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A new method for preparing highly active unsupported Mo sulfide. Catalytic activity for hydrogenolysis of 4-(1-naphthylmethyl)bibenzyl

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Abstract

This paper reports on the catalytic activity of unsupported Mo sulfide (MoS_2 like) catalysts which were prepared by a new and simple method comprised of decomposing ammonium tetrathiomolybdate (ATTM) in an organic solvent with added water under H_2 pressure. Model compound reactions of 4-(1-naphthylmethyl)bibenzyl (NMBB) were carried out at 350–425°C under H_2 pressure in order to examine the activity of the Mo sulfide catalysts generated from ATTM with and without added water for C–C bond cleavage and hydrogenation of aromatic ring. The Mo sulfide catalysts generated from ATTM with added water were much more effective for C–C bond cleavage and hydrogenation of aromatic moieties at 350–425°C than those from ATTM alone. Two-step tests revealed that the addition of water is effective for generating highly active Mo sulfide catalyst from ATTM, but water itself does not promote catalytic conversion. Removal of water after the decomposition of ATTM with added water at 350–400°C under H_2 pressure by hot purging gives highly active Mo sulfide catalyst. These results demonstrate that we have found a new and simple method for preparing highly active, dispersed (unsupported) Mo sulfide catalysts for hydroprocessing. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic activity; ATTM; NMBB; Mo sulfide; Hydrogenolysis

1. Introduction

In this paper we report on the catalytic activity of unsupported Mo sulfide (MoS_2 like) catalysts which were prepared by a new and simple method. The catalytic performance for cleavage of certain C–C bonds and hydrogenation of aromatic rings was studied in the reaction of a model compound containing different C–C bonds and several aromatic rings.

Various catalysts have been tested for conversion and upgrading of liquid and solid fuels. Among them molybdenum sulfide-based catalysts are widely used for hydroprocessing and hydrodesulfurization. The MoS_2 catalyst generated from decomposition of ammonium tetrathiomolybdate (ATTM) is more active than that from sulfidation of molybdenum oxide or the reagent MoS_2, and thus ATTM has been used as catalyst precursor for generation of active MoS_2 catalyst [1–10] for hydrogenation of hydrocarbon [1–4,6] and for coal liquefaction [5,7–10]. In our recent work on catalytic coal liquefaction, we have found that adding water has a very strong promoting effect on

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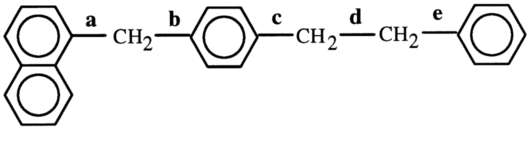
catalytic hydrogenation of Wyodak coal using ATTM as a catalyst precursor [9,10]. Subsequently, we conducted a model compound study using dinaphthyl ether, DNE [11]; the results indicate that the catalysts prepared from ATTM with added water are much more active that those from ATTM alone. For example, the conversion of Wyodak coal with ATTM at 350°C increased from 29.5 to 66.5 wt% upon water addition [9]; the conversion of DNE at 350°C with ATTM increased from 46 to 84 mol% upon water addition [11]. However, the catalytic conversion of DNE and coal also produces water. To clarify the real activity of the catalyst generated from ATTM and added water, it becomes necessary to conduct a reaction using a model compound that does not contain oxygen.

The present study aims at clarifying the activities of the catalyst generated from ATTM with added water on C–C bond cleavage and aromatic hydrogenation. We carried out the reaction of 4-(1-naphthylmethyl)-bibenzyl, abbreviated as NMBB, using ATTM as a catalyst precursor in the absence and presence of added H_2O. NMBB has been used as a model compound for examining activity and selectivity of various catalysts [12–24], since there are different types of potential cleavage sites of C–C bonds and both monocyclic and bicyclic aromatic moieties in the compound, as illustrated in Scheme 1. For upgrading of heavy oil and for hydroprocessing of coal-derived liquids and coal, cleavage of aromatic-aliphatic or aliphatic-aliphatic C–C bonds is believed to be important. Therefore it is also important, in terms of practical application, to examine the catalytic performance of the in situ generated Mo sulfide catalyst from ATTM with added water for NMBB conversion. The present results on NMBB indicate that we have found a new and simple method for producing highly active unsupported Mo sulfide (MoS_2) catalysts.



