Introduction

The electrocatalytic activity toward the oxygen reduction reaction (ORR) in acid medium, as well as the selectivity in the presence of methanol, has been studied on ruthenium chalcogenide-like clusters. We have shown that the clustertype compound Ru\(_2\)Se\(_y\), prepared from the precursor Ru\(_3\)(CO)\(_{12}\) and addition of selenium in xylene or 1,2-dichlorobenzene has superior properties against pure Ru clusters with respect to its structural stability and its resistance to oxidation in the presence of oxygen in the gas phase. Albeit ruthenium and selenium are immiscible in the bulk phase but only form the single compound Ru\(_2\)Se\(_2\): no separate Se-containing phase has been observed during the cluster formation, and the electronic state of Se in our Ru\(_2\)Se\(_2\) cluster compound is still an open question. Using the same chemical synthesis route, other authors prepared similar compounds with a consecutive sintering in selenium (Merck). The reaction is conducted in an inert atmosphere of nitrogen under refluxing conditions. The synthesis temperature was determined by the boiling point of the solvent at 180 °C. The complex in the solution was recovered and cooled down after a reaction time of 60 min to \(T < 0\) °C to stop the reaction. The solvent was evaporated in a rota-vapor at 70 °C and 13 mbar. The resulting solid was dissolved in dichloromethane. Thin-layer chromatography was applied to separate the complex from unreacted Ru\(_3\)(CO)\(_{12}\), which was very little. This separation was carried out in a mixture of ethyl ether and ethyl acetate (50:50) using a 1-mm-thick immobilized silica layer on a glass plate. The complex did not migrate and was extracted with dichloromethane and dried. The purity of the complexes thus separated could be controlled by high-performance liquid chromatography on column. By comparing the XRD diffraction measurements with the ICSD data (collection code 73582), the structure of Ru\(_4\)Se\(_2\)(CO)\(_{11}\) was identified, see Figure 1. This synthesis route is particularly very facile in comparison to a synthesis reported some time ago by Layer et al. using Ru\(_3\) (CO)\(_{12}\) and PhSeSePh in a closed ampule under vacuum at 185 °C for 19 h.

X-ray Diffraction and Debye Function Analysis (DFA).

X-ray patterns were obtained with a Guinier powder diffractometer (HUBER), set to the 45° transmission position. A Johansson-type Ge monochromator produces a focused monochromatic Cu K\(_{\alpha1}\) primary beam (\(\lambda = 1.5406\) Å). Structural changes in different ambient and elevated temperatures can be studied with a specially designed in situ cell attached to the goniometer. The powder samples were pressed slightly to pellets 8 × 15.5 × 0.1 mm\(^3\) in size. These pellets were mechanically unstable and were accordingly fixed tightly, but...
not gastight, between two 0.1 mm beryllium plates before inserting them into the sample holder. In the so-called open slit (OS) mode, the counter slit was set stationary to one or two prominent peaks of the sample. In this mode, time-resolved in situ studies of particle growth or oxide formation are possible. Some angular scans were performed ex situ. In this case, the samples were fixed between two 0.003 mm polyethylene foils and immediately measured in ambient conditions. The background-corrected patterns were subjected to the usual angular correction for absorption, polarization, and geometrical factors and plotted versus the reciprocal scattering length \( b = 2 \sin(\theta)/\lambda \).

**DFT Calculations.** To study the stability of all low-index RuSe\(_2\) surfaces, density functional theory (DFT) pseudopotential slab calculations were preformed using the SeqQuest code.\(^{16,17}\) Throughout the calculations, the PBE\(^{18}\) generalized gradient approximation (GGA) exchange-correlation functional was used together with a standard (nonlocal) norm-conserving pseudopotential\(^{19}\) invoking a nonlinear core correction.\(^{20}\) The basis sets were optimized “double-\(\zeta\) plus polarization” contracted Gaussian functions.

With these calculated parameters, we first studied the bulk properties of RuSe\(_2\) in the well-known pyrite structure. The optimized lattice constant of 6.07 Å deviates from the experimental value by only 2.4% and is also in good agreement with all-electron calculations\(^{21}\) (\( a_0 = 6.0 \) Å). In addition, the formation energy gained by forming a unit of RuSe\(_2\) bulk out of Ru bulk and Se bulk of 0.41 eV and the bulk modulus of 1.34 Mbar conform to corresponding all-electron calculations of 0.41 eV and 1.36 Mbar, respectively. On the basis of the calculated lattice constant, all low-index RuSe\(_2\) surfaces were studied using slabs of at least 17 layers (showing convergence with slab thickness) separated by 20 Å vacuum. In each case, the entire geometry of the system was allowed to freely optimize (to <0.01 eV/Å), resulting in symmetric top and bottom slabs.

