

DOE/MT/94010--T8

RECEIVED
USD OE/PET O

36 SEP 13 PM 1:20

ACQUISITION & ASSISTANCE DIV.

QUARTERLY REPORT #6

For Period: January 1, 1996 - March 31, 1996

Project Title: ADVANCE CONCEPTS FOR THE CONVERSION
OF SYNGAS TO LIQUIDS

RECEIVED

NOV 26 1996

OSTI

Grant #: DOE-FG22-94MT-94010

Project Director: Dr. Rosemarie Szostak
Telephone Number: (404) 880-6861

Prepared by: Dr. Rosemarie Szostak
Dr. Conrad Ingram

Institution: Clark Atlanta University
223 James P. Brawley Drive
Atlanta, Georgia 30314

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *dy*

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1.0 Summary

Research activities for the period January 1, 1995 to March 31, 1996 have been focused on the characterization of catalyst samples, mainly by Diffuse Reflectance Infrared Spectroscopic Techniques. These studies revealed the strong presence of hydroxyls in our synthetic metal substituted aluminophosphate (MeAPO-36) samples, the amount of which appear to vary depending on the type of metal in the framework. In this report, cases of magnesium, cobalt and manganese are highlighted and compared. The hydroxyl groups present in these samples also shows some interaction with basic probe molecules such as ammonia. Details studies are in progress.

2. Work in Progress

Introduction of divalent metals (e.g. Co, Zn, Mn or Mg) into AlPO_4 frameworks are expected to generate a negative framework charge which are balanced by cations such as Na^+ , NH_4^+ or Ca^{2+} and therefore possess ion exchange characteristics. If the cation is H^+ , Bronsted acid sites are expected to be created which can be observed by Infrared Spectroscopy as vibration bands in the 3600 cm^{-1} region. To reveal the internal distribution of Bronsted and possibly Lewis acid sites and their relative strengths, suitable basic probe molecules such as NO, NH_3 , pyridine and CO can be used. These molecules possess spectroscopic properties which are altered upon interaction with acid centres within the pores of MeAPO molecular sieves. The acidic properties of MeAPO samples containing different metals are therefore currently being investigated by Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS).

2.1 Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) studies of the acidic properties of MeAPOs

Experimental procedure: Various metal containing MeAPO-36 samples were typically calcined in a quartz tube furnace at 500°C in flowing dry nitrogen for 2 hr followed by 500°C - 550°C in air for 4 hr, but conditions varied as was necessary to preserve the crystallinity of the samples. Following calcination, the IR spectra of each sample was recorded using a Nicolet FTIR equipped with diffuse reflectance attachments. Approximately 20 mg of each sample was placed as a thin surface on top of a lower KBr layer in a DRIFT cell. The sample was evacuated at 1×10^{-4} torr for 0.5 hr at 25°C , 100°C , 200°C , 300°C and 400°C and IR spectra were recorded at each temperature. The cell was then water cooled to 100°C and a spectrum was recorded to be used as reference. 10 torr of dry ammonia was passes over the sample for 0.5 hr, followed by evacuation for 0.5 hr. Another spectrum was recorded. The sample was then heated to 400° for 2 hr under vacuum in order to desorb ammonia, then re-cooled to 100°C and a final was spectrum recorded. The results are shown in Figure 1-6.

