INTERACTION OF OXYGEN WITH ZIRCONIA SURFACE

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The influence of surface heat treatment, electron (50 - 800) eV irradiation and UV (180-300) nM illumination of adsorption system on the state of oxygen adsorbed on zirconia surface have been investigated. On the temperature-programmed desorption (TPD) profiles from high temperature (1200 K) treated surface peaks of molecular and atomic oxygen are observed at ca. 450 K. On the basis of experimental results obtained by investigation of photon emission accompaning oxygen adsorption (AL) and TPD data existence of adsorption sites on the surface is suggested on which irreversible dissociative adsorption of oxygen occurs. These very sites are associated with emission processes. Conclusion is made that the only type of adsorption sites connected with anion vacancy is present on zirconia surface and this is its charge state that determines the state of adsorbed oxygen. One of the important mechanisms by which the electron and UV photon exitation affects the adsorption interaction is the change of the charge state of the adsorption site.

1. INTRODUCTION

The first stage of interaction of the gas phase molecules with the solid surface or heterogeneous reaction is the adsorption of the particle on the surface. The nature of adsorption sites determines the state of adsorbed particle and its reactivity. Irreversible changes which may take place on the surface with time cause corresponding changes in the structure of the adsorption sites and hence influence the state of adsorbed particle and following surface processes.

Interaction of the gas phase molecules with the surface of refractory oxides attracts at present time great attention in view of fundamental and applied importance of such investigations, in particular for purposes of heterogeneous catalysis, electronics, corrosion protection, gas sensors. Pure, doped and stabilized by various admixtures zirconia is a very promising material for gas sensors applications, especially oxygen sensors. Zirconia is an oxide with considerable disturbance of stoichiometry depending on the temperature which, in dependence on conditions, may demonstrate n- or p-type conductivity. At constant oxygen pressure above the surface the defect concentration decreases sharply with temperature lowering. Besides, negligible admixtures essentially influence it properties. Under the usual conditions zirconia demonstrates oxygen deficiency and the main kind of defects is the oxygen vacancy.

In some adsorbing systems gas chemisorption on the surface is accompanied by photon and electron emission. Such phenomena were observed, in particular, in the case of oxygen adsorption on the surface of magnesium oxide [1] and are observed for the O_2- ZrO_2 system. The nature of the adsorption sites, responsible for emission processes, as adsorption sites on the whole. is of primary importance for understanding the mechanisms of chemisorption. In the present work attempt is made to determine the nature of adsorption sites on zirconia surface by the way of investigation of the adsorbed oxygen states and influence on them of the adsorption system exitation with electrons (50 - 800) eV and UV photons (180 - 300) nM and accompaning emission phenomena studies.

2. EXPERIMENTAL

Experiments were carried out in UHV apparatus at residual gas pressure not higher then 10^{-7} Pa. Zirconia samples were obtained from high purity grade oxide powder. Water solution of the powder was spread on a metal heater and baked in vacuum at 373K for 1 hour. Residual gas and desorbed species analysis was carried out by unipolar mass spectrometer MX7303 with sensitivity threshold towards argon not less then 2 nPa. Oxygen gas obtained in a separate reservoir by thermal decomposition

of previously outgassed KMnO$_4$ powder was introduced through a variable leak valve. TPD was measured by linear heating of the sample with the temperature increase rate of (1 - 5)KS^{-1} up to 1100 K. To normalize the sensitivity of the spectrometer a small amount of Ar was constantly leaked into the system. The UV light source was a water cooled deuterium lamp with band of wavelengths (180 - 300) nM in UV region and roughly estimated photon flux (3 - 10)10^{15}S^{-1}. The sample was irradiated through quartz window. The electron irradiation was carried out with electron gun which provided electron current of (5 - 150) μA with electron energies of (50 - 800) eV mounted in the region of the sample.

Adsorboluminescence measurements were carried out in counting mode with photomultiplier PHEM-130 sensing in the wavelength range of (200-650) nM.

