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RHEED STUDY OF Au/KCl SYSTEM FOR ESTIMATION OF THE DEPENDENCE OF DIFFRACTION SPOT PROFILES ON THE PARTICLE SIZE

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The reflection high energy electron diffraction (RHEED) method has been used for the investigation of Au cluster growth on KCl substrate. The formation of three-dimensional particles was observed. The morphological parameters of the particles (i.e. diameter and density) were estimated ex-situ by transmission electron microscopy (TEM) and the results were compared with the RHEED spot profiles. Au particles were chosen, because they did not change their parameters by the reconstruction caused by oxidation during the preparation for TEM measurements.

1. *Introduction*

Reflection high energy electron diffraction (RHEED) is attractive as a technique for the investigation of surface structures. Because of a favourable geometry (grazing angle of incidence and exit) it is possible to investigate in-situ epitaxial thin film growth in real time as well as the film morphological changes during the desorption experiments with the sample in line-of-sight of a mass spectrometer.

The diffraction pattern analysis permits to distinguish between different modes of overlayer formation. The RHEED method offers a simple and readily applicable mean of in-situ observations of supported particle model catalysts. It gives essential information on the structure, orientation and morphology of the substrate and deposit.

The most reliable method commonly used to characterise the morphological parameters of supported particles is transmission electron microscopy (TEM). The difficulties of in-situ examination of catalysts by this result from the necessity of special particle supports and preparation.

The goal of this work is to estimate the correlation between spot profiles of RHEED patterns and the average particle size obtained from TEM observations. To exclude the possibility of particle reconstruction under the exposure to the atmosphere during the preparation of samples for electron microscopy, the Au particles were used. The Au particles are supposed to be air–stable.

2. *Experimental*

The RHEED experiments were performed in an UHV chamber equipped with a special evaporation cell MEBES (Micro Electron Beam Evaporation Source) operating on the principle of electron bombardment. The magnetically focused electron gun provides an electron beam of a primary energy of 30 keV. A 512×512 and 256–grey–level CCD camera and an AT 486 DX computer data acquisition system permit both image processing and real time analysis of intensity profiles of diffracted beams.

The substrate, the KCl (001) plane cleaved in air, was cleaned by heating at the temperature of 300 °C for one hour before deposition. The Au deposits were prepared at substrate temperature from 20 to 210 °C at a pressure of about 5×10^{-6} Pa. At the end of the measurement the particles were investigated by TEM using the method of transfer carbon replica. This standard method as well as the method of investigation of the deposit granulometry is described in details in Ref. 1. The morphological parameters of the Au particle deposits evaluated by TEM are presented in Table 1.

TABLE 1.
The morphological parameters of the Au *particle deposits evaluated by TEM.*

Sample number	Preparation temperature [°C]	RHEED $k = a(\mathrm{KCl})/a(\mathrm{Au})$	RHEED $< L >$ [nm]	TEM $< L >$ [nm]
1	20	1.54	2.0	2.9
2	210	1.53	3.6	5.0
3	130	1.53	2.4	4.0
4	20	1.55	1.6	2.2

3. Results and discussion

Figure 1 shows an example of RHEED diffraction pattern from Au deposit on KCl (001) substrate along the [110] crystallographic direction. The arrangement of diffraction spots gives following epitaxial parameters of adlayer–substrate system:

$$\text{Au } (001)||\text{KCl } (001)$$

$$\text{Au } [110]||\text{KCl } [110].$$

Spot-like form of the diffraction pattern indicates the three-dimensional particle growth. The diffraction spots are elongated along the circles which are centred at

