ELECTRON SPECTROSCOPY STUDY OF METAL PARTICLE – GAS MOLECULE INTERACTION

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Investigation of the chemical changes in an electronic structure induced by the gas molecules adsorption and particle reconstruction has been performed on the non-continuous Rh film deposited onto γ-Al_2O_3 substrate. The combination of different methods, such as Auger electron spectroscopy, electron energy loss spectroscopy and elastic peak electron spectroscopy allow to follow the behaviour of studied systems, it means to determine the actual surface morphology, chemical state and an electronic structure of the metal deposit.

Introduction

The changes of the physical properties occurring on the model system of noble metal non continuous film deposited onto ceramic support and interacting with impinging gas molecules CO and O_2 exhibit a point of interest in a heterogeneous catalysis. Gas molecule adsorption can evoke the energy shift of the Auger peak of deposited material. This effect can be affected both by the gas molecule adsorption behaviour and by the morphology changes caused by the particle reconstruction.

We have deposited rhodium onto Al_2O_3 substrate to study these effects. The sample was treated to a special cleaning and stabilising procedure [1] and later the surface interaction with the CO and O_2 molecules was performed. The Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and elastic peak electron spectroscopy (EPES) have been used to monitor the surface processes. The goal of this paper is to characterise the metal particles condition in situ and to contribute by this way to our knowledge of the surface processes in heterogeneous catalysis.

Experimental

Experiments were performed in an ultra high vacuum chamber (base pressure typically 2×10^{-8} Pa) equipped by the double pass CMA analyser DESA 100 with the coaxial electron gun, produced by Staib Instruments. The Auger spectra were measured with a primary electron energy E_p = 2.5 keV. Elastic peak electron spectroscopy (EPES) results were obtained at the both primary electron energies E_p = 0.5 keV and 1 keV because the surface sensitivity of EPES differs for different E_p [2]. Electron energy loss spectroscopy (EELS) was performed using the primary energy 300 eV. The exposure of sample with CO and O_2 was performed by a simple molecular beam system. The vacuum chamber is equipped also by the Rh evaporating source and Ar^+ gun. The samples can be heated up to 800 K.

The alumina substrates were prepared from aluminium plates $10\times10\times1$ mm^3, produced by Goodfellow, purity of 99.999%. The plates were polished by the mechanical and chemical procedure and then heated under atmosphere at 870 K during 24 hours. This procedure leads to the formation of polycrystalline γ-alumina layer with a thickness of about several tens of nm [3]. Before the first Rh deposition the substrates as well as the reference Rh foil (Goodfellow, 99.9%) were heated for 5 minutes at temperature 770 K and then sputtered by Ar^+ ions, using the density of ion current 1.5 $\mu A/cm^2$, ion energy 1 keV and sputtering time 10 min.

Rh deposit was evaporated in-situ from the cell working on the principle of an elec-

tron bombardment of Rh wire. Rh was deposited at a support temperature 300 K.

Deposited sample was heated up to 800 K and later stabilised in gas mixture of 3×10^{-7} Pa CO and 3×10^{-7} Pa O_2 at temperature of 800 K for 60 minutes. This procedure is used to avoid the non-reversible changes stimulated by a sample treatment during the regular TDS experiments. Stabilised Rh particles are probably oxidised, so the reduction by the CO molecules flux is performed.

Following CO adsorption was performed at temperature of 300 K, while the oxidation at the temperatures of 500 K and 700 K consequentially, O_2 exposure being about 17 L. A sample reduction was achieved by the CO exposure of about 5 L at the temperature of 450 K.

Finally, the morphology parameters of deposited films were determined by means of TEM using the method of transparent carbon replica.

Results and discussion

Elastic peak electron spectroscopy (EPES) represents very simple method based on the measurement of elastically reflected electrons current. The intensity of elastic peak depends on the atomic number, structure of the target material, incident angle of electrons and the primary electron energy [2]. The metal surface coverage of sample Θ_{Rh} was calculated using the obtained EPES results according to a model presented in [4]. The development of Θ_{Rh} calculated by this way is shown in Fig. 1a.

