The bond lengths and angles found in the 4-nitroimidazolato ligand are similar to those found in other cobalt(III) pentaammine imidazolate complexes[18–20] although the quality of the data set obtained has allowed a more accurate determination in the present case. The geometry of the nitro group is similar to that found in the structure of another 4-nitroimidazole molecule.[21]

Results of the mean-plane calculations indicate that the imidazole ring and the nitro group are coplanar. The three equatorial N_4 donor atom planes are very nearly orthogonal to each other, making angles of 88.2, 89.6, and 89.5° to one another. The principal deviation from regular octahedral symmetry arises from the planes containing the cobalt–imidazole bond, at 88.2° to each other. The imidazole plane is not coplanar with either of the N_4 equatorial atom planes but is about equally inclined to each of them (44.2, 47.9°) as is also found in a similar cobalt(III) imidazolato complex.[18]

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Registry No. $[Co(NH_3)_5(NO_2Im)]Cl_2$, 84040-89-1; $[Co(NH_3)_5(ImH)](ClO_4)_3$, 15279-15-9.

Supplementary Material Available: Listings of thermal parameters and their esd's for the positional parameters in Table I, $Co(NH_3)_5X^{n+}$ structures and bond lengths and angles, final values for F_o and F_c for the 2315 reflections used in the refinement process, bond lengths and angles for 4-nitroimidazolate, imidazoles, and the imidazolium ion, hydrogen bond lengths and selected angles for $[Co(NH_3)_5(NO_2Im)]Cl_2$, and coefficients of least-squares planes and a figure showing the packing of the unit cell and hydrogen-bonding parameters (17 pages). Ordering information is given on any current masthead page.

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Formation of Paramagnetic Adsorbed Molecules on Thermally Activated Magnesium and Calcium Oxides. Characteristics of the Active Surface Sites

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Thermal activation of MgO, CaO, SrO, BaO, and ThO_2 yields diamagnetic active surface defects that are capable of reducing adsorbed nitrobenzene, *p*-benzoquinone, tetracyanoquinodimethane (TCNQ), tetracyanoethylene, bipyridine, pyridine, acetophenone, benzophenone, naphthalene, anthracene, and phenanthrene to radical anions at room temperature. The reduction appears to occur as a one-step process on the "reducing sites", and monolayers of many of the respective radical anions are formed. The same active sites are capable of reduction/polymerization of CO to $(CO)_x$ radical anions, dianions, and trianions. However, lower concentrations of these radical anions are formed, and this is a consequence of the need for either special steric requirements and/or higher reactivity of the sites (both reduction and polymerization are required for CO). The defect sites are highly basic and can be poisoned by Lewis acids/proton donors such as CO_2, CS_2, H_2O, H_2S, CH_3OH, HCl, NH_3, acetylene, and acetone as well as alkylating agents such as CH_3I. It is likely that the active sites are surface defects that exist because of cation vacancies, perhaps of the Schottky or Frenkel type. However, residual OH groups aid in the reduction process.

Introduction

Alkaline-earth oxides possess a multitude of structural defects.[1–3] These defects can be due to an irregularity in the crystalline lattice structure (thus, a perfect crystallite has defects at the corners and edges) or due to atom displacements, free electron centers, radiation damage sites, UV–visible absorption sites, etc. Some defects are due to ion vacancies; for example, a Frenkel defect is an ion vacancy with the ion located in an interstitial vacancy, while a Schottky defect is a pair of vacancies with opposite signs (cf. Figure 1). Frenkel and Schottky defects are the result of thermodynamics.[4,5] Thus, a vacant lattice site is higher in energy than an occupied site. However, the occurrence of point defects increases the disorder of the systems, and the entropy term increases. (Sondor and Sibley have proposed a nomenclature for defects based on an ionic crystal defect scheme).[6] The method of

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Table I. Methods of Preparation and Properties of MgO[8]

	properties				
method	surf. area, m^2/g	pore size distrib, Å	particle size distrib, Å	appearance	ref
MgO smoke ($Mg + O_2$)	10	no pore structure	400-800	cubes, hexagonal plates	9-13
$Mg(OH)_2$ pyrolysis		25-75		irregular[a]	14-18
$Mg(CO_3)$ pyrolysis				irregular, highly defective	10, 19-23
$Mg(NO_3)_2$ pyrolysis		25-50	10 000	pitted, topographically irregular with octahedral pieces in some cases	24, 25

