

## EQUILIBRIUM ADSORPTION OF MOLYBDATE BY COAL

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**Keywords:** Surface Charge, Catalyst, pH Effects

**Abstract:** To investigate the effect of solution pH on the adsorption of molybdate, two Argonne Premium coals were equilibrated with aqueous solutions of ammonium heptamolybdate at pH 2 and 4. The extent of molybdate adsorption by the coal was calculated from the decreased concentration of molybdate in solution as determined by atomic absorption. The time necessary to reach equilibrium was always less than 24 hours; the majority of the adsorption occurred within the first hour. The Wyodak coal adsorbed more molybdate with better reproducibility than did the Illinois No.6 coal. The amount of Mo adsorbed by both coals increased with a decrease in the pH of the solution and with increased concentrations of molybdate. The increased adsorption under acidic conditions is consistent with increased positive sites on the coal surface at the lower pH.

**Introduction:** Electrokinetic studies of coal-water suspensions demonstrate that the surface charge of the coal particle is dependent upon the pH of the solution.<sup>1</sup> At lower pH values, the coal surface becomes positively charged due to protonation of basic sites. For demineralized bituminous coals, the surface usually becomes positively charged below pH 6. Lower rank and oxidized coals have lower isoelectric points; they develop a net positive charge at lower pH levels.

One would expect that the ability to disperse the negatively charged catalyst precursors, such as molybdenum anions, would be affected by the charge on the coal surface. If the coal surface has a net negative charge, the molybdate anion should tend to aggregate at the small localized positive regions. Increasing the number of the positively charged regions would be expected to provide more sites for the precursor to bind. This could lead to a more evenly dispersed catalyst with a smaller particle size.

Experiments with carbon supports indicate that the mechanisms of dispersion can be related to the carbon surface chemistry.<sup>2</sup> When a number of carbons were treated with molybdate solutions at a pH above their isoelectric points, only small amounts of molybdenum were adsorbed. When the same carbons were treated in the same way at a pH lower than the carbon isoelectric point, considerably larger amounts of molybdenum were adsorbed. The higher molybdenum adsorption at lower pH was taken as evidence that the lower solution pH resulted in a more positively charged carbon particle.

The effect of surface charge on the application of dispersed phase catalysts to coals has been examined only recently.<sup>3</sup> Such effects may be important to the art of catalyst impregnation. To investigate the effect of solution pH on the adsorption of molybdate, two Argonne Premium coals were equilibrated with solutions of ammonium heptamolybdate at pH 2 and 4. The results

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\* M.Tate was a participant in the Professional Internship Program administered by the Oak Ridge Associated Universities, Oak Ridge, Tennessee.

of these studies indicate that control of the pH during catalyst application may lead to more effective impregnation techniques.

**Experimental:** To a 1 g sample of coal in a 50-mL pyrex centrifuge tube was added 40 mL of a buffered catalyst solution. The slurry was mixed for periods from 0.5 to 24 hours at ambient temperature, then centrifuged. Aliquots (3 mL) were removed for atomic absorption analysis (AA) and the pH was measured. Mixing was then resumed. The solution pH remained relatively constant. The measured pH values over the 3 days of equilibration were  $1.90 \pm 0.06$  for the solution with an initial pH of 1.8 (20 determinations) and  $4.14 \pm 0.05$  for the solution with an initial pH of 4.1 (24 determinations). The average pH of the solutions containing larger amounts of molybdate tended to be slightly higher than those containing lower concentrations, but the difference was always less than 0.1 pH unit.

**Coals:** The Wyodak and Illinois No.6 coals were obtained from the Argonne Premium Coal sample bank'. Vials were tumbled prior to opening in accord with the Argonne instructions. The coals were pre-equilibrated with the same buffers that were used to prepare the catalyst solutions. Although the purpose of the pre-equilibration was to adjust the pH of the coal surface, it also removed all of the alkali and alkaline earth metal cations Na, K, Mg, and Ca. However, no iron was removed. It was also noted that the Illinois #6 coal samples wetted more easily and formed fewer clumps than did the Wyodak samples.

