Dispersed Catalysts for Co-processing and Coal Liquefaction

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Objective:

The basic goal is to improve dispersed catalysts employed in the production of clean fuels from low value hydrocarbons. The immediate objective is to determine how the properties of the catalysts may be altered to match the demands placed on them by the properties of the feedstock, the qualities of the desired end products, and the economic constraints put upon the process.

Several interrelated areas of the application of dispersed catalysts to co-processing and coal conversion are under investigation. The first involves control of the selectivity of MoS_2 catalysts for HDN, HDS, and hydrogenation of aromatics. One means of controlling selectivity lies in the manipulation of the morphology of the slab-like particles of MoS_2. The main concern is to gain control of the relative number of edge and rim sites on the catalyst. Rim sites, those located at the juncture of the edge and basal planes, are regarded as active for hydrogenation, while edge sites participate in the direct removal of sulfur (1). A prime example of the later reaction is the conversion of dibenzothiophene to biphenyl and H_2S. A method of preparing MoS_2 catalysts with varying ratios of edge to rim sites will be employed to investigate the importance of controlling the selectivity. The method makes use of published procedures for the exfoliation and restacking of MoS_2. The prepared materials then will be tested in coal liquefaction and as upgrading catalysts using various resids.

A second area of research is the development and use of methods to evaluate dispersed catalysts by means of activity and selectivity tests. A micro-flow reactor has been developed for determining intrinsic reactivities using model compounds, and will be used to compare catalysts prepared in different ways. Micro-autoclaves will also be used to develop data in batch experiments at higher partial pressures of hydrogen.

The third area under investigation concerns hydrogen spillover reactions between MoS_2 catalysts and carbonaceous supports. Preliminary results obtained by monitoring H_2/D_2 exchange reactions with a pulse-flow microreactor indicate the presence of spillover between MoS_2 and a graphitic carbon. A more complete study will be made at a later stage of the project.

Accomplishments & Conclusions:

Exfoliation, that is, the dismantling of multilayered MoS_2 into single layers, has been used to generate interesting new materials (2,3). An extension of this technique has been used to apply exfoliated MoS_2 as a catalyst in the direct liquefaction of coal (4). The first step is the intercalation of MoS_2 with lithium. Briefly, MoS_2 was mixed with n-butyllithium in hexane for two or three days. The resulting lithium intercalated molybdenum sulfide was filtered, dried, and then added to a protic solvent, such as water. The reaction between the protic solvent and the intercalated lithium produced hydrogen gas, effectively blowing the multilayered molybdenum sulfide apart.

$$Li_x \cdot MoS_2 + xH_2O \rightarrow 1/2xH_2 + xLiOH + MoS_2$$

Single-layer exfoliated metal sulfides are reported to stay in suspension for several days due to the formation of a hydroxylated surface. The restacking of the single-layer MoS_2 can be accelerated by the addition of dilute acids. The changes in the stacking dimension of MoS_2 crystallites that occur over the course of exfoliation and reassembly may be conveniently followed using X-ray diffraction. The average crystallite size perpendicular to the plane of the layers may be estimated from the half-width of the (002) line. Measured by this method, the untreated MoS_2 had an average stacking dimension of 375 Å. Examination of the untreated MoS_2 by SEM revealed a wide assortment of slab widths ranging from about 10 μ down to a few hundred angstroms. After exfoliation in water and with restacking induced by drying, the (002) peak was broadened and corresponded to a reduction in the average stacking dimension to 185 Å. The BET surface area was 10.0 m^2/g for the dried material.

The exfoliated MoS_2 catalysts were tested for their activity in microautoclaves using 3 g of a high volatile bituminous coal (hvBc) from Blind Canyon, Utah (DECS-17), 3 g of a coal-derived recycle solvent (Wilsonville distillate V-178), and 0.12 g of elemental sulfur (Fisher) when applicable. The initial H_2 pressure was 6.8 MPa (1000 psi) at room temperature and the loading for the catalysts was 2000 ppm Mo calculated on a weight basis using daf (dry, ash-free) coal. The reaction temperature was 375°C, with a reaction time of 1 or 2 hours.

