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PROGRESS IN THE THERMAL ANALYSIS OF OXIDES AND REFRACTORIES

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ABSTRACT

Selected papers dealing with catalysts, electrode materials, solid electrolytes and non-stoichiometric oxides are reviewed and discussed.

During this Conference a series of interesting contributions about oxides and their properties have been presented [1-9]. The reported results concern the following materials:

Catalysts:	FeS_2 (effects of SiO_2 and Fe_2O_3) [1] Fe_2O_3–V_2O_5–MoO_3 system [4,9] Ni–U–O system [6]
Electrode materials:	Na_xCoO_2 bronzes, alkalines, intercalation electrodes [5] Ag_2O (cathode for Ag–Zn cells) [3]
Solid electrolytes:	$CaCr_2O_4$ (Ca–Cr–O) [2]
Non-stoichiometric oxides:	UO_{2+x}, CeO_{2-x}, $PrO_{1.5+x}$ and $U_yRe_{1-y}O_{2\pm x}$ [8]

In these contributions several important aspects can be considered from the viewpoint of thermal analysis.

First, it was shown to be useful, if not essential, to make combined measurements involving both thermal analysis and other techniques in order to obtain sufficient data to evaluate a solid-state reaction or the properties of a material. This was demonstrated, e.g., by Kurzawa [4] and Walczak et al. [9], who used combined ETA and X-ray measurements to establish the phase diagram for the Fe_2O_5–V_2O_5–MoO_3 system and the existence of several new compounds in this system. Similarly, combined TG, DTA and X-ray measurements were used by Banerjee [1] to study the effect of silica and iron(III) oxide additives on the oxidation of iron pyrites in static air. In this study it was shown that the presence of these additives enhances the direct oxidation of pyrites, its interaction with iron(II) sulphate and the

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decomposition of sulphates. Finally, combined TG and X-ray measurements proved very helpful in the studies by Murray [6] on the reduction behaviour of nickel–uranium oxide catalysts. Using a new TG technique, by means of which the amount of hydrogen used during heating of the sample could be monitored, it was shown that the reduction of uranium oxides is facilitated in the presence of nickel. From powder X-ray diffraction data the results obtained by these TG measurements could be interpreted in terms of the structural properties of the solids.

In studies of reactions in oxides involving the release of oxygen, measurements by thermal analysis combined with EGA (evolved gas analysis) are very useful. In this case EGA can be elegantly performed with a galvanic concentration cell based on a solid zirconia electrolyte, which can be placed either in a separate furnace or near the sample directly in the furnace of the thermoanalyser. Using the latter arrangement, Havlica and Ambruz [2] studied the phase stability in the system Ca–Cr–O. From combined measurements of the equilibrium oxygen pressure and DTA and TG data, the standard Gibbs free energy of formation of the phase $CaCr_2O_4$ was determined as a function of temperature, which verifies the importance of this method. Further, the pressure and temperature range could be established for the formation of compounds with six-valent chromium, e.g., $CaCrO_4$, which are poisonous.

Koller and Fiedlerová [3] studied the thermal decomposition of silver oxide and measured the oxygen release using a galvanic concentration cell of this type. In this instance, however, this cell was placed in a separate furnace, through which the carrier gas (N_2) was flowing. This method proved to be sensitive and very useful in Ag_2O quality control, as it can be used to determine the content of carbonates, water and organic substances and the presence of structural imperfections.

Finally, the elegant coulometric titration technique used in studies of various non-stoichiometric oxides by Teske and Nebelung [8] should also be emphasized. By this technique the change in the partial pressure of oxygen in the effluent gas from the sample furnace is coulometrically titrated to a pre-determined level, probably corresponding to that of the incoming gas, with a galvanic cell (pump) that again is based on a zirconia–calcium oxide solid electrolyte. This method was found to be very sensitive and in studies of various non-stoichiometric oxides (UO_{2+x}, CeO_{2-x} and other oxides) a standard deviation of $x = 0.0007$ was obtained. The technique is therefore promising for studying non-stoichiometric oxide systems where the defect structure and the thermal, electrical, optical, magnetic and other properties are very sensitive to small compositional changes.

Another example of a study using combined measurements is the work of Molenda and Stoklasa [5], who analysed the dominant defect types in Na_xCoO_2 bronzes. TG and electrical conductivity measurements were carried out as a function of oxygen pressure in the temperature range 990–670 K and the oxygen pressure range 100–10 kPa. By comparing the deviations from stoichiometry and the electrical conductivity with theoretical expressions derived for various possible defect types it was shown that the dominant ionic defects in cobalt bronze are Co^{3+} ions substituted for sodium.

Finally, the dilatometric method developed by Shvaiko-Shvaikovsky [7] for evaluating defect types in non-stoichiometric oxides is also worth mentioning. With a new design, identical thermal conditions could be obtained for the push-rod and the sample holder, which considerably improves the accuracy of these measurements. By this technique measurements are carried out as a function of oxygen pressure at constant temperature and the changes in relative density, volume and coefficients of thermal expansion are determined as a function of deviations from stoichiometry. From these data the type of defect and the mean volume per defect can be determined. For single crystal 0.9 $Zr(Y_2O_3)O_{2-x}$, preliminary measurements showed that single oxygen vacancies are formed during reduction at 1600 K, as indicated by the observed decrease in density and increase in volume. However, as the defect concentration reached $x = 10^{-3}$ (atomic fraction), interactions between the defects resulted in a decrease in volume. The mean volume per defect was calculated to be 10 $Å^3$. This method appears to be very promising for studies on non-stoichiometric compounds, as it apparently can give unambiguous information about the predominant defect type.

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