[a] Low pressures of H_2O (even 1 mtorr) can cause severe sintering during this process.[19,20]

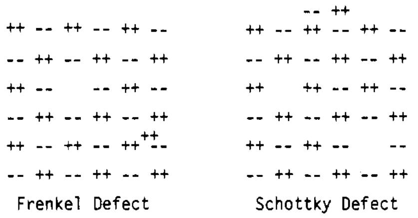

Figure 1. Schematic representation of Frenkel and Schottky defects in alkaline-earth oxides.

preparation of the MgO has a vital role in the occurrence of many defects. These preparation methods and discussions of the resultant properties of MgO are summarized in Table I.

From a chemist's viewpoint the interesting feature about these defects is that they exhibit a rich chemistry with added adsorbing molecules.[7] Of course, different defects behave differently chemically. As a sampling, Schottky defects on MgO have been proposed to be the active sites for the oxidation of carbon monoxide.[26] Likewise, Boudart and co-workers have studied the activity of V sites for H_2–D_2 exchange at −196 °C.[24]

Table II. Adsorbed Anion Radical Species on Alkaline-Earth Oxides

source	adsorbate	color, ESR parameters[a,b]	ref
MgO	nitrobenzene *m*-dinitrobenzene trinitrobenzene *p*-fluoronitrobenzene *p*-nitrotoluene	gray-green, $g = 2.0018$, 2.006	27-30
MgO	7,7,8,8-tetracyanoquinodimethane	blue-green, $g = 2.0011$	31
MgO	pyridine	purple, $g = 2.0022$, 2.0030, $A(^{14}N) = 8.2$	32
MgO	carbon monoxide	peach, $g = 2.0021$, 2.0055	33
MgO	tetracyanoethane	...	34
MgO	nitric oxide	NO_2^{2-} $g = 2.0025$, 2.0068	35, 36
MgO	bipyridyl	blue	28
CaO	nitrobenzene	...	29
CaO	bipyridyl	blue	28
CaO	pyridine	purple, $g = 2.0022$, 2.0026, $A(^{14}N) = 7.4$	32
SrO	pyridine	purple, $g = 2.002$, 2.003, $A(^{14}N) = 7.2$	32

[a] g represents the ESR absorption value or g factor. [b] A is the hyperfine splitting in gauss for ^{14}N.

Of the many defects known, some are diamagnetic and some are paramagnetic. Some can be diamagnetic, but when treated with diamagnetic added molecules, adsorption can take place, leading to paramagnetic adsorbed species. This requires that an electron be transferred to or from the defect to or from the adsorbing molecule. The most common form this process takes is for electron transfer from the defect to the adsorbing molecule, thus yielding an adsorbed anion radical. Table II summarizes much of this work.

The first example of an electron transfer to an adsorbed organic molecule on outgassed MgO was the formation of the nitrobenzene anion radical.[27] *sym*-Trinitrobenzene and *m*-dinitrobenzene also formed anion radicals upon adsorption at room temperature on MgO. Further experiments indicated that preadsorption of CO_2 or H_2O prevented nitrobenzene reduction, and Tench and co-workers concluded that the electron-transfer site was a coordinatively unsaturated oxygen species and that this basic, diamagnetic site could be blocked by Lewis acids (CO_2, H_2O). Since O_2 (EA = 0.5 eV) did not form $O_2^{-}\cdot$ upon adsorption and nitrobenzene did (EA = 0.7 eV), it was also concluded that molecules with an electron affinity (EA) equal to or greater than 0.7 were necessary to extract an electron from this electron-rich site.[27]

By the activation of MgO at 500 or 900 °C different active sites were apparently generated, one containing a reactive OH group.[27,30,31] When nitrobenzene was adsorbed, two anion