Table 1 contains results illustrating the various effects of the addition of sulfur, solvent pretreatments, and the technique of catalyst addition in terms of THF conversion, cyclohexane conversion, and the amount of hydrogen taken up. It may be seen that the catalytic performance of a particular sample of MoS_2 may be improved by exfoliation in the presence of coal. A number of variables in the application technique were surveyed. It was found that catalyst application techniques likely to promote a high degree of exfoliation coupled with extensive swelling of the coal

gave better results.

Three basic methods of applying the catalyst to coal were compared. First, the original material was mixed with coal without intercalation or exfoliation. The mixing took place in a binary solvent, 1:1 THF/water, using an ultrasonic bath for 4 h to promote dispersion. Separate experiments demonstrated that mixing in the ultrasonic bath led to higher oil yields than when the catalyst and coal were mixed by hand with a stirring rod. For the sake of consistency, the ultrasonic bath was used even in cases where no catalyst was added to the coal (Exps. 3 & 4). The combined effect of the solvents and ultrasound on coal reactivity when measured in the absence of catalyst is small, as may be seen by comparing the results of Exps. 1 - 4. In the second method, the MoS_2 was exfoliated in water, recovered by drying, then mixed with coal as in the first case. In the third, the intercalated MoS_2 was exfoliated directly in slurries of coal in THF/water or other solvent systems, thus providing greater opportunity for increasing the dispersion of catalyst on a swollen coal structure. All of the coal/catalyst mixtures were then dried and subjected to the microautoclave test.

Comparison of the three methods reveals best results were obtained by conducting the exfoliation and dispersal in a single step (Exp. 14). Once the improvement of using a single exfoliation/dispersal step was realized, several solvent systems were compared for use in this single step. None of the other choices provided performance better than using THF/water.

Table 2 provides results obtained with a longer residence time. Here, a comparison was made with MoS_2 catalysts prepared *in situ* by conventional means. This method involves the deposition of MoS_2 precursors on the coal from solution prior to liquefaction. Impregnation of ammonium heptamolybdate or ammonium tetrathiomolybdate was accomplished by dissolving the salts in THF/water, then mixing the solution with coal for 4 h in an ultrasonic bath in the same manner as used with the particulate MoS_2 catalysts. In this comparison, the method of exfoliation of particulate MoS_2 in THF/water with coal (Exp. 19) gave a somewhat higher cyclohexane conversion and a greater amount of hydrogen uptake than both catalysts derived from the impregnated precursors.

In summary, exfoliation of MoS_2 in the presence of coal has produced a catalyst with good liquefaction performance. The results indicate that for the same amount of catalyst, a combination of reduction in MoS_2 stacking and improved coal/catalyst dispersion is beneficial.

TABLE 1. LIQUEFACTION OF BLIND CANYON BITUMINOUS COAL; ONE HOUR AT 375° C, EXFOLIATION OF MoS_2 WITH COAL PRESENT (EXCEPT AS INDICATED).

Exp.	Catalyst	Dispersing Solvent	Conversion, % daf Coal		H_2 Uptake, psi	Added Sulfur
			THF	Cyclohexane		
1	None	None	75	16	24	yes
2	None	None	70	18	8	no
3	None	THF/H_2O	78	21	31	yes
4	None	THF/H_2O	69	19	14	no
5	MoS_2[1]	THF/H_2O	77	18	56	no
6	MoS_2[2]	THF/H_2O	82	20	96	yes
7	MoS_2[2,3]	THF/H_2O	79	18	98	yes
8	MoS_2[1]	THF/H_2O	87	27	120	yes
9	MoS_2	H_2O	88	26	146	yes
10	MoS_2	EtOH	85	25	148	yes
11	MoS_2	i-PrOH	86	26	141	yes
12	MoS_2	H_2O/i-PrOH	86	27	149	yes
13	MoS_2	THF/i-PrOH	88	28	126	yes
14	MoS_2	THF/H_2O	88	32	160	yes

1 MoS_2 was exfoliated in H_2O, recovered, dried, and dispersed onto coal in a THF/H_2O slurry..

2 MoS_2 was used as received from Aldrich, without exfoliation; material was dispersed onto coal in THF/H_2O slurry.

3 Lithium hydroxide added in equimolar amount with molybdenum.

TABLE 2. LIQUEFACTION OF BLIND CANYON BITUMINOUS COAL; TWO HOURS AT 375° C, COMPARISON OF EXFOLIATED MoS_2 WITH OTHER MOLYBDENUM CATALYSTS.

