



Temperature dependent XPS study of CO dissociation on small Rh particles

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We have used temperature dependent X-ray Photoelectron Spectroscopy (XPS) to study the heating-induced CO dissociation on oxide-supported Rh particles through observation of changes undergone by the adsorbate CO and the formation of atomic carbon from the dissociation process. Different behaviour upon heating was observed for the two CO species on the islands. Our study indicates that one of the species is desorptive and that the other is dissociative. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

CO dissociation is a fundamental process in heterogeneous catalysis. This step is crucial for e.g., the so-called Fischer-Tropsch process (conversion of CO into hydrocarbons).¹ This has motivated investigations devoted to the fundamental properties of CO dissociation on different substrates using surface science techniques, such as Thermal Desorption Spectroscopy (TDS). Concerning CO dissociation on Rh single crystals it has been shown that no dissociation occurs on close-packed surfaces, such as Rh(100)² and Rh(111),³ but that it does occur on at least some of the more open surfaces, such as Rh(210).⁴ TDS studies of the particle size-dependence of the CO dissociation on Rh particles have however given seemingly contradictory results.⁵⁻⁷

An alternative way to study the CO dissociation process is to directly monitor changes of the adsorbed CO and the formation of atomic carbon on the surface. This can be done with X-ray Photoelectron Spectroscopy (XPS), which has the advantages of atomic selectivity and high surface sensitivity. XPS has previously been used to complement TDS, e.g., in studies of CO dissociation on Rh(210).⁴ For small supported Rh particles we have used XPS to establish the existence of a size-dependent maximum in the dissociation activity.⁸⁻¹⁰ We have also shown that CO is adsorbed in two different sites upon these clusters and that these sites play different roles in the dissociation process.¹⁰ In this paper we will perform a detailed analysis of heating series on two such islands of different size, demonstrating how the present approach to temperature-dependent XPS can yield information about the CO dissociation process. Analysis of the changes in the CO C 1s

supports the suggestion that one of the species desorbs upon heating and that the other dissociates.

2. Experimental

The experiments were carried out at Beamline 22 at the Swedish synchrotron facility MAX-lab in Lund. The setup at the beamline consists of a modified Zeiss SX-700 monochromator in conjunction with a large hemispherical electron energy analyzer for photoemission.¹¹ XP spectra were recorded at a photon energy of 380 eV for C 1s (total resolution 0.4 eV). The XPS binding energies are referred to the Fermi level of the NiAl(110) substrate. The preparation of the well-ordered Al₂O₃-film has been extensively described elsewhere.¹²

Rh (Heraeus, >99.9%) was deposited using a commercial evaporator (Focus EFM 3) based on electron bombardment which allows evaporation from a rod. During evaporation the sample was put on a retarding potential to avoid effects due to ions produced in the evaporation source which are accelerated towards the sample. The evaporator had previously been calibrated using a quartz microbalance, which gives the nominal film thickness. During deposition the substrate was held at room temperature. Initially the growth of two-dimensional Rh islands is observed, but as the size increases the islands start to grow three-dimensionally.¹³ The islands studied in this work both have three-dimensional character. Measurements with STM have given estimates for the average island sizes.⁹ In this paper we will present data for islands with an average of 500 and 10,000 atoms, respectively.

The Rh islands were subsequently exposed to 40 L CO at a temperature of 90 K. This dose should be sufficient to saturate the islands with adsorbed CO.¹⁴ The samples were then quickly

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annealed to different temperatures and thereafter cooled to 90 K again before the spectra were recorded. The heating-induced changes were studied using XPS. The temperature of the sample was determined using a K-type thermocouple spot-welded to the crystal, and the heating was performed by passing a current through the tungsten wire holding the sample.

3. Results and discussion

First we will present the heating-induced changes in the CO-Rh system as can be directly observed from the XPS raw data. We will then proceed with a more detailed quantitative analysis of these changes and extract information about the CO dissociation process.

Figure 1 shows the evolution of the C 1s XPS peaks for islands with an average of 10,000 atoms as a function of sample annealing temperature. The spectra are normalized with respect to the background at binding energies lower than the C 1s peaks, so that the intensities for the different temperatures can be directly compared. The 90 K spectra show a distinct peak at ~ 286.0 eV due to the adsorbed CO. This binding energy is consistent with those found for CO adsorbed on Rh(111); 286.0 eV for CO adsorbed on-top and 285.4 for CO in a three-fold-hollow site.¹⁵ After the first two heating steps to 200 K and 300 K no significant change is observed for the intensity of the CO C 1s peak. After heating to 350 K the CO C 1s intensity has decreased and this