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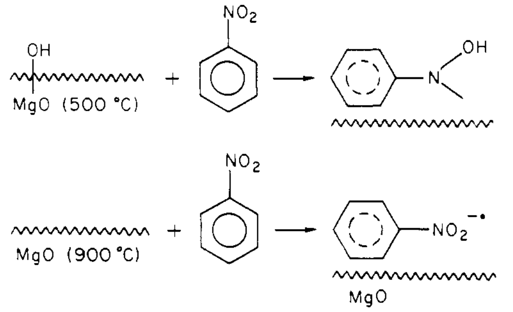
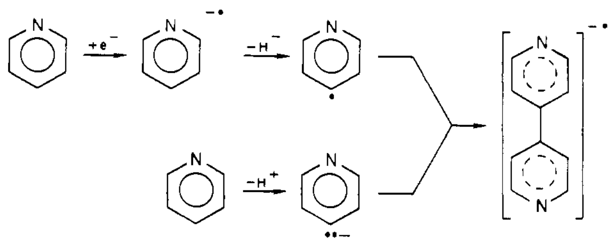
radicals were formed, one containing a proton:



The surface of outgassed calcium oxide is also active in nitrobenzene reduction to the anion radical.[29] The anion radical concentration varied with CaO activation temperature, the highest concentration of $C_6H_5NO_2^{-}\cdot$ being found when 480–500 °C was the activating temperature. These "reducing sites" were compared with "basic sites" (by titration) and were found to correspond poorly with each other as the activation temperature was varied. Also, the basic sites were 10^3 higher in concentration than the reducing sites.[29]

Pyridine is also reduced on these activated oxides.[32,37-39] Since the ESR splitting parameters could only be satisfied by two nitrogen atoms being present in the anion radical, it was proposed that the 4,4′-bipyridyl anion radical was formed as shown:



As expected, 2,2′-bipyridine and 4,4′-bipyridine are reduced to anion radicals when adsorbed directly.[28,38]

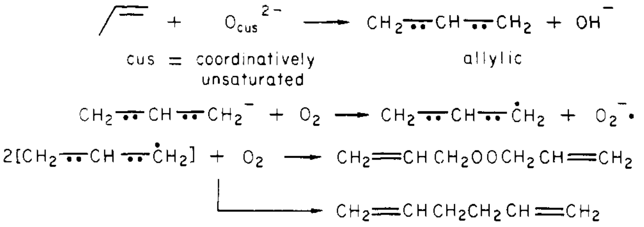
Sulfur-containing anion radicals can also be prepared.[40,41] Elemental sulfur at 400 °C reacted in the following way to yield paramagnetic $S_3^{-}\cdot$:

$$(S)_n + \underset{MgO}{(OH)_4} \rightarrow 2H_2S + 2S_3^{-}\cdot + SO_4^{2-} + (S)_{n-9}$$

Table III. Sources of Magnesium Oxides

identification	source	comment
MgO-I	Research Organic/Inorganic Chemical Corp.	99.99%
MgO-II	Research Organic/Inorganic Chemical Corp.	99.99%, powder 200 mesh
MgO-III	Fisher Scientific Co.	99.5%
MgO (OH)	Fisher Scientific Co.	$Mg(OH)_2 \xrightarrow[\text{vacuum}]{800\ ^\circ C} MgO + H_2O$
MgO (NO_3)	Mallinckrodt Chemical	$Mg(NO_3)_2 \xrightarrow[\text{in air}]{\Delta} MgO + 2NO_2 + {}^1/_2O_2$
MgO (smoke)	Fisher Scientific Co.	$2Mg + O_2 \xrightarrow[\text{in air}]{\text{flame}} 2MgO$
MgO (cryst)	Atomergic Chemetals Corp.	single cryst

In a related process, sensitizers have allowed the formation of $O_2^{-}\cdot$ on thermally activated MgO, CaO, and SrO.[42] Recall that paramagnetic F_s^+ centers will react with O_2 to form $O_2^{-}\cdot$, but diamagnetic MgO will not.[33,37,42,43] However, prior adsorption of hydrogen, ethylene, carbon monoxide, propene, 1-butene, acetylene, or pyridine followed by O_2 will result in $O_2^{-}\cdot$ formation.[32,37,39,42-47] Garrone, Zecchina, and Stone[42] believe that a sensitization mechanism based on the presence of strong basic sites operates. Thus, adsorption of an alkene yields a carbanion, which can shuttle an electron to O_2:[42,48]



Hydrogen must behave in a similar manner:[42]

$$H_2 + O^{2-}{}_{cus} \rightarrow H^- + OH^-$$
$$H^- + O_2 \rightarrow O_2^{-}\cdot + H\cdot$$

It would appear from the previous work that it is still not at all clear what types of sites are "reducing sites" and whether the presence of basic sites is also necessary. The remainder of this report deals with recent work we have done in an attempt to learn more about the properties of the so-called "reducing sites".

