Co-Mo/Al$_2$O$_3$ CATALYSTS   IN THE HYDROCRACKING OF ATHABASCA BITUMEN:
EFFECTS OF THE PRESENCE OF Na and F ON THEIR COMPOSITION AND PERFORMANCE.

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Co-Mo/Al$_2$O$_3$ Catalysts in the Hydrocracking of Athabasca Bitumen:

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Composition and Performance

by

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ABSTRACT

A series of catalysts was prepared using different procedures to
incorporate sodium and fluoride into the Co-Mo/Al$_2$O$_3$ system. A bench-scale
high pressure continuous-flow system was used for reactivity tests. The
experimental results have shown that sodium is an inhibitor and fluoride
is a promoter for the hydrodesulphurization of bitumen derived from the
Athabasca Oil Sands. The fluoride ion was considered to enhance the cata-
lyst Bronsted acidity and therefore cracking of carbon-carbon bonds. This
could improve the access to the catalyst of sterically hindered sulphur
atoms in the bitumen. The slower rate of catalyst deactivation when molyb-
denum and cobalt were added to the catalyst before the first calcining step
was attributed to the greater interaction of the molybdenum with the alumina.
This would decrease the number of bare alumina sites which may be prime
candidates for coke formation. It would also decrease sintering tendencies
in MoS$_2$ crystallites.

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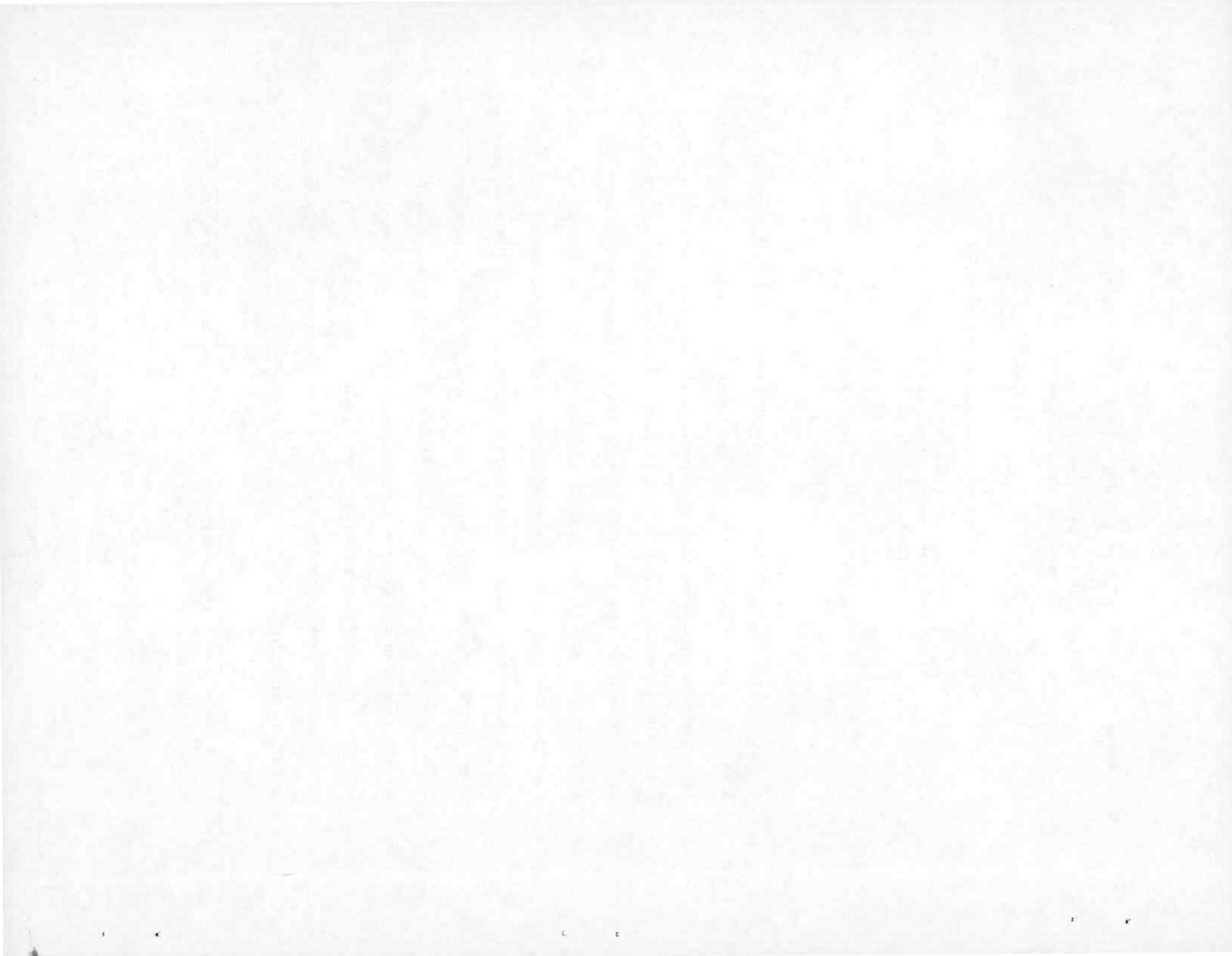
INTRODUCTION

The diminishing world supplies of conventional crude oils have stimulated research into the utilization of alternative sources of liquid fuels. Oil sands and heavy oils are important unconventional sources of hydrocarbons in Canada.