**Thermodynamic Considerations.** To compare the stability of different surfaces, the important quantity is the surface free energy

\[
\gamma = \frac{1}{A} \left[ G_{\text{slab}} - N_{\text{Ru}} \mu_{\text{Ru}} - N_{\text{Se}} \mu_{\text{Se}} \right] \tag{1}
\]

where \( A \) is the surface area (in the case of our slab geometries, both the top and bottom layers have to be considered) and \( G_{\text{slab}} \) is the Gibbs free energy of the slab containing Ru and Se atoms (\( N_{\text{Ru}} \) and \( N_{\text{Se}} \)) with the chemical potential \( \mu_{\text{Ru}} \) and \( \mu_{\text{Se}} \) of their corresponding reservoirs. Because in the present work we concentrate on RuSe\(_2\) surfaces, we assume that bulk RuSe\(_2\) is in equilibrium with both reservoirs, leading to

\[
\mu_{\text{RuSe}_2}^{\text{bulk}} = \mu_{\text{Ru}} + 2\mu_{\text{Se}} \tag{2}
\]

Using this condition to replace \( \mu_{\text{Se}} \), eq 1 becomes

\[
\gamma = \frac{1}{A} \left[ G_{\text{slab}} - \frac{N_{\text{Se}}}{2} \mu_{\text{RuSe}_2}^{\text{bulk}} + \left( \frac{N_{\text{Se}}}{2} - N_{\text{Ru}} \right) \mu_{\text{Ru}} \right] \tag{3}
\]

where we replaced \( \mu_{\text{RuSe}_2}^{\text{bulk}} \) by the Gibbs free energy \( \mu_{\text{RuSe}_2}^{\text{bulk}} \) of the bulk compound. Because in our calculation we only consider solid surfaces, entropy contributions are expected to be small, allowing us to use the DFT total energies instead of \( G_{\text{slab}} \). This equation allows us to study the surface phase diagram as a function of \( \mu_{\text{Ru}} \) (in the following we referenced \( \mu_{\text{Ru}} \) to \( \mu_{\text{RuSe}_2} \) by using \( \Delta \mu_{\text{Ru}} = \mu_{\text{Ru}} - \mu_{\text{RuSe}_2} \)).

This method allows us to connect the surface with both bulk reservoirs, assuming a continuous exchange of atoms between the surface and both reservoirs. Besides the thermodynamic equilibrium, which can be described by this approach, the actual process of atom diffusion out of or into the particle itself would be very interesting. But especially on nanoparticles there is a large variety of different processes possible (e.g., on different surface planes, near step edges or kinks, or even more importantly at surface defects), which so far extends the capabilities of quantum-mechanical calculations. Corresponding simulations with larger scale methods will be performed in the near future.

In addition, we would like to point out that because thermodynamics is one of the main driving forces during the compound formation or the genesis, respectively, studying the thermodynamic stable RuSe\(_2\) surface structures already provides useful insight into the final surface and bulk structures of the compounds.

**Results and Discussion**

**XRD Analysis.** Figure 2 shows an open slit measurement (receiving slit width \( \Delta \theta = 1^\circ \)) of the intensity around the strongest peak of the carbonyl compound Ru\(_4\)Se\(_2\)(CO)\(_{11}\) (upper curve, Bragg window at \( b = 0.2 \) Å\(^{-1}\) (\( \theta = 8.6^\circ \)) in Figure 1),
and at the same time the intensity around the diffuse peak expected for nanoscale ruthenium particles (lower curve, Bragg window at \( b = 0.47 \) Å\(^{-1} \) (\( \theta = 21.4^\circ \)) in Figure 1). During the measurement, the sample was treated by flowing nitrogen (purity 6.0) or alternatively in helium with a temperature ramp of 8 °C/min or 2 °C/min. It is evident that the crystalline structure of the carbonyl phase breaks down at around 220 °C, which is related to the rapid loss of intensity of the Ru\(_{2}\)Se\(_2\)(CO)\(_{11}\) peak.