Experimental Section

General procedures and spectral analysis procedures have been reported previously.[8,49,50] Seven different MgO samples were used and are summarized in Table III. Samples Mg-I–Mg-III were washed with boiling distilled water for 1 h, recovered by hot filtration, dried in air at 110 °C for ~6 h, and stored in vials awaiting thermal activation. Each sample was chopped (not ground since grinding produced higher concentrations of paramagnetic defects) into small pieces <1.5 mm. All seven MgO samples were heat-treated as follows: About 100 mg was placed in a 10–15-cm quartz cell equipped with a graded pyrex seal to a high-vacuum stopcock (4 mm). The cell was evacuated slowly, and heating was begun very slowly. About $2^1/_2$ h was needed to attain 380–400 °C, and then several more hours were needed to slowly reach the desired temperature. The extremely slow heating was necessary to avoid violent degassing of the oxide sample. The desired temperature was maintained for about 14 h followed by

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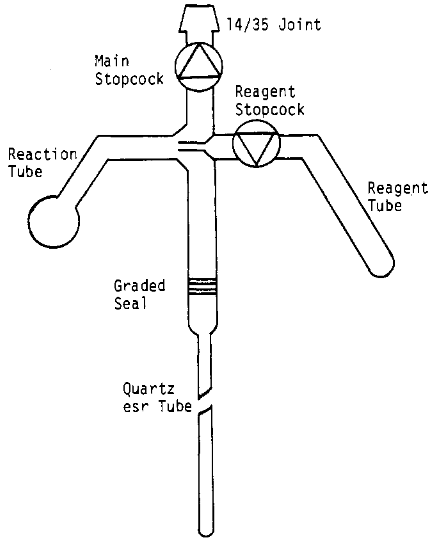

Figure 2. Diagram of the cell used for the addition of solid reagents to oxide samples.

cooling to room temperature. Typical pressures at the conclusion of this process were 2 × 10^{-6} torr.

Calcium oxide was obtained from Research Organic/Inorganic Chemical Corp. (purity 99.99%) and treated as Mg-I–Mg-III were.

Purification of Reagents. Reagents used were purified by passing through a −196 °C trap (CO, H_2, O_2, N_2, CH_4, C_2H_6), −78 °C trap (CO_2, NH_3, HCl, C_3H_6, C_2H_4, CH_3OCH_3), −38 °C trap ($CH_3C{\equiv}CH$, $CH_3CH_2CH{=}CH_2$, $N(CH_3)_3$), or −20 °C trap (H_2S). Liquids were distilled and freeze–thaw degassed prior to use. Solids were distilled or sublimed. Other purification steps were taken as necessary: CH_3OH and CH_3CH_2OH were dried over 4-Å molecular sieves; $C_2H_5OC_2H_5$ was dried with $LiAlH_4$; n-C_5H_{12} was dried with sodium metal, $HC{\equiv}CH$ was passed over alumina and bubbled through concentrated H_2SO_4 prior to passing through a −78 °C trap; C_6H_5CN and C_5H_5N were dried over $CaSO_4$; ^{13}CO from Prochem/Isotopes was passed over a freshly regenerated BASF R3-11 deoxygenation catalyst followed by passing through a −196 °C trap.

Treatment of Activated Oxides with Reagents. Generally the activated oxide under vacuum was exposed to the vapor of the reagent for at least several minutes. The exact addition procedure was very dependent upon the type of reagent at hand. For gases or volatile liquids, vapor transfer was easily carried out on a vacuum line, but for solids with little or no vapor pressure, a special technique was employed, which used toluene as a solvent. Toluene did not interfere with anion radical formation with added reagents. Therefore, 10 mmol of reagent was dissolved in 5 mL of dry, purified toluene contained in the reagent tube of the apparatus (Figure 2). The solution was freeze–thaw degassed. The oxide powder sample was thermally activated in the quartz section (ESR tube) and then transferred to the reaction tube (Figure 2). The solution was allowed to pour onto the oxide and left to equilibrate for 5 min. Then the reagent tube was cooled with liquid nitrogen, and the toluene was cryogenically pumped back into the tube. After toluene removal the treated oxide was transferred to the ESR tube, which was sealed off with a flame, and spectrally analyzed.

