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AD-A227 990

REPORT DOCUMENTATION PAGE **DTIC FILE COPY**

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		1b. RESTRICTIVE MARKINGS	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
6a. NAME OF PERFORMING ORGANIZATION Kansas State University	6b. OFFICE SYMBOL (if applicable)	5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 24939-12-CH	
7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
6c. ADDRESS (City, State, and ZIP Code) Dept. of Chemistry, Willard Hall Kansas State University Manhattan, KS 66506	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-87-K-0130		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
3c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		PROGRAM ELEMENT NO	PROJECT NO.
11. TITLE (Include Security Classification) Final Report - "Activated Metal Oxide Surfaces as Highly Reactive Environments"		TASK NO.	WORK UNIT ACCESSION NO.
12. PERSONAL AUTHOR(S) Kenneth J. Klabunde			
13a. TYPE OF REPORT Final Report	13b. TIME COVERED FROM Aug. 87 to Aug. 90	14. DATE OF REPORT (Year, Month, Day) August 3, 1990	15. PAGE COUNT 16
16. SUPPLEMENTARY NOTATION The view, 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.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	metal oxide, adsorbents, high surface, toxic substance, hazardous waste, surface chemistry, surface sites, destructive adsorbent, organophosphorus.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A final report on surface chemistry of high surface area metal oxides, especially magnesium oxide, is presented. Thermal activation yields a highly reactive surface capable of destroying and immobilizing toxic chemicals. Understanding of surface reactive sites was gained by studying RH/D ₂ exchange reactions, catalytic activities and electron transfer properties, chemisorption of spin traps, Lewis Bases, organophosphorus compounds, and carbon monoxide. Progress was also made on developing new aerogel procedures for synthesis of ultra-high surface area magnesium oxide. Finally, some metal oxide molecules were studied in chemical reactions and by theoretical methods. Three students earned Ph.D. degrees and one an M.S. degree. A visiting professor and two postdoctoral associates were also trained in this research area.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DTIC ELECTED OCT 25 1990

**Activated Metal Oxide Surfaces
as Highly Reactive Environments**

Final Report

Kenneth J. Klabunde

August 3, 1990

U.S. Army Research Office

DAALO3-87-K-0130

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I. Introduction

The development of catalysts for use in air purification is an extremely important endeavor in all of environmental science. Catalytic converters for automobile exhaust cleanup is a relevant, related area.¹ However, toxic substances that may be airborne, and need to be efficiently destroyed, often contain heteroatoms such as phosphorus and sulfur, particularly chemical agents and pesticides. These heteroatoms are notorious for catalyst poisoning.

"As an alternative to high performance catalysts, highly reactive solid-state reagents that undergo stoichiometric reactions can be used to destroy these toxic compounds. These reagents, for example, activated metal oxides, should be chosen on the basis of their widespread and inexpensive availability, their rapid dealkylative, hydrolytic, and/or oxidative decomposition of the target chemical, and their extensive reaction capacity. For best results, volatile non-polar products such as hydrocarbons and ethers, would form and be desorbed, while polar components containing the heteroatom would bind strongly to the metal oxide, for example as PO_4^{3-} . After decomposing large amounts of reagents, the oxides would eventually lose activity and be discarded."²

Our earlier work, supported by ARO, has shown that thermally activated MgO shows a great deal of promise as such a reactive solid state reagent.³ Defect sites and high surface areas were shown to be important contributors to the destructive adsorptive properties with organophosphorus compounds. Thus, the development of the most useful and efficient solid reagents depends on our ability to prepare ultra-fine powders with very high surface areas, which may maximize defect site concentration and high reactivity/capacity.