The small further decrease of the intensity at higher temperatures ca. 500 °C can be attributed to growth processes. The simultaneous intensity increase in the second Bragg window relates to the formation of a nanoscale phase of ruthenium.\(^{22}\) Figure 1 shows the diffraction pattern of the precursor carbonyl compared with the structure factors of the bulk carbonyl as referred to the Joint Committee on Powder Diffraction Standards International Center for Diffraction Data (JCPDS-ICDD) database, while Figure 3 shows the diffraction pattern of the same material taken after pyrolysis in helium was stopped at 220 °C. The solid line in this figure is a simulation calculation using \( hcp \)-type ruthenium model particles of sizes around 1–3 nm. The related size distribution resulting from the simulation is given in the inset of Figure 3. This data have been achieved by the method of Debye function analysis (DFA) explained elsewhere.\(^{8,9}\) The result of thermal decomposition in the gas phase is very similar to our earlier investigation of cluster-like compound Ru\(_x\)Se\(_y\) prepared by the decomposition in dichlorobenzene: \( hcp \) nanoparticles with an average size of 1.7 nm, an interatomic distance equal to bulk ruthenium, and no indication of a separate Se-containing phase is detected.

When the treatment temperature in He is increased to 430 °C (Figure 4), no dramatic changes are visible in the diffraction pattern, except a narrowing of the \( hcp \) ruthenium lines due to a certain growth of the particles. The two arrows in the figure inset point to two weak and diffuse peaks assigned to a first formation of very small pyrite-type RuSe\(_2\) particles. Figure 5 shows the DFA simulation of the corrected diffraction pattern (beryllium background removed) after final heating in helium at 430 °C for 80 min. The particles have a surprisingly uniform size of 3.1 nm at that stage; see the inset of Figure 5.

After treatment in N\(_2\) at a temperature around 600 °C (cf. Figure 2), the diffraction pattern splits into two phases: a ruthenium phase, probably free of selenium, and the ruthenium diselenide phase (RuSe\(_2\)). This result is evident from the structure factors of both phases that are plotted as vertical bars in Figure 3, and cf. Figure 1. The inset shows the mass fraction vs cluster diameter. The last four averaged scans of Figure 4 are shown after correction of the background and the application of angular correction factors (dotted curves). The solid line is a DFA simulation of the diffraction pattern using \( hcp \) ruthenium model clusters. The inset shows the resulting mass fraction vs cluster diameter.

Ru\(_{2}\)Se\(_2\), Surface Morphology. Studying the structure of realistic Ru\(_{2}\)Se\(_2\) nanoparticles usually requires large system sizes and long time scales, which is far out of the range of quantum-mechanical calculations. However, as a first step toward understanding the structure of those compounds we idealized to (semi-)infinitely extended surfaces (length scale) and the thermodynamic equilibrium (time scale). This already allows us to study the preferred surface structure, which due to thermodynamics at least the larger particles try to adopt, for different environmental conditions (given by the Ru-chemical potentials). The structure and composition of smaller particles might also be influenced by so-called quantum-size effects, but this is out of the scope of the present work.

For the surface morphology of Ru/Se nanoparticles, we have to consider two cases:

1. \( \mu_{\text{RuSe}_2} > \mu_{\text{Ru}} + 2\mu_{\text{Se}} \): Under this condition, the formation of bulk RuSe\(_2\) is thermodynamically unfavorable. Therefore, it
can be assumed that all Se present in a particular Ru$_x$Se$_y$ particle will be at or near the surface of a pure Ru particle (Ru core). However, besides forming a layer of adsorbed Se on the surface it might also be possible that the Ru core is covered with a thin shell of a certain Ru$_x$Se$_y$ phase. With regard to the phase diagram shown in Figure 7, this corresponds to the area in which $\Delta \mu_{\text{Ru}} < 0$. Compared to the bulk-terminated surface of RuSe$_2$, which would result in a horizontal line in the phase diagram, under those conditions even the pyrite crystal structure seems to prefer a Se-rich surface, which under these conditions might also support the picture of the particle structure, consisting of a Ru core with a selenide phase on the surface. The exact structure will be subject of a forthcoming publication.

2. $\mu_{\text{RuSe}_2} \leq \mu_{\text{Ru}} + 2\mu_{\text{Se}}$. Under this condition, the formation of RuSe$_2$ is thermodynamically favorable. To investigate the preferred surface composition for this case, all low-index surfaces of RuSe$_2$ with different surface terminations were calculated and will be discussed in the following.

