

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

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| 1. AGENCY USE ONLY (Leave Blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED FINAL 01 Jul 96 - 30 Jun 00 |
| 4. TITLE AND SUBTITLE Nanoscale Metal and Metal Oxide Particles Chemistry. Reagents for Decontamination and Remediation | | 5. FUNDING NUMBERS DAAH04-96-1-0166 |
| 6. AUTHOR(S) Kenneth Klabunde | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Kansas State University | | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 | | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 35177.13-CH |

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

| | |
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| 12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited. | 12 b. DISTRIBUTION CODE |
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13. ABSTRACT (Maximum 200 words)
The goal was to understand the surface chemistry of nanoscale metallic and metal oxide particles as they react with chlorocarbons, organophosphorous compounds, organosulfur compounds, sulfur dioxide, and other toxic materials. This work has led us to propose and try to develop such nanoparticles (a) for use in high temperature processes as Destructive Adsorbents (DAT - destructive adsorbent technology for bulk quantities of toxic substances, (b) for room temperature processes for protection of soldiers from warfare agents, and (c) for use in ground water purification, (Metal Assisted Remediation Technology - MART) and (d) for air filtration/purification.

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|--|---|--|----------------------------------|
| 14. SUBJECT TERMS | | 15. NUMBER OF PAGES | |
| | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED | 18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED | 19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED | 20. LIMITATION OF ABSTRACT UL |

Final Progress Report
DAAH04-96-1-0166
Kenneth J. Klabunde

Note: A subsequent renewal contract DAAD19-99-1-0228 became effective about July 1999. By October of 1999 all the funds in DAAH04-96-1-0166 were expended. Therefore, some of the students supported on -0166 were then transferred to -0228. Therefore, some of the students involved were the same and -0228 allowed them to continue their projects.

1) List of Manuscripts

Lucas, E.; Klabunde, K., "Nanocrystals as Destructive Adsorbents for Mimics of Chemical Warfare Agents," Nanostructured Materials, 12, 179-182 (1999).

Khaleel, A.; Li, W.; Klabunde, K.J.; "Nanocrystals as Stoichiometric Reagents with Unique Surface Chemistry. New Adsorbents for Air Purification," Nanostructured Materials, 11, 459-468 (1999).

Sun, N.; Klabunde, K.J.; "Nanocrystal Metal Oxide-Chlorine Adducts: Selective Catalysts for Chlorination of Alkanes," J. Am. Chem. Soc., 121, 5587-5588 (1999).

Wagner, G.W.; Bartram, P.W.; Koper, O.; Klabunde, K.J.; "Reactions of VX, GD, and HD with Nanoscale MgO." J. Phys. Chem. B., 103, 3225-3228 (1999).

Sun N.; Klabunde, K.J.; "High Activity Solid Super Base Catalysts Employing Nanocrystals of Metal Oxides: Isomerization and Alkylation Catalysis, Including Conversion of Propylene-Ethylene Mixtures to Pentenes and Heptenes," J. Catalysis, 185, 506-512 (1999).

Koper, O.; Klabunde, K.J.; "Development of Reactive Topical Skin Protectants Against Sulfur Mustard and Nerve Agents," J. Appl. Toxicology, 19, S 59-S 70 (1999).

Boronina, T.N.; Dieken, L.; Lagadic, I.; Klabunde, K.J.; "Zinc-Silver, Zinc-Palladium, and Zinc-Gold as Bimetallic Systems for Carbon Tetrachloride Dechlorination in Water," J. Hazardous Substances Research, on line vol.1, pg. 1 (1999), http://www.engg.ksu.edu/HSRC/JHSR/v1_no6.html.

Carnes, C.; Klabunde, K.J.; "Synthesis, Isolation, and Chemical Reactivity Studies of Nanocrystalline Zinc Oxide," Langmuir, 16 3764-3772 (2000).

Wagner, G.W.; Koper, O.B.; Lucas, E.; Decker, S.; Klabunde, K.J.; "Reactions of VX, GD, and HD with Nanosize CaO: Autocatalytic Dehydrohalogenation of HD," J. Phys. Chem. B, 104, 5118-5123 (2000).

Richard R.; Li, W.; Decker, S.; Davidson, C.; Koper, O.; Zaikovski, V.; Volodin, A.; Rieker, T.; Klabunde, K.J.; "Consolidation of Metal Oxide Nanocrystals. Reactive Pellets with Controllable Pore Structure That Represent a New Family of Porous, Inorganic Materials," J. Am. Chem. Soc., 122, 4921-4925 (2000).

Klabunde, K.J.; Koper, O.; Khaleel, A.; U.S. Patent 6093236, June 25, 2000
"Porous Pellet Adsorbents Fabricated From Nanocrystals."

2) *Scientific Personnel*

Aldo Ponce (partial support)
Erik Lucas, Graduate Student (partial support)
Corrie Carns, Graduate Student (partial support)
Ryan Richards, Graduate Student (partial support)
Ravi Mulukutla, Postdoc (partial support)

3) *Report of Inventions*

Klabunde, K.J.; Khaleel, A.; "Method for the Destruction of Unwanted Compounds Using Metal Oxide Composites," U.S. Patent 5,914,436; June 22, 1999.

4) *Scientific Progress and Accomplishments*

Specific Aims: To understand the surface chemistry of nanoscale metallic and metal oxide particles as they react with chlorocarbons, organophosphorus compounds, organosulfur compounds, sulfur dioxide, and other toxic materials. This work has led us to propose and try to develop such nanoparticles (a) for use in high temperature processes as Destructive Adsorbents (DAT – destructive adsorbent technology for bulk quantities of toxic substances, (b) for room temperature processes for protection of soldiers from warfare agents, and (c) for use in ground water purification, (Metal Assisted Remediation Technology – MART) and (d) for air filtration/purification.

A. Corrie Carnes – New Metal Oxide Nanoparticles

Appendix A

B. Erik Lucas – Probing Active Sites on Nanocrystalline MgO

Appendix B

C. Ryan Richards – Nanoparticle Surface Characterization and New Catalysts (work in Novosibirsk, Russia for 6 months, and work at KSU for 6 months)

Appendix C

D. Ravi Mulukutla – AP-MgO as a Chlorination Catalyst

Appendix D

E. Aldo Ponce – Active Copper Nanoparticles

Appendix E

Appendix A

Corrie Carnes
Review of 1999

Over the time period from January to December 1999 several studies were completed. Nanoparticles of copper oxide and nickel oxide were prepared and characterized. A study concerning zinc oxide pressed into pellets was also conducted to note the physical and chemical differences once pressed. The preparation of a mixed ZnO/ZnS nanoparticle material was prepared by pulsing CS₂ over ZnO. The catalysis of methanol from CO₂ and H₂ was studied using ZnO, CuO and NiO nanoparticles. Lastly an EXAFS study was conducted on ZnO to determine the disorder of the crystal system.