3.0 Results and Discussion

On calcination in N_2 followed by air of a cobalt containing MeAPO-36 sample, the catalyst underwent a colour change from blue to yellow-green with small patches of blue remaining distributed throughout. This colour change is ascribed to the oxidation of framework Co^{2+} to Co^{3+} while the remaining blue portion is proposed to be due to unoxidized Co^{2+} present in the pores of the molecular sieve on ion exchange sites. Figure 1 shows stack DRIFT spectra of this calcined sample evacuated at various temperatures up to $400^\circ C$. The band around 3665 cm^{-1} to 3675 cm^{-1} is assigned to the weak or non-acidic P-OH and Al-OH groups¹ whereas the band around 3599 cm^{-1} is not yet fully characterized, but is tentatively assigned to acidic hydroxyls of Al-OH-Me bond (Me = Zn, Co Mg or Mn). Similar vibration bands were observed by other researchers in zeolite faujasite and have been assigned to Bronsted OH groups.² These bands were also observed in a synthetic sample of the highly acidic, proton exchanged zeolite mordenite (Figure 2). Figure 3 shows stack spectra of a calcined magnesium containing MeAPO-36, which underwent similar thermal treatment. The vibration bands in the OH region of these spectra were similar to those observed in the cobalt containing sample. From a visual comparison of the spectra however, it can be observed that the intensity ratio of the 3590 to 3670 band is higher for CoAPO-36 compared with MgAPO-36, though both samples were prepared with equivalent amounts of each metal in their respective reaction mixtures. Figure 4 shows the stack spectra of a calcined sample of manganese containing MeAPO-36, which also underwent similar thermal treatment as previously described for Co and Mg containing samples. The vibration band around 3595 cm^{-1} was absent in this sample and may be due to the partial loss of crystallinity, and a resulting loss of acid sites during the calcination process.

Ammonia sorption on MeAPO-36: On exposure of CoAPO-36 to ammonia, a partial reversal of colour change from green-yellow back to grey-blue occurred. Figure 5 shows the difference spectrum of the sample after exposure to 1×10^1 torr of dry ammonia for 0.5 hr followed by evacuation. It can be observed that the vibration band around 3590 cm^{-1} disappeared while a negative peak was observed at 3683 cm^{-1} possibly due to interaction of NH_3 with hydroxyls. On desorbing ammonia at $400^\circ C$, vibration band at 3590 cm^{-1} returned, while the negative peak around 3683 cm^{-1} persisted (Figure 6). These IR studies are preliminary and further experiments are currently in progress that will hopefully clarify the acid-base interaction phenomena observed in these samples.

4. Other activities

4.1 The Catalytic activities of MeAPO samples will be evaluated using a continuous flow microreactor currently under construction.

4.2 Dr. C. W. Ingram presented paper on Catalytic Hydroxylation of Phenol over MeAPO-11 Molecular Sieves at the Symposium on Selective Hydrocarbon Oxidation at ACS National Meeting in New Orleans, March, 1996. The full paper from this research effort will be published by Applied Catalysis and is currently in press.

