

Steps and catalytic reactions: CO oxidation with preadsorbed O on Rh(553)

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Industrial catalysts often comprise of nanoparticles supported on high-area oxides, in order to maximize the catalytically active surface area and thereby minimize the amount of active material needed. Furthermore, nanoparticles contain steps and corners that, thanks to low coordination to neighbouring atoms, are more reactive [1] and, as a consequence, are often assumed to have higher catalytic activity. We have investigated the reaction between CO and preadsorbed O on a stepped Rh(553) surface, and show that the reaction indeed occurs at lower temperature than on the flat Rh(111) surface. We do, however, find that this is not thanks to reactions on the steps, but rather on the terraces close to the steps. Hence it is not the steps as such that are more active, but the presence of steps allows for relaxation of the atomic structure on the terraces, which lowers the corresponding reaction barrier. This finding can assist in optimizing the shape of the nanoparticles to further improve the activity of certain reactions.

Figure 1 shows the reaction between CO and preadsorbed O on a Rh(553) surface [2] at room temperature and 2×10^{-8} mbar as followed in situ by XPS. Initially the reaction occurs with approximately the same speed on Rh(553) at room temperature as on Rh(111) at 100°C, showing that the reaction indeed is faster on the stepped surface. But the reaction slows down after removal of 50% of the oxygen and seem to stop with about 25% of the oxygen still on the surface. Further analysis shows that the remaining oxygen is attached to the steps, suggesting that the step edge is not the active site, as one might expect. This is indeed confirmed by DFT calculations, that instead shows that the O in site 2, on the terrace but close to the step, is easiest to remove. The O atoms in site 3 reacts with the same speed after diffusing to site 2, while the diffusion from site 1 is slower giving rise to the change in reaction rate at a coverage of 0.2 ML as shown in the middle panel. The diffusion barrier for the oxygen in site 4 is very high explaining the convergence towards 25% of the oxygen remaining at the surface.

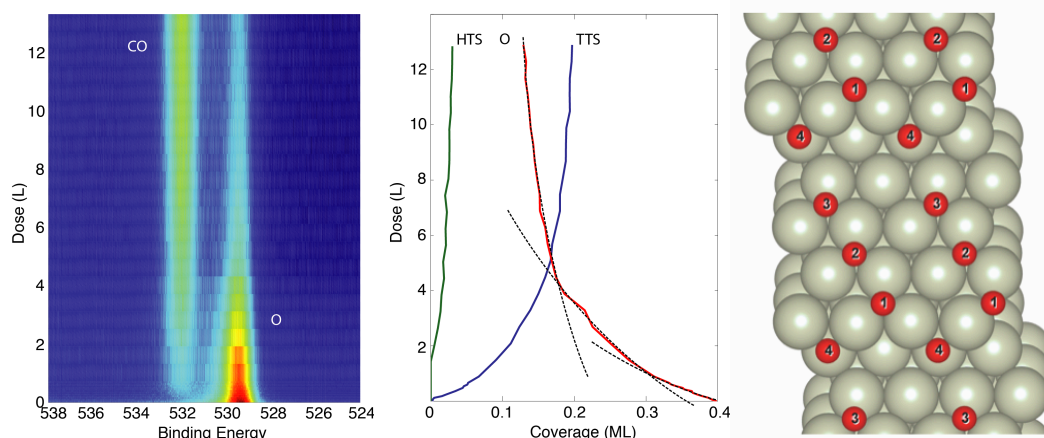


Figure 1: Reaction between CO and preadsorbed O on a Rh(553) surface.

[1] A. Stroppa, F. Mittendorfer, J.N. Andersen, G. Parteder, F. Allegretti, S. Surnev and F.P. Netzer, J. Phys. Chem. C, 113(3), 942-949 (2009).

[2] J. Gustafson, A. Resta, A. Mikkelsen R. Westerstrom, J. Andersn, E. Lundgren, J. Mittendrfere and G. Kresse Phys. Rev. B 60, 10, 1103 (2006).