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ELECTRONIC CONCEPTS APPLIED TO COKE FORMATION ON
HYDROCRACKING AND HYDRODESULPHURIZATION CATALYSTS

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ELECTRONIC CONCEPTS APPLIED TO COKE FORMATION ON
HYDROCRACKING AND HYDRODESULPHURIZATION CATALYSTS

by

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ABSTRACT

A simple model of a hydrocracking catalyst employing two types of reaction sites is used to explain coke formation. Electron holes are associated with hydrogen adsorption-desorption. Uncharged electron acceptor sites are associated with hydrocarbon adsorption-desorption. Previous studies have shown that varying the catalyst composition; adding alkali metal cations to the support, changing the MoS_2 content, changing the sulphur content, and adding promoters (cobalt or nickel), influences catalyst performance. The above model was used to explain changes in catalyst coke content which have been reported to accompany these changes in catalyst composition.

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INTRODUCTION

When high molecular weight hydrocarbon mixtures, containing significant amounts of asphaltenes and organometallic compounds, are hydrocracked a rapid decline in catalyst activity occurs. Both coke formation and metals deposition contribute to the decline. However coke formation has by far the larger effect. Recent studies (1,2,3) at the Energy Research Laboratories have reported the quantity of coke on the catalyst as a function of catalyst composition. The purpose of this paper is to attempt to explain these findings in terms of a simple model of the catalyst's electronic properties.

All of the catalysts were prepared by mixing acid and aqueous solutions of various compounds into an alpha alumina monohydrate (boehmite) powder. Because the resulting gel was essentially homogeneous the surface composition of the catalyst was expected to be the same as the bulk composition. This expectation was confirmed in a recent XPS study (4) in which the surface composition of the oxide form of catalyst was analyzed. The catalyst was subsequently ground into a fine powder, thereby creating new surfaces from the bulk, and analyzed by XPS again. The analyses were similar. One interpretation would be that the surface and bulk compositions were comparable.

CONCEPTS DESCRIBING THE CATALYST

Concepts described in the literature have been employed to explain coke formation phenomena. It is postulated that the catalyst contains two types of reaction sites. The first type consists of electron holes (p-conductivity in the catalyst) which are associated with hydrogen adsorption-desorption. This concept was developed by Aoshima, Wentrcek, and Wise (5,6,7,8,9). Electron holes have a major impact on the rates of all the hydrocracking reactions; however they do not influence the catalyst coke content at the reaction conditions which have been used (1,2,3).

The second type consists of uncharged electron acceptor sites which are associated with hydrocarbon adsorption-desorption. The S^{2-} vacancies in MoS_2 are considered to be uncharged electron acceptor sites. According to the model of deBeer and Schuit (10) hydrocarbon molecules containing a sulphur atom are adsorbed at these sites. Similarly Wentrcek and Wise (6) concluded that olefins are adsorbed at these sites. The acidic sites associated with the Al^{3+} cations in the alumina support are also considered to be uncharged electron acceptor sites which are associated with hydrocarbon adsorption-desorption. For example, acidic sites are required for molecular weight reduction (cracking) via a carbonium ion mechanism. Also electron transfer cracking (11) requires electron acceptor reaction sites. The uncharged electron acceptor sites responsible for hydrocarbon adsorption are considered to be the ones at which coke formation occurs.

Changing the catalyst composition is known to affect all the hydrocracking reactions in a similar manner. For example molecular weight reduction (12), desulphurization (12), denitrogenation (12) and hydrogenation (13) all had similar conversion patterns with changing catalyst composition. One can speculate that for all the above reactions, hydrogen reacts with a hydrocarbon reaction intermediate before the reaction product is desorbed from the catalyst surface. If the reaction rates are limited by hydrogen addition, then any change in the number of electron holes would effect hydrogen adsorption and would produce similar changes in all the reaction rates.

