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PROGRESS REPORT

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INTRODUCTION

In the work done so far, we have examined the properties of adsorbents prepared by the novel method of depositing a layer of the precursor (metal acetylacetonates) on the alumina surface. These samples were activated by decomposing the precursors to their oxides. It was possible to obtain a fairly predictable trend in the SO_2 adsorption properties of the adsorbents as long as the metal acacs did not dissociate in solution. This was observed in the case of the magnesium supported samples. Lithium supported samples exhibited a high SO_2 pickup rate at low metal loadings on alumina but the incremental SO_2 pickup was poor; one explanation for this observation is the dissociation of Li(acac) prior to its adsorption on alumina from the solution. We decided to investigate the properties of adsorbents prepared by **aqueous** impregnation to investigate the virtues of non-ionizing vs. ionizing precursors.

We also carried out infrared investigations of the supported lithium precursor, in an attempt to determine the nature of this material. Conductivity analyses, presented in earlier reports, suggest that the Li(acac) ionizes in methanol solution. Elemental analyses, also presented in earlier reports, indicate a carbon/lithium ratio of 1.6 for the supported precursor, much less than the value of 5 expected from the precursor stoichiometry. Based on our earlier success using infrared spectroscopy for characterization of the magnesium and copper precursors, we decided to investigate the nature of the supported lithium complex using the same technique.

EXPERIMENTAL

MAGNESIUM IMPREGNATED SAMPLES

Preparation of magnesium supported samples by the aqueous method.

Magnesium acetate was used as the precursor because it is very soluble in water and the organic anion is readily decomposed. Samples were prepared by the following procedure:

> A measured quantity of $Mg(CH3CO_2)_2 \cdot 4H_2O$ was dissolved in 50 ml of de-ionized water and the solution is added to a beaker containing 10 grams of Al_2O_3 in 250 ml of water. The mixture was well stirred for about 24 hours to allow for the deposition of the magnesium on the surface of alumina. The beaker was then heated slowly to remove the solvent. A cake was left in the beaker and it was subsequently dried using a vacuum oven to remove any traces of solvent. Samples of different weight loadings were prepared using this technique.

The samples were analyzed for metal, carbon, and hydrogen content by Applied Technical Services of Marietta, GA.

RESULTS

$Mg(CH_3CO_2)_2$ Aqueous Impregnation.

The dashed line in Figure 1 shows the results of the carbon and magnesium analyses from the impregnated alumina. The impregnation solutions contained 110 to 440 μmol of Mg/g of Al_2O_3, and the line that would have been obtained had all the magnesium ended up on the support, with its associated acetate ligand, is shown as the solid line in Figure 1. The analyzed samples show a metal loading of only 20 to 230 μmol Mg/g Al_2O_3. This observation is difficult to explain at this moment as the preparation technique involved only the removal of the solvent by evaporation. The weight loadings of the four samples prepared from Mg acetate by the aqueous method (hence named MgAq#) are found in Table 1.

Table 1. Measured magnesium concentration for various sorbent formulations.

SAMPLE	MEASURED Mg CONENTRATION
MgAq1	16.46 μmol/g Al_2O_3
MgAq2	123.43 μmol/g Al_2O_3
MgAq3	226.29 μmol/g Al_2O_3
MgAq4	218.06 μmol/g Al_2O_3

The samples apparently contained excess carbon. When the line is extrapolated to zero μmol of Mg ion, a non-zero concentration is found for carbon. Also, the slope of the line is greater than 4, implying that the incremental incorporation of Mg was greater than what was expected from the stoichiometry of the parent complex. It is clear that the acetate complex dissociates in water, but the fate of the residual Mg is not clear.

