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Final Report

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Charge Distribution Analysis of Catalysts under Simulated Reaction Conditions

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Abstract

A new technique has been developed to measure mobile charge carriers in dielectric materials, insulators and catalysts. The technique, Charge Distribution Analysis, is based on the measurement of the dielectric polarization in an electric field gradient, contact-free, at 0 Hertz under minimum perturbation conditions. The measured parameter is the force $F^{\pm}$ experienced by the sample in a gradient of reversible polarity. CDA allows to determine the sign of the majority charge carriers and the density of surface charges which may be correlated to the chemical or catalytic activity. Throughout this work a microbalance has been used as a force-sensing device. CDA can be applied to any dielectric material, compact or porous, in inert or reactive and corrosive gas environments. To conduct CDA experiments under simulated reaction conditions that are relevant to coal liquefaction research, e.g. in reactive and in part chemically corrosive atmospheres, several modifications were introduced to the current design. In particular, the stainless steel sample chamber and furnace/electrode assembly were built, and the gas flow system was redesigned. The CDA instrument was equipped with new data acquisition capabilities. Tests were performed in inert gases and in reactive and corrosive atmosphere between ambient temperature and 500°C on iron oxide and partially sulfidized iron oxide catalysts as well as on pyrite (FeS_2) single crystals.

Introduction

The purpose of the work performed under Contract DE-AC 22 92 PC 92106 was to apply a new technique, **Charge Distribution Analysis** (CDA), to various oxide, sulfide and carbon-black catalysts that are of interest to the Coal Liquefaction Program of the Pittsburgh Energy Technology Center of the U.S. Department of Energy.

CDA is a new technique which measures the dielectric polarization of a material. CDA may be of considerable value to the study of catalysts for heterogeneous reactions. Because CDA is a relatively new technique, it is appropriate to first review its physical basis and to evaluate the information that can, in principle, be obtained. We begin by asking the question: Which specific properties of a given solid come into play when its surface becomes catalytically active?

In heterogeneous catalysis, the purpose of a catalyst is to promote certain chemical reactions among gases or liquids that are in contact with its surface. The function of the surface is to enable reactions that might otherwise be hindered or loose out to competing pathways. The promotion occurs by changing the rate of a given reaction, thus enhancing the kinetics, or by enabling competing reactions, thus changing the overall mechanism of a given set of reactions. A second important requirement is that the catalyst may not be consumed, and a third that is should be capable of performing the reaction on a molecular level over many cycles. Specifically, in coal liquefaction research, the interest is to understand how a highly polymerized coal is depolymerized and hydrogenated, converting into lower molecular weight products, by the help of catalysts.

Background

Every catalytic reaction entails some amount of transfer of charges, either electrons (e^-) or holes (h^+), between the solid surface and the reactants during transient adsorption or chemisorption. The transfer may be transient or permanent for a given reaction step. On the basis of this argument we may predict that catalytic activity should be related to the capacity of a solid surface to donate electrons to or accept electrons from molecules in the gas or liquid phases with which it is brought in contact. Two such processes involving species A and B are outlined schematically in Figure 1.

Surface Charge Transfer Processes

Figure 1:

Schematic representation of a electron or hole transfer between a catalytically active surface and two molecules A or B. Through the transfer of charges A and B become activated A^* and B^* or chemically modified as radicals.

e' and h^+ stand for an electron and hole, respectively. n and μ stand for the number density and mobility of charges. Subscripts s and b designate surface and bulk, respectively.

A specific case is the hydrogen abstraction from CH_4 on oxide contacts at temperatures above $600^\circ C$, a reaction that is fundamental to oxidative coupling of methane and its conversion into higher hydrocarbons. A large number of oxides have been found to be catalytically active including such very simple non-transition metal oxides like MgO and CaO . On the catalyst side the reaction is controlled by the availability of holes h^+ at the oxide surface, e.g. by the availability of O^- states on the surface primarily composed of O^{2-} . As shown by Figure 2, a reaction then occurs between CH_4 and O^- by which an H atom is abstracted from the CH_4 molecule and transferred onto the oxide surface, forming an OH^- at the surface. The CH_4 molecule becomes a methyl radical, $\bullet CH_3$, which remains in the gas phase, $CH_4 + O^- = \bullet CH_3 + OH^-$, while the methyl radicals continue to react to give higher hydrocarbons such as ethane: $\bullet CH_3 + \bullet CH_3 = C_2H_6$.

Though the oxidative coupling of methane is not of direct interest to coal liquefaction, the example shows how, in the case of a simple oxide, its surface may become reduced by hydrogenation while the gas phase reactants become oxidized.

Obviously, the reaction just described depends upon the availability of O^- at the oxide surface. Besides being a chemical species as suggested here, the O^- is also and primarily an electronic charge carrier, more precisely a defect electron in the O^{2-} matrix. As a defect electron it carries a positive charge and is often designated as a "positive hole". Its diffusion from the bulk to the surface is indicated in **Figure 2** by the arrow in the bulk symbolizing the transport of $h^* \equiv O^-$.

Figure 2:

Schematic representation of a typical gas-solid reaction whereby a CH_4 molecule donates an H atom, (H^+ plus an electron) to a surface O^- in an oxide (O^{2-}) matrix.

This particular reaction is of interest in the field of oxidative coupling of methane and its transformation into higher hydrocarbons.

While the CH_4 molecule is oxidized, the surface O^- species are reduced by turning into OH^- . Such OH^- are generally assumed to become H_2O at the temperature of the reaction, $>600^\circ C$, following the "textbook" reaction $OH^- + OH^- = H_2O + O^{2-}$. Such H_2O molecules would then be removed from the catalyst surface, leading to what appears as an irreversible loss of O^- from the catalyst. The question arises: How can an oxide catalyst replenish its O^- reservoir to sustain a large turnover number of repetitive reaction steps?

The way how O^- may be replenished in a given oxide or on its surface has been clarified over the last few years, at least for the simplest catalyst of MgO and CaO . The basic issue concerns the removal of OH^- . It has been shown that OH^- do not necessarily remove themselves as H_2O following the simple reaction scheme $OH^- + OH^- = H_2O + O^{2-}$. Instead, they undergo a redox conversion by which OH^- pairs become H_2 plus O_2^{2-} , peroxy anions: $OH^- + OH^- = H_2 + O_2^{2-}$. The reaction appears to be driven by steep local electric field gradients associated with vacancy sites. The peroxy anions, O_2^{2-} , in turn dissociate at temperatures above $500^\circ C$ to give two mobile O^- which replenish the O^- reservoir.

Following the general argument outlined above that chemical reactions at surfaces always involve the transfer of charges, we predict that, as long as no transferable charges are available at a surface, that surface cannot be catalytically active. Along the same line of arguments, we expect (i) that the activity of a catalyst should depend upon the number density (n_s) and mobility (μ_s) of surface charges, either electrons or holes, and (ii) that the rate at which a reaction can be performed at a

catalyst surface under steady state conditions should be controlled by the flux of charges ($n_s\mu_s$) along the surface or by the flux of charges ($n_b\mu_b$) from the bulk to the surface. If these assumptions are valid, any technique that measures electric conductivity along solid surfaces and in the bulk might be used to obtain information that correlates with catalytic activity.

The simplest way to measure surface conductivity would be by placing a set of electrodes on the sample and measuring the d.c. (direct current) or a.c. (alternating current) surface conductivity as sketched by the upper circuit in Figure 3. In cases where the surface conductivity is enhanced over the bulk conductivity, the surface current ($n_s\mu_s$), if measured by the upper circuit, should be significantly higher than the current ($n_b\mu_b$) measured by the lower circuit.