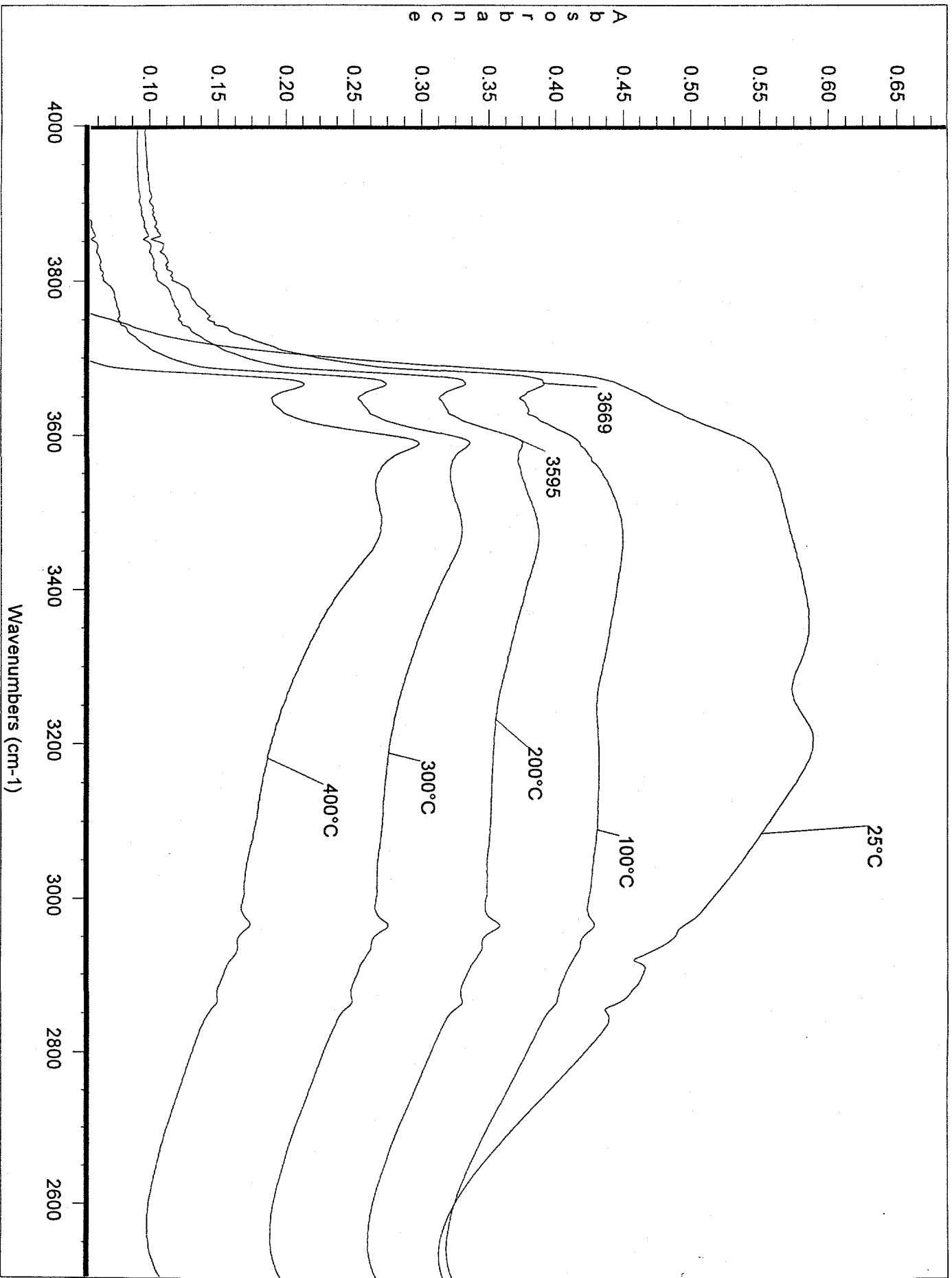


Figure 1. DRIFT spectra of OH region of a Co containing MeAPO-36 at various temperatures