C1s XPS as function of temperature

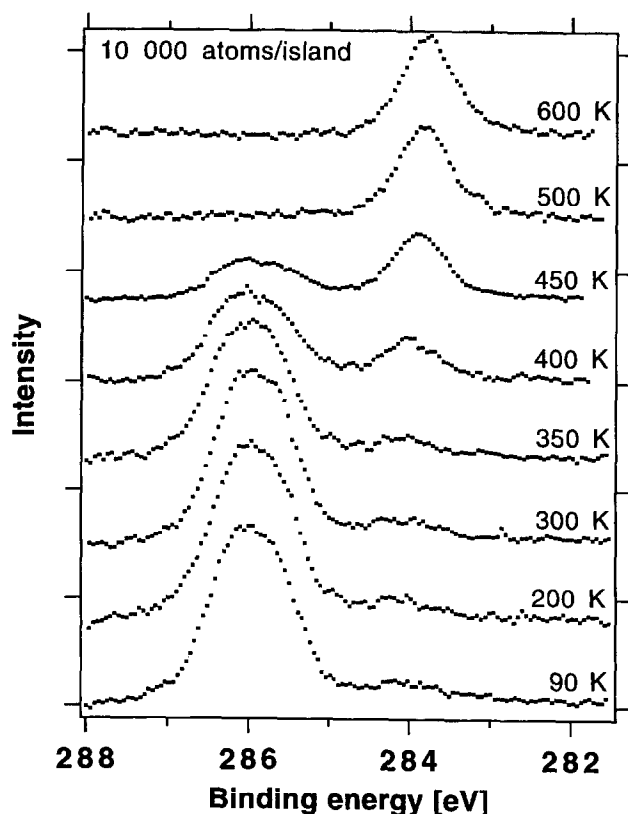


Figure 1. The evolution of the C 1s XPS peaks for islands with an average of 10,000 atoms per island as a function of sample heating. The spectra have been normalized with respect to the background at lower binding energy.

decrease continues upon further heating to 500 K where the CO C 1s has completely vanished. At temperatures above 350 K the formation of a second peak at ~ 286.0 eV is observed. We attribute this peak to atomic carbon produced through CO dissociation. After heating to 500 K and above, only the atomic carbon peak remains.

The dissociation activity of the island is given by the ratio between the intensities of the initial CO peak and the final atomic carbon signal, as presented elsewhere.^{9,10} A more detailed study of the heating induced changes can however give further information about the dissociation process.¹⁰ As mentioned above no significant formation of atomic carbon is seen upon heating to 350 K, while the intensity of the CO peak decreases. This suggests that the initial decrease of the CO peak is mainly caused by desorption, which consequently begins prior to dissociation. It can also be seen that the peak shape of the CO C 1s peak changes during heating to 300 K. These changes have been explained as heating-induced site shifts of the adsorbed CO. It has also been suggested that CO adsorbed in the two different types of sites on the clusters should behave differently during heating above 300 K.¹⁰ To investigate this in detail a careful curve-fitting analysis¹⁶ was performed for both the heating series presented in Fig. 1 and a similar series for islands with an average of 500 atoms.

Figure 2 shows a typical C 1s spectrum from the two heating series. This particular spectrum was recorded for CO adsorbed on Rh islands with an average of 10,000 atoms after consecutive heating steps up to 450 K. The shape of the CO C 1s peak clearly indicates the presence of two components. These two components and the atomic carbon peak, as determined through curve fitting, are also presented in the figure. The dotted line through the data points shows the summation of the three components.

The two CO components A and B have been interpreted as being due to CO adsorbed in two different types of sites on the Rh islands. The coordination is lower for the A-sites than for the B-sites, as indicated by comparison to single crystal XPS-results. It has also been proposed that it is the CO adsorbed in the B-sites which dissociates.¹⁰

The decrease of the total CO intensity is caused by desorption and dissociation. The magnitudes of both these effects can be

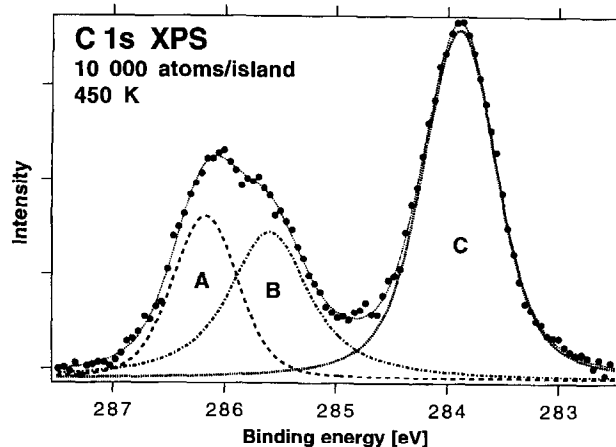


Figure 2. C 1s XPS spectrum for CO adsorbed on Rh islands with an average of 10,000 atoms recorded after consecutive heating steps up to 450 K. Peak components as determined through curve-fitting are also included. Components A and B are identified as due to adsorbed CO. Component C is atomic carbon left by the dissociation process.

directly determined through the curve-fitting analysis. The intensity decrease caused by dissociation is reflected by the increase of the atomic carbon peak. The decrease due to desorption can then be determined as the total decrease of the CO peak minus the decrease due to dissociation. The intensity changes of the two components of the CO peak can also be determined through the analysis.

