

PROGRESS REPORT

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INTRODUCTION

This report describes our efforts to determine the ability of the lithium-promoted alumina samples to adsorb SO_2 . By comparing these results with our previous results for the Mg-impregnated system, we will be able to begin determining the relative efficiencies of group IA vs group IIA metals with regard to their ability to promote SO_2 adsorption on alumina. We have conducted x-ray diffraction studies on our $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ -impregnated alumina, with the goal of measuring the dispersion of the precursor on the alumina surface.

RESULTS

SO_2 Adsorption on Lithium-Promoted Alumina.

Samples of lithium acetylacetonate [$\text{Li}(\text{acac})$] on alumina were thermally decomposed prior to their use as an adsorbent. The procedure adopted was similar to that followed for the Mg-impregnated alumina samples discussed in the last progress report. The sample was heated in an atmosphere of 20% oxygen and 80% nitrogen, flowing at $150 \text{ cm}^3/\text{min}$, in the TGA from 20°C to 550°C at the rate of $15^\circ\text{C}/\text{min}$ and held at 550°C for one minute. The sample was then cooled to 20°C . A maximum temperature of 500°C was found sufficient in the case of $\text{Li}(\text{acac})$ to complete the decomposition, in contrast to the temperature of 550°C required for complete decomposition of the magnesium precursor on alumina. The weight and temperature of the sample were recorded simultaneously as a function of time.

The SO_2 adsorption was carried out in a gas stream flowing at $150 \text{ cm}^3/\text{min}$ consisting of the following mixture: 1100ppm SO_2 , 20% O_2 , balance N_2 . The samples were exposed to this mixture for 15 minutes and then purged in nitrogen ($150 \text{ cm}^3/\text{min}$) for 20 minutes.

The desorption cycles involved heating the samples from 20°C to 500°C at the rate of $20^\circ\text{C}/\text{min}$ in a nitrogen atmosphere flowing at $150 \text{ cm}^3/\text{min}$, and then cooling the samples to 20°C . Each sample was subjected to four continuous cycles; each cycle comprising an adsorption step and a desorption step. The results of these experiments are shown in Figure 1, along with results presented earlier for magnesium-promoted alumina.

For the same concentration of metal on the surface of alumina, lithium is a more effective promoter for SO_2 adsorption than is magnesium, at least at lower loadings. This may be attributed to the higher basicity of the lithium compared to magnesium. The strongly basic Li^+ ion has a greater affinity for the acidic SO_2 than does the Mg^{2+} ion. The lithium-promoted aluminas have a lower incremental SO_2 pickup compared to the magnesium-promoted samples. Initial impregnation of alumina with the lithium precursor resulted in a dramatic increase in SO_2 adsorption efficiency, compared to bare alumina, with little additional uptake resulting from higher loadings. One explanation for this result could be the poorly dispersed state of lithium on the surface of the alumina. As reported earlier (Annual Report 91-92), $\text{Li}(\text{acac})$ dissociates to a certain extent in methanol. It is possible that the dissociation could result in poor dispersion of lithium on the surface resulting in the formation of ensembles of lithium on the surface. More work is necessary to investigate the dispersion of lithium on the surface and the effect of this dispersion on the SO_2 adsorption capacity.

X-Ray Diffraction Studies.

Our previous studies have yielded ambiguous results with regard to the dispersion of the magnesium promoter on the surface. Infrared results seemed to indicate that initially, the precursor was present on the surface as small crystallites of the anhydrous form of $\text{Mg}(\text{acac})_2$. These crystallites appeared to melt on heating to high temperature (550°C) to form something close to a single layer. We decided to use powder x-ray diffraction to investigate the alumina-supported $\text{Mg}(\text{acac})_2$ to see if we could determine the nature of the supported precursor.

Powder x-ray diffraction spectra were obtained for alumina, $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, and an impregnated alumina with a high loading of the precursor (determined by atomic absorption for magnesium). A physical mixture of $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ (0.82 wt/wt% Mg) and alumina was also examined. This latter sample was examined in order to investigate the sensitivity of the technique. The spectra are shown in Figures 2 - 5.

The absence of any peaks in the spectrum for alumina (Figure 2) is an indication of its amorphous structure. Figure 3 shows the spectrum for the pure precursor, $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$. The presence of the prominent peaks is an indication of its crystalline structure.

