A Microkinetic Model for the Water Gas Shift Reaction on Cu(111) and Fe(111)

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Introduction

The development of lower temperature water-gas-shift (WGS) catalysts is of paramount importance. In particular, an efficient lower temperature WGS catalyst is crucial in improving the reforming process for developing a reformate-fed proton-exchange membrane fuel cell, as well as for the direct methanol fuel cell, intended for transportation and stationary applications. The approach so far has involved random or combinatorial screening of binary and tertiary catalysts of different compositions. Since there are infinite possibilities, not surprisingly, this approach so far has been met with only limited success.

The aim of the present work is to develop a microkinetic model for both lower and higher temperature WGS catalysts. The approach of microkinetics is appealing [1] since it is not based on any arbitrary assumptions regarding rate-determining step (RDS) and is, thus, not restricted to a particular set of conditions. In doing this we follow a novel approach developed recently by us [2] to *derive* a *complete* set of elementary reactions and reaction routes (RRs) for a given set of species, coupled with a reliable prediction of the elementary reaction energetics on a given catalyst based on the Unity Bond Index – Quadratic Exponential Potential (UBI-QEP) approach developed by Shustorovich [3] and the transition-state theory. This new approach allows us to develop *a priori* a complete microkinetic model for the WGSR on a given catalyst and will also provide a rational approach for identifying the rate determining steps (RDS), if any, under different conditions, so that reduced models may also be developed.

Microkinetic Model and Simulation

The mechanism of the WGS reaction is assumed to proceed via a set of elementary reactions (ERs) comprising active sites (S) on the surface of the catalyst, surface intermediates (I_i), and terminal species (T_i). Generically the elementary reactions (s_j) may be written as

$$s_j = \alpha_{jo} S + \sum_{k=1}^{q} \alpha_{jk} I_k + \sum_{i=1}^{n} \beta_{ji} T_i = 0$$

where α and β represent the stoichiometric coefficients assumed to take positive values for products and negative values for reactants. The rate expressions of the elementary reactions are given by

$$r_j = \vec{A}_j \exp\left(-\frac{\vec{E}}{RT}\right)\theta_0^{\vec{\alpha}_{jo}} \prod_{k=1}^{q} \theta_k^{\vec{\alpha}_{jk}} \prod_{i=1}^{n} P_i^{\vec{\beta}_{ji}} - \bar{A}_j \exp\left(-\frac{\bar{E}}{RT}\right)\theta_0^{\bar{\alpha}_{jo}} \prod_{k=1}^{q} \theta_k^{\bar{\alpha}_{jk}} \prod_{i=1}^{n} P_i^{\bar{\beta}_{ji}}$$

where A_j and E are the pre-exponential factors and activation energies, respectively, and θ represents species coverage.

Our starting point in the development of the microkinetic model is the experimental evidence according to which the WGS reaction normally proceed via the following set of surface intermediates H_2OS, COS, CO_2S, H_2S, HS, OHS, OS and HCOOS. Starting with these surface species, a plausible set of ERs may be generated using an appropriate chemical reaction generator. The stoichiometry of ERs is dictated further by the subsequent application of the UBI-QEP method to calculate the energetic characteristics of these ERs. In other words, the ERs are limited to those 3 types for which the UBI-QEP method provides the necessary formulae:

1. AB(g) + S = ABS
2. AB(g) + S = AS + BS
3. AS + BCS = ABS + CS

The set of ERs generated under these stoichiometric constraints for the WGS reaction is presented in Table 1. Next, the UBI-QEP method is utilized to calculate the enthalpy changes as well as activation energies of each ER on both Cu(111) and Fe(111) (Table 2). Further, the pre-exponential factors are estimated using the conventional transition state theory [1]. Following Waugh [4], we assume an immobile transition state without rotation for all of the species that result in a pre-exponential factor of 10^1 $Pa^{-1}s^{-1}$ for adsorption/desorption reactions and 10^{13} s^{-1} for surface reactions. The obtained microkinetic model for the WGS reaction is presented in Table 1. Fine-tuning of some of the pre-exponential factors of the adsorption/desorption reactions, however, is necessary in order to be consistent with the known thermodynamics of the overall reaction. Numerical simulations and analyses were performed for both CSTR and PFR.