Infrared Spectra. Procedures for obtaining IR spectra of thermally activated, chemically treated MgO and CaO pellets have been described previously.[49,51,52]

Results and Discussion

The purpose of our experiments was to establish what properties of metal oxides, in particular MgO and CaO, are necessary in order to produce or possess "reducing sites". For our purposes we define a reducing site as a site capable of effecting the transformation of an adsorbed diamagnetic molecule into an adsorbed anion radical, the starting site being diamagnetic itself.

Table IV. Metal Oxides Tested for Activity for Formation of Paramagnetic Species upon Exposure to Carbon Monoxide

	Active	
MgO	SrO	ThO$_2$
CaO	BaO	
	Nonactive	
BeO	FeS(7%):SiO$_2$	La$_2$O$_3$
Na$_2$O (220 °C)	PbO	CeO$_2$
NaOH(5%):SiO$_2$	SnO$_2$	Nd$_2$O$_3$
Al$_2$O$_3$	TiO$_2$	Eu$_2$O$_3$
Al$_2$O$_3$(45%):SiO$_2$	GeO$_2$	Dy$_2$O$_3$
SiO$_2$	ZnO	UO$_3$/U$_2$O$_5$
Fe$_2$O$_3$(0.05):Al$_2$O$_3$	ZrO$_2$	

Active and Nonactive Oxides. Some preliminary experiments were performed in order to determine the approximate scope of materials capable of "reducing site chemistry". A variety of oxides, hydroxides, and sulfides were tested for activity for formation of carbon monoxide anion radicals.[7] All of the materials listed in Table IV were heat-treated at 600 °C under a vacuum of 10^{-6} torr for 12–18 h before exposure to 150-torr CO at room temperature. All of the activated materials were diamagnetic after heat treatment. The active oxides are unique in that they are the only known materials to convert adsorbed carbon monoxide into paramagnetic molecules at room temperature without the need for an irradiation step. It should be noted that all of the active oxides possess strong Lewis base sites.[53] However, some of the nonactive oxides are also basic. So if basic sites play a role in the conversion of CO to paramagnetic telomers as we concluded previously,[49,50] the alkaline-earth oxides have other unique properties as well that must be acting synergistically with the basic sites.

In fact, all of the active oxides are alkaline-earth oxides with the exception of ThO_2. This oxide behaves considerably differently, and quite different paramagnetic CO species are formed. For example, with the alkaline-earth oxides, CO adsorption causes a rapid color change whereas with ThO_2 no color was generated. Also, the average g value for $(CO)_n^{-}\cdot/ThO_2$ ranged from 1.989 to 2.001, significantly different from the $(CO)_n^{-}\cdot/MgO(CaO)$ value of 2.004. Thus, ThO_2 is unique among the active oxides and should be considered separately.[54]

Another unusual case is BeO, which is the only alkaline-earth oxide inactive in the CO reduction/polymerization process. Although this inactivity may be due to a lower basicity of certain sites, it is interesting to note that BeO is the only one that has a different structure, not the sodium chloride structure as with MgO, CaO, SrO, and BaO.

We consider these CO reduction/polymerization activities as significant and generally indicative of activity for the reduction of other molecules of sufficient electron affinity. This is based on our previous work indicating MgO samples of varying activity for CO reduction/polymerization showed the same activity trends for $C_6H_5NO_2$ reduction to $C_6H_5NO_2^{-}\cdot$. We concluded that the "reducing sites" were similar for both processes.

Electron Micrograph Studies. A comparison was made between the relative activities of various MgO and CaO samples for CO reduction/polymerization vs. their physical appearance under the electron microscope. Table V lists the relative activities of oxides all thermally activated in the same way and gives a brief description of their appearance. Magnesium oxide prepared as a single crystal or as MgO smoke has the least defective surface structure and the lowest surface area. Since neither sample showed any activity for CO reduction/polymerization, it is clear that a defective surface structure is necessary. However, the presence of a very ir-

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(53) K. Tanabe, "Solid Acids and Bases", Academic Press, New York, 1970.

