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PROGRESS REPORT

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3. TITLE OF PROPOSAL: SIMULTANEOUS SO_2/NO_x ABATEMENT USING ZEOLITE-SUPPORTED COPPER.
4. NAME OF INSTITUTION: Clark Atlanta University
5. AUTHOR(S) OF REPORT: Drs. Mark B. Mitchell and Mark G. White

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ABSTRACT

Progress has occurred on several fronts during the past year. We moved into a new facility at Clark Atlanta University, and have acquired several new pieces of analytical equipment. We have succeeded in growing an overlayer or zeolite on cordierite, have prepared an active NO decomposition catalyst, and have preliminary data on a vanadium-impregnated alumina for SO_2 oxidation. We are beginning the studies of a vanadium-impregnated zeolite for SO_2 oxidation.

INTRODUCTION

The goals of this project have evolved from an investigation of ways of preparing Li and Hall's Cu-ZSM-5 catalyst using new methods to yield a more robust catalyst, into an investigation of modified Cu-ZSM-5 catalysts for the simultaneous reduction of NO and oxidation of SO_2. This was not a conscious effort or decision on the part of the investigators, but resulted from a natural evolution of the project. We have developed a zeolite synthesis and characterization capability in our group and have prepared impregnated test materials for the investigation of different catalyst precursors. We have prepared different vanadium-impregnated aluminas, for evaluation of the impregnation method, and have succeeded in reproducing the results of Li and Hall's Cu-ZSM-5 catalyst.

This report reviews the progress during the first three quarters of the year, and includes progress from the last quarter.

RESULTS

Raman Spectroscopy of Precursors.

In the earlier part of the year, we were concerned with successfully preparing a zeolite impregnated with a metal complex. We were successful in preparing a Zeolite A impregnated with $Co(en)_3Cl_3$. We used Raman spectroscopy to characterize Zeolite A, a cobalt ethylenediamine complex, $Co(en)_3Cl_3$, and Zeolite A impregnated with the cobalt complex. We reported the *infrared* spectra of this series of samples in an earlier report using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The spectra were recorded for a powdered zeolite sample containing about 1 wt% Co; the elemental analyses for C and N in this same sample showed the same stoichiometry as that expected for the metal complex. In the infrared work, it was found that the ethylenediamine ligands appeared to remain intact, but the frequencies of the N-H stretch vibrations were shifted to lower frequencies, consistent with an interaction of the N-H dipole of the complex with dipoles in the zeolite framework.

The Raman spectra similarly indicated that the complex was intact, and that most of the vibrational frequencies of the complex appeared to be unchanged except for the NH_2 scissors vibrations. These vibrations appear to be shifted by approximately 15 - 30 cm^{-1} to higher frequency. The rest of the spectrum was found to be remarkably similar to what would be obtained by simply adding the spectrum of the complex to that of the zeolite. These results again imply an interaction of the NH_2 group with the zeolite framework.

Infrared Spectroscopy of Vanadium-impregnated Alumina.

We wanted to investigate the use of vanadium acetylacetonate precursors for the impregnation of alumina with vanadium so that we have some idea of the efficiency of the impregnation procedure with a relatively simple substrate before trying to use the zeolites. We investigated the nature of adsorbed vanadyl acetylacetonate on alumina to determine the nature of the adsorbed complex, and the behavior of the complex as a function of temperature.

We observed that under vacuum, the complex appeared to be remarkably stable with respect to temperature. Even at 500°C, the complex appeared to remain intact. However, under oxygen, the complex appeared to oxidize to form an acetate at 300°C, then to form an infrared-invisible compound by 400°C (probably CO_2 and H_2O which evolve from the surface, and a surface-bound vanadium oxide).

Zeolite Overlayer on Cordierite.

We attempted to grow an overlayer of ZSM-5 on cordierite using typical zeolite gel preparation techniques which have been discussed in previous reports. The x-ray data from the material prepared indicated that the attempt had been successful, with the product containing only peaks which corresponded to either ZSM-5 and cordierite peaks from standard x-ray spectra. This is a very important on-going area of research. This arrangement of catalyst on support has the potential to yield low pressure drop monoliths which have specific catalytic activity and good structural integrity.

Reactivity of Cu-ZSM-5.

We prepared a sample according to the technique of Li and Hall [Li, Y. and Hall, W. K. *J. Catal.*, **1991**, *129*, 202]. Three samples(1.38g, 1.70g, and 2.13g) of this powdered catalyst were placed in a tubular flow reactor for testing in three separate runs at a common temperature (773K) and for a common inlet concentration of NO in He (4.21% NO). The data for the smallest amount of catalyst appeared to show smaller conversions at each spacetime than the data for the larger weights of catalysts. At low spacetimes, the data at the two larger weights appeared to coincide. These results suggest that mass transfer effects appeared to influence the data collected from the run involving the smallest amount of catalyst in the reactor. Therefore this diagnostic confirms that no less than 2.5g of catalyst should be used in the reactor for this temperature so that we may measure the effects of kinetics in the absence of the confounding effects of mass transfer.

Impregnation of Vanadyl Acetylacetonate on Alumina.

The results of the atomic analyses on the vanadyl acetylacetonate-impregnated alumina allowed us to determine an adsorption isotherm for the impregnation procedure using methanol as a solvent. The isotherm is shown in Figure 1. The surface concentration is relatively low, compared to results from copper on silica using the acetylacetonate precursor. In the earlier work with copper, we could routinely obtain surface concentrations of greater than 6 μmoles/m^2, whereas in this work the limiting surface concentration appears to be about 1 - 1.5 μmoles/m^2.