Exp.	Catalyst	Dispersing Solvent	Conversion, % daf Coal		H_2 Uptake, psi
			THF	Cyclohexane	
15	AHM[1]	THF/H_2O	90	37	176
16	ATTM[2]	THF/H_2O	87	37	181
17	MoS_2[3]	THF/H_2O	89	31	156
18	MoS_2[4]	THF/i-PrOH	90	35	178
19	MoS_2[4]	THF/H_2O	90	40	216

1 Ammonium heptamolybdate.
2 Ammonium tetrathiomolybdate.
3 MoS_2 was exfoliated in THF/H_2O and dried before it was impregnated onto the coal by ultrasonication in THF/H_2O.
4 MoS_2 was exfoliated in the binary solvent system in the presence of coal.

Similar techniques for modifying MoS_2 were used to generate catalysts for use in upgrading a vacuum resid from Hondo crude oil. This application provided different challenges. The reactions crucial to conversion of coal are different in kind from those for HDS or HDN of petroleum resid. The Hondo resid used as a test material was 82% soluble in heptane before treatment. In the case of resid upgrading, major interests lie in the extent of the HDS and HDN reactions in addition to conversion to heptane solubles. In the absence of coal, the solid particulate substrate used to carry the catalyst is missing. Accordingly, the exfoliated, restacked catalysts were mixed directly with the resid. The effect of catalyst promoters is conveniently studied in this way by conducting the exfoliation step in aqueous solutions of $Ni(NO_3)_2$ or $Co(NO_3)_2$. Elemental analyses of the finished catalysts were used to determine the atomic ratios of Co/Mo and Ni/Mo which were 0.61 and 0.66, respectively. Nitrogen contents of the catalysts were negligible, indicating the nitrate counterions are not carried along with the washed materials.

The interlayer distance in the stacking dimension may be estimated from the position of the 002 line. Values for the original MoS_2 and restacked MoS_2 are 6.14 Å, as expected. The interlayer distance for both NiMo and CoMo catalysts was ~11.5 Å. A net expansion of the layered structure is evident from these data. These layer expansions are consistent with the observations of Golub et al. (5). They report the formation of MoS_2 intercalated with nickel or cobalt hydroxide as well as other transition metals.

Recovered catalysts were also examined by XRD. The soluble organic material was first removed by extraction with THF. In the case of exfoliated/restacked MoS_2, the recovered catalyst exhibited properties similar to the fresh catalyst. The stacking dimension was unchanged, 185 Å. The diffraction spectrum still gave evidence of an extensive contribution by a turbostratic structure.

The catalysts prepared with Ni and Co were also recovered. In these cases, the XRD spectra of the original and recovered materials were significantly different. The interlayer distances of the recovered materials were reduced from the former values of ~11.5 Å to 6.14 Å, now consistent with MoS_2. Apparently, the intercalated Ni or Co ions were removed from between the layers during the resid upgrading reaction. In the case of Co, there was also a remarkable growth in crystallite size. Only sharp lines for MoS_2 were apparent, leading to an estimate of an average crystallite size of >1000 Å in both the 002 and 11 planes.

The results from hydrotreatment tests are summarized in Table 3 along with some of the physical properties of these catalysts taken before mixing with the resid.

Table 3. Results of hydrotreatment of Hondo resid at 425° C for one hour, and some catalyst properties.

