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13. ABSTRACT *(Maximum 200 words)*

A final report on the study of ultrafine metal oxide particles as destructive adsorbents for toxic substances is presented. Successful treatment of organophosphorous compounds and chlorocarbons, where heteroatoms are extracted forming nontoxic metal phosphates and chlorides, has been carried out. Methods for preparing the nanoscale particles, including core/shell overlayer particles, have been worked out. Surface characterization, surface chemistry, heats of adsorption, surface catalyzed $CH/D_2 \rightarrow CD/HD$ exchange, effect of surface --OH groups, electron transfer processes, $^{16}O/^{18}O$ exchange, and studies of molecular metal oxides have been reported. A patentable invention dealing with Fe_2O_3/MgO core/shell structures is also described. Overall, 11 graduate students, research associates, and visiting professors have been involved in this work.

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Nano-Scale Metal Oxide Particles as Materials for Air Purification

Final Report

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U.S. Army Research Office

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Kansas State University
Department of Chemistry
Manhattan, Kansas 66506

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I. Introduction

The development of solid reagents that adsorb and simultaneously destroy toxic substances is important for air purification and as an alternative to incineration. Toxic chemicals such as organophosphorus, -halogen, -sulfur, and nitrogen compounds are not very amenable to treatment by high performance catalytic processes since these heteroatoms are notorious for catalyst poisoning.

Solid reagents that might serve as effective destructive adsorbents must have high capacity, and convert the toxic materials to non-toxic substances. Ideally, the heteroatoms (P, Cl, Br, N, S) would be extracted from the organic parts of the molecules and "mineralized" (converted to an innocuous metal salt).

In attempts to synthesize and develop such destructive adsorbents, we have concentrated our efforts on nanoscale metal oxides. The development of the most efficient solid reagents depends on our ability to prepare ultrafine powder with very high surface areas and intrinsic surface reactivities.

This research direction leads us into the exciting field of nanostructured materials, which possess novel and hybrid properties between molecular and bulk solid limits. Metal and semiconductor nanoscale materials have already been demonstrated to possess unique magnetic, optical, and physical properties. We are contributing to this field by studying the unique surface chemistry of nanoscale insulator particles.

From these points of view, we believe that continued work on the chemistry of such particles has importance both to basic and applied science. Further understanding of their synthesis, properties, and chemistry and their development into useful materials is the driving force behind the prior and proposed work described herein.

II. Review of Previous Work. Brief Rationale for Carrying Out the Work Plus Abstracts of Papers Published 1990-1993.

A. Synthesis of Nanoscale MgO, CaO, and Fe_2O_3/MgO

The development of the best methods of preparation of nanoscale MgO and CaO was a major accomplishment during the past 4 years. Several approaches were used, including: (1) the oxidation of metal vapor (atoms) by water, (2) controlled oxidation of nanoscale metal particles, (3) precipitation of aqueous metal ions by hydroxide followed by dehydration, and (4) aerogel methods including a hypercritical drying step. Method (4) proved to be the best approach, and abstracts of papers published or in preparation are shown below:

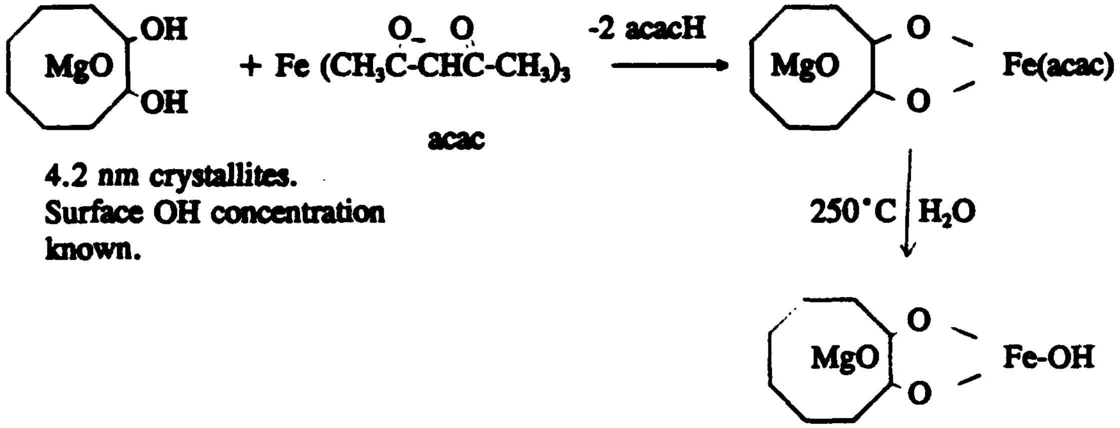
Nanoscale Metal Oxide Particles/Clusters as Chemical Reagents. Synthesis and Properties of Ultrahigh Surface Area Magnesium Hydroxide and Magnesium Oxide