At present all the operating commercial upgrading plants in Canada utilize a coking process to convert the low grade fossil fuel into more volatile liquids. An alternative conversion route is hydrocracking. This process increases the yield of liquid product per unit volume of feedstock and does not result in the formation of cokes as a by-product.

Catalytic hydrocracking of bitumen could be very demanding of the catalyst employed. The feedstocks typically contain metals such as iron, vanadium and nickel and large concentrations of sulfur, nitrogen and oxygen. The catalyst itself should be able to perform two functions. First, it should be able to crack species of high molecular weight into smaller fragments. The second function is to catalyze the hydrogenation of these smaller, unsaturated fragments and thus prevent polymerization. The removal of heteroatoms should also be accomplished in the hydrogenation step.

The design of a hydrocracking catalyst must take into account the above functions. The most crucial aspect is the catalyst lifetime, which is critically dependent upon the rate of coke deposition. Hydrotreating catalysts, such as $Co-Mo/Al_2O_3$, were found by Ternan and Kriz[1]

to be active in the initial stages of the hydrocracking of Athabasca bitumen. However, after 50 h on stream this activity was reduced to only marginal levels. The relatively high temperatures required for cracking also led to the rapid deposition of coke.

In this paper we discuss the modification of Co-Mo/Al$_2$O$_3$ catalysts and their effectiveness in the hydrocracking of bitumen. The purpose of the work was to attempt to lower the temperature at which cracking would be significant, without adversely affecting hydrogenation ability. To accomplish this end, the alumina support has been modified by the incorporation of fluoride. This idea stems from the work of Tanabe et al[2], who have shown that fluoride ion, and various other fluorinated species, can enhance the acid catalyzed reactions of alumina dramatically. Since we began the work Massoth et al[3] have communicated preliminary results of a similar study using model compounds. For comparison we also prepared sodium-doped Co-Mo/Al$_2$O$_3$ catalysts previously shown to be more basic and therefore less reactive towards hydrocracking.

EXPERIMENTAL

Catalyst Preparation

The catalysts used in this study were prepared by spraying aqueous solutions of the appropriate species onto 1 kg of alpha-alumina monohydrate (80% Catapal SB and 20% Catapal N obtained from Continental Oil Company, Peterboro, N.J.). Cobalt and molybdenum were added as solutions of cobalt nitrate and ammonium paramolybdate respectively. Sodium
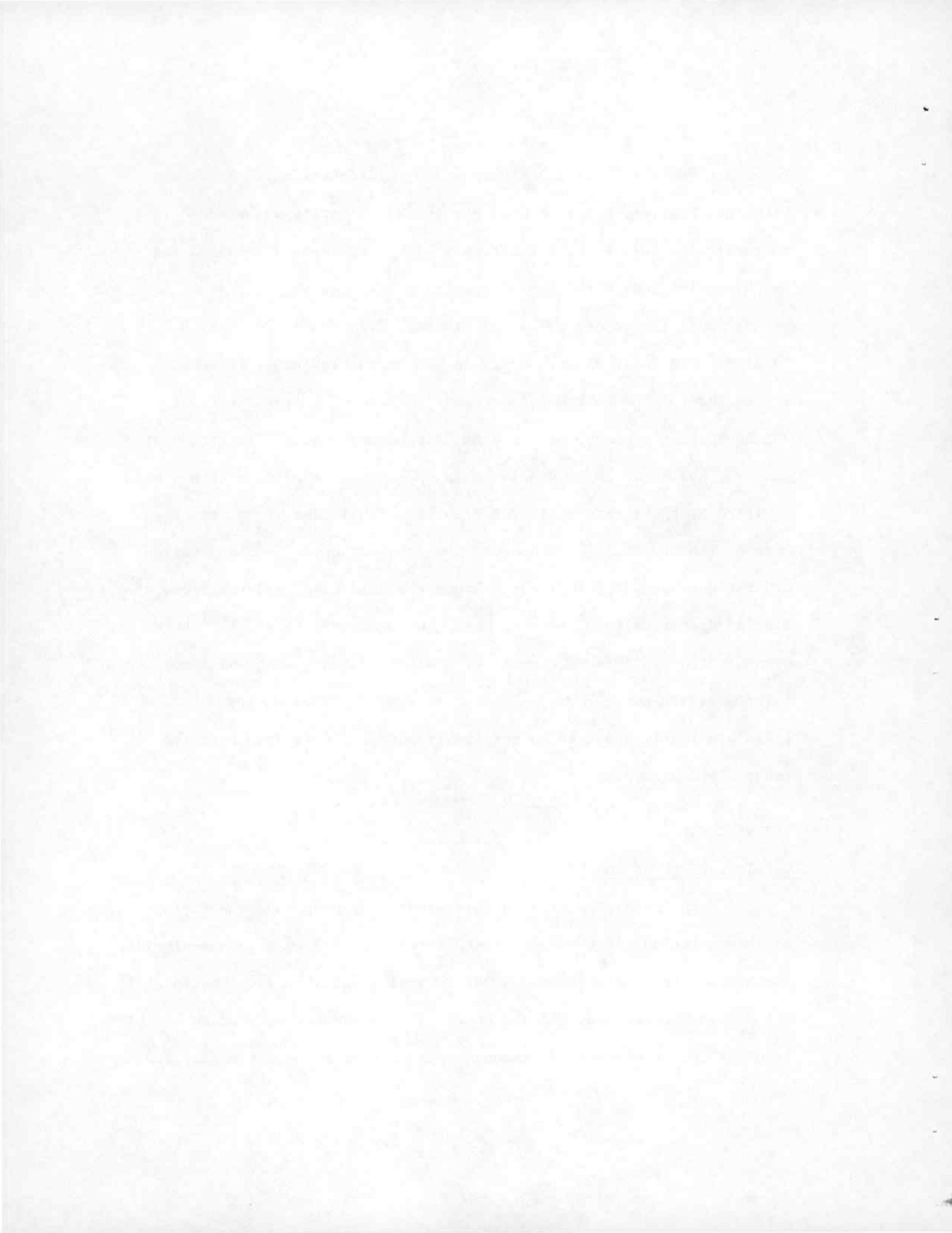
was added as sodium nitrate and fluoride as ammonium bifluoride. After thorough mechanical mixing the mulls were dried at 110°C for 6 h and then calcined at 500°C for 6 h. This procedure applies to catalysts A1, B1 and C1.

