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Bimetallic dispersed sulfide catalysts from organometallic clusters for coal liquefaction

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Several heterometallic complexes consisting of Mo, Co and sulfur in a single molecule were synthesized and tested as precursors of dispersed catalysts for liquefaction of a subbituminous coal. The structure of the precursors, in particular the type of ligands to the metal species, significantly affects the activity of the bimetallic MoCo sulfide catalysts generated in situ. Among the M–M′ type precursors tested, Mo–Co thiocubane, $Mo_2Co_2S_4(Cp)_2(CO)_2$ (Cp = cyclopentadiene), produced the best catalyst.

Keywords: Bimetallic sulfide; clusters; dispersed catalysts; coal liquefaction

1. Introduction

Coal organic matrix consists of relatively small aromatic structural units that are connected together by a number of weak and strong bonds to form a three-dimensional network. The initial step in primary coal liquefaction is thermally initiated fragmentation. The coal-derived reactive fragments (radicals) must be stabilized promptly by hydrogen transfer, otherwise, they undergo retrogressive reactions to form more refractory materials. The desirable roles of a catalyst are the prompt hydrogenation of the coal-derived reactive fragments in the initial stage, and hydroprocessing of unsaturated compounds in the later stage.

It has been recognized recently that dispersed catalysts are superior to supported catalysts for primary hydroliquefaction of coal. The advantage of dispersed catalysts is largely due to their intimate contact with the surface of coal particles, which facilitates the activation and transfer of hydrogen to the coal-derived fragments and reactive sites. Because most active catalysts of interest (e.g., MoS_2) are insoluble in common solvents, the desire to achieve better dispersion leads to the strategy of using a soluble precursor that can be dispersed on to coal surface from

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its solution. The precursor may not itself be active, but it transforms at elevated temperatures into an active catalyst. Both inorganic salts of transition metals [1–3] and organometallic compounds such as metal carbonyls have been tested as precursors for dispersed catalysts, mostly MoS_2 [4–7]. Some recent work on multicomponent catalysts has involved the mixture of two or more inorganic salts [8–11]. However, little work on bimetallic dispersed sulfide catalysts for coal liquefaction has appeared.

The present work is concerned with organometallic precursors which can directly produce bimetallic sulfides upon thermal decomposition. Related to this work are two important general observations from previous investigations: (1) there could be synergistic effects between two different transition metal compounds [1,8,9] and (2), for a given metal, an organometallic precursor may be better than an inorganic one for coal liquefaction [12,13]. From the recent book on metal clusters by Mingos and Wales [14], it seemed to us that highly active bimetallic catalysts may be prepared from the "thiocubane" clusters containing two transition metals such as Co and Mo in a single molecule. Two different metals bound together in a single cluster should have a more systematic spatial arrangement in the resulting catalytic phase upon thermal decomposition than if two separate compounds were used to introduce the two different metals to a catalytic system. Recently, Chianelli et al. [15] and Halbert et al. [16] have used the unsupported sulfides from bimetallic complexes to study the promotional effects of Co on MoS_2 for hydrodesulfurization (HDS). They have shown that the CoMo sulfide catalysts from some organometallic precursors exhibit greatly improved activity for HDS. In this communication we wish to report on a potential bimetallic dispersed catalyst system for coal liquefaction from thiocubane cluster.

2. Experimental

CATALYST PRECURSORS AND COAL SAMPLES

Reagent-grade $Mo(CO)_6$ and $Co_2(CO)_8$ were used as the primary starting materials. We synthesized three Mo–Co bimetallic thiocubane clusters, including $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$, $Mo_2Co_2S_4Cp_2(CO)_2$, and $Mo_2Co_2S_4(Cp')_2(CO)_2$, in which Et, Cp and Cp′ represent ethyl group, cyclopentadiene, and pentamethylcyclopentadiene, respectively. For convenience, we will refer to these three clusters as MoCo-TC1, MoCo-TC2, and MoCo-TC3, respectively. The method of Halbert et al. [17] was used for synthesizing MoCo-TC1, and that of Brunner and Wachter [18] for MoCo-TC3. We prepared MoCo-TC2 using the same procedure as for MoCo-TC3 but with a modification of the starting material for the ligand. For comparative examination, a trianionic complex $(PPh_4)_3Co(MoS_4)_2$, designated as MoCo-S, was also synthesized based on the procedure of Pan et al. [19]. It is a bimetallic sulfide complex containing the cobalt bis(tetrathiomolybdate) trianion, $Co(MoS_4)_2^{3-}$, whose structure is significantly different from those of the thiocubanes.