(54) W. S. Brey, R. B. Gammage, and Y. P. Virmani, *J. Phys. Chem.*, **75**, 895 (1971).

Table V. Relative Activities of Thermally Activated Oxides for CO Reduction/Polymerization

source[a]	rel activity[b]	surf. area, m^2/g[c]	appearance
MgO-I	1.00	134	highly defective flakelike particles
MgO-II	0.94	129	
MgO-III	0.79	163	
MgO (OH)	0.58	177	small, irregular-shaped particles
MgO (NO_3-water washed)	0.84	172	
MgO (NO_3-non water washed)	0.76		
MgO (smoke)	0.00	15	smooth hexagonal plates
MgO (cryst)	0.00	low	smooth, well-formed single cryst
CaO	0.98	190	

[a] See Experimental Section. [b] Areas under the curves obtained by double integration (R. S. Alger, "Electron Paramagnetic Resonance: Techniques and Applications", Interscience, New York, 1968, p 216). [c] BET method (Brunauer, Emmett, Teller method: S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938)). Also see S. Lowell, "Introduction to Powder Surface Area", Wiley-Interscience, New York, 1979, p 20.

regular surface is not the only requirement. This is best illustrated by considering MgO (NO_3), where one sample was water washed and the other was not. Although the sample without water washing had excessive surface irregularities, this was not reflected in increased CO reduction/polymerization activity. The most active samples, MgO-I and MgO-II, possess flakelike particles, whereas MgO (OH) is less reactive and is made up of small irregular-shaped particles. The beautifully shaped hexagonal plates of MgO smoke showed no activity.

Surface Area Studies. Table V lists the surface areas for the same oxides as determined by the gas adsorption method (BET). As expected from their appearance, MgO (smoke) and MgO (cryst) possessed very low surface areas. The areas for the other oxides ranged from 129 to 190 m^2/g, and their CO reduction/polymerization activities did not correlate linearly with surface areas, again demonstrating specific types of defects rather than just a high surface area are necessary.

Pore Size Distribution. Pore size distribution varied significantly for the MgO samples. The distributions were broad over 20–150 Å with the most previous pore radii for MgO-I at 25–100 Å, MgO-II at 25–75 Å, MgO-III at 50–100 Å, MgO (OH) at 25–75 Å, and MgO (NO_3) at 25–50 Å. The activities of these oxides for CO reduction/polymerization did not correspond to pore size.

Scope of Molecule Reductions. Anion radical species were detected with a variety of adsorbed molecules. Table VI lists all the substances that we have studied. These results indicated that only molecules that are easily reduced form anion radicals. Those substances that are easily oxidized such as anisole or aniline do not form radicals, which is further support for our contention that MgO and CaO surface defects are always electron donating.

In earlier work we demonstrated that nitrobenzene forms a very high concentration of anion radicals on MgO,[55] essentially monolayer coverage. This appears to be the case for all of the active molecules shown in Table VI. Specifically, the anion radical concentrations (number of spins/g of MgO) were determined for nitrobenzene (6.7×10^{19}), *p*-benzoquinone (6.0×10^{19}), benzophenone (5.8×10^{19}) 2,2′-bipyridine (6.4×10^{19}), and pyridine (6.3×10^{19}). Also note that the wide variance in reduction potential for these molecules does not affect radical concentrations; for example, compare nitrobenzene (−1.15 V) and *p*-benzoquinone (−0.54) (see Table VI for more data).[56]

Table VI. Survey of Molecules Capable of Forming Anion Radical Species on Calcium and Magnesium Oxides[a,b]

No Radical Formation

hydrogen
oxygen
nitrogen
carbon dioxide
carbon disulfide
ammonia
trimethylamine
methane
ethane
propane
butane
pentane
ethene
propene
1-butene
1-pentene
acetylene
propyne

methanol
ethanol
iodomethane
dimethyl ether
diethyl ether
acetic acid
acetone (−2.84)
benzene
toluene
aniline
anisole
cyanobenzene (−2.31)
perfluoroacetone
fluorobenzene (−2.85)
perfluorobenzene
α,α,α-trifluorotoluene
α,α,α,α′,α′,α′-hexafluoro-*p*-dimethylbenzene
benzene

