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Exfoliated MoS_2 catalysts in coal liquefaction

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A technique is described for the application of MoS_2 to coal particles. The method was used to determine the importance of several parameters to the performance of this direct coal liquefaction catalyst. Improved performance was obtained when MoS_2 was intercalated with lithium, then exfoliated in a mixture of tetrahydrofuran and water in the presence of coal. Performance was compared by subjecting dried coal/catalyst mixtures to uniform microautoclave liquefaction tests. Measurements of coal conversion and hydrogen consumption show that a combination of reduction of the MoS_2 stacking and improved coal/catalyst dispersion is beneficial.

Keywords: MoS_2 catalysts; exfoliation; coal liquefaction

Catalysts have been used to increase the conversion of coal to potentially useful coal liquids by direct coal liquefaction [1]. The thermally induced hydrocracking of the coal matrix produces lower molecular weight radical fragments. These radicals must be stabilized by hydrogen, otherwise undesirable retrogressive reactions will occur to produce insoluble materials. Catalysts are therefore useful to activate molecular hydrogen or otherwise transfer hydrogen to cap these highly reactive radicals. Dispersed catalysts offer an advantage in that their more complete contact with the coal surface and the initial dissolution products makes them better suited to activating and transferring hydrogen to the sites where it is needed. In a recent review is developed an overview of the relevant scientific issues in catalyst dispersion in coal liquefaction in a historical context [2]. The preparation of dispersed MoS_2 catalysts for liquefaction often begins by introducing a precursor by either impregnating the coal with a water soluble molybdenum salt, addition of an oil-soluble organometallic salt, or by introducing an easily volatilized metal carbonyl. The use of another method to produce well-dispersed MoS_2 for the purpose of coal liquefaction is described below.

Exfoliation, that is, the dismantling of multilayered MoS_2 into single layers,

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has been used to generate interesting new materials [3]. Morrison has elaborated on the use of exfoliation of MoS_2 for several purposes, including the preparation of catalysts [4] and other materials with interesting properties [5]. An extension of such methods is described below for the application of exfoliated MoS_2 in the direct liquefaction of coal. The first step in this procedure is the intercalation of MoS_2 with lithium following the method of Dines [6]. Briefly, MoS_2 was mixed with *n*-butyllithium in hexane for two or three days. According to the work of Dines, MoS_2 is reduced, lithium is intercalated between the layers, and octane is produced by coupling of the butyl radical. 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,

$$Li_x{\cdot}MoS_2 + xH_2O \rightarrow \tfrac{1}{2}xH_2 + xLiOH + MoS_2$$

Single-layer exfoliated metal sulfides are reported to stay in suspension for several days due to the formation of a hydroxylated surface. The charged layer causes a repulsion between the separate single layers of molybdenum sulfide that hinders their immediate restacking [5]. Eventually, the molybdenum sulfide will restack to form multilayer particles. The restacking of the single-layer MoS_2 can be accelerated by the addition of dilute HNO_3, for example. The neutralization of the surface-attached hydroxyl groups allows restacking to happen in a matter of minutes rather than days as it would without addition of acid.

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 used in this work (Aldrich) 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 μm 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 interplanar spacing, calculated from the scattering angle of the (002) peaks, increased from 6.14 to 6.24 Å. The increase in average interlayer distance may be due to trace amounts of water remaining between some of the MoS_2 layers. BET surface area measurements using N_2 uptake gave a surface area of 10.0 m^2/g for the dried material and 6.3 m^2/g for the original MoS_2. The relative increase in surface area (1.59×) is reasonable in view of the relative decrease in stacking dimension (0.49×). Morrison found N_2 surface areas for his exfoliated and restacked MoS_2 and untreated MoS_2 samples to be 8.4 and 6.6 m^2/g, respectively [7,8].

The exfoliated MoS_2 catalysts were tested for their activity in coal liquefaction reactions. A brief discussion of the experimental techniques employed in the liquefaction tests is in order. All reactions were carried out in 42 ml 316 stainless steel tubing-bomb reactors in a temperature-controlled fluidized sand bath. Each reactor contained approximately 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 vessels were slowly heated to 375°C in about 50 min, held at this temperature for 1 or 2 h, then rapidly cooled by immersion in cold water. The gas was vented and the liquid products were analyzed by sequential solvent extraction using pressure filtration with tetrahydrofuran (THF) and cyclohexane following the method of Utz et al. [9]. The THF soluble, cyclohexane insoluble material and the THF insoluble residue were vacuum dried. Coal conversions were calculated on a daf basis using the values obtained for cyclohexane and THF insoluble residues. The results using exfoliated MoS_2 in coal liquefaction are shown in tables 1 and 2.

The data in table 1 reveal 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. A rough relative measure of hydrogen uptake was taken to be the drop in pressure between the high-

Table 1
Liquefaction of Blind Canyon bituminous coal; 1 h 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 [a]	THF/H_2O	77	18	56	no
6	MoS_2 [b]	THF/H_2O	82	20	96	yes
7	MoS_2 [b,c]	THF/H_2O	79	18	98	yes
8	MoS_2 [a]	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

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

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

[c] Lithium hydroxide added in equimolar amount with molybdenum.

Table 2
Liquefaction of Blind Canyon bituminous coal; 2 h 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[a]	THF/H_2O	90	37	176
16	ATTM[b]	THF/H_2O	87	37	181
17	MoS_2[c]	THF/H_2O	89	31	156
18	MoS_2[d]	THF/*i*-PrOH	90	35	178
19	MoS_2[d]	THF/H_2O	90	40	216

[a] Ammonium heptamolybdate.