The different, nonequivalent surface structures of RuSe$_2$ are shown in Figure 8. With both the (100) and (110) surfaces, three different surface terminations are possible. For RuSe$_2$(100) configurations 1 and 3 are Se-terminated, whereas the latter one shows the stronger changes in the surface structure due to relaxation. This is certainly because of the large amount of Se atoms on the surface, which are not stabilized by the presence of Ru atoms. Similar to RuSe$_2$(110) there are also two Se-terminated surface configurations (1 and 2). However, compared to (100) the surface relaxation for all three configurations is much smaller. The RuSe$_2$(111) surface is more complex. Here we have to distinguish five different surface structures.

On the basis of the DFT-calculated total energies of the various slabs, the surface free energies, which were evaluated with eq 3, are summarized in Figure 7. Because the RuSe$_2$ bulk phase is only stable for $\Delta \mu_{\text{Ru}} \geq 0$ eV, in the following we will focus on this condition. At $\Delta \mu_{\text{Ru}} = 0$ eV, where both phases (the separated and pyrite phase) are in thermodynamic equilibrium (which is the most interesting condition), we find configuration 5 of RuSe$_2$(111) to be the most stable thermodynamically. Compared to the RuSe$_2$ bulk composition, this surface is rather Se-rich and has two additional Se atoms per surface unit cell. Again, at this phase separation line the close-packed (111) surface is not the most stable, but the more opened (100)-surface.

Figure 6. WAXS pattern of Ru$_x$Se$_y$ after 600 °C treatment. The thick vertical bars show the hcp structure of Ru. The presence of the RuSe$_2$—pyrite phase is also evident (thin bars and some Miller indices).

Figure 7. Surface phase diagram of RuSe$_2$ (pyrite-structure) involving all low-index surfaces. For $\Delta \mu_{\text{Ru}} = 0$ eV ($\Delta \mu_{\text{Ru}}$ is referenced to $\mu_{\text{RuSe}_2}$), where the RuSe$_2$ compound is in equilibrium with both reservoirs (Se bulk and Ru bulk), a Se-terminated surface is the most stable thermodynamically. Increasing $\Delta \mu_{\text{Ru}}$ leads to a depletion of Se from the surface.

Figure 8. Hard-sphere models of the different surfaces studied to calculate the surface phase diagram (see Figure 7). For each surface, different terminations were possible, leading to the various configurations (geometry optimized structures are shown) shown below each system.
high values of $\Delta \mu_{\text{Ru}}$. This already indicates a preference for a Se-terminated surface even under conditions where the bulk compound should form. Interestingly, the phase diagram shows that when $\mu_{\text{Ru}}$ is increased the preferred surface orientation alternates between RuSe$_2$(100) and RuSe$_2$(111). RuSe$_2$(110), which one would expect to have a lower surface free energy than RuSe$_2$(100), plays only a minor role. Although among the bulk-terminated surfaces RuSe$_2$(100) is the most stable (see horizontal lines in Figure 7), it seems that the presence of additional Se on the surfaces of RuSe$_2$(111) increases their stability.

Finally, it should be remarked that the above considerations did not take any kinetic barrier into account, which might be involved in forming RuSe$_2$ bulk out of Ru bulk and Se bulk. As already mentioned above, we are now in the process of performing larger scale molecular dynamic (MD) simulations on the growing process itself. For this, all of the DFT calculations (structures and energies) described in the present paper were used to generate an accurate Ru/Se interaction.

Cluster-like Formation Dynamics during Pyrolysis. As shown in Figures 2 and 3—5, the evolution of the final catalyst particle nanostructure, under temperature-controlled conditions, depends on significant initial fragmentation of the heteronuclear cluster framework followed by preferential nucleation at ruthenium centers. From model calculations, we know that the relative intensity function will not be significantly modified by replacement of some surface Ru atoms by Se atoms, even if the Ru-Se distance is altered against the Ru-Ru distance. After pyrolysis of the precursor molecule, only a single phase remains. This phase can be quantitatively attributed to a nanocrystalline phase of hcp-type. If the selenium atoms did not escape fugacious (which would only be partly possible, because the selenium reappears as RuSe$_2$ at high temperature), then we would have seen it because it cannot be overlooked, due to the fact that the scattering power of Se is about 60% of that of Ru; thus, selenium should contribute about 30% to the total intensity. This proves that Se must be incorporated into the hcp particles. There is no direct proof that Se is located at the nanoparticle surface. But there are two arguments that strongly support this thesis: (i) Se is insoluble in bulk ruthenium, and (ii) if Se would in fact show a solubility to Ru on a nanoscale, then we would expect a measurable change of the mean interatomic spacing, which is not observed.

