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# Kinetic modelling of CO conversion over a Cu/ceria catalyst

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A Cu/ceria/alumina catalyst has been tested for the water–gas shift reaction under fuel reformer conditions for fuel cell applications. These catalysts do not need any reduction before use and are non-pyrophoric. However, their activity is significantly lower than a Cu/Zn/Al catalyst. A detailed kinetic analysis shows that the data can be described by a two-step redox model and that ceria lowers the activation barrier of the water dissociation. The lower activity of the Cu/Ce/Al catalyst compared to the Cu/Zn/Al is due to the lower copper surface area of the former one. The kinetic analysis includes a rigorous procedure based on an analysis of the Jacobian matrix in order to eliminate non-influential parameters from the rate-equations.

*Keywords:* Mathematical modelling; Catalysis; Numerical analysis; Kinetics; Hydrogen purification; Reaction mechanism

## 1. Introduction

Efficient operation of proton-exchange membrane (PEM) fuel cells requires high-purity hydrogen. Reforming of hydrocarbons or alcohols produces a mixture of hydrogen, carbon monoxide, carbon dioxide and steam. The carbon monoxide level must be reduced to levels between 10 and 50 ppm to avoid poisoning of the fuel cell electrodes. This is accomplished in several steps that include the water–gas shift (WGS) reaction. The WGS converts CO into CO<sub>2</sub> by the reaction with water over a suitable catalyst and provides additional hydrogen.

Current industrial catalysts require long and tedious pre-treatment procedures and are pyrophoric, thus they are not suited for onboard applications. A large number of studies report the development of ceria supported metal catalysts that are better suitable for the WGS reaction for fuel cell applications (Fu et al., 2003; Germani et al., 2005; Ghenciu, 2002; Goguet et al., 2004; Hilaire et al., 2004). This study aims at understanding the reaction mechanism of the WGS reaction over a Cu/Ce/Al catalyst through kinetic modelling. This catalyst is compared to a commercial Cu/Zn/Al catalyst. A special procedure has

been applied to eliminate non-influential parameters from the rate-equations. This procedure is outlined for one specific case.

## 2. Experimental

The Cu/Ce/Al catalyst has been prepared by successive impregnation steps as described in Engelhard (2002). The Cu/Zn/Al catalyst was provided by Engelhard. The composition of the Cu/Ce/Al catalyst is 8% CuO, 10% CeO<sub>2</sub>, 82% Al<sub>2</sub>O<sub>3</sub> whereas that of the Cu/Zn/Al catalyst is: 32% CuO, 37% ZnO, 31% Al<sub>2</sub>O<sub>3</sub>. The BET surface areas amounted to 69 and 91 m<sup>2</sup>/g<sub>cat</sub> and the Cu surface areas as measured by N<sub>2</sub>O decomposition were 2 and 12 m<sup>2</sup>/g<sub>cat</sub> for the Cu/Ce/Al and the Cu/Zn/Al catalyst, respectively.

The kinetic data were obtained from integral fixed bed reactor operation. The partial pressures of both reactants and products were varied over a wide range of conditions at a total pressure of 1 bar. The temperature was varied in the range of 150–400 °C. 100–200 mg of catalyst with a sieve fraction between 200 and 300 μm was used and flow rates between 60 and 300 sccm. Around 100 experimental points were collected for each catalyst. Before reaction, the catalyst was reduced by ramping the temperature with 2 °C per minute to 260 °C under a flow of 5% H<sub>2</sub> in helium. The temperature was kept at 260 °C during 30 min after which the temperature was changed to the reaction temperature.

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### 3. Results

Fig. 1 compares the activity of the Cu/Zn/Al and the Cu/Ce/Al catalysts as a function of temperature. The Cu/Ce/Al catalyst is less active than the Cu/Zn/Al but can be used up to temperatures of 400 °C. Moreover, after exposure to oxygen the Cu/Ce/Al catalyst remains active. Fig. 2 shows the carbon monoxide conversion as a function of the  $W/F_{CO}$  at different temperatures for both catalysts.

