Journal of Structural Chemistry, Vol. 48, Supplement, pp. S147-S159, 2007
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DFT QUANTUM-CHEMICAL CALCULATIONS OF NITROGEN OXIDE CHEMISORPTION AND REACTIVITY ON THE Cu(100) SURFACE

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UDC 539.192

A DFT quantum-chemical study of NO adsorption and reactivity on the Cu_{20} and Cu_{16} metal clusters showed that only the molecular form of NO is stabilized on the copper surface. The heat of monomolecular adsorption was calculated to be $\Delta H_m = -49.9$ kJ/mol, while dissociative adsorption of NO is energetically unfavorable, $\Delta H_d = +15.7$ kJ/mol, and dissociation demands a very high activation energy, $E_a = +125.4$ kJ/mol. Because of the absence of NO dissociation on the copper surface, the formation mechanism of the reduction products, N_2 and N_2O, is debatable since the surface reaction ultimately leads to N–O bond cleavage. As the reaction occurs with a very low activation energy, $E_a = 7.3$ kJ/mol, interpretation of the NO direct reduction mechanism is both an important and intriguing problem because the binding energy in the NO molecule is high (630 kJ/mol) and the experimental studies revealed only *physically adsorbed forms* on the copper surface. It was found that the formation mechanism of the N_2 and N_2O reduction products involves formation (on the copper surface) of the ($O_{ad}N$–NO_{ad}) dimer intermediate that is *chemisorbed* via the oxygen atoms and characterized by a stable N–N bond (r_{N-N} ~1.3 Å). The N–N binding between the adsorbed NO molecules occurs through electron-accepting interaction between the oxygen atoms in NO and the metal atoms on the "defective" copper surface. The electronic structure of the ($O_{ad}N$–NO_{ad}) surface dimer is characterized by excess electron density $(ON\text{–}NO)^{\delta-}$ and high reactivity in N–O_{ad} bond dissociation. The calculated activation energy of the destruction of the chemisorbed intermediate ($O_{ad}N$–NO_{ad}) is very low (E_a = 5-10 kJ/mol), which shows that it is kinetically unstable against the instantaneous release of the N_2 and N_2O reduction products into the gas phase and cannot be identified by modern experimental methods of metal surface studies. At the same time, on the MgO surface and in the individual $(Ph_3P)_2Pt(O_2N_2)$ complex, a stable ($O_{ad}N$–NO_{ad}) dimer was revealed experimentally.

Keywords: quantum-chemical calculations, DFT method, molecular structure, ON–NO surface dimer, metal cluster, Cu_{20}, Cu_{16}.

INTRODUCTION

Investigation of NO adsorption and reactivity on the metal surface is important from scientific and technological viewpoints. Knowledge of the NO reduction mechanism on the metal surface is a fundamental problem in selecting effective

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0022-4766/07/48 Supplement-0147 © 2007 Springer Science+Business Media, Inc.