Methanol has recently attracted renewed interest because of its potential importance as a solar fuel. Methanol is also an important bulk chemical that is most efficiently formed over the industrial Cu/ZnO/Al2O3 catalyst. The identity of the active site and, in particular, the role of ZnO as a promoter for this type of catalyst is still under intense debate. Structural changes that are strongly dependent on the pretreatment method have now been observed for an industrial-type methanol synthesis catalyst. A combination of chemisorption, reaction, and spectroscopic techniques provides a consistent picture of surface alloying between copper and zinc. This analysis enables a reinterpretation of the methods that have been used for the determination of the Cu surface area and provides an opportunity to independently quantify the specific Cu and Zn areas. This method may also be applied to other systems where metal-support interactions are important, and this work generally addresses the role of the carrier and the nature of the interactions between carrier and metal in heterogeneous catalysts.