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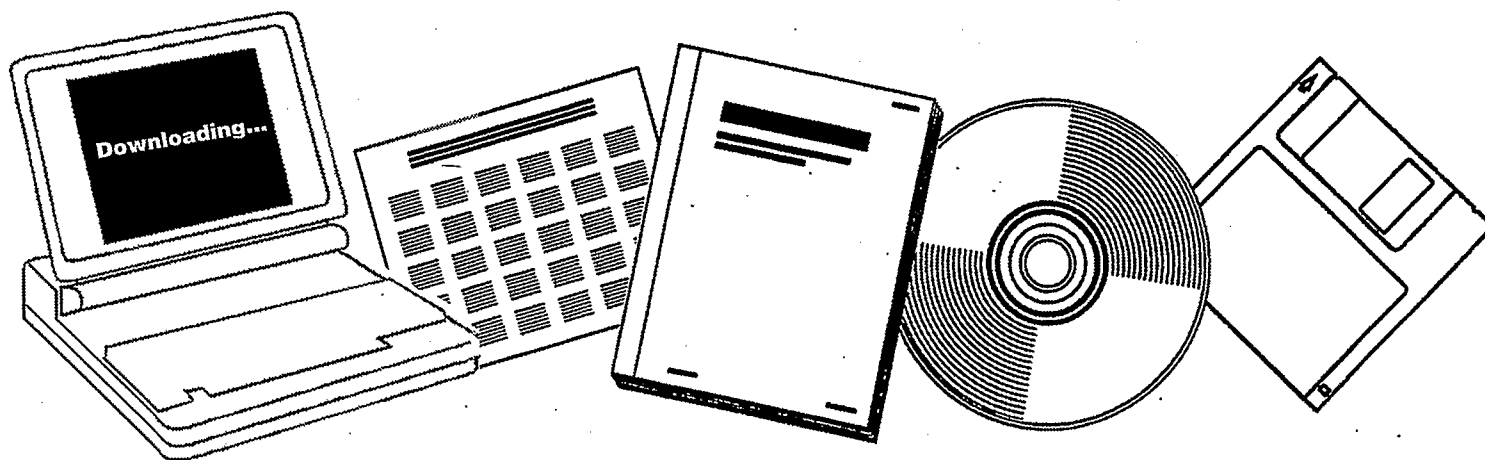
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**DESIGN OF A HIGH ACTIVITY AND SELECTIVITY
ALCOHOL CATALYST. FIFTH QUARTERLY REPORT,
AUGUST 7, 1991--NOVEMBER 7, 1991**

DELAWARE UNIV., NEWARK. CENTER FOR
CATALYTIC SCIENCE AND TECHNOLOGY

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**DESIGN OF A HIGH ACTIVITY AND
SELECTIVITY ALCOHOL CATALYST**

**Fifth Quarterly Report for Period
August 7, 1991 to November 7, 1991**

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During the first quarter of the second year of this project, continued emphasis was placed on developing a better understanding of the secondary dehydration of methanol to dimethyl ether on both the native gamma-alumina surface and our alumina-supported rhodium/molybdenum catalyst. This reaction is important since ethers as well as alcohols are considered to be and are used as octane boosters in reformulated gasoline. Hence, an understanding of the properties of our catalyst which control this chemistry is essential.

Past work in the literature [Perera and Figoli, 1969] suggests that methanol dehydration on alumina occurs via dissociative adsorption of methanol at Lewis acid sites to form surface methoxy and hydroxyl groups. As set forth in our last report, a singular potassium doping experiment has been conducted on both gamma-alumina and on our Rh/Mo catalyst wherein samples were contacted with various concentrations of KNO_3 ion-exchange solution in order to (i) replace hydrogen in surface hydroxyl groups as well as to (ii) cap off Lewis acid sites, leaving both types of sites shielded by an alkali metal oxide layer. The "capping off" of the Lewis acid sites occurs by, first, dissociatively adsorbing water at the sites, followed by ion exchanging hydrogen at the surface hydroxyl groups. The presence of the potassium, then, shields the Lewis acid sites from nucleophilic attack by methanol. In contrast to the Lewis acid sites, which interact directly with methanol, the surface hydroxyl groups are involved in closing the dehydration cycle by associating to form water molecules which desorb from the surface. Here, again, the replacement of the hydrogens at these hydroxyl sites with potassium ions impedes the dehydration. Figures 1 and 2 schematically contrast the expected interaction of methanol with the alumina surface in the absence and presence of an alkali-metal oxide layer.

