

August 10, 2005
Dr. Christopher Ibeh
REU/RET Program Director
Summer 2005

Re: Synthesis and Characterization of Cr- AlMCM-41 and Its Application
toward Photo-catalytic Decomposition of Acetaldehyde

Dear Dr. Ibeh:

Enclosed please find the technical report regarding synthesis and characterization of silica based Cr- AlMCM-41 and Al-MCM 41 and their application toward degradation of acetaldehyde. The results in this study are invaluable in understanding the ideas to synthesize nanoparticles of interest and the application of these nanoparticles in decomposing toxic chemicals. We used different methods of analysis to shed some light on mechanism of reactions on surfaces.

Thank you very much for providing opportunities to work on this project. I also thank my research advisor Dr. Paul for providing continuous assistance.

Sincerely,

Chih-Ang Chang
Pittsburg, KS 66762

Research Topic

REU/RET

Summer 2005

Synthesis and Characterization of CrAlMCM-41 and Its Application
toward Photo-catalytic Decomposition of Acetaldehyde

By

Chih-Ang Chang

Department of Chemistry

Pittsburg State University

Research Advisor

Dr. Dilip Paul

For

Dr. Christopher C. Ibeh

Director REU/RET Program

Department of Engineering

Pittsburg State University

August 10, 2005

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ABSTRACT

Here some novel nanoparticles involving mesoporous MCM -41 were synthesized using sol-gel method and characterized using surface area and XRD measurements. These Cr and Al incorporated MCM-41 nanoparticles were then studied using FT-IR and MS to explore the reactivity towards a common organic pollutant, acetaldehyde. The low temperature reaction of acetaldehyde with Cr-MCM -41 indicates the formation of crotonaldehyde which probably results from the acid-base properties of the surface. As the reaction is carried out in presence of UV-Vis light, further oxidation takes place forming carbon dioxide along with other partially oxygenated species, such as acetate, crotonate etc. Comparing the results of both Cr and Al-doped MCM-41 for acetaldehyde oxidation, it shows that Cr-doped nanoparticles are more reactive toward oxidation.

INTRODUCTION

The discovery of MCM-41 mesoporous molecular sieves has gained interest in developing new nanoparticles for its uniform pore sizes and high surface area. Professor Klabunde's group recently synthesized Cr-AlMCM-41 and AlMCM-41 and characterized these particles. The high reactivity of these nanoparticles sparked interest in using these particles for detoxification of chemical warfare in presence of oxygen. Initial studies by Klabunde group show that these nanoparticles are very reactive toward oxidation of a simple organic having -CHO functionality. During the reaction CO₂ was formed and monitored by a GC-MS. However, in these studies the reaction was carefully monitored using in situ FT-IR in order to understand the reaction mechanism and to identify other surface intermediates. These studies also indicate whether these nanomaterials are effective in detoxifying the environment.

LITERATURE REVIEW

Rodrigues, Shalini; Uma, S., " Visible Light Induced Photocatalytic Activity for Degradation of Acetaldehyde using Transition Metal Incorporated Al-MCM-41 (aluminum doped silica zeolitic material)," Journal of Photochemistry and Photobiology A, 2004, 51-58.

This paper describes the synthesis and characterization of transition metal (Mn, Cr, Cu, or Co) incorporated into MCM-41 in addition to measuring the photoreactivity of

acetaldehyde degradation and carbon dioxide formation in gas phase. The photo source is using 1000 watt Hg lamp. The appropriate filter was used to block UV light in order to investigate the effect of visible light. In this experiment, different concentrations of Co in AIMCM-41 are used to understand the effect of the metal ion. The increasing concentration of Co^{2+} has more photoactivity but the activity is lower than Degussa P25 TiO_2 . Furthermore, the photoactivity of Cr-AIMCM-41 increases because of the presence of Cr^{3+} and Cr^{6+} couple in the catalyst. It also shows that catalysts in visible light and UV light have good activity especially in Cr-AIMCM-41.

Kim, Ji Man; Kwak, Ja Hun, "Ion Exchange and Thermal Stability of MCM-41," Journal of Physical Chemistry, 1995, 16742-16747.

It presents the syntheses and characterization of MCM-41 and compares the ion exchange of AIMCM-41 with that of MCM-41. It is because the Si-OH group does not have enough capacity for ion change. The process of ion change is using slurry-filtration-wash cycle. Slurry is using AIMCM-41 stirred in nitrite solution such as NaNO_3 , KNO_3 , or $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ than filtered and wash with distilled water for about 3 times. The ratio of Na/Al or K/Al will change but it is reversible. It shows that ion change on the MCM framework of Aluminum side. Furthermore, from MAS Al NMR, octahedral aluminum show at the 0 ppm when the sample is fully hydrated but the boarding line might cause difficult to detect. Instead of investigate in intensity of tetrahedral Al NMR, it is better to use ion change capacity.