The surface area was about 35% greater in the work with silica than in the current study, but that does not account for the factor of four difference in metal concentration formed on the surface. There may be some limitations imposed by surface area inside pores. The silica used in the copper study was non-porous, and all the surface area was accessible. However, the alumina used here is porous. We have not characterized the alumina with respect to pore size distribution, however, and so this explanation is simply conjecture at this point. In any case, the alumina work is merely a prelude to work using ZSM-5, and so we do not want to spend more effort on this aspect of the project, now.

The adsorption of the vanadyl acetylacetonate complex onto the alumina surface involves more than simple physisorption as can be seen from Figure 2. This figure is a plot of the surface carbon concentration versus the surface vanadium concentration. The results indicate that the carbon content appears to be rather flat as a function of the vanadium concentration, indicating that some decomposition of the complex may be occurring during adsorption. Another way to view this result is to plot the carbon to vanadium (C/V) atom ratio versus vanadium surface concentration, as is done in Figure 3. The C/V ratio decreases with increasing vanadium content indicating that the complex is not remaining intact. The line at 10 on the C/V axis indicates what the result should be if the complexes remained intact. The high carbon result at low vanadium concentrations may result from the adsorption of methanol onto the alumina surface.

There are implications from the analytical work on the alumina-supported vanadium complexes with regard to the use of DRIFTS as a technique for the determination of the complexes on the support. Figures 4, 5, and 6 show the DRIFTS spectra of three of the supported samples prepared, samples with 0.318, 0.822, and 1.21 μmoles vanadium/m^2 alumina surface, respectively. It is clear that the apparent intensity of the spectra do not scale linearly with the vanadium concentration. If the ligand is remaining intact, the intensity should at least vary linearly with carbon content. In fact, if the integrated intensity of the spectra is plotted as a function of carbon content as is shown in Figure 7, it can be seen that the intensity actually appears to decrease with increasing carbon content. This indicates that the ligand does not appear to remain intact, and that the surface carbon is changing into a chemical form which is less "visible", a species which is less strongly absorbing than the acetylacetonate ligand in the range 1800 - 1200 cm^{-1}.

FUTURE DIRECTIONS

Our work in the next year will focus on the development of a vanadium-impregnated ZSM-5 zeolite for SO_2 oxidation coupled with copper-impregnation for NO reduction. We will begin using the GC/MS catalyst screening capability in Dr. White's lab for characterizing the SO_2 oxidation ability as well as for NO reduction ability of these catalysts.