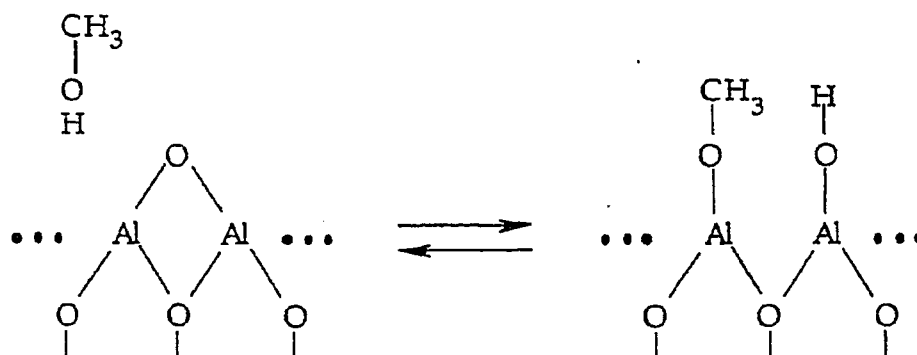


FIGURE 1. Dissociative adsorption of methanol at a Lewis acid site on alumina

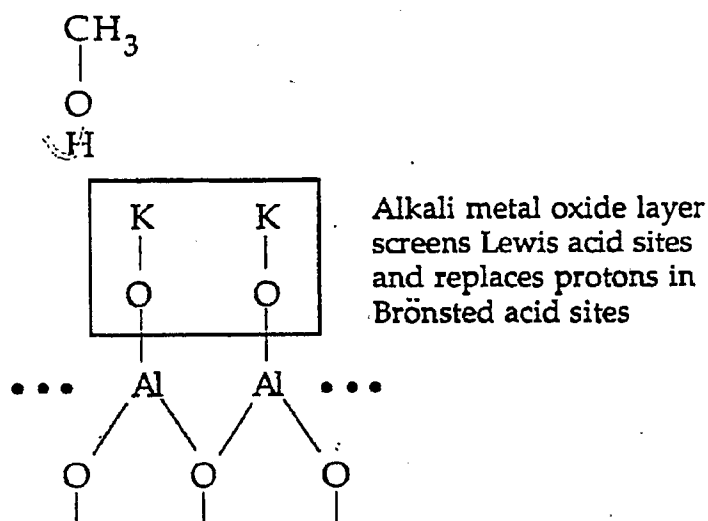


FIGURE 2. Interaction of methanol with the doped surface.

In our last quarterly report, we presented results for a series of samples of native gamma-alumina which had been contacted with increasingly concentrated KNO₃ ion-exchange solutions. These results suggested, as expected, that as the concentration of the ion-exchange solution was increased, the tendency of methanol to dehydrate to dimethyl ether under reaction conditions correspondingly decreased. These trials were conducted in our low-pressure microreactor system at 180° C and approximately atmospheric pressure. Inert helium carrier gas, flowing at approximately 50 sccm, picked up methanol vapor by passing the helium through a bubbler maintained at constant temperature, and the methanol/carrier gas mixture was then fed through a Pyrex microreactor tube packed with a fixed bed of sample. Products were analyzed downstream with our on-line gas chromatograph equipped with a flame ionization detector.

The results of similar trials conducted on our transition-metal loaded samples, again contacted with various concentrations of KNO₃ ion-exchange solutions, were not as straightforward. Representative runs for (i) a base case Rh-Mo/Al₂O₃ catalyst synthesized earlier this year and (ii) the same catalyst after contacting with a 2.3 M solution of KNO₃—estimated to contain ten K⁺ ions for every one hydroxyl group on the support surface—showed relatively the same propensity for DME formation at equivalent reaction conditions. In fact, the ion-exchanged sample produced roughly 11% more DME than the base case run, though this difference may not be statistically meaningful. Nevertheless, the above result was exactly the opposite of that expected.