Scheme 1. Structure of 4-(1-naphthylmethyl)bibenzyl (NMBB) and its potential cleavage sites.

2. Experimental

2.1. Catalyst precursor and reactants

Ammonium tetrathiomolybdate (ATTM) and n-tridecane solvent were purchased from Aldrich, and 4-(1-naphthylmethyl)bibenzyl (NMBB) from TCI America. ATTM and NMBB were used without further purification. It was noted in previous work in this laboratory that long-time storage of ATTM in closed vials that has been exposed to air may lead to degradation of the reagent, which results in deviations in the observed activity of in situ generated MoS_2 catalysts from different bottles of ATTM reagent. In this work, a bottle of newly purchased ATTM was used in all experiments on NMBB runs, and the reagent bottle was stored in a refrigerator in order to minimize oxidative degradation.

2.2. Model compound reactions

A horizontal tubing microautoclave reactor with a capacity of 25 ml was loaded with ca. 0.8 mmol (0.258 g) of NMBB, 1 wt% catalyst precursor ATTM (1 wt% Mo based on NMBB) and 1.48 g or 2.95 g of solvent (*n*-tridecane). ATTM was added to the reactor in its powder form (as in the fresh reagent vial from Aldrich). When water was added, the weight ratio of H_2O to NMBB was kept at 0.56. The amount of water and the amount of NMBB were determined based on our prior work in catalytic coal conversion [9,10] and model compound studies using NMBB [21–23].

The sealed 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 reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction, the microautoclave was quenched in a cold water bath. The contents were washed out with 20–30 ml acetone, and filtered through a low speed filter paper for subsequent GC analysis of the filtrate.

Two-step tests were also carried out. In the first step, the active Mo sulfide catalyst was prepared using ATTM in the presence of *n*-tridecane solvent with added H_2O under H_2 pressure without NMBB in the 25 ml microautoclave. Then the water vapor and H_2S and NH_3 gases generated from ATTM decomposition were removed from the reactor by hot venting at 200°C for 35 min. Subsequently the reactor was opened and NMBB was added into the reactor and then the reaction was conducted at 350°C in a similar manner as described above.

The products were identified by GC–MS using a Hewlet-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 and W DB-17 column; 30 m×0.25 mm, coated with 50% phenyl-50% methylpolysiloxane with a coating film thickness of 0.25 mm. For quantification, a Perkin-Elmer 8500 GC flame ionization detector and the same type of DB-17 column were used. Both GC and GC–MS were programmed from 40°C to 280°C at a heating rate of 6°C/min, with a initial holding time of 5 min and a final holding time of 18 min. The GC response factors for NMBB and seven of the products were determined using pure compounds.

The NMBB conversion is defined as {[NMBB (wt) charged – NMBB (wt) recovered]/NMBB (wt) charged]}×100, and the molar yields of products are defined as [product (mol)/NMBB (mol) charged]×100. Since the products mainly include the compounds from both C–C bond cleavage and partial hydrogenation of NMBB, the sums of product yields are generally less than twice the value of the conversion.