CuO nanoparticles (NC-CuO) were synthesized from CuCl₂ through a non-aqueous sol method. XRD and TEM agree giving the crystallite size to be 7-9 nm, and BET methods give surface areas to be 120-140 m²/g, figure 1. Elemental analysis shows the samples to be 95% pure, with no detectable amounts of chlorine remaining. The chemical reactivity was also tested against commercial CuO (CM-CuO) using adsorption studies. First a pulse reaction with CCl₄ was studied ($\text{CCl}_4 + 2\text{CuO} \rightarrow \text{CO}_2 + 2\text{CuCl}_2$), having a theoretical ratio of CCl₄:CuO is 1:2. The results show CCl₄:NC-CuO to be 1:23, and CCl₄:CM-CuO to be 1:290, figure 2. Next the adsorption of SO₂ gas was carried out and the results show that CM-CuO adsorbs about a monolayer, whereas NC-CuO efficiently adsorbed multilayers. Lastly a reaction was carried out between paraoxon and CuO, here NC-CuO was also found to have enhanced abilities to destructively adsorb the paraoxon when compared to CM-CuO.

NiO nanoparticles were prepared by a similar method to the CuO. Here BET methods give surface areas to be in the range of 320-350 m²/g, figure 3, and XRD along with TEM gives the crystallite size to be 2-4 nm, and. Elemental analysis shows the samples to be 94% pure, with only trace amounts of hydrogen, carbon, excess oxygen and chlorine remaining. The chemical reactivity was found to be very enhanced when tested against commercial NiO (CM-NiO) using adsorption studies. A pulse reaction with CCl₄ was studied ($\text{CCl}_4 + 2\text{NiO} \rightarrow \text{CO}_2 + 2\text{NiCl}_2$), having a theoretical ratio of CCl₄:NiO is 1:2. The results show CCl₄:NC-NiO to be 1:8.3, and CCl₄:CM-NiO to be 1:6000, figure 4. Next the adsorption of SO₂ gas was carried out and the results show that CM-NiO adsorbs about a monolayer, whereas NC-NiO efficiently adsorbed multilayers. Lastly a reaction was carried out between paraoxon and NiO, in this study NC-NiO shows a huge increase in activity to destructively adsorb an organophosphorous compound. Results of these reactions give the molar ratios of paraoxon:CM-NiO to be 1:14000, and paraoxon:NC-NiO to be 1:38.

A ZnO pellet study was conducted to see how the material would change physically and chemically when pressed into pellets. Pellets were made at 1000, 2000, 3000, 4000, and 5000 pounds load. At 1000 pounds the pellets surface area, pore volume and pore

diameter were relatively unchanged. To test each samples chemical reactivity a pulse reaction was used where CCl_4 was pulsed through a bed of the sample. By pressing the samples into pellets the chemical reactivity was slightly lessened, however the NC-ZnO pellets were still many times more reactive then the CM-ZnO samples.

A study where CS_2 was pulsed through a ZnO bed was performed to results in a ZnO/ZnS material. As CS_2 was pulsed through the ZnO, gas chromatograph was used to detect CO_2 , and excess CS_2 coming through the bed. It was found again that the NC-ZnO was much more reactive than the CM-ZnO samples reacting with more CS_2 to result in a higher ZnS content. XRD was unable to confirm ZnS, possibly due to the amorphous nature of the NC-ZnO samples, but XPS confirmed that ZnS was present.

The catalysis of methanol from CO_2 and H_2 was studied using ZnO, CuO and NiO as the catalyst. To test this reaction a flow reactor was setup so that a continuous flow of CO_2 , H_2 and ethane was passed through a bed of the catalyst at a given temperature. At set time intervals gas samples were taken and checked via gas chromatograph. The results show that the NC-ZnO produced more methanol continuously than the CM-ZnO samples. The CM-CuO samples did produce methanol continuously, whereas the NC-CuO was quickly reduced to Cu^0 metal and reactivity ceased. The CM-NiO samples had no reactivity, although the NC-NiO samples produced a large amount of methanol continuously.

An EXAFS study was conducted on CM-ZnO, NC-ZnO, and NC-ZnO after CCl_4 pulse reaction. This study was able to clearly show how NC-ZnO is much more disordered than the CM-ZnO samples. By looking at the Zn K edge the CM-ZnO has complete first (Zn-O) and second (Zn-Zn) shells, whereas the NC-ZnO samples have only 70% of a full first shell, and 40% of the second shell, Table 1. The NC-ZnO + CCl_4 samples showed a higher deterioration of order having 50% of the first shell, and 20% of the second shell. The Cl K edge was also looked at and confirmed that there was a Zn-Cl bond present. This would explain the deterioration in order of the ZnO in the NC-ZnO + CCl_4 sample if Cl is replacing some of the O. Overall this study confirms that the NC-ZnO samples are indeed more amorphous, and contain many more defect sites than the CM-ZnO samples. This helps us to explain why the NC-ZnO is much more reactive than the CM-ZnO samples.

