatic rings[1], as given in Fig. 1.

In the sub- or supercritical water conditions(Tc: 374°C; Pc: 22.1MPa), CO is supplied by the oxidation of hydrocarbons, and then the in-situ H_2 produced from water gas shift reaction (WGSR, $CO+H_2O \rightarrow CO_2+H_2$) with sub- or supercritical water is thought to hydrocrack NMBB[2,3,4].

In this study, the effect of sub- and supercritical water on the NMBB conversion and products selectivity has been discussed.

2. Experimental

The 5 wt% Ni catalyst on an activated carbon (AC) was used as catalyst, denoted as 5%Ni/AC. Catalytic cracking of NMBB reaction was carried out in a 20 mL steel batch autoclave reactor (HASTELLOY alloy). As a typical run, 0.5 g of Ni/AC, 3 g of NMBB and a certain amount of deionized water were placed in an autoclave reactor using an electric furnace swinging. The reaction system was purged three times with 1MPa H2 or N2 to remove the trapped air. After the purging, the reactor was pressurized with H2 or N2 to 3.0–6.0MPa, and then heated up to 350 °C or 400 °C. After reaction, the reactor was cooled down and then depressurized to atmospheric pressure. Water phase and oil phase products were recovered by acetone. The liquid products were analyzed by a capillary chromatography (GC-14B, FID, Shimadzu, Japan). The solid products were first dissolved in toluene and filtered. The solids still remaining were placed on a petri dish, dried at 120 °C for 12 h and weighed. This toluene insoluble was defined as coke and spent catalyst [24]. The conversion of NMBB was calculated by the unreacted NMBB.

3. Results and discussion

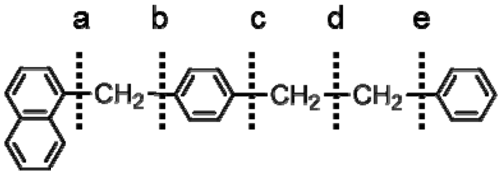
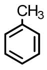
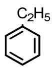
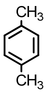
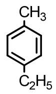
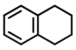
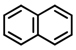
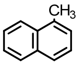
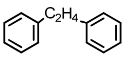
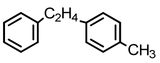


Fig.1 Structure of NMBB and five potential cleavage sites

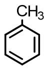
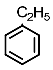
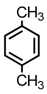
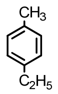
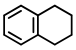
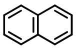
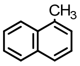
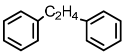
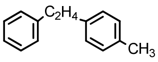
Table 1 summarizes the catalytic activity and product distributions of NMBB cracking with the presence of sub- and supercritical water in H_2 or N_2. Under the supercritical water, the NMBB conversion of 58% is significantly higher than that under the subcritical water in H_2 atmosphere (44%). In the N_2 atmosphere, the result is similar to that in H_2 atmosphere. NMBB conversion increases from 23% to

Table 1 Catalytic cracking of NMBB under sub- or supercritical water in N_2 or H_2.

Temp. (°C)	Atmos.	Conv. (%)	Yield of product (mol%)										Coke (wt%)
													
350$^{1)}$	N2	23	0	0.1	0.04	0	0	0	4.5	0.2	0.4	6.4	27
350$^{1)}$	H2	44	0	0	0.17	0	0.13	0.5	8.2	0.3	0.7	14.3	22
400$^{2)}$	N2	55	0	0.5	0.12	0.6	0	0	18.6	0.9	2.6	18.3	31
400$^{2)}$	H2	58	0.4	2.0	0.7	1.0	0.3	0.3	22.4	1.2	3.7	27.8	28

a) subcritical water; b) supercritical water, NMBB: 3g; H_2O: 11g; 5%Ni/AC: 0.5g; 60 min; 3MPa

Table 2 Catalytic cracking of NMBB under subcritical water in N_2 or H_2.

Temp. (°C)	Atmos.	Conv. (%)	Yield of product (mol%)										Coke (wt%)
													
350	N2	67	0.8	9.9	0.1	3.5	0	0	22.9	1.5	2.5	12.9	32
350	H2	75	1.7	38.9	0.3	4.1	0.2	0.7	26.4	1.7	6.5	21.9	25
400	N2	77	5.0	23.2	0.4	8.6	0	0	24.0	1.5	1.8	4.9	23
400	H2	80	7.6	36.3	0.9	11.6	0.5	0.5	22.1	1.2	1.3	2.4	20

NMBB: 3g; H_2O: 2g; 5%Ni/AC: 0.5g; 60 min; 3MPa

55% after the reaction temperature reaching to the critical temperature (Tc). In the supercritical water, the dominated products are naphthalene and 4-methylbibenzyl, indicating that the cracking conditions effectively promote the cleavage of aromatic-aliphatic C-C bond **a** in NMBB. Moreover, since other products with small amount, the possible cleavage sites (bonds **c**, **d**, **e**) are less likely to be attacked by the H_2 on catalyst surface. In the supercritical water, NMBB conversion enhances slightly from 55% in N_2 atmosphere to 58% in H_2 atmosphere. The supplied H_2 effectively restrains the formation of coke, possibly because of the small amount of in-situ H_2 from WGSR and condensation reaction.

In order to investigate the subcritical water conditions, the effect of reaction pressure below critical pressure (Pc) was examined (Table 2). Surprisingly, if the reaction pressure is lower than Pc, the catalyst exhibits an amazing hydrocracking ability on NMBB in the subcritical water whatever the temperature reaches to Tc or not. As reaction temperature increasing, NMBB conversion increases and coke formation decreases, indicating that higher temperature can promote the hydrogenation ability of the catalyst. The coke amount in subcritical water decreases, because of the higher reaction temperature. On the other hand, the coking reaction is slowed down, because of the mass-transfer resistance between different emulsion droplets in subcritical water. The subcritical water enhances the reaction since it has the partial properties of supercritical water and has also excellent solubility as an organic-like solvent. In addition, it has better potential of industrial application for coal derived liquid product upgrading since the operation temperature and pressure of subcritical water are milder than that of supercritical water, and coke formation rate is lower, keeping catalyst active. According to the results, the cracking of NMBB with subcritical water under H_2 can be regarded as a suitable reaction condition.

4. Conclusions

The cracking of NMBB was investigated under sub- and supercritical water. The sub- and supercritical water provided additional in-situ H_2 source, which was more active than the supplied H_2. Interestingly, it showed excellent NMBB catalytic hydrocracking in the subcritical water. In contrast to N_2, H_2 showed better NMBB conversions. The subcritical water and H_2 showed the best hydrocracking ability of NMBB and the least coking formation, which seems to be a promising method for coal derived liquid upgrading.

References

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