PROMOTING EFFECT OF WATER ON IN-SITU GENERATED MoS_2 CATALYST FOR HYDROGENATION AND C-O BOND CLEAVAGE OF DINAPHTHYL ETHER

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INTRODUCTION

In our recent work, we found a strong promoting effect of water on low-severity catalytic coal liquefaction using molybdenum sulfide catalyst in-situ generated from ammonium tetrathiomolybdate (ATTM): addition of H_2O to the run using ATTM as a catalyst precursor increased the conversion of Wyodak coal at 350 °C from 29.5 to 66.5 wt% [1]. Initially, this strong promoting effect of water was surprising to us, because it has been shown that better drying method for moisture removal results in higher coal conversion in catalytic liquefaction using molybdenum sulfide catalyst [2]. It was also observed that addition of water to catalytic coal hydroliquefaction has negative effect [3-5]. On the other hand, water addition to non-catalytic coal conversion reactions and some model reactions has been shown to have positive impacts [6-10]. More recently, it has been reported that ether compounds such as 1-phenoxynaphthalene and 9-phenoxyphenanthrene cleave in water at 315 °C, and this cleavage is enhanced at higher temperature; since water becomes a stronger acid as temperature increased, this cleavage reaction was shown to proceed through ionic process [9,10].

In the present study, in order to clarify the role of water in catalytic hydroliquefaction of coal, we carried out hydrogenation and hydrogenolysis of 2,2'-dinaphthyl ether (DNE) using ATTM as a catalyst precursor in the absence and presence of H_2O or D_2O. There are many connecting linkages in coal structures; the aromatic C-O and aromatic-aliphatic C-C bonds are believed to be important linkages between aromatic moieties of coal structures. Therefore, in order to increase the conversion of coal to liquids, it is necessary to cleave these connecting linkages. Coal structures have not been clarified at the molecular level. The use of coal-related model compounds is suitable for understanding fundamental chemistry. The products from the hydrogenation of model compounds can be easily identified by GC/MS. DNE has been shown to be thermally unreactive in the absent of catalyst, but its conversion is enhanced by some metal sulfide catalyst [11]. Here we used DNE to investigate the effect of the addition of water on cleavage of ether-linkages and on hydrogenation of aromatic rings using ATTM under the conditions of coal liquefaction.

EXPERIMENTAL

Catalyst Precursor

Ammonium tetrathiomolybdate (ATTM) was purchased from Aldrich, and 2,2'-dinaphthyl ether (DNE) from TCI America. ATTM and DNE were used without further purification. It was noted in previous work in this laboratory that long-time storage of ATTM in reagent vials in air may lead to degradation of the reagent, which results in deviations in the observed activity of in-situ generated MoS_2 catalyst from different bottles of ATTM reagent. In this work, a bottle of newly purchased ATTM was used in all the experiments on DNE runs, and the reagent bottle was stored in a refrigerator in order to minimize oxidative degradation.

Model Compound Reactions

A horizontal tubing bomb microautoclave reactor with a capacity of 25 mL was loaded with ca. 0.216 g DNE, 1 wt% catalyst precursor (1 wt % Mo based on DNE) and 1.47 g solvent (n-tridecane). When water was added, the weight ratio of H_2O to DNE was 0.56, unless otherwise mentioned. The reactor was purged four times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source, and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in a cold water bath. The contents were washed out with 30-40 mL acetone, and filtered through a low speed filter paper for subsequent GC analysis of the filtrate. Two-step reaction was also carried out in a similar manner as described above, except that the active MoS_2 catalyst was prepared first using ATTM with and without H_2O in the first-step reaction, and subsequently, the reactor was opened, and DNE was then added into the reactor. DNE was treated with and without H_2O in the second-step reaction.

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971 A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m x 0.25-mm, coated with 50% phenyl 50% methylpolysiloxane with a coating film thickness of 0.25 μm. For quantification, a Perkin Elmer 8500 GC with flame ionization detector and the same type of column (DB-17) was used. Both GC

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and GC-MS were programmed from 80 to 280 °C at a heating rate of 4 °C/min and a final holding time of 8 min. The response factors for 5 of the products were determined using pure compounds.

RESULTS AND DISCUSSION

One-Step Reaction

Table 1 shows the results of non-catalytic and catalytic runs of DNE with in-situ generated dispersed MoS_2 catalyst at 350, 375 and 400 °C. Without ATTM, the conversions of DNE are very low, even at 400 °C. Adding water alone seems to inhibit the conversion of DNE completely. However, in the presence of ATTM conversions are significant. An addition of water to the runs with ATTM substantially increases the conversion of DNE. Upon addition of water to the catalytic runs, the conversion of DNE increases from 46.0 % to 83.8 % at 350 °C. The principal products are tetralin, naphthalene, 2-naphthol, 5, 6, 7, 8-tetrahydro-2-naphthol, octahydroDNE, and tetrahydroDNE. Formation of these products suggests that both the ether linkage cleavage reaction and hydrogenation of aromatic rings occur simultaneously. Because the yields of tetralin are higher for the runs with added water than for those without water, the hydrogenation of aromatic ring prevails in the run with water and ATTM.

