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PROGRESS REPORT

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2. PERIOD COVERED BY REPORT: October 1, 1992 - December 31, 1992

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

The proposed research seeks to advance/improve current flue gas cleanup catalyst technology by modifying promising copper-exchanged zeolite NO decomposition catalysts which reduce NO to elemental nitrogen and oxygen in the absence of an added reducing gas. We believe that this approach has great potential. Copper on alumina has been investigated by the Pittsburgh Energy Technology Center (PETC) as a NO_x/SO_2 abatement catalyst. Copper on alumina acts as a sorbent for SO_2, forming a surface sulfate upon adsorption in an oxygen-containing atmosphere, and as a catalyst for selective catalytic reduction (SCR) of NO_x using ammonia; both CuO and $CuSO_4$ on the surfaces of these materials are active SCR catalysts. SO_2 adsorption in the PETC studies was carried out at 673K, a temperature well within the range for active NO decomposition by the Cu-ZSM-5 catalyst. We believe that by beginning with a material which decomposes NO without needing an added reducing gas, we will be able to design a catalyst which will act as a regenerable NO_x/SO_2 abatement catalyst which does not need ammonia to accomplish NO_x reduction, and which will accomplish SO_2 abatement by adsorption, similar to the copper on alumina catalyst. Coupled with a SO_2 oxidation catalyst, this successful system will be able to remove both NO_x and SO_2 from flue gases with no added reducing agent and no waste.

INTRODUCTION

Restrictions on coal-fired power plant emissions of SO_2 and NO_x, mandated by the Clean Air Act, are expected to tighten significantly over the next ten years. Though much of the emphasis is placed on SO_2 emissions control, NO_x control is seen as a major hurdle as well. In order to comply with the SO_2 and NO_x reduction goals, the utility industry must have a wide selection of abatement technologies from which to choose, given the different designs, ages, and capacities of existing power plants. This proposal, involving collaborative efforts at Clark Atlanta University, the Georgia Institute of Technology, and Arthur D. Little, Incorporated, addresses this need by investigating a promising new technology for catalytic NO decomposition which does not need an added reducing gas, the application of this technology to power plant emissions control, and the additional potential of these catalysts for SO_2 abatement.

The proposed research seeks to advance/improve current flue gas cleanup catalyst technology by modifying promising copper-exchanged zeolite NO decomposition catalysts which reduce NO to elemental nitrogen and oxygen in the absence of an added reducing gas. We believe that this approach has great potential. Copper on alumina has been investigated by the Pittsburgh Energy Technology Center (PETC) as a NO_x/SO_2 abatement catalyst. Copper on alumina acts as a sorbent for SO_2, forming a surface sulfate upon adsorption in an oxygen-containing atmosphere, and as a catalyst for selective catalytic reduction (SCR) of NO_x using ammonia; both CuO and $CuSO_4$ on the surfaces of these materials are active SCR catalysts. SO_2 adsorption in the PETC studies was carried out at 673K, a temperature well within the range for active NO decomposition by the Cu-ZSM-5 catalyst. We believe that by beginning with a material which decomposes NO without needing an added reducing gas, we will be able to design a catalyst which will act as a regenerable NO_x/SO_2 abatement catalyst which does not

need ammonia to accomplish NO_x reduction, and which will accomplish SO_2 abatement by adsorption, similar to the copper on alumina catalyst. Coupled with a SO_2 oxidation catalyst, this successful system will be able to remove both NO_x and SO_2 from flue gases with no added reducing agent and no waste.

We have begun efforts in two areas. The first involves developing the synthetic expertise needed to carry out the synthesis of the zeolites themselves. We have prepared sodium and hydrogen Y-type zeolites and the sodium and reduced forms of the ZSM-5 zeolite using standard techniques, and the x-ray results indicate that we have been successful.

The second area of investigation involves the selective impregnation of zeolite surfaces. Our goal is the development of a zeolite-based catalyst which will accomplish both NO_x decomposition and SO_2 oxidation. We envision accomplishing this goal by carrying out these reactions simultaneously in different regions of the catalyst, with the NO decomposition occuring on the inside of the zeolite cage, catalyzed by copper, and the SO_2 oxidation occuring on the outside of the cage, catalyzed by an oxidation catalyst such as vanadia. Our synthetic design requires that we be able to accomplish the copper exchange preferentially on the inside surfaces of the zeolite, and leave the outside surfaces available for treatment with, for example, a vanadium-containing precursor. We have begun these efforts by passivating the external surfaces of amorphous silica (Cab-O-Sil) and a ZSM-5 zeolite with hexamethyldisilazane. The silica experiment provides a simple test of the overall procedure, and is easier to characterize than ZSM-5. By silating the surface hydroxyls, we hope to remove the sites to which our copper precursor attaches.