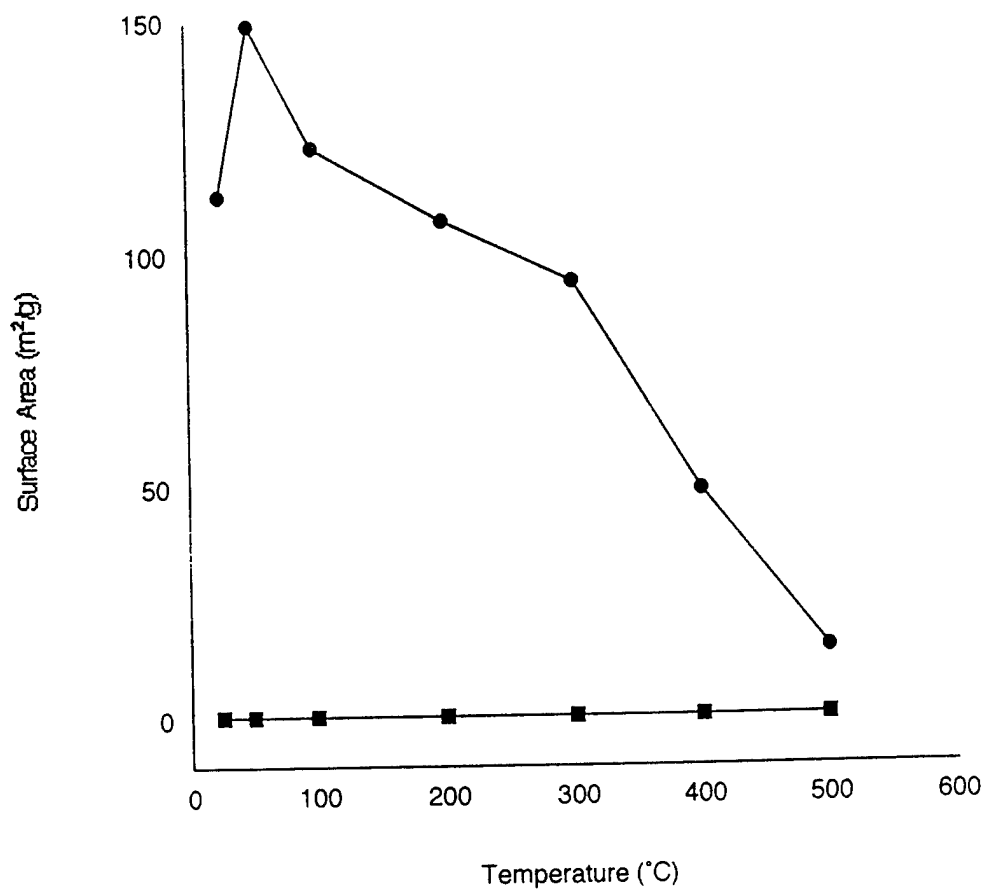


Figure 1: Surface Area vs. Temperature for NC-CuO (circles), and CM-CuO (squares).

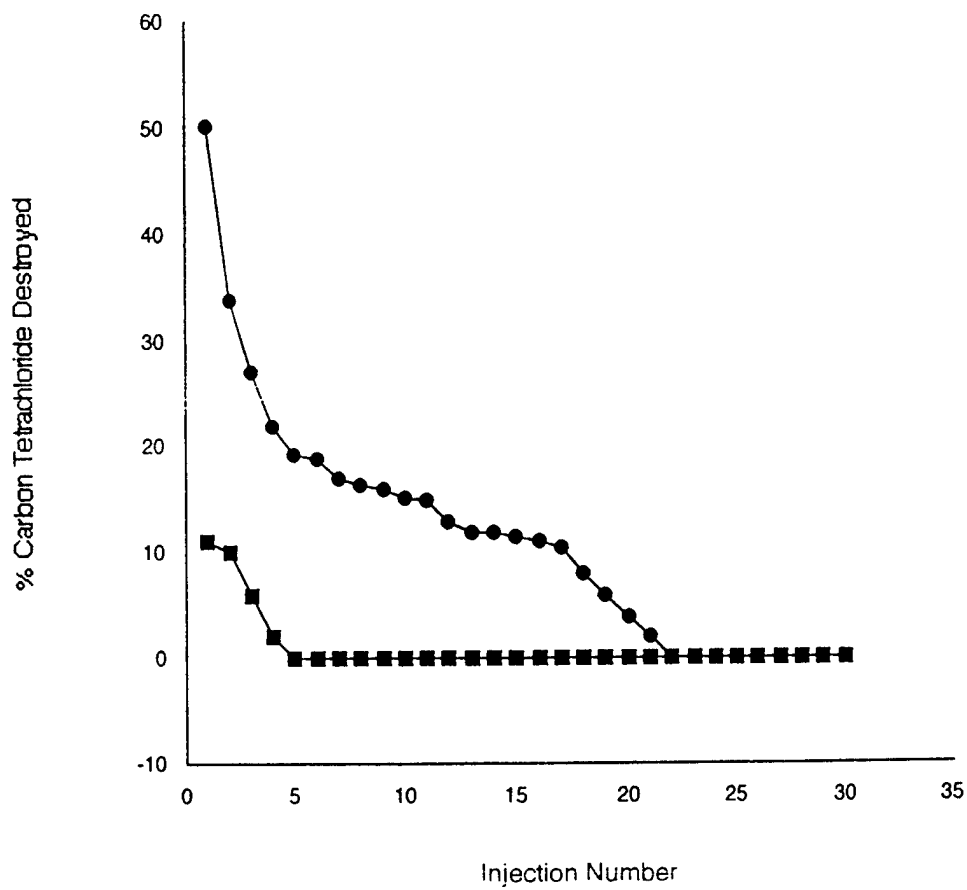


Figure 2: % CCl₄ Destroyed vs. Injection Number;
(squares) CM-CuO, and (circles) NC-CuO.