The different elementary steps for the WGS reaction over copper catalyst that are proposed in the literature are shown in Table 1. Based on these elementary steps, eight different reaction paths were derived as indicated by the stoichiometric numbers in the left columns of Table 1. The eight corresponding rate-equations are listed in Table 2.  $\beta$  in these equations is defined as:

$$\beta = \frac{P_{H_2} P_{CO_2}}{K_{eq} P_{CO} P_{H_2O}}, \quad (1)$$

$$K_{eq} = \exp\left(\frac{-36.0}{R}\right) \exp\left(\frac{38060}{RT}\right) \quad (\text{Moe, 1962}). \quad (2)$$

Rate-equation (1) is based on a two-step redox mechanism, including associative adsorption terms for all reactants and products. The two-step redox model has been put forward by Temkin to describe the reaction mechanism over Cu/Zn catalysts (Temkin, 1979). Reaction path (2) corresponds to a Langmuir–Hinshelwood mechanism with associative adsorption terms and the reaction between adsorbed carbon monoxide and water as rate-limiting step. Rate-equation (3) is also based on a Langmuir–Hinshelwood mechanism, but with dissociative chemisorption of hydrogen and the formation of a carboxylic species as rate-determining step. The change of the rate-determining step does not change the form of the rate-equation when compared to Eq. (2).

Both reaction paths (4) and (5) are Eley–Rideal type mechanisms with reactions between gas-phase carbon monoxide and

adsorbed water (path 4) or a reaction between gas-phase water and adsorbed carbon monoxide (path 5). Rate-equation (6) has been proposed by Van Herwijnen and De Jong (1980) for their data over a commercial Cu/ZnO catalyst. Their reaction mechanism is based on the formation and subsequent decomposition of formate species. Rate-equation (7) is similar as the Langmuir–Hinshelwood equation (2) except that it involves two active sites. Carbon monoxide is adsorbed on copper related sites, whereas water is activated by ceria. Rate-equation (8) is also based on a dual site mechanism this time through a formate intermediate species.

These rate-equations contain between 6 and 10 parameters. For example, the 10 parameters in rate-equation (3) were estimated by regression analysis of the experimental data for the Cu/Zn/Al catalyst. Only five out of the 10 parameters were estimated with correct 95% confidence intervals (i.e., intervals smaller than the actual value of the parameter). This situation is caused by a linear combination of parameters giving the same model response. The columns in the Jacobian matrix then become linearly dependent, characterized by a high condition number, making the optimization process much more difficult. Here a systematic procedure to eliminate the least influential parameters was used, originally developed for parameter estimation in microkinetic models (Jansson, 2002). The first step of this procedure consists of calculating for each parameter the norm of the Jacobian matrix, defined as:

$$\text{norm}(J_k) = \sqrt{\sum_i \left(b_k \frac{\delta y_i}{\delta b_k}\right)^2}, \quad (3)$$

where  $y_i$  is the model response corresponding to experiment  $i$ , and  $b_k$  is parameter  $k$  in the model. This norm gives information about the relative influence of the parameters. A low value indicates that the parameter has very little influence on the model response. In Fig. 3 the values of the norm of the 10 parameters of rate-equation (3) are plotted separated into

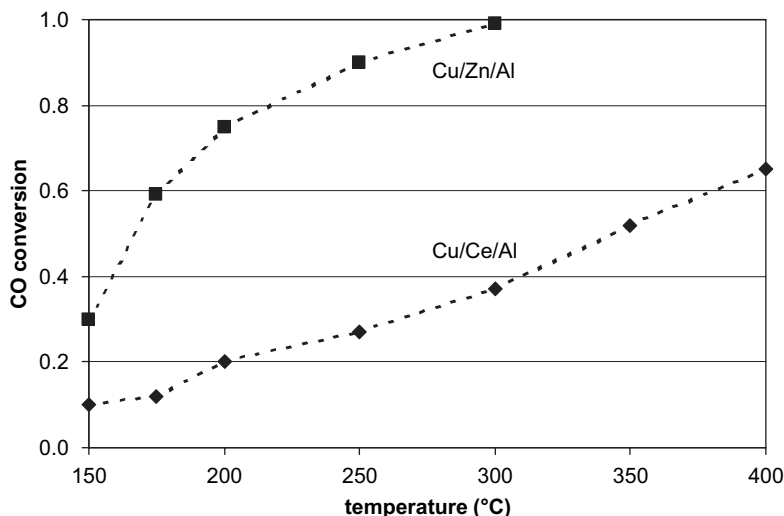


Fig. 1. CO conversion as a function of temperature for the Al/Zn/Al and Cu/Ce/Al catalysts. Conditions: 200 mg catalyst, 3%CO, 10% $H_2O$ , total flow rate 100 cm<sup>3</sup>/min.