Radical Formation

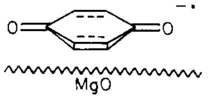
p-benzoquinone (−0.54)
benzophenone (−1.75)
acetophenone (−1.87)
naphthalene (−2.50)
phenanthrene (−2.44)

anthracene (−1.94)
nitrobenzene (−1.15)
pyridine
2,2′-bipyridine

[a] The results are essentially identical for both calcium and magnesium oxides. [b] Reduction potentials are listed in volts with respect to SCE (DMF solvent, 0.1 M $R_4N^+X^-$).[56]

We conclude that a reduction potential of at least −2.5 V is needed in order for reduction to radical anions to occur on MgO and CaO surface sites. However, if an adsorbed molecule possesses a more than adequate reduction potential, complete reduction to monolayer coverage takes place.

However, it must again be pointed out that CO is unique among the reducible compounds. Monolayer anion radical coverage does not occur. This is most likely a result of the fact that CO reduction must be accompanied by CO telomerization, and this puts certain steric requirements on the defect sites that can be active. However, recall our previous work, indicating that by the varying of thermal activation procedures the reducing activities of various MgO samples can be varied but that the samples that show the highest activity for nitrobenzene reduction also show the highest activity for CO reduction/polymerization.[49] These considerations led to the conclusion that the same types of defect sites are responsible for nitrobenzene reduction and for CO reduction/polymerization but that slight steric restrictions are placed on the sites for CO interaction. It would be logical that the same defect sites are responsible for reduction of the other reducible molecules shown in Table VI. Since no steric restrictions are apparent for all molecules except CO, we conclude that the anion radicals formed lie flat on the surface of the MgO but rotate and sweep out an area equal to their spinning diameters (monolayer coverage was determined on the basis of this conclusion):[27,55]



Another interesting aspect we must consider is the rate of anion radical formation for these molecules vs. that for CO. All of the active molecules in Table VI are reduced quite

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(56) M. E. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

Table VII. Survey of Molecules That Will Block Radical Formation on Magnesium and Calcium Oxides[a]

Blocking Reagents	
water	iodomethane
hydrogen sulfide	acetic acid
hydrochloric acid	acetone
ammonia	aniline
acetylene	carbon dioxide[c]
methanol	carbon disulfide[c]
ethanol	
Nonblocking Reagents	
hydrogen	ethene
oxygen	propene
nitrogen	1-butene
trimethylamine	1-pentene
methane	propyne
ethane	dimethyl ether[b]
propane	benzene
butane	toluene
pentane	

[a] Results are identical for both calcium and magnesium. [b] Required 70 °C heating under vacuum for removal to prevent blocking on magnesium oxide only. [c] CO_2 and CS_2 do not possess removable protons but can function as Lewis acids through the carbon atom.

rapidly (48 h at most) on the surface of MgO at room temperature. Even CO is reduced/polymerized to diamagnetic dianions quite rapidly.[50] However, anion radial formation is very slow, and 40 days are required for maximum concentrations of $(CO)_x$ anion radicals to form. This difference can possibly be attributed to (1) the notion that CO reduction/polymerization to an anion radical requires defect sites of specific steric properties and/or (2) the fact that a three-electron reduction to $(CO)_6{}^{3-}\cdot$, (which we believe is the predominant but not the only anion radical formed with (CO)[50] requires defect sites of especially powerful reducing properties.

Thus, although similar defect sites are probably responsible for all these reduction processes, slight variations in the sites account for differences encountered in nitrobenzene (and similar molecules) vs. CO. Different reduction mechanisms are obviously also occurring. Nitrobenzene (and similar molecules) appear to be directly reduced in one step by surface sites. However, for CO three steps are likely: (1) instantaneous adsorption of CO, with removal of the CO atmosphere not changing the rate for the final concentration of anion radicals formed; (2) Orientation and migration of CO molecules into the proper sites, with color formation due to the formation of $(CO)_x{}^{2-}$ species being noticeable in 5–10 min; (3) reduction of the CO polymers to trianion radicals and monoanion radicals. A likely sequence for the C_6O_6 species is shown by eq 1–3.

