ACTIVATED METAL OXIDE SURFACES AS HIGHLY BASIC AND REDUCING ENVIRONMENTS(U) KANSAS STATE UNIV MANHATTAN DEPT OF CHEMISTRY K J KLABUNDE 21 MAY 87
UNCLASSIFIED ARO-21367.6-CH DAAG29-84-K-0051
Activated Metal Oxide Surfaces as Highly Basic and Reducing Environments

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May, 1987

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Alkaline earth oxides of high surface area were thermally activated at 400-1100°C. Super base properties and electron transfer sites were generated. These materials serve as catalysts for selective deuteration of hydrocarbons, alkene isomerization, CO telomerization and reduction, carbonyl compound condensation, and as a destructive adsorbent for organophosphorus compounds and other toxic substances. Some fundamental understanding of the reactive sites involved has been gained by studying adsorbed species and by metal ion doping. Studies of single metal oxide molecules in matrices has begun.

Metal oxide, super base, thermal activation, defect sites
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Final Report

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I. Introduction

Although metal oxides play an important technological role in the chemical industry (polymer additives, food additives, catalyst supports and promoters, chromatography, paints, etc.), the rich surface chemistry of metal oxides has only recently begun to be appreciated. This is especially true of the alkaline earth oxides which are capable of exhibiting "super base" and "super reducing" abilities. The key to further understanding of this rich area of chemistry is to appreciate that surface defects are generally the reactive sites, and that the defects generated are very dependent on preparative method and activation procedure.

Thephysics community has done a considerable amount of work trying to outline the multitude of defects that can occur on alkaline earth oxide surfaces. However, presumably due to their complexity, the chemistry community has dealt with the subject sparingly. Admittedly, these are very difficult systems to understand. However, the potential technological payoff now dictates that these studies be undertaken more seriously. (The Japanese and French scientific communities have been most active in metal oxide surface work, especially as it relates to catalysis.)

Unique Physical Properties of Metal Oxides:

1. The high heats of formation of the insulator oxides (e.g., MgO, CaO, SiO₂, and Al₂O₃) and their ionic character allow them to form high surface area, nearly amorphous states with very good thermal stabilities. Reactive defect sites are often formed in high concentrations during preparation.

2. The defect sites are of several types: (a) steps and kinks on surfaces; (b) ion vacancies called Frenkel or Schottky defects; and (c) paramagnetic defects called F or V centers formed by electron capture or loss from ion vacancies. A myriad of variations are possible depending on the surrounding geometrical and electronic environment around the defect in question, and whether OH groups exist on the surface.

3. Cation size and M:O stoichiometry can cause unusual crystallite structures to be formed. For example, BeO has the Wurtzite structure (hexagonal close packed arrangements of O⁻) while MgO, CaO, SrO, and BaO adopt the rock salt structure. Al₂O₃ can have different phases; the γ-structure possesses tunnels which allow ionic conductive properties when doped with Li⁺ or Na⁺.

4. Metal oxide surfaces can be activated by irradiation, which dislodges electrons which are captured at defect sites, or by heating under vacuum or under a rapid flow of N₂ or Ar to a specified temperature in the range of 400-1200°C. Heating causes structural defects to form, and to become available through a cleaning process. Thus, H₂O, CO₂, and other adsorbed species are removed. In addition, chemical processes such as H₂ elimination from surface OH groups can lead to additional reactive sites such as electron deficient centers:
(5) Activation temperature and doping with other ionic metal oxides can have a dramatic effect on chemical reactivities.

Unique Chemical Properties of Metal Oxides:

(1) Super base properties can be generated.\(^{12}\)

(2) Super acid (e.g., ZrO\(_2\) - Na\(_2\)SO\(_4\)) properties can be generated.\(^{13,14}\)

(3) Activated MgO is basic enough that it can be used conveniently as a deuteration catalyst for hydrocarbons such as methane by the reaction CH\(_4\)+D\(_2\) \rightarrow CH\(_3\)D + HD.\(^{15}\)

* (4) MgO can also be used for selective deuteration of toluene, ethylbenzene, and other hydrocarbons.\(^{16}\)

* (5) Relative acidities of hydrocarbons such as toluene, xylene, and even neopentane can be determined using activated MgO as a deuterium exchange catalyst.\(^{17}\)