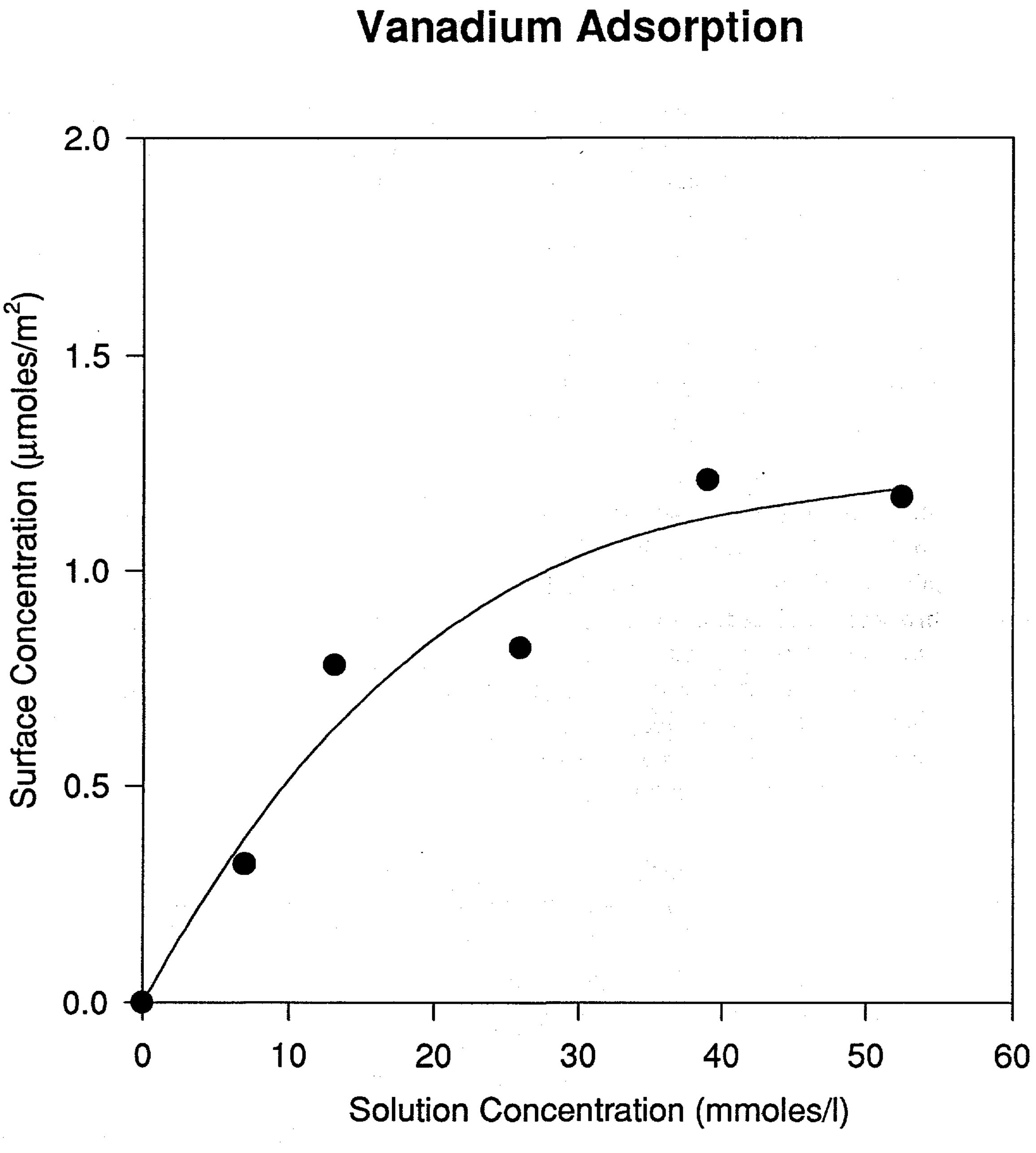

Vanadium Adsorption
2.0
1.5
1.0
0.5
0.0
Surface Concentration (µmoles/m²)
0
10
20
30
40
50
60
Solution Concentration (mmoles/l)

Figure 1.

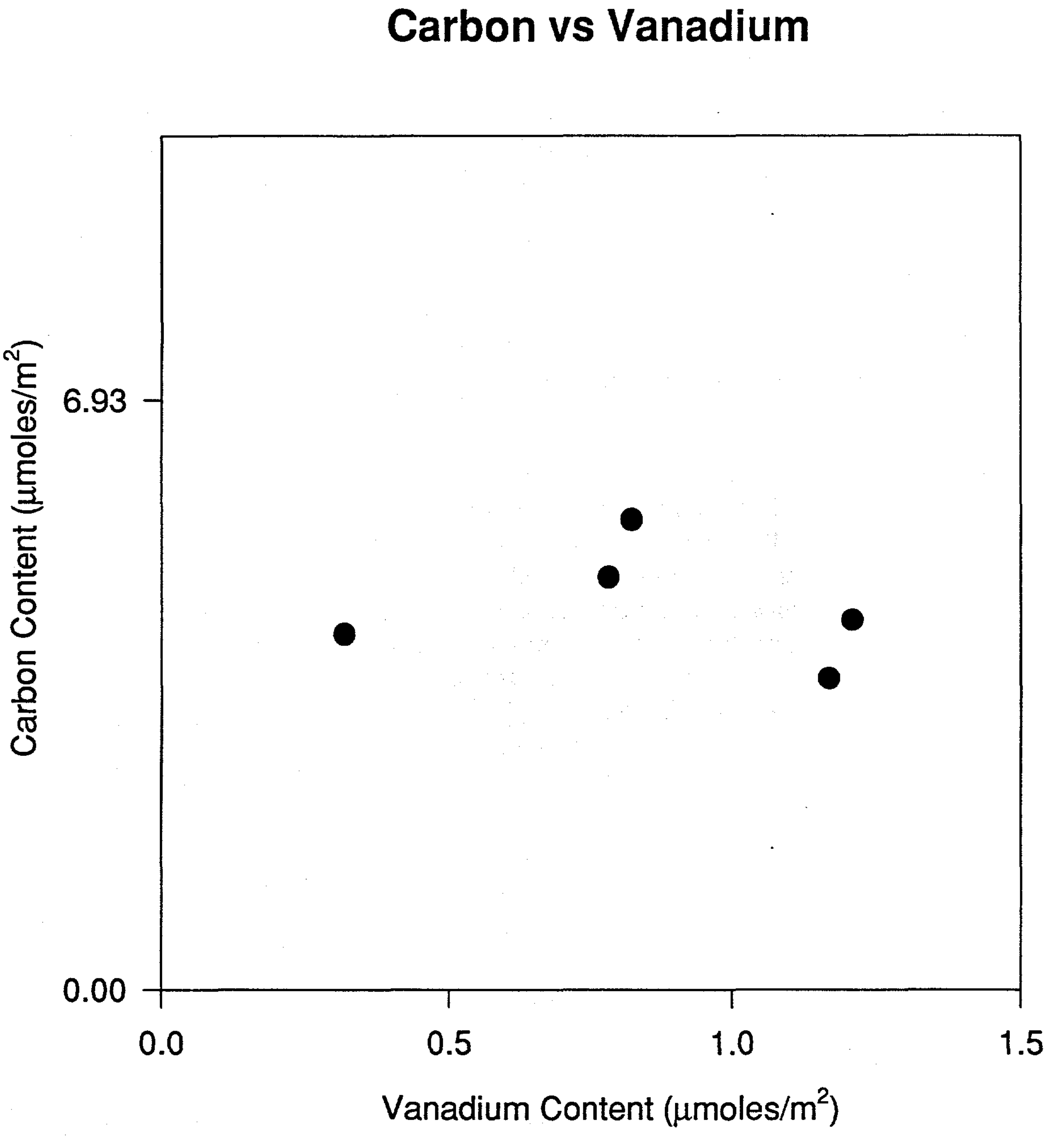

Carbon vs Vanadium
Carbon Content (µmoles/m²)
6.93
0.00
0.0
0.5
1.0
1.5
Vanadium Content (µmoles/m²)

Figure 2.