Does CrAIMCM-41 decompose toxic chemical?

The experiments on acetaldehyde decompose on TiO_2 has been investigated and researched for a long time. However, it has not been investigate in Cr-AIMCM-41. Does this nanomaterial decompose acetaldehyde? Does it forming other materials that it is toxic? And, how well it is?

SYNTHESIS AND CHARACTERIZATION

This Cr-AIMCM-41 and AIMCM-41 were prepared by Klabunde and coworkers following a procedure by Lin et al. The preparation of these specific compounds was carried out in Dr. Klabunde's Lab according to the procedure given here. 10 mL of diethyl amine solution was added to a solution containing 72 mL of deionized water, 2.04 g of cetylammonium bromide, and 0.386 g of $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ and stirred vigorously. Then CrCl_3 in 3.6 mL of NH_4OH was added to the above mixture.

The resulting solution was stirred and to it was added 8.9 mL of tetraethylortosilicate drop-wise. Finally the mixture was stirred at room temperature for 4 h followed by heating at 110 deg C for 4 days in a polypropylene container. The product was filtered, washed with water, and dried overnight. The sample was calcined at 600 deg C at a heating rate of 1 deg C/min. Upon calcinations the nanoparticles were shipped here at PSU for further analysis.

Powder x-ray diffractograms (XRD) of the samples, BET surface area and UV-vis NIR with an integrated sphere were determined by Klabunde's group.

METHODOLOGY

EQUIPMENT USED

For synthesis and characterization purposes (at K-State) following equipment were used:

Parr Reactor, Calcination oven, XRD, Surface area analyzer, UV-Vis spectrometer

And here at PSU we used the following equipment:

- i) Ultra high vacuum system
- ii) FTIR (Fourier Transform Infrared) Spectrometer, Mattson Instrument ---to receive IR spectral data using Winfirst software
- iii) Xenon short arc and Filters ---150 watt UV lamp with broadly band irradiation (PTI Inc)
- iv) Hydraulic press --- for pressing the sample on to mesh
- v) Temperature Controller (Honey well UDC 3000)
- vi) MKS Mass Spectrometer
- vii) Power Supply ---to heat the sample as needed during the reaction
- viii) OriginPro 6. ---for manipulating the IR spectral data
- ix) Sonicator ---for cleaning the sample holder and Tungsten grid

MATERIAL USED

- i) Nanomaterial Cr-ALMCM-41 and ALMCM-41
- ii) 0.002" thick photoetched tungsten me - used for sample holder (the transimission of grid is about 58%)
- iii) Dry ice and acetone - use for conduction cooling
- iv) E-type thermocouple (0.12mm constant and chromega wires)

- v) Highly pure hydrogen gas
- vi) High purity oxygen gas
- vii) High purity acetaldehyde obtained from Aldrich
- viii) High purity crtonaldehyde obtained from Aldrich Chemical

PROCEDURE

Experiments were carried out in a bakeable stainless steel IR cell capable of operating at sample temperatures from 180 to 1200 K. The detailed description of IR cell had been reported previously. In brief, the nanoparticle powder (~4-8 mg) was pressed into a tungsten grid which was held rigidly by a power/thermocouple feedthrough via a pair of nickel clamps. An E-type thermocouple was spot-welded on the top central region of the tungsten grid to measure the temperature of the sample. The sample temperature could be easily adjusted using dry-ice acetone mixture and electrical heating of the grid via a programmable controller.

Upon transferring the sample into the cell, the cell is evacuated over night at room temperature. Then the sample is heated slowly at different temperature up to ~500°C to dehydroxylate the sample which then undergoes calcinations in presence of oxygen (~15 Torr) for 30 min. followed by evacuation at 650°C. The sample is then cooled to 233 K to record the background spectrum before exposing the sample to any gas or reactant.

The IR cell was connected to a stainless steel vacuum system pumped by a turbomolecular pump and the base pressure was 1×10^{-8} Torr. The system base pressure was measured by the ion current drawn by the ion pump, while the reactant gas pressures were measured by a capacitance manometer. A FT-IR spectrometer and a quadrupole mass spectrometer were used in this system.