**Catalyst Solutions:** Ammonium heptamolybdate tetrahydrate (Fisher, Certified A.C.S.) was used as received to prepare the various concentrations of molybdate in two buffers listed in Table 1. Concentrations are expressed in ppm molybdenum. An additional solution at 6000 ppm formed a white precipitate, presumed to be  $MoO_3$ , after a couple of days. Because of this instability at higher concentrations, experiments were limited to solutions containing 3000 ppm or less.

**Buffer Solutions:** All solutions were prepared using deionized water which had been deaerated by purging with argon for at least 30 minutes prior to use. An acetate buffer of nominal pH 4 was prepared using acetic acid and sodium acetate. This gave a solution with a measured pH of 4.1. Similarly, a sulfate buffer of nominal pH 2 was prepared using sulfuric acid and sodium sulfate. This gave a solution with a measured pH of 1.8.

**Calculations:** The molybdate on the coal was calculated from the loss of molybdate from solution according to the equation

$$Mo_{coal,i} = Mo_{coal,i-1} + (Mo_{soln,i-1} - Mo_{soln,i}) \frac{V_{soln,i}}{W_{coal}}$$

where  $Mo_{coal}$  is the molybdenum concentration in ppm on the coal,  $Mo_{soln}$  is the molybdenum concentration in the solution in ppm,  $Vol_{soln}$  is the volume of solution remaining in mL, and  $W_{coal}$  is the weight of the coal in grams. It was necessary to take into account the change in volume of the solution with each successive sample  $i$ , because the aliquot size was not negligible in comparison to the solution volume. The concentration of molybdate in solution was measured by AA as described below.

**AA Analysis:** Atomic Absorption (AA) analyses were performed using a Perkin Elmer Model 503 flame atomic absorption spectrophotometer. Ammonium chloride modifier was added to provide a final concentration of 1% in all determinations. The molybdenum

concentration was determined by reference to a linear regression calibration curve derived from four standard solutions ranging from 0 to 10 ppm Mo. Samples which exceeded this range were diluted as needed to fall within the calibrated range.

The agreement of the AA results with the concentrations determined from the weights of molybdate and buffer used in the solution preparations is shown in Table 1. The last column of the Table lists the concentration determined by AA and the fifth column lists the concentration of Mo determined gravimetrically in each of the solutions used in this study. The agreement between the two determinations is very good; the gravimetric determination is always within two standard deviation units of the AA result and is often within one unit. There may be a small bias in one of the methods since the gravimetric determination is always lower than the AA determination, but the difference is considered insignificant for the purpose of these experiments.

The standard deviations and relative standard deviations were derived from a series of control samples analyzed over the several days of the experiment. The magnitudes of the deviations are similar to those found for the AA technique itself. For example, the nominal 600 ppm controls gave a standard deviation of 27 ppm at both pH levels. This compares favorably with the precision of the AA technique of 42 ppm as determined in separate quality assurance experiments. Thus, the solutions themselves were stable with time and precipitation cannot account for the loss of Mo from solution. A false positive was never obtained for blank samples which were also analyzed routinely in single blind experiments.

**Results:** Aqueous solutions of ammonium heptamolybdate containing up to 3000 ppm molybdenum were allowed to equilibrate with samples of the Argonne Premium Wyodak and Illinois No.6 coals. The loss of molybdate from solution was monitored by AA analyses of aliquots of the supernatant solution. The results obtained using the Wyodak coal at a pH of 2 are shown in Figure 1. Molybdate was adsorbed quickly and equilibration occurred within the first 24 hours. At the lowest initial concentration, 60 ppm, the adsorption of Mo was complete; the supernatant solution contained no detectable Mo after the first hour of contact. At 600 ppm, 90% of the Mo was adsorbed resulting in about 2 g of molybdenum being adsorbed per 100 g of as-received Wyodak coal. Increasing the solution concentration by a factor of 2.5 to 1500 ppm resulted in increased adsorption by a factor of about 2. A further doubling to 3000 ppm resulted in an even smaller incremental increase in adsorption, indicating that the amount of molybdate that can be adsorbed is limited. Inspection of the graphs in Figure 1 suggests that under these conditions the limiting value is in the neighborhood of 5%.