The x-ray diffraction spectrum of the highest weight loading of the precursor on the alumina that we were able to obtain (using the Soxhlet extraction device), $164 \mu\text{mol}$ precursor/g Al_2O_3 , is shown in Figure 4. Its spectrum displays only the diffuse features observed in the alumina spectrum but none of the peaks that were present in the spectrum of the pure precursor, Figure 3. The spectrum of the physical mixture is shown in Figure 5. This spectrum exhibits the highest intensity peaks found in the spectrum of the pure precursor, and indicates that it is possible to detect crystals of the precursor mixed in amorphous alumina even at low loadings. Comparison of this result with the x-ray spectrum of the supported precursor must be carried out with some care, since the size of the crystals in the physical mixture could easily be orders of magnitude larger than any present on the alumina surface. This would clearly have a significant impact on the sensitivity of the x-ray experiment for the supported precursor.

CONCLUSIONS

Lithium can be used with good effectiveness as a promoter for SO_2 adsorption on alumina due to its high basicity. The difficulty of depositing a layer on the surface of alumina must be overcome to achieve this goal.

The x-ray diffraction studies indicate that the Mg precursor is well-dispersed on the alumina surface, and that the crystals formed, if any, are too small to be detected by the diffractometer. Further work must be done on the lithium-promoted samples to examine the dispersion on alumina.

FUTURE WORK

We plan to examine loadings of lithium on alumina less than the lowest value shown in Figure 1. At low lithium loadings, the uptake of SO_2 must approach that of bare alumina, measured by us to be $264 \mu\text{mol SO}_2/\text{g Al}_2\text{O}_3$. This is clearly not the value one obtains by using the line generated from the present lithium samples and determining the intercept at zero lithium. Information regarding this low loading behavior will be invaluable in the determination of the mechanism by which these promoters act.

● Mg

Li(repeat)