Pursuing this direction of surface chemistry leads us into the new and exciting field of cluster and cluster assembled materials.⁴ Aggregation of a few to several hundred metal oxide molecules to form a metal oxide cluster in the nanometer size range of 1-100 nm yields a nano-scale particle, that should possess novel and hybrid properties between molecular and bulk solid state limits.⁴ Indeed, metal, semiconductor, and insulator clusters in this size range have exhibited unique optical and chemical reactivity properties. "The ability to produce significant quantities of such clusters, and the possibility of their controlled assembly into both non-interacting and interacting arrays, highly porous aggregates, and densely consolidated materials, may offer opportunities for novel properties in these new materials."⁴

From these points of view, we believe our continued work in the chemistry of nano-scale metal oxide particles has importance to both basic and applied science. Further understanding of their properties and surface chemistry and their development into useful materials is the driving force behind the prior and proposed work described herein.

II. Review of Previous Work

A. Overview

We have concentrated our efforts on the elucidation of surface chemistry of thermally activated MgO. It serves in one sense as a model of other oxides since it has a simple crystal structure (NaCl structure) and stoichiometry. However, since defect sites are important, surface sites can be of various forms, and MgO is known to possess a rich surface chemistry due to such sites.⁵ In spite of a great deal of work on MgO and other

"basic" oxides, there is still considerable disagreement about specific sites involved in important catalytic and stoichiometric processes.

Our approach has been to carry out detailed studies of probe reactions on MgO and doped MgO. In the process we have found specially prepared and activated samples are selective CH/D₂ exchange catalysts and, as an added benefit, we have developed ways to use kinetic CH/D₂ exchange as a way to estimate hydrocarbon acidities (both solution and gas phase).

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- (1) V. Haensel, R. Burwell, Sci. Am., **225**, 46 (1971).
- (2) J. G. Ekerdt, K. J. Klabunde, J. R. Shapley, J. M. White, and J. T. Yates, Jr., J. Phys. Chem., **92**, 6182 (1988).
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- (5) K. J. Klabunde, M. F. Hoq, F. Mousa, and H. Matsushashi, in "Preparative Chemistry Using Supported Reagents", P. Lazslo, editor, Academic Press, New York (1987), pg. 35; a review of metal oxides and thin physico-chemical properties in catalysis and synthesis; see references therein, especially the early work of Rees, Wertz, Taylor, Sondor, Tench, and others.

Abstracts of Papers Published Under ARO Support

1986 - 1990

**Thermally Activated Magnesium Oxide as a Selective
Deuteration Catalyst Under Mild Conditions**M. Fazlul Hoq and Kenneth J. Klabunde, J. Am. Chem. Soc., 1986, 108, 2114.

The surface of microcrystalline, thermally activated MgO was found to serve as an excellent catalyst for CH/D₂ exchange in hydrocarbons. The rate of the gas-solid surface exchange reaction correlated with the acidity of the C-H bond in question. Ethylbenzene, for example, could be selectively deuterated first in the benzylic position at 25°C, then the ring C-H bonds at 150°C, and then the CH₃ at 300°C. Activation energy for benzylic deuteration was found to be only 0.9 kcal/mole, while the E_a for aromatic ring deuteration = 8 kcal/mole. Proton abstraction by the "superbase" MgO was rate determining, and defect sites appear to be the catalytically active sites.

**A Comparison of Electron Donor and Proton Abstraction Activities of
Thermally Activated Pure Magnesium Oxide and Doped Magnesium Oxides**

Kenneth J. Klabunde and Hiromi Matsushashi

J. Am. Chem. Soc., 1987, 109, 1111.

Thermal activation of microcrystalline MgO at 400-700°C has been carried out under vacuum and under rapid flows of N₂, Ar, O₂, and H₂/N₂. Some samples of MgO were impregnated or coprecipitated with LiOH, NaOH, or Al(OH)₃ before activation. The activities for 1-butene isomerization, where

proton abstraction is rate limiting, were compared with activities for CO telomerization/reduction, where electron donation capability is most important. These studies suggest that defect sites are involved and that localized electron rich domains can be enhanced by Li^+ substitution for Mg^{2+} but that localized more electron deficient domains can be enhanced by Al^{3+} substitution for Mg^{2+} . These studies also show that high-temperature thermal activation with gas flow of N_2 or Ar is possible, but that O_2 and H_2/N_2 anneal out defects and activity is lost.