Figure 3:

Schematics for measuring surface versus bulk conductivities of a solid sample.

Upper circuit: surface conductivity between electrodes (1) and (2).

Lower circuit: bulk conductivity between electrodes (1/2) and (3).

(4): Ground ring electrode

Unfortunately, surface conductivity measurements are difficult, and they become intractable when the samples to be studied are highly insulating materials in either compact or pressed powder form as is often the case for catalysts. Whenever a sample is highly insulating, the application of metal contacts creates contact potentials and thus alters the distribution and density $[n]$ of charge carriers at the interface. Therefore, a measurement of the surface conductivity becomes ambiguous because one does not know the charge carrier density on the unperturbed surface. In cases of pressed pellet samples good electrical contacts between the sample surface and the metal electrode cannot be achieved and grain-grain contacts are generally poorly constrained.

Alternatively, one can employ higher frequency a.c. techniques such as impedance measurements which obtain information about the conductivity by determining the attenuation and phase shift of a sinusoidally alternating voltage sent through the sample in a symmetrical capacitor arrangement. Impedance measurements are usually performed with contacting electrodes. They thus suffer from the same experimental constraints as d.c. techniques. In addition, neither conventional d.c. nor

a.c. conductivity measurements can provide information about the sign of the majority charge carriers. To obtain such information one normally carries out Hall effect measurements. Such measurements are commonly done for semiconductors. As they require contacting electrodes they suffer from the same limitations as mentioned above. They are inapplicable to highly insulating materials which contain an insufficient charge carrier density of charge carriers.

As a technique that does not require contact electrodes, CDA addresses some of the fundamental concerns listed above. CDA obtains information about bulk charge carriers and surface charges by immersing the sample, contact-free, into a static electric field gradient of different polarities and measuring the force acting on the sample.

Charge Distribution Analysis — A New Technique

When a dielectric is placed in an external electric field of field strength E_{ext} it becomes polarized, and its polarization $\mathbf{P}$ is given by:

$$\mathbf{P} = \frac{\epsilon_0 \chi_{\text{diel}}}{4\pi} \mathbf{E}_{\text{ext}} \quad (1)$$

where ϵ_0 is the permittivity of vacuum and χ_{diel} is the dielectric susceptibility, related to the dielectric constant ϵ by $\chi_{\text{diel}} = (\epsilon - 1)$.

$\mathbf{P}$ contains at least four contributions, $\mathbf{P}_{\text{el}} + \mathbf{P}_{\text{ion}} + \mathbf{P}_{\text{local}} + \mathbf{P}_{\text{space}} + \mathbf{P}_{\text{surface}}$, of which the first two refer to the ideal dielectric¹¹. $\mathbf{P}_{\text{el}}$ reflects the field-induced polarization of the electronic shells of atoms and ions which is characterized by a very short response time, of the order of 10^{-16} sec, and gives rise to the refractive index via the Mosotti equation. $\mathbf{P}_{\text{ion}}$ reflects the field-induced polarization of atoms and ions which is characterized by yet another very short response time, of the order of 10^{-12} sec, and is fundamentally related to the dielectric constant, ϵ . The next two contributions arise from defects and impurities. $\mathbf{P}_{\text{local}}$ reflects contributions from local dipoles that may rotate in the electric field or deform like a "jelly" but cannot diffuse over larger distances. $\mathbf{P}_{\text{space}}$, the contribution arising from space charges, reflects the presence or appearance of mobile charges in the bulk that can diffuse over macroscopic distances. Finally, $\mathbf{P}_{\text{surface}}$ is a contribution which specifically refers to surface charges, either positive or negative, that may build up on the surface of the sample. Such surface charges appear in any insulating or semiconducting material when mobile charge carriers are present in the bulk. The sign of the surface charge then indicates the sign of the majority charge carriers in the bulk.

CDA uses the effect that, when a dielectric is placed in an electric field gradient along a direction z , a force $\mathbf{F}_z^\pm$ acts on the sample accelerating it towards the region of higher field density. Using Maxwell's equations $\mathbf{F}_z^\pm$ is given to first approximation by:

$$\mathbf{F}_z^\pm = - \int_V \nabla (\mathbf{P} \cdot \mathbf{E}_{\text{ext}}) dV \quad (2)$$

where the volume integral includes the sample but not the sources of the field.

In the case of a material which only contains $\mathbf{P}_{el}$, $\mathbf{P}_{ion}$, $\mathbf{P}_{local}$, and $\mathbf{P}_{space}$, contributions $\mathbf{F}_z^\pm$ is invariant to the direction of the field gradient: $\mathbf{F}_z^\pm = \mathbf{F}_z^+(\mathbf{E}_{ext}) = \mathbf{F}_z^-(\mathbf{E}_{ext})$. By contrast, the $\mathbf{P}_{surface}$ term is variant to the reversal of the field gradient direction, causing an attraction to or repulsion from the region of higher field density, depending upon the sign of the surface charge and polarity of the field.

To separate the gradient-invariant contributions ($\mathbf{P}_{el} + \mathbf{P}_{ion} + \mathbf{P}_{local} + \mathbf{P}_{space}$) from the gradient-variant $\mathbf{P}_{surface}$ contribution we form the linear combinations:

$$\mathbf{F}_\Sigma \equiv \frac{1}{2}(\mathbf{F}^- + \mathbf{F}^+) = -\frac{\epsilon_0 \chi_{diel}}{4\pi} \int_V \nabla \cdot \mathbf{E}_{ext}^2 dV \quad (3)$$

$$\mathbf{F}_\Delta \equiv \frac{1}{2}(\mathbf{F}^- - \mathbf{F}^+) = -\int_V \nabla(\mathbf{P}_{surface} \cdot \mathbf{E}_{ext}) dV \quad (4)$$

To evaluate $\mathbf{P}_{surface}$ we introduce $a_\pm U^2$ where $a_\pm$ is a constant:

$$\mathbf{F}^\pm = \mathbf{F}_1^\pm + a_\pm U^2 \quad (5)$$

$\mathbf{F}_1^\pm$ is a constant which depends upon the surface charge density and the internal electric field, while $a_\pm U^2$ describes the behavior of the ideal dielectric. In summary $\mathbf{F}_\Sigma$ and $\mathbf{F}_\Delta$ are given as:

$$\mathbf{F}_\Sigma = \frac{1}{2}(\mathbf{F}_1^- + \mathbf{F}_1^+) + \frac{1}{2}(a_- + a_+) U^2 \quad (6)$$

$$\mathbf{F}_\Delta = \frac{1}{2}(\mathbf{F}_1^- - \mathbf{F}_1^+) + \frac{1}{2}(a_- - a_+) U^2 \quad (7)$$

To first approximation we have: $\mathbf{F}_1^+ = \mathbf{F}_1^- + \Delta\mathbf{F}$, and $a_- = a_+ + \Delta a$, with $\Delta\mathbf{F} \ll \mathbf{F}_1^\pm$ and $\Delta a \ll a_\pm$. This is equivalent to a small perturbation by the surface. At high voltage we have $a_\pm = \frac{1}{2}(a_- + a_+)$. Thus, $\mathbf{F}_\Sigma$ can be defined at the high voltage limit as $\mathbf{F}_\Sigma \approx \frac{1}{2}(a_- + a_+) U^2 \equiv a_\pm U^2$.