* (6) Acidity determinations over MgO parallel solution acidities rather than gas phase acidities.\(^{18}\)

* (7) H-D exchange from H\(_2\)+D\(_2\) and RH(benzylic) + D\(_2\) have extremely low Ea (-1-2 kcal/mol) which indicates a strong bifunctional catalytic mechanism where both M\(^{++}\) and O\(^{-}\) are involved simultaneously.\(^{19}\)

(8) Activated MgO can be used as a hydrogenation catalyst for organic dienes. When D\(_2\) is used, no H-D scrambling occurs if the MgO activation is carried out at 1100\(^\circ\)C. Thus, catalytic sites for D\(_2\) addition or H-D exchange are different, and one or the other can be favored by activation procedure.\(^{20}\)

(9) Methane can be partially converted to ethane in a slightly oxidizing environment over MgO.\(^{21}\) Activity can be enhanced by Li doping.

* (10) Doping of MgO with Li\(^+\), Na\(^+\), and Al\(^{3+}\) can have dramatic effects on catalytic reaction rates for 1-butene isomerization vs electron transfer to CO to form (CO)\(_6\).\(^{22}\)

* (11) Chemisorption processes on activated MgO often involve electron transfer from defect sites to the adsorbed molecule. Thus, nitrobenzene, benzophenone, naphthalene, anthracene, and others chemisorb at room temperature to form monolayers of anion-radicals.\(^{23,24}\)
Chemisorption of CO at 25°C causes both telomerization and electron transfer, yielding a variety of \((\text{CO})_n^x\) species, particularly \((\text{CO})_6^2\) and \((\text{CO})_6^3\).\(^{24}\)

Organic carbonyl compounds are strongly chemisorbed and base induced condensation reactions readily carried out over activated MgO.\(^{26}\)

Activated MgO is an extremely effective material, due to its high surface area and high concentration of very basic defect sites, for adsorption and destruction of organophosphorous compounds, and it shows promise as a sorbent for air purification systems.\(^{26}\)

II. Summary of Work Completed Under the Past ARO Contract (3/84-3/87)

A. Unique Chemical Properties of Activated MgO

In the Introduction a list of Unique Chemical Properties is given. Those marked with an asterisk are areas we have contributed to (see pages 6-7).

B. Structural Aspects Regarding Reactive Sites

When dealing with the complexities of metal oxide surfaces and the knowledge that a variety of reactive defect sites are possibly important, the major problem becomes one of understanding chemical reactivity on the molecular level. Here we outline some of our recent investigations aimed at improving our current understanding at this level.

1. Doping with Li\(^+\), Na\(^+\), and Al\(^{3+}\)

   To encourage the formation of Frenkel and Schottky defects as well as electron deficient/excess centers, MgO was doped with Li\(^+\), Na\(^+\), and Al\(^{3+}\) as their oxides. Chemical probes \(\text{CO} + (\text{CO})_6^3\) and 1-butene isomerization have been employed, and suggested that electron rich and electron deficient substructures were formed, as illustrated by \([\text{Mg}_2\text{Li}_3\text{O}_{12}]^{3+}\) and \([\text{Mg}_9\text{Al}_3\text{O}_{12}]^{3+}\). Unique reaction properties were described.

2. Spin Traps

   Organic nitroso and nitronc compounds are capable of trapping transient free radicals (R\(\cdot\)) or free electrons to form stable, paramagnetic adducts that exhibit ESR spectra characteristic of R\(\cdot\) (or e\(\cdot\)) trapped. In addition, nitroxide radicals adsorbed on surfaces can yield information about adsorption sites.

   Since activated MgO can possess paramagnetic defect sites (that are difficult to detect by ESR due to relaxation times), and electron transfer sites, we carried out a study of species formed upon adsorption of NOMP and PNP on its surface. We made the following observations: depending on
activation temperature three species were formed NOMP'-o-surface (trapped surface O'), PNP' or NOMP' (electron donated to NOMP or PNP), and di-t-butynitroxide (decomposition of NOMP and subsequent trapping of (CH₃)₂C• by additional NOMP). These studies have helped delineate what activation temperatures favor certain kinds of sites.