EXPERIMENTAL

Zeolites are typically prepared in the sodium form by mixing a source of alumina with a source of silica and a source of sodium in aqueous solution. Most of the solutions are very basic, pH 12 or higher. The sodium source can be the same as the source for the alumina or it can be the same as the silica source. That is, sodium metasilicate can be used as the sodium/silica source, for example, or sodium aluminate can be used as the sodium/alumina source. The Na-Y zeolite is prepared by mixing a suspension of silicon dioxide in water ($SiO_2 \bullet nH_2O$) from Dupont (Ludox-40) with sodium aluminate ($NaAlO_2$) from Pfaltz and Bauer in basic solution. The Na-ZSM-5 zeolite is prepared in much the same way but with a different ratio of silica to aluminate, no base is added, but with the addition of a templating agent (tetrapropyl ammonium hydroxide). The mixtures are placed in a teflon-lined stainless steel bomb and heated at 100 - 150°C for approximately 100 - 150 hrs. Table 1 shows the relative molar ratios of the reaction components which were used for the preparations, normalized to 1 mole for the sodium aluminate. For the preparation of Na-Y zeolite, additional NaOH is added to bring up the sodium oxide concentration. The zeolites are converted to the hydrogen form by ion exchanging the sodium with ammonium ion using ammonium nitrate, followed by heating to approximately 500°C to drive off ammonia gas.

Table 1. Reaction Mixture (Molar Ratios)/Conditions

Zeolite	$NaAlO_2$	SiO_2	Na_2O	H_2O	Template	Temperature (^oC)	Time (hr)
Na-Y	1	20	8	320	none	105	96
ZSM-5	1	28	1	453	34.2 (TPAOH)	150	166

The surface passivation with the silating agent was accomplished by bubbling nitrogen through hexamethyldisilazane (HMDS) at 120°C, which then flowed onto the zeolite bed in an oven at 180°C. The exit vapors were passed through a cold trap at 0°C to remove any unreacted silating agent. The silated supports were then examined by diffuse reflectance infrared Fourier transform (DRIFT) spectrosocpy.

The silated ZSM-5 was placed in a solution of copper ethylenediamine ($Cu(C_2N_2H_8)_2(ClO_4)_2$) in acetonitrile at room temperature for six hours. The impregnated zeolite was then washed with an excess of solvent to remove any complex which did not ion-exchange with the zeolite support.

RESULTS AND DISCUSSION

Powder x-ray diffraction of the hydrogen form of the Y-type zeolites are shown in Figure 1. The diffraction pattern shown in this figure shows sharp peaks which correlate well with those peaks observed in other literature for Y-type zeolites.

A DRIFT spectrum was taken of unsilated amorphous silica and this spectrum is shown in Figure 2. The sharp peak near 3750 cm^{-1} is due to non-hydrogen-bonded surface silanol (Si-OH) groups. The DRIFT spectra of the silated silica samples, Figures 3-5, show the loss of this sharp peak and the introduction of peaks in the C-H stretching region (2850 - 3000 cm^{-1}). The loss of the silanol stretching mode implies that the silating agent has reacted at the OH sites to form silyl ethers. This is also indicated by the presence of C-H modes due to the symmetric and asymmetric stretching modes of the HMDS. The difference between the samples whose spectra is shown in Figures 3-5 is the HMDS exposure time. Figure 3 corresponds to a contact time of 2 hours, Figure 4 corresponds to a contact time of 4 hours, and Figure 5 corresponds to a contact time of 6 hours. The spectrum shown in Figure 5 shows bands in addition to the symmetric and asymmetric methyl vibrations, presumably due to CH_2 vibrations, indicating the formation of a surface polymer. Thus, the reaction time should be limited to less than 4 hours to prevent the formation of these side proucts.