Buffering the solution pH to 4 resulted in less molybdate adsorption, as can be seen in Figure 2. Although increasing the initial Mo concentration from 60 through 600 to 3000 ppm resulted in increased amounts of Mo being adsorbed, the equilibrium values are noticeably lower at this higher pH. For the case at 3000 ppm, equilibration at a pH of 4 resulted in the coal adsorbing 3.4% of its weight in Mo; equilibration at a pH of 2 resulted in 4.3% adsorption by coal. Only at 60 ppm where both solutions were depleted in Mo was the amount adsorbed the same. Thus, lowering the pH of the medium effects a larger adsorption of molybdate from solution.

Different levels of adsorption occurred when a bituminous coal was used. Similar experiments using the Argonne Illinois No.6 coal resulted in the data presented in Figures 3 & 4. In contrast to the rather smooth trends discernible at all Mo concentrations for the Wyodak coal, the results for the Illinois coal contained appreciable scatter at the highest Mo concentration. Despite this scatter, some comparisons between the Wyodak and Illinois coals can be made by focusing on the results obtained at the 60 and 600 ppm concentrations. At these lower initial molybdenum concentrations, a rapid equilibration apparent within the first 24 hours was consistent with the rapid equilibration seen for the Wyodak coal. However, the amount of Mo adsorbed was much smaller than was seen for the lower rank coal. At 60 ppm, the molybdenum adsorbed was barely above the detection limits at a pH of 2 and at the detection limits at a pH of 4. By contrast, the Wyodak coal adsorbed all of the available Mo under similar conditions. At an initial Mo concentration of 600 ppm, the amount of Mo adsorbed by the Illinois No.6 coal is only 10% of that adsorbed by the Wyodak coal. Thus, on a weight basis, the Wyodak coal is 10 times more effective at adsorbing molybdenum anions than is the Illinois coal at a pH of 2. Substituting a pH 4 buffer (Figure 4) for the pH 2 buffer (Figure 3) effected an even greater decrease in Mo adsorption for the Illinois No.6 coal than it did for the Wyodak coal. At the 600 ppm level, the higher pH resulted in the coal adsorbing only 0.13% of its weight in molybdate instead of the 0.51% seen at the lower pH. Thus, the Illinois No.6 coal adsorbs less Mo from solution than does the Wyodak coal and the amount adsorbed is more sensitive to the pH of the aqueous solution.

**DISCUSSION:** The results obtained for these two coals appear to be consistent with an adsorption mechanism in which molybdate in solution is in equilibrium with surface-bound molybdate. The extent of surface adsorption is expected to depend on both the concentration of molybdenum in solution and the number of adsorption sites available on the coal surface. Because the coal surface develops more net positive charge at the lower pH, more anion binding sites are expected to become available. Thus, both increasing molybdate concentration and decreasing pH are expected to result in more molybdate being removed from solution.

However, the nature of the molybdenum species in solution changes with changes in total concentration of molybdenum(VI) and pH.<sup>5</sup> For example, at a total Mo(VI) concentration of 50 ppm the predominate species is  $\text{Mo}(\text{OH})_6$  at a pH of 2, but  $\text{MoO}_4^{2-}$  predominates at a pH of 4. At a total Mo(VI) concentration of 2000 ppm the predominate species is  $\text{Mo}_2\text{O}_7^{4-}$  at a pH of 2, whereas  $\text{HMo}_2\text{O}_7^{3-}$  predominates at a pH of 4. This rich chemistry provides alternate explanations to the observed adsorption trends. Each of these species as well as a number of other minor species may all adsorb with different equilibrium constants. Thus, the details of the adsorption mechanism are not clear.