The samples were subjected to a cycle of adsorption and desorption steps similar to the method followed for the earlier samples prepared from acetylacetonates. The samples were decomposed to the oxide by heating in a stream of oxygen and nitrogen (80% Oxygen and 20% Nitrogen) and heating the sample to 500°C. SO_2 was passed over the adsorbent for 20 min. in a stream of air (SO_2 1100 ppm., balance a 71% N_2 and 29% O_2 mixture.) The weight change, temperature and the first derivative were recorded as described earlier. These steps were conducted four times (five in the case of MgAq3) to determine the reproducibility of the results. Figures 2.1-2.4 show the results of the sorption studies. The X-axis is the step number; all odd numbers correspond to adsorption steps and the even numbers correspond to desorption steps. The Y-axis is the percentage weight change in a particular step.

The results of the adsorption studies are summarized and shown along with the earlier data in Figure 3.

LITHIUM IMPREGNATED SAMPLES

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the supported Li(acac) complex and the pure complex are shown in Figure 4 over the frequency range which is characteristic for the acetylacetonate ligand. The spectra are only useful for qualitative purposes, but clearly indicate the presence of the same material in the four impregnated alumina samples.

DISCUSSION

MAGNESIUM IMPREGNATED SAMPLES

Unlike the magnesium samples prepared from $Mg(acac)_2$, these samples produced very random results. The bar graphs in Fig. 2 show the different behavior of various samples during sorption cycles. Samples MgAq4 and MgAq1 exhibited repetitive results after the first cycle. But, MgAq3 shows a 'decay' in the percentage of weight change. This 'decay' may be a result of sulfate formation or a manifestation of the poor distribution of the metal ion on the surface of alumina. From our earlier work with the acacs, we have concluded that the behavior of the metal to adsorption is strongly dependent on the ability of the precursor to remain undissociated. It is for this reason that magnesium gave us results close to the theoretical values whereas lithium was far from the theoretical values but some of the molecules maintained their original structure and there is a correlation between the different data points although it is only 12% of the theoretical value. The SO_2 adsorption appears to show some variation over MgO/Al_2O_3 prepared from the acetate; e.g. consider the results for a Mg loading between 210 and 225 μmol Mg/g of Al_2O_3. The SO_2 pickup varies between 200 and 430 μmol SO_2/g Al_2O_3. As another example of this unusual variation in the SO_2 pickup, consider the sample with a magnesium loading of 16 and 123 μmol Mg/g Al_2O_3. The sample with the smaller weight loading (16 μmol) shows a higher SO_2 pickup (364 vs. 260 μmol SO_2/g Al_2O_3 for the higher loading sample). This implies that the adsorption phenomena for the aqueous samples cannot be explained solely by the factors that govern the adsorption on the supported adsorbents prepared from metal acetylacetonates. We believe that other factors may be governing the SO_2 adsorption properties of the aqueous samples. Perhaps the micro-porosity varies in the samples prepared from magnesium acetate. One possible explanation is that the large crystallites of MgO are formed which block the pores on the alumina surface.

Surface area analysis and the pore size distribution of some of the aqueous samples will be conducted to examine the surface characteristics of these samples in order to explain some of the observations mentioned earlier.

LITHIUM IMPREGNATED SAMPLES

As mentioned in the introduction and described in earlier reports, the precursor being used for the lithium impregnation, lithium acetylacetonate, ionizes significantly in methanol solution. Also, the apparent ratio between carbon and lithium on the surface was too low for the lithium to be accounted for solely by the lithium acetylacetonate. The measured ratio of C/Li on the

surface was 1.6, the expected ratio is 5. We investigated the infrared of the supported material to determine the nature of the supported species, and to examine the signature bands due to the acetylacetonate ligand.

As can be seen from Figure 4, there is apparently some acetylacetonate on the surface of the alumina. The spectra are not quantitative, but from these results it appears that the acetylacetonate ligand is the only species absorbing in the spectral region presented. Carbonate species would absorb in this region, but no bands due to carbonate are seen. It is not certain that the acetylacetonate is bound to the lithium and, given the conductivity results indicating dissociation in solution, the bands observed are likely due to a combination of lithium acetylacetonate and an aluminum-containing acetylacetonate species. It is possible that some of the lithium simply ion-exchanged with surface protons, forming surface Al-O-Li groups and neutral pentanedione in solution. This process would create a surface with an apparent excess of lithium, and is probably the most likely mechanism to yield this result. It is also possible that an $Al(acac)_3$ is created which would then go into solution and effectively remove carbon from the surface. However, this is thought to be much less likely.