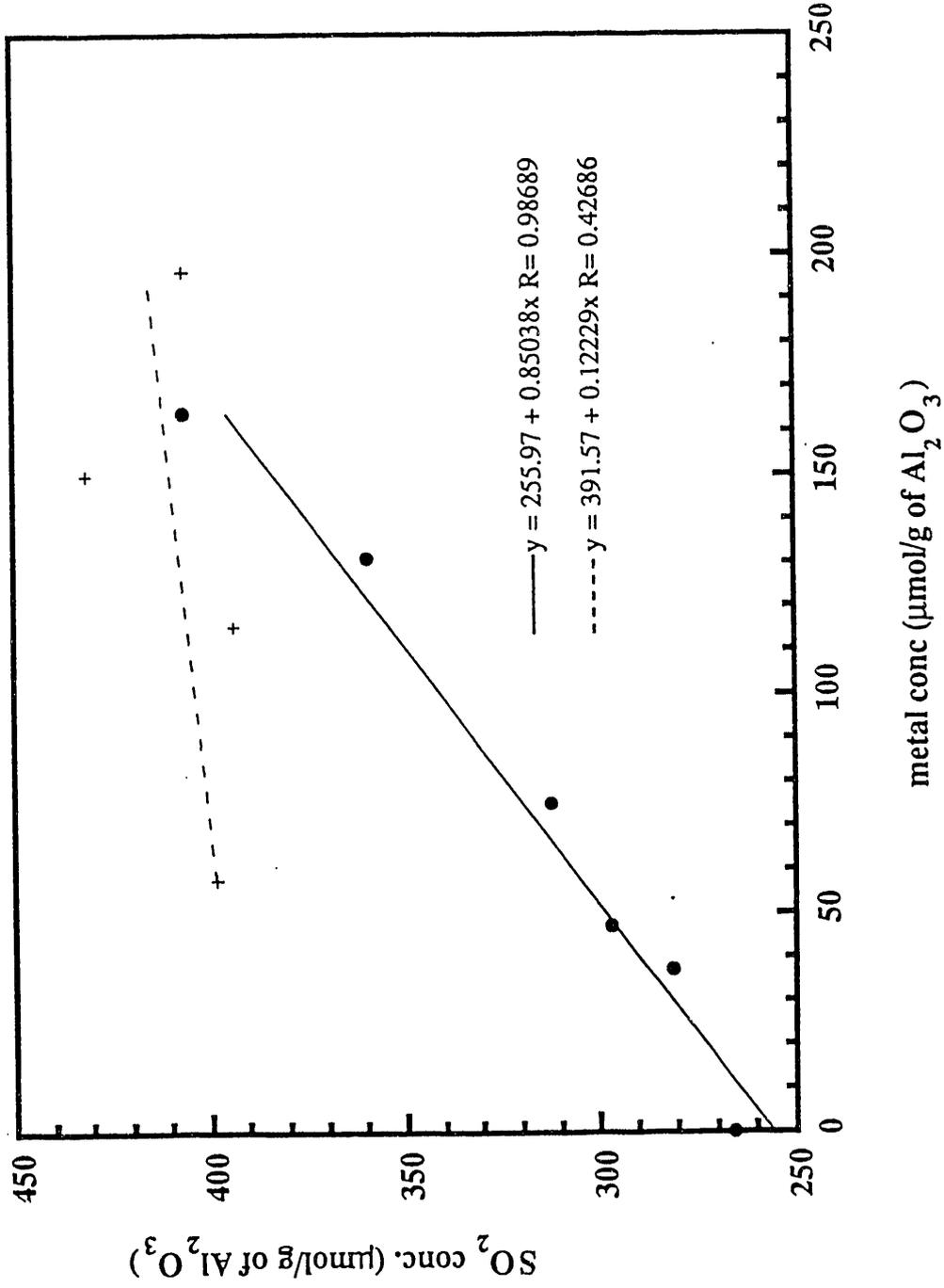


Figure 1. Comparison of SO₂ Adsorption on Lithium and Magnesium-Promoted Aluminas.

Sample: alumina File: AL203.SM

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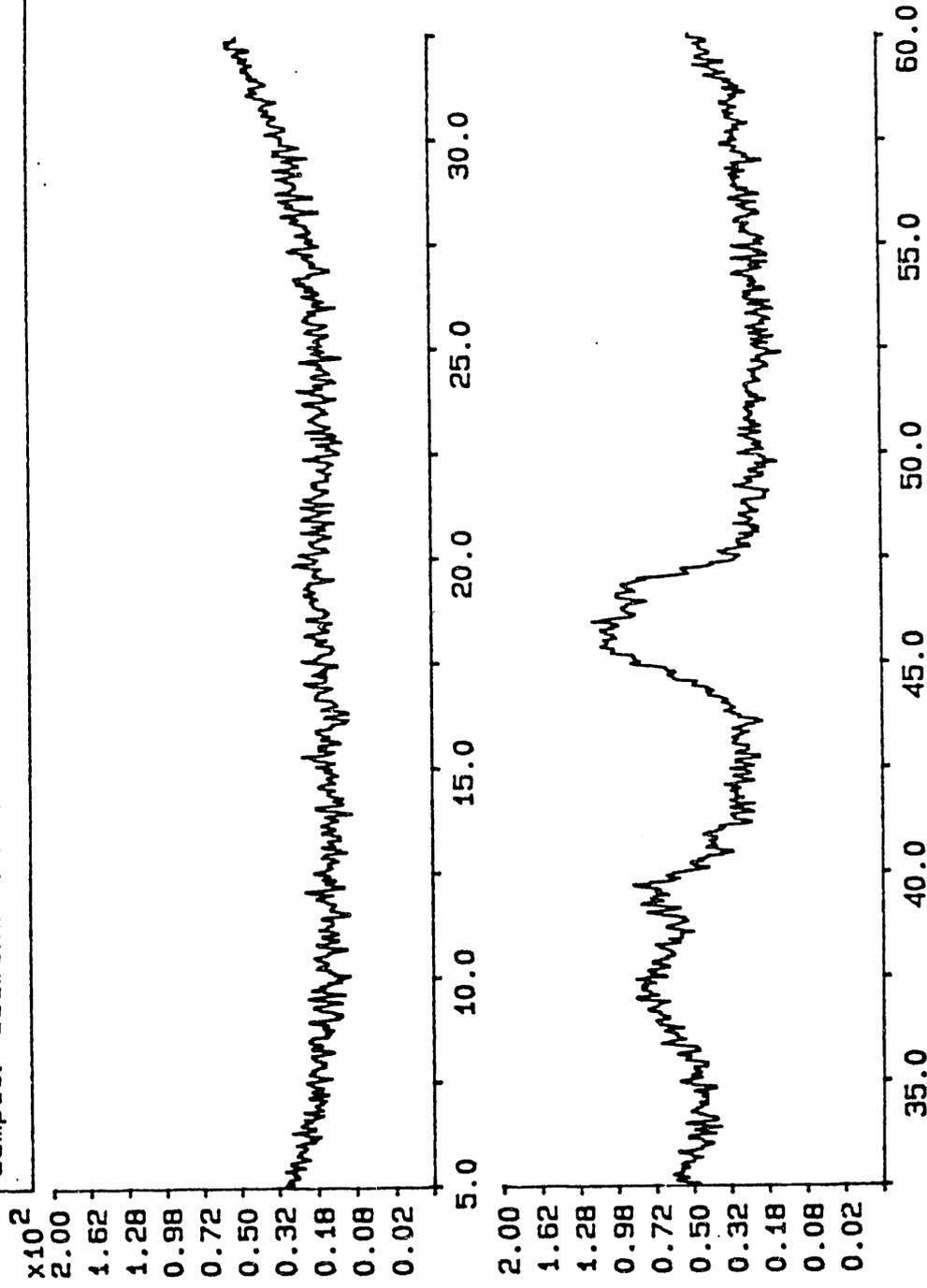