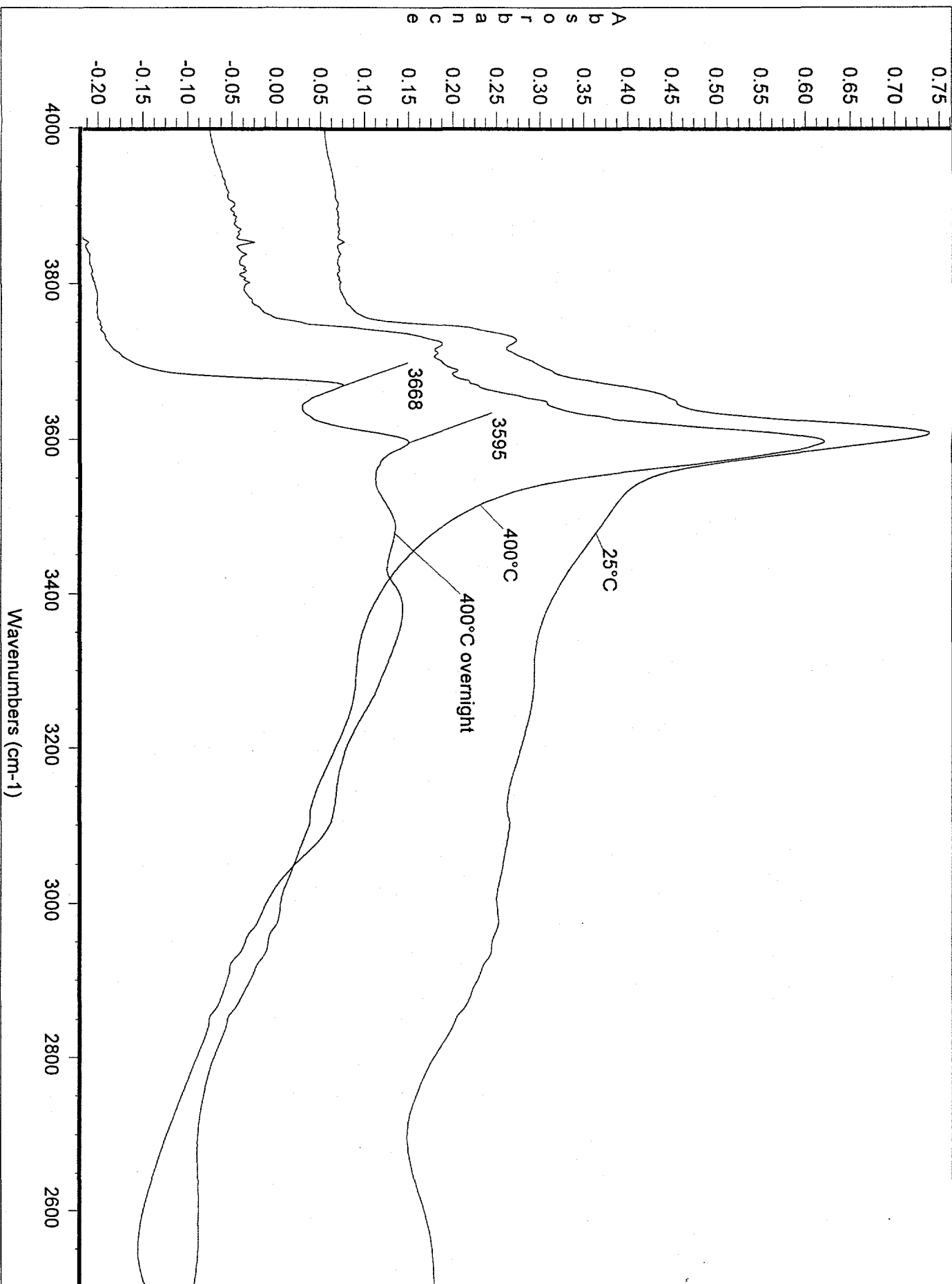


Figure 2: DRIFT spectra showing OH region of H-mordenite at various temperatures

