Low Temperature VOC Combustion Over Manganese, Cobalt and Zinc Alpo$_4$ Molecular Sieves

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By
Rosemarie Szostak

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

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1.0   Introduction

The objective of this project is to prepare manganese, cobalt and zinc containing $AlPO_4$ molecular sieves and evaluate their catalytic activities for the removal of low levels of volatile organic compounds (VOCs) from gas streams. This report highlights our research activities for period October 1,1996 to March 31, 1997.

2.0   Experimental Procedure

Preparation and characterization of catalysts

Procedures for the catalysts preparation and their characterization by X-ray Diffraction (XRD) and Diffuse Reflectance Infrared Spectroscopy (DRIFTS) were outlined in Semi-Annual Report #1 (period August 1, 1995 to February 31, 1996).

Conversion of methylene chloride in a fixed bed continuous flow reactor

The design and construction of the fixed bed upflow microreactor used in the following catalytic studies was reported in Semi Annual Report # 2 (March 1,1996 to August 31, 1996). The procedure for a typical catalytic run was as follows: A 0.50 g sample of catalyst was placed on the frit inside the reactor tube and was kept in place by a small plug of glass wool. The reactor tube was heated to the desired reaction temperature. Air was bubbled at flow rate of 1 cc/min through methylene chloride contained in a 200 mL Dreshel bottle which was ice cooled to 0°C. The methylene chloride saturated stream of air was made up with an additional 15 mL/min of air to give a combined flow rate of 16 mL/min of gas going through the catalyst bed at space velocity of approximately (1920 mL gas/mLcatalyst/hr). 250 µL sample of the reactor effluent was injected into the gas chromatograph (GC) at regular intervals using the Valco six port valve gas sample loop. The operating conditions for the GC were as follows: Injector port temperature 200°C, FID Detector temperature 200°C, and oven temperature isothermal at 100°C. Separation was done using an Altech stainless steel packed column of dimensions 6 ft x 1/8 inch, containing Porapak Q stationery phase. The retention time (RT) of methylene chloride under these conditions was 8.87 minutes.

Studies on methylene chloride using DRIFTS

While we awaited the modification of the reactor to characterize and quantify the reaction products, DRIFTS was used to give some insight into the possible nature of these products. The adsorption and oxidation of methylene were performed in the DRIFT cell over both CoAPO-36 (sample D) and CoY. The catalysts powder was placed on a KBr bed inside the reaction cell which was then evacuated to 10^{-5} torr while heating to 400°C for a minimum of 12 hrs. After cooling the cell to 300°C, the catalyst was allowed to interact with 15 torr of methylene chloride

vapor for 1 hr. The cell was then evacuated at 10^{-5} torr for 1 h to remove physisorbed methylene chloride. Spectra were recorded (1000 scans) and ratioed against the pure activated molecular sieve to observe the interaction of chemisorbed methylene chloride with the catalyst surface.

Oxidation of the chemisorbed methylene chloride was conducted as follows: 100 torr of dry oxygen was allowed to interact with the chemisorbed methylene chloride at 300°C under static conditions. The transformation of the surface products was observed over time. The spectrum of chemisorbed methylene chloride was used as a background to obtained the spectra of the oxidized species.

3.   Results and Discussion

The results from the reactor runs for the oxidation of methylene chloride using various molecular sieves are tabulated in Table 2. Though all catalysts, with the exception of TS1 and CoY were synthesized from reaction mixtures of similar molar composition ratios, wide variation in their catalytic activities were observed. CoAPO-36 showed catalytic activity closest to the reference catalyst, CoY, which showed highest methylene chloride conversion. The Ti, Mn, Mg and Zn containing molecular sieves all showed low catalytic activities at 400°C. Further experiments was therefore focused on Co containing samples.

Figure 1 shows the catalytic activity of CoAPO-36 as a function of temperature and cobalt content of the catalysts. Methylene chloride conversion showed distinct temperature dependency. Exponential increase in conversion levels was observed in the temperature range from 250°C to 400°C, reaching 100% conversion at the higher temperature. Chatterjee and Greene reported similar results using zeolite Y exchanged with H, Ce and Cr.[1] Catalytic activity increased with Co content until approximately 4.8 wt % Co. No further increase in activity was observed for samples with higher Co content. CoY consistently showed higher conversion than CoAPO-36, though the former contained a lower Co content (2.5 Wt. %). This may be a result of the higher concentration of Bronsted acid sites that is available in its structure in comparison with CoAPO-36, as was revealed by DRIFTS.