Table 1. A microkinetic model for the WGSR

s_1 = - H_2O - S + H_2OS =0
s_2 = - CO - S + COS = 0
s_3 = - CO_2S + CO_2 + S = 0
s_4 = - HS - HS + H_2S + S = 0
s_5 = - H_2S + H_2 + S = 0
s_6 = - H_2OS - S + OHS + HS = 0
s_7 = - COS - OS + CO_2S + S = 0
s_8 = - COS - OHS + HCOOS + S = 0
s_9 = - OHS - S + OS + HS = 0
s_{10} = - COS - OHS + CO_2S + HS = 0
s_{11} = - HCOOS - S + CO_2S + HS = 0
s_{12} = - CO_2S - OHS + HCOOS + OS = 0
s_{13} = - H_2OS - OS + 2OHS = 0
s_{14} = - H_2OS - HS + OHS + H_2S = 0
s_{15} = - OHS - HS + OS + H_2S = 0

Model Analysis and Reduction

Typical results of numerical simulations using the proposed microkinetic models for Cu(111) and Fe(111) are presented in Figures 1 and 2. As can be seen, the model can satisfactorily reproduce the main features of the WGSR on both Cu LTS catalyst and Fe HTS catalyst without any further fine-tuning, e.g., coverage dependence of the activation energy, etc. Notice, for Cu(111) a much better description of the experimental data may be obtained if the last two elementary reactions, s_{14} and s_{15}, are dropped from the mechanism. The reason for this behavior is not yet clear. More detailed and exact kinetic measurements are necessary in order to discriminate among the full 15-elementary step and 13-elementary step microkinetic model on Cu.

To get a deeper insight into the nature of the WGS reaction mechanism we next use the RR formalism to reduce and simplify the microkinetic model. First, we enumerate a complete list of stoichiometrically distinct direct overall RRs (Table 3). The individual contributions of these overall RRs may be estimated by performing numerical simulations for each of the RRs separately. An example of such simulations in a CSTR for Cu(111) is presented in

Table 2. Preexponential factors ($Pa^{-1}s^{-1}$ for adsorption/desorption steps and s^{-1} for surface reaction) and activation energies (kcal/mol) microkinetic model for the WGSRs

			Cu(111)		Fe(111)	
ERs	$\vec{A}_j$	$\bar{A}_j$	$\vec{E}_j$	$\bar{E}_j$	$\vec{E}_j$	$\bar{E}_j$
s_1	10^1	10^{14}	0	13.6	0	17.2
s_2	10^1	10^{14}	0	12.0	0	32.0
s_3	$4\ 10^{12}$	10^1	5.3	0	6.9	0
s_4	10^{13}	10^{13}	15.5	13.0	24.5	7.6
s_5	$6\ 10^{12}$	10^1	5.5	0	7.1	0
s_6	10^{13}	10^{13}	25.4	1.6	19.9	12.0
s_7	10^{13}	10^{13}	0	17.3	20.6	4.5
s_8	10^{13}	10^{13}	0	20.4	9.0	12.2
s_9	10^{13}	10^{13}	15.5	20.7	12.4	29.1
s_{10}	10^{13}	10^{13}	0	22.5	10.3	10.9
s_{11}	10^{13}	10^{13}	1.3	3.5	4.4	1.8
s_{12}	10^{13}	10^{13}	4.0	0.9	19.3	0
s_{13}	10^{13}	10^{13}	29.2	0	24.6	0
s_{14}	10^{13}	10^{13}	26.3	0	24.8	0
s_{15}	10^{13}	10^{13}	1.3	4.0	3.4	3.2

