EFFECTS OF REACTION CONDITIONS ON COPPER-CATALYZED WATER-GAS SHIFT REACTION: A KINETIC MONTE CARLO STUDY

Hèctor Prats[a],* Leny Álvarez[a], Francesc Illas[a] and Ramón Sayós[a]

a: Departament de Química Física and Institut de Química Teòrica I Computacional, Universitat de Barcelona, C. Martí I Franquès 1, 08028, Barcelona, Spain
e-mail: hpratsga@ub.edu

The water-gas shift reaction (WGSR: $CO + H_2O \rightarrow CO_2 + H_2$, $\Delta_r H^o_{(298.15\ K)} = -41.2$ kJ/mol) is an industrial important reaction for H_2 production, where iron oxide-based and copper-based catalysts are used at high- and low-temperature stages, respectively. Multiple reaction mechanisms have been proposed for this reaction. Moreover, several theoretical and experimental studies have been carried out over different model systems, including metallic surfaces (e.g., Au(111), Pt(111), Cu(111),..) and nanoparticles deposited in these surfaces (e.g., CeO_x/Cu, CeO_x/Au, Cu/ZnO, …), which a significant increase of the rate of H_2 production.

In the present work, we present a complete first-principles kinetic Monte Carlo (kMC) study of WGSR reaction over Cu(111), a typical benchmark catalyst for this reaction. A total of 34 elementary processes are considered, including the diffusion of the main adsorbates. Rates for all processes were obtained from DFT data [1] along with the application of both transition state theory and collision theory. Some additional DFT calculations were carried out to complete the published data. In the present lattice-gas model the surface of Cu(111) was represented as a hexagonal periodic grid of 25 x 25 adsorption sites with periodic boundary conditions. All kMC simulations have been performed by means of a C++ code developed in our group. Gas mixtures of several partial pressures of CO and H_2O and temperatures were considered to study the effect of the reaction conditions in the total turnover frequency of this reaction.

The present kMC results will be compared with mentioned microkinetic model data [1], available experimental data [2] and with some previous kMC results presented for Cu(111) in the study of the WGSR reaction over Cu/ZnO [3]. Conclusions will be presented at the meeting.

1) A.A. Gokhale, J.A. Dumesic, M. Mavrikakis. *J. Am. Chem. Soc.* **2008**, 130, 1402.
2) K. Mudiyanselage, S.D. Senanayake, L. Feria, S. Kundu, A.E. Barber, J. Graciani, A. B. Vidal, S. Agnoli, J. Evans, R. Chang,
S. Axnanda, Z. Liu, J. F. Sanz, P. Liu, J.A. Rodriguez, D. J. Stacchiola. *Angew. Chem.* **2013**, 125, 5205.
3) L. Yang, A. Karim, J.T. Muckerman. *J. Phys. Chem. C.* **2013**, 117 3414.