Coke formation is known to occur by dehydrogenation and polymerization reactions. Experiments (13) showed that hydrogenation rather than dehydrogenation predominated since the liquid product had a larger hydrogen content than the reactant. On this basis it will be assumed that coke is formed primarily by polymerization reactions rather than dehydrogenation reactions. Presumably polymerization will occur on sites where hydrocarbon species are adsorbed. Therefore

coke formation will be associated with uncharged electron acceptor sites where hydrocarbon adsorption-desorption occurs rather than with electron holes where hydrogen adsorption-desorption occurs. The discussion which follows will use this concept in an attempt to explain the changes in hydrocracking catalyst coke content with changing catalyst composition.

DISCUSSION

Results from three separate experimental studies will be discussed. Different feedstocks or slightly different methods of coke measurement were used in each study. The changes in the relative amount of coke on the catalyst may be considered to be accurate for any particular study. However results of catalyst coke content from different studies should not be compared. In each case the statistical number of coke monolayers on the catalyst surface has been calculated. This has been done by assuming that the coke has a density of 1.2 g/mL and that the thickness of an aromatic molecule is 34 pm.

The effects caused by incorporating alkali metal compounds into a catalyst composed of 2.2 wt % MoO₃, 1.1 wt % CoO and gamma alumina have been described (3). Figure 1 shows a two dimensional arithmetic diagram which has been devised in order to count the number of outer shell electrons associated with each ion in the catalyst. It does not represent the catalyst structure or any real situation. The surface can terminate with either hydroxyl groups or O²⁻ anions. In Figure 1A every two Al³⁺ cations are associated with three O²⁻ anions corresponding to Al₂O₃. Each O²⁻ anion is surrounded by an outer shell of eight electrons. Each Al³⁺ cation is surrounded by six electrons. The missing two electrons correspond to the uncharged electron acceptor reaction sites associated with the Al³⁺ cations in the alumina. When an alkali metal ion, for example potassium, is incorporated into the support the two dimensional arithmetic diagram is shown as Figure 1B. In this case the K¹⁺ cation can donate one electron to another part of the catalyst and still be surrounded by an outer shell of eight electrons. This extra electron can then occupy one of the uncharged electron acceptor sites associated with the Al³⁺ cations. Figure 1A shows that each Al³⁺ cation donates one of its electrons to each adjacent O²⁻ ion. The K¹⁺ ion could donate two of its electrons to each adjacent O²⁻ ion. Depending on the number of O²⁻ ions which are coordinated with each K¹⁺ ion an additional three or four electrons could be available to occupy uncharged electron acceptor sites. Coke formed by polymerization should decrease as more and more uncharged electron acceptor sites are occupied by electrons.

The data in Figure 2 support this explanation. The amount of molybdenum was identical in each of the catalysts shown. As the number ratio of alkali metal ions to molybdenum ions increased, the coke formed on the catalyst decreased.

The effect of molybdenum content in the catalyst on coke formation has been described previously (2). Some of the data points in Figure 3 are for unpromoted catalysts containing only molybdenum and aluminum cations. It is apparent that the catalyst coke content decreases as the content of molybdenum ions in the catalyst increases. A simple explanation for this phenomenon is possible. As the number of Mo⁴⁺ cations in the catalyst increases the fraction of the catalyst surface covered by Mo⁴⁺ cations will increase and the fraction covered by Al³⁺ cations will decrease. The number of uncharged electron acceptor sites (S²⁻ vacancies) per Mo⁴⁺ cation may be smaller than the number of uncharged electron acceptor sites (electron pair vacancies) per Al³⁺ cation. Therefore as the molybdenum content of the catalyst increases, the number of uncharged electron acceptor sites decreases, and coke formation via polymerization should decrease. This concept of surface coverage appears to be a simple way to explain the data in Figure 3.