S. Utamapanya, K. J. Klabunde and J. R. Schlup, Chem. of Materials, 1991, 3, 175-181.

A modified autoclave hypercritical drying procedure has been used to prepare a hydrated form of MgO from $Mg(OCH_3)_2$ in a methanol-toluene solvent mixture. This material was prepared with 1000 m^2/g surface area and 35-Å crystallite size. Heat treatment of this precursor at 500°C under vacuum yielded the dehydrated MgO with 500 m^2/g surface area and 45-Å crystallite size. The samples were further characterized by Fourier transform infrared/photoacoustic spectroscopy (FT-IR/PAS), X-ray diffraction, scanning electron microscopy, and chemical analyses. The hydrated precursor contained some residual $-OCH_3$ groups and was much less crystalline in appearance than conventionally prepared MgO-$Mg(OH)_2$ samples. The dehydrated material was free of $-OCH_3$ groups and was made up of much smaller crystallites than conventionally prepared MgO.

A. Khaleel and K. J. Klabunde, work in progress

A well characterized sample of nanoscale MgO prepared by the aerogel method was treated with $Fe(acac)_3$:



4.2 nm crystallites.
Surface OH concentration
known.

In this way a monolayer of iron oxide was deposited on the magnesium oxide surface. Characterization by XPS, x-ray diffraction, Mossbauer, CO_2 adsorption, pyridine adsorption, and as a destructive adsorbent for DMMP and CCl_4 is in progress. Significant chemical reactivity differences are being realized. For example, under the same conditions the iron oxide coated MgO converts CCl_4 to CO_2 more cleanly and apparently without the intermediacy of Cl_2CO.

$$2\,MgO(FeO_x) + CCl_4 \longrightarrow 2\,MgCl_2(FeO_x) + CO_2$$

B. Surface Characterization of Nanoscale Metal Oxides Surfaces

Exhaustive studies of adsorbed pyridine, nitrobenzene, benzene and reaction of surface -OH with $AlEt_3$ were carried out for two well characterized MgO samples of varying crystallite sizes. Intrinsic surface chemistry differences were demonstrated for the first time, based only on crystallite size difference.

Heats of adsorption were also determined for a wide array of toxic organic chemicals, and these results demonstrated strong surface binding for a variety of functional groups.

Nanoscale metal Oxide Particles as Chemical Reagents. Intrinsic Effects of Particle Size on Hydroxyl Content and Reactivity, and Acid/Base Properties of Ultrafine Magnesium Oxide

H. Itoh, S. Utamapanya, J. V. Stark, K. J. Klabunde, J. Schlup
Chem. of Materials, 1993, 5, 71-77

Two sizes of ultrafine magnesium oxide particles have been carefully compared for intrinsic surface chemistry differences. Ultra-high surface MgO (400-650 m^2/gm) prepared by an autoclave hypercritical drying (aerogel) procedure has been compared with conventionally prepared MgO (100-300 m^2/gm) for hydroxyl surface concentration (also residual OCH_3), pyridine, benzene, xylene, and nitrobenzene adsorption. The aerogel prepared material exhibited the highest surface area (650 m^2/g) after a 300°C heat treatment, while the conventional sample's surface area went up to 300 m^2/g) after a 400°C treatment. Both FT-IR/ Photoacoustic and conventional transmission IR spectroscopies were employed to monitor the adsorbed species. Amounts of material adsorbed were also quantitatively determined. Careful comparisons between the smaller and larger particle MgO were made. It was shown that surface-OH concentrations were similar but that the larger particles allowed more geminal pair reactions of -OH with $AlEt_3$ to yield $EtAl-(O_2)(ad)$. It was also found that the MgO particles adsorbed pyridine on the Mg^{2+} sites, not the Bronsted sites. However, benzene did adsorb on Bronsted sites and IR shifts showed that the smaller particles exhibited weaker Bronsted acidity. Nitrobenzene adsorption suggested weaker Lewis basicity as well. It is proposed that basic/reducing character depends more on domains and is encouraged by larger particle size and Bronsted acidity is also encouraged by -OH surface island domains. Overall, the results show that particle size can have intrinsic effects on surface chemistry.