Figure 3**.** From these simulations, we conclude that, for Cu(111), the main contributions come from four overall RRs, namely, RR_1, RR_2, RR_3 and RR_{18}. The first three RRs are the formate, redox and associative RRs, respectively. As can be seen from Figure 3, the formate and associative RRs are dominant at lower temperatures, while the redox RR is significant at higher temperatures. This result is of particular significance since it shows that both the formate and redox mechanisms may be important in different temperature ranges and for different feed compositions. RR_{18} represents a new RR and is due to the elementary reaction s_{15}. As already mentioned above, the prominence of this RR still needs to be proved. Similar evaluations for the WGS reaction on Fe(111) reveal that the dominant RRs are RR_1, RR_3, RR_{18} and RR_{19}, their contributions being equal. Further, when these dominant overall RRs are summed up, it is seen that the elementary reactions s_{13} and s_{14} drop out and, consequently, may be disregarded. We thus arrive at a simplified mechanism involving only the first 12 ERs and the elementary reaction s_{15}.

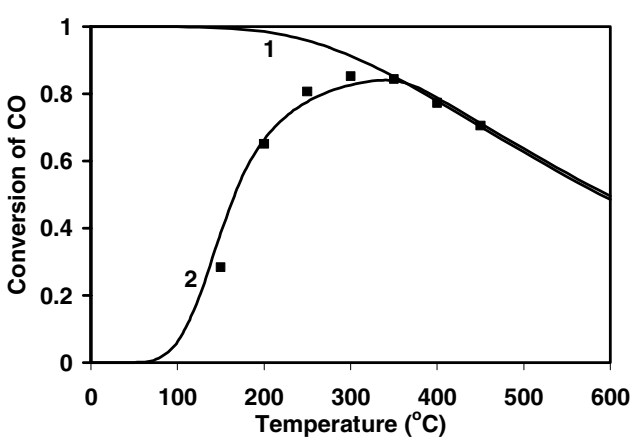

Figure 1. CO conversion vs. temperature on Cu(111).
1-equilibrium conversion; 2-microkinetic model; squares-experimental data from [5].

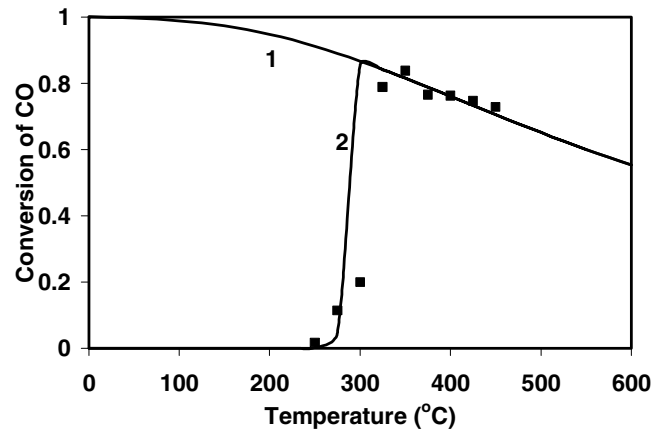

Figure 2. CO conversion vs. temperature on Fe(111).
1-equilibrium conversion; 2-microkinetic model; squares-experimental data from present work.

Table 3. A complete list of unique overall reaction routes for the 15-step microkinetic model of the WGS reaction microkinetic model.