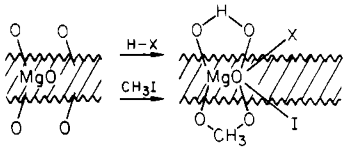
$$\begin{aligned} CO + \text{surface} &\rightarrow CO(\text{ads}) \\ 6CO(\text{ads}) &\rightarrow (CO)_6(\text{ads}) \end{aligned} \qquad (1)$$

$$(CO)_6(\text{ads}) + 2e^- \rightarrow C_6O_6{}^{2-}(\text{ads}) \qquad (2)$$

$$C_6O_6{}^{2-}(\text{ads}) + e^- \rightarrow C_6O_6{}^{3-}\cdot(\text{ads}) \qquad (3)$$

As would be expected, lower temperatures impede the formation of both $C_6O_6{}^{2-}$ and $C_6O_6{}^{3-}\cdot$. No formation of anions or anion radicals occurs at 77 K, but at 215 K the rate of anion radical growth is nearly the same as at 300 K.

Reducing-Site Blockage. Thermally activated MgO and CaO samples were exposed to a series of reagents to determine which would block the active sites for CO reduction/polymerization. Vapors of the materials shown in Table VII were allowed to contact the oxides for several minutes, then the samples were evacuated, and then CO was added. Certain trends are noted from Table VII. All the reagents that were inactive for blocking were relatively nonpolar and did not possess easily removable protons. All the reagents active in blocking are Lewis acids or possess removable protons and thus could block a basic site, with the exception of iodomethane. Iodomethane is a very active alkylating agent and would also be expected to react with a basic surface site. These results lead to the conclusion that the active sites are strongly basic and are poisoned by Lewis acids, protons, and alkylating agents:



High-temperature treatment of activated MgO with H_2 or O_2 at 800 °C for 24 h did not change the surface structures or activity of the samples significantly. However, water treatment in this way caused gross surface structure changes and sintering of the MgO with almost complete loss of activity for CO reduction/polymerization (at 25 °C.). Water is known to be destructive in this way,[14,15,21,24,57,58] and care must be used to avoid the presence of water vapor during thermal activation procedures.

Conclusions

(1) The active sites are surface defects with very high basicity. They are probably made up of cation vacancies, yielding clusters of oxygen dianions at a corner, edge, or step on the crystallite surface.[55] Frenkel or Schottky type defects at the surface would fit the requirements. However, lower activation temperatures (400–500 °C) yield more active oxides than higher activation temperatures (800–1000 °C), and this would suggest that the higher temperatures anneal out defect sites. Thus, cations in the Frenkel or Schottky picture (Figure 1) may migrate, eventually neutralizing some of the oxide cluster defect sites.

(2) The surface reduction of nitrobenzene (and similar organic molecules) occurs by direct electron transfer from the defect (sensitization is not necessary). Sufficient defects are available such that monolayers of nitrobenzene radical anions form, which lay flat and rotate on the MgO or CaO surface.

(3) Direct electron-transfer reduction/polymerization of CO is also indicated. Similar sites are involved, but the mechanism is stepwise such that CO is adsorbed, migrates, polymerizes, and is reduced. In the case of CO two- and three-electron reductions are common to yield predominantly $C_6O_6{}^{2-}$ and $C_6O_6{}^{3-}\cdot$, and this requires especially active defect sites.

(4) The oxides MgO, CaO, SrO, BaO, and ThO_2 possess active reducing sites, but ThO_2 behaves somewhat differently from the others. Only materials possessing Lewis basicity also possess reducing character. This suggests a synergistic effect where basic surface sites may serve to rapidly chemisorb reducible reagents, which then slowly migrate to the proper reducing sites. The basic character of the oxide also allows the production of highly basic reducing sites.

(5) The requirements of the adsorbed molecules are that they possess a reduction potential of about −2.5 V. However, CO reduction is a special case in that telomerization occurs so that $(CO)_x$ species of sufficient reduction potential are formed (monomeric CO is not reducible).

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Registry No. MgO, 1309-48-4; CaO, 1305-78-8; SrO, 1314-11-0; BaO, 1304-28-5; ThO_2, 1314-20-1; carbon monoxide, 630-08-0.

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