With regards to stability of the catalysts under reaction conditions, CoAPO-36 samples maintained high crystallinity as was indicated by XRD. Peak positions (2θ values) and peaks heights in the X-ray diffractograms remained unchanged from a comparison of the calcined catalysts before and after catalytic runs.

The promising activity shown by the Co containing molecular sieves prompted us to investigate the activity of other Co containing topologies from the aluminophosphate family. Thus large pore CoAPO-5 (pore dimension of 0.73 nm) and medium pore CoAPO-11 (pore dimensions 0. 63 nm x 0. 39 nm) were investigated and compared with large pore CoAPO-36 (pore dimension of 0.65 nm x 0.75 nm).[2] Here again CoAPO-36 shows highest catalytic activity among the three. Though CoAPO-36 and CoAPO-5 are both large pore materials, it is known that the former container stronger Bronsted acid sites was demonstrated in its n-butane cracking activity.[3] Since acid sites seems to play an important role in methylene chloride oxidation, this may explain why CoAPO-36

show greater catalytic activity. In the case of CoAPO-11 which is also know to possess strong Bronsted acid sites, its lower catalytic activity may be related to its smaller pore dimensions causing slow diffusion of methylene chloride into its pores.

Efforts are ongoing to improve the reactor so that products can be analyzed proper mass balance can be conducted. In the meantime, qualitative analysis for the presence of HCl as a reaction product was assessed as a function of temperature by passing the reactor effluent through 20 mL of deionized water for 10 minutes using CoAPO-36 (D). The change in pH was monitored using a pH meter and the increase in H_3O^+ concentration was determined as a function of temperature. A direct correlation was observed between methylene chloride conversion and HCl (Figure 3).

Figures 4 and 5 show the spectra of CoAPO-36 (D) at 300°C before and after methylene chloride was chemisorbed respectively. The negative peaks observed at 3672 cm^{-1} and 3589 cm^{-1} after the adsorption of methylene chloride are due to the interaction of the VOC with the hydroxyls on the catalyst surface. Figure 6 shows results from oxidation of chemisorbed methylene in air at 300°C. The hydroxyl band at 3666 cm^{-1} gradually reappears as the time of oxidation was increased, suggesting the gradual oxidation of the VOC and an important role played by these acidic centers. The spent catalyst was observed to undergo a color change from yellow green to blue and this is attributed to a change in the oxidation state of the cobalt from 3^+ to 2^+. The above suggests that the VOC is simultaneously interacting with both the acid site and the Co center.

Among the main reaction products expected from this reaction are CO_2 and CO. The double bands appearing at 2363 cm^{-1} and 2326 cm^{-1} in Figure 7 is assigned to CO_2.[4] The intensities of these bands and therefore the amount of CO_2 produced increased with oxidation time up 60 minutes. The band at 2170 is assigned to CO and its intensity did not appear to increase with oxidation time (Spectra 1-4). In Figure 8 bands at 1788 cm^{-1} and 1735 cm^{-1} corresponds to the C=O stretching and CCl_2 assymetric stretching respectively in accordance with published work. The intensities of both peaks increased with increase in the time of oxidation, and could possibly be due to the formation of phosgene on the surface of the catalysts.

In these studies both CO and CO_2 were identified in the reaction products along with some intermediates which were tentatively identified.

4.0   Summary and Future work

A range of molecular sieves were screened for their catalytic activities in the destruction of the chlorinated VOC, (methylene chloride). CoAPO-36 showed best catalytic activity for the process and compared well with CoY. Catalytic activity increased with cobalt content up to 4.8 wt.%. The Ti containing zeolite TS1, as well as the Mg, Co and Zn containing MeAPOs showed much lower activities compared with CoAPO-36.

Future work will focus on further qualitative and quantitative analysis of reaction products so that trends in selectivity towards CO and CO_2 can be assessed by DRIFTS and gas chromatography. MeAPOs will also be screened for their activities in the decomposition of other other VOCs such as carbon tetrachloride.

5.0 Presentation of results

Preliminary results from this project were presented by undergraduate student Miss Keera Cleare at the Fifth Annual Historical Black College and Universities and Other Minority Institution/ Private Sector Energy Research and Development Technology Transfer Symposium in Baton Rouge Louisiana; March 2-4, 1997, for which she placed first in a poster competition.

Table 1: Synthesis gel compositions and wt. % Co and Al in products of CoAPO-36 samples.