Infrared spectra were obtained with a dry CO₂ free air purged Mattson FTIR spectrometer equipped with a narrow band HgCdTe detector. The sample spectra shown here were recorded with 4 cm⁻¹ resolution using 300 scans.

RESULTS AND DISCUSSION

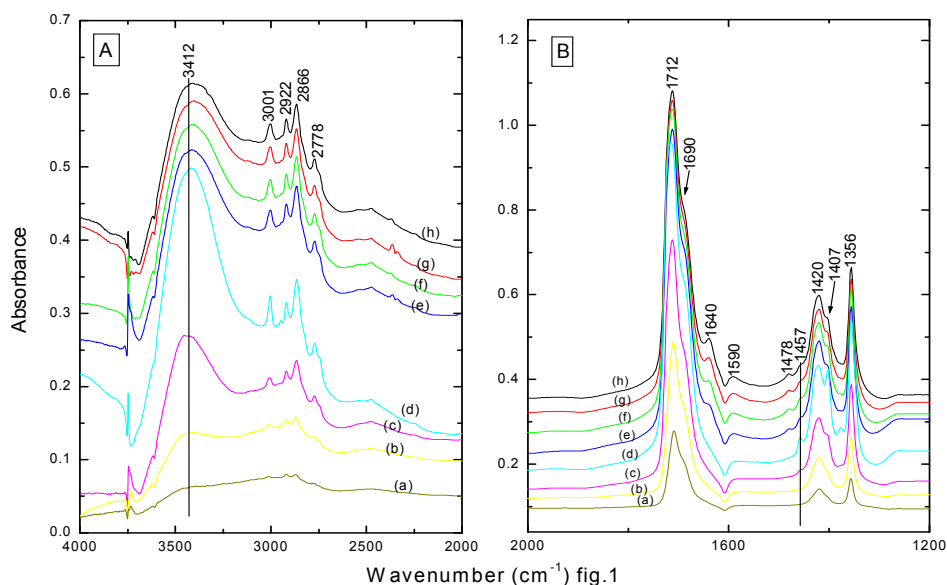


Figure 1 (spectra a, b, c, and d) shows the development of IR spectra as acetaldehyde is introduced onto the surface at different pressures as indicated: (a) 0.085 Torr, (b) 0.09 Torr, (c) 0.13 torr, and (d) 0.21 torr. The spectra e, f, and g indicate the development of spectral behavior upon introduction of oxygen (15 Torr) at different time intervals. The left panel of Figure 1 [A] shows the C-H and O-H stretching modes whereas the right panel [B] shows the bending modes of all surface species. As the acetaldehyde is introduced onto the surface, the isolated OH stretching mode at 3691 cm^{-1} gradually diminishes and a new peak develops at 3412 cm^{-1} . In addition, the C-H stretching and bending modes develop in the corresponding region. This unique spectral behavior indicates the formation of H-bonding through surface OH and carbonyl oxygen of acetaldehyde molecule. The enormous increase in the O-H mode intensity at 3412 cm^{-1} and the red-shift of OH mode from 3691 cm^{-1} to 3412 cm^{-1} are the main characteristics for H-bonding. The tentative peak assignment of all surface species is given in Table 1.

Table 1.

Acetaldehyde		
Assignment	Gas Phase (cm^{-1})	Cr-AIMCM-41 (cm^{-1})
$\nu_a(\text{CH})\text{ sp}^2$		
$\nu_s(\text{CH})\text{ sp}^2$		

$\nu_a(\text{CH}_3)$ sp^3	3014	3011
$\nu_s(\text{CH}_3)$ sp^3	2968/ 2923	2962/ 2946/ 2920
$\nu(\text{CH}_{\text{ald}})$	2716	
$\nu(\text{C}=\text{O})$	1743	1712
$\nu(\text{C}=\text{C})$		
$\delta_a(\text{CH}_3)$	1433	1422
$\delta_s(\text{CH}_3)$	1395	1407
$\delta(\text{CH})$	1352	1356
$\nu(\text{C}-\text{C})$	1114	
$\nu(\text{C}-\text{CH}_3)$		
$\rho(\text{CH}_3)$	920/ 867	932
$\rho(\text{CH})$	764	
Crotonaldehyde		
Assignment	Gas Phase (cm^{-1})	CrAIMCM-41 (cm^{-1})
$\nu_a(\text{CH}) \text{ sp}^2$	3058	
$\nu_s(\text{CH}) \text{ sp}^2$	2995	3002
$\nu_a(\text{CH}_3)$ sp^3	2963	2964
$\nu_s(\text{CH}_3)$ sp^3	2938	2946/ 2920
$\nu(\text{CH}_{\text{ald}})$	2805/ 2738	2772/2748
$\nu(\text{C}=\text{O})$	1720	1690
$\nu(\text{C}=\text{C})$	1649	1640
$\delta_a(\text{CH}_3)$	1455	1458
$\delta_s(\text{CH}_3)$	1391	1377
$\delta(\text{CH})$	1304	
$\nu(\text{C}-\text{C})$	1147	
$\nu(\text{C}-\text{CH}_3)$	1074	
$\rho(\text{CH}_3)$	973	
Crotonate		
Assignment	Paper (cm^{-1})	CrAIMCM-41 (cm^{-1})
$\nu_a(\text{OCO})$	1590	1593