The adsorption sites on the coals are effected by the solution pH. These sites may reside in the organic portion, the mineral portion, or both portions of the coal. Organic functional groups play an important role in the electrokinetic behavior of coal-water suspensions<sup>1</sup> and the adsorption of molybdate by carbon supports can be related, in part, to the degree of surface oxidation.<sup>2</sup> Nitrogen heteroatoms, which become positively charged in acid, may also play an important role. It is interesting to note that an atomic Mo to nitrogen ratio of 1 corresponds to a 5

weight % Mo loading on the Wyodak coal. Thus, it is reasonable to suspect that the extent of molybdate adsorption and the pH dependence are related to the organic heteroatom content. Also, mineral matter may play an important role in the adsorption. The protonation of alumina hydroxyl groups is responsible for the creation of adsorption sites for molybdate on catalyst supports.<sup>6</sup> The clays or other minerals in the coal could behave in a similar fashion.

It is of interest to compare these results with those obtained for some other coal samples. Table 2 compares the results obtained by Abotsi et al.<sup>3</sup> with the results obtained here. Since some of the experimental procedures are different, and the coals are not identical, the results are not strictly comparable. The solution concentration used by Abotsi was 4800 ppm whereas our highest concentration was 3000 ppm. However, the main points are readily discernable. There is a fairly large difference in the % Mo adsorbed between the bituminous and subbituminous coals. This may be due to the higher oxygen content of the latter. However, there are also differences within rank. The Montana Rosebud subbituminous coal (PSOC 1493) adsorbed about half as much Mo as did the Wyodak coal. Thus, the nature of the coal is also important to the adsorption mechanism.

**CONCLUSIONS:** The extent of molybdate adsorption by coal is affected by the nature of the coal and the pH and molybdate concentration of the equilibration solution. Lower pH and higher molybdate concentrations favor molybdate adsorption. Such effects may be important to the art of catalyst impregnation.

**ACKNOWLEDGEMENTS:** The authors thank Ms. Deborah Hreha and Ms. Jodi Schuster who performed the AA analyses reported in this work and José Solar for many helpful discussions.

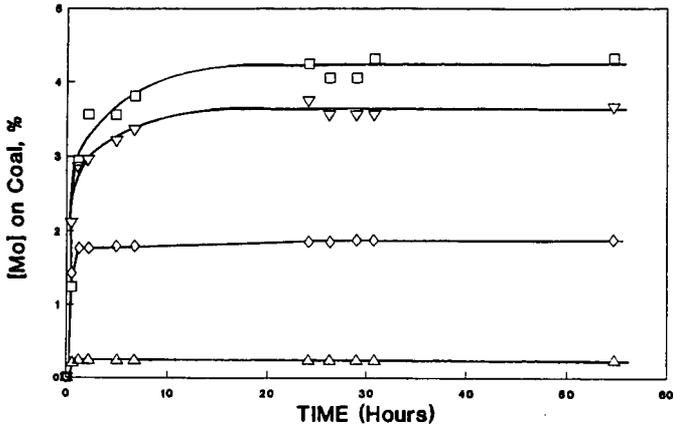
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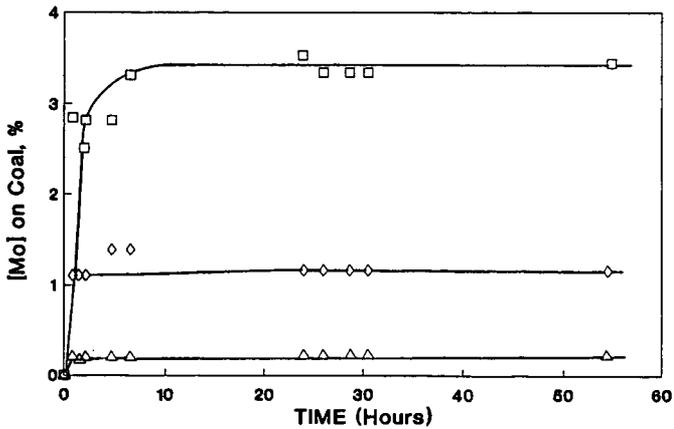
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Table 1. Concentration of Molybdenum in Buffered Solutions					
Nominal pH	Nominal Concentration (ppm Mo)	Ammonium Heptamolybdate (grams)	Amount of Buffer (grams)	Calculated Concentration (ppm Mo)	Concentration Measured by AA (ppm Mo)
4	60	0.0116	100.72	63	66±5 (±8%)
	600	0.1078	100.37	583	598±26 (±4%)
	3000	0.5487	100.20	2960	2968±225 (±8%)
2	60	0.0114	100.60	62	66±5 (±8%)
	600	0.1077	101.46	576	584±27 (±5%)
	1500	0.1325	50.21	1430	1550±71 (±5%)
	3000	0.5484	100.22	2957	3152±175 (±6%)

