The development of novel (electro-)catalysts is commonly based on a trial-and-error approach without detailed understanding of the catalytic processes at the atomic scale. Reaching such understanding would be desirable, but, practically, it is not possible with real catalysts due to their structural and chemical complexity, and the presence of reaction environment. These limitations can be overcome following the model catalysis approach. In this thesis the elementary aspects of model catalysis are applied on electrochemical reactions to reach detailed understanding of fundamental electrocatalytic processes at the atomic level of various catalysts applicable in energetically relevant reactions. The studied model catalysts consist of rare metals (Pd, Pt) and reducible oxides (Co_3O_4, CeO_2). The main focus lied on the study of morphological and chemical properties of these systems in ultrahigh vacuum (UHV) and electrochemical environment combining surface science and electrochemical methods. The results show a clear link between the structural properties of the catalysts and their stability and performance in the electrochemical environment. The obtained level of understanding allows us to define key parameters to optimize the catalyst properties, identify adsorption sites and describe the elementary steps of catalytic reactions.