Figure 2. XRD Spectrum of Alumina.

Sample: Mg(acac) File: MGACAC.SM 15-NOV-92 17:20

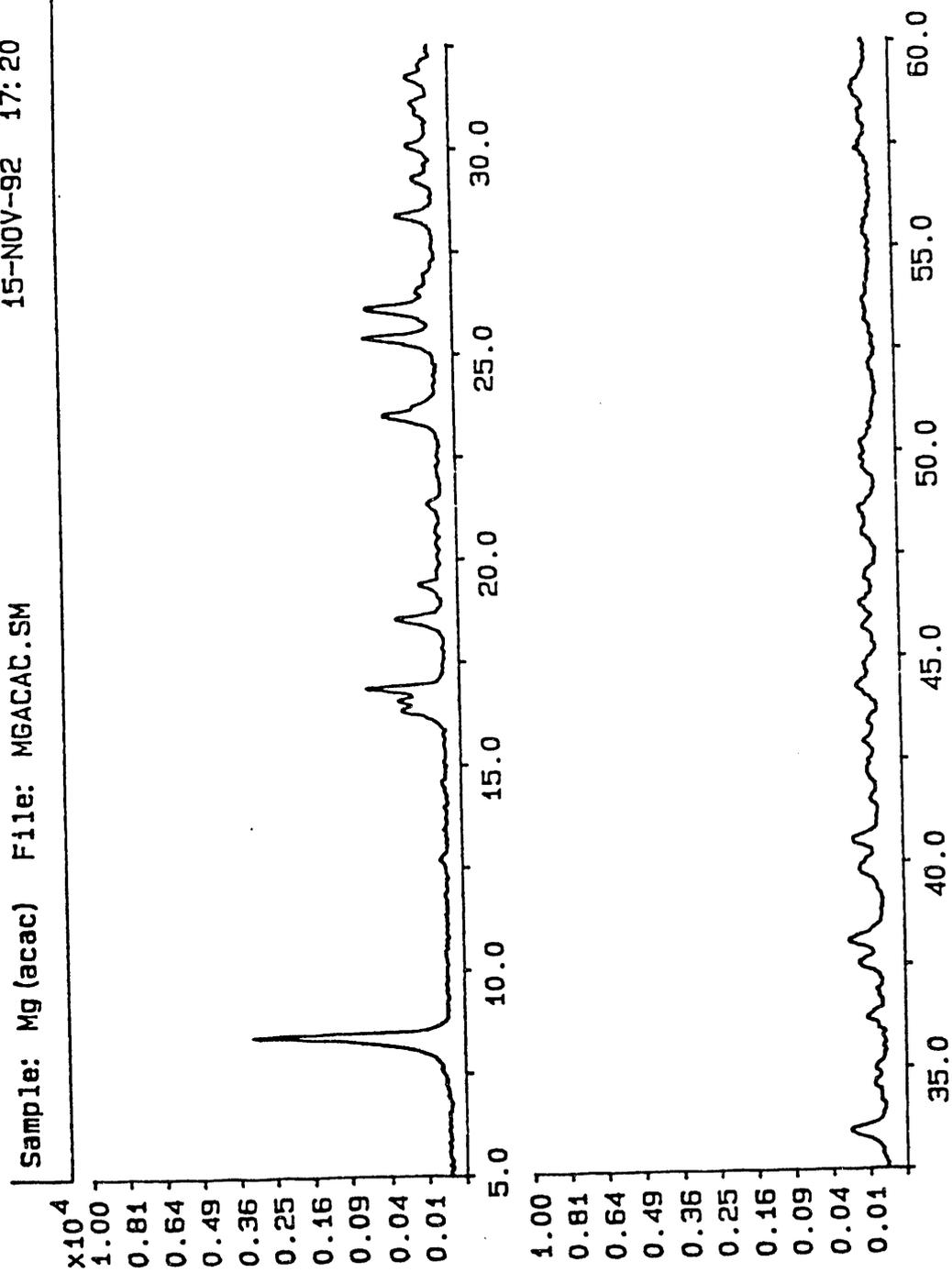


Figure 3. XRD Spectrum of Magnesium Acetylacetonate Dihydrate, Mg(acac)₂•2H₂O.

