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SURFACE PROPERTIES OF ZrO$_2$ IN EQUILIBRIUM WITH THE GAS PHASE

J. NOWOTNY and M. SŁOMA

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, PL-30-239 Kraków, Poland

Résumé - Le potentiel de surface de ZrO$_2$ stabilisée par Y$_2$O$_3$ a été mesuré à 1035 K pendant la re-équilibration en cours d’oxydation et de réduction sous pression partielle d’oxygène entre 0,21 et 10$^{-4}$ atm. Le changement du travail d’extraction des électrons consiste en une variation initiale rapide liée à l’équilibration ionique et en une lente dérive de même signe. La comparaison des résultats obtenus avec les résultats précédents sur l’émission électronique de ZrO$_2$ rapportés par Odier et Loup permet de déterminer l'exposant n de la loi de variation avec la pression partielle d’oxygène pour le platine recouvert d’une mince couche superficielle de PtO$_2$/n = 8.1/.

Abstract - The surface potential of Y$_2$O$_3$ stabilized ZrO$_2$ was measured at 1035 K during the re-equilibration involving oxidation and reduction at oxygen partial pressure between 0.21 and 3.10$^{-4}$ atm. Changes in work function consist of a rapid initial increase due to ionic equilibration and a slow drift of the same sign. Comparison of the obtained results with former electronic emission data of ZrO$_2$ reported by Odier and Loup enables to determine the exponent of oxygen partial pressure dependence of Pt covered with a thin layer of PtO$_2$ /n = 8.1/.

I - INTRODUCTION

Despite numerous works devoted to ZrO$_2$, there are very limited reports on its surface properties /1-3/. It has been namely observed that yttria doped ZrO$_2$ crystals are not homogeneous but involve a strong composition gradient of Y within the near-surface layer as a result of Y segregation /3/. Odier and Loup /1,2/ have reported work function data obtained by electronic emission. Their data correspond to the equilibrium state at very low oxygen pressure below 10$^{-6}$ atm. The purpose of the present work is to re-investigate the work function of Y$_2$O$_3$ doped ZrO$_2$ under higher pO$_2$ range using the dynamic condenser method which enables to monitor the re-equilibration kinetics "in situ".

II - DEFINITION OF TERMS

The interaction between ZrO$_2$ and oxygen may be expressed by the equilibrium:

$$\frac{1}{2} O_2/_{gas} + V_0^\ast + 2e \rightarrow O_0$$

/1/

By application of the mass action law to defects in crystal and also assuming the Maxwell-Boltzmann statistics, we obtain the following relation between changes in work function and pO$_2$/4/:
where \( n \) is the parameter corresponding to the structure of point defects in crystal and \( \Delta \Phi_X \) corresponds to work function changes of oxide sample. It has been reported that for \( \text{ZrO}_2 \) \( n = 4/1,2/ \). In the dynamic condenser method, \( \Delta \Phi_X \) is related to changes in contact potential difference \( \Delta \text{CPD} \) between the condenser plates:

\[
\Delta \text{CPD} = \Delta \Phi_X - \Delta \Phi_{\text{Pt}}
\]

where \( \Delta \Phi_{\text{Pt}} \) is work function changes of the Pt reference electrode.

III - EXPERIMENTAL

The dynamic condenser method was applied in the present studies /4/. Its recent modifications involving the vibrating system and the electronic set-up led to a high accuracy of determinations of the CPD at 1000°C up to \( \pm 2 \) mV. The polycrystalline sample of \( \text{ZrO}_2 \) doped with 9 at.\% \( \text{Y}_2\text{O}_3 \) was taken for investigations. The experimental procedures consist in heating the system in the Ar-\( \text{O}_2 \) gas mixture \( /\text{P}_{\text{O}_2} = 3.10^{-4}\) atm/ for 10 h at 1035 K. Then a slow drift of CPD of a constant rate (-25 mV/h) was observed. Then air was admitted into the reaction system /oxidation run/ and the CPD was monitored in time (Fig. 1). As seen the CPD suddenly increases, then exhibits slight changes around maximum and finally slowly decreases with the same rate as before the experiment. Similarly the reduction experiments consist in admission of the Ar-\( \text{O}_2 \) mixture \( /\text{P}_{\text{O}_2} = 3.10^{-4}\) atm/. Appropriate changes of CPD in time are shown in Fig. 2. As seen these changes are markedly slower. Finally CPD assumes a stationary value when the same drift appears. The results are well reproducible for several independent experimental runs. The same experiments were also performed for the \( \text{NiO-Pt} \) system where \( \text{NiO} \) serves as a standard for calibration of the Pt electrode. Appropriate changes in the CPD were +25 and -25 mV for oxidation and reduction, respectively. No drift was observed in this case.