Given the puzzling result above, we endeavored to evaluate the effectiveness of our ion-exchange procedures using x-ray microanalysis. Four representative energy-dispersive x-ray

spectra (EDS spectra) are attached. Due to the inherently rough morphology on these amorphous samples, this analytical technique provides only qualitative results as to elemental content under the present collection procedures. Nevertheless, the accompanying spectra differ little from those collected at various positions on the sample surface and hence provide a reasonable representation of the elemental content of the samples analyzed. Note that due to the presence of a beryllium window between the detector and the sample in the particular system used, x-ray emissions of lighter elements above the third row of the periodic table are not detected (hence the oxygen in the alumina is not fingerprinted by this process). Spectrum 1, bare gamma-alumina, displays the characteristic K_{α} x-ray emission for aluminum at 1.490 keV. The presence of the peak for gold is a remnant of the sample preparation, wherein the sample is sputtered with gold to reduce charge-cloud formation upon electron bombardment in the scanning electron microscope used to position the sample for x-ray analysis. Spectrum 2 depicts the alumina after treatment with ion-exchange solution and shows a characteristic peak for the K valence shell of potassium indicating that the ion-exchange procedure was successful in depositing potassium on the surface. The result depicted in Spectra 1 and 2 differs significantly from that demonstrated by the other two spectra. Spectrum 3, base case Rh-Mo/ Al_2O_3 without ion exchange, confirms the presence of Rh and Mo on the support surface; the small Si peak is most likely due to impurities introduced in the alumina during its initial formation. Spectrum 4, which depicts the same material after it has been contacted with ion-exchange solution for 36 hours, has a label indicating where a potassium peak should appear, but the potassium emission is absent. Note that the samples depicted in Spectra 2 and 4 were subjected to identical ion-exchange treatment, but in the case of the transition-metal loaded sample (Spectrum 4), no significant indication of potassium doping is seen. This result, then, is consistent with the reactor testing results mentioned above. Namely, no change in methanol dehydration was observed because the Lewis acid sites had not been modified.

The results for the transition-metal loaded samples dictate the need for a new ion-exchange procedure, and these experiments will be the focus of our near-term work. Thus far, samples were immersed in the ion-exchange solution for 36 hours at room temperature and then dried for 24 hours at 120° C. Future efforts to improve on this procedure will take two forms: (i) ion-exchange will be conducted instead by pore volume saturation of the sample to incipient wetness (rather than immersion) and then dried as above and (ii) the sample immersion approach will be repeated, but an effort will be made to maintain the ion-exchange solution above the isoelectric point of the gamma-alumina surface using a combination of a pH meter and the addition of KOH to the ion-exchange supernatant.

In addition to suggesting the need for a new ion-exchange procedure, an encouraging aspect of the metal-loaded results is that they shed some light on the role of Lewis acid sites in the sequential chemisorption of the Mo and Rh carbonyls on the alumina during initial catalyst

preparation. It is possible that the Mo and Rh precursors react with surface acid sites during deposition of Mo and Rh and reduce the number of acid sites which would otherwise be available for dissociative adsorption of water and potassium ion exchange. Figure 3 schematically demonstrates one possible route for oxidative chemisorption of metal carbonyls using Mo(CO)_6 as a representative precursor. Why these transition-metal oxide sites would not also shield the surface from nucleophilic attack by methanol remains to be seen, though they may form alkoxide ligands with the methoxy groups directly under reaction conditions and hence allow DME formation via a separate mechanism. In the coming months, we intend to explore these ideas further in light of future ion-exchange results.

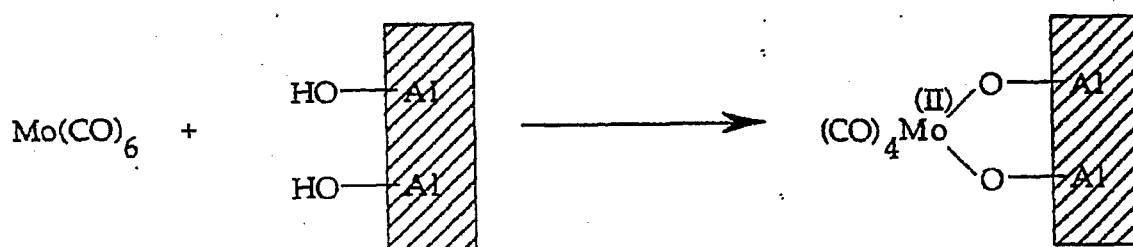


FIGURE 3. Oxidative adsorption of molybdenum hexacarbonyl at adjacent Brønsted acid sites.