Actually the situation is more complex. As the concentration of Mo⁴⁺ ions in the catalyst increases, depending on the sulphur content, it is possible that the number of electron holes will also increase simultaneously. Since electron holes are considered to affect desirable reaction rates and not coke formation, this aspect will not be discussed further.

The effect of catalyst sulphur content on catalyst coke content has already been described (1). Some of these results are shown in Figure 4. The catalyst with the greatest amount of coke in Figure 4 was the one sulphided with gas oil and was shown in a figure of reference 1. The catalyst with the least amount of coke was the one sulphided with H_2S followed by two reaction experiments and was shown in the same figure of reference 1. The catalyst containing the intermediate amount of coke was sulphided with H_2S followed by four reaction experiments and was described in the text of reference 1. The data clearly show that catalysts having a greater sulphur content also contain less coke.

Coke formation via polymerization was ascribed to S^{2-} vacancies, the uncharged electron acceptor sites, in MoS_2 . Incorporating additional S^{2-} anions into the catalyst fills some of the sulphur vacancies. As a result there are fewer sites on which coke can form. This explains the results in Figure 4.

Figure 5, the two dimensional arithmetic diagram, shows MoS_2 and MoS_2 with additional non-stoichiometric sulphur. It is apparent that the additional S^{2-} anions fill the uncharged electron acceptor sites (S^{2-} vacancies) and provide additional electron holes. The data in Figure 4 show that two of the catalysts contained more sulphur than the 2.97 wt % S - stoichiometric value. This is consistent with the work of Wentrcek and Wise (6) in which S^{2-} anions in excess of the stoichiometric requirement were related to filling S^{2-} vacancies and forming electron holes.

Adding a promoter ion, Ni or Co, does not affect the coke content of the catalyst. This is illustrated in Figure 3 where it is evident that the nickel promoted catalysts contain approximately the same amount of coke as the unpromoted catalysts. However, the nickel promoted catalysts (2) have considerably higher activity than do the unpromoted catalysts (12). Similarly another set of experiments with nine different promoters (2) showed that all catalysts contained the same amount of coke regardless of the promoter cation. However, the nickel and cobalt promoted catalysts had much higher activities for hydrogenation (13), desulphurization (12) and denitrogenation (12).

The observation that the promoter does not affect coke formation can be explained in terms of Figure 5C. Incorporating an additional promoter cation into the catalyst creates an additional two electron holes which can be used for hydrogen adsorption, and therefore can affect all of the desirable reactions; hydrogenation (13) desulphurization (12) and denitrogenation (12). However the incorporation of a promoter does not affect the number of uncharged electron acceptor sites at which polymerization reactions and coke formation occur. Therefore it would not be expected to affect the catalyst coke content, which is in agreement with the data in Figure 2 and in reference 2.

By combining these previously described concepts, electron holes and uncharged electron acceptor sites, it has been possible to qualitatively explain data describing coke formation phenomena on hydrocracking catalysts. All the desirable reactions, hydrogenation, desulphurization, denitrogenation, and to some extent molecular weight reduction require both hydrogen (adsorbed on electron holes) and hydrocarbon species (adsorbed on uncharged electron acceptor sites). Results from the experiments referred to in this paper have indicated that the desirable reaction rates were limited by hydrogen adsorption (electron holes). On this basis there should be no correlation between desirable reaction rates and uncharged electron acceptor sites (S^{2-} vacancies, Mo ion valence, etc.). In contrast the undesirable reaction, coke formation by polymerization, requires reaction between hydrocarbon species (adsorbed on uncharged electron acceptor sites). Electron holes are not involved. Therefore there should be a correlation between coke formation and uncharged electron acceptor sites (S^{2-} vacancies, Mo ion valence, etc.).

CONCLUSIONS

The concepts of electron holes and uncharged electron acceptor sites

have been combined to describe phenomena occurring on hydrocracking catalysts. Electron holes were used to explain the rates of formation of desirable reaction products whereas uncharged electron acceptor sites were used to explain coke formation. This combination of concepts produced qualitative agreement with all of the data present here.