In order to test the importance of the sequence of impregnation and calcination, two further series of catalysts were made. A2 and C2 were prepared by adding the cobalt and molybdenum in the first step, followed by drying and calcining. In the second step the calcined catalysts were crushed, and then impregnated with sodium and fluoride respectively. Drying and calcining were repeated, as above. Catalysts A3 and C3 were also prepared by a two-step process in which the sodium and fluoride were added in the first step, and the cobalt and molybdenum in the second step. The drying and calcining steps were carried out after each phase of impregnation. The quantities of sodium, fluoride, cobalt and molybdenum added were calculated to give catalysts containing 3 wt % CoO, 15 wt % MoO_3 and atomic ratios of 10 Al:1Na, or 10 Al:1F respectively. The compositions of the seven catalysts, and the impregnation sequence used for each, are presented in Table I.

Catalyst Characterization

Bulk elemental analysis of catalyst C1 confirmed that the expected concentrations of Co and Mo were present. Of more importance, however, are the surface concentrations of the components of the catalyst. The catalyst exterior surface concentrations were estimated by an X-ray photoelectron spectroscopic study of the catalysts. The results are presented in Table II,

and are considered accurate to ±10%. The spectra were obtained using
a model 548 Physical Electronics X-ray photoelectron spectrometer with
an accessory specimen introduction system (PHI 2100) and multiple-tech-
nique analytical computer system (MACS). Each specimen was pressed into
a KBr-type pellet (13 mm diameter x 2 mm thick) and dried at 105°C over-
night prior to XPS analysis. A Mg anode was utilized for this study.
X-ray radiation of energy 1254 eV was directed onto an $\simeq$10 mm^2 area of
the sample. Samples were analyzed in two scanning modes: (a) initial
surveying for determining all elements present, (b) "multiplexing"
specific regions at greater resolution to obtain quantitative information.
A charge neutralizer was used to compensate for sample charging. The
carbon C(1s) signal was corrected to 284.6 eV.

Surface area measurements were carried out by the BET method
on catalysts in their oxide forms after degassing. These results
(m^2/g) are given below:

A1, 147; A2, 180; A3, 155; B1, 197; C1, 175; C2, 166; C3, 151

Catalyst Testing Procedures

The catalysts were tested in hydrocracking experiments involving
Athabasca bitumen as the feedstock. The Athabasca bitumen was obtained
from Great Canadian Oil Sands Ltd. (now Suncor) at Fort McMurray, Alberta,
and its general properties have been reported previously[4]. The catalyst
evaluation experiments were performed in a bench-scale fixed-bed reactor
system, described elsewhere[4]. The reactor had a volume of 155 ML and a
length to diameter ratio of 12. It was completely filled with catalyst,
which was in the form of particles U.S. Standard mesh sizes -5 + 30 (from
0.6 to 4 mm). The bitumen, mixed with hydrogen, was fed into the bottom

of the reactor. Catalysts were evaluated at a pressure of 13.9 MPa, and at a temperature 420°C. The liquid volumetric space velocity was 1 h^{-1} based on the total empty reactor volume. Hydrogen flow rate was set at 36.0 mL/S at S.T.P. (5000 scf/bbl). The reactor was kept at a steady state for 2 h during the liquid product collection period. Prior to the evaluation experiments each catalyst was presulfided in the presence of bitumen and hydrogen for 4 h at 420°C. The feedstock and liquid products were normally analyzed for C, H, S and N, and the relative density was measured. The results quoted are the mean values from two to four experiments.