Sample: 170 File: 170.SM2 25-NOV-92 00:24

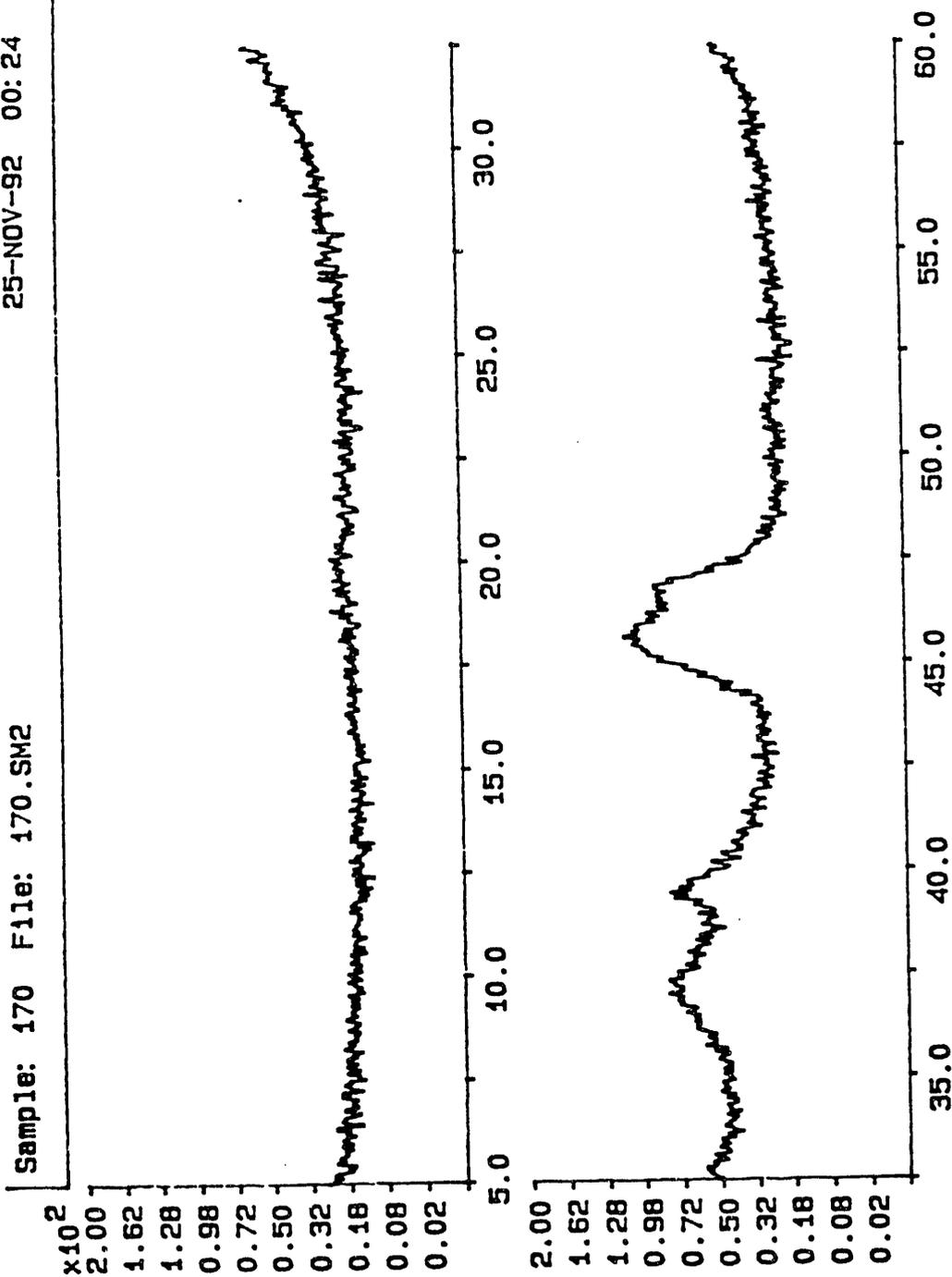


Figure 4. XRD Spectrum of Alumina-Supported $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, 164 $\mu\text{mol Mg/g Al}_2\text{O}_3$.