A DRIFT spectrum of ZSM-5 before silating is shown in Figure 6. The silated samples of ZSM-5 are shown in Figures 7 and 8. Changes observed in these spectra are similar to those observed with the silated amorphous silica. There is a large reduction in the peak heights in the O-H stretching region (3200 - 3800 cm^{-1}) and the introduction of new features in the C-H stretching region (2850 - 3000 cm^{-1}). This reduction in O-H absorption is attributable to the formation of ethers from surface Si-OH and Al-OH groups. Also, the ether groups are less attractive to water so less adsorbed water is

present. The increased absorbance in the C-H stretching region is primarily due to absorbance by the methyl groups from the HMDS silating agent. Some of the absorbance in this region is due to residual material from the synthesis of the zeolite which did not decompose during preparation. The decrease in the O-H region is noticable but not complete, even after six hours of silation treatment. The remaining absorbance in the silated samples is probably from Al-OH and Si-OH groups present in the pores or holes of the zeolite not silated by the bulky HMDS silating agent.

STUDENT PARTICIPATION

Much of the synthesis and characterization work reported here was carried out by David Bruce, a graduate student at Georgia Tech who has been working with Dr. Mark White and Dr. Aaron Bertrand. Enid Gatimu, an undergraduate student at Clark Atlanta University, is being trained on the use of FT-IR and DRIFT spectroscopy so that we can begin the in situ adsorption/characterization studies.

FUTURE WORK

We plan to prepare NO decomposition catalysts by repeating Hall's work,[2] using a copper nitrate precursor in aqueous solution, and by using the acetylacetonate and ethylenediamine copper complexes as precursors in non-aqueous solution.

We look forward to the results of metals analysis from ZSM-5 impregnated with copper using the copper ethylenediamine precursor.

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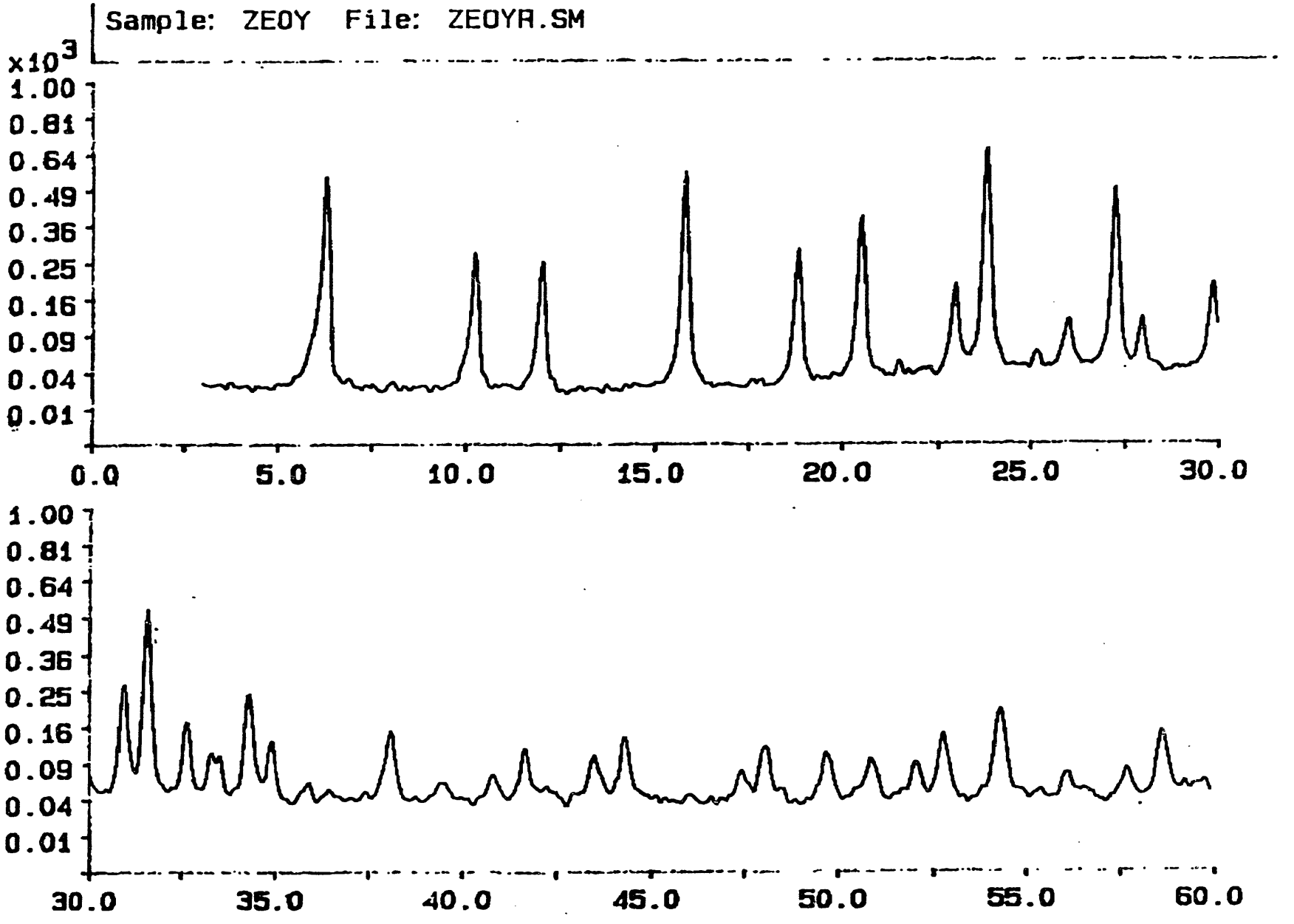