Sample ID	** Molar composition of reaction mixtures	* Wt % composition by chemical analysis	
		% Co	% Al
A	$2.0R:0.05CoO:0.98Al_2O_3:1P_2O_5:40H_2O$	2.5	25.0
B	$2.0R:0.10CoO:0.96Al_2O_3:1P_2O_5:40H_2O$	4.8	23.5
C	$2.0R:0.18CoO:0.98Al_2O_3:1P_2O_5:37H_2O$	6.5	24.4
D	$1.9R:0.26CoO:0.91Al_2O_3:1P_2O_5:40H_2O$	5.0	22.1
E	$1.9R:0.40CoO:0.84Al_2O_3:1P_2O_5:40H_2O$	10.8	20.1
CoY	nd	2.5	nd

**   R = trypropylamine
*   Wt. % of metal in product determined by ICPMS
      nd = not determined

Table 2: Catalytic activities of various molecular sieves for methylene chloride oxidation

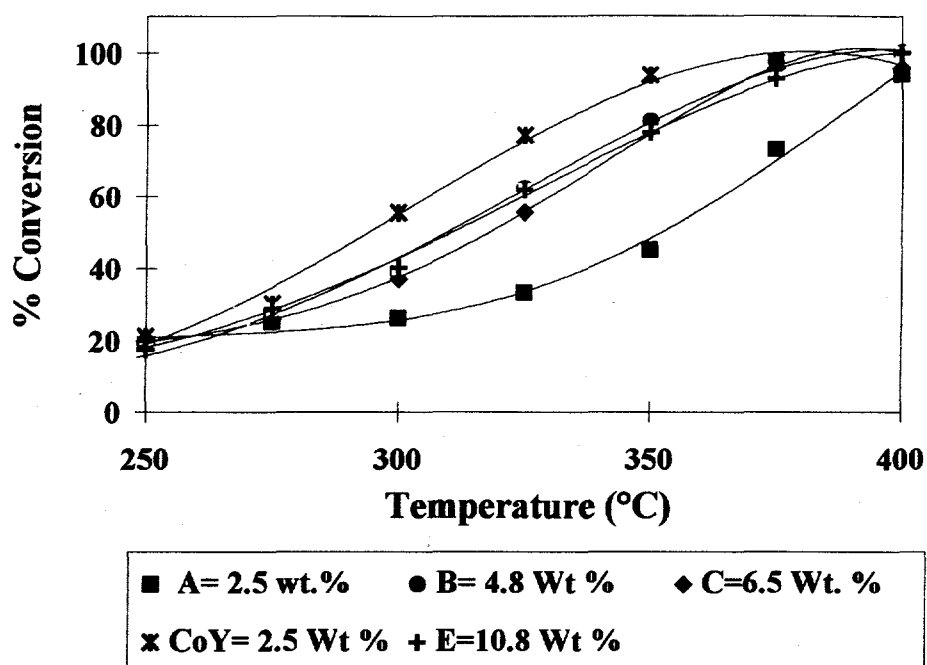| Catalysts	Conversion (%)		
	300°C	350°C	400°C
CoY	45.4	93.6	97.5
CoAPO-36 (B)	37.1	77.6	100
MnAPO-36	7.5	16.4	37.2
MAPO-36	7.8	12.3	19.8
ZnAPO-36	3.9	4.1	12.7
TS1	2.1	11.6	14.6
Homogeneous run	0		14.1

Figure 1: Methylene chloride conversion vs. reaction temperature and Co content of CoAPO-36.
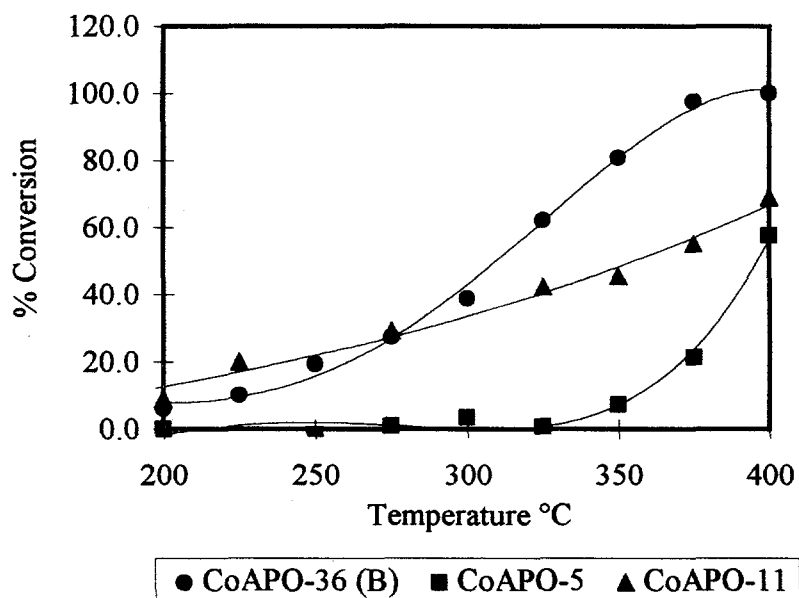