The EPES data obtained for an electron primary energy $E_p = 500$ eV and 1 keV are presented. It is well recognised that calculated Θ_{Rh} is higher for $E_p = 500$ eV than for 1 keV after the deposition. This difference becomes lower after the sample annealing up to 800 K and stabilisation. The values obtained for both E_p decreased both during the annealing and during the stabilisation. We explain this decrease as the deposit reconstruction. Under the deposition conditions, especially low substrate temperature (300 K) we can suppose the growth of two dimen-

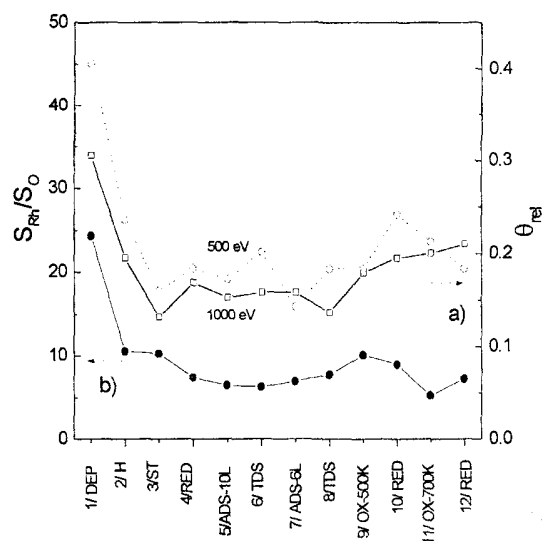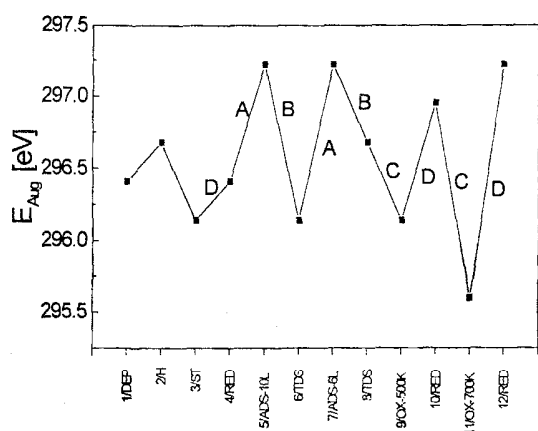sional formations (2D) due to low substrate diffusion of deposited Rh atoms [5].

Fig. 1. Rh deposit relative coverage Θ_{Rh} of sample calculated by EPES (a) and the ratio of Rh and O AES peaks intensity S_{Rh}/S_O (b). The particular steps in sample treatment are marked N/Y, where N stands for the step sequence and Y stands for the step character: DEP $\Leftrightarrow$ deposition, H $\Leftrightarrow$ heating, ST $\Leftrightarrow$ stabilisation, RED $\Leftrightarrow$ reduction, ADS $\Leftrightarrow$ CO adsorption, TDS $\Leftrightarrow$ thermodesorption, OX $\Leftrightarrow$ oxidation. In a case of the adsorption and oxidation the CO exposure and sample temperature, respectively, are also marked.

After the sample annealing and later stabilisation the surface diffusion is stimulated by elevated temperature and the 3D particles are created. This process results in the increase of uncovered substrate area and so in the lower Θ_{Rh}. The difference in the values of Θ_{Rh} obtained for the different primary energies is explained by the different information depth. So the signal at $E_p = 1000$ eV is more influenced by the underlying substrate than at $E_p = 500$ eV. Furthermore, the different values of calculated Θ_{Rh} demonstrate the two dimensional character of the deposit. During the procedures consequentially performed, i.e. CO adsorption and desorption, oxidation and reduction, the value of Θ_{Rh} seems to be independent on E_p and it changes in a narrow interval of $\approx 0,15 - 0,20$. The change of calculated values can be the

result both of the morphological changes and of the sample purity change due to the gas interaction and probable CO dissociation on deposited Rh particles [6].

Let us have a look at a Fig. 1b now. The ratio (S_{Rh} /S_O), where S_{Rh} and S_O stand for the rhodium and oxygen Auger signal intensities, respectively.

The decrease of S_{Rh}/S_O ratio during the sample annealing after the depositions can be seen. Later, the S_{Rh}/S_O changes are not so evident, maybe excluding the last sample oxidation at 700 K and consequent reduc-

tion.

Fig. 2. Auger electron energies E_A of Rh($M_{45}N_{45}N_{45}$) peak. Typical E_A changes are marked so: A: E_A increase with CO adsorption, B: E_A decrease after TDS, C: decrease after oxidation and D: E_A increase after reduction. The step sequence and character are marked identically as in Fig. 1.