RESULTS

Initially the catalysts A1, B1 and C1 were prepared and evaluated in the hydrocracking of bitumen at 420°C. The results of these experiments are presented in the bar graphs of Figure 1. The trend observed is that which we anticipated. The more acidic, fluoride-treated CoMo/Al$_2$O$_3$ catalyst, C1, gives the lowest sulfur content, the lowest relative density and the highest H:C ratio. Indeed its performance at this relatively low temperature is very encouraging. As expected, the sodium-treated catalyst, A1, is less effective than B1, which is the "control" catalyst in this group. In Figure 2 and Figure 3 the effect of impregnation sequence in the preparation of catalysts is examined. Surprisingly, for F-containing catalysts there is little difference in the results. The negative influence of the presence of sodium ions in the catalysts A1 and A3 is diminished significantly

when sodium is impregnated into a Co-Mo/Al$_2$O$_3$ catalyst in the second step of the preparation, in catalyst A2. This may be due, in part, to the larger surface area in A2. For both A1 and A3 the surface areas are lower than that of the "control" catalyst B1, but generally, other differences in catalyst performance could not be ascribed to surface area effects.

The performance of 5 different catalysts at relatively short times on stream is indicated in Figure 4. The data are consistently with Figure 1 in that the fluoride containing catalysts (C2 and C3) perform better than the "control" catalyst (B1) which performed better than the sodium containing catalysts (A2 and A3). When the addition of sodium or fluoride followed the calcining of alumina-molybdenum-cobalt gels (catalysts A2 and C2), rather than in the reverse order (catalysts A3 and C3), improved results were observed. In addition, catalysts A3 and C3 deactivated more rapidly than catalysts A2 and C2 as evidenced by the slopes in Figure 4 for catalysts A3 and C3 being twice as steep as for catalysts A2 and C2.

The XPS studies we have made on the unused catalysts (Table II) (i.e. oxide forms) have yielded some information on the chemical species present at the catalyst surfaces. In considering these results, however, it must be remembered that, as yet, we do not have any comparable XPS information on the catalysts in their surfided states. Subtle differences in the species of Mo present on the surface of the various oxide-form catalysts may be neutralized if upon sulfiding the Mo is converted exclusively to MoS$_2$.

Some of the XPS peaks are shown in Figure 5. The intensities of these peaks were adjusted by the computer so that the peak heights would be identical, regardless of the real signal intensity. This permits a comparison of peak positions and shapes. The real relative intensities of the peaks were related to the concentrations shown in Table 2.

Adjustments were made for sample charging. This was done by matching the C(1s) peak centers which were obtained at one half of the peak height. In all cases the C(1s) peak centers were within 0.1 eV of 284.6 eV, suggesting little difference in charging between samples. All element peak positions were adjusted so that they would be consistent with C(1s) peak centers at 284.6 eV.

Four catalysts are compared: B1, C2, C3 and a catalyst containing only alumina and fluoride. The well-performing catalysts C2 and C3 are illustrated in Figure 5. The F(1s) peaks for all three catalysts (catalyst B1 did not contain fluoride) were superimposed on one another. The aluminum (2p) peak in catalyst C3 (fluoride added before first calcining, cobalt-molybdenum added after) is at a higher finding energy than in catalyst C2 (cobalt-molybdenum added before first calcining, fluoride added after). This suggests that addition of the fluoride before the first calcining results in direct Al-F bonding interactions, and thus is responsible for the shift of the Al (2p) peak to higher binding energies. The Mo(3d)

peaks were superimposed for catalyst B1 (molybdenum-cobalt only) and
catalyst C2 (molybdenum-cobalt added   before the first calcining).
The Mo(3d) peaks for catalyst C3 (molybdenum-cobalt added **after** the
first calcining) are at lower binding energies. This shift in Mo(3d) peak
position may indicate that when the molybdenum is added after the first
calcining, it does not interact as much with   either fluoride
or alumina as when it is added before the first calcining. In contrast,
when the fluoride is added first it interacts more strongly with aluminum,
as described above, and therefore has less influence on the molybdenum
added last.

DISCUSSION

The inhibition effect of sodium on cobalt-molybdenum-alumina
catalysts has been investigated previously in our laboratory (1, 4).
Briefly, sodium can donate electrons which neutralize the desirable elec-
tron holes and electron acceptor sites in the catalyst. A more detailed
discussion will not be given here. Instead, the beneficial catalytic
effects of fluoride illustrated in Figure 1 will be considered.