Figure 2: Conversion of methylene chloride on Co containing MeAPOs of various topologies.
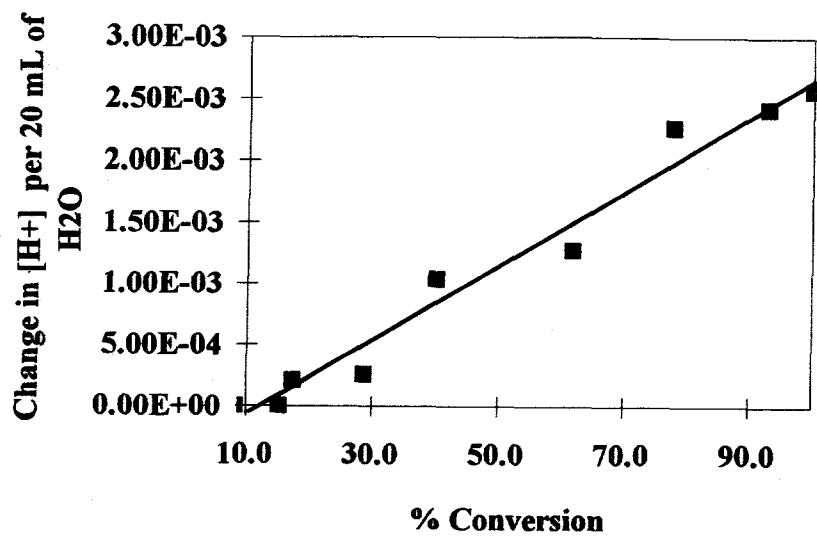
Figure 3: HCl production vs. methylene chloride conversion on CoAPO-36 (B)
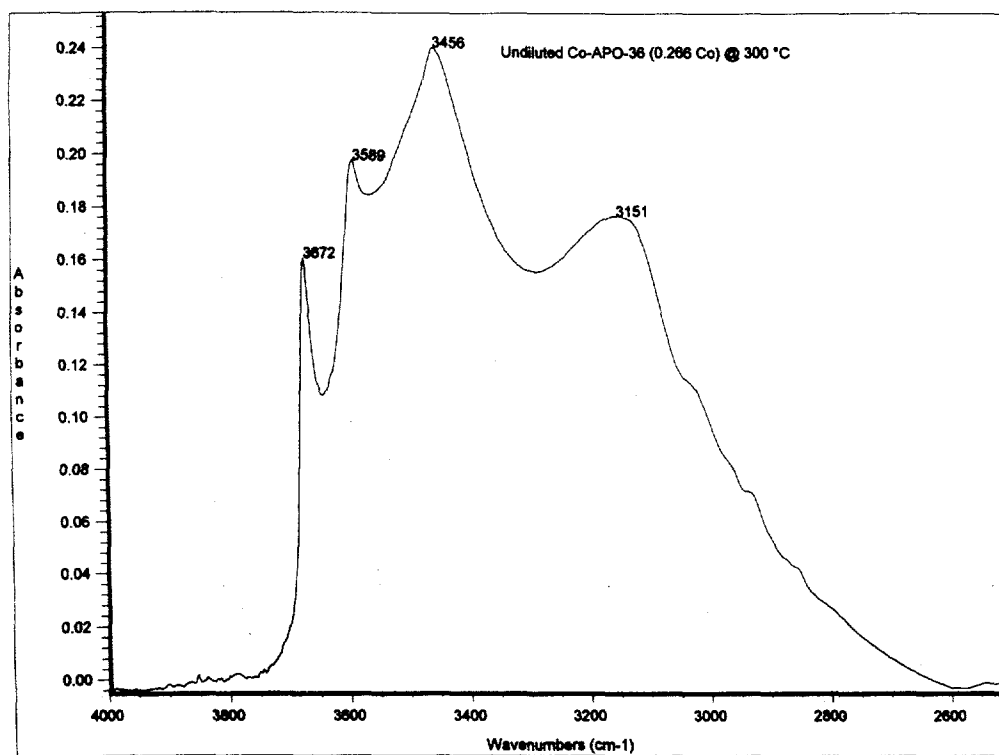