In order to clarify the role of water, DNE was hydrogenated with ATTM and D_2O. Because some aryl ethers cleave in H_2O at high temperature above 315 °C through ionic mechanism [9,10], this ionic effect of H_2O on the cleavage of C-O bond in DNE is investigated. Even though water alone has inhibition effect on conversion of DNE as described above. Table 2 represents the results of catalyst run of DNE with dispersed catalysts and H_2O or D_2O at 350, 375 and 400 °C. Comparing the results using H_2O and D_2O, the conversions of DNE are almost the same in each pair of corresponding runs. There are no apparent isotopic effect on the conversion of DNE and the yields of the products. The results of GC/MS analysis indicate that the products and recovered DNE contain a few deuterium atom, and the fragmentation of mass spectra of the products indicate that deuterium atoms are introduced into the products unselectively. These results show that the hydrogen from water has a little effect on the conversion of DNE. In other words, we have found no clear evidence that H_2O enhanced ether bond cleavage: the ionic effect of water on cleavage of ether-linkage in DNE is not significant, under the conditions employed.

Two-Step Reaction

As shown in Tables 1 and 2, the conversion of DNE increases with an addition of water. In order to further clarify the role of addition of water on the hydrogenation of DNE, two-step reaction was carried out. In the first-step, the Mo sulfide catalyst was prepared from decomposition of ATTM in the presence and the absence of water at 350, 375 and 400 °C under hydrogen pressure for 30 min. Subsequently the reactor was quenched, vented, and opened to allow the loading of DNE followed by purge and repressurization with H_2. The hydrogenation of DNE, as the second-step, was carried out with and without H_2O at 350 °C under hydrogen pressure for 30 min. Table 3 shows the results of the two-step reactions. Using the catalyst prepared from ATTM alone at 350, 375 and 400 °C, the conversions of DNE are almost the same at 64-67 %: the activities of the catalysts are very similar. However, highly active catalysts are generated from ATTM with added H_2O, the conversion of DNE is the largest at 375 °C: the catalyst prepared at 375 °C is most active. This finding corroborates with our previous results on coal liquefaction [12]. After the preparation of catalyst, the addition of water decreases the conversion of DNE. For example the conversion of DNE decreased from 64.4 % to 32.9 % at 350 °C (first-step) after the addition of water to the second-step run. In addition, after the preparation of catalyst from ATTM and water at 350 °C complete removal of water caused about 100 % conversion of DNE at 350 °C at the second-step. These results suggest that water itself does not have promoting effect on hydrogenation of DNE, but that it is effective for the preparation of active catalyst for hydrogenation and bond cleavage of DNE.

Effect of H_2O/DNE Ratio

In the test discussed above, the weight ratio of H_2O/DNE was maintained at 0.56 for the determination of role of water addition on hydrogenation of DNE. We have also attempted to determine the optimum amount of added water. This was done by examining the relationship between the conversion of DNE and amount of added D_2O. Figure 1 shows the relationship between the amount of D_2O added and the conversion of DNE from the runs at 350 °C for 30 min. The conversions of DNE gradually increase from 46 % to 100% with increasing water amount from 0 to 0.2 g corresponding to a D_2O/DNE weight ratio of about 0.93, and they decrease from 100% to 60 % with further addition of water. These results also clearly indicate that 0.026 of the ratio of ATTM to D_2O is optimum for conversion of DNE under the conditions employed. It seems that since water is used for the preparation of effective catalyst from ATTM for hydrogenation and bond cleavage of DNE, the conversion of DNE is large up to 0.235 g of D_2O. However water itself has a negative effect for the hydrogenation of DNE, further additions of D_2O over 0.235 g seem to cause the decrease of the conversion of DNE.

CONCLUSION

A proper amount of added water has a strong promoting effect on hydrogenation and hydrogenolysis of DNE using molybdenum sulfide catalyst in-situ generated from ATTM. We have found that the addition of water is not effective for DNE conversion, but is effective for the preparation of active catalyst from ATTM for hydrogenation and hydrogenolysis of DNE.

