Atomic Structure of Copper Surfaces in the Presence of CO, CO_2 and Methanol Gases

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Using high pressure scanning tunneling microscopy (HPSTM), we show here that the most compact and stable surfaces of Cu undergo massive reconstructions in the presence of CO at room temperature at pressures in the Torr range, and they decompose into two-dimensional nanoclusters, which is a double effect of low cohesive energy of Cu and the high gain in adsorption energy at the newly formed under-coordinated sites.[1,2,3] Here we discuss the atomic structure of the nanoclusters as a function of CO pressure, their energetics for formation, and the growth mechanisms, as well as their importance for heterogeneous catalysis. Whilst 19-atom large hexagonal clusters are the building blocks of larger clusters on the Cu(111) surface, linear clusters form on Cu(100) and Cu(110) surfaces. Surface- sensitive spectroscopy techniques such ambient pressure photoelectron spectroscopy (APXPS) and infrared reflection absorption spectroscopy (IRRAS) are used to corroborate the HPSTM results.

The surfaces which are broken up into clusters are more active for water dissociation, a key step in the water gas shift reaction. Such a behavior opens a new paradigm, especially for other soft metals like gold, silver, zinc, etc., and it is clear that we need more of such studies.

Similar to CO, Cu(100) surface also breaks up into clusters in the presence of CO_2, however at an order of magnitude higher pressures.[4] Gas-phase CH_3OH, on the other hand, does not cause the break-up of Cu into clusters because methoxy already adsorbs strongly on Cu terraces.[5]

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