3. Matrix Isolation of Single Metal Oxide Molecules

We are well equipped and experienced in the study of high temperature species such as free atoms and coordination deficient molecules. We are now initiating studies of single metal oxide molecules in low temperature matrices. This work is in the beginning stages and is intended to yield bench mark data as the ultimate model of the surface of metal oxides. Up to this point we have used laser, electron beam, and resistive heating methods to generate free molecules of TiO and VO since these are the most amenable to this approach. We have found that solid TiO₂ and V₂O₅ are better sources of molecular TiO and VO than are solid TiO and VO. Reaction chemistry with Cl₂, 2,4-pentanedione, cyclopentadiene, and bipyridine have been investigated. One surprising result is the facile loss of oxygen as H₂O whenever mildly acidic hydrogens are available as a reaction partner. Matrix isolation spectroscopic studies are beginning.

4. Theoretical Approaches to Understanding MgO and CaO Isolated Molecules: Spectroscopic Properties and Coordination to CO.

One Ph.D. candidate working jointly with KJK and JOV is investigating MgO and CaO by theoretical methods. Matrix isolation experimental studies will be carried out in conjunction later.

Ab initio calculations on CO complexes with metal oxides have yielded several results that will motivate further experimentation. The standard program package Gaussian 82 has been employed in these studies. Additional codes for performing SCF calculations with effective core potentials have also been employed when the metal atom belongs to the fourth period. Geometries can be fully optimized, with gradients of the total energy evaluated analytically.

The first target of this study was complex formation between MgO and CO. Weak van der Waals binding occurs when the CO attacks at the O of MgO, regardless of whether the C or the O of CO is pointed at MgO. A stable complex is formed when the CO donates an electron pair to the Mg. The electronic structure is roughly that of a Mg²⁺ ion with a CO and oxide ligands. No back donation into the σ* of the CO occurs, as Mg²⁺ has no valence electrons. It is possible to optimize another stable geometry in which the CO is bound to the metal through the oxygen atom. Both structures are approximately linear. These two geometries are optimized at the SCF double t plus polarization level; correlation corrections at these geometries are estimated with second order perturbation theory. Vibrational frequencies are also calculated in the even that experimental spectra can be observed.
When the metal is changed to Ca, several differences from the Mg results become prominent. Upon choosing reasonable values for bond distances in an approximately linear geometry, the carbonyl and isocarbonyl structures spontaneously convert to highly bent structures. The latter guess geometry connects smoothly to a planar, four-member ring with the C and Ca atoms opposite each other. The electronic structure is approximately a Ca$^{2+}$ ion with a CO$_2$ chelating ligand. In this C$_2$ structure, the anion is isoelectronic with CF$_2$. The HOMO of the free anion donates in a σ fashion to the empty σ, π and d orbitals of the cation. Upon assuming the former initial guess geometry, a smooth conversion to another ring-containing structure occurs. A three-member ring with Ca, O and C forms. One can understand this species as a complex of the same anion and cation as before, but with the latter bridging between the C and one of the O atoms. These Ca results suggest that similar ring structures may exist for the Mg case. A four-member ring structure with Mg has been found, but no stable three-member ring was obtained.

Further work on complexes with early transition metals is now in progress to examine the effects of d electrons on the bonding. The alternatives of simple CO binding or formation of CO$_2^-$ suggest that subtle differences in metal atom size and electronegativity may have great consequences for catalytic reactivity on metal oxide surfaces.

REFERENCES


4. Japanese scientific teams at Hokkaido University (Tanabe, Hattori), U. of Tokyo (Yoneda), Kyushu Univ. (Mochida), Tokyo Inst. (Akal) and others are heavily involved. French teams at U. of Paris (Che) and CNRS-Lyon (Telchner) are also active. However, each group has its own interest and special direction.


17. M. F. Hoq and K. J. Klabunde, Unpublished results (in preparation)


27. a) C. A. Evans, *Aldrichimica Acta*, 12, 23 (1979); 


**Publications resulting from ARO Grant**


Three other papers in are in preparation.
Scientific Personnel

M. F. Hoq, Ph.D. expected in August 1987

S. Utamapanya, Ph.D. expected in December 1988.

I. Nieves, visiting professor from U. of Puerto Rico

H. Matsuhashi, postdoctoral research associate

F. Mousa, postdoctoral research associate

T. Groshens, Ph.D. expected May 1988
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