Metal Oxides and Their Physico-Chemical Properties
in Catalysis and Synthesis

Kenneth J. Klabunde, M. Fazlul Hoq, Faleh Mousa, and Hiromi Matsushashi

"Preparative Chemistry Using Supported Reagents"

P. Laszlo, editor, Acad. Press, New York, 1987, pg. 35.

The purpose of this chapter is to critically, but not exhaustively, review the uses of common metal oxides as reagents for carrying out a variety of catalytic and stoichiometric transformations of small molecules and organic compounds. In order to understand why metal oxides such as Al_2O_3 or MgO can possess or be given highly reactive sites, structural features and defects will be discussed. Activation of metal oxides by irradiative and thermal means is a very important aspect of this work, thus allowing metal oxides to be active in acid-base chemistry, telomerization and polymerization, electron transfer, C-C bonding breaking, H-D exchange, and other important processes.

Interaction of Activated Magnesium Oxide Surfaces with Spin Traps

Kenneth J. Klabunde and Ileana Nieves, J. Phys. Chem., 1988, 92, 2521.

Thermal activation of high surface polycrystalline MgO at 200-1100°C produced room temperature surface reactivity with subsequently adsorbed spin traps such as N- α -diphenylnitrone (PNP) and 2-nitroso-2-methylpropane (NOMP). ESR measurements indicate the MgO surface to be initially diamagnetic. The added spin traps are also initially diamagnetic. However, upon interaction high concentrations of paramagnetic species are formed. Two primary reactions appear to be (1) electron transfer from electron-rich defect sites on MgO to PNP and NOMP to form PNP $^{\bullet-}$ and NOMP $^{\bullet-}$. In the case of PNP the anion radical is stable and strongly adsorbed. In the case of NOMP $^{\bullet-}$, decomposition to tert-butyl radical and presumably O-NP $^{\bullet-}$ occurs, and the alkyl radical is trapped by NOMP to form the stable di-tert-butyl nitroxide. (2) Surface Mg-oxy radicals are trapped by NOMP to form -O-NOMP $^{\bullet}$ which subsequently also decomposes to tert-butyl radical which is then also trapped by NOMP. Activation temperature for the MgO profoundly affects the course of these radical-forming processes. Thus, addition of spin traps to such active oxide surfaces serves as a method of distinguishing different types of surface reactivity and features. Partially dehydroxylated surfaces are unusually reactive, suggesting the importance of OH groups next to exposed cations as important sites.

Nature of Chemisorbed Species on Metal Oxide Surfaces.

Electron Transfer and Bond-Breaking Processes

I. Nieves and K. J. Klabunde, Materials Chem. and Physics, 1988, 18, 485.

Highly ionic insulator oxides, in particular MgO, can be prepared in high surface area form possessing many surface defect sites. The nature of

these thermally robust defects are either structural (edges, planes, kinks, cation and anion vacancies) or electronic (electron excess or deficient sites). Extremely basic, electron rich sites are capable of strongly interacting with chemisorbing molecules. Proton abstraction, electron transfer, molecular oligomerization, base condensation, and radical trapping reactions have been observed with various adsorbing organic molecules. Adsorbed species can be readily detected with appropriate spectroscopic tools. Further technological use of thermally activated MgO and other oxides appear promising, especially in such areas as selective hydrocarbon H-D exchange catalysts, and destructive adsorbants for air purification purposes.

Surface Chemistry of Organophosphorus Compounds

J. G. Eckerdt, J. K. Klabunde, J. R. Shapley, J. M. White, and

J. T. Yates, Jr, J. Phys. Chem., 1988, 92, 6182.

This paper reviews the known decomposition chemistry of organophosphorus compounds interacting with metal and metal oxide surfaces. Three kinds of processes -- oxidation, dealkylation, and hydrolysis -- are known to be important, but the fundamental knowledge base in this technologically and environmentally important area is presently inadequate. Some significant research directions are identified for surface chemical science, surface reaction chemistry, solid-state synthesis, and organometallic cluster chemistry.