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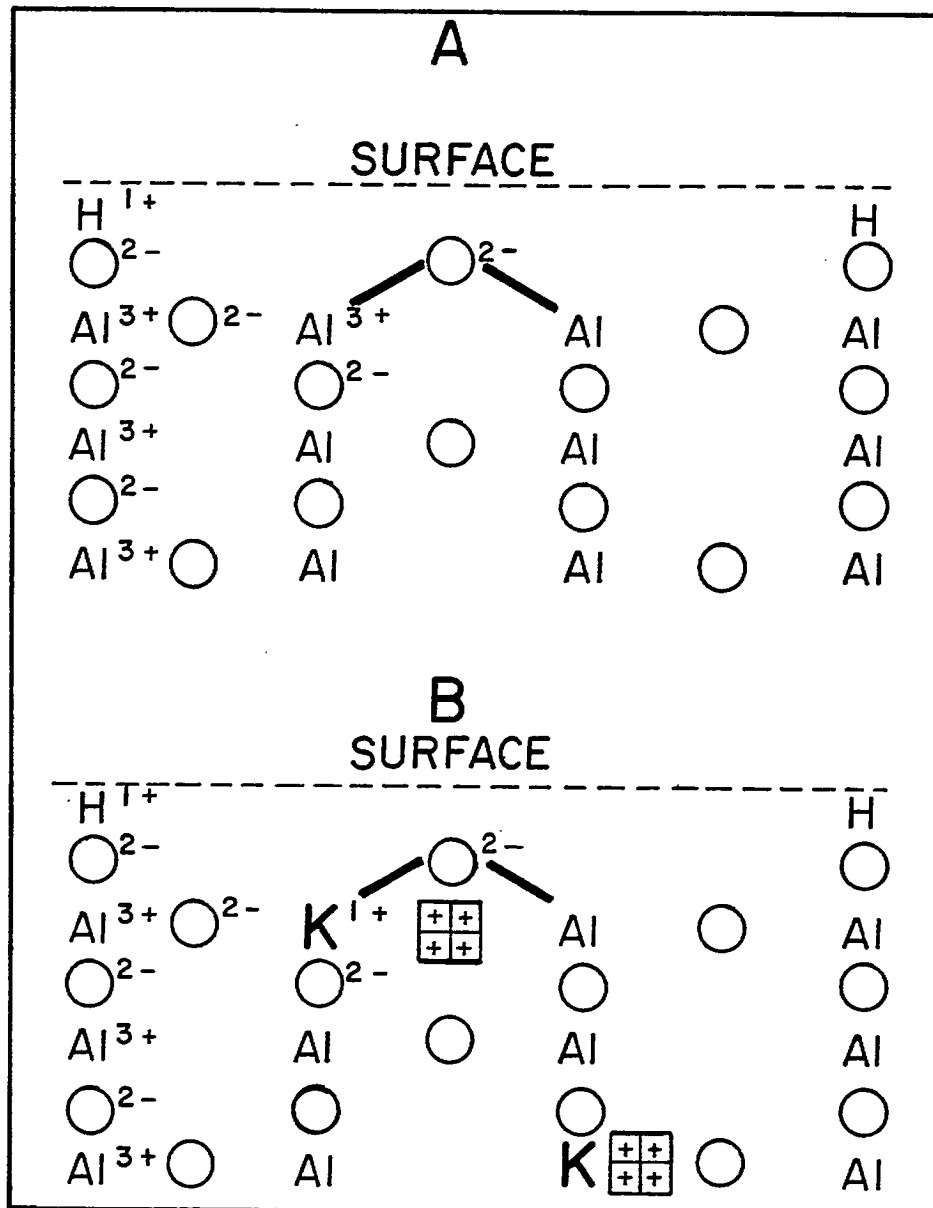