Nanoscale Metal Oxide Particles as Chemical Reagents. Heats of Adsorption of Heteroatom-Containing Organics on Heat-Treated Magnesium Oxide Samples of Varying Surface Areas

M. Atteya and K. J. Klabunde, Chem. of Materials, 1991, 3, 182-187

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 demonstrate the nature of heat-treated MgO as a destructive adsorbent for many toxic chemicals. Since MgO is nontoxic and inexpensive and can be prepared in highly surface activated forms, it shows promise for use in air-purification schemes.

C. Catalytic Properties of MgO for CH/D_2 Exchange in Hydrocarbons

The special properties of nanoscale MgO as a selective catalyst for deuterium exchange in hydrocarbons were studied in some detail. Mechanistic features were elucidated, and acidity of many hydrocarbons were compared with each other. A striking finding was that the acidities determined by the MgO catalyzed CH/D_2 exchange correlated with gas phase acidities of several of the hydrocarbons.

Mechanistic Studies of Hydrocarbon CH/D_2 Exchange Over Thermally Activated Magnesium Oxide

M. F. Hoq, I. Nieves, and K. J. Klabunde, J. Catalysis, 1991, 123, 349-363

The CH/D_2 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 O^{2-} ions, which abstract protons from carbon acids, as well as acidic Mg^{2+} ions, which stabilize resulting carbanions; (2) the active site is probably a defect site of high electron density (perhaps a cation vacancy) and contains an O-H (or O-D) group; (3) the transition state in the

$R\text{-}H(g) + D_2 \xrightarrow{MgO} R\text{-}D(g) + HD(g)$ exchange reaction probably involves O^{2-}-D^+ attack on adsorbed R^-—H^+ in the active site. A reaction coordinate diagram is proposed that explains our findings that exchange rates roughly correlate with literature solution-phase pK_a values for R-H.

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
<u>Proceedings of International Symposium on Acid-Base Catalysis</u>
Sapporo, Japan **1988**, Nov. 28-Dec. 1; pg. 105-121

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 $\Delta H^\dagger$ were calculated. It was found that $\Delta H^\dagger$ values correlated linearly with literature gas phase acidities (enthalpies for $R\text{-}H_{(g)} \rightarrow R^-_{(g)} + H^+_{(g)}$; 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 $\Delta H^\dagger$ 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/D_2 exchange over solid base MgO.

D. Destructive Adsorption of Organophosphorus and Organochlorine Compounds

The most intense effort during the prior grant period was devoted to understanding the adsorption and bond breaking processes of organophosphorus compounds on nanoscale MgO. It was shown for example that DMMP was destructively adsorbed at relatively low temperatures and with high capacities. Several analytical techniques were applied including FT-IR-Photoacoustic Spectroscopy and Pulsed Reactor-GC-MS. Complete material balances were possible, and structures of permanently adsorbed phosphorus residues were determined.

Analogous work with organochlorine compounds is underway.

Adsorption and Decomposition of Organophosphorus Compounds on Nanoscale Metal Oxide Particles. In Situ GC-MS Studies of Pulsed Microreactions over Magnesium Oxide

Y.X. Li, O. Koper, M. Atteya and K. J. Klabunde, Chem. of Materials, 1992, 4, 323-330.

Using an in-situ pulsed reactor GC-MS system, the thermal decomposition of organophosphorus compounds (as models of nerve agents) has been compared with their destructive adsorption on high surface area magnesium oxide. Dramatically lower temperatures are required when MgO is present. Volatile products evolved were formic acid, water, alcohols, and alkenes. At higher temperatures CO, CH_4, and water predominated. Phosphorus residues remained completely immobilized. Addition of water enhanced the facility of MgO to destroy these compounds, and in fact, water pulses were found to partially regenerate a spent MgO bed. Using ^{18}O labeling, some aspects of the reaction mechanisms were clarified and in particular showed that oxygen scrambling occurred. Surface OH and MgO groups transferred oxygen in the formation of formic acid, and surface mobility and reactivity of adsorbed groups was very high. The substantial capacity of high surface area MgO for destruction and immobilization of such toxic substances makes it attractive for air purification schemes as well as solid reagents for destruction and immobilization of bulk quantities of hazardous phosphorus compounds or organohalides.