Theoretical Calculations on the Interaction of CO with MgO and CaO

Suchada Utamapanya, J. V. Ortiz and Kenneth J. Klabunde

J. Am. Chem. Soc., 1989, 111, 799.

Ab initio calculations have been performed on linear and cyclic structures resulting from the interaction of CO with MgO and CaO. For the MgO case, linear carbonyl (OC-MgO) and isocarbonyl (CO-MgO) minima are higher in energy than a four-member ring geometry with C_{2v} symmetry. Linear carbonyl and isocarbonyl structures spontaneously rearrange to two cyclic minima in the CaO case. The first of these resembles the Mg cyclic structure, but the second has a Ca-O-C three-membered ring. All of the cyclic structures contain a metal dication coordinated to a bent CO_2^{2-} ligand.

Activation Energies for Carbon Acid/ D_2 Exchange

Over a Solid Base Catalyst. Correlation with Gas Phase Acidities

M. F. Hoq and K. J. Klabunde

Proceedings of International Symposium on Acid-Base Catalysis

Sapporo, Japan, 1988, Nov. 28-Dec. 1;

pg. 84 of Abstracts, Kodansha Ltd., Tokyo, 1989, 105-21

Thermally activated MgO has been employed as a highly basic solid catalyst for carrying out CH/D_2 exchange in hydrocarbons. A series of benzylic, aromatic, and alkane C-H bonds were studied. Reaction rates at various temperatures yielded activation energies E_a , and from these enthalpies of activation ΔH^\ddagger were calculated. It was found that ΔH^\ddagger values correlated linearly with literature gas phase acidities (enthalpies for $R-H(g) \rightarrow R^-(g) + H^+(g)$; ΔH_a°). This surprising result was rationalized by proposing a reaction cycle with a transition state involving $O^{2-}D^+$, $Mg^{2+}R^-$, and $O^{2-}H^+$. These results mean that, although bifunctional catalysis on MgO

allows for very low ΔH^\ddagger values (analogous to a strong solvent assist in a solution environment), this bifunctional catalytic assistance in proton abstraction is about the same energetically no matter what carbon acid is under study. These results imply that gas phase acidities can be estimated for other carbon acids by carrying out CH/D₂ exchange over solid base MgO.

**Mechanistic Studies of Hydrocarbon CH/D₂ Exchange
Over Thermally Activated Magnesium Oxide**

M. F. Hoq, I. Nieves, and K. J. Klabunde, *J. Catalysis*, **1990**, 123, 349-363

The CH/D₂ exchange reaction over thermally activated solid base catalyst MgO, where CH represents a hydrocarbon (carbon acid), has been investigated from a mechanistic point of view. Extensive kinetic studies of the exchange, analyses of hydroxyl content of MgO activated at various temperatures, spectroscopic studies, and consideration of pore sizes and possible reaction sites on MgO, have led to the following conclusions: (1) the active site on MgO involves basic O²⁻ ion, which abstract protons from carbon acids, as well as acidic Mg²⁺ ions, which stabilize resulting carbanions; (2) the active site is a defect site of high electron density and containing a O-H (or O-D) group. Its structure is best described as a cation vacancy near an edge defect on the MgO crystallite; (3) the transition state in the R-H(g) + D₂(g) $\xrightarrow{\text{MgO}}$ R-D(g) + Hd(g) exchange reaction probably involves O²⁻-D⁺ attack on adsorbed R⁻---H⁺ in the active site. A reaction coordinate diagram is proposed that explains our findings that exchange rates correlate with solution phase pK_a values for R-H but that ΔH^\ddagger (+E_a - MRT) correlate better with gas phase acidities of R-H.