FIGURE 1
TWO DIMENSIONAL ARITHMETIC DIAGRAM FOR ALUMINA (1A) AND
FOR ALUMINA CONTAINING POTASSIUM (1B)

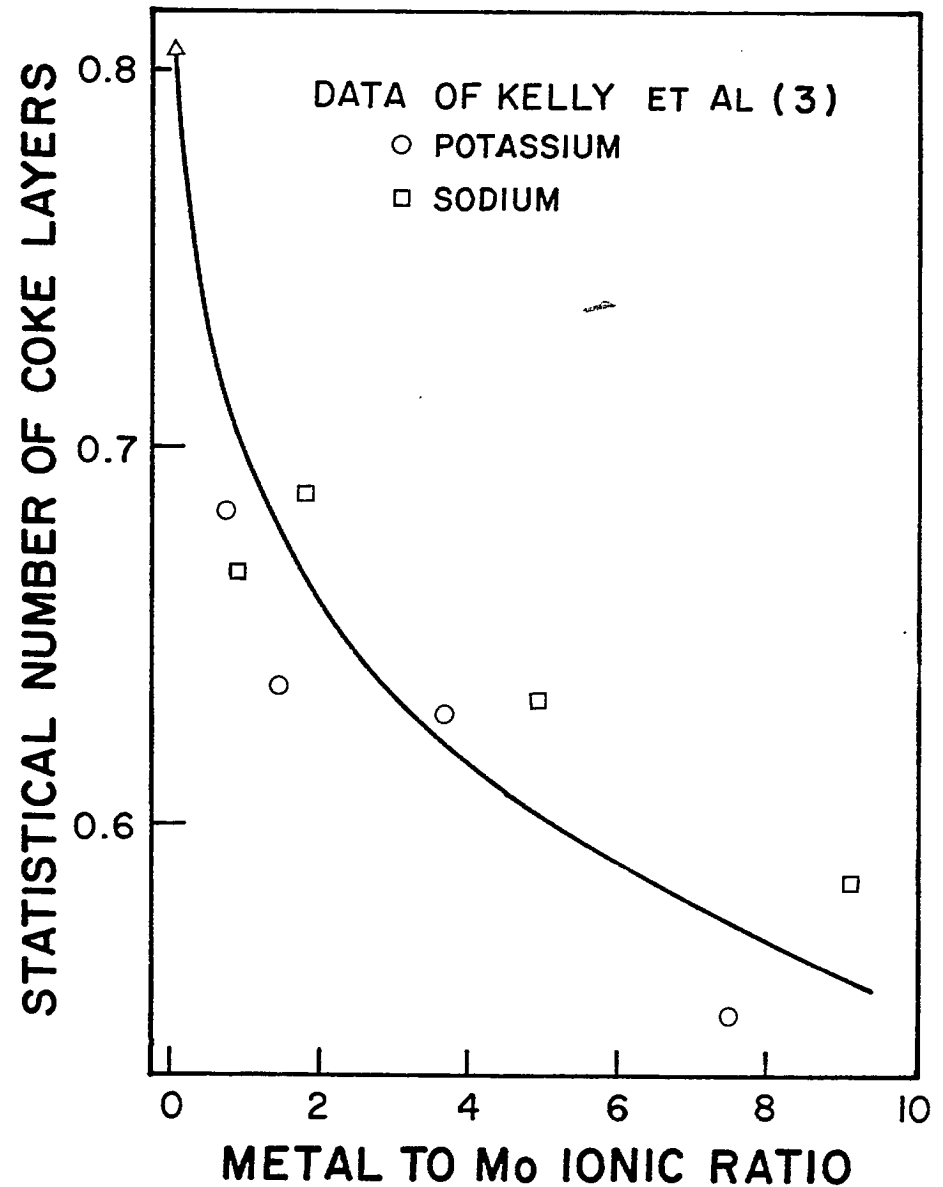


FIGURE 2
STATISTICAL NUMBER OF COKE LAYERS VERSUS