The determined intensity changes for the two heating series are presented in Fig. 3. The changes observed for the two CO components A and B are presented with filled markers. The two different causes for CO intensity decrease, desorption and dissociation, are presented with unfilled markers. The intensity changes have been internally normalized to unity being the total original CO C 1s intensity. For both situations the same correlation is observed. The determined changes of component A clearly follows the changes observed for the desorption indicating that it is the CO adsorbed in the A-sites which desorbs. A similar correspondence exists between the changes of component B and the dissociation suggesting that it is the CO adsorbed in the B-sites which dissociates. This strongly supports the suggestion that species A exhibit a desorptive behaviour and that species B

exhibit a dissociative behaviour upon heating to temperatures above 300 K.¹⁰ The figure also shows that, for our heat-treatment, desorptions set in earlier and is initially faster than dissociation.

Although these results are internally consistent, comparison to TDS measurements on these islands¹⁷ demonstrates the influence of the heat-treatment on the obtained results. For the TDS measurements no desorption was seen below 300 K, consistent with the measurements reported here. However, in the TDS study the desorption maximum was found at around 500 K, where we no longer observe any adsorbed CO on our islands. This discrepancy is due to the different heating procedures used. TDS involves the uniform and slow (1.5 K s^{-1} in the data we compare to ours¹⁷) heating of the sample throughout the measured temperature range. For our XPS measurements, the sample was both heated and cooled again for each temperature, and at an uncontrolled rate, so that the total desorption is not comparable for the same indicated measurement temperature. This comparison clearly shows that the qualitative information obtained in the present work is valuable, especially in the comparison of, e.g., different sites or cluster sizes. However, as for all such measurements of kinetics-dependent processes, the trends

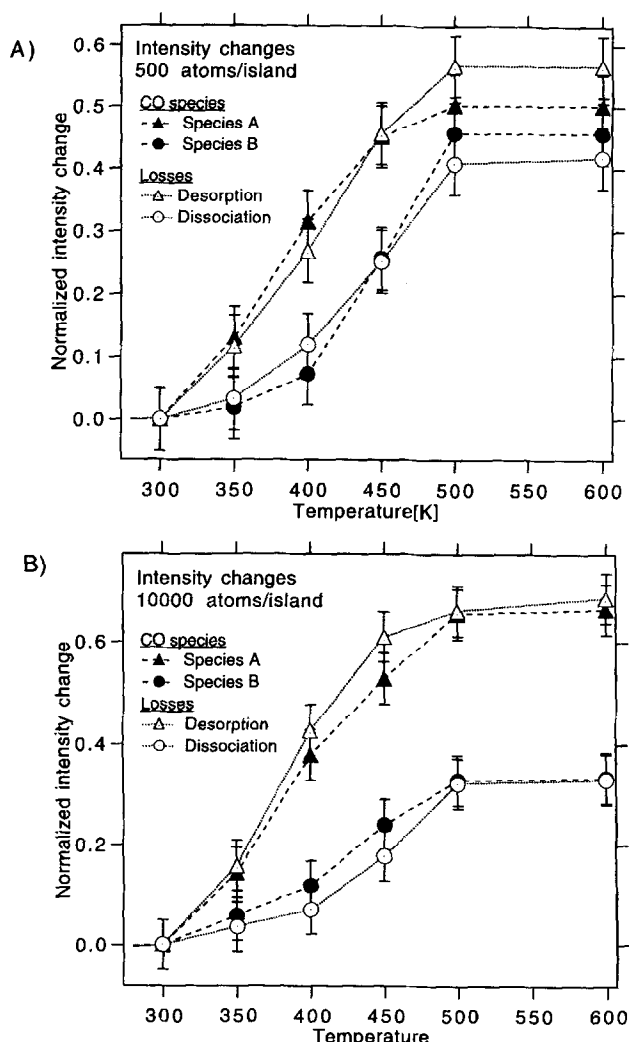


Figure 3. The determined intensity changes for the different components in the C 1s XP-spectra for islands with an average of 500 and 10,000 atoms, respectively.

observed have to be considered with caution, as, e.g., the temperature scale of the data can be strongly dependent on the heating procedure.

4. Conclusions

We have used temperature dependent XPS to observe changes undergone by adsorbed CO and the formation of atomic carbon upon heating-induced dissociation of CO on oxide-supported Rh islands. The observed changes suggest that the two different CO species on the islands exhibit different behaviour upon heating. The CO adsorbed in sites with lower metal-coordination desorb, whereas CO in more highly-coordinated sites dissociate.

Acknowledgements

This work has been supported by the Swedish Materials Research Consortium on Clusters and Ultrafine Particles (which is funded by the Swedish National Board for Industrial and Technical Development (NUTEK) and the Swedish National Science Research Council (NFR)), Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen. The authors thank the staff at MAX-lab for invaluable experimental assistance. M.F. and J.L. thank the Studienstiftung des deutschen Volkes for a fellowship.

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