Figure 4:

Defining the geometry of a sample (shaded) placed in a asymmetrical capacitor (solid) composed of a circular bias electrode (top) and a cup-shaped cylindrical ground electrode acting as the furnace.

Besides providing the sign of the majority charge carriers, $\mathbf{F}_\Delta$ can be used to calculate the surface charge carrier density. For a simple, axially symmetrical geometry as defined in Figure 4 and a homogeneous, non-porous sample the number of charge carriers N per unit area is then given by ⁸:

$$F_{\Delta} = 8 \pi^2 \epsilon_0 U (N \cdot e) \frac{D^2}{a^2} \sum_{n=1}^{\infty} \beta_n \left[\int_0^b \rho J_0(k_{0n} \rho) d\rho \right] [\cosh(k_{0n} g) - \cosh(k_{0n} (g+c))] \quad (8)$$

$$\text{where } \beta_n = k_{0n} \frac{\text{cosech}(k_{0n} L)}{J_1(k_{0n} a)} \left[\int_0^d \rho J_0(k_{0n} \rho) d\rho \right].$$

where D is the dipole layer thickness, a the radius of the cylindrical bias electrode, b the radius of the sample, c the sample thickness, d the radius of bias electrode, L the length of cylinder, g the distance of sample-bias electrode, e the charge of the carriers and ϵ_0 the permittivity of the vacuum. J_n are the Bessel functions of n -th order, where $k_{0n} = x_{0n}/a$, with x_{0n} being the solutions of the zero order Bessel function $J_0(x_{0n}) = 0$.

Experimental Set-Up

The configuration used for the work under this Contract is based on a PERKIN-ELMER Thermo-gravimetric Analyzer TGS-2. A lay-out of the entire system in an early configuration is shown in **Figure 5**. It consisted of the microbalance with a sensitivity of 10^{-7} N, the stainless steel Test Cell with an internal Pt-wire resistance furnace built as part of this Contract, the Control Package for regulating the balance and the furnace, a custom-designed Data Acquisition Package based on National Instruments LabVIEW 2.0, and an Apple Quadra 700 with a 20" color monitor.

In this early version, the electrode-sample arrangement was such that the bias electrode was placed below the sample as sketched in Figure 6. For most CDA measurements reported here the geometry was similar to that shown in Figure 6, using a PERKIN-ELMER Thermogravimetric Analyzer TGS-2 modified by the introduction of a circular ground electrode above the sample and a spherical bias electrode below the sample. The ground electrode was made of 0.1 mm gold foil. The bias electrode were made of a sphere of gold melted onto either a Pt wire or the stainless steel sheath of a 1 mm diameter coaxial thermocouple.

Figure 6:

Schematic cross section through the CDA furnace with approximate field lines between the circular bias electrode (bottom) and the annular grounded counter electrode (top). The position of the sample is indicated by the stippled area. In both configurations the sample rests on a fused silica loop or a stirrup made of either Pt or stainless steel wire, and insulated from ground by a long fused silica hang-down fiber. The bias electrode-sample distance was adjusted within $\pm 10 \mu\text{m}$. The counter electrode (always grounded) consisted of a Pt shield surrounding the furnace or of a circular Au electrode placed above the sample on the inside wall of the furnace or the glass tube.

A disadvantage of any resistance furnace is that the heating wire produces a magnetic field that can interfere with the CDA measurements. The effect can be alleviated, though not eliminated, by using a resistance furnace with a bifilar winding. Initially, a Pt resistance furnace was used. It measured 16 mm diameter, 18 mm high, and used bifilar Pt wire on aluminum oxide ceramic. Because Pt reacts with H_2S , this furnace was later replaced by Inconel wire on Macor glass ceramic. But Inconel was also found to be destroyed by H_2S . In addition, even with bifilar winding, a residual magnetic field and an associated field gradient were found to exist. If the magnetic field gradient couples to a ferromagnetic sample, a force will act on the sample which interferes with the CDA measurements. Some of the samples to be studied under this Contract were ferromagnetic iron oxides. Therefore, the question of magnetic interference had to be addressed.

A solution can be found by using d.c. current to run the furnace and to regulate the temperature either manually or by means of a proportional controller. Manual control was tried during an intermediate period, but the accuracy of the temperature control was found to be insufficient. A more radical solution was to do away with the resistance furnaces altogether and use infrared (IR) lamps as heating sources. Two IR lamps with a temperature control were procured, using funds from non-DOE sources. A new stand for the PE microbalance was built as depicted in Figure 7.

Figure 7: Double stand for the new CDA instrument using two 1000 W clam-shell IR heaters.

Various modes of operation have been used involving either stepwise heating and cooling or a variety of linear heating and cooling programs. The bias voltages are usually applied in ± 100 V steps up to ± 400 or ± 600 V as shown schematically in **Figure 8**. After reaching the upper voltage limit, the bias voltage was either removed to 0 V (**Figure 8 top**) or decreased in a stepwise fashion (**Figure 8 bottom**). The time-dependent variations of $F^{\pm}$ were measured over periods of the order of several minutes to evaluate charge carrier diffusion processes.

Atmospheres of Ar, N₂ were used at 1 bar total pressure and flow rates of 10-40 ml/min. Provisions to use controlled N₂-H₂S mixtures have been put into operation, using three MKS flow controllers. One controller, set at a high rate to 10-20 ml/min, directed a flow of pure Ar or N₂ through the balance housing. The two remaining controllers were used to mix Ar or N₂ with H₂S at a ratio of 10 to 1 and direct this mixture at a low flow rate of 1-2 ml/sec directly into the sample chamber. Due to the extremely corrosive nature of H₂S, several mishaps occurred. At one instance, while using the configuration shown in **Figure 6**, H₂S penetrated the balance housing and caused irreparable damage to the balance. Even in the configuration shown in **Figure 7** the stainless steel parts in the lower end of the sample chamber, in particular the micrometer, suffered corrosion and had to be replaced several times during the period of this contract.

Figure 8: Two different voltage time profiles used in the present work during isothermal periods. The voltage increments and decrements V_n were typically 100 V. The time t_1 during which the voltage was applied was typically 20–60 sec, and the depolarization time t_d of the order of 200 sec.

II Prior Work

II.1 MgO Single Crystals

The most complete study so far of the electric and dielectric characteristics of a highly insulating oxide material was done MgO single crystals. MgO is an insulator with a theoretical band gap of the order of 8.5 eV¹². MgO should therefore behave as an ideal dielectric. However, it has been known for quite some time that, between 450–800°C, MgO exhibits an unusual increase in its electrical conductivity¹³. Concurrently MgO develops a pronounced catalytic activity towards the oxidative coupling of methane^{14–17}. Because of its high resistance the electric conductivity of MgO is difficult to measure by conventional techniques.

Fig. 9 Typical electrical conductivity behavior of high purity MgO single crystals heated Ar. The open squares are adopted from data by *Kathrein and Freund (1983)*. The small maximum around 3500°C was confirmed by *Kathrein et al. (1980)*. The steep section of the solid line delineates the high temperature Arrhenius branch as reported by many authors including *Mitoff (1959, 1962, 1964)*, *Lewis and Wright (1970)* and *Osburn and Vest (1971)*. The dashed extension is adopted from graphical representations given by *Lewis and Wright (1970)* and from *Kathrein and Freund (1983)*. The conductivity is given in Siemens/meter.