3. RESULTS AND DISCUSSION.

Freshly prepared samples were heated up to 1100 K in vacuum, cooled and exposed to oxygen at 350 K. Then TPD measurements were carried out. Composition of desorbed species in the first several temperature sweeps is presented in Fig.1, where temperature positions and relative hights of peaks on corresponding TPD profiles are indicated.
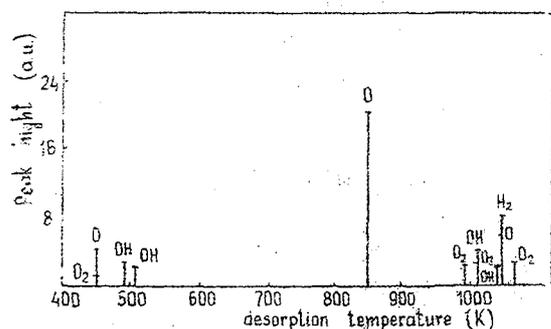

Fig.1.Composition of desorbed species from freshly prepared zirconia surface.Exposition to oxygen at 350K.

Peak hights of desorbed species vary in successive temperature sweeps, some of them diminishing to minor proportions. It may be

concluded that some of the desorbed species and adsorption sites are connected with the process of water decomposition in the bulk and on the surface of the sample. After a short time heat treatment at elevated temperatures atomic oxygen remains the only substantial desorbed species, corresponding TPD profile is shown in Fig.2. Two peaks of atomic oxygen at 450 K and 850 K (I$_1$ and I$_2$ respectively) dominate on TPD profile.
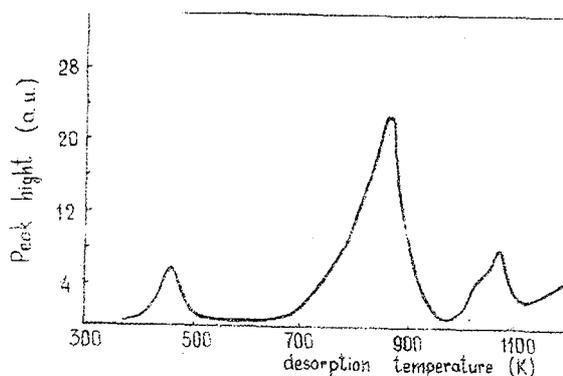

Fig.2.TPD profiles of atomic oxygen desorbed from freshly prepared zirconia surface. Exposition to oxygen at 350K,exposition ca.10^{5}L .heating rate 3K/S.

Peak hights ratio I$_2$/I$_1$ decreases with the time of heat treatment. Besides, ratio I$_2$/I$_1$ depends on the surface temperature upon adsorption and exposition value, higher temperatures and lesser expositions cause relative increase of I$_2$. The third peak on TPD profile in the high temperature region is not connected with adsorbed oxygen. It is shown in [2], that dissolution of water molecules in the magnesium oxide lattice is accompanied by their dissociation and formation of V$_H$ centres. These centres decay at elevated temperatures and transform to V centres, released hydrogen atoms recombine on the surface and desorb from it. Decay of V centres, in their turn, gives rise to release of free holes which diffuse to the surface and are captured by surface anions which after neutralization desorb from the surface. Taking into consideration Figs. 1, and 2 it may be concluded that similar processes take place in our case. Continuous desorption of atomic oxygen observed at temperatures above 1100 K is due to another processes. Most likely it is

related to mobility of oxide lattice atoms in the bulk as well as at the surface which is supposed begin at Tamman temperatures equal to (0,3 - 0,5) of the melting temperature of the sample substance and is expected take place in our case.

Changes in composition of desorbed species and shapes of TPD curves testifies to irreversible processes on the surface in the course of heat treatment. They are due to several reasons, particularly removal of water decomposition species and other contamination from the surface, processes on grain boundaries and changes in defect structure on the surface. It is known that ideal surface of oxide is usually inert toward adsorption and adsorption sites are connected with defects of various kinds [3]. The main type of defects on zirconia surface is oxygen vacancy which, depending on temperature, may be partially or completely ionized.

Long heating (6 hours) of the sample in vacuum at 1200 K causes further changes in adsorptive properties of zirconia surface. Oxygen adsorbed at 350 K desorbs in atomic and molecular from with peak maxima at ca. 450 K as shown in Fig.3 TPD profiles don't change with time what testifies to stabilization of adsorptive properties of the surface.
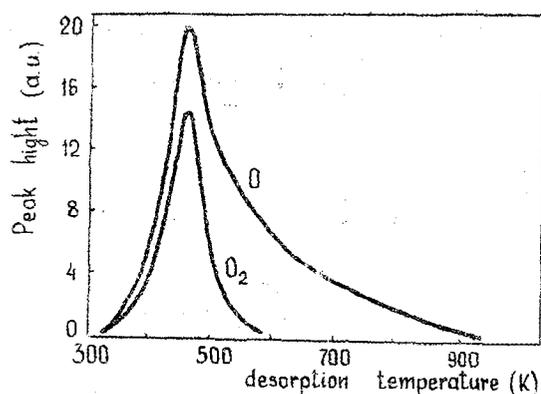
of adsorbing surface in the course of heat treatment.