3. Result and discussion

3.1. *Effect of ATTM precursor and H_2O on NMBB conversion*

Tables 1 and 2 show the results of noncatalytic and catalytic runs of NMBB, respectively, at 350°C, 375°C, 400°C, 425°C and 450°C using a small amount of *n*-tridecane solvent (1.48 g). Without ATTM, the conversions of NMBB were negligible at 350–375°C, low but observable at 400–425°C. Only when temperature is increased to 450°C, noncatalytic conversion becomes significant, reaching 67.5%. When ATTM was used as a catalyst precursor, both C–C bond cleavage and hydrogenation were promoted, and NMBB conversions are over 70% in all the catalytic runs. As shown in Table 2, adding water to the runs with ATTM substantially enhanced the catalytic reaction: NMBB conversions increased from 78.9% to 99.3% for runs at 350°C. The promoting effect of water is still apparent for runs at 375–400°C, but the net increase in conversion becomes smaller because the NMBB conversions are already over 92% with ATTM without added water. It is clear from these results that the use of ATTM with added water is more effective than ATTM alone for NMBB conversion, particularly at lower temperatures.

Table 1
Noncatalytic hydrogenolysis of NMBB in 1.48 g tridecane

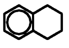
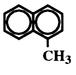
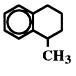
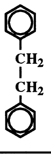
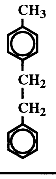
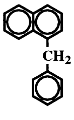
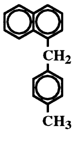
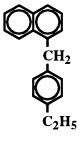
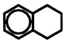
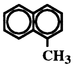
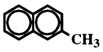
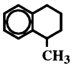
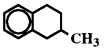
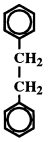
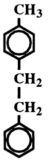
		Yield (mol%) of product											
Temp. (°C)	Conv. (wt%)												4H-NMBB
350	0	0	0	0	0	0	0	0	0	0	0	0	0
375	0	0	0	0	0	0	0	0	0	0	0	0	0
400	5.9	0.4	0	0.9	1.5	0	0	0.1	0	0	0.2	0	0.5
425	16.1	16.6	1.2	3.4	1.7	0.6	0	0.6	5.2	1.2	6.0	0.8	1.2
450	67.5	33.2	9.0	16.4	0	4.8	0	2.2	8.5	3.0	20.1	2.3	1.0

Table 2
Effect of Mo catalyst precursor on hydrogenolysis of NMBB in 1.48 g tridecane

			Yield (mol%) of product										
Catalyst Precursor	Temp. (°C)	Conv. (wt%)											**4H-NMBB**
ATTM	350	78.9	0	0	49.4	11.4	4.7	0.3	0.8	0.2	8.3	57.7	8.2
ATTM	375	92.4	0	0	56.8	18.5	5.9	0.7	1.3	0.6	11.8	74.5	7.7
ATTM	400	92.9	2.2	1.6	55.1	21.3	5.4	0.6	1.4	0.6	12.6	72.5	2.6
ATTM	425	96.3	10.6	7.8	52.1	22.2	5.0	0.6	1.3	0.6	11.8	63.4	0.4
ATTM + H_2O	350	99.3	0	0	56.1	21.1	4.6	0.4	1.6	0.6	10.3	75.6	9.1
ATTM + H_2O	375	99.9	0	0	60.2	25.0	5.0	0.9	1.6	0.9	13.6	82.9	4.0
ATTM + H_2O	400	99.7	2.3	1.7	54.5	27.9	4.9	0.9	1.8	0.9	14.4	77.6	1.3
ATTM + H_2O	425	100	13.5	10.7	55.7	24.9	5.5	1.1	1.4	0.9	14.6	63.3	0

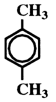
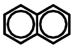
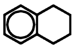
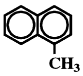
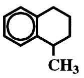
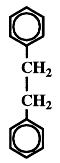
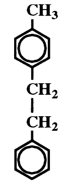
Both types of catalytic runs (ATTM, and ATTM+H_2O) show similar patterns of product distributions. For the run with ATTM and ATTM+H_2O, naphthalene and 4-methylbibenzyl are the major products, indicating that both catalysts effectively promote the cleavage of aromatic–aliphatic C–C bond <u>a</u> in NMBB. However, for noncatalytic run at 425°C toluene and 1-(*p*-tolylmethyl)naphthalene, abbreviated as TMN, are the major products. This indicates that the cleavage of band <u>d</u> in NMBB occurs predominantly in noncatalytic runs at higher temperatures. The weakest bond in NMBB is bond <u>d</u> [24]. The cleavage of the bond <u>d</u> in NMBB seems to occur predominantly under thermal reaction conditions over 400°C. For the run with Mo sulfide catalyst only catalyst-mediated reactions occur below 375°C, but at over 400°C both catalytic and thermal reactions occur. Disappearance of TMN in the products at 425°C seems to be due to secondary reaction of TMN or quick decomposition of NMBB in early stage of catalytic reaction. It is clear that the reaction pathways in catalytic and noncatalytic runs are different (see below).