Catalyst	Heptane extract, wt%	S, wt%	N, wt%	Spins/g x 10^{-17}	Stacking height, Å	Surface area, m^2/g
(Resid)	82	5.1	0.9	--	--	--
None	89	3.5	0.8	--	--	--
MoS_2, as received	93	3.2	0.8	6.0	375	6.2
MoS_2, exfoliated /restacked	95	3.3	0.7	7.1	185	10
$CoMoS_2$	95	2.6	0.7	1.9	110	22
$NiMoS_2$	96	2.2	0.8	9.4	98	6.1

The main difference in performance between the catalysts is in the extent of HDS. Cobalt and especially nickel significantly promote desulfurization. Review of the catalyst properties in Table 3 does not produce a simple, consistent correlation of a property with HDS performance. For example, the surface area of the CoMo catalyst is 3.6 times that of the NiMo catalyst, but the latter exhibits a greater amount of HDS. A correlation between the EPR signal intensity assigned to Mo(IV) and the rate of catalytic conversion of dibenzothiophene for a series of MoS_2 catalysts has been reported [6]. This correlation fails when promoted and unpromoted catalysts in Table 3 are compared. The CoMo catalyst has the lowest EPR signal intensity, but performed quite well in HDS. In contrast to the significant HDS activity, HDN activity is negligible for all catalysts tested here. These preliminary results are encouraging in that a variety of related dispersed catalysts can be prepared for comparative studies, although it is evident that no single physical parameter can be used to correlate with all of the differences in performance.

Evaluation of the intrinsic reactivity and selectivity of dispersed catalysts has been carried out using a micro-flow reactor constructed at PETC (7). An exfoliated/restacked MoS_2 catalyst was prepared by drying after exfoliation in water. This typically leads to a catalyst with a moderate degree of stacking. The catalyst was mixed with sand before it was packed in the stainless steel reactor. The test conditions were 350°C with a H_2 flow of 1.3 mL/min at a gauge pressure of 350 kPa. A solution of 1% dibenzothiophene in tetralin with 0.8% dimethlydisulfide (DMDS) added was pumped through the reactor at various flow rates from 2 to 5 μL/min. DMDS is a convenient source of H_2S, and was added to maintain a constant degree of sulfidation of the catalyst. The recovered products were analyzed quantitatively by gas chromatography. The products included biphenyl, naphthalene

derived from the tetralin solvent, and unconverted dibenzothiophene.

The conversion of dibenzothiophene followed a pseudo-first order rate law over this set of conditions. A plot of the ln of the molar ratio of unconverted dibenzothiophene to the total of dibenzothiophene and its products versus the space time was well fit by a straight line. The rate constant for dibenzothiophene conversion was 4.17×10^{-5} mmol dibenzothiophene/g catalyst·min. This result may be compared with a value determined for a high surface area MoS_2/carbon catalyst (BCP 287, surface area = 262 m^2/g) prepared by A. Cugini (8). Under the same conditions of hydrogen pressure and flow rate but at the lower temperature of 275° C, the rate constant was 2.85×10^{-4} mmol dibenzothiophene/g catalyst·min. The latter catalyst thus had an activity seven times greater although it was measured at a significantly lower temperature. An additional product, phenylcyclohexane, was also found among the products. The appearance of both biphenyl and phenylcyclohexane among the products can be accounted for using the reaction network proposed by Singhal et al. (9). This network includes parallel paths, one that begins with hydrogenation of dibenzothiophene followed by removal of sulfur, and another that results in direct sulfur removal producing biphenyl. From our results it may be seen that two nominally similar MoS_2 catalysts prepared by different methods may be significantly different in both activity and selectivity.

PLANS

The exploration of the use of exfoliated/restacked catalysts for co-processing Hondo resid will be continued. Of prime interest will be the effect of various preparation techniques on the relative amount of sulfur and nitrogen removal. This information may indicate whether controlling MoS_2 particle morphology can result in an optimum reduction in heteroatom content at the least cost in hydrogen. The selectivity for HDS and HDN will be determined for the exfoliated/restacked MoS_2 catalyst now under evaluation in the micro-flow reactor by use of mixtures of dibenzothiophene and quinoline. These data will be correlated with that obtained from the high-pressure microautoclave study with Hondo resid.

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