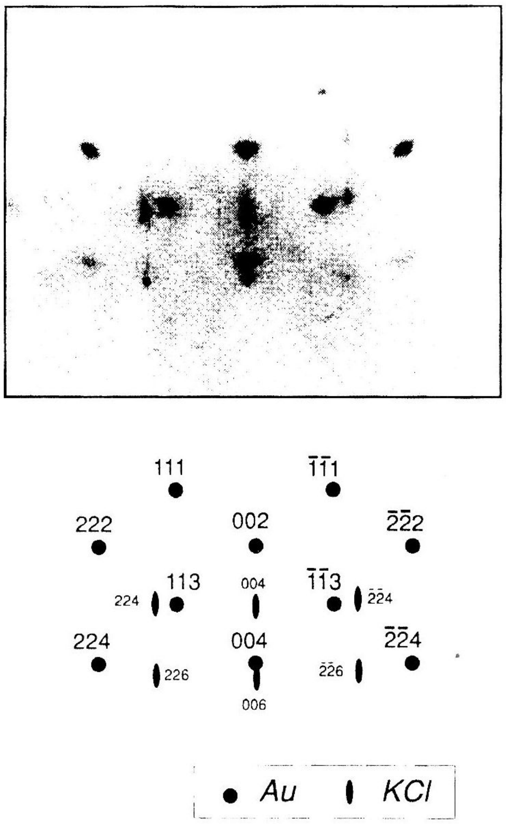

Fig. 1. RHEED pattern and its simulated diagram of Au *particles supported by* KCl *(001) substrate along the [110] crystallographic direction.*

the position of the (000) spot on the screen. This elongation is probably given by the weak azimuthal disorder of Au particles along their [001] crystallographic direction perpendicular to the substrate surface. The azimuthal disorder is probably a consequence of a lattice mismatch. Its measured values are introduced in Table 1. Corresponding k parameter gives a ratio between the lattice parameter of KCl substrate and Au particles in the direction parallel to the substrate surface.

The broadening of the spots is caused by the finite extent of the crystallites [2]. In the case of TEM, the angular breadth β of an electron diffraction ring intensity profile, measured at half–peak height, can be used to provide an estimate of the average crystallite diameter L by application of the Scherrer equation [3] $L = K\lambda/\beta$, where λ is the electron wavelength and K is a constant determined by the crystal shape; it is usually between 0.85 and 1.0. By replacing β by b/D, (b is a diffraction spot breadth and D the distance between the sample and the screen) one can write $L = KD\lambda/b$. We have used this equation for the derivation of epitaxial Au particles from the RHEED spot profiles. For simplicity, we took $K = 1$. A special software equipment, described in detail in Ref. 5, performing an image analysis of the diffraction pattern, permitted the determination of lattice parameter and FWHM parameter (full width at half maximum) with a high precision.

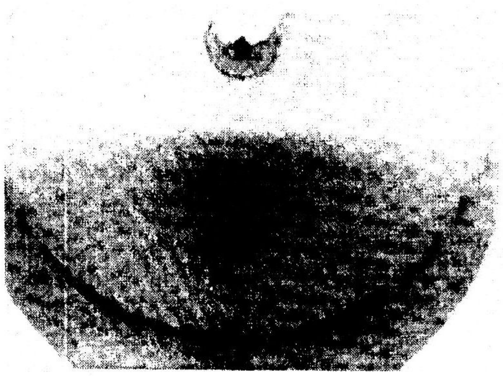

Fig. 2. RHEED pattern of sapphire (0001) surface. The incident beam is parallel to the crystallographical direction [100].

For precision analysis, true profiles would have to be generated by a deconvolution process requiring an accurate experimental instrumental profile, corresponding to that produced by infinite crystals illuminated under identical conditions [3]. The corrected value of b, corresponding to a measured value b_m was obtained using the following formula: $b^2 = b_m^2 - b_i^2$. The instrumental profile, b_i, was determined from an intensity profile obtained under identical conditions (30 keV) for a high quality single crystal of sapphire (0001). The corresponding RHEED diffraction pattern is presented in Fig. 2. The distribution of diffraction spots along a Laue circle indicates a crystal surface without defects. The high quality of the sapphire surface was confirmed by the atomic force microscope analysis. The results are not presented in this paper.