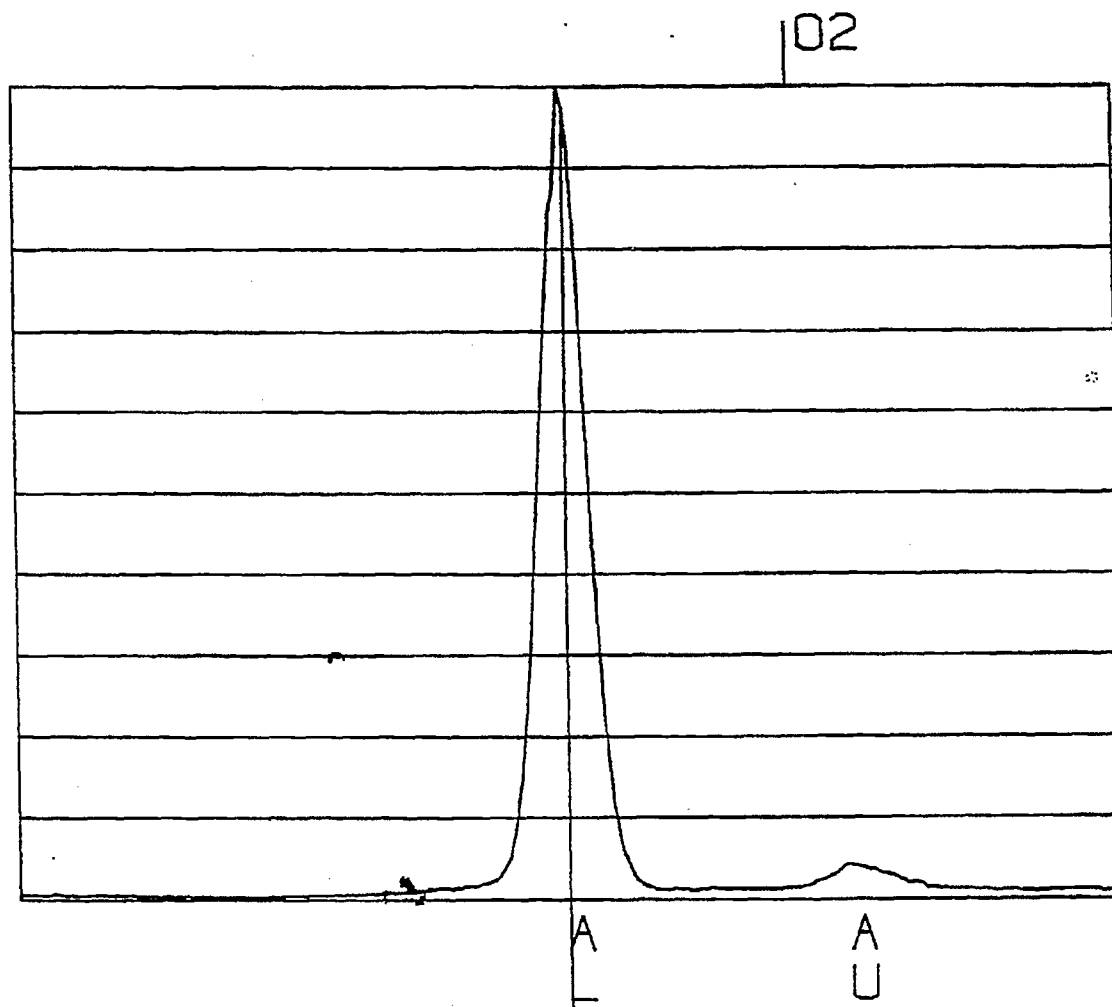
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RATE: CPS TIME 83LSEC

00-20KEV: 10EV/CH PRST: 100CSEC

A: G-AL203 B:

FS= 9438 MEM: A FS= 200



CURSOR (KEV) = 01.490

EDAX

SPECTRUM 1.
Bare gamma-alumina, no ion exchange.