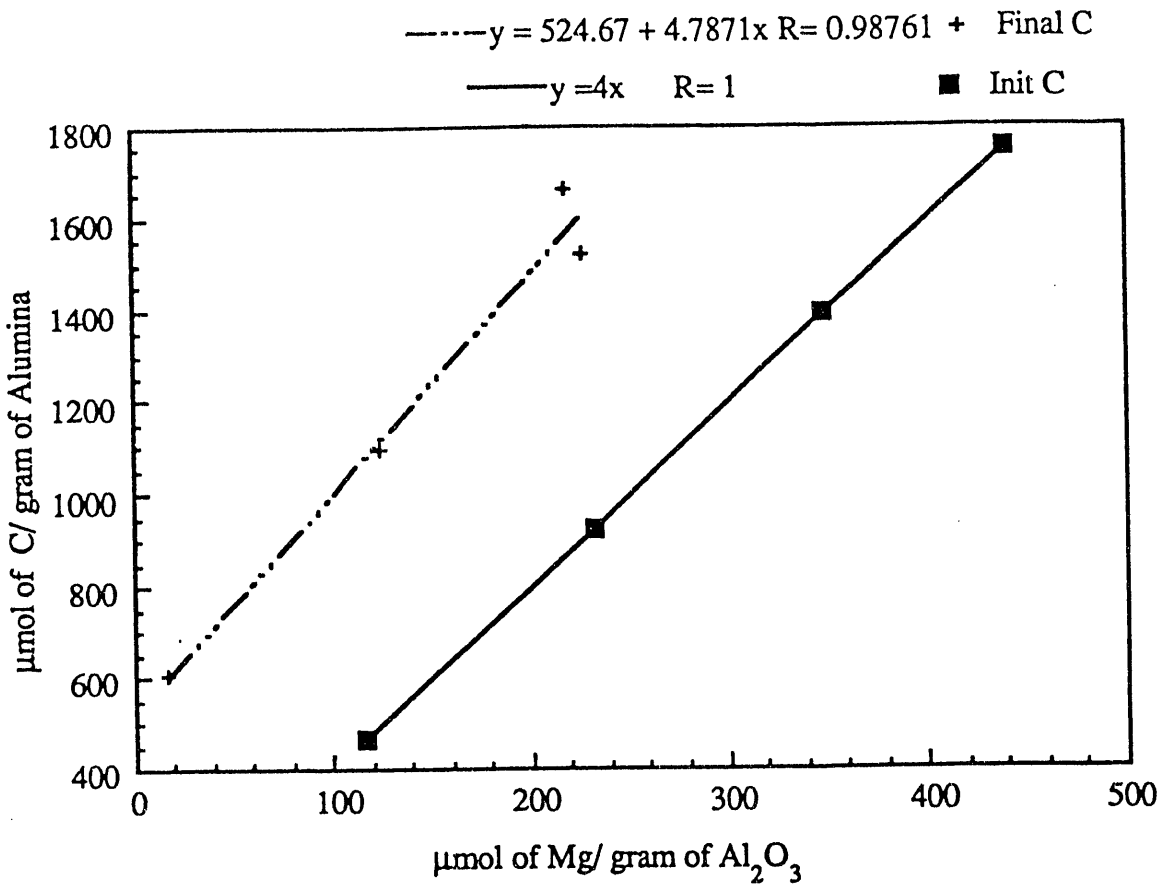

Figure 1. Graph of observed and predicted carbon vs magnesium ratios for the impregnated alumina samples.

