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Charge Distribution Analysis of Catalysts under Simulated Reaction Conditions

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As pointed out in our Ninth Quarterly Technical Progress Report, the CDA instrument had to be rebuilt in its entirety, using a replacement weighing mechanism from Perkin-Elmer Corporation. In addition, it was equipped with two 1000 W infrared heaters as outlined in our Eight Quarterly Progress Report as depicted in Fig. 1.

Fig. 1: Rebuilt CDA instrument on a twin stand, using two 1000 W clam-shell IR heaters.

The new unit has since been taken into operation. Some problem arose initially with thermal convection currents. The problem was alleviated by breaking the thermal convection currents with loosely packed fused silica wool packed at the plane of the bias electrode beneath the sample. This arrangement still allows for a smooth flow of purge nitrogen from above but restricts our ability to perform measurements under corrosive gas atmospheres (H₂S).
Following extensive tests with the new system using single crystal MgO calibration standards, we prepared a pressed pellet of the high surface area Iron Oxide Catalyst #7 from the available powder and began its dielectric polarization and surface charges. The protocol for the measurements was modified with respect to earlier series. 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 then 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 to differentiate between polarization that occurs during initial voltage application and remnant polarization that relaxes upon voltage removal. Since the polarization rate varies with the temperature, at some temperatures the time available for depolarization may be too short. The protocol outlined above and depicted in Fig. 2 minimizes the danger of erroneous data.

![Cat#7, Force vs. Time](image)

**Fig. 2**: Plot of the raw data versus time showing the sequence of voltage applications at 100°C. The approximately parabolic shape of the force vs. voltage curves is apparent.
During the experiment the sample lost weight, most markedly above 250°C. This weight loss led to a non-linear sloping background which is a complicated function of time. An example is shown in Fig. 3, showing data acquired at 425°C. The sloping background created problems with the data evaluation and made it very time-consuming, due to the need for correction terms.

**Fig. 3:** Plot of the raw data versus time showing the sequence of voltage applications at 425°C.

A selection of parabolas recorded in Region II is shown in Fig. 4. The depth and "steepness" of the parabolas is a measure of the bulk dielectric polarization, their "skewness" a measure of the surface charge. Inspection of the parabolas depicted in Fig. 4 suggests that the bulk polarization increased markedly above 350°C and that the sample acquires a negative surface charge.
To evaluate the bulk polarization, expressed in the $F_\Sigma$ parameter, we have introduced a procedure designed to minimize errors due to remnant polarization effects. Each of the parabolas shown in Fig. 4 was curve-fitted to a quadratic equation: $y = M_0 + M_1x + M_2x^2$. It is the $M_2$ parameter containing information on the bulk polarization, equivalent to $F_\Sigma$ as defined in previous reports.

**Fig. 4:** Parabolic plots, force versus voltage, for selected temperatures recorded in Region II.
In Fig. 5 we plot the $M_2$ parameter as a function of temperature for all temperatures. The three curves shown represent Regions I to III. The parabolas obtained for Regions I and III refer to the positive and negative voltages only. The $M_2$ parameters for Region II (open squares) 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 probably due to remnant polarization and are considered of secondary importance.

Cat#7, Force vs. T

Fig. 5: $M_2$ of the parabolic curve fit function, equivalent to the $F_\Sigma$ parameter, plotted versus temperature for all Regions I – III.
The overall $F_x(T)$ behavior of this iron oxide catalyst under study is consistent with either an increased polarization of structural defects in the iron oxide grains or the appearance of mobile charge carriers which polarize in the applied electric field.

![Diagram of Cat#7, Force vs. T](image)

Fig. 6: $F_\Delta$ calculated from pairs of three different voltages from Region II, plotted versus $T$.

In Fig. 6 we plot $F_\Delta$ versus temperature, using $F^\pm$ data at 100V, 300V and 600V from Region II. As we had already found in a 1992/93 study for Dr. Farcasiu the surface of the iron oxide catalyst tends to be negatively charged. The negative surface charge increases weakly up to 350°C and much more strongly above 350°C.

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