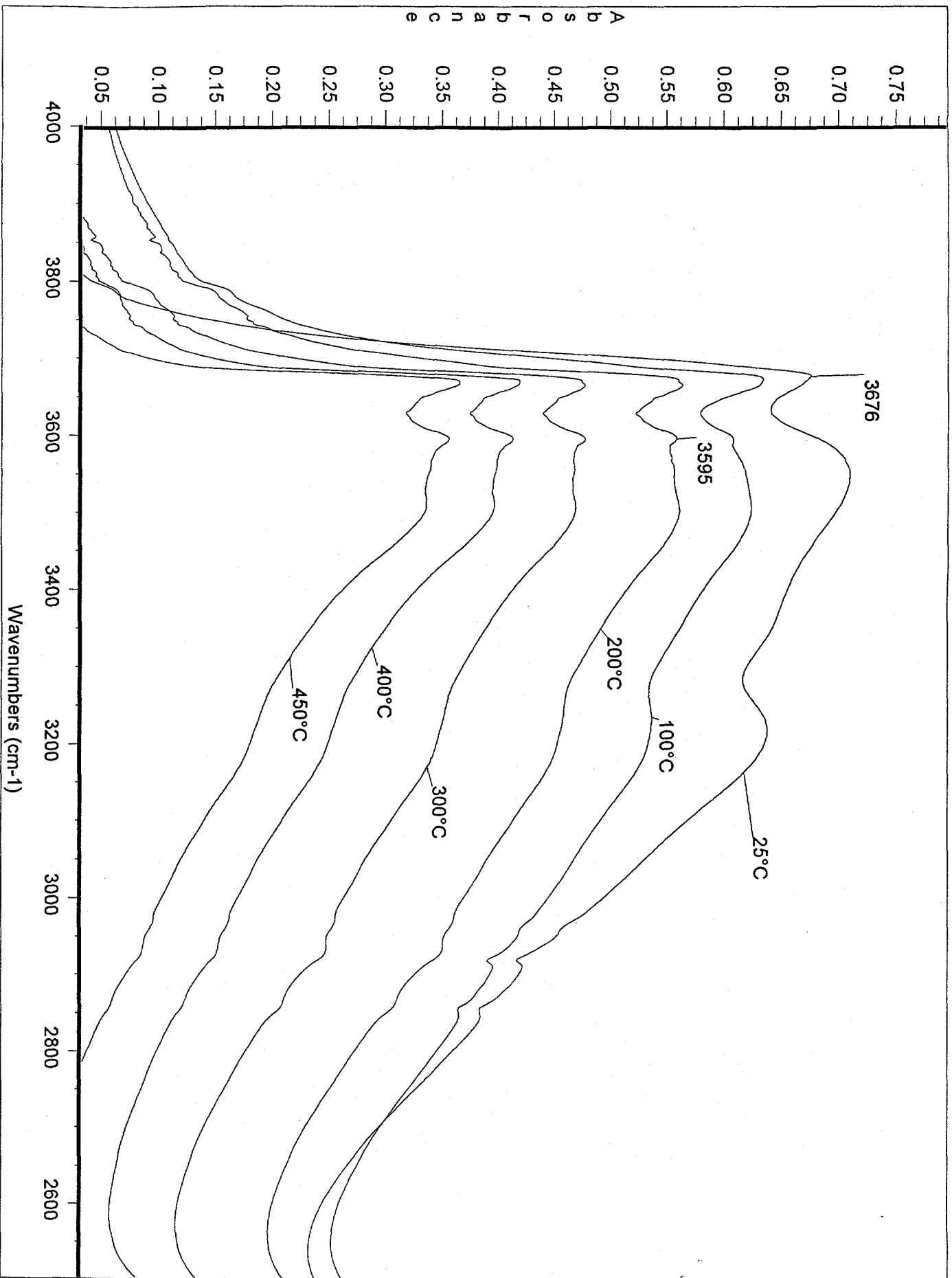


Figure 3: DRIFT spectra showing the OH region of a Mg containing NeAPO-36 at various temperatures