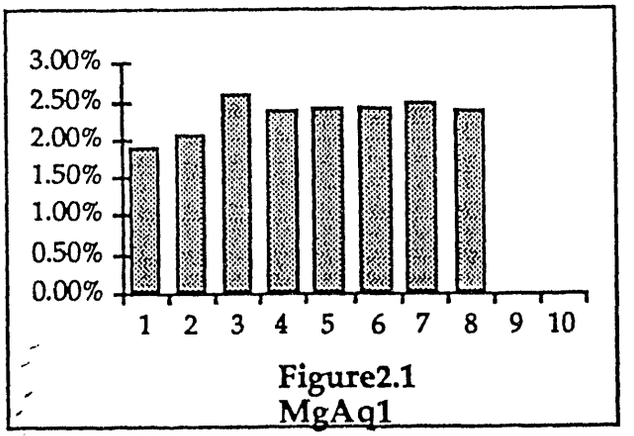

Figure2.1
MgAq1

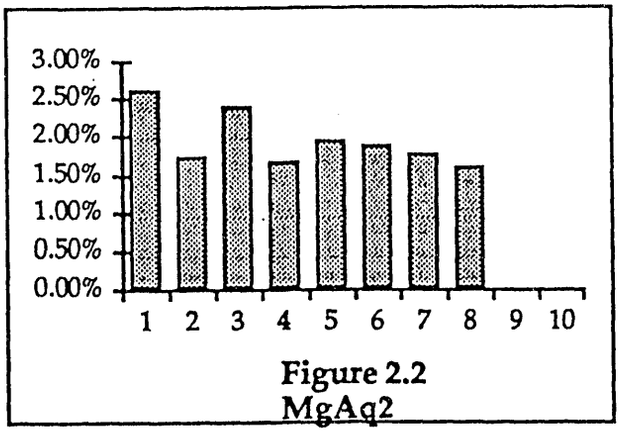

Figure 2.2
MgAq2

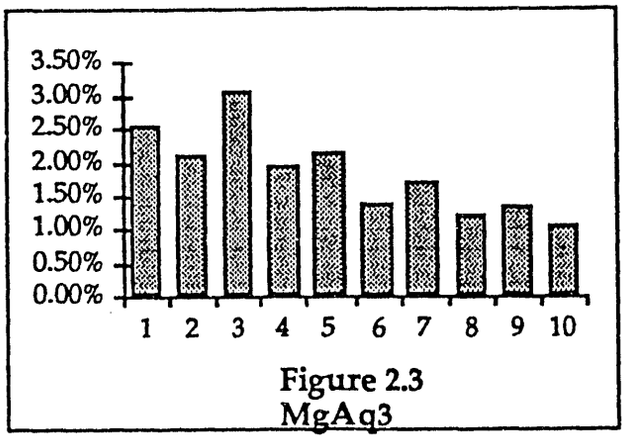

Figure 2.3
MgAq3

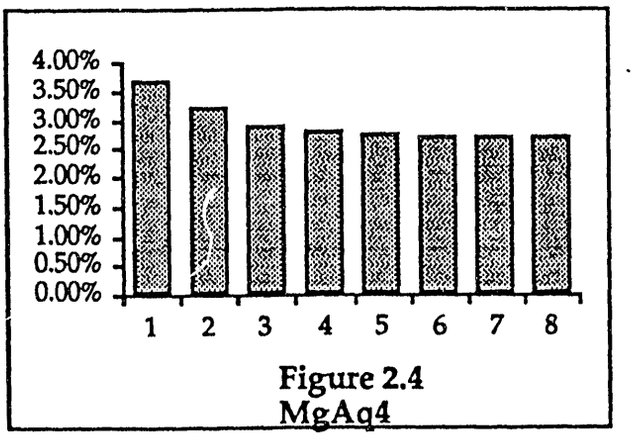

Figure 2.4
MgAq4

Figure 2. Bar graphs of the SO_2 adsorption/desorption amounts for different magnesium weight loadings. The odd numbers along the X-axis refer to adsorption steps, the even numbers refer to desorption steps. The Y-axis refers to percent weight change.