**NANO-SCALE METAL OXIDE PARTICLES/CLUSTERS AS CHEMICAL REAGENTS.
SYNTHESIS AND PROPERTIES OF ULTRA-HIGH SURFACE AREA MAGNESIUM OXIDE.**

Suchada Utamapanya, Kenneth J. Klabunde* and John Schlup

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ABSTRACT

A modified autoclave hypercritical drying procedure has been used to prepare a hydrated form of MgO from $\text{Mg}(\text{OCH}_3)_2$ in a methanol-toluene solvent mixture. This material was prepared with $1000 \text{ m}^2/\text{g}$ surface area and 35 \AA crystallite size. Heat treatment of this precursor at 500°C under vacuum yielded the dehydrated MgO with $500 \text{ m}^2/\text{g}$ surface area and 45 \AA crystallite size. The samples were further characterized by Fourier Transform Infra Red/Photoacoustic Spectroscopy (FT-IR-PAS), X-ray diffraction, scanning electron microscopy, and chemical analyses. The hydrated precursor contained some residual $-\text{OCH}_3$ groups and was much less crystalline in appearance than conventionally prepared $\text{MgO-Mg}(\text{OH})_2$ samples. The dehydrated material was free of $-\text{OCH}_3$ groups and was made up of much smaller crystallites than conventionally prepared MgO.

(Submitted to Chemistry of Materials)

**Molecular Vapor Synthesis:
The Use of Titanium Monoxide and
Vanadium Monoxide Vapors as Reagents**

Thomas J. Groshens and

Kenneth J. Klabunde*

Abstract

The production and reactivity of titanium monoxide (TiO) and vanadium monoxide (VO) on synthetically useful scale were studied using the techniques and apparatus previously developed for reactions of metal atoms. Cocondensation reactions with chlorine showed that greater amounts of metal atoms were produced as impurities in the vapor when stoichiometric metal monoxides were used as vapor sources than when metal sesquioxides were used. It was found that evaporation of MO and M_2O_3 solids from open tungsten boats yielded vapor compositions of M, MO, and MO_2 similar to those reported earlier from Knudsen cells in the case of vanadium, but somewhat different in the case of titanium. The monoxide molecules reacted with chlorine to produce oxometal chlorides in high yields. They reacted with 2,4-pentanedione and other organics containing relatively acidic hydrogen, to form water as a by-product via protonation of the oxo moiety; coordination compounds of titanium and vanadium were isolated as acac complexes in high yields.

(Inorganic Chemistry, in press)

NANO-SCALE METAL OXIDE PARTICLES AS CHEMICAL REAGENTS.**HEATS OF ADSORPTION OF HETEROATOM CONTAINING ORGANICS ON HEAT TREATED
MAGNESIUM OXIDES SAMPLES OF VARYING SURFACE AREAS**Maher Atteya and Kenneth J. Klabunde^{*}

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Abstract

Heats of adsorption (immersion) were measured via a solution calorimeter for a series of heteroatom (oxygen, sulfur, phosphorus) containing organic compounds on thermally activated magnesium oxide (heat treated at 700°C overnight in vacuo followed by cooling to room temperature). For phosphates, phosphites, and phosphines the heats of adsorption were high and showed a small dependence on substituent effects. For sulfur compounds -S-H containing compounds yielded the highest values. For oxygen systems very high heats of adsorption were found for carbonyl compounds. In addition, the strongly basic nature of the MgO surface was demonstrated by the extremely high heats of adsorption/reaction with carboxylic acids. Heats observed for 1-butanol adsorption varied linearly with MgO surface area. Surprisingly, cyclohexane dilution of 1-butanol caused a dramatic lowering of adsorption heats, demonstrating the competitive nature of even such unreactive solvents. The observed heats of adsorption/reaction combined with spectroscopic data allowed some conclusions about the type of surface bonding that took place. The strong interactions of several of these organics demonstrated the nature of heat

(Submitted to Chemistry of Materials)

treated MgO as a destructive adsorbent for many toxic chemicals. Since MgO is non-toxic, inexpensive, and can be prepared in high surface activated forms, it shows promise for use in air purification schemes.

Current Ongoing Projects**"Further Characterization of Nano-scale Magnesium Oxide Particles"****Suchada Utampanya**

Over the past six months Suchada wrote her thesis and completed her final defense. She also carried out further experiments on characterization of ultra-high surface area MgO. She quantitatively determined how much pyridine was adsorbed on heat treated MgO.

