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Unraveling the effect of Rh steps on the NO reduction by CO

Content

Tracking the active site of metallic nanoparticles is mandatory for tailoring new catalysts and promote a green environment. The activity of each of the facets of the nanoparticle will differ depending on the orientation and coordination of surface atoms [1]. However, isolating their individual activity is challenging. Within this context, curved single crystals possess different planes, hence they are ideally suited for selectively probing different types of under-coordinated atoms [2,3]. Using this methodology, we have studied the NO reduction by CO at 1 mbar on Rh stepped surfaces using a cylindrical section of a Rh(111) crystal. This peculiar sample features the flat (111) face at the center of the crystal, and surfaces with an increasing density of either A- (square) and B- (triangular) steps as one approaches each of the edges of the sample.

As a first step towards understanding the NO reduction, we exposed the sample to just NO to probe its dissociation. Upon slight annealing (100 °C), we observe a significant NO cracking occurring at the steps leading to atomic oxygen and nitrogen at the step edges. At the same time, NO remains molecularly adsorbed at terraces. The oxygen coverage increases steadily with temperature, while that of NO decreases. Before surface saturation, we observe the highest amount of NO at the terraces and oxygen at steps independent of the substrate temperature, revealing that steps are more active than terraces towards the NO reduction.

During reaction conditions (CO+NO gas mixture), we observe three different regimes depending on the sample temperature. At low temperatures (100 °C), the surface is covered by a mixed CO-NO layer, with the peculiarity that CO does not adsorb on the steps at any temperature under reaction conditions. Further heating (150 °C) yields a stage where the NO dissociation dominates the scenario: large amounts of atomic N, atomic O and uncharacterized C-O and N-O species (possibly reaction intermediates) are clearly observed at steps, while only NO and CO are detected at terraces. As extracted from the mass spectrometer signal, there is a considerably large CO₂ production at 150 °C. Such turnover doubles after heating to 190°C, reaching its maximum. At this high temperature the chemical composition at the surface has changed. Most of the chemical species containing C or N have vanished from the surface, which is now heavily oxidized. Interestingly, the amount of atomic N is now smaller at steps rather than at terraces. This is surprising, since the adsorption energy of atomic N is larger at steps [4], therefore pointing towards a larger reactivity of steps as compared to terraces during the NO reduction reaction on Rh surfaces.

References

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