Fourier Transform Infrared Photoacoustic Spectroscopy Study of the Adsorption of Organophosphorus Compounds on Heat-Treated Magnesium Oxide

Y.X. Li, J. R. Schlup and K. J. Klabunde, Langmuir, 1991, 7, 1394-1399.

A series of magnesium oxide samples of varying surfaces area were prepared and heat treated (thermally activated) at 500 or 700°C. Dimethyl methylphosphonate (DMMP), trimethyl phosphate (TMP), and triethyl phosphate (TEP) were allowed to adsorb on the MgO samples both in a vacuum environment and in a helium stream. Analyses of the powdered samples were carried out by Fourier transform infrared photoacoustic spectroscopy. These studies revealed that adsorption occurred on all samples in proportion to surface area. Physisorbed organophosphorus molecules were easily removed by evacuation or under helium flow. However, substantial amounts strongly chemisorbed through the oxygen atom of the P=O bond. Even at room temperature and up to 190°C the chemisorbed compounds began to decompose, but decomposition products remained adsorbed. At 500°C complete decomposition took place releasing mainly formic acid plus some methanol. The phosphorus moiety remained immobilized as a $[CH_3OPCH_3]$ residue.

Nanoscale Metal Oxide Particles as Chemical Reagents. Destructive Adsorption of a Chemical Agent Stimulant, Dimethyl Methylphosphonate, on Heat-Treated Magnesium Oxide

Y.X. Li and K. J. Klabunde, Langmuir, 1991, 7, 1388-1393.

Nanoscale particles of MgO were prepared as fine powders of varied surface areas and crystallite sizes. The capacities of these samples for dissociative (destructive) adsorption of dimethyl methylphosphonate (DMMP), a chemical reagent stimulant, were determined by using a pulsed microreactor. Surface stoichiometric reactions were encountered and large amounts of DMMP were destroyed, about one DMMP molecule to two surface MgO moieties. Volatile products were formic acid and methanol. Elemental analyses of the spent MgO samples coupled with Fourier transform infrared photoacoustic spectroscopy indicated that the phosphorus-containing molecular fragment was immobilized as $[CH_3OPCH_3]_{ads}$. Effects of contact time, temperature, and surface area were studied. A proposed reaction scheme for the decomposition is given, which involved loss of CH_3O followed by its oxidation by a second DMMP molecule.

Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide

Olga Koper, Yong-Xi Li, and Kenneth J. Klabunde, Chem. of Materials, 1993, 5, 500-505.

Ultrafine particles of CaO react with CCl_4 to yield $CaCl_2$ and CO_2. Phosgene is an intermediate product but can be avoided if excess CaO is employed. The reaction with $CHCl_3$ yields $CaCl_2$, CO, and H_2O, while C_2Cl_4 yields $CaCl_2$ and carbon. Thermodynamically these are all favorable reactions, but kinetic parameters demand that high surface area CaO be used. However, under the right conditions multiple layers of the CaO particles can be converted to $CaCl_2$. An aerogel/autoclave method for the preparation of high surface area CaO is described.

Y. X. Li and K. J. Klabunde, work in progress.

Studies of aromatic chlorocarbons passed over these destructive adsorbents have shown that: (a) The presence of MgO or CaO greatly enhances decomposition compared with straight thermolysis; (b) Capture of Cl is efficient when MgO or CaO are present, and $MgCl_2/CaCl_2$ are formed; (c) The presence of H_2 as a flow gas greatly suppresses carbon formation and accelerated decomposition; (d) High surface area is beneficial; (e) Carbon formation is encouraged by air or He as flow gas; (f) The presence of air as a flow gas is not good in that traces of dioxins can form; (5) Products formed include benzene, CO, H_2O, HCl, CH_4, and carbon.

E. Chemistry of O_2 with Oxygen Deficient Metal Oxide Surfaces.

Studies directed toward understanding the chemistry of oxide anion vacancy sites led to a detailed analysis by ESR of the interaction of O_2 with heat treated CeO_2. The reversible $O_2 \rightleftarrows 2O^{2-}$ reaction was elucidated.