Sample: t1 File: T1.SM

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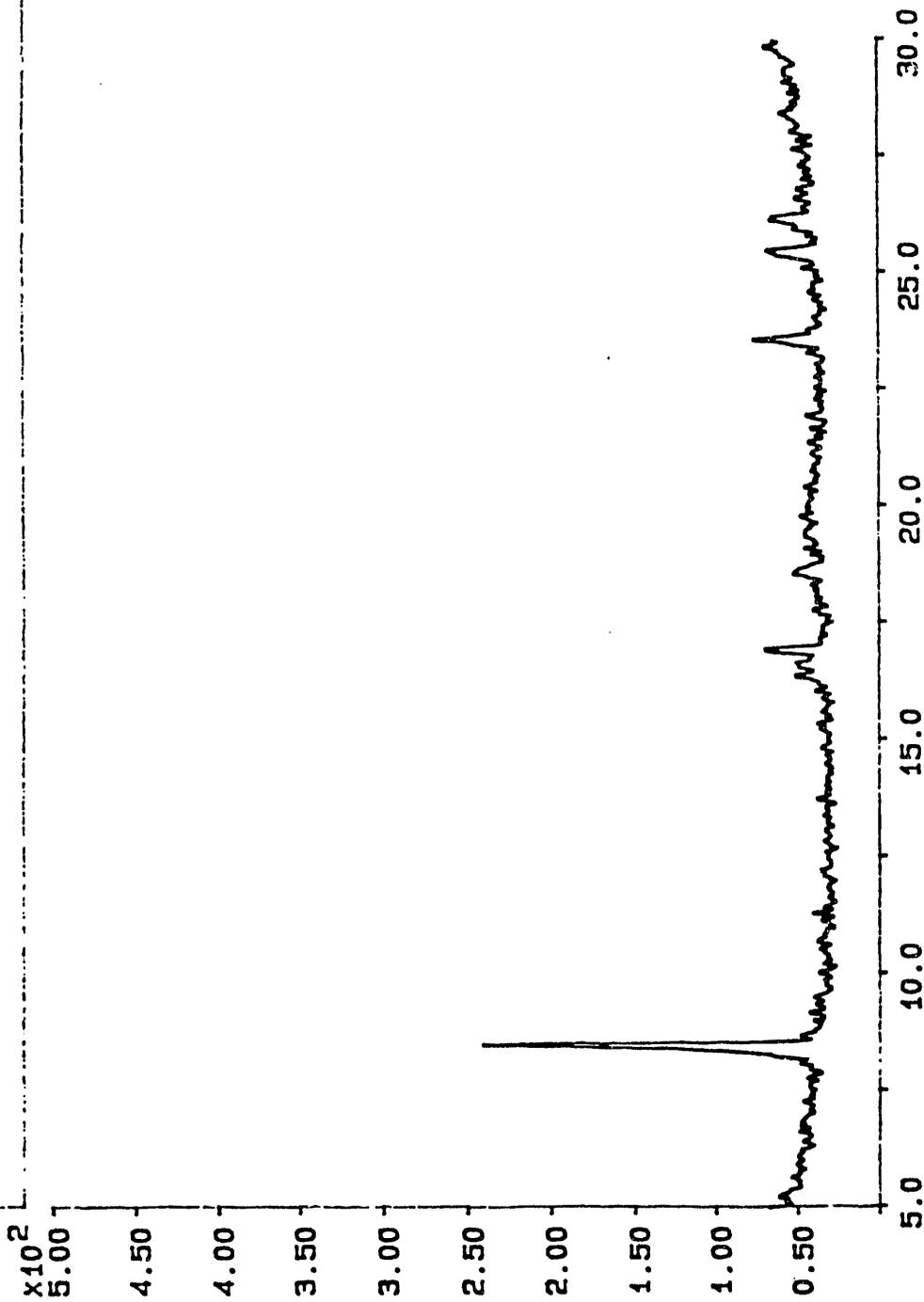


Figure 5. XRD Spectrum of a Physical Mixture of $\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ and Alumina (0.82 wt/wt% Mg).

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