$RR_1 = s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_8 + s_{11}$
$RR_2 = s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_9$
$RR_3 = s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_{10}$
$RR_4 = s_1 + s_2 + s_3 + s_4 + s_5 + 2s_6 + s_7 - s_{13}$
$RR_5 = s_1 + s_2 + s_3 + s_4 + s_5 + s_{10} + s_{11} - s_{12} + s_{13}$
$RR_6 = s_1 + s_2 + s_3 + s_4 + s_5 + s_9 + s_{10} + s_{13}$
$RR_7 = s_1 + s_2 + s_3 + s_4 + s_5 + s_8 + s_{11} - s_{12} + s_{13}$
$RR_8 = s_1 + s_2 + s_3 + s_4 + s_5 - s_8 + 2s_{10} - s_{12} + s_{13}$
$RR_9 = s_1 + s_2 + s_3 + s_4 + s_5 + s_8 + 2s_9 + s_{12} + s_{13}$
$RR_{10} = s_1 + s_2 + s_3 + s_4 + s_5 + s_8 + s_9 + s_{11} + s_{13}$
$RR_{11} = s_1 + s_2 + s_3 + s_4 + s_5 + s_7 + 2s_{11} - s_{12} + s_{13}$
$RR_{12} = s_1 + s_2 + s_3 + s_4 + s_5 + s_7 + 2s_9 + s_{13}$
$RR_{13} = s_1 + s_2 + s_3 + s_4 + s_5 - s_7 + 2s_{10} + s_{13}$
$RR_{14} = s_1 + s_2 + s_3 + s_4 + s_5 - s_7 + 2s_8 + 2s_{11} + s_{13}$
$RR_{15} = s_1 + s_2 + s_3 + s_4 + s_5 + 2s_6 + s_8 + s_{12} - s_{13}$
$RR_{16} = s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_8 + s_9 + s_{12}$
$RR_{17} = s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_{11} - s_{12}$
$RR_{18} = s_1 + s_2 + s_3 + s_5 + s_6 + s_7 + s_{15}$
$RR_{19} = s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{12} + s_{15}$
$RR_{20} = s_1 + s_2 + s_3 + s_5 + s_7 + s_9 + s_{14}$
$RR_{21} = s_1 + s_2 + s_3 + s_5 + s_{10} + s_{14}$
$RR_{22} = s_1 + s_2 + s_3 + s_5 + s_8 + s_{11} + s_{14}$
$RR_{23} = s_1 + s_2 + s_3 - s_4 + s_5 + s_7 - s_{13} + 2s_{14}$
$RR_{24} = s_1 + s_2 + s_3 - s_4 + s_5 + s_7 + s_{13} + 2s_{15}$
$RR_{25} = s_1 + s_2 + s_3 - s_4 + s_5 + s_7 + s_{14} + s_{15}$
$RR_{26} = s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{12} + s_{14}$
$RR_{27} = s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{12} + s_{14}$
$RR_{28} = s_1 + s_2 + s_3 + s_5 + s_{10} + s_{13} + s_{15}$
$RR_{29} = s_1 + s_2 + s_3 + s_5 + s_8 + s_{11} + s_{13} + s_{15}$
$RR_{30} = s_1 + s_2 + s_3 - s_4 + s_5 + s_8 + s_{12} - s_{13} + 2s_{14}$
$RR_{31} = s_1 + s_2 + s_3 - s_4 + s_5 + s_8 + s_{12} + s_{14} + s_{15}$

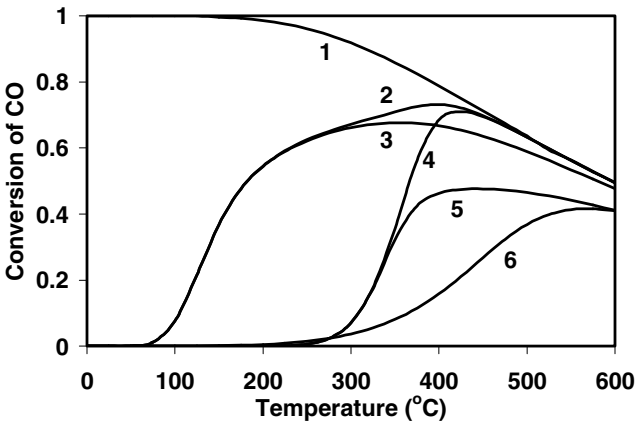

Figure 3. CO conversion vs. temperature for Cu(111) 1-equilibrium; 2-13-step mechanism; 3-RR_1 and RR_3, 4-RR_2; 5-RR_{16}; 6-RR_{17}.