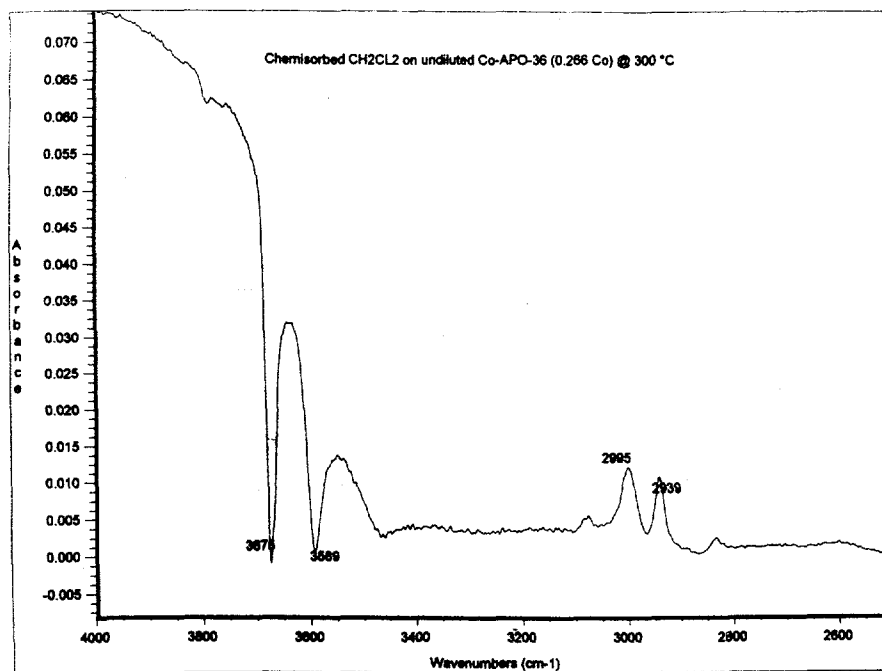Figure 4. IR Spectrum showing OH region of CoAPO-36 (D) after heating and evacuation.

Figure 5: IR Spectrum showing OH region of CoAPO-36 (D) after methylene chloride was chemisorbed at 300°C.
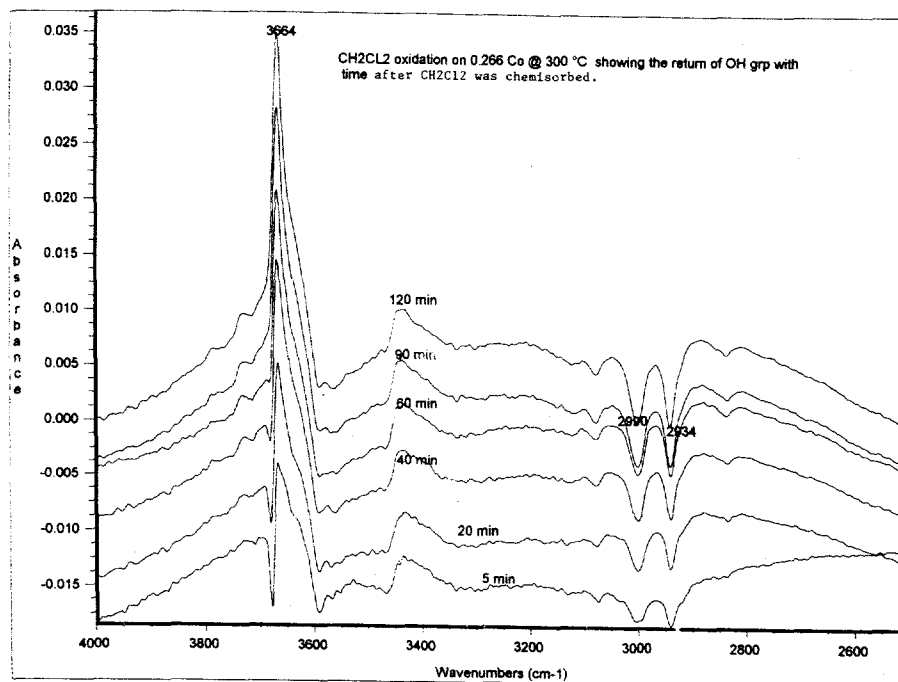