FTIR Spectra showing OH region of Mn containing MeAPO sample

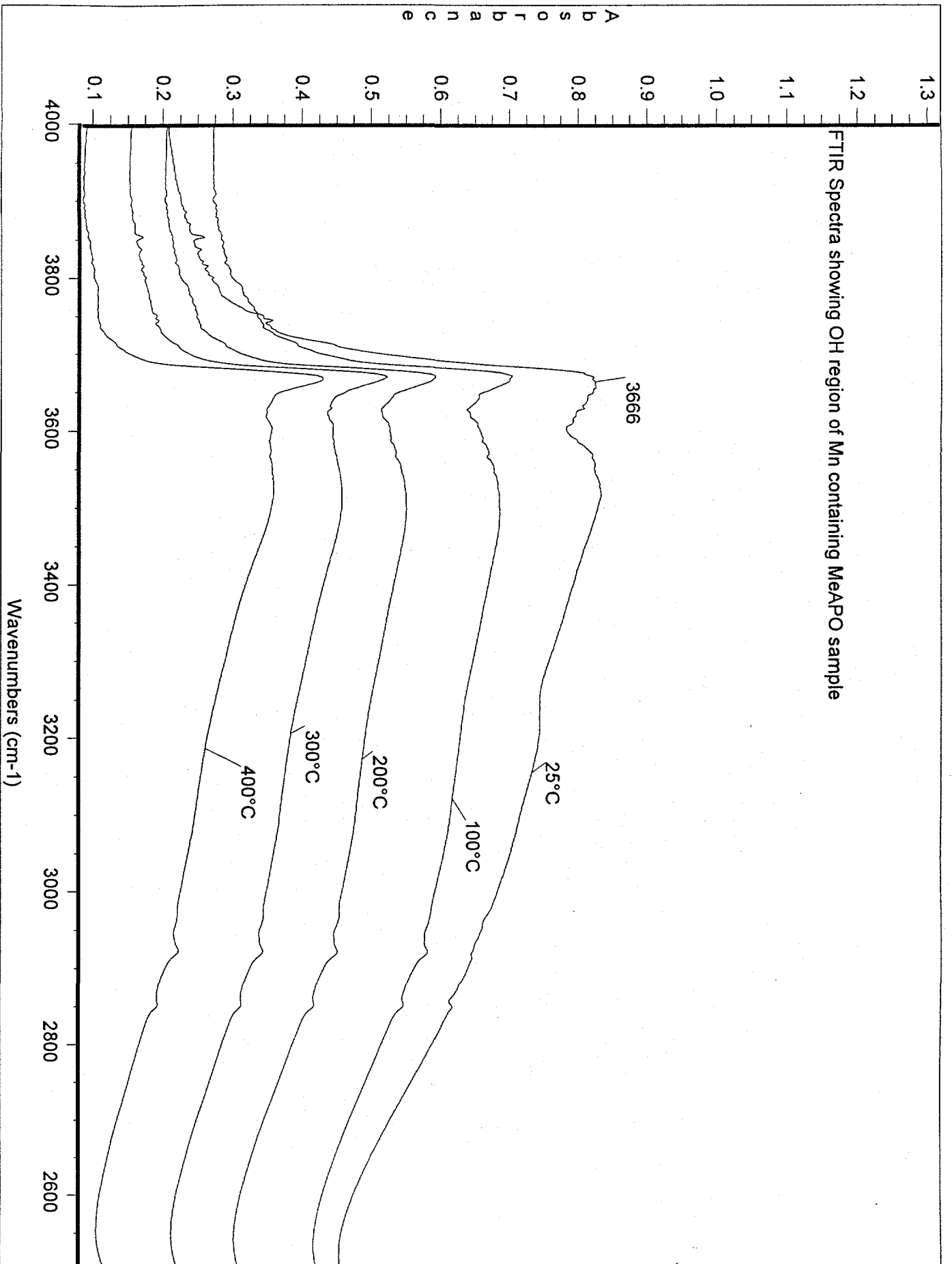


Figure 4: DRIFT spectra showing OH region of a Mn containing MeAPO-36 at various temperatures