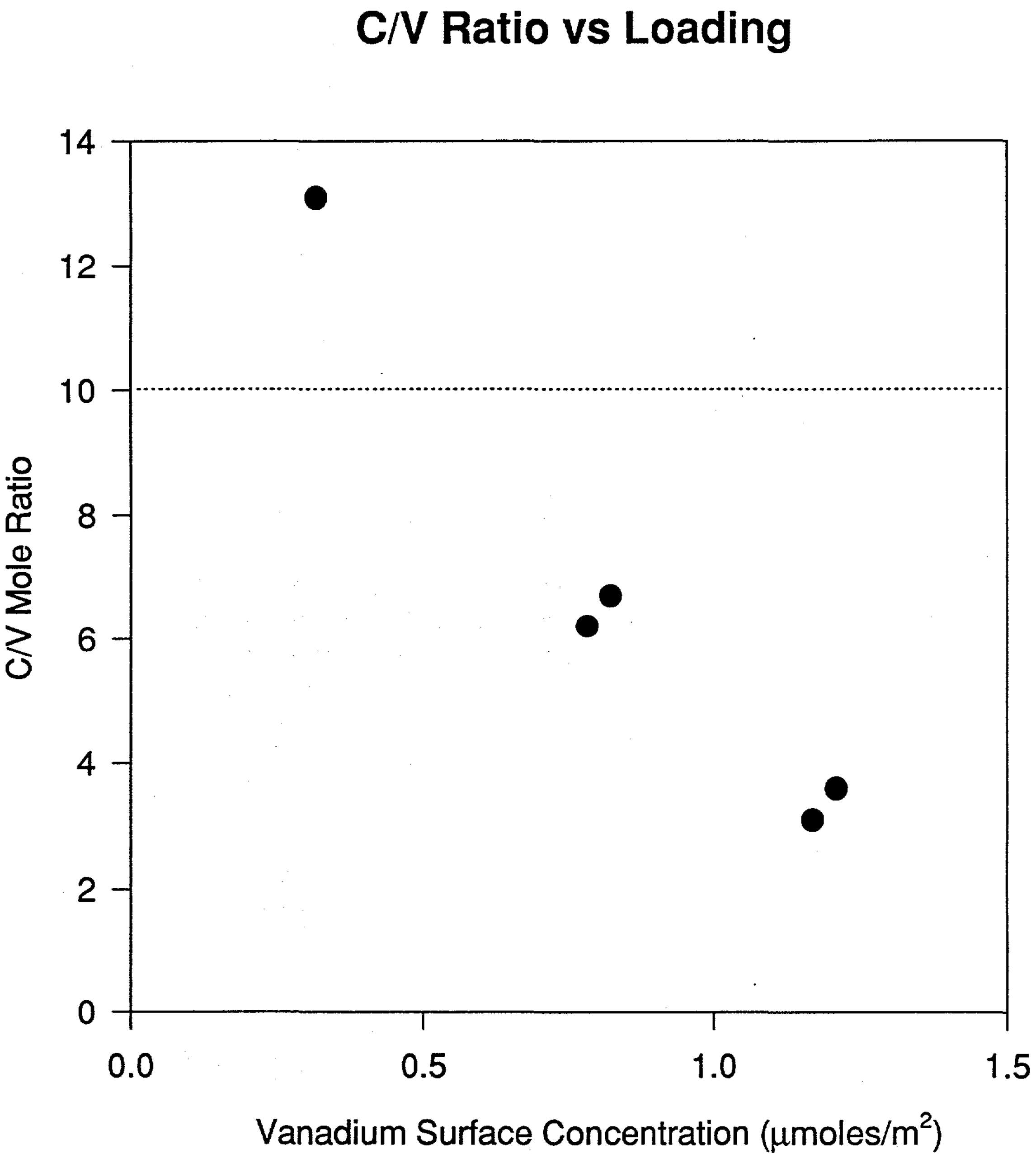

C/V Ratio vs Loading
C/V Mole Ratio
Vanadium Surface Concentration (μmoles/m²)
0
2
4
6
8
10
12
14
0.0
0.5
1.0
1.5

Figure 3.