$\nu_s(\text{OCO})$	1478	1475
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As the adsorbed acetaldehyde allowed to react with surface acid-base sites, several changes are observable--- formation of new peaks for ν (C=O) at 1690 cm^{-1} and ν (C=C) at 1640 cm^{-1} . These new peaks indicate the formation of crotonaldehyde [$\text{CH}_3\text{CH}=\text{CHCHO}$] surface species via aldol condensation and dehydration. The formation of crotonaldehyde appears to increase in presence of oxygen as shown by the increase in intensity of IR spectral features. This indicates that probably basic sites on the surface increases as oxygen is introduced to the surface which is consistent with the existing literature.

Figure 2 shows the development of infrared spectra as the surface is exposed to UV/vis light using a xenon lamp (100 watt) after dark oxidation for an hour. These spectra are obtained by subtracting the background just before UV-Vis lamp was turned on. These subtracted spectra shows the changes that occurred due to light exposure onto the surface. The O-H stretching modes at 3748 and 3497 cm^{-1} gradually diminishes in intensity along with CH stretching modes at 2865, 2815, and 2780 cm^{-1} . It indicates that OH groups are involved in further oxidation of adsorbed acetaldehyde and crotonaldehyde that formed during the exposure and during dark oxidation processes. The negative peaks at 1712 and 1685 cm^{-1} shows that the C=O modes is gradually depleting forming other species having infrared features at 1661, 1644, 1593, 1475, and 1451 cm^{-1} . There is an increase in carbon dioxide indicated by a spectral feature at 2346 cm^{-1} . The peaks at 1593 cm^{-1} and 1478 cm^{-1} increased substantially during photooxidation and these may be assigned to asymmetric stretching mode (OCO) and symmetric stretching mode (OCO) respectively.

