A Microkinetic Analysis and Mechanism for the Water Gas Shift Reaction over Industrial Cu Catalysts

Rostam. J. Madon[1*], Drew Braden[2], Peter Nagel[1], Shampa Kandoi[2], James. A. Dumesic[2]
[1]*BASF Corporation, 25 Middlesex/Essex Turnpike, Iselin, NJ, USA 08830*
[2]*Dept. Of Chemical and Biological Engineering, Univ. of Wisconsin, Madison, WI 53706*
*rostam.madon@basf.com

Introduction

Low temperature water gas shift (LTS) is a commercially important reaction that takes place over Cu-ZnO-Al_2O_3 catalyst. A very large number of fundamental studies have been carried out for this reaction including investigations of the reaction mechanism as typified by Refs [1-4]. In short, discussions have centered around (a) the redox mechanism in which adsorbed H_2O is dissociated to O* and OH* and the O* is removed via CO* to form CO_2 – where * is an active site, and (b) formate as a reactive intermediate. Recently, Gokhale et al. [5] using a DFT investigation of the LTS reaction on Cu(111) proposed a new mechanism that involves a reactive surface carboxyl. Our study described in this presentation is aimed at resolving some of the argument over the elementary steps that best describe the catalytic cycle for the LTS reaction. To achieve this, we have started with parameters obtained via DFT calculations [5] for activation energies (E_a) of all reactions and binding energies (BE) as well as entropies of surface intermediates. These parameters form the initial basis of our approach which uses the microkinetic modeling method [6].

Materials and Methods

We carried out all our studies with CuO:ZnO:Al_2O_3 catalysts made via the coprecipitation of carbonates. The catalysts were reduced in flowing H_2/He at 200°C before use. Cu dispersion was measured by the reactive chemisorption of N_2O [7] at 60°C. The LTS reaction was studied at 2.7 and 30 bars total pressure, a temperature range from 453 to 503 K, and a wide range of CO_2:CO ratios from 0.33 to 1.46. We used a fixed bed reactor, varied CO conversion by varying space velocity, kept the average catalyst bed temperature constant, and calculated rates as site-time-yields. The inlet gases consisted of CO, CO_2, H_2O, and N_2.

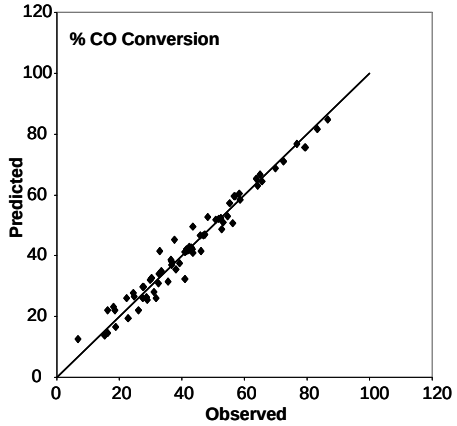
Microkinetic modeling was carried out using the Athena Visual Studio program. By basing the kinetic model on thermodynamic values for gaseous and surface species, we ensured that all kinetic parameters of the model were thermodynamically consistent. By first using parameter values from DFT calculations [5], we initially carried out microkinetic analyses using a transient continuous stirred tank reactor (CSTR) model, since with this approach it is relatively facile to fit the experimental data. With the adjusted parameters thus obtained, we used the plug flow reactor (PFR) model to finalize the parameter set. We used this parameter set to probe the nature of the dominant catalytic cycle for low-temperature water-gas shift over copper.

Results and Discussion

We analyzed a set of data *using all elementary steps* including those that described the redox mechanism, the formate mechanism, and the carboxyl mechanism. Importantly, by using all reactions together, we ensured that there was no bias towards any particular reactions to fit our data. We found the catalytic cycle for LTS on Cu to be described by (a) the equilibrated adsorption – desorption of CO, H_2O, and CO_2, and the non-equilibrated desorption of H_2; (b) the dissociation of H_2O* to H* and OH*; (c) the reaction of CO* and OH* to form COOH*: (d) and the reaction of COOH* with OH* to form CO_2* and H_2O*.

The key reactions that describe the redox mechanism: dissociation of OH*, OH* + OH* disproportionation, and CO* oxidation were all unimportant and were not part of the catalytic cycle. We found the reaction of CO_2* and H* to form formate to be equilibrated but an important reaction, because even though its net rate was significantly lower than the rates of the reactions in the LTS catalytic cycle, the step ensured that there was significant coverage of formate species on the Cu surface. The bidentate formate is a spectator species whose coverage increases with increasing pressure and decreases with increasing temperature. However, this coverage is important and influences the overall LTS reaction. The Cu surface is mainly covered by H* and HCOO** with very low coverage by all other surface intermediates.

With the parameter set, obtained from the initial CSTR model, we analyzed 72 experiments using a PFR model at the wide variety of conditions given earlier. The only adjustable parameter was the binding energy of H*. The figure shows a parity plot, with BE of H* being 262 kJ/mol. The fit is excellent over a wide range of experimental conditions and conversions.



Over all the various data that we analyzed, the key parameter that needed to be varied was the BE of H*, and, that to, by just a few kJ/mol. The other important parameter that sometimes needed to be adjusted was the binding energy of HCOO** which was ca. 278 kJ/mol.

Our investigation over a very large set of industrial conditions confirms that the redox mechanism is unimportant, and that the LTS catalytic cycle involves the formation and reaction of surface carboxyl.

References

1. Ovesen, C. V., et al. *J. Catal.* 158, 170 (1996).
2. Koryabkina, N. A. et al. *J. Catal.* 217, 233 (2003).
3. Rhodes, C., Hutchings G.J., and Ward A.M. *Catal. Today* 23, 43 (1995).
4. Herwijnen, T.V., and Jong, W. A. D. *J. Catal.* 63, 83 and 94 (1980).
5. Gokhale, A. A., Dumesic, J. A., and Mavrikakis, M. *J. Am. Chem. Soc.* 130, 1402 (2008).
6. Dumesic, J. A., et al. "The Microkinetics of Heterogeneous Catalysis", American Chemical Society, Washington, D. C., 1993.
7. Chinchen, G. C. et al. *J. Catal.* 103, 79 (1987).