3.2. *Effect of solvent amount*

The difference in NMBB conversion between the two types of catalytic runs is large at 350°C using 1.48 g of *n*-tridecane, about 20%; however, the difference becomes smaller at 375–425°C because the conversions are very high. We expected from the results of our DNE study [11] that the catalysts generated from ATTM+H_2O are much more active than those from ATTM alone. Therefore in order to further clarify the difference in activity between the catalysts prepared from ATTM and ATTM+H_2O, NMBB reaction was conducted using larger amount of *n*-tridecane solvent (2.95 g).

Table 3 summarizes the results. Figs. 1 and 2 compare the performance of the in situ generated catalysts for the NMBB reaction at 350°C in the presence of 2.95 g and 1.48 g of solvent, respectively. NMBB conversions at 350–425°C with the catalyst in situ generated from ATTM+H_2O are still high, ranging from 91.2% to 99.9%. These values are similar to the corresponding data in Table 2 with smaller amount of solvent. However, NMBB conversions with the cata-

Table 3
Effect of Mo catalyst precursor on hydrogenolysis of NMBB in 2.95 g tridecane

Catalyst Precursor	Temp. (°C)	Conv. (wt%)	Yield (mol%) of product								
											4H-NMBB
ATTM	350	37.4	0	0	28.7	6.4	2.7	0	4.1	30.0	8.3
ATTM	375	67.6	0	0	43.5	11.5	4.2	0.8	8.0	51.4	5.7
ATTM	400	83.4	0	0	53.0	15.1	5.2	1.0	11.3	63.3	2.4
ATTM + H_2O	350	93.1	0	0	55.4	12.6	4.7	1.0	7.9	65.8	13.5
ATTM + H_2O	375	99.9	0	0	57.6	27.9	4.6	1.8	12.6	80.9	4.7
ATTM + H_2O	400	91.2	0	0	54.7	20.4	4.9	1.3	12.4	70.8	1.7

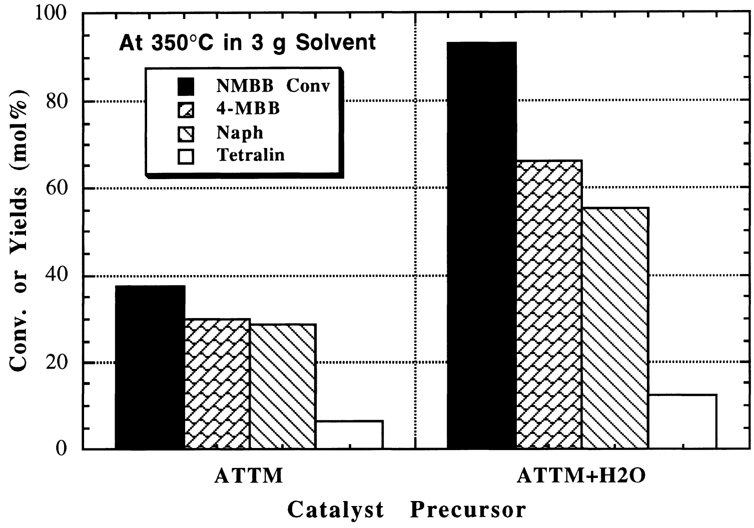


Fig. 1. Comparison of catalytic activity of Mo sulfide in situ generated from ATTM (left) and ATTM+H_2O for NMBB conversion in about 3 g *n*-tridecane solvent at 350°C.