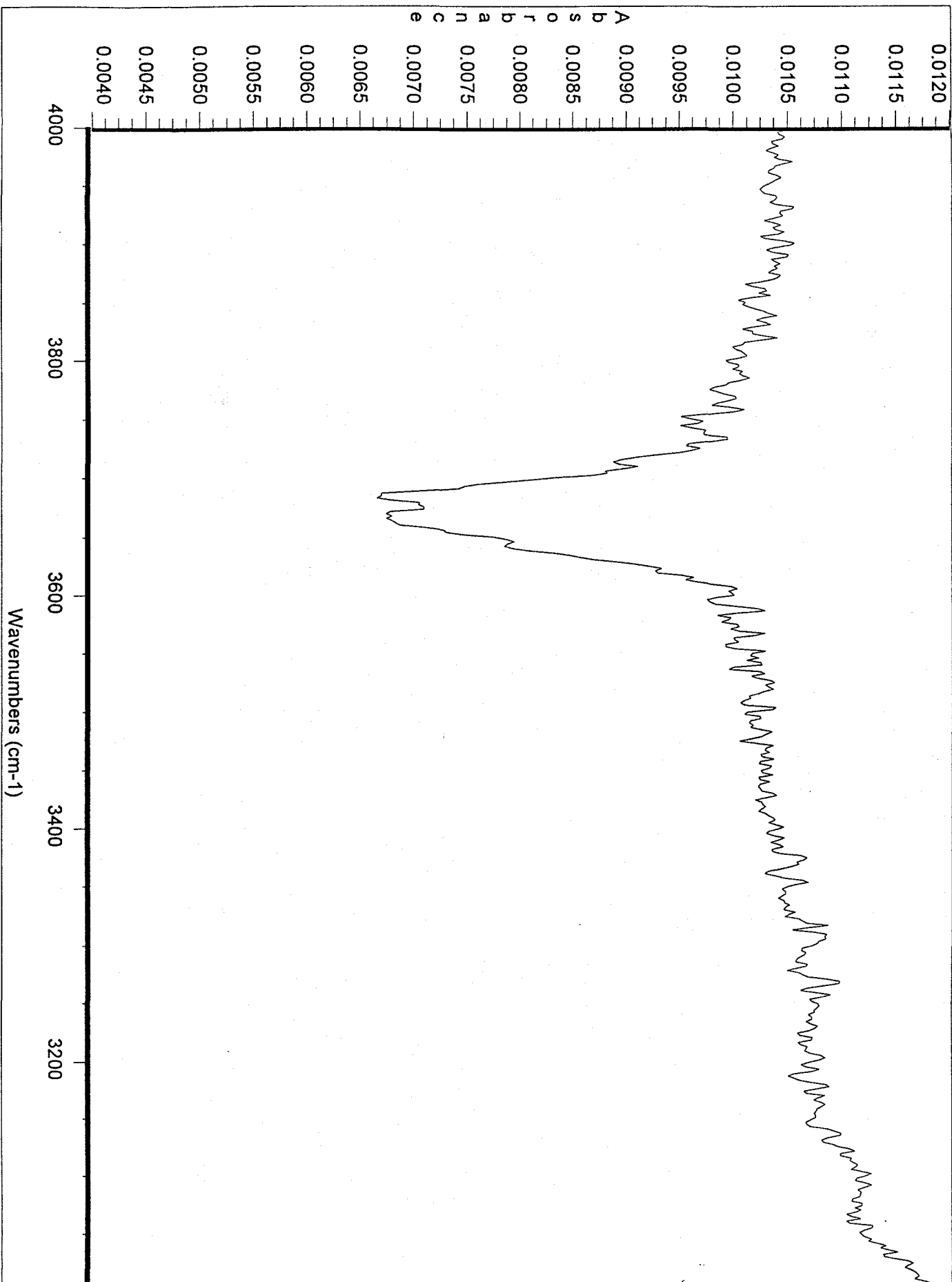


Figure 5: Difference spectra of ammonia chemisorbed on a CoAPO-36 sample at 100°C