Figure 1. Powder x-ray diffraction spectrum of our preparation of Na-Y zeolite.

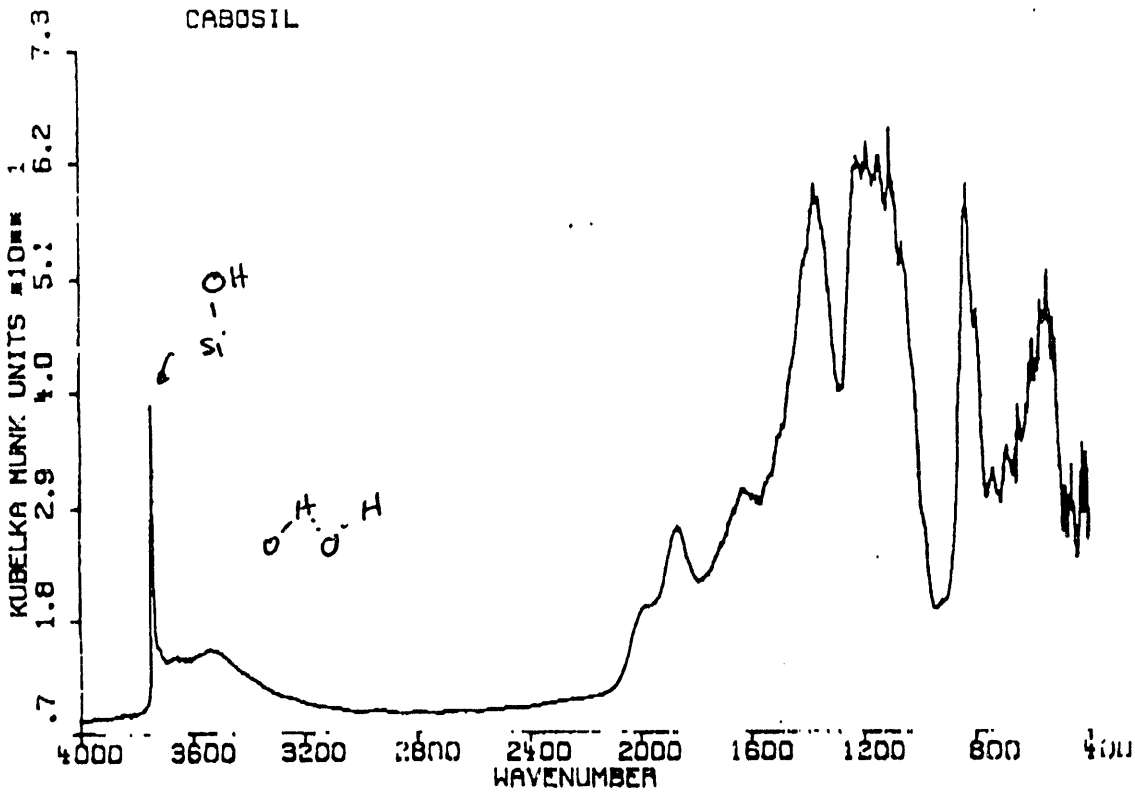

Figure 2. DRIFT spectrum of Cabosil.