ALKALI METAL TO MOLYBDENUM IONIC RATIO

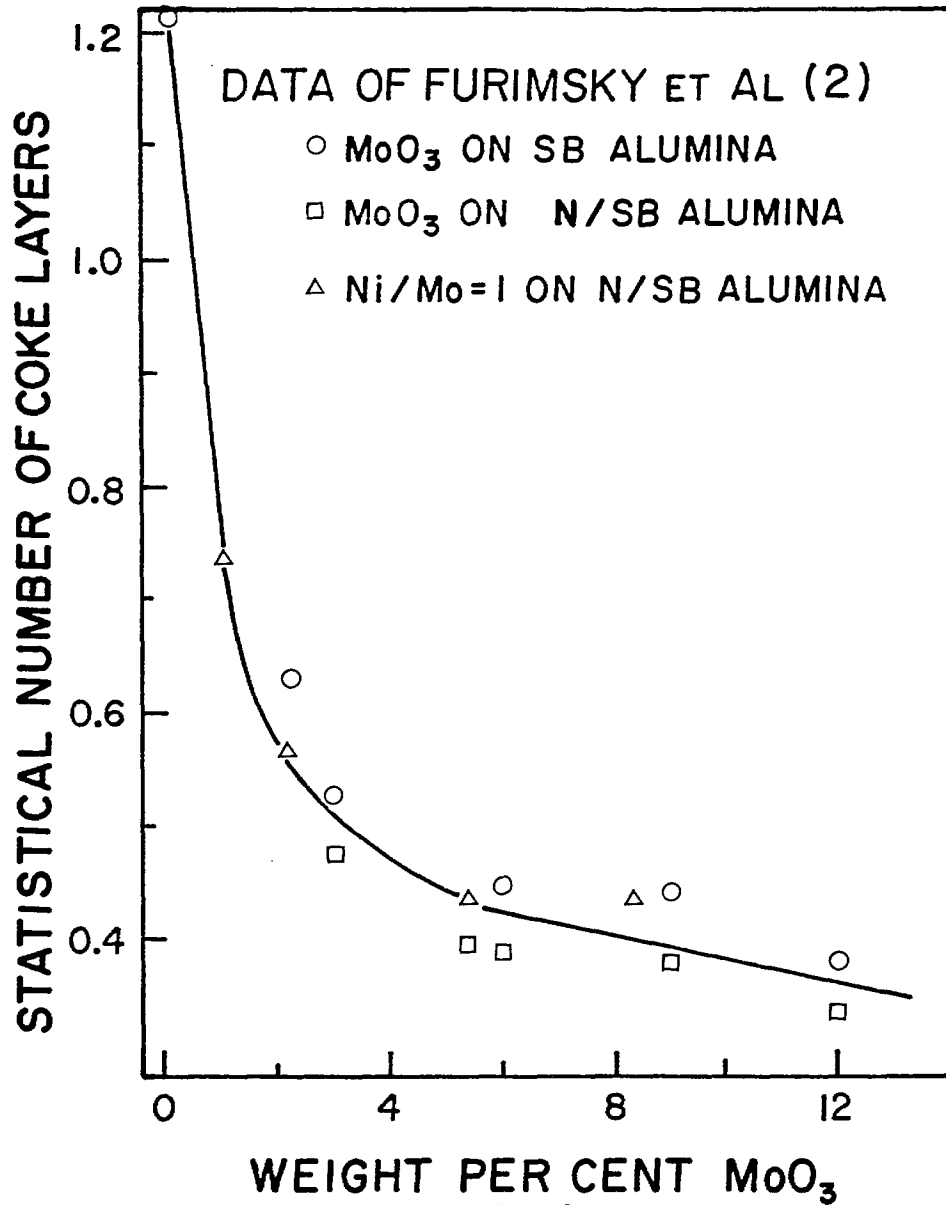


FIGURE 3
 STATISTICAL NUMBER OF COKE LAYERS VERSUS
 WEIGHT PER CENT MoO₃ IN THE CATALYST