CP-MgO(219m²/g)2.16 X 10²⁰ molecules pyridine/gm MgOAP-MgO-5(409 m²/g)12.5 X 10²⁰ molecules/gm MgO

The results demonstrate that the higher surface area material, which has smaller particle sizes, has significantly more Lewis Acid sites available on its surface.

"Point Defects on CeO₂ as Studied by O₂ Adsorption**Xiaolong Zhang**

Cerium dioxide is unusual in that oxygen vacancies can be produced by heat treatment, even with crystalline samples. Since oxygen vacancies are probably important as reactive sites on other oxides as well, we have undertaken a study of CeO₂ with the hope of developing a probe for oxygen vacancies. Thus, ESR was used to study O₂-CeO₂ interactions at low temperature. We observed some new types of ESR signals. One of these is from superoxide ion located in a surface oxygen vacancy; another is superoxide ions located on surface cations. Further study showed that higher heat treatment temperature led to higher concentrations of oxygen

species on surface oxygen vacancies. The reaction of the surface superoxide ions with carbon monoxide led to their total disappearance. By readsorbing oxygen the superoxide ions appeared again, which shows the character of the catalytic cycle. The results also show that the superoxide ions are important species in this catalysis cycle, where oxygen vacancies serve as catalytic sites for oxidation of CO.

"Effect of Water on DMMP Decomposition Over MgO"

Maher Atteya

An important discovery has been made. It has always been assumed that water would poison the activity of MgO for decomposition of toxic phosphorus compounds. However, we have recently found that the decomposition of DMMP over MgO at 500°C is aided by small amounts of water. Up to 10% wt.% water in DMMP is helpful, but more water is detrimental (see attached figure). Further work on understanding this effect is underway.

"Synthesis of Ultra-High Surface Area Fe₂O₃ by Precipitation Methods"

Yong-Xi Li

A series of precipitations of Fe(OH)₃ (from FeCl₃) at different pH followed by heat treatments in flowing gases or in vacuum has allowed the synthesis of α-Fe₂O₃ in surface areas of 10 m²/g, 60 m²/g, 150 m²/g, and 250 m²/g. Mossbauer spectra were very characteristic for each sample.

***Synthesis of Ultra-High Surface Area Fe₂O₃ by Oxidation
of Iron Atoms With Water**

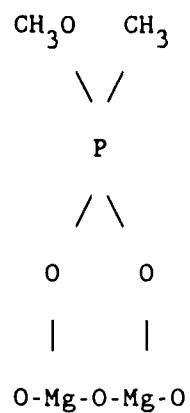
Hiroshi Fujitsu

Preparation of high surface area iron oxide by metal vapor synthesis was investigated by using water as an oxidant. Iron metal and water were simultaneously codeposited on the reactor wall at 77 K under vacuum, and then the evaporated mixture was warmed slowly to room temperature. The resultant black precipitate was filtered and dried at room temperature. Surface areas of products were 70 ~ 100 m²/g (estimated particle sizes were 115 ~ 150 Å). Exposure to air changed the color of the products to brown. XRD patterns of products revealed that they are magnetite or Fe₂O₃. Measurements of the pressure in the reactor during the synthesis suggested that the iron atom was oxidized to give FeO₋₁ during evaporation on the reactor wall around 77 K, and then further oxidized to Fe₂O₃ or Fe₂O₃ around 273 K, evolving more hydrogen. Decreasing the temperature at which the matrix of ice starts to be loose and flexible may be expected to provide much higher surface area of the oxide by preventing the aggregation of the intermediate products.

Further Work on DMMP Adsorption/Decomposition on MgO

Yong-Xi Li

After MgO has decomposed DMMP and is exhausted, the MgO samples were dried and analyzed for P, Mg, C, and H. FT-IR-photoacoustic spectroscopy has also been used to study this residue as well as fresh MgO with DMMP adsorbed at room temperature. We are writing up these results in the papers listed. We have found that DMMP adsorbs on MgO and decomposes to formic acid (mostly) plus some methanol and dimethyl ether. A likely surface species left behind is:



Scientific Personnel

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