Fig. 9 summarizes electrical conductivity measurements of MgO carried out by different authors over the temperature region 350–800°C. The solid line represents the typical conductivity σ versus temperature behavior measured during cooling after long time equilibration at temperatures above 1000°C when ionic conductivity prevails. The exact location of the solid line reportedly changes as a function of sample purity and pretreatment. The square dots show the anomalous conductivity increase observed by nearly all prior researchers, contributed to surface conductivity and, hence, believed to be non-intrinsic. Between 450°C and 750°C the conductivity rises from 10^{-12} – 10^{-14} S/m, equivalent to 10^{-14} – 10^{-16} (Ωcm) $^{-1}$ to 10^{-4} – 10^{-5} S/m¹⁸⁻²⁴. Only by CDA was it possible to show that, while the conductivity increase in the 450–750°C region carries indeed a strong surface contribution, the cause is intrinsic to the sample and not due to adventitious surface contamination as all previous researchers had claimed.

Figure 10: (a) $F^+(T)$ and $F^-(T)$ isochrones of MgO at 50 V, measured for up to 10 min. Below 230°C the $F^\pm$ response is independent of T, indicating a nearly ideal dielectric behavior. Between 230 and 425°C, F^+ and F^- increase slightly but differently for F^+ and F^- . Above 450°C, F^- increases rapidly and F^+ becomes repulsive, indicating a strongly positive surface charge. (b) $F_\Sigma(T)$ increases in two steps between 200 and 375°C and 425 and 550°C. The increase in bulk polarization must be due to an increase in polarizability of point defects or the appearance of mobile charge carriers, or both. (c) $F_\Delta(T)$ from the same data set. Starting with a weakly negative surface charge the MgO crystal develops a strongly positive surface charge above 450°C.

The feeble d.c. conductivity maximum around 350°C in Figure 9 and the sharp d.c. conductivity increase above 450°C are both much more clearly expressed in the CDA response as illustrated by Figure 10(a/c). Figure 10a depicts $F^\pm$ of an MgO crystal previously cooled from 800°C, recorded as a function of time (up to 10 min) and temperature at the relatively low bias voltages of ± 50 V. From the beginning F^- is seen to be larger than F^+ , indicating that the surface charge is slightly positive. Starting around 200°C both F^+ and F^- increase slowly, reaching a plateau around 350–400°C. Above 450°C F^- increases sharply, while F^+ goes into a repulsive mode, indicating an overall increase in the polarization and the appearance of a strong positive surface charge.

Taking these $F^\pm$ data, F_Σ has been plotted in Figure 10b. It shows a two-step increase in the bulk polarization of the MgO crystal. Such a behavior suggest the successive mobilization of some highly polarizable entities in the MgO structure, either local defects which change their intrinsic polarizability or mobile charge carriers which diffuse in the externally applied electric field. During step I, between 200–400°C, the process is quite sluggish, but it becomes fast above 450°C and appears to reach a level above 550°C.

The particular and, to the best of our knowledge, unique feature of CDA is demonstrated in the plot of **Figure 10c**, depicting the temperature and time-dependence of F_A . The most pronounced feature is the sharp increase in F_A above 450°C , indicating a strong positive surface charge. Assuming that the surface charge layer is $300 \text{ \AA}$ thick, the O^- carrier density within this layer was calculated to be of the order of $5 \times 10^{21} \text{ cm}^{-3}$, corresponding of a fraction of a monolayer equivalent ⁷. Such a high charge density lies within the range of chemical activity, if the positive charges at the surface possess some degree of chemical reactivity. It has been shown by a variety of other techniques, combining infrared spectroscopy ²⁵, electron spin resonance spectroscopy ²⁶, magnetic susceptibility ²⁷, gas evolution mass spectrometry ²⁸ and wet-chemical techniques ²⁹ that the charge carriers which cause the positive charge on the MgO crystals are O^- states.

Figure 11: Temperature dependence of F_A of MgO single crystals between 550 – 1000°C measured under Ar, indicating that the surface charge and, hence, the surface O^- density pass through a maximum between 750 – 800°C .

Physically, the O^- states act as defect electrons, but from a chemical standpoint they represent O^- radicals. As such they are extremely reactive oxidation agents capable, for instance, of abstracting H from CH_4 . It can therefore be expected that, if the positive surface charge as measured by CDA is a function of the O^- density at the MgO surface, F_A will correlate with the catalytic activity of MgO with respect to oxidative coupling of methane*. $F_A(T)$ is depicted in **Figure 11**. In order to minimize the perturbation of the surface charge during measurements, the data were obtained at the lowest bias voltages that could be achieved with the existing CDA instrument. They show that F_A reaches a maximum between 750 – 800°C which indeed coincides with the maximum catalytic activity of MgO towards oxidative coupling of methane.

* The question of how to establish a truly catalytic activity by regenerating the active sites will not be treated here.

II.2 Applications: Examples of CaO Catalysts

Besides MgO catalytic activity towards the oxidation of methane is also observed in CaO. The reaction probably occurs by a similar reaction as in the gas phase³², e.g. by O^- abstracting one H from CH_4 , forming a methyl radical:

Figure 12: F_{Δ} of a NaOH-promoted (a) and La_2O_3 -promoted (b) CaO catalyst. Note the narrow region of positive surface charge with maximum at 575°C.

Finely divided CaO catalysts have attracted much attention because of their oxidative activity towards the conversion of methane into C₂ hydrocarbons or methanol and similar partly oxidized products¹⁴⁻¹⁷. Of particular interest is the fact that doping can significantly shift the temperature interval in which F_A of the CaO catalysts becomes positive. This is illustrated in **Figure 12a/b** for two CaO catalysts³³ with different promoters, Na⁺ and La³⁺, which are reported to be more active towards oxidative coupling of methane than pure CaO¹⁷.

F_A shifts from 750°C in undoped CaO to 650°C in NaOH-doped CaO and 575°C in La₂O₃-doped CaO³³. The data presented in **Figure 12** were obtained under inert gas. It would be of interest to perform the same experiments under the reactive gas mixtures, e.g. in CH₄ with additions of O₂.

II.3 Conclusions

The case of the catalytic activity of MgO and CaO towards oxidative coupling of methane illustrates that CDA, which measures the bulk polarization at the limit of 0 Hz and the appearance of surface charges, can provide important clues about to on-set of catalytic activity. In MgO and CaO the positive surface charge has been shown to be due to O⁻ states which, when diffusing to the sample surface, represent oxidizing centers at which H abstraction from CH₄ can take place. Not all positive surface charges, however, are necessarily caused by O⁻ states which are defect electrons residing on or traveling via the O²⁻ sublattice of oxides. In other cases defect electrons may reside on and diffuse via a cation sublattice. Such defect electrons may give rise to a positive surface charge. Of considerable interest to catalysis are also non-oxide, non-silicate solids such as carbon black or sulfides.

From a purely physical viewpoint, however, a quite general argument can be made. Whenever a defect electron arrives at a surface site, this site becomes an electron acceptor, hence, an oxidation site. Conversely, whenever an electron arrives at a surface site, this site is likely to become an electron donor, hence, a reduction site. The potential for catalytic activity will then occur when the flow of charges, either positive or negative, to the surface is sustained and when the charges at the active sites are replenished. This statement holds irrespective of the chemical nature of the solid.

Both processes can be measured by CDA under conditions which minimize the perturbation of the catalyst. As part of this Contract, work was performed to test this hypothesis on realistic and model catalyst materials, in particular highly dispersed ferric-oxide catalysts, Fe₂O₃, in inert gas and corrosive H₂S-containing environments as well as on partially sulfidized Fe₂O₃ and single crystal pyrite, FeS₂, a natural mineral.