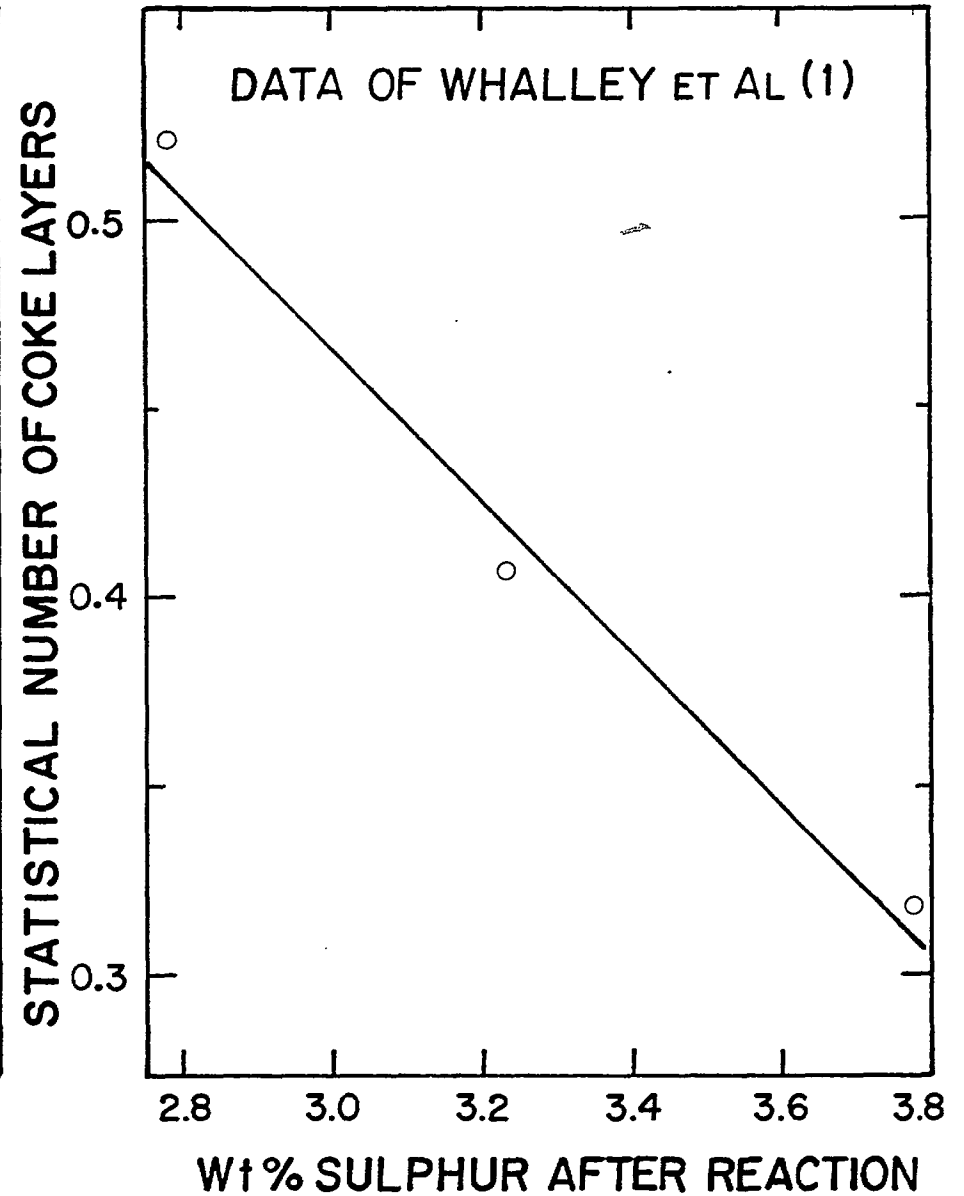


FIGURE 4
 STATISTICAL NUMBER OF COKE LAYERS VERSUS
 WT % SULPHUR IN CATALYST AFTER REACTION

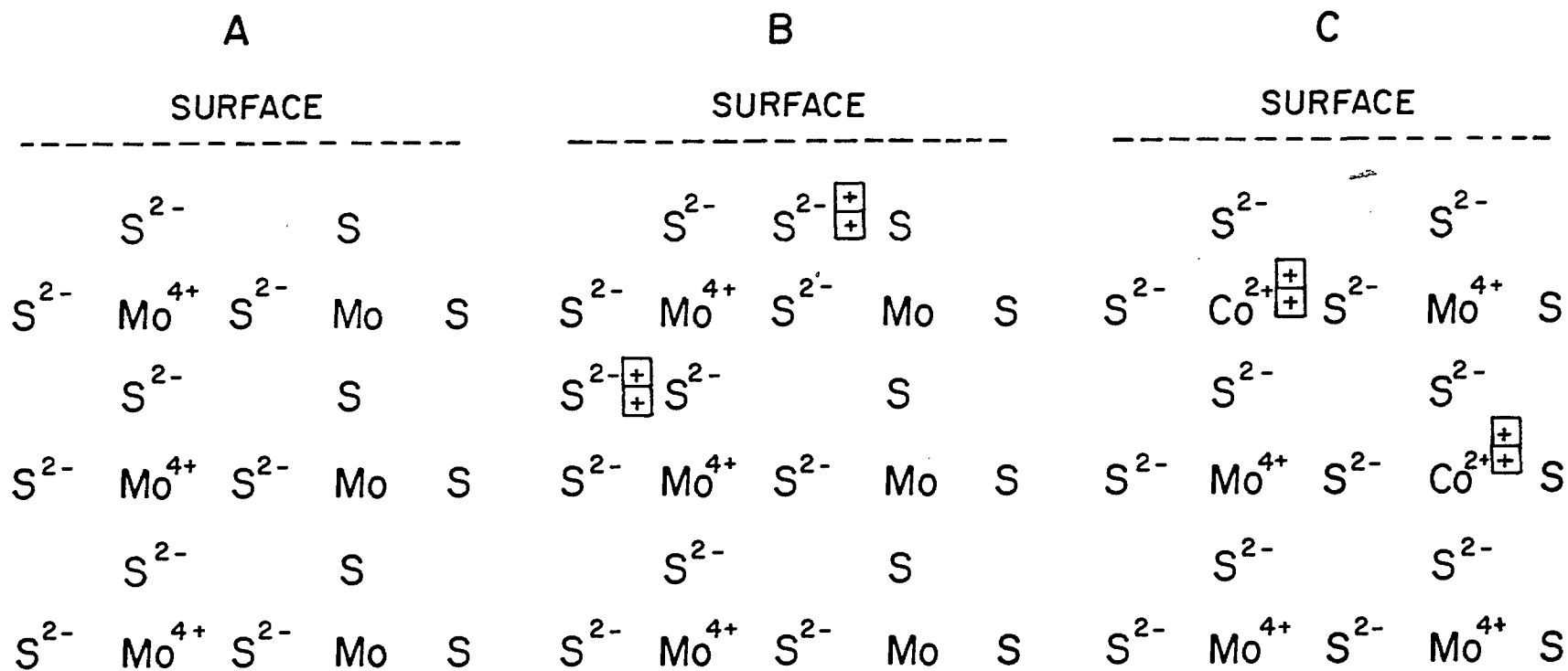


FIGURE 5

TWO DIMENSIONAL ARITHMETIC DIAGRAM FOR STOICHIOMETRIC MoS_2 (5A)

MoS_2 CONTAINING EXCESS SULPHUR (5B), AND MoS_2 CONTAINING A COBALT CATION PROMOTER (5C)