For catalytic activity tests, we used a Montana subbituminous coal, which is one of the US Department of Energy Coal Samples (DECS-9) stored under argon atmosphere in the Penn State/DOE Coal Sample Bank. The DECS-9 (<60 mesh) has the following composition: 76.1% carbon, 5.1% hydrogen, 0.9% nitrogen, 0.3% organic sulfur, and 17.5% oxygen on a dry and mineral matter free (dmmf) basis. The catalyst precursors were dispersed on to the coal (predried at 100°C in vacuum) by the incipient wetness impregnation method using organic solvents, followed by vacuum drying at 100°C for over 2 h to remove the impregnating solvent. The loading for the bimetallic thiocubanes was 0.5 wt% of Mo on dmmf coal. It should be noted that the incipient wetness method used in our work is different from the conventional one in that we only use a certain amount of solution defined by the estimated incipient wetness volume to achieve a constant metal loading. Practical application of this method in a larger scale is possible by means of a spray. When the metal carbonyls $Mo(CO)_6$ and $Co_2(CO)_8$ were used, the loading was 0.5 wt% for Mo and 0.3 wt% for Co metal based on dmmf coal.

The coal liquefaction was carried out in 25 ml microautoclaves in a fluidized sandbath at 400 or 425°C for 30 min under an initial (cold) H_2 pressure of 7 MPa (1000 psi). Each reaction used approximately 3 g dried coal and 3 g of 1-methylnaphthalene as the reaction solvent. After the reaction, the gaseous product was vented, and the liquid and solid products were separated by sequential soxhlet extraction into oil (hexane soluble), asphaltene (toluene soluble but hexane insoluble), preasphaltene (THF soluble but toluene insoluble) and residue [20,21]. In general, the experimental errors were within ± 2 wt% for conversion, and the average data from two or three runs are reported here.

3. Results and discussion

Table 1 shows the results of liquefaction of the Montana subbituminous coal at 400°C for 30 min. We first prepared and tested MoCo-TC1, which has a cubane-like structure as shown in fig. 1 and was first synthesized and used recently by Halbert et al. [16,17] in preparing a hydrotreating catalyst. Using MoCo-TC1 impregnated on to DECS-9 coal from acetonitrile, however, showed little catalytic effect for increasing conversion. Replacing CH_3CN with THF for impregnating MoCo-TC1 increased coal conversion relative to the non-catalytic run by 14 wt%, but dit not improve oil formation to any significant extent. It seems that the acetonitrile solvent is not good for catalyst impregnation. More importantly, the dithiocarbamate and acetonitrile ligands in MoCo-TC1 seem to poison the resulting catalyst under the conditions employed. This consideration prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of MoCo-TC3 using the published method of Brunner and Wachter [18], and subse-

Table 1
Catalytic liquefaction of DECS-9 subbituminous coal

Catalyst precursor	Solvent for catalyst loading[a]	In situ pretreat at LT[b]	Reaction temp. (°C)	Oil + gas dmmf (wt%)	Asphaltene dmmf (wt%)	Preasph. dmmf (wt%)	Conversion dmmf (wt%)
none	none	no	400	16.0	9.4	6.8	32.2
MoCo-TC1	CH_3CN	no	400	22.8	4.8	5.2	32.8
MoCo-TC1	THF	no	400	18.7	12.8	14.8	46.3
MoCo-TC2	toluene	no	400	32.4	18.0	24.2	74.6
MoCo-TC2	THF	no	400	25.8	17.9	23.7	67.4
MoCo-TC3	toluene	yes	400	33.8	17.8	19.9	71.5
MoCo-S[c]	$CHCl_3$	no	400	21.3	12.6	16.0	49.8
MoCo-S[d]	CH_2Cl_2	no	400	25.2	16.0	27.1	68.3
$Mo(CO)_6$	1-MN	no	400	25.2	10.6	16.5	52.3
$Co_2(CO)_8$	1-MN	no	400	23.7	12.6	15.0	51.3
none	none	yes	400	18.9	8.2	7.0	34.1
MoCo-TC2	toluene	yes	400	37.0	19.8	22.0	78.7
MoCo-TC2	toluene	yes	425	46.7	19.5	15.0	81.1
MoCo-TC3	toluene	yes	425	46.3	17.5	12.9	76.6
$Mo(CO)_6$	1-MN	yes	400	24.2	11.8	16.4	52.4
$Co_2(CO)_8$	1-MN	yes	400	23.6	12.4	14.2	50.2

[a] The impregnating solvent was removed by evaporation in vacuum before the reaction solvent 1-MN was added.