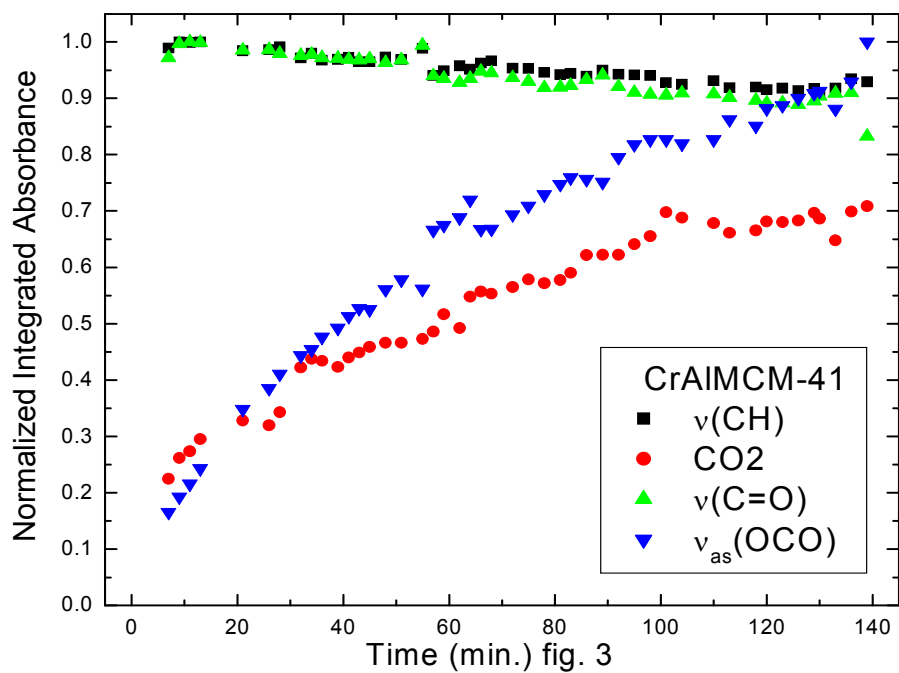
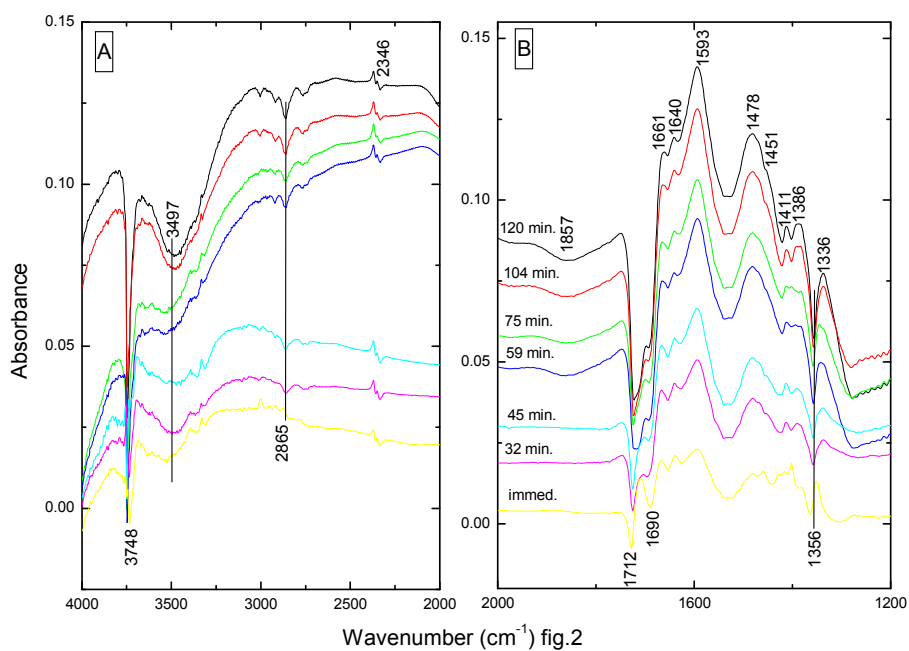


Figure 3 indicates the kinetic plot of photooxidation of acetaldehyde over Cr- AIMCM-41 in presence of UV/Vis light. Here in this plot the disappearance of CH and C=O modes and appearance of different infrared modes were obtained by integrating corresponding modes from the infrared data collected continuously every

2 ½ min. (collection time for 300 coadded scans) during photooxidation at constant temperature of 273 K. The gradual disappearance of ν (CH) and ν (C=O) modes indicates that over a time of 140 min. a fraction of 1/10 th of adsorbed species underwent decomposition forming CO₂(g) and carboxylate species. It appears that the rate of decomposition of CH mode was quite slower than the rate of formation CO₂ and carboxylate species. However, the critical analysis of these data is not possible because of complex mechanism of reactions and the extinction coefficient for different surface species may be significantly different.

Following are mass spectral studies of residual gases and other desorbed species upon warming after photooxidation reaction shows the presence of different oxidized products as shown in Table 2.

Fragments	Possible Compound
29, 43, 44, 15, 42	Acetaldehyde
41, 70, 39, 69, 27, 29, 42	Crotonaldehyde
57, 72, 39, 29, 41, 43, 27	Crotyl Alcohol
29, 28, 58, 27, 26, 59	Propionaldehyde
78, 77, 52, 51, 50, 79	Benzene

Table 2.

It is found that acetaldehyde, crotonaldehyde, croton alcohol, propionaldehyde, and benzene contain in the gas phase.

CONCLUSIONS

Synthesis through sol-gel method and characterization indicates that Cr-ALMCM-41 has good activity in photooxidation. The formation of H-bonding causes OH-mode shift to lower energy (Red-shift). Crotonaldehyde and other species are forming by acetaldehyde decomposed as well in photooxidation. Mass spectrum identify the organic species are relate with Aldol Condensation. Though The decompose rate of acetaldehyde and crotonaldehyde is lower, it might be complex mechanism is not well define.

RECOMMEDIATIONS

It is difficult to find the data in synthesis and characteristic of Cr-ALMCM-41, thought there are some journals talk about the transition metal incorporate on

AlMCM-41. So, it might be easy to get started in finding information from AlMCM-41 or MCM-41. The photooxidation of Titanium dioxide in the presence of acetaldehyde has been discussed a lot in IR study. It could be used to compare with Cr-AlMCM-41.

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