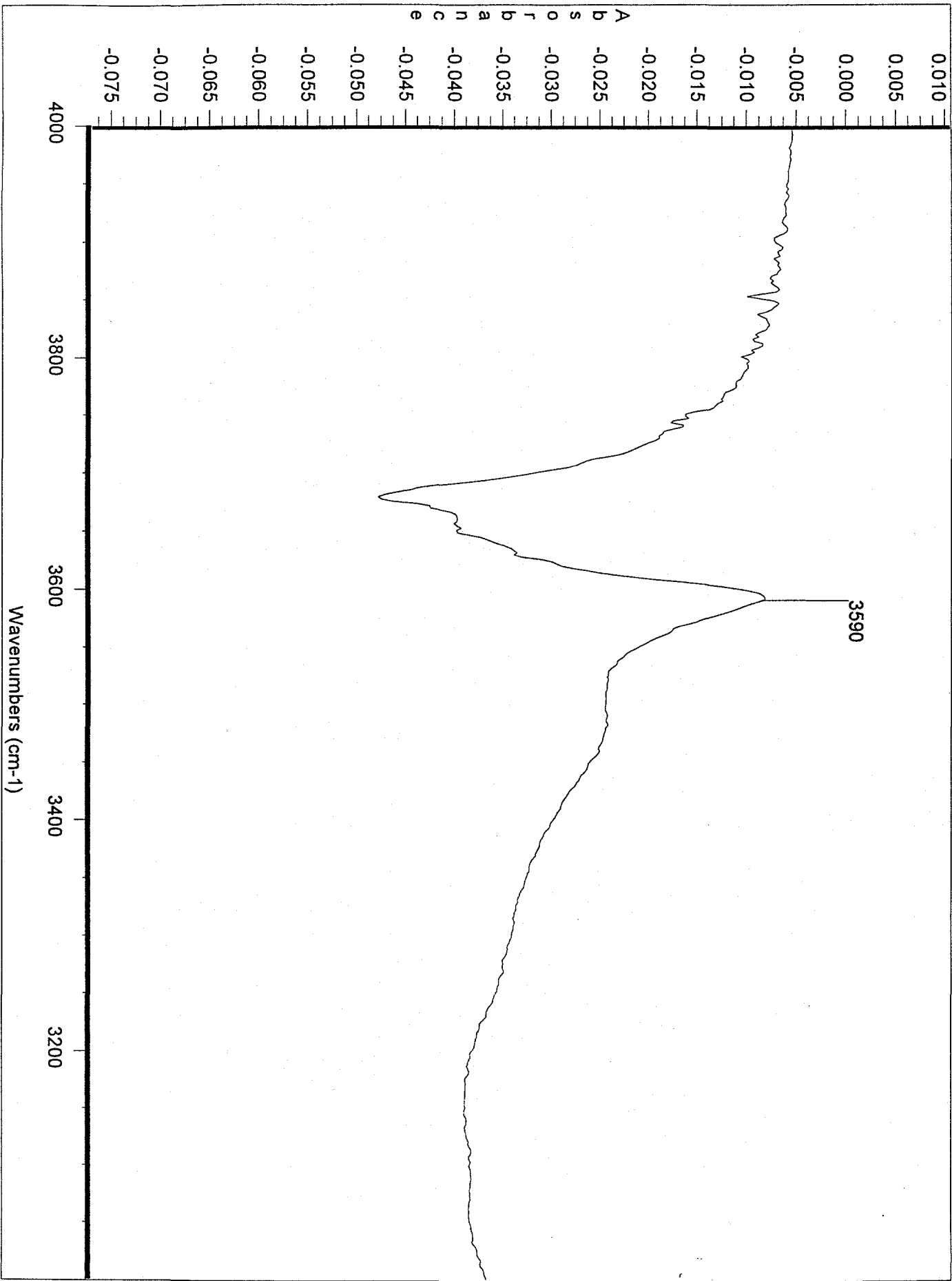


Figure 6: Difference spectra of CoAPO-36 after ammonia desorption at 400°C

Appendix 3

References

¹ J. Janchen, M. J. Haanepen, M. P.J. Peeters, J. H. M.C. van Wolput, J. P. Wolthuizen, J. H. C. van Hooff, *Studies in Surface Science and Catalysis* **84**, (1994) 365.

² M. A. Markarova, A. Garforth, V. I. Zholobenko, J. Dwyer, G. J. Earl, D. Rawlence, *Studies in Surface Science and Catalysis* **84**, (1994) 365.