[b] In situ low-temperature pretreatment at 200°C for 15 min followed by heat-up to reaction temperature.

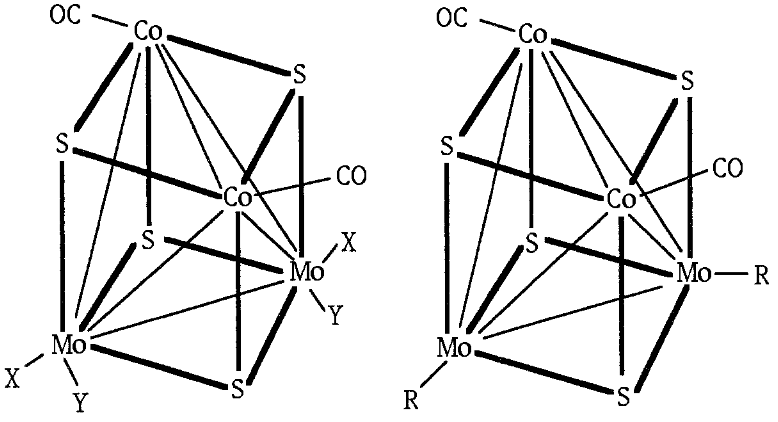
[c] Used shortly after synthesis without further purification. Decomposition during storage was noticed.

[d] Used after further purification immediately before use. The purified MoCo-S was impregnated on to coal using excess amount of CH_2Cl_2 solution.

quently the synthesis of MoCo-TC2 using the same procedure but replacing C_5Me_5 with a simpler and cheaper C_5H_5 ligand. Therefore, the basic differences between these three thiocubanes are the type of ligands bound to the Mo, as indicated in fig. 1.

MoCo-TC2 impregnated from toluene afforded much higher conversion and oil yield; its appears to be much more active than MoCo-TC1. MoCo-TC3 exhibited slightly lower catalytic activity compared to MoCo-TC2. It was expected that MoCo-TC2 would afford greater conversion when THF is used as the impregnating solvent. THF is known to be a better swelling solvent than toluene and using THF for impregnation of metal carbonyls has been shown to increase the conversion of Wyodak subbituminous coal due to improved metal dispersion [22]. Surprisingly, the catalytic liquefaction using MoCo-TC2 gave both higher oil yields and total conversion when toluene was used rather than THF for precursor impregnation.

The structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that pentamethylcyclopentadiene ligand in MoCo-TC3 is replaced by cyclopentadiene in MoCo-TC2. In an attempt to examine the role of bonding



MoCo-TC1

$X = \eta_2\text{-}S_2CNEt_2$
$Y = CH_3CN$

MoCo-TC2 & MoCo-TC3

MoCo-TC3: $R = C_5Me_5$
MoCo-TC2: $R = C_5H_5$

Fig. 1. Structure of the three different bimetallic thiocubane clusters (MoCo-TC1: $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$; MoCo-TC2 : $Mo_2Co_2S_4Cp_2(CO)_2$; MoCo-TC3: $Mo_2Co_2S_4(Cp')_2(CO)_2$).

between Co and Mo, we further tested $Co(MoS_4)_2^{3-}$ which has a distinctly different structure than the above-mentioned thiocubanes, as can be seen from comparison of fig. 2 with fig. 1. The results in table 1 reveal that MoCo-S is more active than MoCo-TC1, comparable (after further purification) to MoCo-TC3, but is less active compared to MoCo-TC2. A technical problem with MoCo-S is its air-sensitive nature: it decomposes during storage even in a refrigerator. Overall, the order of catalytic activity of the precursors appears to be MoCo-TC2 > MoCo-TC3 ⩾ MoCo-S > MoCo-TC1. Since $Mo(CO)_6$ and $Co_2(CO)_8$ were used for synthesizing the bimetallic thiocubanes, we also tested these starting materials as precursors. They did show good catalytic effects in promoting coal conversion and oil yield when compared to MoCo-TC1. However, MoCo-TC2 and MoCo-TC3 are much better precursors than the Mo and Co carbonyls (table 1) as well as their combinations.