Additional excitation of adsorption system may influence surface interaction through various mechanisms. It is possible to disturb the equilibrium of surface electronic system, excite or dissociate gas phase molecule, change the state of the particle adsorbed on the surface [4].

The influence of the UV preillumination of the zirconia surface on the state or amount of adsorbed oxygen was not revealed in our experiments. But illumination during adsorption not changing temperature positions of TPD peaks enhances atomic adsorption of oxygen and conversely influences amount of molecularly adsorbed oxygen.

Besides, illumination of the surface with adsorbed oxygen increases amount of atomic oxygen desorbed in the next TPD process and considerably diminishes the signal of molecular oxygen, which after 0,5h illumination disappears completely. Electron irradiation influences by similar way. In this case amount of molecularly desorbed oxygen is decreased, independently on what state of adsorption process irradiation is carried out. Atomic adsorption as in the case of UV illumination is enhanced, but besides this a strong enhancement by pre-irradiation is observed too, which depends on electron energy (Fig.4).
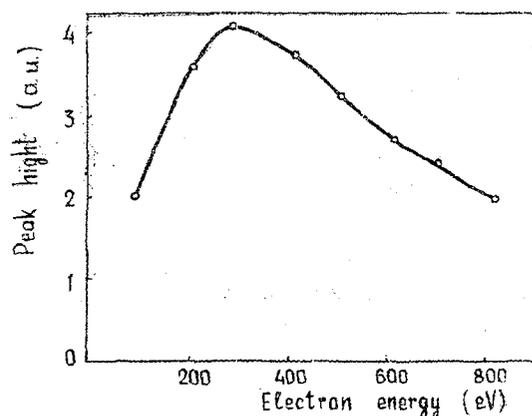

Fig.3. TPD profiles of molecular and atomic oxygen desorbed from zirconia surface after heat treatment (6h) at 1200K.Exposition to oxygen at 350K.Exposition ca. 10^5L.heating rate 3K/S.

Fig.4. Peak hight of atomic oxygen desorbed from pre-irradiated zirconia surface in dependence on electron energy. Exposition to oxygen and irradiation at 350K,exposition ca.10^5L. electron beam current 100 µA ,irradiation time 2 min.

Intensity of emission processes upon oxygen adsorption is diminished due mainly to decrease

Pre-irradiation effect is conserved at the surface

for a long time, and disappears completely after heating the surface up to 800 K as is shown in Fig.5. AL intensity from pre- irradiated surface is considerably enhanced.
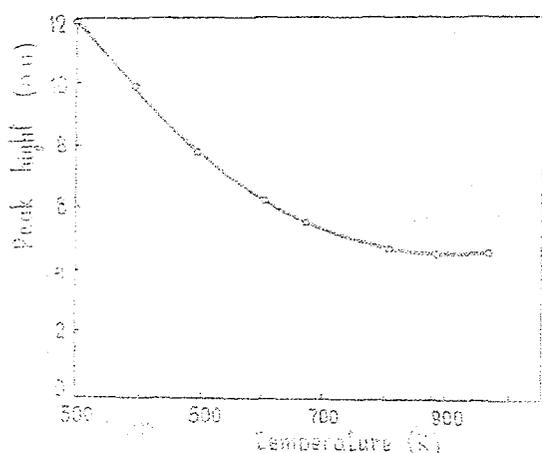

Fig.5 Peak high of atomic oxygen, desorbed from pre-irradiated zirconia surface in dependence on the following temperature rise. Exposition to oxygen and irradiation at 350K, exposition ca.10⁵L, electron energy 300eV, electron current 100 μA, irradiation time 2 min.