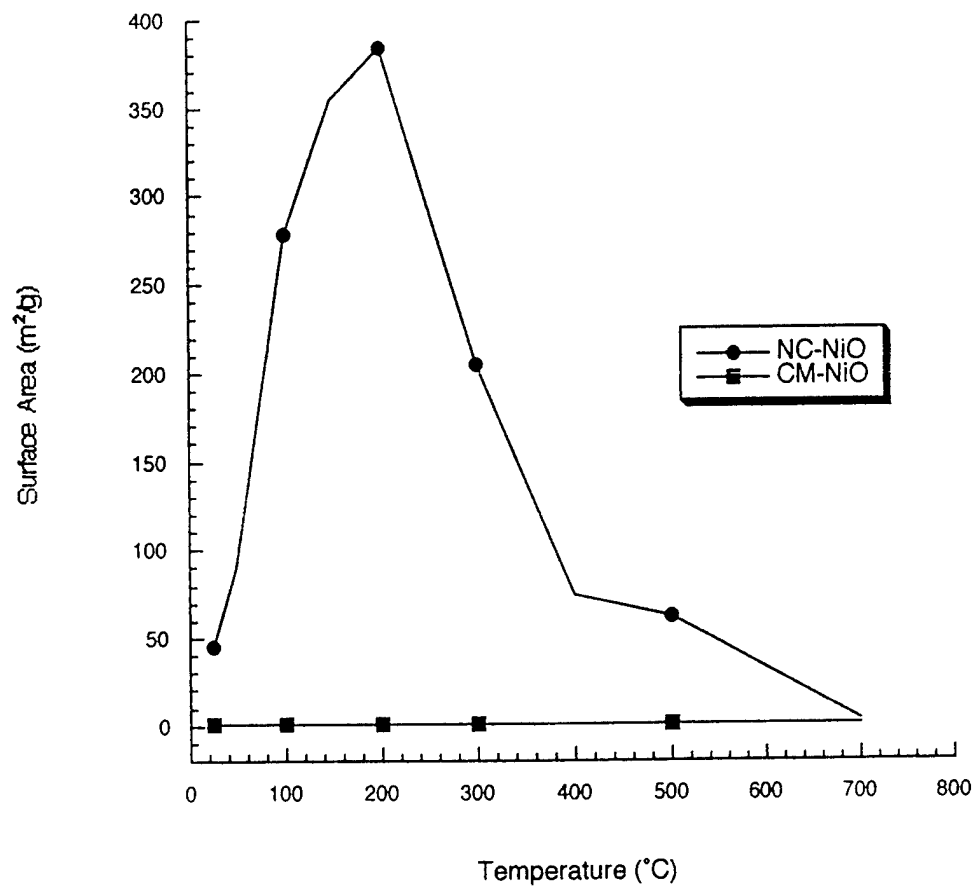


Figure 3: Surface Area vs. Temperature; (squares) CM-NiO, and (circles) NC-NiO.

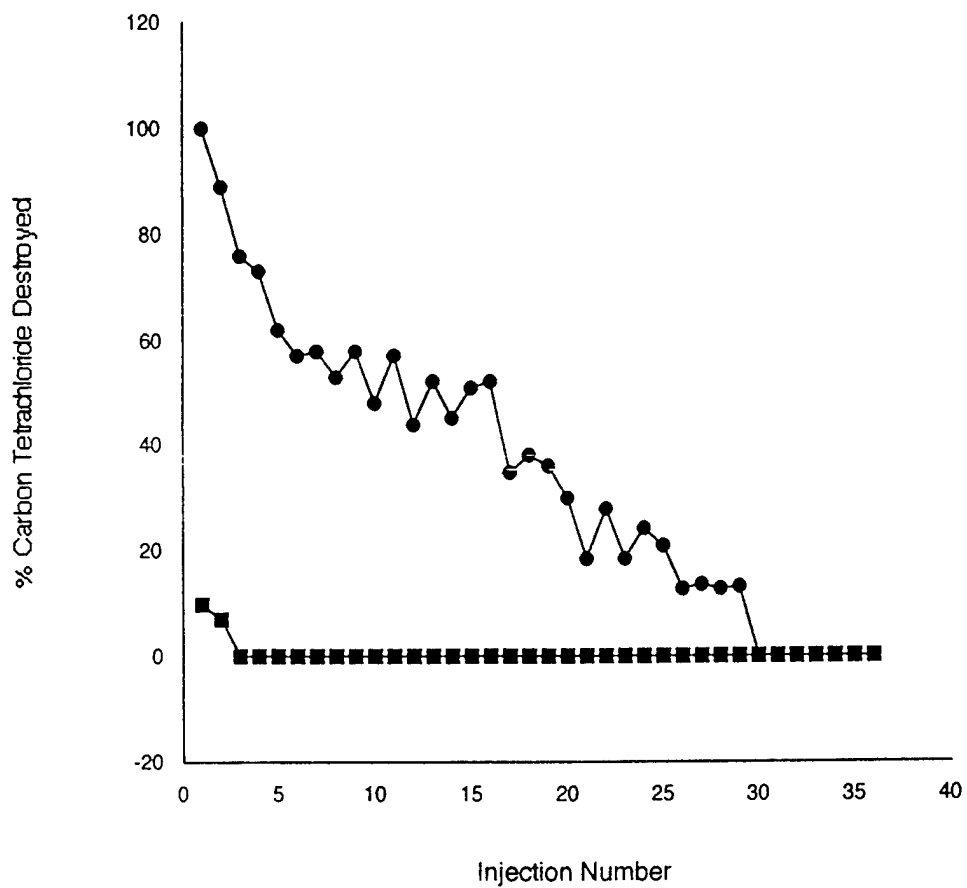


Figure 4: % CCl₄ Destroyed vs. Injection Number;
(squares) CM-NiO, and (circles) NC-NiO

Table I

Zn-O Shell

| Sample | # Oxygen's | Distance (Angstroms) |
|---------------------------|-------------------|-----------------------------|
| CM-ZnO | 4 | 2.02550 |
| NC-ZnO | 2.75 | 2.03470 |
| NC-ZnO + CCl ₄ | 1.94 | 2.06210 |

Zn-Zn Shell

| Sample | # Zinc's | Distance (Angstroms) |
|---------------------------|-----------------|-----------------------------|
| CM-ZnO | 13 | 3.20230 |
| NC-ZnO | 5.77 | 3.2476 |
| NC-ZnO + CCl ₄ | 2.933 | 3.25990 |

Appendix B

Erik Lucas

Review of Research Year 1999

Research year 1999 was spent completing the last stages of research into the destructive adsorbance of mimics of possible war agents. Specifically chloro-acetonitrile (ClCH_2CN), a mimic of the very dangerous compound chloronitrile (ClCN). Work was also completed on the use of CO as a molecular probe of the three different morphologies of MgO . Lastly CD_3CN was used as a molecular probe of the three different morphologies of MgO .

ClCH_2CN as a mimic, is the third target molecule used in the destructive adsorption studies. As a molecule ClCN is very dangerous to handle given chlorine's propensity as a leaving group, leaving a very reactive cyanide radical. For adsorption studies with a methylene group is used, ClCH_2CN , which is much safer to handle.