The method used to prepare the fluoride containing catalysts
is also important. Figures 2 and 4 show that superior hydrodesulphuriza-
tion is obtained when the cobalt and molybdenum are added prior to the
first calcining rather than after. When cobalt and molybdenum species

are added before the first calcining they are completely mixed with the alumina gel. When they are added after the first calcining, the gamma alumina structure will have already formed. Thus, there will likely be some parts of the alumina which are topographically separated from the cobalt and molybdenum. One would expect an increase tendency for separate crystallites of molybdenum to form when cobalt and molybdenum species are added after the first calcining. This is confirmed by the Mo(3d) spectra in Figure 5. When molybdenum was added after the first calcining the Mo 3d peak is at lower binding energies which indicates less interaction with other species. Also, the molybdenum surface concentrations shown in Table II are much higher when molybdenum is added after the first calcining (A3 and C3) than when added before (A2 and C2).

This suggestion may be consistent with the data in Figure 4. When cobalt and molybdenum are added after the first calcining, both sodium and fluoride containing catalysts deactivate more rapidly. Catalyst deactivation at short times on stream has been attributed primarily to coke formation[1]. Coke tends to form on the electron acceptor sites associated with the alumina more readily than on those with the molybdenum species. As indicated above, the catalyst with separate molybdena crystallites would have more bare alumina and therefore more coke. Furthermore, if the separate crystallites sintered more readily via a surface diffusion mechanism, the rate of catalyst deactivation would be greater. In contrast when the molybdenum interacts with the alumina, surface diffusion and sintering of the molybdenum can be more difficult. If the dispersion of molybdenum on the alumina were

maintained, coke formation and catalyst deactivation would be less severe. Evidence for the simultaneous sintering of molybdena crystallites and catalyst deactivation has been reported by Pollack, Makovsky and Brown[5].

The beneficial effect of the presence of fluoride can be attributed to bond breaking or cracking reactions rather than an enhancement of the hydrodesulphurization reaction itself. Presumably some of the sulphur atoms in bitumen molecules are sterically hindered from contacting the catalyst surface. If the fluoride ions enhanced the breaking of carbon-carbon bonds, the sulphur atoms could be more accessible to the catalyst surface. This would increase hydrodesulphuriza- tion. On the other hand, enhancement of hydrodesulphurization of access- ible sulphur atoms can exhibit similar effects. Splitting of sulphur bonds with the remaining parts of molecules can result in immediate cleavage or subsequent cracking while the molecule is still at the surface. Both mechanisms would lead to molecular weight reduction.

The most popular explanation for catalytic cracking (although other explanations have been proposed) has been the carbonium ion theory, which involves proton transfer. The Bronsted acidity of a catalyst is its ability to donate a proton. For example, the maximum catalytic cracking activity of amorphous silica-alumina catalysts[6] corresponds with the maximum in Bronsted acidity[7]. On this basis the enhanced catalytic effect caused by the fluoride ion should be related to increased Bronsted acidity. The fluoride ion has almost the same ionic radius (0.133 nm) as the oxygen ion (0.132 nm). Therefore the fluoride ion could occupy
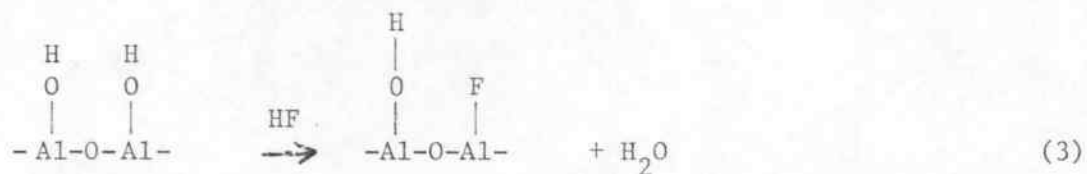
oxygen anion positions at the catalyst surface. One can imagine that the following reactions occur during catalyst preparation:

$$NH_4 HF_2 \rightarrow NH_3 + 2HF \tag{1}$$

$$OH^- \text{ (catalyst)} + HF \rightarrow H_2O + F^- \text{ (catalyst)} \tag{2}$$
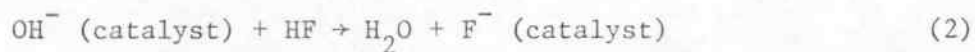
On the surface of the catalyst the reaction may occur as follows:

$$
\begin{array}{ccc}
& & & H \\
& & & | \\
H \quad H & & & O \quad F \\
O \quad O & & & | \quad | \\
| \quad | & \xrightarrow{\text{HF}} & -Al-O-Al- & + H_2O \\
-Al-O-Al- & & &
\end{array}
\tag{3}
$$

The fluoride ion is highly electronegative. Its electron attracting effect will be passed from ion to ion, thereby decreasing the hydrogen-oxygen bond strength in the OH group. This increases the Bronsted acidity and the availability of protons for cracking reactions. Equation 3 is similar to concepts used to explain the effects of SbF_5 [2].