According to Figure 2, the thermal decomposition process can be subdivided into three regions related to the time of treatment, namely, (i) 20—30 min (150—240 °C) breakdown of the carbonyl and formation of ruthenium clusters; (ii) 30—65 min (240—440 °C) slow growth of the preformed cluster by coalescence; and (iii) 65—80 min (440—500 °C) formation of a phase separation.

All of these processes describe the cluster evolution. The curve discontinuity, observed at $t = 30$ min, shows a sudden completion of the metallic cluster formation. As support, the dynamics leading to the formation of segregated core structures finds precedent in other bimetallic systems. The insight, however, in this work is that chalcogen coordination takes place onto ruthenium surface atoms and that there is formation of a narrow size distribution in the nonsupported chalcogenide particles with a compositional distribution, of 2:1 [Ru/Se], in a narrow size distribution in the nonsupported chalcogenide particles with a compositional distribution, of 2:1 [Ru/Se], in full agreement with previously reported works on the catalyst synthesized in organic solvent.

Moreover, the spectrum taken at 430 °C (Figure 4) already indicated the beginning of the formation of pyrite-type domains. As a matter of fact, according to the fixed ratio of Ru/Se (2:1) given by the initial compound Ru$_x$Se$_y$(CO)$_{11}$, the proposed segregation of selenium to the surface of hcp clusters will go into a saturation with the increasing cluster size, as shown in Figure 9.

The number of surface atoms, $N_s$, related to the core atom number, $N_c$, is plotted versus the cluster diameter $D$ for $N = 13$, 57, and 153. The extrapolated curve to $N_s/N_c = 0.5$ furnishes a critical cluster size of 3.4 nm. The circle in Figure 9 indicates the cluster size determined in Figure 5, at the beginning of the formation of pyrite RuSe$_2$. Further growth would lead to an excess of selenium onto the ruthenium surface, favoring pyrite formation. In full agreement with these considerations, the embryonic nucleation of pyrite RuSe$_2$ domains is observed at the cluster size of 3.1 nm; see Figures 4 and 5. Furthermore, as clearly shown by DFT calculations, the Ru—Se system evolves with the temperature up to a thermodynamically stable phase formation within a pyrite structure: RuSe$_2$. The latter is a low-band gap semiconductor (0.76 eV). Summing up, the material dynamics takes place from a heteronuclear cluster compound to a semiconductor, crossing through a chemically stable selenium coordinated ruthenium core. This chemical phenomenon leading to a catalyst material, totally tolerant for the oxygen reduction reaction in the presence of methanol, represents the bottom-up approach of ruthenium selenide Ru$_x$Se$_y$. It also explains the catalytic activity nature of ruthenium-black’s surface modified with selenium and/or the ruthenium chemical-generated and further modified by selenium.

Conclusions

In summary, nanodivided Ru$_x$Se$_y$ cluster-like materials are derived from pyrolysis of a heteronuclear transition-metal complex compound. This phenomenon takes place between 200 and 240 °C. Under this condition, the chalcogen atoms organize preferentially on the surface of the core-formed agglomerated ruthenium atoms. The Ru$_x$Se$_y$ represents a prior intermediate state before reaching a more stable compound with a pyrite structure. As a combination of DFT calculations and thermodynamic considerations indicate, even under conditions where RuSe$_2$ is the thermodynamically stable bulk phase, a Se-rich surface is preferred. If the two separated bulk phases (Ru bulk and Se bulk) are thermodynamically more stable, then Se might coordinate forming a thin selenide phase on the surface of a Ru particle.

Figure 9. Ratio of the number of surface to core atoms, $N_s/N_c$, as a function of cluster diameter, $D/D_0$. The “magic-numbers” of hcp clusters are shown as crosses in the figure. $D_0$ is the interatomic distance ($D_0 = 2.71$ Å for Ru).
Acknowledgment. N.A.V. expresses his thanks to the Alexander von Humboldt Stiftung and the Max-Planck-Society for funding his stay at the Fritz-Haber-Institut. T.J. greatly acknowledges support by the “Fonds der Chemischen Industrie” (VCI) and P.K. by the German Academic Exchange Service (DAAD). We are grateful to Dr. T. Lana-Villarreal for her help in the complex preparation.

References and Notes

(22) The small drop of the intensity before the dramatic increase can be explained by the breakdown of the carbonyl structure in the Bragg window at 21.4°, cf. Figure 2.