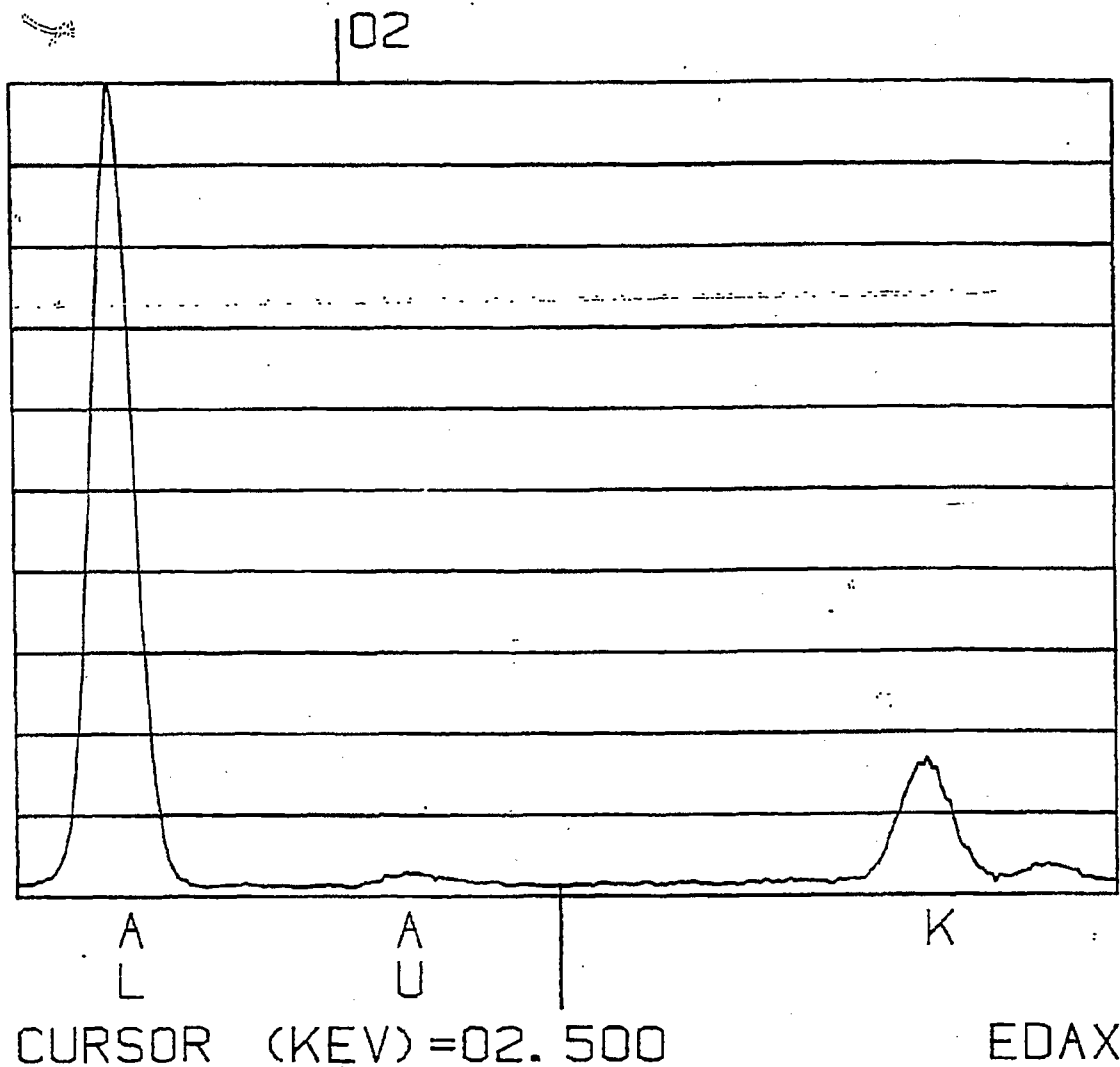
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RATE: CPS TIME 82LSEC

00-20KEV: 10EV/CH PRST: 100CSEC

A: CASE3, RUN3 B:

FS= 6776 MEM: A FS= 200



Spectrum 2.