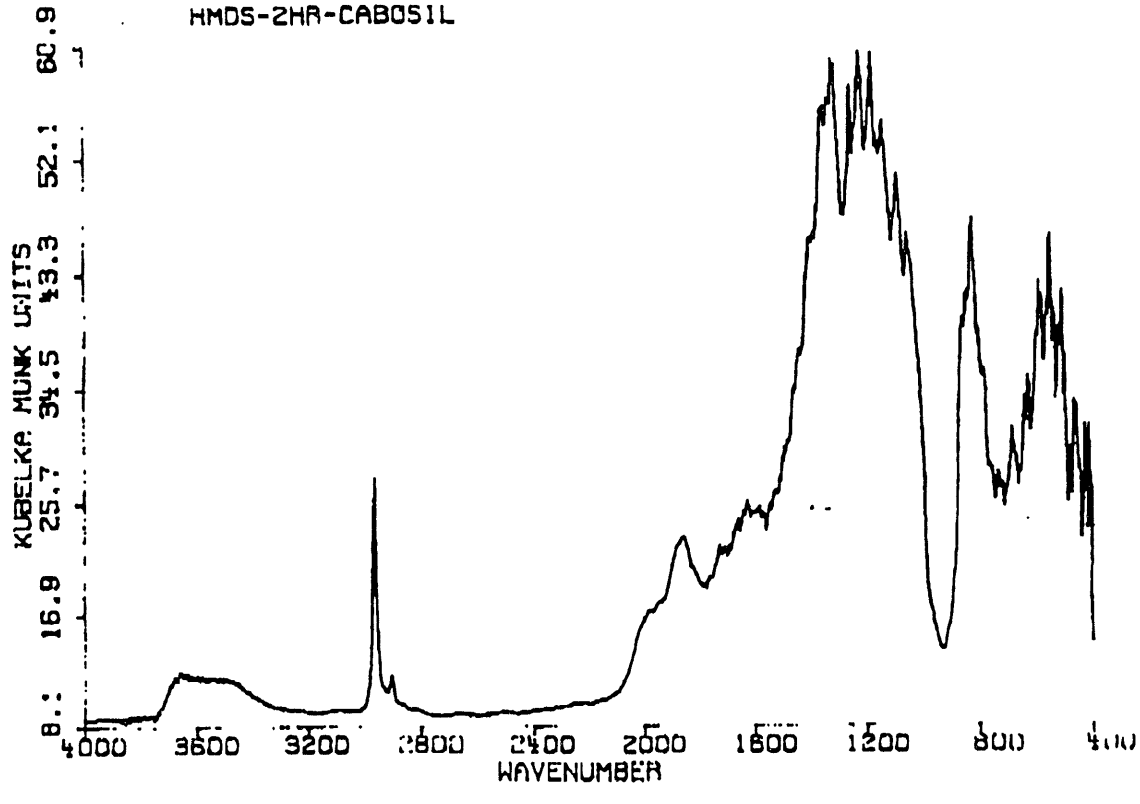

Figure 3. DRIFT spectrum of Cabosil after 2 hour treatment with HMDS.