Thus excitation of the substrate electronic system by both the UV and electron irradiation not changing qualitatively the shape of TPD profiles of atomic and molecular oxygen influences the amount of the species adsorbed and causes redistribution between various adsorbed forms. It may be concluded that no other types of adsorption sites arise from excitation and only two of them are present on the surface. Electron pre-irradiation of the surface increases the amount of atomically adsorbed oxygen and, consequently, the concentration of corresponding adsorption sites. Most probable effect of such irradiation is formation of oxygen vacancies via Auger process according to Knotek-Feibelman mechanism [5]. The shape of the curve in Fig. 4. testifies to such assumption. The threshold energy of electrons at which the influence of pre-irradiation is observed is related to ionization of the upper most filled level of zirconium ion in the lattice and is determined by its position on the energy scale. Decrease in the efficiency of vacancy formation at the electron energies above 300 eV is explained by

increasing of the mean free path of electrons for inelastic scattering. Electron irradiation results in nonequilibrium concentration of oxygen vacancies on the surface. Following irradiation heating of the sample causes diffusion of nonequilibrium vacancies into the bulk and restoration of the equilibrium which is shown in Fig.5. The increase of AL intensity from pre-irradiated sample indicates that these adsorption sites are simultaneously AL centers. The temperature dependence of AL intensity demonstrates monotonous increasing with the surface temperature whereas the amount of atomically desorbed oxygen from such surface decreases in the following TPD experiment. Absence of correlation between the AL intensity and the amount of desorbed oxygen can not be explained by desorption processes so as the shape of AL kinetic curves remains unchanged qualitatively in the temperature range indicated. The only possible explanation consist in assumption that AL accompanies dissociative chemisorption of oxygen which occurs at oxygen vacancy, one of the atoms healing the vacancy and another is stabilized on the surface. The latter is responsible for the signal of atomic oxygen in the next TPD experiment. As a result of vacancy healing equilibrium between the surface and the bulk of the sample is disturbed. Following temperature rise renew equilibrium concentration of oxygen vacancies on the surface owing to their diffusion from the bulk and enables observation of AL repeatedly upon oxygen admission. AL intensity is slowly decreasing in the successive AL measurements which is connected with the general decrease of vacancies concentration in the bulk and subsurface region of the sample. Initial intensity may be restored after continuous thermal treatment of the sample in vacuum at elevated temperature in the course of which the process of oxygen vacancies formation takes place.

Redistribution between the molecular and atomic forms of adsorbed oxygen which is observed under external excitations at different stages of adsorptive interaction does not affect the shape of corresponding TPD profiles. This testifies to the mutual transformation of the indicated adsorption sites under excitation. Hence it may be assumed that in both cases the

adsorption sites are connected with oxygen vacancy and their charge state determines the form of adsorbed oxygen. Oxygen dissociation occurs at the vacancy with the two captured electrons (analogue to Fs centers in alkaline earths oxides) whereas in the case of one captured electron molecular adsorption takes place presumably in the form of O_2^-. Quantitative comparison of the TPD profiles gives evidence that the main part of vacancies has two captured electrons analogously to the case of magnesium oxide and other alkaline earths oxides. The presence in minor quantities. of positively charged vacancies (one captured electron) on the surface supposes existence of other electron traps on the surface or subsurface region necessary for the charge compensation. Decreasing of the amount of molecularly adsorbed oxygen under irradiation may be explained by trapping of released electrons at the centers where oxygen is adsorbed in the form of O_2^- which results in the molecule dissociation and healing of the oxygen vacancy.

REFERENCES

1. Ivankiv L.I., Komarovsky Z.P.,Ketsman I.V., Pentsak O.M. Adsorboluminescence spectrum of MgO upon oxygen chemisorption. // Ukr. Fiz. Zur. 1982. Vol.27. ? 9. P. 1422 - 1424.
2. Kathrein H., Freund F. O$^-$-ions and their relation to traces of H_2O and CO_2 in magnesium oxide. // J.Phys. Chem. Solids. 1984. Vol. 45. ? 11/12. P. 1155 - 1163.
3. Henrich Victor E. The surfaces of metal oxides. // Rep. Prog. Phys. 1985. Vol. 48. P.1481 - 1541.
4. Cunningham J. Radiation and Photoeffects at gas/solid Interfaces. // Chem. Kinetics. 1984. Vol. 19. P. 291 - 427.
5. Knotek M.L. Stimulated desorption. // Rep. Prog. Phys. Vol. 47. P.1499 - 1561.