Gamma-alumina after ion exchange with a 2.3 M KNO_3 solution.

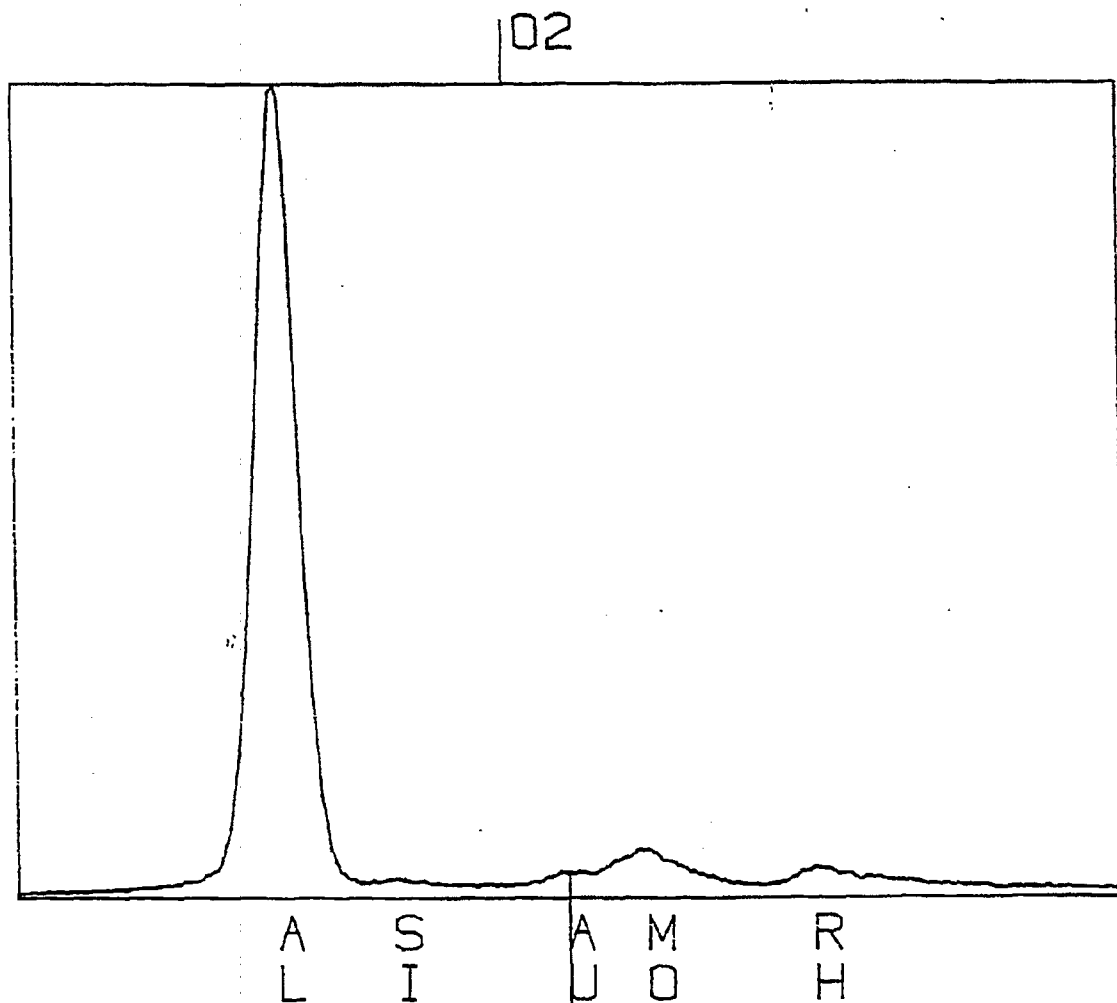
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RATE: CPS TIME 100LSEC

00-20KEV: 10EV/CH PRST: 100CSEC

A: BT2R2: RH/MO/ALB:

FS= 12150 MEM: A FS= 200



CURSOR (KEV) = 02.140

EDAX

Spectrum 3.
Rh-Mo/ Al_2O_3 sample, no ion exchange.