lyst from ATTM alone at 350–425°C dropped significantly when *n*-tridecane solvent was increased from 1.48 to 2.95 g. For example, the conversions with ATTM alone decreased from 78.9% to 37.4% at 350°C, and from 92.4% to 67.6% at 375°C. These results suggest that the Mo sulfide catalysts in situ generated from ATTM+H_2O are substantially more active than those from ATTM alone. Moreover, the Mo sulfide catalysts in situ generated from ATTM+H_2O are highly effective for the cleavage of C–C bond a in NMBB even when its concentration is relatively low.

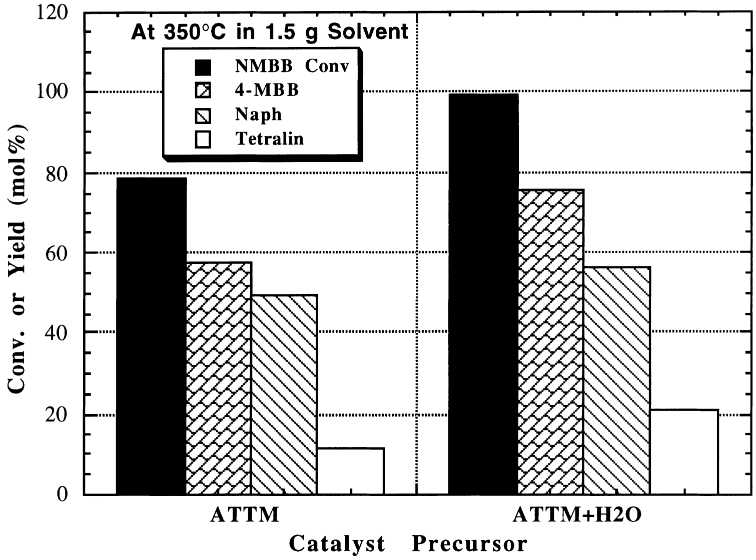


Fig. 2. Comparison of catalytic activity of Mo sulfide in situ generated from ATTM (left) and ATTM+H_2O for NMBB conversion in about 1.5 g *n*-tridecane solvent at 350°C.

A question that arises is, why does more solvent decrease conversion with ATTM? The use of more tridecane solvent lower the reactant concentration, and may also slow down, rather than speed up, the supply of H_2 to the catalyst surface. Relative to the samples from ATTM alone, the more porous catalysts from ATTM+H_2O (see below) have larger area for gas–liquid–solid contact, and therefore can produce more active hydrogen species (such as H atom) for the catalytic reaction. This may partially rationalize the much higher activity of the latter than the former in the presence of larger amount of solvent (Fig. 1).

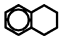
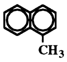
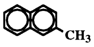
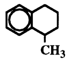
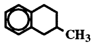
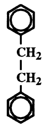
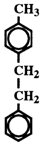
With respect to the effect of temperature for catalyst preparation, the catalyst prepared from ATTM+H_2O at 375°C is generally more active than those prepared at 350°C and 400°C. This result is consistent with our previous results on coal liquefaction [10] and hydrogenation of DNE [11].

3.3. Two-step test

An issue that remains unclear in the one-step tests is the role of water addition in catalytic conversion of NMBB. Does water promote the catalytic reaction, or does water addition result in highly active catalyst? To clarify the role of water and the activity of the catalyst from ATTM+H_2O, we also conducted the two-step tests. In the first step, the ATTM precursor was first decomposed in the presence of 2.95 g of *n*-tridecane with added water under H_2 pressure at 350°C, 375°C and 400°C, respectively. In the second step, the water vapor and the NH_3 and H_2S gases generated from ATTM decomposition under H_2 pressure were removed from the reactor by hot venting at 200°C, and then NMBB was charged into the reactor and reaction was conducted at 350°C for 30 min.