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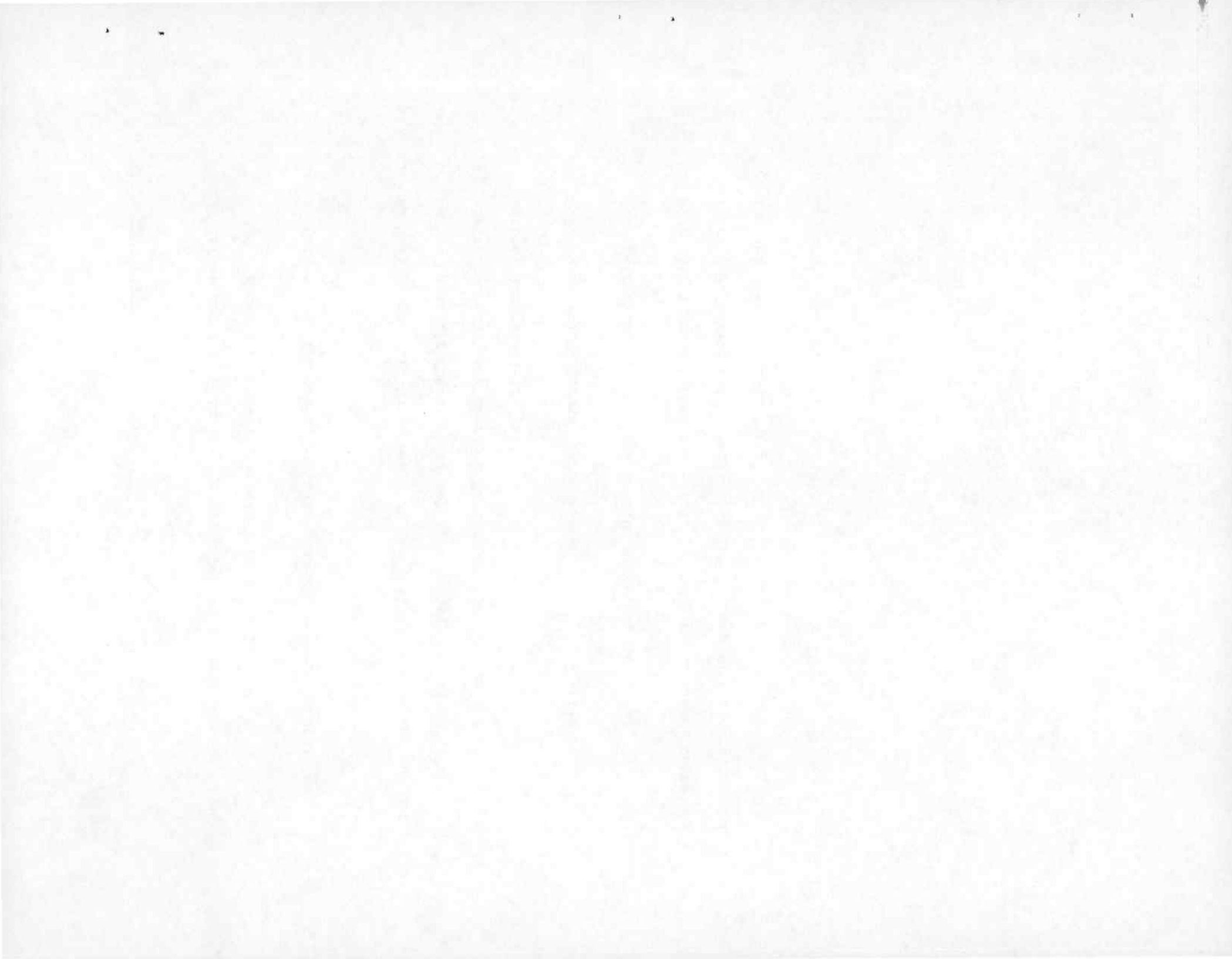
TABLE I