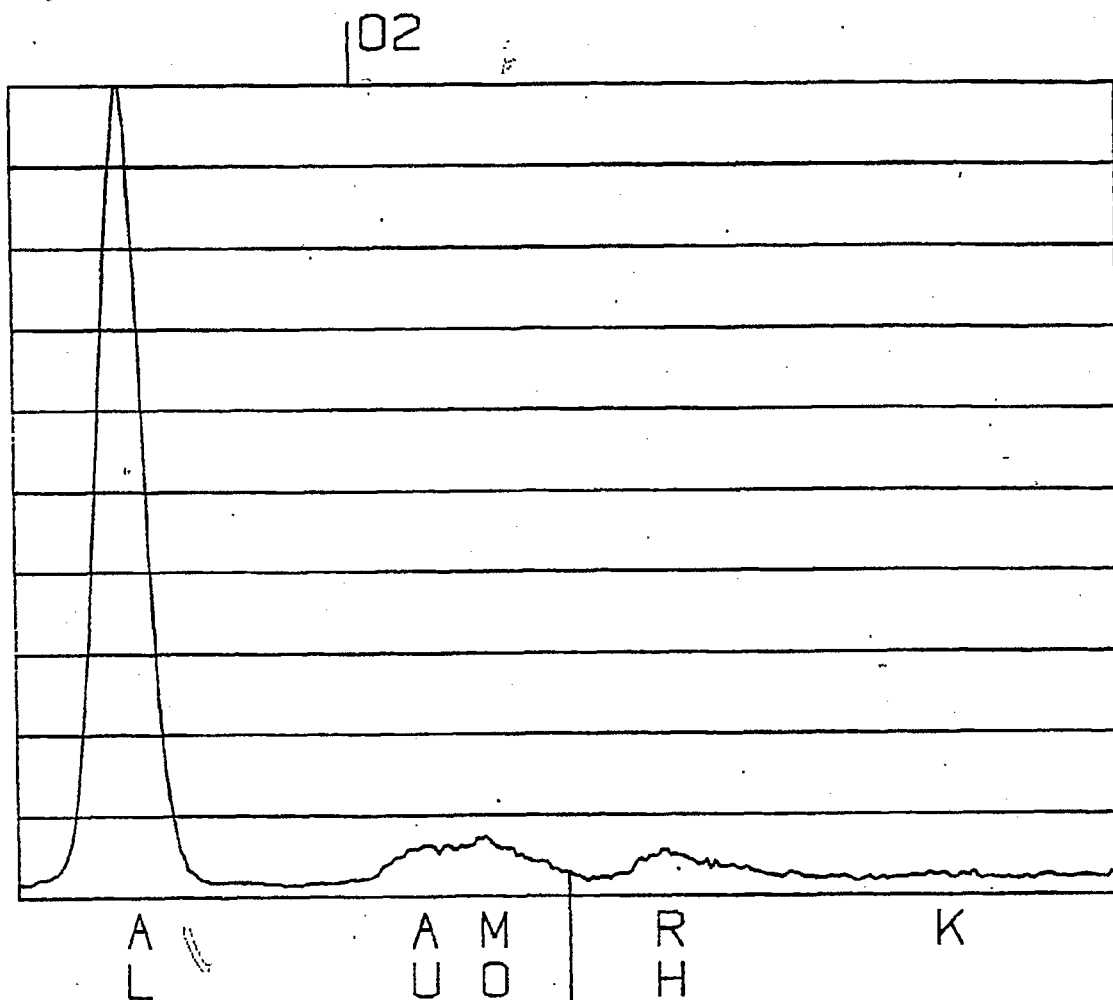
30-OCT-91 13:56:08

RATE: CPS TIME 80LSEC

00-20KEV: 10EV/CH PRST: 100CSEC

A: CASE3A: S2, R2 B:

FS= 5413 MEM: A FS= 200



CURSOR (KEV) = 02.490

EDAX

Spectrum 4.

Rh-Mo/ Al_2O_3 sample after ion exchange with a 2.3 M KNO_3 solution.

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