Figure 6. IR spectra of CoAPO-36 (D) showing the return of OH groups with time during the oxidation of chemisorbed methylene chloride.
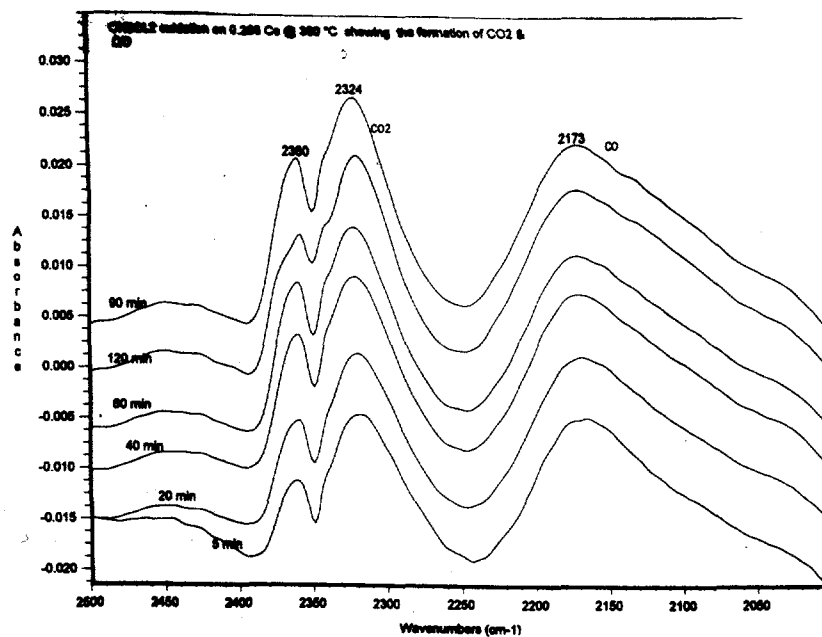
Figure 7. IR spectra of CoAPO-36 (D) showing the formation of CO and CO_2 with time during the oxidation of chemisorbed methylene chloride.
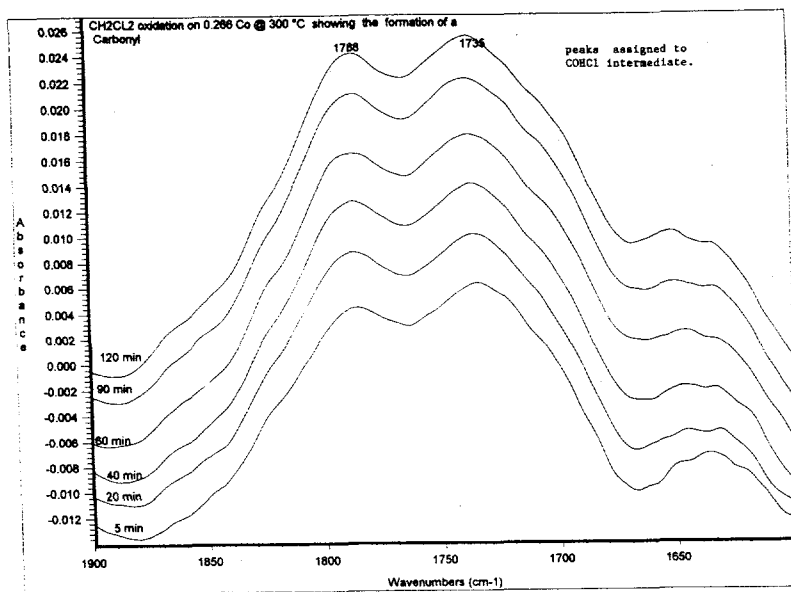

Figure 8. IR spectra of CoAPO-36 (D) showing the formation of carbonyl species (possibly COHCl intermediate) with time during the oxidation of chemisorbed methylene chloride.

References

[1] Chaterjee, S., Greene, H., *Appl. Catal. A: General* 98 (1993)139-158.

[2] Meier, W. M., Olson, D. H., Atlas of zeolite structure types 3rd ed., Butterworth-Heinemann, MA (1992)

[3] Nakashiro, K., Y. Ono, *J. Chem. Soc. Faraday Trans.* 1, 87 19 (1991).

[4] Ramachandran, B., Greene, H., Chatterjee, S., *Appl. Catal. B., Environmental* 8 (1996)157-182