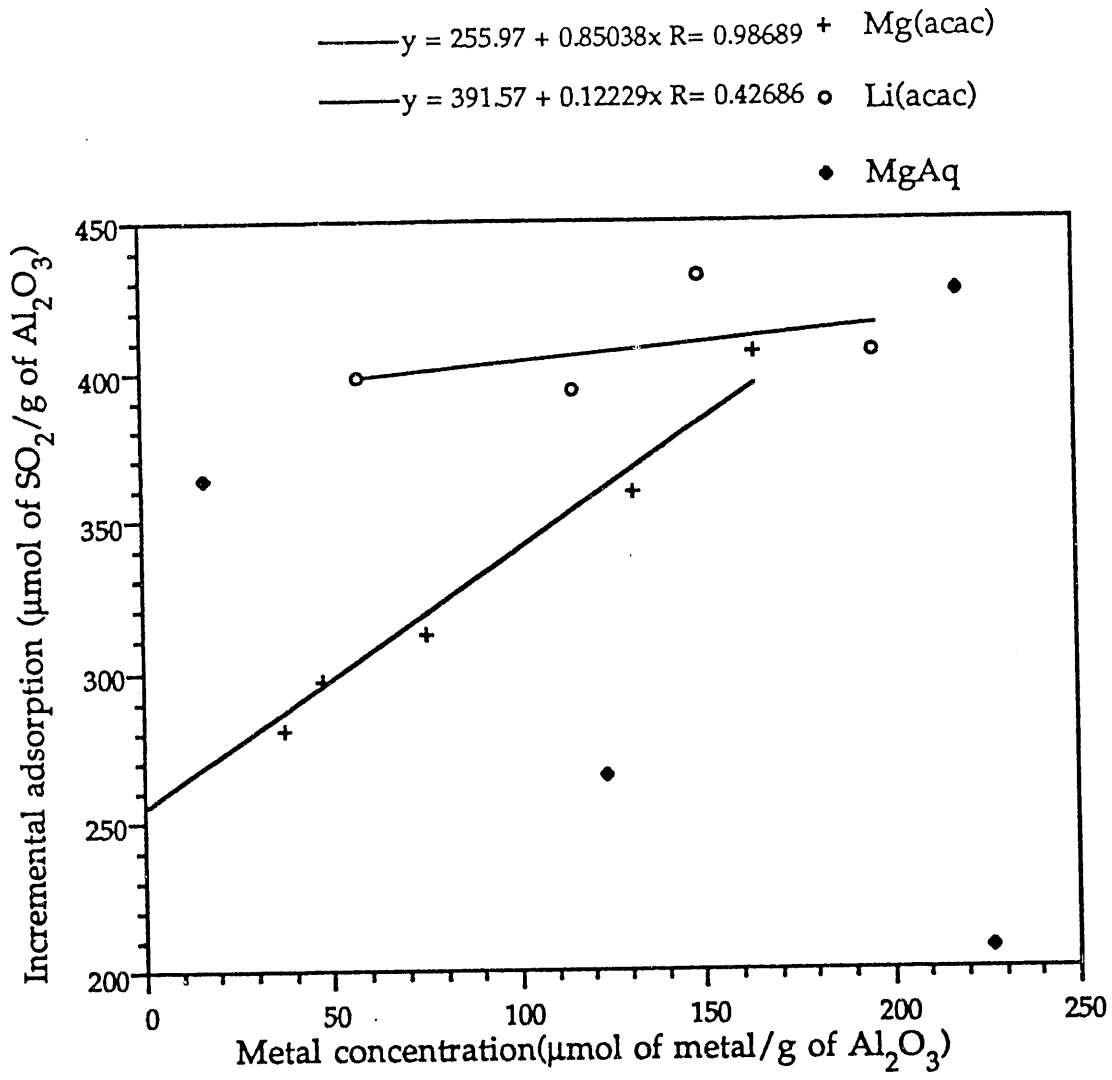

Figure 3. Results of the SO_2 Adsorption/Desorption studies.