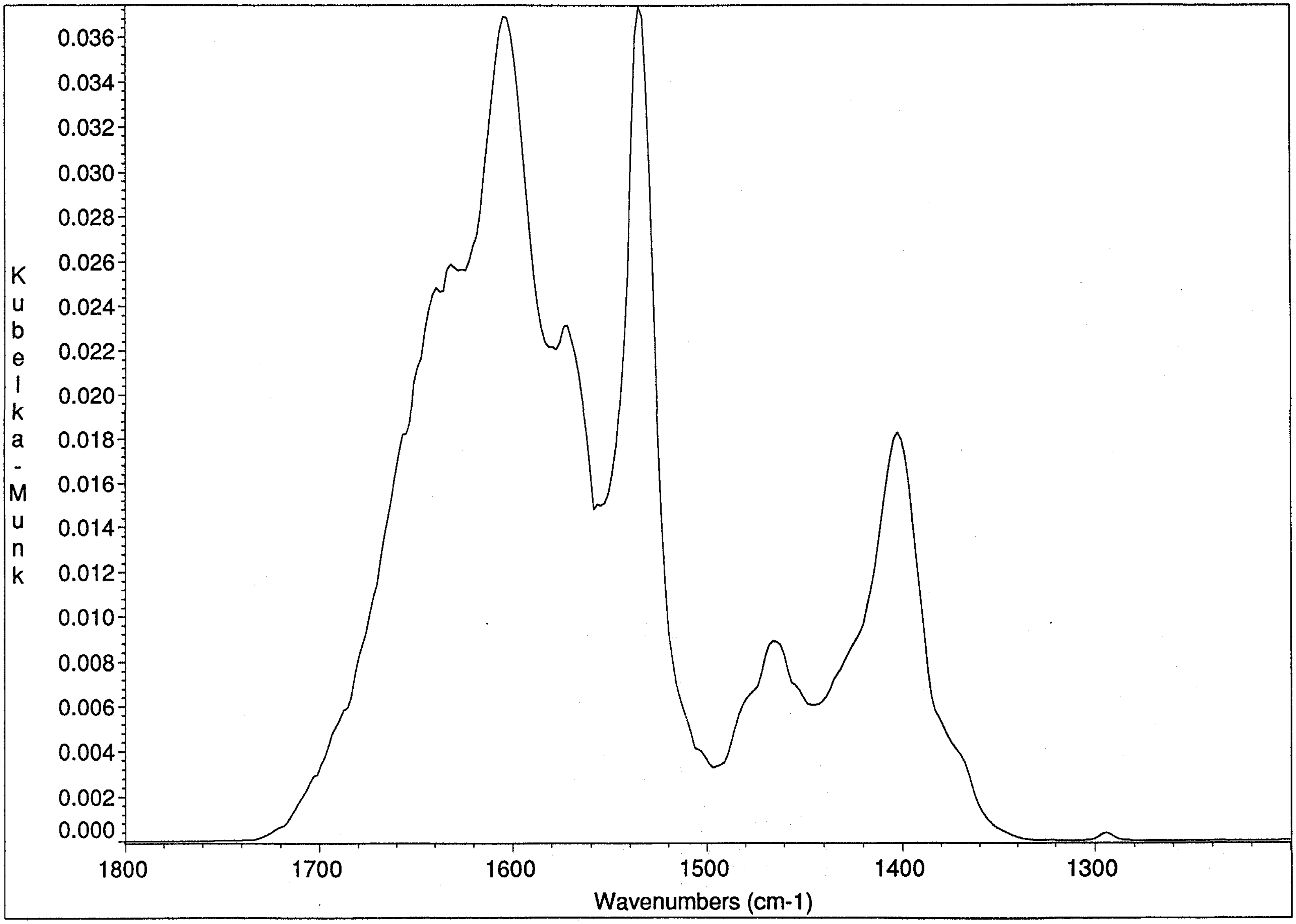


Figure 4. DRIFTS Spectrum of Catalyst Precursor Containing 0.38 μmoles V/m^2 Al_2O_3.

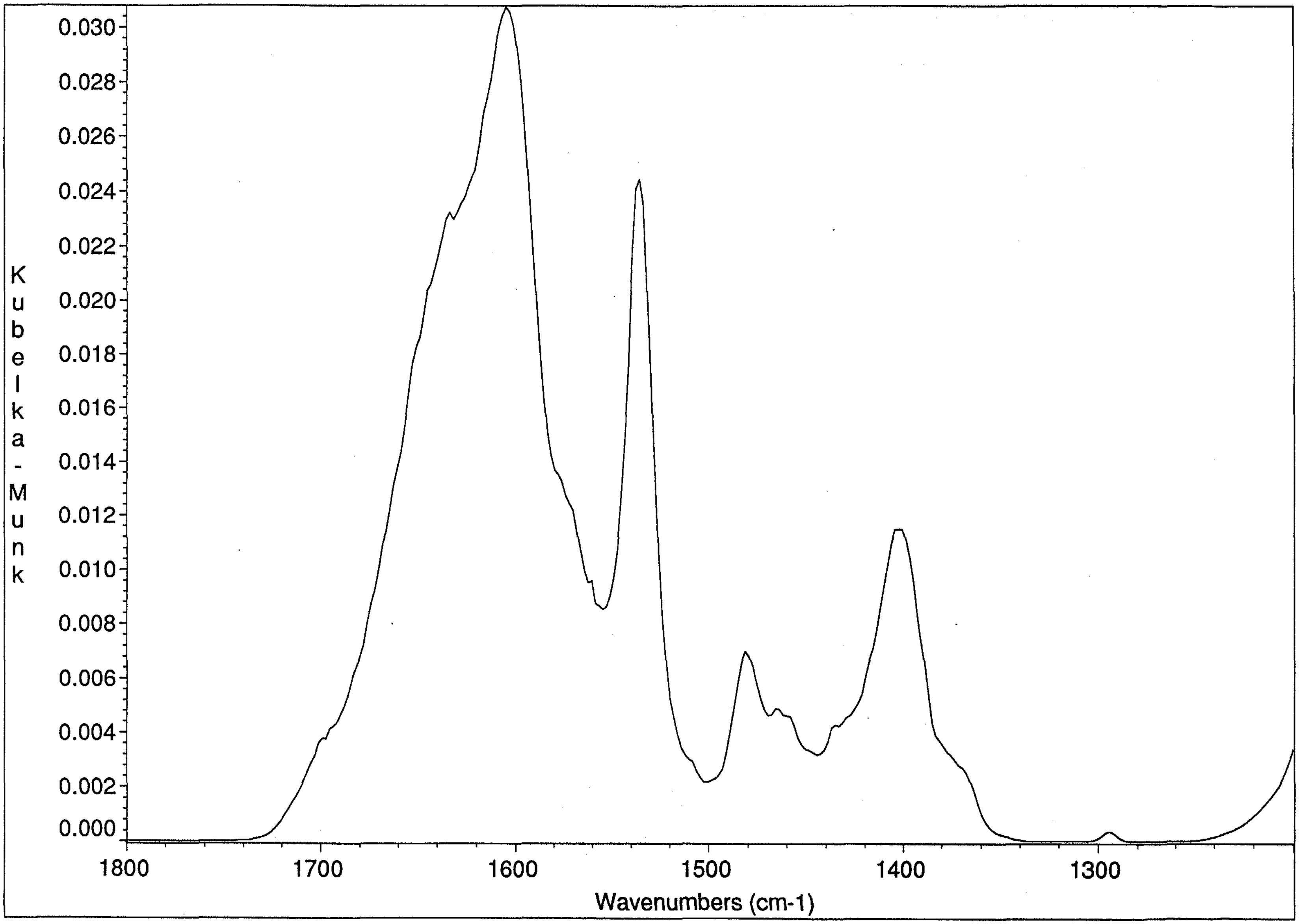


Figure 5. DRIFTS Spectrum of Catalyst Precursor Containing 0.82 μmoles V/m^2 Al_2O_3.