III References

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IV. Results and Discussion

IV.1 Fe₂O₃ Catalyst #7 under Nitrogen

The catalyst samples were obtained from Dr. Malvina Farcasiu. They consisted of loose powders which had to be pressed into pellets prior to CDA analysis. A stainless steel evacuable pellet press of 6 mm i.d. was used for this purpose in conjunction with a hydraulic press. In many cases the sample tended to stick to the polished stainless steel surfaces of the press and fractured when removed. The idea of adding a lubricant was rejected because it would have affected the properties of the material in a potentially uncontrollable manner. Partial success was achieved by inserting thin sheets of waxy paper between the pistons and the sample, though the edges of the pellets then became somewhat fuzzy and easily chipped during removal. However, since CDA does not require a specific geometry of the sample (unless quantitative data was sought), it was practical to use somewhat irregular pellets for the experiments described below.

CDA runs of the iron oxide catalyst #7 (with SO₄) were performed under nitrogen atmosphere. The weight loss of the sample due to removal of adsorbed or chemisorbed H₂O created some difficulties, both during data acquisition and data analysis. Due to the large surface area of the catalyst under study the amount of desorbable H₂O was quite large. On the other hand, the CDA forces to be measured were typically 1-10 % of the weight loss due to dehydration. This meant that, in temperature intervals where rapid weight loss occurred, the CDA measurements had to be performed on steeply sloping baselines. The only way to overcome this difficulty with the present equipment was to wait for the weight loss to come to taper off so that the baseline shift was not too large. (A newer version of the CDA under development during the time of the contract overcomes this problem by measuring the polarization-induced force orthogonal to the gravitational vector.)

The correction for the sloping baseline required further modification of the data acquisition procedure. This was achieved by writing a series of new macros in MICROSOFT EXCEL 4.0. They consisted typically of several pages of code and allowed for baseline corrections during the automated evaluation of the raw data. The macros were debugged and found to work satisfactorily. They provided for a significant time saving during data evaluation.

A typical experimental procedure followed for the CDA measurements under N₂ is chronicled in the TABLE "*Fe₂O₃ History*". It comprised stepwise heating to various temperatures to remove adsorbed or chemisorbed H₂O and to approach weight constancy as far as possible. During heating to 145°C, flushing with N₂ and an attempt to identify a leak, the furnace temperature briefly rose to 412°C. The furnace was then shut off, allowing the sample to cool quickly to ambient temperature. After correcting the leak and repairing the electrical short the run was resumed with the same pellet.

The subsequent heating was carried on up to 440°C with long periods of isothermal heating to achieve weight constancy. The atmosphere at all times was pure N₂. The voltages were applied in 50 V increments in the following sequence, each for 30 secs: 0, +50, +100, +150, +200, +150, +100, +50, 0, 0, -50, -100, -150, -200, -150, -100, -50, 0, 0 Volts. The increased interval

(60 secs) at 0 V was intended to give the sample enough time to depolarize. However, it will be noted at most temperatures that depolarization was not always complete, resulting in an off-set of the baseline at 0 V. This 0 V off-set was software-corrected by a second order averaging protocol. The polarization was repeated several times, typically four times, at specified time intervals to learn more about the sample response under the chosen experimental conditions. These repetitive runs will be designated below as Run 00, Run 01, Run 02 and Run 03 respectively.

DATE	COMMENTS	TIME
12/16/93	Brought temperature up to 125°C for 15 minutes to evaporate off any H ₂ O Decreased temperature to Room temperature. Attempted to take data at 29°C but the sample was gaining weight and our reading were thus going off scale. Increased temperature to 45°C. Attempted to take data but sample was still gaining weight. Increased temperature back up to 125°C Attempted to take data but sample was now losing weight. Increased temperature to 145°C. Attempted to take data but sample weight was still fluctuating. Temperature lowered to 125°C and kept constant Data taken at 126°C with no drifting in the weight	
12/20/93	Temperature increased to 145°C Data taken at 145°C with a small amount of drifting Flushed chamber out with N ₂ . Problems with apparatus. The chamber was leaking. Temperature decreased to room temperature Furnace short circuited raising the sample to a temperature of 412°C very quickly. Turned power off, allowed the sample to cool to ambient Sample subjected to air Sample replaced. Apparatus sealed.	
12/22/93	Temperature increased to 150°C for 30 minutes, while N ₂ flushing Decreased temperature to 125°C Data taken at 125°C. 2 days since last data taken Problems with sensitivity. Removed the dome to adjust balance, contaminating the system with Air. Replaced lid, heated sample to 150°C for 30 minutes while flushing chamber with N ₂ . Decreased temperature to 146°C Data taken at 146°C. 30 minutes since last data taken No weight fluctuation Increased temperature to 165°C Data taken at 165°C. 30 minutes since last data taken 2 units weight loss Increased temperature to 186°C Data taken at 186°C. 45 minutes since last data taken	

1 unit drop in weight
 Data taken at 186°C 15 minutes since last data taken
 Data taken at 186°C. 2 minutes since last data taken
 No weight fluctuation.
 Increased temperature to 206°C.
 Data taken at 206°C. 22 minutes since last data taken
 1 unit drop in weight.
 Data taken at 206°C. 5 minutes since last data taken
 no weight fluctuation.
 Increased temperature to 225°C
 Data taken at 225°C. 5 minutes since last data taken
 Not sure if weight lost.
 Leave at 225°C

12/23/93

Data taken at 225°C. Approx. 18 hours since last data
 No weight fluctuation
 Increased temperature to 245°C
 Data taken at 245°C. 10 minutes after last run.
 1 unit drop in weight. 3 minutes after temp. reached 245°C
 Increased temperature to 265°C.
 Data taken at 265°C. 8 minutes after last run.
 1.75 unit drop in weight. 2 minutes after temp. reached 265°C
 Data taken at 265°C. 10 minutes after last run
 .5 unit drop in weight. Approx. 14 minutes after reached 245°C
 Increased temperature to 285°C.
 Data taken at 285°C. 5 minutes after last run.
 1 unit drop in weight. 2 minutes after temp. reached 285°C
 Increased temperature to 305°C.
 Data taken at 305°C. 7 minutes after last run
 1.5 unit drop in weight 2 minutes after temp reached 305°C
 Data taken at 305°C. 15 minutes after last run.
 No weight change. 19 minutes after reached 305°C
 Increased temperature to 325°C
 Data taken at 325°C. 6 minutes after last run
 1.5 unit drop in weight 2 minutes after 325°C was reached
 Data taken at 325°C. 3 minutes after last run
 .5 unit drop in weight 7 minutes after 325°C was reached
 Decreased temperature to 126°C

1/5/94

Increased T to 200°C, flushing N2 for 10 min
 Increased temperature to 345°C (takes 15 minutes)
 Data taken at 345°C. 1.5 weeks after last run.
 1.75 units drop in weight. started run 2 minutes after reached 345°C
 5 minutes after last run.
 Data taken at 345°C. 8 minutes after reached temp. of 345°C
 Little drop in weight
 Increased temperature to 365. (takes 3 minutes)
 Data taken at 365°C. 8 minutes after last run.
 .5 unit drop in weight. 1 minutes after temp. reached 365°C
 Data taken at 365°C. 4 minutes after last run.
 .25 units drop in weight 7 minutes after temp. reached 365°C
 Increased temperature to 385°C (takes 6 minutes)
 Data taken at 385°C. 8 minutes after last run.