Table 4 shows the result of two-step tests of NMBB. The conversions of NMBB from the two-step tests are considerably higher than those of one-step tests at 350°C. As can be seen from comparison of Table 4 with Table 2, the conversion increased from 93.1% in one-step to 99.6% in two-step. After the removal of water, the catalyst became more active. In the work on DNE, we found that the catalysts generated from ATTM+H_2O in one-step tests are highly active for C–O bond cleavage [11]. The two-step tests indicated that added water is effective for generating highly active catalyst, but (when the active catalyst has been generated) H_2O addition itself have an inhibiting effect on catalytic conversion of DNE [11]. In other words, water itself does not promote catalytic or noncatalytic conversion of DNE. These results indicate that water addition is effective for generation of active Mo sulfide from ATTM; but when the active

Table 4
Conversion of NMBB in two-step tests using ATTM+H_2O as catalyst precursor in the first step

Catalyst Precursor	1st Step Temp. (°C)	2nd Step Temp. (°C)	Conv. (wt%)	Yield (mol%) of product										
														4H-NMBB
ATTM + H_2O	350	350	99.6	0	0	59.8	20.0	5.9	2.2	1.6	1.1	15.8	74.6	2.7
ATTM + H_2O	375	350	100	0	0	54.6	25.8	5.2	2.4	2.0	1.4	17.6	74.2	1.7
ATTM + H_2O	400	350	99.0	0	0	58.4	20.3	5.9	2.4	1.7	1.2	17.0	72.6	2.3

catalyst has been generated, the water has an inhibiting effect on the C–O bond cleavage or hydrogenation of aromatic ring in DNE reaction [11].

In addition, as mentioned above we have found that the catalyst prepared from ATTM+H_2O at 375°C is generally more active than those prepared at 350°C and 400°C in the one-step tests. In the two-step tests, NMBB conversions with all the catalysts prepared at 350°C, 375°C and 400°C are almost 100%. However, the yield of the major hydrogenation product, tetralin, is the highest with the catalyst generated from ATTM+H_2O at 375°C, as shown in Table 4.

We are currently performing physico-chemical and spectroscopic characterization of the Mo sulfide catalysts generated from ATTM+H_2O and from ATTM alone, and the results will be reported in the near feature. The preliminary results [25] have shown that the surface area of MoS_2 generated from ATTM with added water is much higher (>300 m^2/g for sample prepared at 375°C) than that from ATTM alone (<100 m^2/g at 375°C). Because of their important potential applications, methods for preparing more active transition metal sulfides have been attracting attention from researchers and this trend will continue. Mo-based slurry catalysts have been prepared in situ from ammonium molybdate for heavy oil hydroprocessing [26–28] and for coal conversion [29], where hydrogen sulfide is used for sulfiding the oxygen-containing Mo compound. There are also methods in patent literature for preparing molybdenum sulfide catalysts from oil-soluble precursor [30], carbon-containing molybdenum sulfide from ammonium molybdate or thiomolybdate [31], and from metal oxide and ammonium sulfide [32]. The best available patent claims for the MoS_2 catalysts from decomposition of ATTM have surface areas of from 50 to about 150 m^2/g [33,34]. Based on these previous studies, it is expected that the new method reported in this work is promising and warrants further study.

The reason why ATTM+H_2O is better than ATTM alone for generation of more active catalyst (Fig. 1) is not yet completely clarified. Probably the solubility and dispersion effects are at work in our system. ATTM is soluble in water but insoluble in *n*-tridecane solvent. We believe that the solubility of ATTM in water is responsible, at least partly, for the generation of very fine and porous MoS_2-like particles from ATTM+H_2O in the presence of *n*-tridecane solvent under H_2 pressure. In other words, the added water can dissolve ATTM, and the presence of the organic solvent help to disperse the ATTM-containing water droplet during agitation, which give rise to the finely dispersed precursor molecules isolated by organic solvent prior to and during their decomposition and hydrogen reduction. The extremely large surface area (BET) and small particle sizes (SEM) of the catalysts from ATTM+H_2O [25] support the above considerations. Although the possibility that an oxygen-containing sulfide MoO_xS_y may be the more active material cannot be ruled out at the present stage, XPS indicates the oxygen content for the catalyst from ATTM+H_2O is considerably less than that from ATTM, despite the use of H_2O [25]. The chemical analysis of the catalysts from ATTM alone and ATTM+H_2O gives S-to-Mo atomic ratios of 2.03–2.04, identical to that of the commercially available MoS_2 reagent. Therefore, the