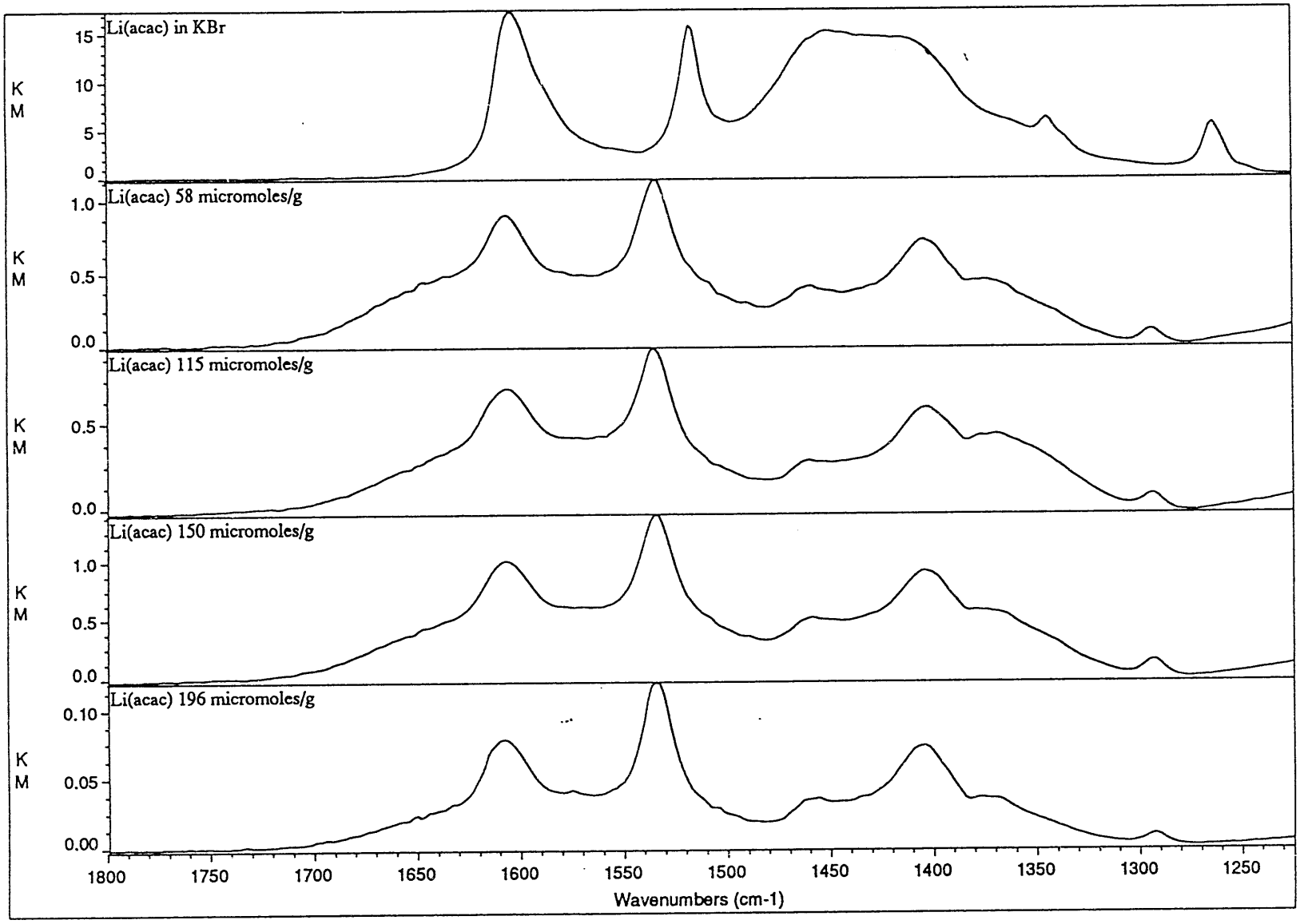

Figure 4. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of pure lithium acetylacetonate and four different loadings of lithium acetylacetonate on alumina. The spectra are, from top to bottom, pure lithium acetylacetonate, 58 μmol Li/ g of Al_2O_3, 115 μmol Li/ g of Al_2O_3, 150 μmol Li/ g of Al_2O_3, and 196 μmol Li/ g of Al_2O_3. The vertical axis scale is Kubelka-Munk units.

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