.75 unit drop in weight.	1 minute after reached 385°C
Left at 385°C for 1 hour.	
Increased temperature to 405°C	(takes 10 minutes)
Data taken at 405°C.	1 hour 11 minutes after last run.
1.5 units drop in weight.	1 minute after temp of 405°C was reached
Data taken at 405°C.	5 minutes after last run.
.75 unit drop in weight	8 minutes after temp reached 405°C
Increased temperature to 425°C.	(takes 2 minutes)
Data taken at 425°C.	5 minutes after last run.
2.5 unit drop in weight.	2 minutes after temp of 425°C was reached
Data taken at 425°C.	4 minutes after last run.
2 unit drop in weight	8 minutes after temp of 425°C was reached
Data taken at 425°C.	10 minutes after last run.
1.5 unit drop in weight	20 minutes after temp of 425°C was reached
Increased temperature to 439°C.	
Data taken at 439°C.	17 minutes after last run.
3.25 unit drop in weight	
Data taken at 439°C.	15 minutes after last run.
3.5 unit drop in weight.	Approx. 20 minutes after 439°C were reached
Data taken at 439°C.	30 minutes after last run.
2.5 unit drop in weight.	52 minutes after temp of 439°C was reached.
Decreased temperature by 20°C then waited 3 minutes.	
repeated above until a temperature of 245°C was reached.	

1/6/94

Decreased temperature to 127°C.

END

Figure 13: Raw data as obtained during a repetitive isothermal CDA run with $\pm$ designating the intervals during which positive and negative bias voltages were applied.

An example of the raw data obtained at 405°C during repetitive application of positive and negative bias voltages is shown in Figure 13. The sample still lost mass as evidenced by the overall downward trend of the curves. The forces measured at positive bias are slightly higher than those measured at negative bias, indicating a moderately negative surface charge.

Figure 14a/b: Uncorrected force versus voltage plots for four consecutive runs at 125°C. The ordinate indicates the microbalance reading in units of 0.2×10^{-5} g.

The

Two typical plots of data "as received" are shown in Figure 14a/b, recorded isothermally at 125°C and represent the composite of the 10 sec averages during stepwise positive up and down polarization from 0 to +200V and negative up and down polarization from 0 to -200V.

(a)

(b)

(c)

(d)

Figure 15: Fe₂O₃: Corrected force vs. voltage plots with parabolic fits for selected temperatures.

After correcting for weight loss through the EXCEL 4.0 macros, the curves coincide much better, though not yet perfectly, as illustrated in **Figures 15a-d** for four selected temperatures, 225, 285, 305 and 325°C, showing force vs voltage plots together with their parabolic fits, both in graphical and numerical presentation. The improvement over the plots shown in **Figure 14** is obvious, though a slight time-dependent shift of the curves is still to be noted. This residual shift is due to the fact that the correction was based on a linear fit between the zero bias points while in reality the weight loss is amore complex function of time.

Two other obvious features of the plots shown in **Figures 15a-d** is that (i) the parabolas become progressively narrower, indicating an increase in the overall bulk polarization, F_{Σ} , over the specific temperature interval, and (ii) the force measured under positive bias is always lower than when measured under negative bias, indicating a positive surface charge as reflected in $F_{\Delta} > 1$. The positive surface charge was found to increase with time below 300°C, as shown in **Figure 16**, obtained by plotting the linear term in the parabolic fit equations contained in **Figures 15a-d**. Above 300°C the surface charge appears to evolve rapidly toward negative values.

Figure 16: Fe_2O_3 : Surface charge on the Fe_2O_3 catalyst #7 during repetitive runs 00 to 03.

Figures 17a-d show $F_{\Sigma}(T)$ plots for a wider temperature interval, 225–440°C, from data obtained after the catalyst has been carefully heated to remove adsorbed and chemisorbed H_2O . Between 225–350°C F_{Σ} is only weakly temperature-dependent, indicating a nearly ideal dielectric response. However, the bulk polarization does not increase quadratically with the applied voltage as theoretically predicted. Instead, the functional relationship between F_{Σ} and V corresponds to a power law with an exponent < 2 . At present we have not definite explanation for this behavior.

Figure 17a-d: Fe₂O₃: bulk polarization $F_{\Sigma}(T)$ of the Fe₂O₃ catalyst #7 during run 03.

In Figure 18 we plot F_{Δ} over the same temperature range, 225–450°C, recorded with a new pellet from the same powder sample. The trend of F_{Δ} toward negative values above 300°C is confirmed, and the surface charge of the Fe_2O_3 catalyst becomes negative at about 375°C.

Figure 18: Fe_2O_3 : $F_{\Delta}(T)$, corresponding to the surface charge of the Fe_2O_3 catalyst #7.

The iron oxide catalyst #7 under inert atmosphere shows the same general response as observed earlier with using the pre-Project CDA instrument. Initially, at low temperatures, the bulk polarization given by F_{Σ} exhibits the expected weak temperature dependence which is typical for materials that behave as a nearly-perfect dielectric. Unfortunately, due to an electric short which developed in the furnace, the temperature of the sample temporarily increased to 420°C at a crucial moment of the measurement. In the range of 420°C the iron oxide is known to acquire a positive surface charge. To save the furnace the power was shut off, causing the sample to cool rapidly from 420°C to ambient. As a result the positive surface charge which apparently built up during the brief exposure to the high temperature, remained positive. If the cooling had been slow, the surface charge would have returned toward the weakly negative values typical at 20°C. The expected behavior of the iron oxide sample was confirmed by reheating it in a stepwise fashion and cooling it likewise in a stepwise fashion. As a result the frozen-in positive surface charge relaxed and reverted to negative. This confirms earlier measurements that the iron oxide catalyst #7 exhibits n-type behavior that increases with increasing temperature.

IV.3 γ -Fe₂O₃ Catalyst under Dry and Wet Nitrogen

Pelletized samples of the γ -iron oxide #5210-LKLO 5352B were prepared using the evacuable pellet die made from corrosion resistant stainless steel. A sample of 59 mg was carefully placed into the bore of the cylinder and slightly compacted. The die was then evacuated with a rotary pump, separated by a liquid nitrogen trap to prevent back-streaming of oil vapors. The sample was pressed for 30 min at 5000 lb. of load, gradually increased to 9000 lb. in 2 hours, using a hydraulic press capable of delivering 4 tons pressure. After numerous attempts to obtain clean pellets it was found that a load of 10,000 lb. was typically required to produce a smooth, glassy quality of the pellet surface. Difficulties were encountered during pressure release which led to lamination of the pellets. Partial success was achieved by using wax paper to separate the pistons from the iron oxide material and by releasing the pressure slowly, over a period of about 15 min.

Further difficulties were encountered because the γ -Fe₂O₃ #5210-LKLO 5352B is ferromagnetic and thus susceptible to even the slightest residual magnetic fields within the furnace cavity. At the time this sample was studied the original bifilar Pt furnace had failed. In preparation for the CDA measurements under H₂S it had been replaced with a double-wound Ni-Chrome wire furnace. A heavy gauge 80%Ni20%Cr heating wire was used, tightly wound on a grooved MACOR glass ceramic body and held in place by high temperature OMEGA ceramic cement. The new furnace achieved 800°C. However, this new furnace did not fully compensate for the magnetic field. Each current pulse from the PID controller caused a pulse in magnetic field. Optimizing the PID control parameters did not solve the problem. Eventually, the controller was replaced by a d.c. power supply which was manually adjusted to approximate the desired temperature.