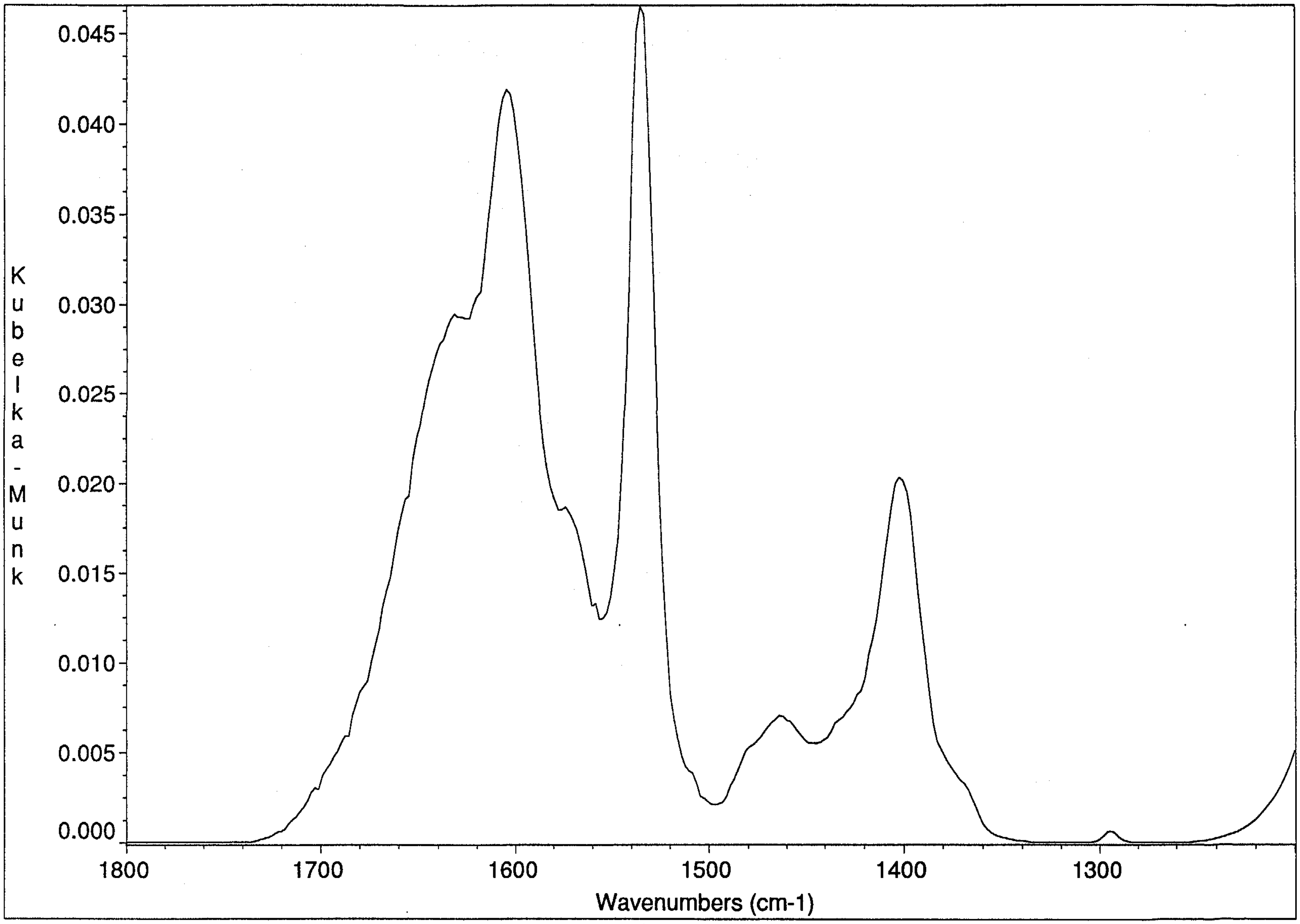


Figure 6. DRIFTS Spectrum of Catalyst Precursor Containing 1.21 µmoles V/m^2 Al_2O_3.