Description of the Catalysts Used in this Study

Catalyst Number	% CoO	% MoO₃	Element added (X) in ratio 10Al:1X	Preparation type (see text)
A1	3	15	Na	One step
A2	3	15	Na	Two steps: Co, Mo in first step; Na in last step.
A3	3	15	Na	Two steps: Na in first step; Co, Mo in last step.
B1	3	15	None	One step
C1	3	15	F	One step
C2	3	15	F	Two steps: Co, Mo in first step; F in last step.
C3	3	15	F	Two steps: F in first step; Co, Mo in second step.
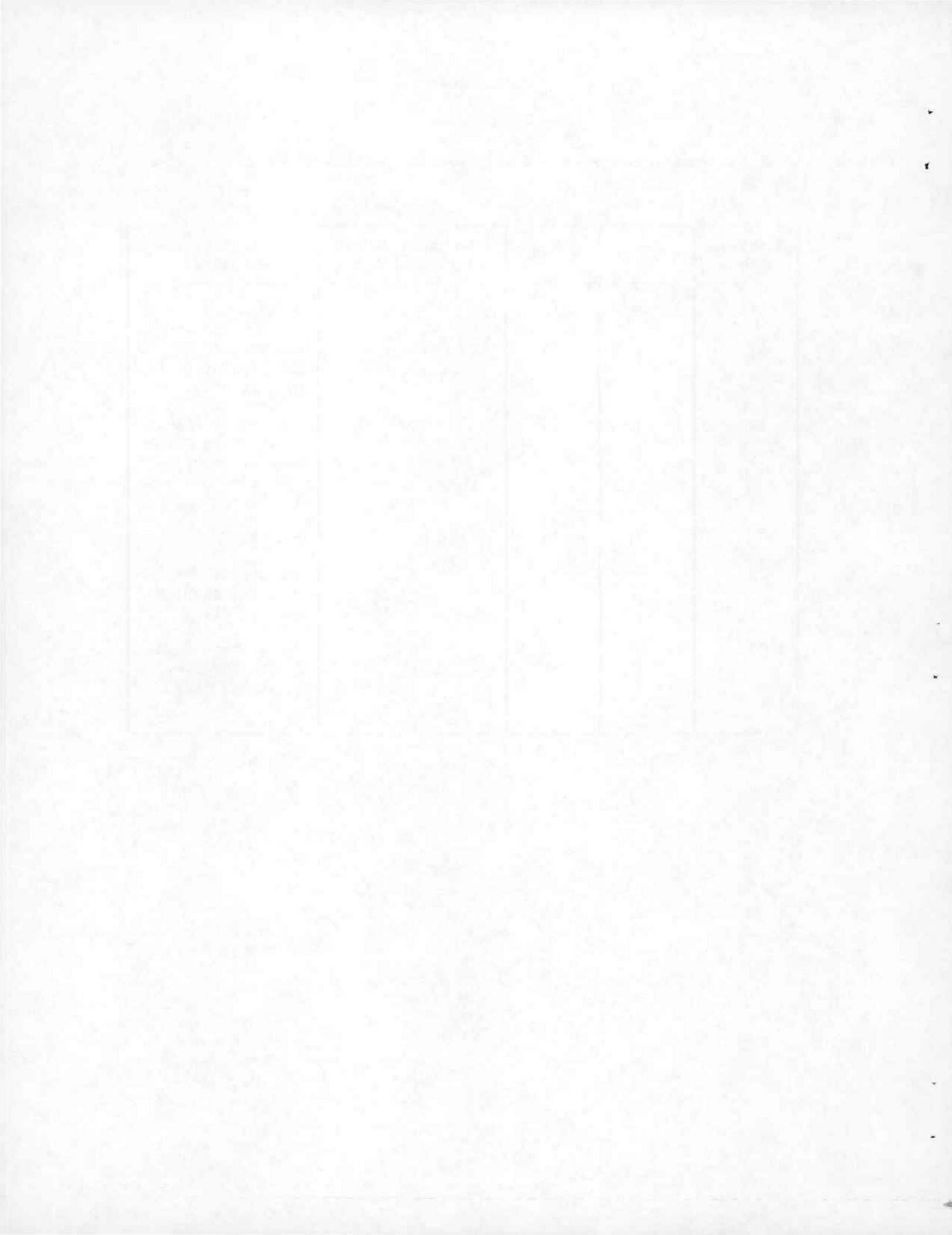
TABLE II

Surface Composition (wt %) of the Catalysts as Determined by XPS

Catalyst Number	Weight % of Element						
	O	C	Mo	Co	Al	Na	F
A1	37.3	6.4	12.3	4.3	30.4	9.3	-
A2	35.6	6.4	11.5	3.0	33.6	9.1	-
A3	33.0	7.0	16.5	6.0	28.2	10.0	-
*A3'	39.9	6.5	-	-	38.8	12.0	-
B1	41.9	7.0	15.5	3.0	32.6		
C1	39.6	3.5	11.8	2.7	39.0	-	3.4
C2	39.8	5.4	10.2	trace	39.0	-	5.6
C3	34.8	6.3	29.2	3.2	20.6	-	1.4
*C3'	42.9	5.2	-	-	46.2	-	5.7