The pellets were run under dry and wet nitrogen over a temperature range 25–400°C in 25°C increments and the application of the bias voltages in 25 V increments up to +600V and in 25 V decrements to –600 V. The time interval for each sub-steps was 20 seconds except at 0 volt., which was applied for 60 seconds to provide enough time for depolarization. A series of CDA runs was completed. During initial heating, the samples suffered significant mass losses, due to a loss of adsorbed H₂O. The software program was modified to be able to account for these losses through interpolation of the measured raw data and zero-point correction.

Results of the runs, expressed as $F_{\Sigma}(T)$ and $F_{\Delta}(T)$, are depicted in **Figures 19a/b** and **20a/b**. The seemingly erratic response, temperature-dependent variations and apparent negative F_{Σ} values (which are physically not meaningful) suggest that these runs failed to characterize this sample.

Figure 19: Bulk (a) and surface (b) polarization of $\gamma\text{-Fe}_2\text{O}_3$ heated in dry nitrogen.

While incomplete correction for the weight loss during experiment may be the cause of some of the rapid temperature-dependent F_Σ and F_Δ changes seen in **Figures 19a/b** and **20a/b**, besides interferences from magnetic coupling, the runs under dry and wet N_2 do exhibit some differences with respect to earlier results. Under dry N_2 the positive surface charge below 300°C reverts to negative. Under wet N_2 the negative surface charge does not persist. Instead, the surface becomes essentially neutral.

Figure 20: Bulk (a) and surface (b) polarization of $\gamma\text{-Fe}_2\text{O}_3$ heated in wet nitrogen.

Another iron oxide sample provided by Dr. Farcasiu, prepared under reducing conditions in H_2 atmosphere and presumably consisting of a non-stoichiometric magnetite, Fe_3O_4 , was not further studied due to the extreme sensitivity of this sample to exposure to air.

IV.3 New Measurements of the γ -Fe₂O₃ Catalyst under Nitrogen

In view of the somewhat conflicting results obtained in previous runs with the Fe₂O₃ catalyst #7, we prepared a new pellet from the available powder batch. The CDA instrument was recalibrated using MgO single crystal standards. The protocol for the measurements was modified as follows: After 24-48 hrs purging in dry N₂ at 120°C the sample was subjected to a continuous string of voltage increments, lasting for 20 sec each, from 0 to +600 V to 0 V and then from 0 to -600 V and back to 0 V. The sample was subsequently heated to the next step in the 14 step temperature protocol (from 100-425°C) and the string of voltage increments was repeated. This protocol was adopted so as to differentiate between polarization during initial voltage application and remnant polarization that relaxes upon voltage removal. Since the polarization rate varies with temperature, at some temperatures the time available for depolarization may have been too short to reach steady state. The protocol is depicted in **Figure 21a/b** for two temperatures, 100°C and 425°C.

Figure 21a/b: Plot of the raw data versus time showing the sequence of voltage applications at 100°C and 425°C. The approximately parabolic shape of the force vs. voltage curves is apparent.

A selection of parabolas recorded in Region II and corrected in the usual way for attendant weight loss is shown in **Figure 22**. The depth and "steepness" of the parabolas is a measure of the bulk dielectric polarization, their "skewness" a measure of the surface charge. Casual inspection of the parabolas show that the bulk polarization increases sharply above 350°C and that the surface acquires a negative charge. To evaluate the bulk polarization, expressed in the F_{Σ} parameter, we have introduced a new procedure designed to minimize errors due to remnant polarization effects.

Each of parabola shown in **Figure 22** was fitted to a quadratic equation: $y = M_0 + M_1x + M_2x^2$. The M_2 parameter contains the same information on bulk polarization as F_{Σ} defined above. Likewise, M_1 contains the same information on the surface charge as F_{Δ} defined above. By plotting M_1 and M_2 rather than F_{Δ} and F_{Σ} , respectively, a significant improvement of the signal-to-noise ration was achieved.

Figure 22: Parabolic plots, force versus voltage, for selected temperatures recorded in Region II.

In **Figure 23a** we plot M_2 as a function of T for all temperatures, equivalent to F_2 as discussed above. The three curves shown represent Regions I, II and III. The parabolas obtained for Regions I and III respectively refer to positive and negative voltages only. The M_2 parameters for Region II (open squares) are experimentally most reliable. They give an essentially flat curve between 100–300°C, followed by a sharp increase between 325–350°C and a plateau above this temperature. Small differences between the data pertaining to Regions I, II and III are due to remnant polarization and they are considered to be of minor importance.

Cat#7, Force vs. T
DE-AC 22 92 PC 92106

Figur

e 23a: M_2 of the parabolic curve fit function, equivalent to the F_{Σ} parameter, plotted versus temperature for Regions I – III.

In **Figure 23b** we likewise plot M_1 as a function of T for all temperatures, equivalent to F_{Δ} as discussed above. The overall $F_{\Delta}(T)$ behavior is consistent with the appearance of negative charge carriers above 350°C . These data thus confirm the trend which had become apparent from all the other CDA measurements reported here.

Therefore, in the final analysis of this set of Fe_2O_3 catalyst #7 samples, we conclude that the iron oxide surface acquires the characteristic of an electron donor above 350°C which should translate into a reducing activity in chemical surface reactions.

Figure 23b: M_1 of the parabolic curve fit function, equivalent to the F_{Δ} parameter, plotted versus temperature for Regions I – III.

This response of the $\gamma\text{-Fe}_2\text{O}_3$ -based catalyst is in sharp contrast with the observations with MgO and CaO described in Sections II.1 and II.2. In the case of these two oxides the surfaces acquired a positive charge above 450°C , meaning that they become hole donors or electron acceptors, capable to abstract H from CH_4 and to perform other oxidative surface reactions. It is our understanding that, in the case of catalysts used in coal liquefaction, the function of the solid is to depolymerize the C_{∞} network by breaking C-C bonds and simultaneously activating a hydrogen donor compound which then transfers H onto the broken C bonds, stabilizing them as C-H.

IV. 4 Partially Sulfidized Iron Oxide Catalyst

Since coals as extracted from mines invariably contain sulfur as mentioned earlier, they generate an H₂S-laden environment when subjected to conditions conducive to depolymerization reactions. Any iron oxide catalyst added to the coal to aid such a reaction will therefore be exposed to H₂S and is likely to become sulfidized or partially sulfidized. The reaction product is pyrrhotine, a non-stoichiometric, predominantly Fe²⁺-containing sulfide of the simplified formula FeS_{1+δ}.

As part of this Contract we were asked to carry out sulfidation reactions on the Fe₂O₃ catalysts and investigate by CDA the bulk polarization response and surface charge of the reaction product. There was some concern that an *in situ* sulfidation of an oxide pellet might cause problems.

First, the sample will gain weight during the reaction which can be written, in a simplified way, as:

Second, due to the attendant volume change, it was feared that the pellet might disintegrate and shed particle, making meaningful CDA measurements impossible.

After setting up an H₂S gas line with a dedicated MKS flow controller, testing it, and performing preliminary runs under H₂S atmosphere, CDA data were collected under simulated reaction conditions with the iron oxide catalyst #7 sample. Unfortunately, it became soon apparent that the on-set of the sulfidation reaction was accompanied by a pronounced volume increase, even at moderate degrees of sulfidation. It caused the pellet started to crumble at the corners, leading to an early termination of this run. The sulfidation was then carried out separately, using the loose powder, in a separate gas handling system built with glass and fused silica.