The Auger electron energies E_A of Rh Auger peak ($M_5N_{45}N_{45}$ transition) measured at the particular steps of the experiment are presented in Fig. 2. According to the obtained Auger energy E_A the small Rh particles were deposited because the Auger energy after the deposition and sample heating reaches the values about 296.5 eV, which is lower compared to the bulk value measured on our experimental set up of 298.5 ± 0.2 eV. The E_A increase during the sample annealing can be explained also by the particle coalescence 2D → 3D, that results in the structure change towards the bulk material. Consequent stabilisation represents the oxidation,

because CO molecules do not adsorb at $T =$ = 800 K, while O_2 can dissociate and diffuse to the particle volume [6]. That is why this E_A decrease can be explained as the oxidation of Rh atoms, that will be described later. Generally, these E_A shifts can be observed:

(a) E_A increases after CO adsorption – marked A in Fig. 2.

(b) E_A decreases after TDS – marked B in Fig. 2.

(c) E_A decreases after oxidation – marked C in Fig. 2.

(d) E_A increases after reduction – marked D in Fig. 2.

It is well seen from the presented experimental data that the E_A changes reproduce regularly. The E_A increase can be caused by the chemical bond creation (e.g. oxidation - see Fig. 2) or metal particles dispersion. Both effects result in a lower number of free electrons that screen the positive charge in the metal particle after the electron emission during the Auger process - see e.g. [7, 8]. On the other hand the E_A decrease can be caused by the metal particle coalescence or breaking of the chemical bond (e.g. reduction - see Fig. 2). It should be decided now which of the two effects - either the morphology change or the chemical state change - occurs in our experiment.
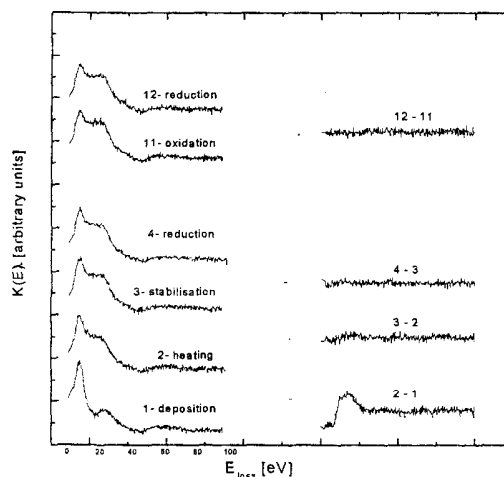

Fig. 3. EELS results converted to $K(E)$ curves (left side of the figure) and the differences between the adjoining spectra. The step sequence (see Figs. 1, 2) and character of procedure is marked near every spectrum.

The EELS results presented in Fig. 3 can help us to solve this problem. Metal surface coverage of non-continuous sample can be determined by the analysis of EELS peak [9]. The Rh/Al_2O_3 sample EELS curves obtained at the particular steps of our experiment and the differential curves are shown. The presented results were measured at $E_p = 300$ eV. We can recognise the curve development only between the deposition and the annealing and also a low change between the annealing and stabilisation procedure. Later the EELS results do not change. It can be interpreted that there is none or very low particle morphology reconstruction. So probably the obtained changes in E_A values express only the chemical change of the metal deposit surface.

TEM determined metal coverage of the sample after the finishing the experiments $\Theta_{Rh}^{TEM} = 0.15$–0.22, that is in a good agreement with the results shown previously - 0,2 calculated by EPES and presented in Fig. 1a after the last reduction. The average particle size was determined to 5 nm.

Conclusions

The results obtained by electron spectroscopy methods exhibit the irreversible morphological change of the rhodium deposited onto polycrystalline Al_2O_3 substrate. The reconstruction is stimulated by sample annealing and stabilisation procedure. On the other hand the reconstruction by the gas molecule-Rh particle interaction was not demonstrated.

The metal particle-gas molecule interaction can be in principle monitored *in situ* by the methods of electron spectroscopy. The chemical and morphological changes can be separated.

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ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ МІЖ ЧАСТИНКАМИ МЕТАЛУ ТА МОЛЕКУЛАМИ ГАЗУ МЕТОДАМИ ЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ

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На несуцільній родієвій плівці, напиленій на підкладку з γ-Al_2O_3 , проведено дослідження хімічних змін в електронній будові, викликаних адсорбцією молекул газу і реконструкцією частинок. Поєднання таких різних методів, як електронна Оже-спектроскопія, електронна спектроскопія енергетичних втрат і електронна спектроскопія пружного піка, дозволило простежити поведінку досліджуваних систем, тобто визначити реальну морфологію поверхні, хімічний стан і електронну структуру осадженого металу.