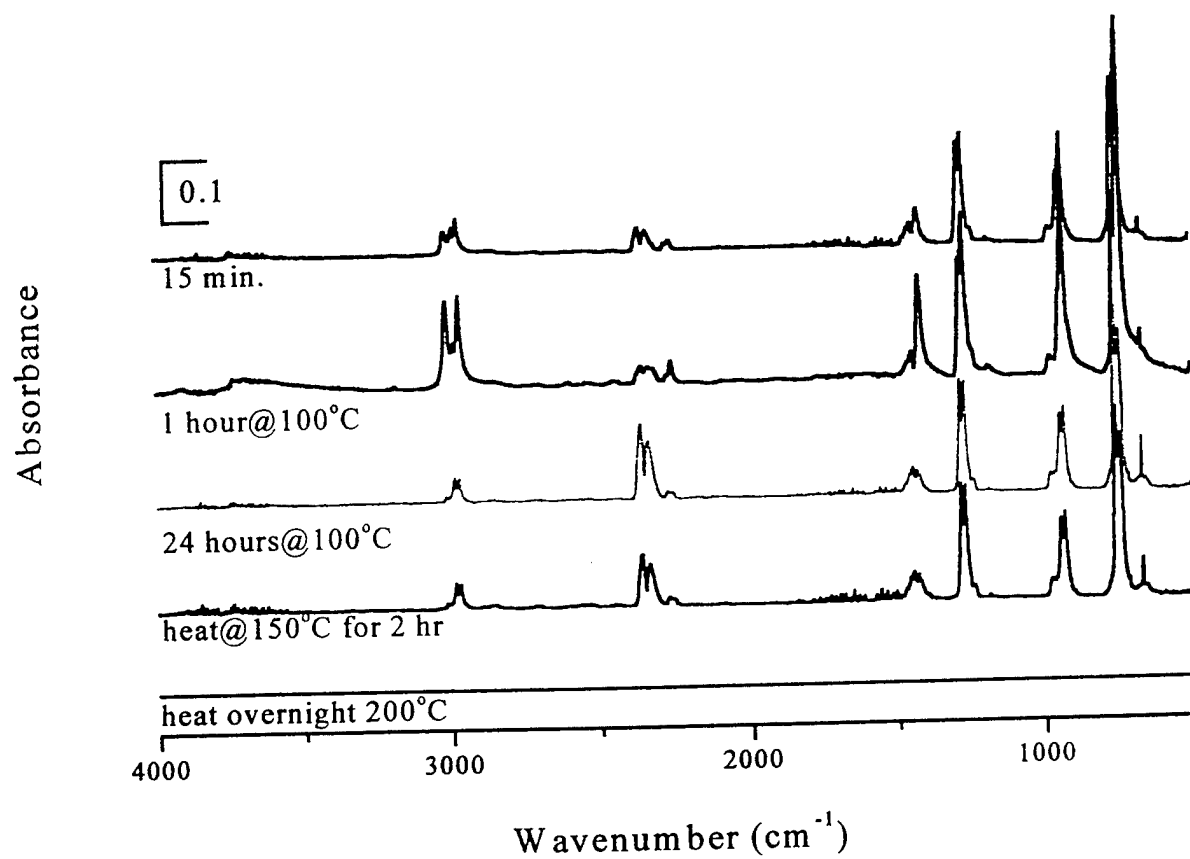
Initial studies, performed using the round bottom flask IR cell previously used for the 2-CEES work, showed some ability to adsorb ClCH_2CN . Vapor phase spectra were taken of several reaction conditions to measure the disappearance of the chloride. When the system is heated to 200°C overnight the ClCH_2CN appears to fully adsorb onto the surface, as evidenced by the spectrum showing nothing in the vapor phase. There was also a noticeable brown shade on the surface of the AP- MgO . Spectra were taken of the solid after reaction (see figure), nothing positive could be identified from the spectra. To try and find out possible intermediaries of the reaction, the reaction was held for 15 minutes at 150°C and then the vapors pulled off into a separate chamber (the ClCH_2CN was subtracted out). XRD of the solid after reaction showed no change in the crystal structure from perovskite MgO .

G.C. Pulse reactions of ClCH_2CN were discouraging. While AP- and CP- MgO were better at destroying the ClCH_2CN samples than commercial samples, AP and CP had the same destructive ability at 250°C . Upon heating the system higher, AP- MgO showed no greater ability to destroy ClCH_2CN and actually dropped in ability at 500°C . G.C. pulse studies showed an approximate 4 surface oxide-to-1mol ClCH_2CN ratio.

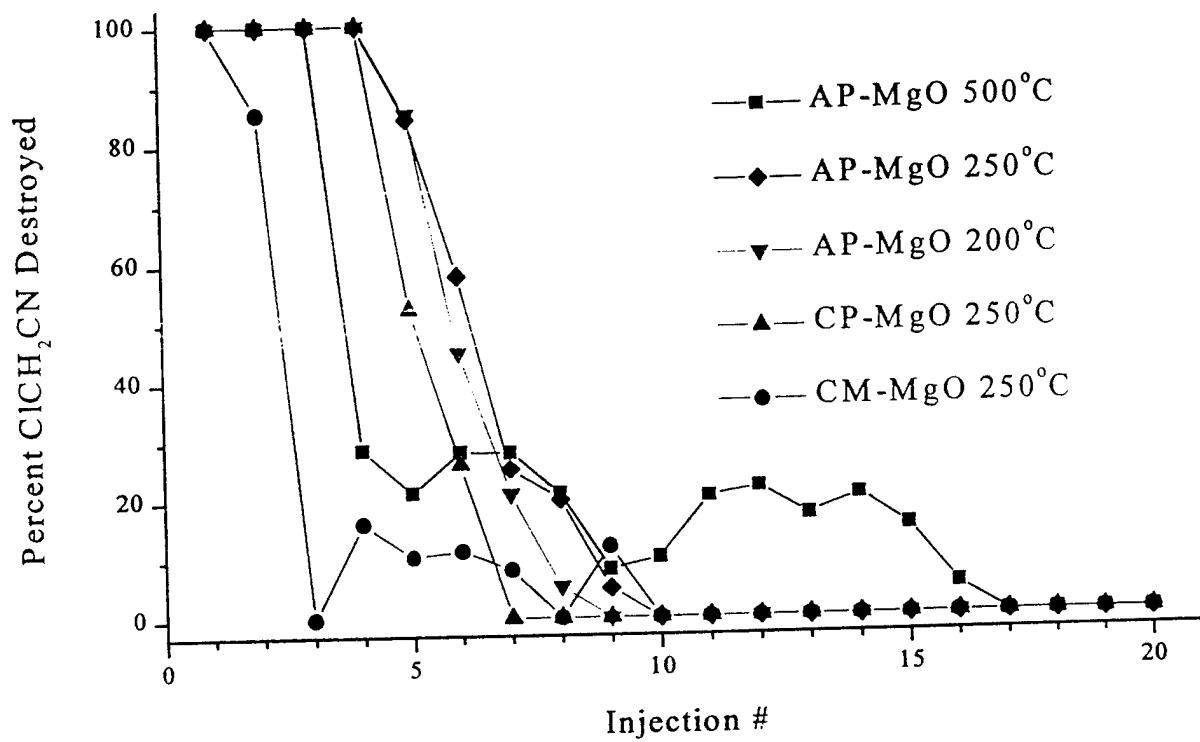
CO studies were finally refined to see individual surface sites of the three MgO forms. These liquid nitrogen temperature studies were performed using the stainless steel high vacuum IR cell from 0.05-10.0 Torr. The CO studies showed that the number of edge and corner sites on CP- MgO were so low that they couldn't be identified by probes. AP- MgO showed edge sites that were much more acidic than standard edge sites. Both AP- and CP- MgO showed acidic (001) plane sites, but CP showed a much smaller number, approximately 10 times less, and they were quickly filled. The corner sites on AP- MgO were not clearly visible, but a polymeric carbonate species formed only on the AP sample, which indicated the presence of cleaved corners. The commercial MgO samples showed some edge structure but the amounts of CO adsorbed were so small that these numbers were insignificant.