The reliability of this method was controlled by comparing the RHEED and TEM results (see Table 1). A similar approach has been used in Ref. 4.

Due to the elongated form of the diffraction spots, we have evaluated the FWHM parameter in the direction of the narrowest intensity profile. From the RHEED study of disordered surfaces [2], it is known that the formation of flat islands gives the RHEED diffraction pattern in form of strikes perpendicular to the substrate surface. Therefore, in our case we can suppose that the particles are three–dimensional. So, the L parameter can be considered as the average particle size. Figure 3 shows an example of intensity profiles of Au 113 spots (from Fig. 1). From the measured FWHM values (corrected for the natural width of the electron beam) we have calculated the average particle size in accordance with the above mentioned expression. These values as well as the average particle sizes obtained by observation of TEM micrographs are presented in Table 1.

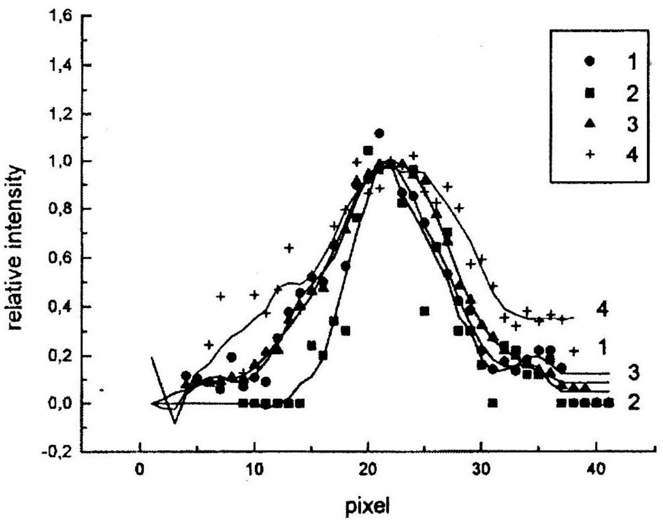

Fig. 3. Example of intensity profiles of 113 Au *diffraction spot for four different samples. The incident beam is parallel to the crystallographic direction [110].*

The particle sizes obtained by RHEED method are approximately of 30 % smaller than that ones obtained from TEM micrographs. Several effects can contribute to this discrepancy, the additional broadening of the diffraction spots can be caused by the following phenomena:

a) azimuthal disorder of Au particles

b) existence of polycrystalline phase of Au particles without any preferential orientation. These particles, detected by TEM and not seen by RHEED, can be smaller that the epitaxial ones

c) internal stress inside the Au particles. The KCl/Au lattice parameter ratio k shows the Au lattice dilatation up to 0.8

On the other hand this discrepancy could be smaller if the morphological constant K is taken higher than unity, at about 1.4. We can not ascertain whether this is justified due to the relatively small number of results available at this time.

4. Conclusion

In situ investigation of small supported particle morphology is very important from the point of view of the investigation of size effects in heterogeneous catalysis [6]. The above presented results show that the RHEED method can be used for particle size evaluation. We have found a relatively good agreement between the values of average particle sizes determined from the TEM and RHEED methods. Namely, the use of RHEED for observation of relative particle size variations during the catalyst – gas interaction seems to be very promising.

We shall continue to investigate this method in order to increase the precision of particle size determination. Namely, the role of constant K has to be elucidated.

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PROUČAVANJE Au/KCl SUSTAVA POMOĆU RHEED-A RADI OCJENE OVISNOSTI PROFILA DIFRAKCIONIH TOČAKA O VELIČINI ČESTICA

Primijenjena je refleksijska difrakcija elektrona više energije (RHEED) u istraživanju rasta Au nakupina na KCl podlozi. Opaženo je oblikovanje trodimenzijskih zrnaca. Oblici zrnaca naknadno su odredeni transmisijskom elektronskom mikroskopijom i rezultati su uspoređeni s analizama RHEED profila točaka.