IV - DISCUSSION

The measured changes in CPD for the \( \text{ZrO}_2\)-Pt system should be subdivided into the main electronic effect corresponding to chemical reactions of oxygen with the surface of the condenser electrodes and a slow CPD drift which is independent of the equilibration process. Thus determined changes in the CPD are almost the same for both runs concerning their absolute values:

\[
\begin{align*}
\text{CPD}_{\text{ox}}^1 &= (\Delta \Phi_{\text{ZrO}_2} - \Delta \Phi_{\text{Pt}}) \frac{1}{e} = 80 \text{ mV} \\
\text{CPD}_{\text{red}}^1 &= (\Delta \Phi_{\text{ZrO}_2} - \Delta \Phi_{\text{Pt}}) \frac{1}{e} = -79 \text{ mV}
\end{align*}
\]

when subscripts "ox" and "red" correspond to oxidation and reduction runs, respectively. A good reproducibility of the measured electronic effect for both oxidation and reduction runs indicates that the system \( \text{ZrO}_2\)-Pt is well equilibrated with the gas phase. Application of the \( \text{ZrO}_2 \) oxygen sensor /5/ to monitor oxygen activity in the dynamic condenser during the re-equilibration process indicates that the long equilibration time for reduction runs is rate controlled by diffusion through the gas phase. Accordingly the CPD changes for oxidation are more adequate to the equilibration kinetics.

Determination of the \( \text{P}_{\text{O}_2} \) power dependence for \( \text{ZrO}_2 \) from Eq./2/ requires to solve Eq./3/ in respect to \( \Delta \Phi_{\text{Pt}} \). Therefore the standard system \( \text{NiO-Pt} \) was taken for CPD measurements involving the same procedure as that for the \( \text{ZrO}_2\)-Pt system.
Corresponding CPD changes may thus be expressed in the respective forms:

\[
\text{CPD}^2_{\text{ox}} = (\Delta \Phi_{\text{NiO}} - \Delta \Phi_{\text{Pt}}) \frac{1}{e} = 25 \text{ mV} /5/ \\
\text{CPD}^2_{\text{red}} = (\Delta \Phi_{\text{NiO}} - \Delta \Phi_{\text{Pt}}) \frac{1}{e} = -25 \text{ mV}. /5/
\]

Doubly ionized cation vacancies as predominant defects were assumed for NiO in calculation of the surface electronic effect /6,7/.

Fig. 1 - CPD changes for the ZrO$_2$ - Pt system at 1035 K for oxidation runs.

Fig. 2 - CPD changes for the ZrO$_2$ - Pt system at 1035 K for reduction runs.
Although a higher concentration of cation vacancies were reported for the surface layer of NiO /8/, this segregation effect has a negligible influence on the crystalline structure which still can be considered in term of the NaCl-type structure /9/. Accordingly we may assume that both crystalline bulk and the surface layer exhibit the same power of the $P_{02}$ dependence /$n=6$/ . Thus Eq./2/ serves to calculate work function changes of NiO in the experimental conditions applied:

\[
\frac{1}{e} (\Delta \phi_{\text{NiO}}) = 97 \text{ mV}. \quad /6/
\]

Therefore, taking into account expressions /4/ and /5/, we have:

\[
\frac{1}{e} (\Delta \phi_{\text{ZrO}_2}) = \frac{1}{e} (\Delta \phi_{\text{Pt}}) + CPD^1 = CPD^1 + \frac{1}{e} (\Delta \phi_{\text{NiO}}) = 151 \text{ mV}
\]

Thus, from Eq./2/ we obtain that the parameter $1/n$ for ZrO$_2$ is equal $1/3.84$. This value is in a good agreement with data reported already by Odier and Loup /1,2/ and indicates that the defect structure of the surface layer of ZrO$_2$ is essentially the same as it has been reported for the crystalline bulk /10/. Changes due to segregation, if any, may consist either in concentration of anion vacancies or $Y_2O_3$ or both.

Experimental data obtained in this work enable to determine the electronic effect of the Pt electrode:

\[
(\Delta \phi_{\text{Pt}}) \frac{1}{e} = (\Delta \phi_{\text{NiO}}) \frac{1}{e} - CPD^2 = 72 \text{ mV} / \text{oxidation} /.
\]

This value corresponds to $n = 8.1$ in Eq./2/ and should be considered in term of the defect structure of a thin layer of PtO$_2$ which covers the metallic reference Pt electrode.

**V - CONCLUSIONS**

As it results from the work function measurements, there is no evidence of segregation in yttria doped ZrO$_2$ which might lead to changes in the structure of the surface layer. The segregation, if any, may consist in changes in concentration of anion vacancies or $Y_2O_3$ or both. The obtained $P_{02}$ dependence of work function for Pt may serve in determination of absolute values in work function changes using the dynamic condenser method at higher temperatures. At lower and moderate temperatures, the changes in work function of the Pt reference electrode are usually assumed negligible compared with the investigated oxide sample /11/. However, at elevated temperatures, work function changes of Pt assume comparative values to those of the investigated sample.

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