Adsorption studies using CD_3CN confirmed the presence of acidic corner defects with a large population of adjacent $\text{Mg}^{2+}_{3\text{C}}$ sites on AP- MgO , more of these sites exist than edge sites. Some of these sites do exist on the CP- MgO but they are in very small quantities, which makes sense considering the smaller Lewis basicity of CP- MgO . Commercial MgO has such a small basic character, compared to the other two forms that adsorption of CD_3CN wasn't successful until pressures of 1.0 Torr were achieved, and only showed the expected edge and planar sites.

Vapor Phase FT-IR of Rxn of $\text{ClCH}_2\text{CN} + \text{AP-MgO}$



Percent of ClCH_2CN Destroyed Per injection in G.C. Pulse reactions
 (20 inj. is 1:1 surface oxide-to- ClCH_2CN)



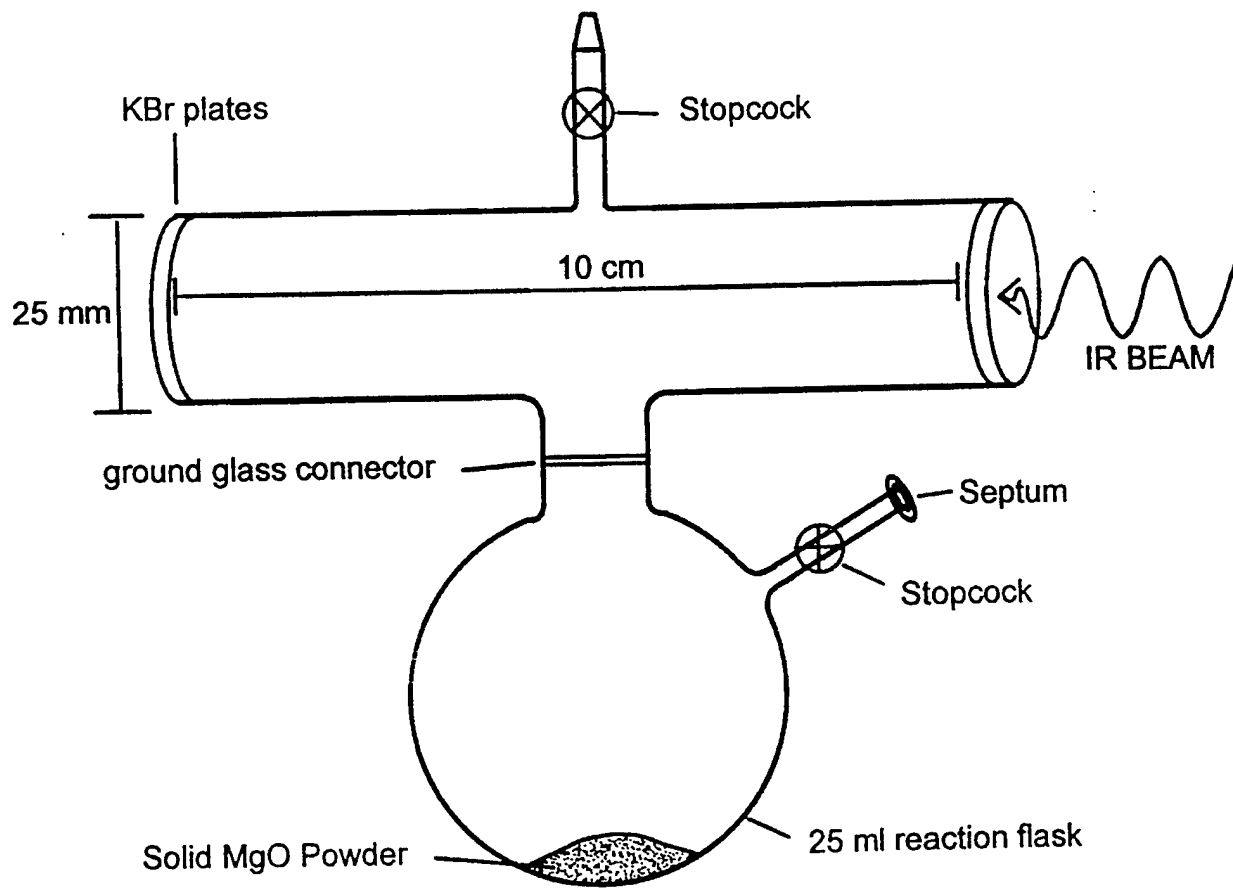
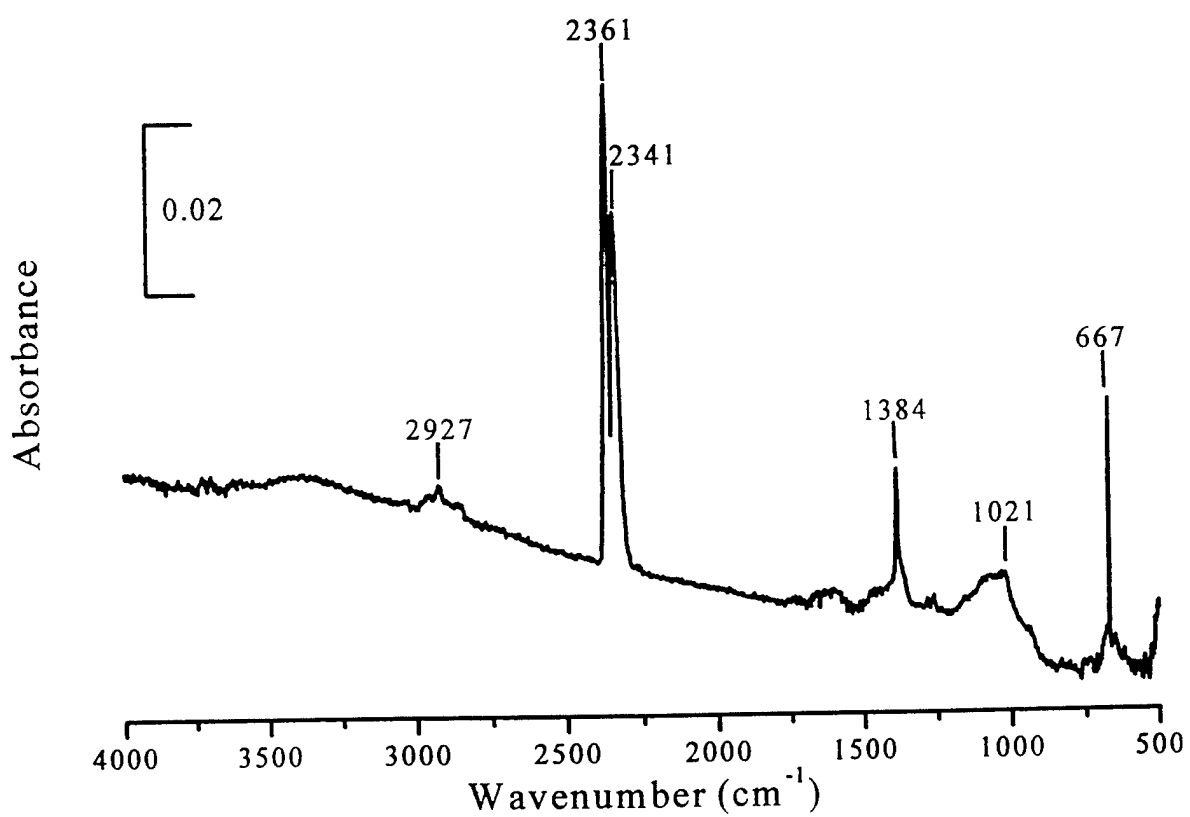
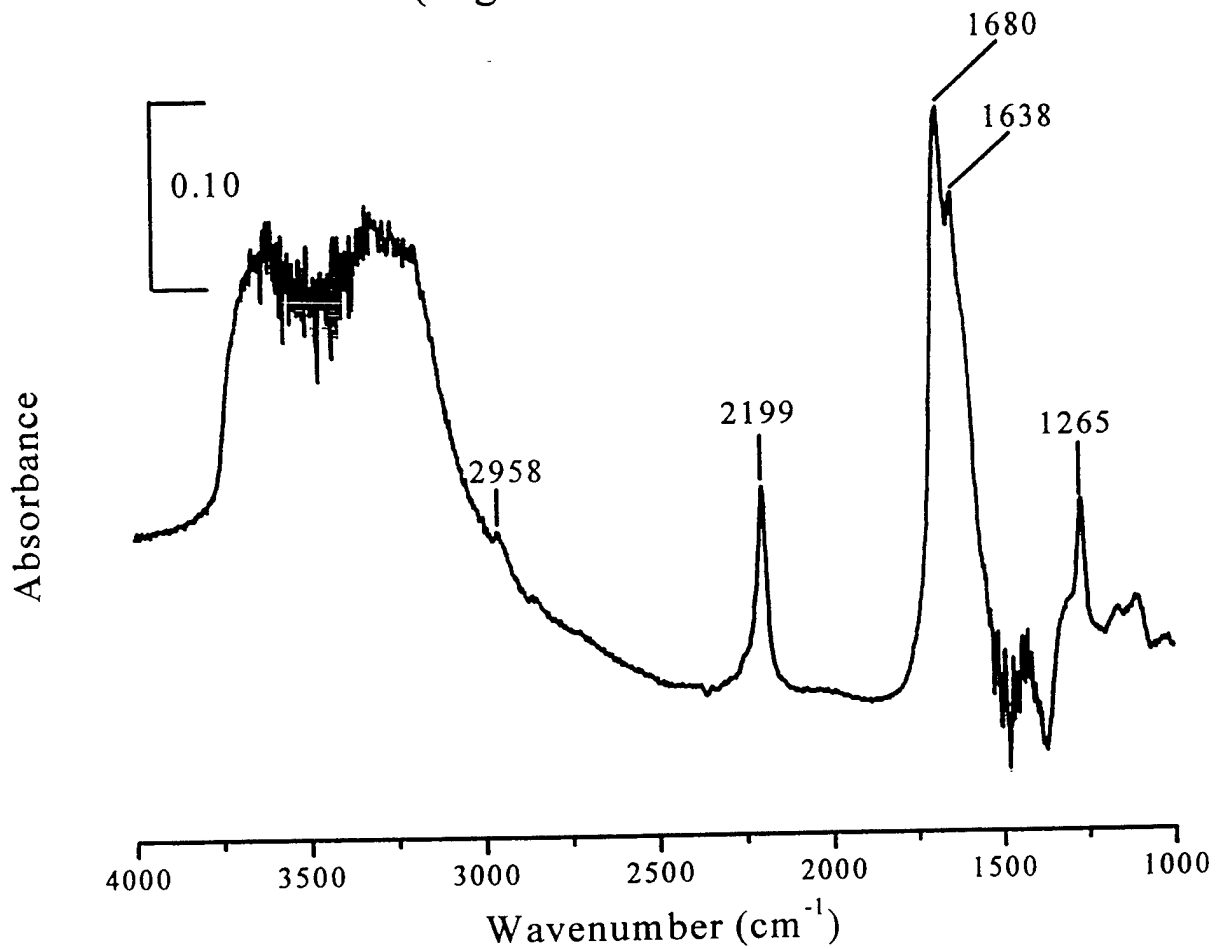


Figure 1. IR reaction cell

Vapor Phase of Rxn of AP-MgO + ClCH₂CN
(ClCH₂CN spectra subtracted out)



FT-IR of Solid After Rxn: AP-MgO + ClCH₂CN
(MgO Subtracted out)



Appendix C

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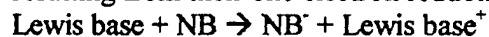
Ryan Richards

Report summary of 1999 Research

Metal oxide nanoparticles and their interaction with nitroxyl radicals have been examined by electron paramagnetic resonance (epr).