Table 4. A 10-Step Reduced Mechanism for WGSR

s_1:	$H_2O + S = H_2OS$	EQ
s_2:	$CO + S = COS$	EQ
s_6:	**$H_2OS + S = OHS + HS$**	**RDS**
s_8:	**$COS + OHS = HCOOS + S$**	**RDS**
s_9:	**$OHS + S = OS + HS$**	**RDS**
s_{10}:	**$COS + OHS = CO_2S + HS$**	**RDS**
s_{12}:	**$CO_2S + OHS = OS + HCOOS$**	**RDS**
s_{15}:	**$OHS + HS = OS + H_2S$**	**RDS**
$s_2 + s_3 + s_7$:	$CO + OS = CO_2 + S$	EQ
s_3:	$CO_2S = CO_2 + S$	EQ
$1/2(s_4 + s_5)$:	$HS = 1/2H_2 + S$	EQ
$s_3+1/2s_4+1/2s_5 + s_{11}$:	$HCOOS = CO_2 + 1/2H_2 + S$	EQ

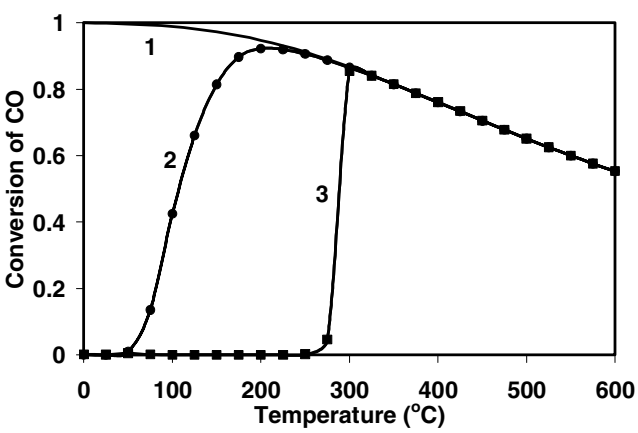

Figure 4. CO conversion vs. temperature for Cu(111) and Fe(111) 1-equilibrium; 2-13-step mechanism on Cu(111), dots-simplified microkinetic model for Cu(111); 3-15-step mechanism on Fe(111), squares-simplified microkinetic model for Fe(111).

The microkinetic model was further reduced using quasi-equilibrium and quasi-steady state approximations. Based on affinity calculations, elementary reactions s_1, s_2, s_3, s_4, s_5, s_7, and s_{11} were determined to be quasi-equilibrium (QE) reactions. Using the intermediate RRs formalism [2] one may next appropriately combine the QE elementary reactions into a set of intermediate reactions. Substituting the QE elementary reactions with the intermediate reactions result in an 12-step, 5-route and 5-RDSs simplified mechanism that is presented in Table 4.

The elementary reactions s_6, s_8, s_9, s_{10}, s_{12} and s_{15} may therefore be considered rate determining steps. The next natural step in the reduction of the mechanism is to assume that the remaining surface intermediate OHS is a quasi-steady state (QSS) species. Under these conditions, the rates along the dominant RRs, i.e., RR_1, RR_2, RR_3, RR_{19} and RR_{18} are equal to r_8, r_9, r_{10}, r_{12} and r_{15} and are given by

$$r_8 = \frac{\vec{k}_6\vec{k}_8K_1K_2P_{H_2O}P_{CO}\theta_0^2}{\frac{\left(\bar{k}_6+\bar{k}_{15}\right)P_{H_2}^{1/2}}{\left(K_4K_5\right)^{1/2}K_6}+\bar{k}_9+\left(\vec{k}_8+\bar{k}_{10}\right)K_2P_{CO}+\vec{k}_{12}K_3^{-1}P_{CO_2}}\left(1-\frac{P_{CO_2}P_{H_2}}{KP_{H_2O}P_{CO}}\right)$$