Superoxide (O_2^-) on the Surface of Heat-Treated Ceria. Intermediates in the Reversible Oxygen to Oxide Transformation

X. Zhang and K. J. Klabunde, Inorganic Chemistry, 1992, 31, 1706-1709.

Powder X-ray diffraction (XRD) and electron spin resonance (ESR) studies were employed for the study of oxygen interaction with nonstoichiometric ceria $CeO_2 \rightarrow CeO_{2-x}$. The crystal structure of CeO_2 is maintained during heat treatment in vacuo from 573 to 1073 K. Oxygen adsorption yields ESR signals for three species believed to all be due to O_2^- adsorbed at different surface sites. Studies of temperature dependence, reactivity, and stability suggested that two side-on bonded O_2^- species were formed along with an end-on bonded species probably inserted into a surface oxygen vacancy. This end-on bonded species behaves as an intermediate in the pathway to re-formation of a lattice oxide dianion.

F. Oxygen (^{18}O) Isotope Exchange.

An unprecedented transformation of nanoscale MgO to $Mg^{18}O$ was discovered. Pulsing $H_2{}^{18}O$ over ultrafine MgO particles at 300°C led to surface OH exchange; at 500°C surface O^{2-} was exchanged, and at 700°C interior lattice O^{2-} was also exchangeable. The availability of $Mg^{18}O$ ultrafine particles allowed further clarification of DMMP destructive adsorption.

Heterophasic Isotope Exchange in Nanoscale Metal Oxide Particles. Lattice Oxygen and Surface OH Groups with Water Vapor (D_2O and $H_2{}^{18}O$)

Y.X. Li and K. J. Klabunde, Chem. of Materials, 1992, 4, 611-615.

Ionic solids MgO, CaO, and Fe_2O_3 exchange surface and lattice oxide anions with $H_2{}^{18}O$ as monitored by pulsed reactor-GC-MS studies. Depending on the temperature, the process can be controlled to exchange only OH, or additional surface lattice O^{2-}, or additionally, interior lattice O^{2-} (up to 16 layers deep). Exchange of surface oxide has an activation energy 5 times lower than exchange of bulk-lattice oxide, and the latter is probably controlled by E_a(diffusion). High surface area, small particle size MgO samples exchange most readily. Exchange studies with D_2O have shown that surface OH can be quantitated by the same pulsed reaction-GC-MS technique. These experiments have allowed the synthesis of isotopically labeled $Mg^{18}O$, which has proven useful for clarifying surface adsorption/decomposition chemistry. An example is given where the $Mg^{18}O$ yielded labeled formic acid in the surface decomposition of an organophosphorus compound, proving that surface and lattice oxide can take part in such adsorption/decomposition processes.

G. Related Studies

New approaches to the study of molecular metal oxides led to an experimental study of the chemical reactions of TiO and VO molecules with halogens and organics, and to theoretical calculations on the interaction of MgO and CaO molecules with carbon monoxide.

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

T. J. Groshens and K. J. Klabunde, Inorganic Chemistry, 1990, 29, 2979-2982.

The production and reactivity of titanium monoxide (TiO) and vanadium monoxide (VO) on a synthetically useful scale were studied by 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 byproduct via protonation of the oxo moiety; coordination compounds of titanium and vanadium were isolated as acac complexes in high yields.

III. Students, Postdoctorals, and Research Associates Involved in this Research 1990-1993.

Suchada Utamapanya, Ph.D. 1990 (Now a Research Associate at U. of Nebraska)
Maher Atteya, M.S. 1990 (Now a Ph.D. candidate at Colorado School of Mines)
Xiaolong Zhang, past research assistant (Now a Ph.D. candidate at Albert Einstein Univ.)
Jane Stark, current M.S. Student
Olga Koper, current Ph.D. Student
Cathy (Rogers) Mohs, current Ph.D. Student
Abbas Khaleel, M.S. Degree completed
Yong Xi Li, Research Associate, now a manager of an analytical lab in industry.
Paul Hooker, postdoctoral, now an Assistant Professor at a small college.
Hidenobu Itoh, past visiting professor (now an Associate Professor at the Kitami Inst. in Japan).
Hiroshi Fujitsu, past visiting professor funded by Japanese government (now an Associate Professor at Kyushu Univ. in Japan)

IV. Reportable Inventions

Recent results describing the overlayer Fe_2O_3 on nanoscale MgO particles, designated as $[Fe_2O_3]MgO$, we believe are patentable. These core/shell particles have much more capacity for destructive adsorption of chlorocarbons than just nanoscale MgO, CaO, or Fe_2O_3. Apparently a unique "spillover catalysis" takes place where 2 Cl^- and O^{2-} are exchanged, and the MgO is converted to $MgCl_2$.

An invention disclosure has been submitted to the Kansas State University Research Foundation.