*Intermediate after one step of the impregnation: $A3' = Al_2O_3/Na$

$C3' = Al_2O_3/F$
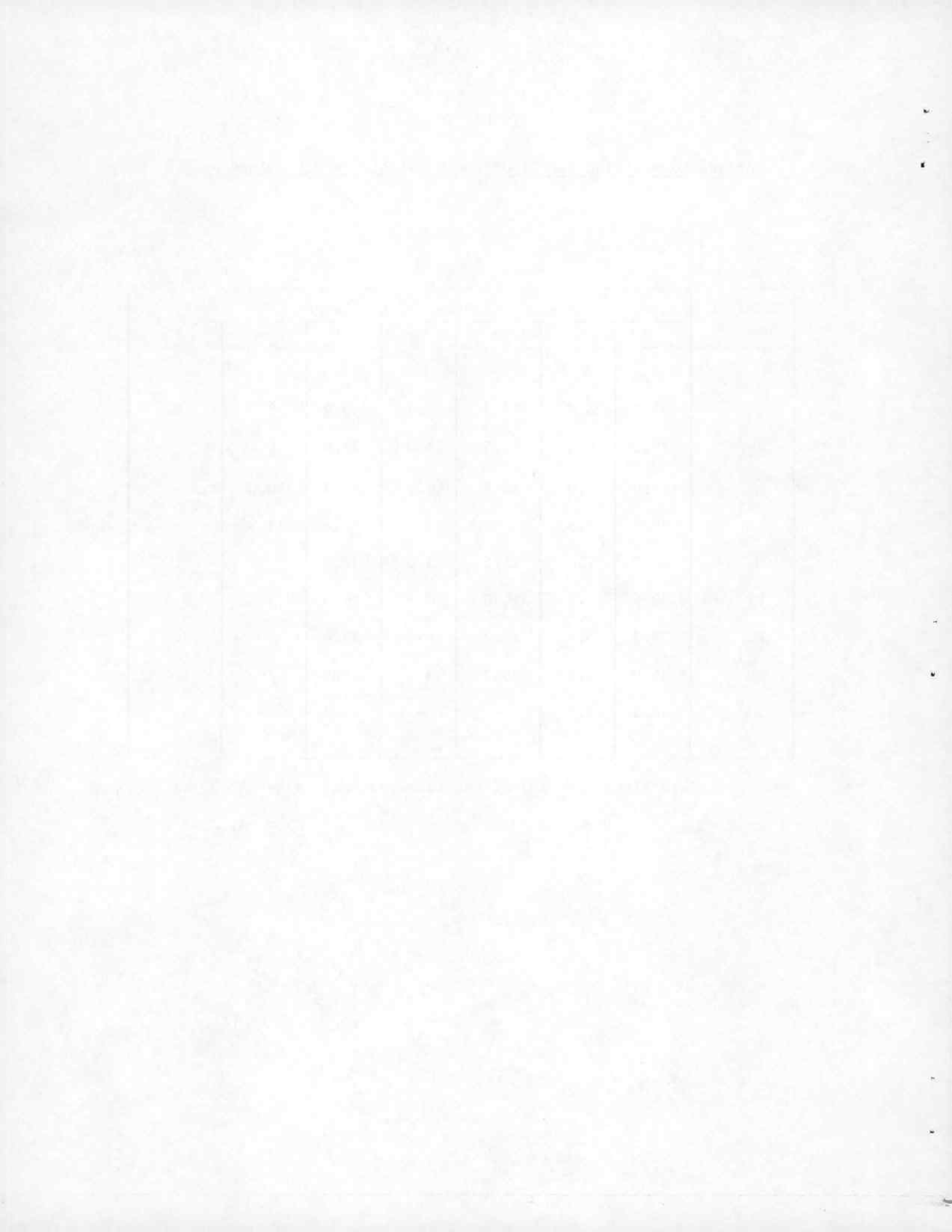
FIGURE CAPTIONS

Figure 1. Comparative Performance of Three Catalysts (Al, Bl, and Cl)
in Hydrocracking Athabasca Bitumen at 420°C. Bar 1 represents
hydrogen to carbon atomic ratio. Bar 2 represents relative
density. Bar 3 represents mass per cent sulphur in the hydro-
cracked liquid product.

Figure 2. Effects of Impregnation Sequence on Catalyst Performance:
Fluoride containing catalysts at 420°C. Bar 1 represents
hydrogen to carbon ratio. Bar 2 represents relative density.
Bar 3 represents mass per cent sulphur in the hydrocracked
liquid product.

Figure 3. Effects of Impregnation Sequence on Catalyst Performance:
Sodium Containing Catalysts at 420°C. Bar 1 represents
hydrogen to carbon atomic ratio. Bar 2 represents relative
density. Bar 3 represents mass per cent sulphur in the
hydrocracked liquid product.

Figure 4. Mass per cent Sulphur in Hydrocracked Liquid Product versus
Catalyst Time-on-Stream (h) for Catalysts Al, A2, Bl, C2 and C3.

Figure 5. X-ray Photoelectron Spectra showing the positions of the
aluminum 2p peak and the molybdenum 3d peak for catalysts C2
and C3.

Fig 1

RELATIVE   DENSITY

HYDROGEN TO CARBON
ATOMIC   RATIO

MASS   %   SULPHUR

RELATIVE DENSITY

HYDROGEN TO CARBON
ATOMIC RATIO

MASS % SULPHUR

Mo 3d

C2   C3

C3   Al 2p

C2

BINDING ENERGY eV

240 238 236 234 232 230   78 76 74 72 70

Fig 5.