$$r_9 = \frac{\vec{k}_6\vec{k}_9K_1P_{H_2O}\theta_0^2}{\frac{\left(\bar{k}_6+\bar{k}_{15}\right)P_{H_2}^{1/2}}{\left(K_4K_5\right)^{1/2}K_6}+\bar{k}_9+\left(\vec{k}_8+\bar{k}_{10}\right)K_2P_{CO}+\vec{k}_{12}K_3^{-1}P_{CO_2}}\left(1-\frac{P_{CO_2}P_{H_2}}{KP_{H_2O}P_{CO}}\right)$$

$$r_{10} = \frac{\vec{k}_6\vec{k}_{10}K_1K_2P_{H_2O}P_{CO}\theta_0^2}{\frac{\left(\bar{k}_6+\bar{k}_{15}\right)P_{H_2}^{1/2}}{\left(K_4K_5\right)^{1/2}K_6}+\bar{k}_9+\left(\vec{k}_8+\bar{k}_{10}\right)K_2P_{CO}+\vec{k}_{12}K_3^{-1}P_{CO_2}}\left(1-\frac{P_{CO_2}P_{H_2}}{KP_{H_2O}P_{CO}}\right)$$

$$r_{12} = \frac{\vec{k}_6\vec{k}_{12}K_1K_3^{-1}P_{H_2O}P_{CO_2}\theta_0^2}{\frac{\left(\bar{k}_6+\bar{k}_{15}\right)P_{H_2}^{1/2}}{\left(K_4K_5\right)^{1/2}K_6}+\bar{k}_9+\left(\vec{k}_8+\bar{k}_{10}\right)K_2P_{CO}+\vec{k}_{12}K_3^{-1}P_{CO_2}}\left(1-\frac{P_{CO_2}P_{H_2}}{KP_{H_2O}P_{CO}}\right)$$

$$r_{15} = \frac{\vec{k}_6\vec{k}_{15}K_1\left(K_4K_5\right)^{1/2}P_{H_2O}P_{H_2}^{1/2}\theta_0^2}{\frac{\left(\bar{k}_6+\bar{k}_{15}\right)P_{H_2}^{1/2}}{\left(K_4K_5\right)^{1/2}K_6}+\bar{k}_9+\left(\vec{k}_8+\bar{k}_{10}\right)K_2P_{CO}+\vec{k}_{12}K_3^{-1}P_{CO_2}}\left(1-\frac{P_{CO_2}P_{H_2}}{KP_{H_2O}P_{CO}}\right)$$

The overall rate, r, is a sum of the rates along the dominant RRs:

$$r = r_8 + r_9 + r_{10} + r_{12} + r_{15}$$

Notice, for Cu(111) we neglected r_{12} and r_{15} while for Fe(111) we neglected r_9. These simplified rate expressions are in perfect agreement with the full microkinetic model (Figure 4).

Also under the QSS condition for OHS, all of the dominant RRs may be combined into a final, two-step, one-route mechanism

$H_2O + S = OHS + 1/2H_2$	1
$CO + OHS = CO_2 + 1/2H_2 + S$	1
Net: $H_2O + CO = CO_2 + H_2$	

This reduced mechanism could be compared to that proposed by Temkin, which is based on adsorbed O rather than OH.

Conclusions

In this work we have shown that a quite reliable microkinetic model for the WGS reaction on Cu(111) and Fe(111) may be developed based on a rather simplistic evaluation of the pre-exponential factors coupled with energetic estimations using the UBI-QEP method. The fact that these microkinetic models quantitatively describes the kinetics of the WGS reaction on a commercial Cu-Zn LTS and Fe HTS catalysts is quite surprising since some of the approximations involved are rather crude.

We further applied a simplification and reduction technique based on the RRs formalism. It was shown that only a very limited number of RRs dominate the kinetics of the process. This allows a dramatic simplification and reduction of the micriokinetic model. The numerical performance of the final explicit rate expression is excellent when compared with the complete microkinetic model.

References

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