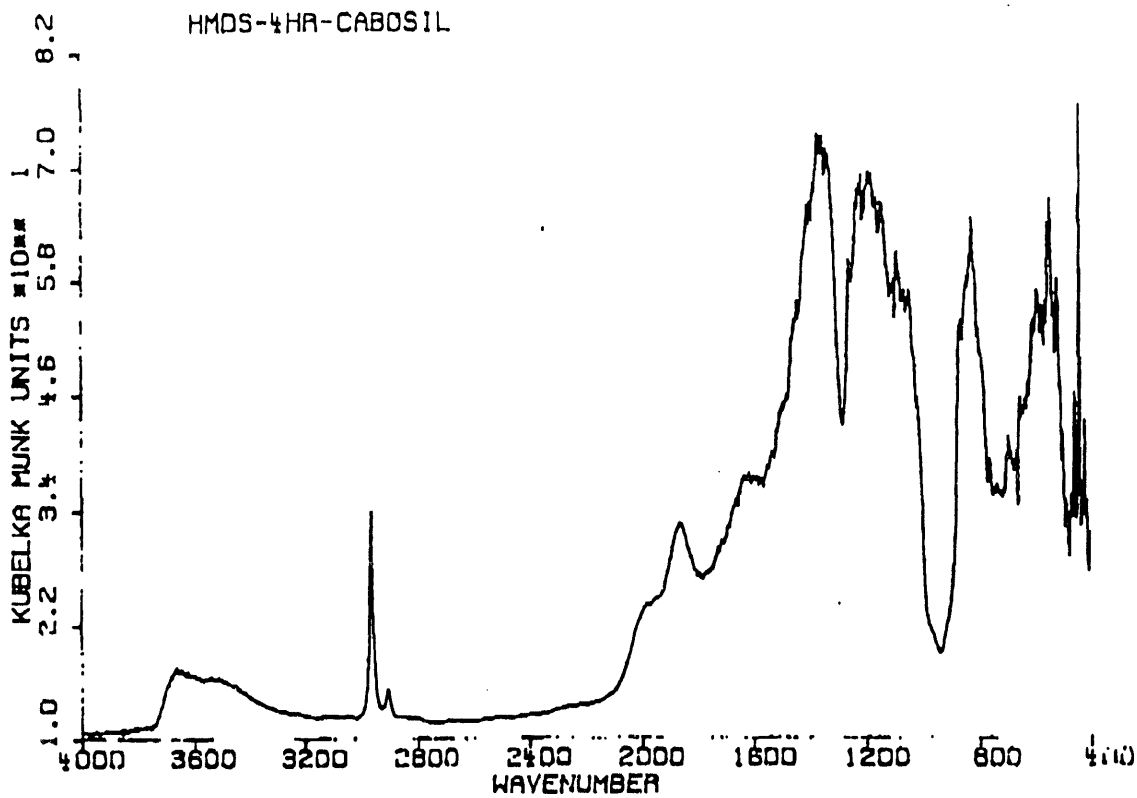

Figure 4. DRIFT spectrum of Cabosil after 4 hour treatment with HMDS.

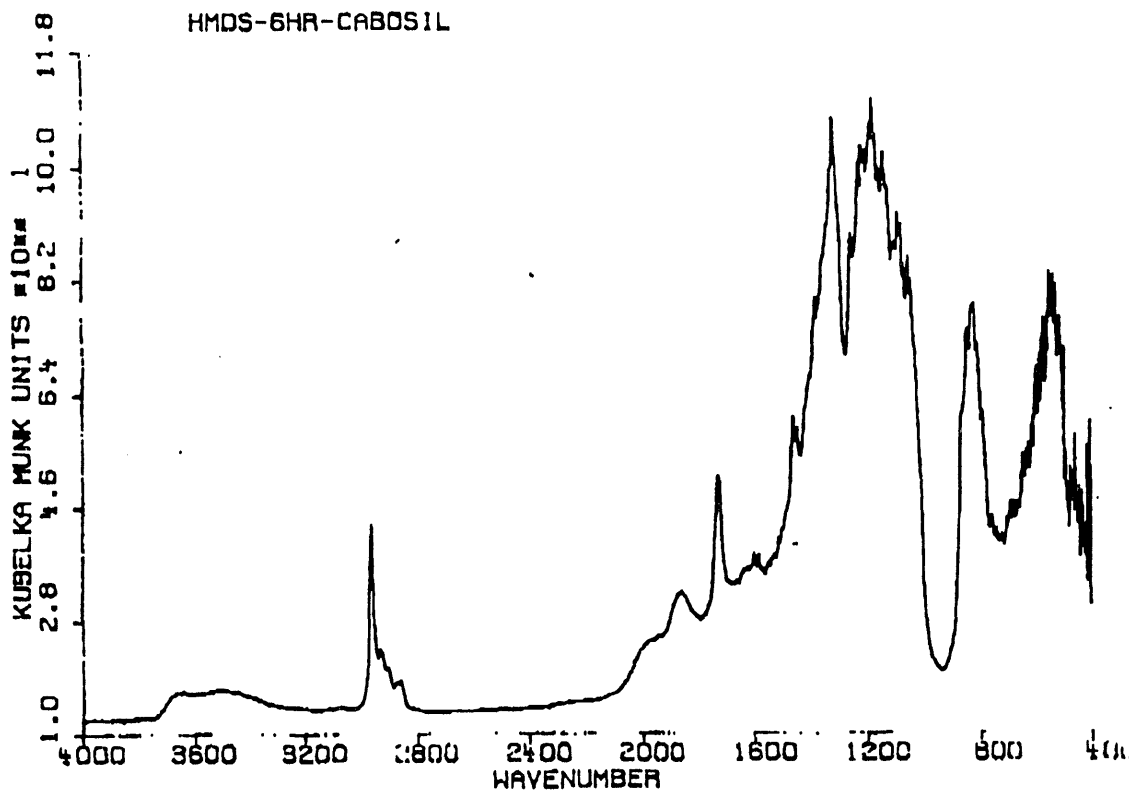

Figure 5. DRIFT spectrum of Cabosil after 6 hour treatment with HMDS.