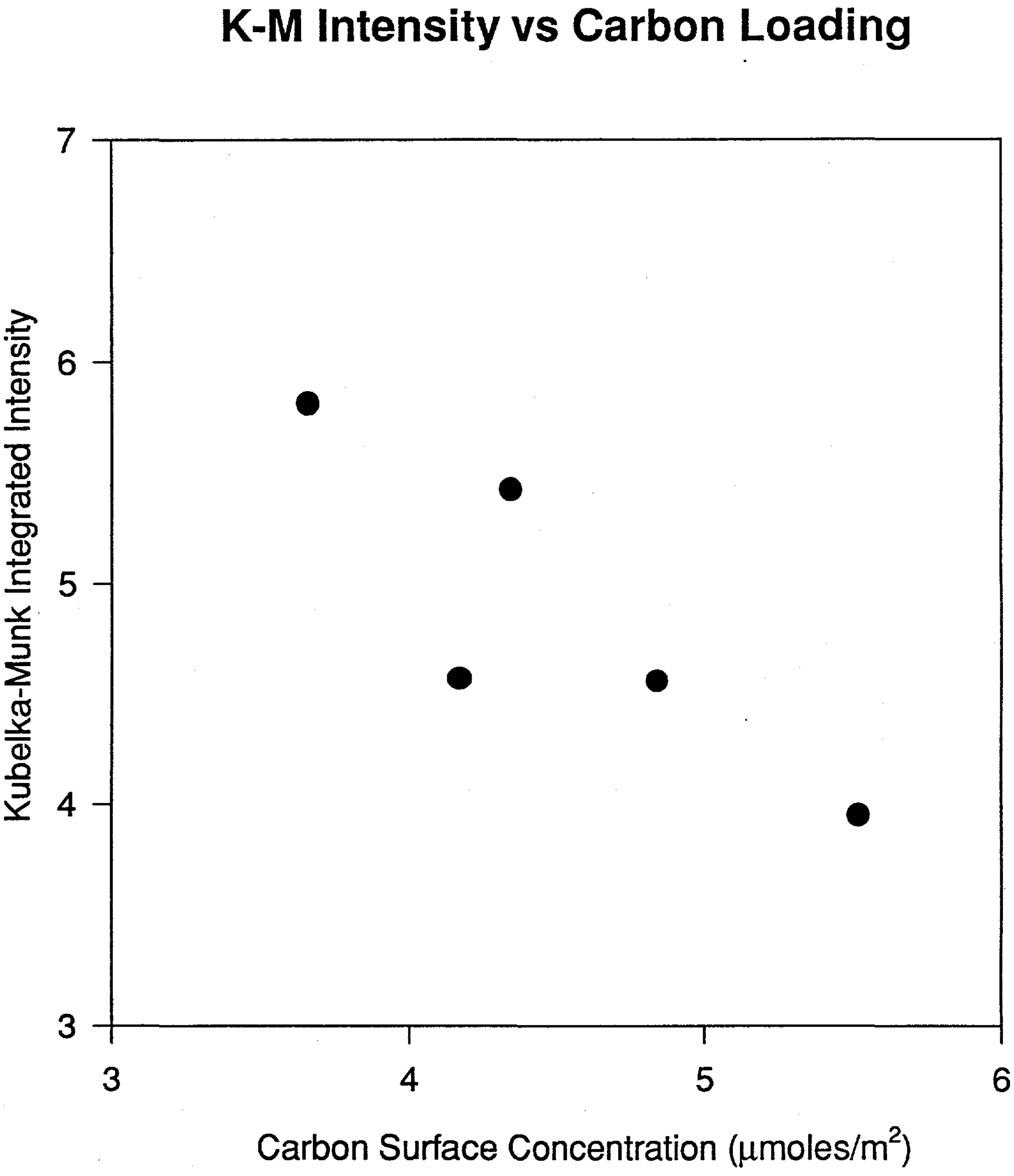
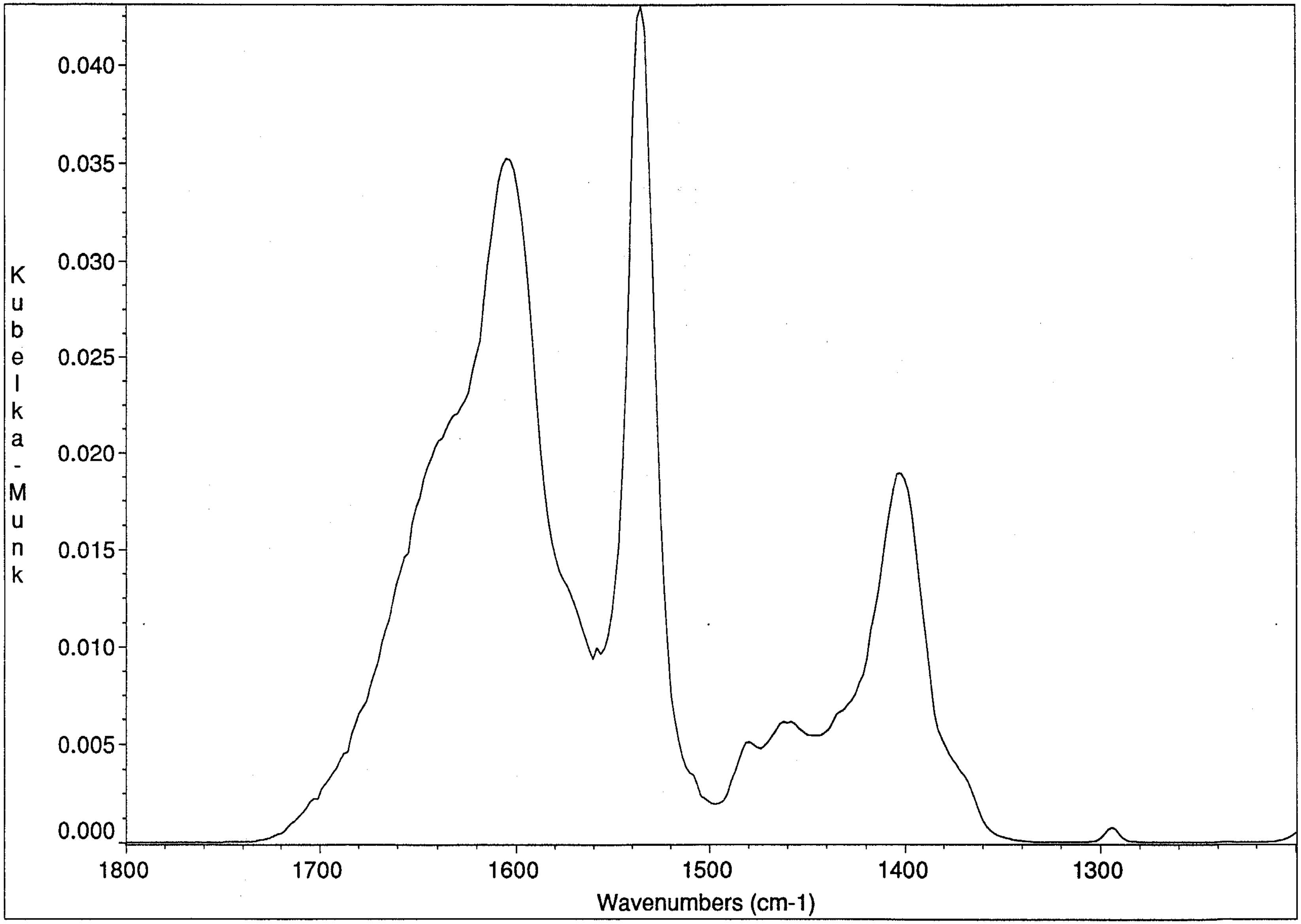
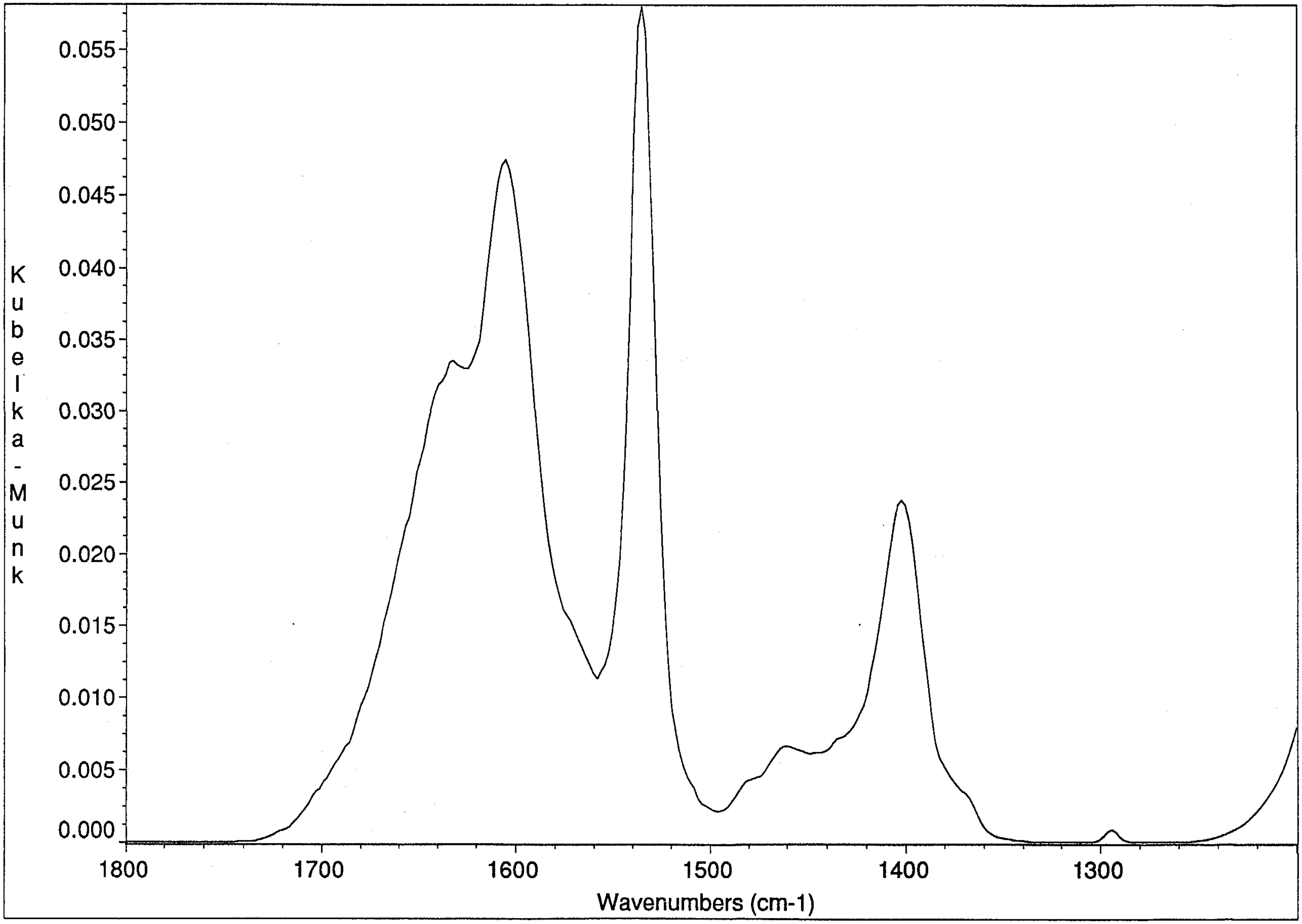


Figure 7. Integrated Infrared Spectral Intensity versus Carbon Loading on Precursor.



Kubelka-Munk
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
1800
1700
1600
1500
1400
1300
Wavenumbers (cm-1)


0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
Kubelka-Munk
1800
1700
1600
1500
1400
1300
Wavenumbers (cm-1)