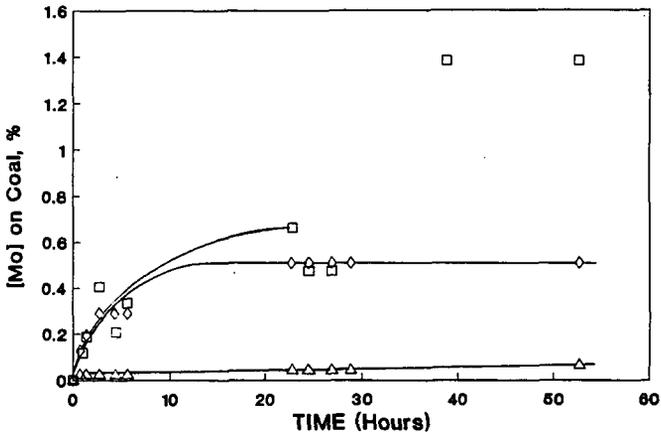
TABLE 2. Comparison of Molybdate Adsorption for Different Coals			
COAL	pH	% Mo on Coal (Ref. 3)	% Mo on Coal (This Work)
SUBBITUMINOUS	2	2.11	4.1
	4	1.25	3.5
BITUMINOUS	2	0.29	≥0.5
	4	0.19	≥0.3



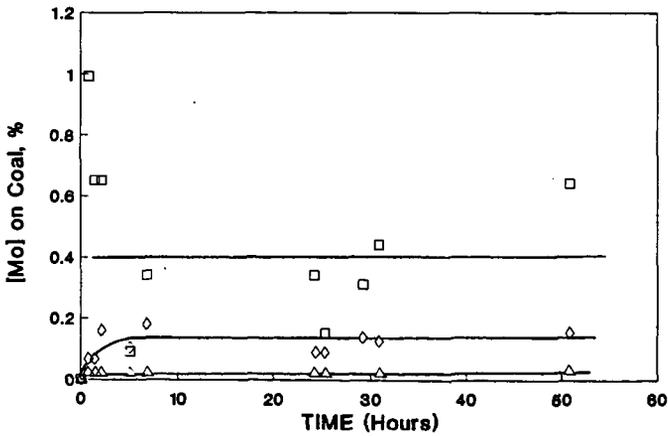
**FIGURE 1.** Adsorption of Molybdate from Solution by Wyodak Coal at a pH of 2. □ Initial solution concentration = 3000 ppm. ▽ Initial solution concentration = 1500 ppm. ◇ Initial solution concentration = 600 ppm. △ Initial solution concentration = 60 ppm.



**FIGURE 2.** Adsorption of Molybdate from Solution by Wyodak Coal at a pH of 4. Symbols the same as on Figure 1.



**FIGURE 3.** Adsorption of Molybdate from Solution by Illinois No.6 Coal at a pH of 2. Symbols the same as on Figure 1.



**FIGURE 4.** Adsorption of Molybdate from Solution by Illinois No.6 Coal at a pH of 4. Symbols the same as on Figure 1.