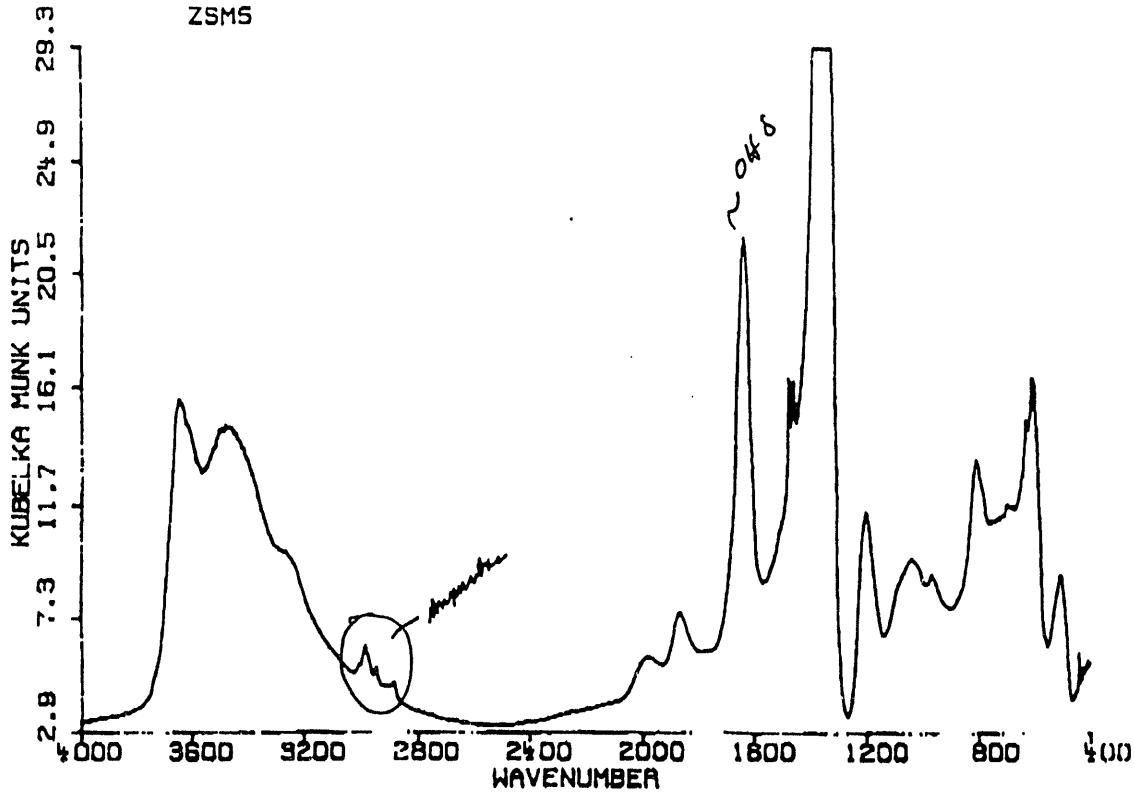

Figure 6. DRIFT spectrum of ZSM-5.