The sulfidation reaction was carried out at 1 bar H₂S atmosphere. The degree of sulfidation is unknown, but certainly the reaction did not go to completion. The black reaction product was pressed into a 13 mm diameter pellet, reduced in size to fit the CDA furnace and studied over a temperature range 20–440°C using a counterflow of 10-20 ml/min N₂ through the microbalance housing and a 1-2 ml/min 10:1 N₂-H₂S mixture through the sample chamber as described above.

The sulfidized sample appeared to be normal until about 200°C as evidenced by **Figure 24a**. Above 200°C the sample began to behave strangely, with $F^\pm$ values shifted between repetitive runs as is demonstrated by **Figure 24b**. Around 225°C the forces became repulsive under positive and negative voltages, as shown in **Figure 24c**. Such a behavior had been seen before and is believed to be caused by unusually high conductivity in a thin surface layer, causing displacement of highly mobile charges of either sign along the surface and concomitant formation of surface dipole layers. The sample was then cooled to test whether this behavior could be duplicated upon reheating. The results showed that the repulsive action was repeatable. At 260°C the sample began to act normally again until temperatures around 400°C were reached when the partially sulfidized sample began to

decompose or undergo some other irreversible reaction. As an example this behavior is illustrated in **Figures 24d/e** representing data obtained at 300 and 400°C, respectively. At the higher temperatures the surface charge became positive – an observation that is at variance with the CDA results obtained with the non-sulfidized iron oxide samples.

Dr. Farcasiu informed us that 400°C is the highest temperature at which iron oxide catalysts are operated in a coal liquefaction reactor. Since coals generally contain sulfides which create an H₂S reaction environment, the CDA experiments under H₂S bear directly upon the potential use of the catalysts. According to the insight gained from the CDA data presented in **Figures 24a/e**, the positive surface charge above 300°C suggests that the partially sulfidized iron oxides become electron acceptors (or hole donors). As a consequence, their surfaces are expected to become chemically oxidizing above 300°C.

Unfortunately, this series of CDA measurements under H₂S could not be extended nor repeated, due to damage to the furnace by the corrosive gas. Unexpectedly, the NiChrome windings of the furnace became brittle and eventually broke. At the same time the Macor body onto which the NiChrome wire had been wound exhibited multiple cracks, probably due to the effect of H₂S on the Omega High Temperature Cement that was used to hold the doubly wound wire in place. With the furnace out of commission it could not be established whether the repulsive response of the partially sulfidized sample, observed around 225°C, was repeatable after cooling and reheating.

Filename: G Fe2O3 124 A 940324

○	Run 00	$y = 0.000x^2 - 0.011x - 3.381$
○	Run 01	$y = 0.000x^2 - 0.011x - 3.465$
○	Run 02	$y = 0.000x^2 - 0.011x - 3.539$
○	Run 03	$y = 0.000x^2 - 0.011x - 3.740$

Sample 1: (5210) LKLO 5352 B
Gamma Fe2O3

Figure 24a/e: Selection of force versus voltage plots of partially sulfidized γ -Fe₂O₃ catalyst, representing the typical CDA response at various temperatures. Note the repulsive response at positive and negative bias voltages at 225°C and the positive surface charge at 300°C and above.

IV. 5 Pyrite, FeS_2 , Single Crystal

Due to the experimental difficulties experienced under H_2S , further measurements in this highly corrosive gas were limited to a maximum temperature around 250°C . Following a suggestion by Dr. Farcasiu, when higher temperatures had to be reached, the H_2S was replaced by inert N_2 without detrimental effect on the CDA measurements.

The next sample to be studied was pyrite, FeS_2 , a natural mineral that may be considered an acceptable model for partially sulfidized iron oxide sample and pyrrhotine. The pyrite sample available was a single crystal several cm in size. A rectangular piece, approximately $6 \times 6 \times 1.5$ mm, was cut with a diamond saw and used as cut, without additional polishing. Initially, a major concern with this sample was that pyrite, which is metallic in appearance, also has a high intrinsic conductivity. Since CDA was basically developed for insulators, the question arose whether the technique was applicable at all to a material like pyrite.

The experiments were conducted in the usual manner, first under H_2S , then under N_2 , following procedures described above. The first heating under H_2S was limited to a maximum temperature of 253°C . A set of force vs. voltage plots with their parabolic fits is shown in **Figure 25**. They indicate a smooth increase of the bulk polarization, F_Σ , and an evolution of the surface charge, F_Δ , toward slightly positive values.

Figure 25: $F^\pm(V)$ of pyrite single crystal, FeS_2 , during first heating in H_2S up to 255°C .

Figure 26a/b: $F^{\pm}(V)$ of pyrite single crystal in N₂ during heating below and above 242°C.

It is encouraging to note that parabolic $F^{\pm}(V)$ curves were at all obtained in spite of the high conductivity of the pyrite single crystal under study. This suggests that CDA was applicable to materials which have a metallic appearance and a high intrinsic conductivity.

Figure 27a/b: $F_{\Delta}(T)$ and $F_{\Sigma}(T)$ respectively of the pyrite single crystal, FeS₂, in N₂.

After slow cooling from 250°C to ambient, the H₂S was flashed out with N₂, and the pyrite crystal was reheated in N₂ in closely spaced temperature increments up to 400°C. The force vs. voltage plots thus obtained are shown in **Figure 26a/b** together with their parabolic fits for temperatures intervals below and above 220°C.

Up to 200°C the response was nearly perfectly parabolic, with the bulk polarization increasing only slightly and no sign of any surface charge as shown in **Figure 26a**. At higher temperatures, most notably above 260°C, the parabolas became skewed under positive bias as shown in **Figure 26b**. At about 280°C, F⁺ became strongly repulsive, indicating that the surface had acquired a strong positive charge. No measurable mass loss or gain occurred during heating.

These findings translate into $F_{\Delta}(T)$ and $F_{\Sigma}(T)$ graphs in **Figures 27a/b** respectively. Below 200°C the surface charge is essentially zero as already mentioned above. This may be due to the nearly metallic conductivity of the pyrite single crystal under study. The positive surface charge reaches a maximum around 325°C and decreases upon further heating as shown in **Figure 27a**. The bulk polarization, $F_{\Sigma}(T)$, passes through a maximum at 300°C as shown in **Figure 27b**. Above this temperature $F_{\Sigma}(T)$ decreases sharply. The reason for this behavior is not understood.

V Summary

Charge Distribution Analysis (CDA) is a newly developed technique that has considerable interest for the characterization of catalysts. CDA measures the bulk polarization at the limit of 0 Hz and determines the sign and density of surface charges. The measurements are typically carried out as a function of temperature under various atmospheres. Since the catalytic activity of a solid is fundamentally related to the presence of charges on the solid surface, specifically of transferable charges, CDA data obtained at different temperatures can provide insight into the on-set of catalytic activity. The sign of the surface charge provides information whether electrons or holes become available at the solid surface and, hence, whether the surface becomes reducing or oxidizing.

As part of this Contract, we have applied CDA to iron oxide, partially sulfidized iron oxide and ferrous sulfide (pyrite, FeS₂) samples over the temperature range from ambient to about 500°C. The original expectation that we could perform the CDA measurements in corrosive H₂S atmosphere could not be fully satisfied, due to recurring problems with the corrosiveness of H₂S. These problems can only be overcome by a complete redesign of the CDA instrument, avoiding the exposure of any metallic parts in the reaction chamber to the H₂S gas except Au. Such a design is currently under development but was not yet available for the work performed under this Contract.

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