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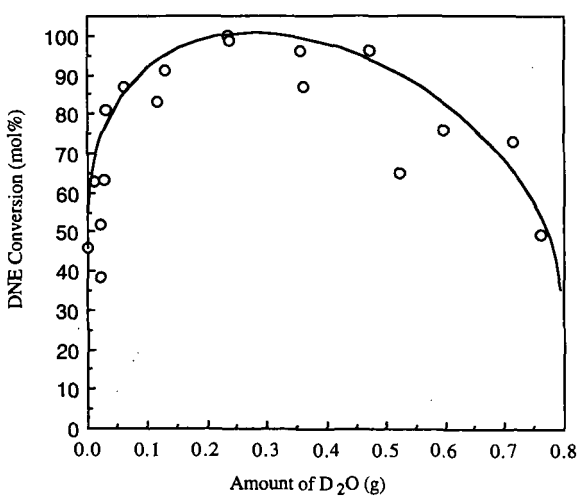

Fig. 1 Effect of addition of D_2O on conversion of 2,2'-dinaphthyl ether (DNE) at 350 °C for 30 min in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C_{13}: 1.47g

Table 1 Effect of addition of H_2O on reactions of DNE at 350-400 °C under 6.9 MPa H_2.

Run No.	16	17	15	19	18	20	7	6	8	5	3	4
Catalyst Precursors	None	None	None	H_2O	H_2O	H_2O	ATTM	ATTM	ATTM	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O
Temperature (°C)	350	375	400	350	375	400	350	375	400	350	375	400
DNE Conversion (mol %)	0.7	0.5	4.6	0.0	0.0	0.0	46.0	86.4	82.4	83.8	95.2	94.2
Products (mol %)												
Tetralin		0.7	5.4				31.4	70.9	66.7	72.7	106.1	109.1
Naphthalene		0.3	2.0				33.1	74.1	73.4	57.1	66.2	70.8
5,6,7,8-Tetrahydro-2-naphthol							8.0	6.2	3.6	8.1	9.5	6.0
2-Naphthol							2.2	4.7	12.6	3.4		
OctahydroDNE			0.3				1.3	2.0	1.0	2.5	2.2	
TerahydroDNE	0.6		0.6				7.4	6.5	3.2	10.6	2.1	1.2

Table 2 Catalytic reactions of DNE using ATTM and D_2O at 350-400 °C under 6.9 MPa H_2

Rnu No.	29	5	32	3	27	4
Catalyst Precursor	ATTM + D_2O	ATTM + H_2O	ATTM + D_2O	ATTM + H_2O	ATTM + D_2O	ATTM + H_2O
Temperature(°C)	350	350	375	375	400	400
DNE Conversion (mol%)	82.9	83.8	95.5	95.2	95.6	94.2
Products (mol%)						
Tetralin	68.8	72.3	106.5	106.1	106.5	109.1
Naphthalene	59.7	57.2	71.2	66.2	64.7	70.8
5,6,7,8-Tetrahydro-2-naphthol	7.9	8.0	9.0	9.5	6.6	6.0
2-naphthol	2.2	3.2			1.1	
OctahydroDNE	2.4	3.1	0.7	2.2	1.1	
TetrahydroDNE	11.2	11.3	1.5	2.1	1.2	1.2

Table 3 Two-step reactions of DNE under 6.9 MPa H_2.

Run No.	44	48	49	41	42	51	68	67	50	96*
1st-step Catalyst	ATTM	ATTM	ATTM	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O	ATTM	ATTM	ATTM	ATTM + H_2O
1st-Step Temperature(°C)	350	375	400	350	375	400	350	375	400	350
2nd-step Addition	None	None	None	None	None	None	H_2O	H_2O	H_2O	None
2nd-Step Temperature(°C)	350	350	350	350	350	350	350	350	350	350
Conversion (mol %)	64.4	66.7	66.0	82.7	96.0	76.9	32.9	29.7	41.2	97.0
Products (mol%)										
Tetralin	49.1	46.9	44.7	58.6	76.5	53.1	26.8	22.9	31.9	89.6
Naphthalene	67.5	72.6	72.6	79.5	85.1	75.9	26.6	25.5	39.5	104.4
Tetrahydronaphthol	0.8	0.6	1.0	1.4	1.6	4.2	1.2	0.6	0.7	
2-naphthol	0.8	0.6	1.0	0.4	0.1	2.2	1.6	0.8	1.0	
OctahydroDNE	0.3	0.3	0.4	0.8	2.1	0.7	0.2	0.2	0.2	
TetrahydroDNE	5.1	6.1	6.0	12.0	12.2	8.5	4.6	4.6	4.4	

* After the first-step reaction, water was completely removed by hot venting at 200 °C for 35 min., prior to the addition of DNE for second-step reaction.