The epr spectrum of the initial state of AP-MgO was examined for the presence of solid defects or other paramagnetic species. The spectrum revealed the presence of a solid defect as well as another species which appeared to be a triplet. This sample was examined at a number of microwave frequencies to resolve the species present in the spectrum. The presence of a solid defect is observed in the epr spectrum of AP-MgO taken at 26 dB at room temperature with a g factor of 2.0026 and contains 2.51 E16 spins/g. This solid defect is stable through 500 °C with a maximum concentration of spins at 300 °C. Above 500 °C sintering takes place and by 600 °C the concentration of spins in the solid defect has decreased significantly. Also present in the spectra is a triplet with a g factor of 2.0035 with relative intensities of 1:2:1. This triplet is believed to be due to the presence of CH₂ radical species based upon hyperfine splitting constant a=17.3 and relative intensities. A decrease in the intensity of this species is observable upon heating to 200 °C and after heating to 300°C the species is no longer observable. It is important to note that this species was not removed during the calcination step under vacuum during the original preparation, but is easily removed through oxidation when heated while exposed to air.

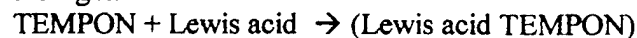
The adsorption of the nitroxyl radicals TEMPON and *m*-dinitrobenzene (*m*-dnb) on the Lewis acid and base sites of magnesium oxide nanoparticles has also been studied. Lewis base sites on magnesium oxide nanoparticles can be studied by their adsorption of aromatic nitrocompounds. In a number of cases their adsorption is accompanied by the formation of paramagnetic particles. The appearance of radicals after nitrobenzene adsorption is assumed to be anion radicals of adsorbed compounds resulting from their one electron reduction on surface Lewis base sites.



Counterion (Ds⁺) formation for these reactions can not be observed in the epr spectra. The concentration of donor centers (Ds) is determined by the maximum concentration of radical particles (NB⁻) produced by adsorption.

Paramagnetic species due to the formation of DNB radicals can be observed at all temperatures between 25° C and 500 °C. Similar to the solid defect the maximum concentration of paramagnetic species is observed at 300 °C which is 1.295 e18 spins/g.

From experiments examining the interaction of TEMPON with MgO it was concluded that the surface of the oxides has Lewis acid sites which possess sufficiently high adsorption heats for TEMPON, the room temperature equilibrium is shifted to the right.



This is very interesting since MgO is typically not associated with acid catalysis and it is believed that this is the first observation of this type of Lewis acid activity on MgO.

This knowledge of the Lewis acid and base sites of the nanosize magnesium and calcium oxides can lead to a number of interesting catalytic properties. Their high activity and selectivity in the C_4H_9Cl dehydrochlorination are most notable.

In contrast to $\gamma-Al_2O_3$, MgO and CaO aerogels have been found to have high selectivity in the C_4H_9Cl dehydrochlorination to butylene. Their activity grows with temperature. However, the temperature growth also results in the acceleration of the transformation of the oxides to chlorides. While at 20-100°C only surface chlorination occurs, at 300-400°C a bulk solid-phase reaction takes place. The activity of the catalysts studied changes in the following row: $\gamma-Al_2O_3 > CaCl_2 > MgCl_2 > MgO > CaO$, the specific activity of calcium and magnesium chlorides being at least by two orders of magnitude higher than that of the corresponding oxides.

Table 1

MgO activity in the C_4H_9Cl dehydrochlorination measured in successive experiments on the same sample

| Reaction temperature, °C | C_4H_9Cl conversion, % |
|--------------------------|--------------------------|
| 100 | 0.5 |
| 200 | 5 |
| 300 | 70 |
| 400 | 90* |
| 200 | 30 |

* - small amounts of ethane and ethylene are formed besides butylene

Table 2

CaO activity the C_4H_9Cl dehydrochlorination measured in successive experiments on the same sample

| Reaction temperature, °C | C_4H_9Cl conversion, % | Product composition***, % | | |
|--------------------------|--------------------------|---------------------------|----------|------------------|
| | | n- C_4H_9Cl | C_4H_8 | i- C_4H_9Cl ** |
| 100 | 0 | 100 | 0 | 0 |
| 200 | 0.4 | 97.6 | 0.3 | 0.1 |
| 300 | 85 | 15 | 84.7 | 0.3 |
| 400 | 95 | 5 | 95* | 0 |
| 300 | 95 | 5 | 94.9 | 0.1 |
| 200 | 55 | 45 | 50 | 5 |
| 100 | 24 | 76 | 20 | 4 |

* - small amounts of ethane and ethylene are formed besides butylene

** - exact isomer has not been identified

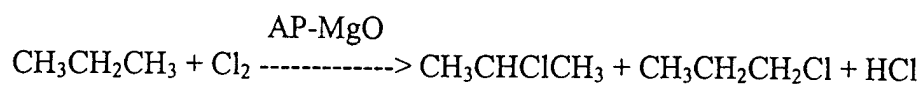
***- without argon

Appendix D

Ravi Mulukutla

AP-MgO as a Chlorination Catalyst

In previous reports we have described the synthesis and properties of the chlorine adducts of AP-MgO. This adduct is a solid "storage bin" for active chlorine. Recently we have been designing, building, and implementing, a catalytic reaction system for chlorination of alkanes using this new form of active chlorine. This work is intended to give full elucidation of this new material. In addition to catalysis,



spectroscopic investigation using Raman and XPS is underway.

Appendix E

Aldo Ponce

Active Copper Nanoparticles

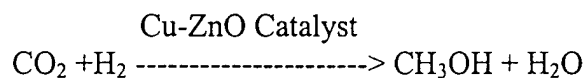
Two aspects of nanoparticle metal chemistry are being explored, where Cu is chosen as a prototype.

First of all, reactive nanoparticles of copper have been prepared by depositing Cu vapor with solvent vapors at liquid nitrogen temperature. These active powders derived from Cu atoms clustering in THF, toluene, and pentane were tested for surface reactivity by an Ullman type reaction:



The rate of biphenyl production under a certain set of conditions showed that the reaction was strictly surface area controlled.

Another aspect of this work is to combine Cu nanoparticles with ZnO nanoparticles in order to obtain a unique, very active methanol synthesis catalyst



This work is ongoing. The ZnO nanoparticles alone make an excellent catalyst, surpassing other known systems. The combination of Cu so far has not improved things, but it appears this is because of Cu nanoparticle aggregation. Some new approaches to attaching the Cu particles to the ZnO are being considered.