Mo sulfide samples from both ATTM and ATTM+H_2O have very similar chemical composition, but different morphology such as particle shape (SEM), surface area (BET) and degree of layer stacking of MoS_2 slab (XRD) [25]. Further work is needed for developing a clear understanding.

3.4. Mechanistic considerations for NMBB conversion

The mechanisms for catalytic reactions of NMBB are not established and there are different propositions and arguments [12,13,17,18,20]. It is interesting to note that the weakest bond (**d**) is preserved, but the strong bond (**a**) [24] is cleaved in the catalytic reaction with ATTM and ATTM+H_2O. Here we consider the possible mechanisms for the cleavage of bond **a**, **b** and **d** in NMBB (Scheme 1). Because of its higher electron density in the highest occupied molecular orbital (HOMO) [24], the naphthyl group in NMBB should be adsorbed preferentially on the surface of the catalyst. Then the dissociatively adsorbed hydrogen on the catalyst surface attacks on ipso position in naphthalene ring (the carbon connected to methylbibenzyl group), leading to the cleavage of bond **a** and the formation of naphthalene and methylbibenzyl. Since one of the phenyl ring of the bibenzyl group is near the surface when naphthyl ring of NMBB is adsorbed on the catalyst, hydrogen on the surface of the catalyst could also attack on ipso position of phenyl group (the carbon connected to methylnaphthyl group). This can leads to the cleavage of bond **b** to produce 1-methylnaphthalene and bibenzyl. It is known that polycyclic aromatic ring can stabilize intermediate radical more than monocyclic aromatic ring, because of delocalization of radical. The radical formed in the naphthyl group of NMBB is more stable than that formed in phenyl group [24]. These two factors rationalize the dominance of the bond **a** cleavage over bond **b** cleavage involving radical intermediate.

Since other possible cleavage sites (bond **c**, **d**, **e**) are relatively far from the catalyst surface, those bonds are far less likely to be attacked by the hydrogen generated on the catalyst surface. Noncatalytic (thermal) reactions of NMBB involves homolytic cleavage of bond **d**, and thus generated radicals can react with gas-phase hydrogen (at a much lower rate) to form toluene and TMN. This also leads to the formation of hydrogen radical, which can attack ipso carbon on naphthalene ring resulting in the formation of naphthalene and 4-methylbibenzyl. In the catalytic reactions, the cleavage of bond **e** does not appear to occur to any significant extent because the corresponding products were not detected. Because yields of toluene in the catalytic reactions are comparable to those in non-catalytic reactions, the cleavage of bond **d** seems to be a thermally driven reaction. At this stage we do not have strong supporting evidence for the above consideration, but it seems to rationalize our experiment results.

4. Conclusion

Mo sulfide catalysts generated from ATTM in the presence of *n*-tridecane solvent with added H_2O under H_2 pressure at 350–400°C are much more active than those from ATTM alone for cleavage of C–C bond **a** and hydrogenation of naphthalene ring in NMBB. Addition of water to ATTM can more than double the conversion of NMBB in the presence of a larger amount of *n*-tridecane solvent at 350°C. Water addition is effective for generation of highly active catalyst, but water itself does not promote catalytic conversion of NMBB. Removal of water after ATTM decomposition at 350–400°C under H_2 pressure gives highly active Mo sulfide catalyst. These results clearly demonstrate that we have found a new and simple method for preparing highly active, unsupported Mo sulfide.

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