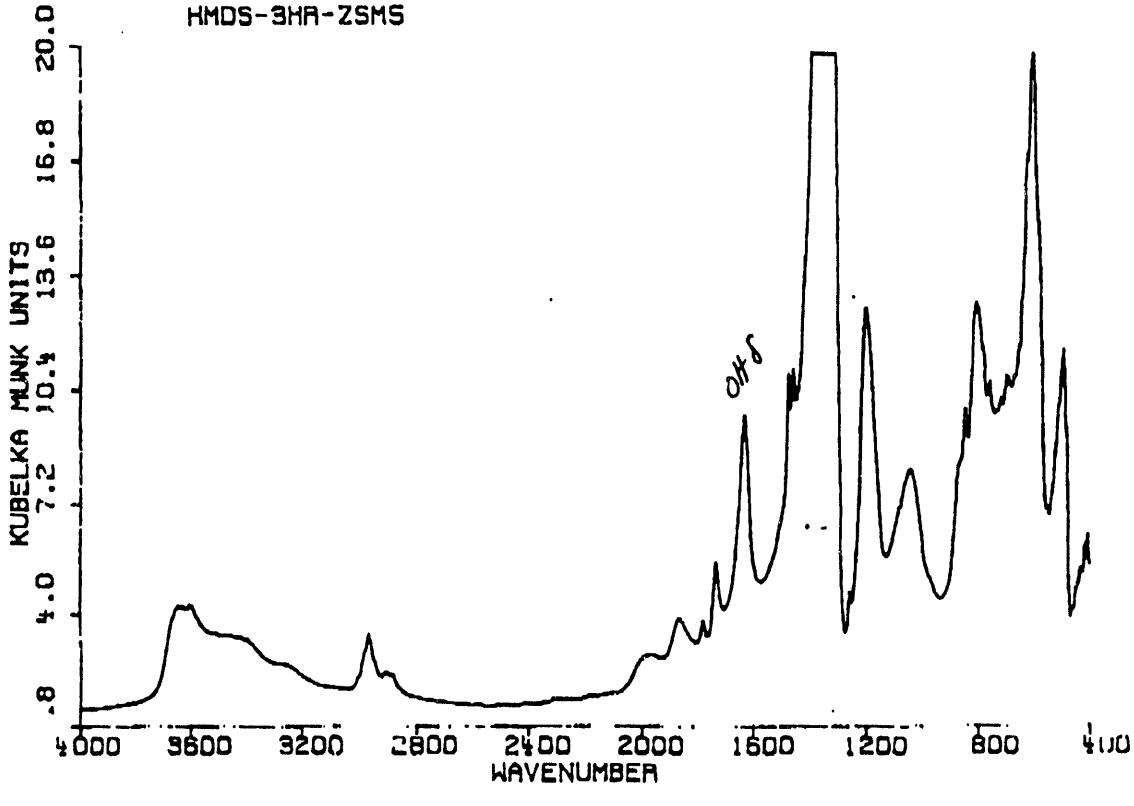

Figure 7. DRIFT spectrum of ZSM-5 after 3 hour treatment with HMDS.

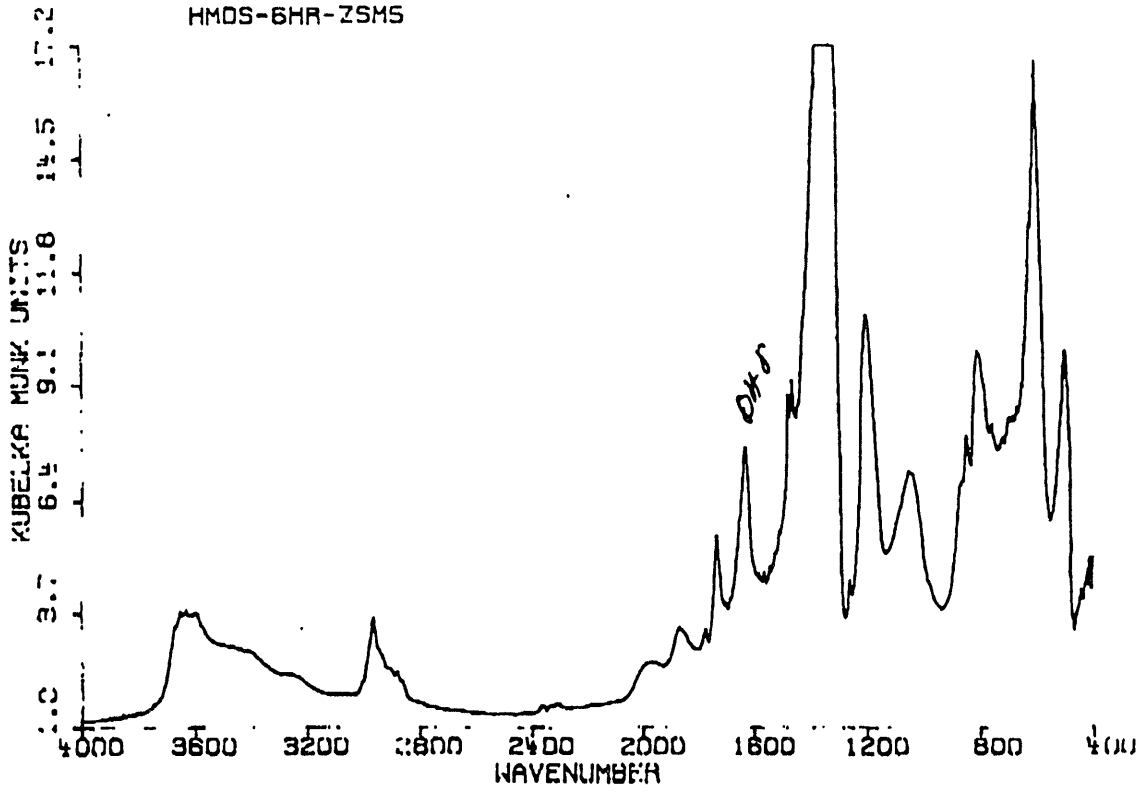

Figure 8. DRIFT spectrum of ZSM-5 after 6 hour treatment with HMDS.

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