[b] Ammonium tetrathiomolybdate.

[c] MoS_2 was exfoliated in THF/H_2O and dried before it was impregnated onto the coal by ultrasonication in THF/H_2O.

[d] MoS_2 was exfoliated in the binary solvent system in the presence of coal.

est value observed when the reaction temperature was first reached and the value recorded just before the reactor was cooled at the end of the experiment. The difference is due mostly to hydrogen consumption because the amount of hydrocarbon gas made at this low liquefaction temperature is minimal. The nominal hydrogen pressure for all experiments was 6.8 MPa (1000 psi) at room temperature before the liquefaction started. The amount of hydrogen consumed in the liquefaction runs using the exfoliated MoS_2 catalysts generally had a direct relationship to the cyclohexane conversion: as hydrogen consumption increased, so did cyclohexane conversion. The data in table 1 show 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.

To gain an idea of the change the various application techniques might make in performance, three basic methods of applying the catalyst to coal were compared. In the 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 and 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 and recovered by drying the suspension. The restacked material was 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. In this method, greater opportunity exists 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 of catalyst addition reveals exfoliation in itself increases performance. When the catalyst was added as received (exp. 6) without exfoliation, the THF conversion was slightly higher than the comparable experiment without catalyst (exp. 3) and a moderate amount of H_2 was taken up. The sequence of exfoliation, restacking and recovery, then dispersion (exp. 8) led to a significant improvement. Still better 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. This binary system offers a double advantage in that water enhances the exfoliation of MoS_2, while THF increases the area of the coal structure open to catalyst deposition. Systems less able to swell coal (H_2O, EtOH, *i*-PrOH, H_2O/*i*-PrOH) [10,11], or less effective for exfoliation (THF/PrOH) provide somewhat inferior cyclohexane conversions and lesser amounts of hydrogen uptake.

Physical characterization of the catalyst after it is deposited on the coal is difficult. The small amount that is used was undetectable by X-ray diffraction. Examination by SEM indicates that the MoS_2 is well dispersed over the entire surface of the coal particles. However, the resolution of the instrument was insufficient to determine stacking dimensions. A further effort to employ X-ray diffraction was made by examination of the THF-insoluble residue recovered after the liquefaction experiment number 8. This residue was subjected to a standard extraction procedure using aqueous HF/HCl to remove the native mineral matter present in the coal. Thus, the X-ray diffraction pattern was relatively free of the extraneous peaks due to the crystalline components of coal-derived mineral matter. However, the lines observed that might be ascribed to MoS_2 were too weak to allow structural information to be derived. At this point, MoS_2 is estimated to represent approximately 1.5% of the mass of the residue. Catalyst performance remains the main indicator of differences induced by the various catalyst application techniques.

A few additional observations can be made on the data in table 1 concerning the individual effects of sulfur, exfoliated MoS_2, and their combination. The Blind Canyon bituminous coal that was used in these experiments had a very low, 0.4%, sulfur content. In most of the experiments, elemental sulfur was added to the reactor to keep the MoS_2 sulfided under liquefaction conditions. The addition of sulfur by itself improved THF conversions slightly (exps. 1 and 3 vs. 2 and 4). H_2S has been shown to have some catalytic ability [12,13]. When exfoliated/restacked MoS_2 was added to the system without any extra sulfur (exp. 5), the cyclohexane conversion was about the same as when neither sulfur nor MoS_2 was added (exp. 4), even though the amount of hydrogen consumed, 0.38 MPa (56 psi) was greater. When both MoS_2 and sulfur were added to the system (exp. 8), both cyclohexane and THF conversions, and hydrogen uptake increased dramatically to 27%, 87%, and 0.82 MPa (120 psi). It is known that MoS_2 is partially oxidized by exposure to air at room temperature [14]. Thus, it is presumed that the MoS_2 may have been partially oxidized before reaching the liquefaction reactor. Without a supplement, the small amount of sulfur in the coal apparently was insufficient to complete its activation. Since neither addition of catalyst nor sulfur by itself increased performance as well as their combination, it appears that in addition to the direct influence sulfur has on conversion, it has another important role, that of assuring a supply of H_2S for maintaining a more active form of MoS_2.

Comparison of the first four entries in table 1 also shows that the choice of solvent used in the impregnation step has by itself only a small effect, if any. In all of the cases where exfoliation was used, the amount of lithium taken up by the MoS_2 during the intercalation was retained in the liquefaction experiment. To determine whether the addition of a similar amount of lithium could influence the liquefaction results, lithium hydroxide was added to the solvent system used to disperse the as-received MoS_2 on the coal in a 1 : 1 molar ratio to molybdenum. This addition did not lead to improved performance (exps. 6 and 7). Thus, exfoliation and/or its combination with dispersion of catalyst on coal are responsible for the majority of the observed improvements in performance.

Table 2 provides results obtained with a longer residence time at the same liquefaction temperature. By comparison with the analogous entries in table 1, it may be seen that the extension of the reaction to 2 h somewhat increased both cyclohexane conversions and the amount of hydrogen taken up. The order of catalyst performance was the same: exfoliation/dispersion in THF/H_2O > exfoliation/dispersion in THF/*i*-PrOH > exfoliation, then dispersion. A further 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. Comparisons with other particulate catalysts and recycled catalysts are in progress to determine the relative importance of catalyst/coal contacting and catalyst morphology.

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