Since the precursors may not be very active by themselves, their decomposition at low temperature, which could serve as an in situ activation/generation of the active catalyst, may contribute to more effective hydrogenation of reactive fragments and aromatics at high temperature. Therefore, we also examined the influence of in situ pretreatment at 200°C for 15 min. Our results clearly show that such pretreatment in the presence of MoCo-TC2 (or TC3) is beneficial and contributes to substantially increased coal conversion and oil yield, especially at higher reac-

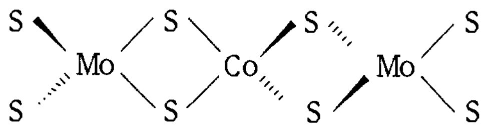


Fig. 2. Structure of the bimetallic sulfide complex $Co(MoS_4)_2^{3-}$ (cobalt bis(tetrathiomolybdate) trianion).

tion temperature (425°C). However, when the metal carbonyls were used, neither conversion nor oil yield increased upon such an in situ pretreatment. This comparison suggests that an active catalyst can be formed from MoCo-TC2 and MoCo-TC3 upon heat treatment at relatively low temperatures. With an attempt to examine the decomposition behavior of MoCo-TC2, TGA analysis was performed in atmospheric N_2, but was unsuccessful because of the volatilization. The question as to what are the exact decomposition temperatures of the precursors remains to be answered.

By combining the information in table 1 and figs. 1 and 2, it becomes very clear that MoCo-TC2 is the best precursor and MoCo-TC1 is the worst precursor among the three thiocubanes, which differ from each other only in the type of ligands to Mo. Bimetallic sulfide complex MoCo-S also produces a catalyst whose activity is comparable to that of MoCo-TC3 at 400°C. In MoCo-S, the Co and Mo are bonded through sulfur-bridge bonding (fig. 2), but in MoCo-TC2 or TC3, there are direct metal–metal bonds between Co–Mo, Co–Co, and Mo–Mo (fig. 1) in addition to the sulfur bridges. Since the central $Co_2Mo_2S_4$ core structure of MoCo-TC1, MoCo-TC2, and MoCo-TC3 in fig. 1 should be nearly identical, the differences between the three thiocubanes clearly indicate the importance of ligand type. On the other hand, MoCo-S does not have Co–Mo, Co–Co, and Mo–Mo bonds that exist in the three thiocubanes. The superiority of MoCo-TC2 over MoCo-S may suggest the importance of direct metal–metal bonding. The chemical composition and structure of the active phases of the in situ generated catalysts, however, need to be clarified in future work.

The solvents used for loading the precursors are also influential. Both toluene and THF were tested for impregnating MoCo-TC2 but toluene solvent seems to be better in terms of higher oil yield. There is a possibility that the dispersion of the precursors on the coal surface is influenced by the nature of the solvent. Different compounds may differ from each other in solubility, and in the pattern of interaction, if any, with the solvent molecules and coal surface. In fact, the solubilization of different bimetallic precursors often requires different solvents; the optimum solvent and method for loading catalyst precursors are not known yet. Further work is now in progress.

4. Summary

In summary, the results indicate that the structure of the precursors, in particular the type of ligands to the metal species, affect the activity of the resulting bimetallic MoCo sulfide catalyst significantly. For a given precursor, the solvent used for catalyst impregnation also affects coal conversion, although the impregnating solvent was removed before reaction by evaporation and vacuum drying. Among the M–M′ type precursors tested, Mo–Co thiocubane, $Mo_2Co_2S_4(Cp)_2(CO)_2$ (Cp = cyclopentadiene) impregnated onto coal from toluene, generated in situ the best catalyst (MoCo-TC2) for coal liquefaction. The performance of the MoCo-TC2 catalyst was further enhanced by using an in situ thermal pretreatment.

We realize that the bimetallic catalysts reported in this work would be rather expensive for use in an industrial process. However, the knowledge derived from this work on the dependence of catalyst activity on the structure and fundamental chemistry of the bimetallic precursors is very important for the development of novel catalysts and advanced catalytic processes. Another potential application of the precursors reported in this paper is preparation of supported Co–Mo catalysts which are usually prepared from inorganic salts [23]. Some of the bimetallic precursors will be used for preparing supported hydrotreating catalysts for more efficient upgrading of coal liquids as well as residual oils to high quality gasoline, jet fuels and diesel fuels.

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