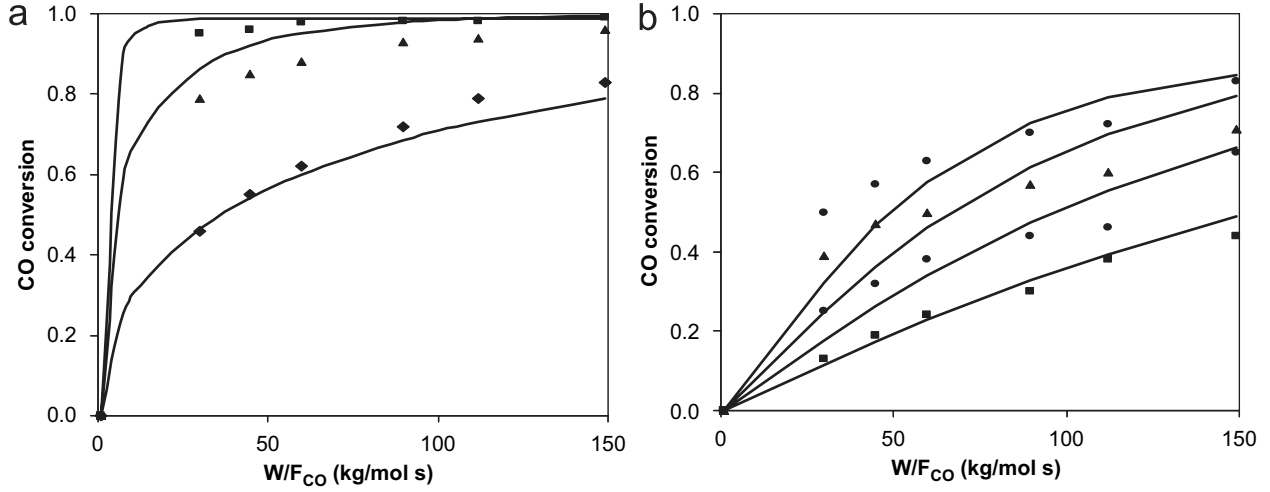


Fig. 2. CO conversion as a function of the  $W/F_{CO}$  at different temperatures: temperature for the Al/Zn/Al (graph A) and Cu/Ce/Al (graph B) catalysts. Conditions: 200 mg catalyst, 3%CO, 10%H<sub>2</sub>O, graph A: 200, 250 and 300 °C, graph B: 250, 300, 350 and 400 °C. Symbols experimental data, full lines model simulations based on rate-equation (8). Note that this data set was not used for the regression analysis.

Table 1  
Possible elementary steps for the WGS reaction over copper

No	$K_i$	Elementary step	1	2	3	4	5	6	7	8
1	$K_{H_2O}$	$H_2O + * \rightleftharpoons H_2O^*$	1	1	1	1		1		
2	$K_{CO}$	$CO + * \rightleftharpoons CO^*$	1	1	1		1	1	1	1
3	$K_{CO_2}$	$CO_2 \rightleftharpoons CO_2 + *$	1	1	1		1		1	1
4	$K_{H_2}$	$H_2 \rightleftharpoons H_2 + *$	1	1		1		1		
5	$K_5$	$H^* + H^* \rightleftharpoons H_2 + 2^*$			1					
6	$k_6, k_{-6}$	$CO^* + H_2O \rightleftharpoons CO_2^* + H_2^*$		1						
7	$k_7, k_{-7}$	$CO^* + H_2O \rightleftharpoons HCOO^* + H^*$			1					
8	$K_8$	$HCOO^* + * \rightleftharpoons CO_2^* + H^*$			1					
9	$K_9, k_{-9}$	$CO^* + H_2O \rightleftharpoons H_2CO_2^*$						1		
10	$k_{10}, k_{-10}$	$H_2CO_2^* \rightleftharpoons H_2^* + CO_2$						1		
11	$k_{11}, k_{-11}$	$CO + H_2O^* \rightleftharpoons CO_2 + H_2^*$					1			
12	$k_{12}, k_{-12}$	$CO^* + H_2O \rightleftharpoons CO_2^* + H_2$					1			
13	$k_{13}, k_{-13}$	$H_2O^* + * \rightleftharpoons H_2^* + O^*$	1							
14	$k_{14}, k_{-14}$	$CO^* + O^* \rightleftharpoons CO_2^* + *$	1							
15	$K_{15}$	$H_2O + Ce \rightleftharpoons H_2O-Ce$							1	
16	$K_{16}$	$H_2-Ce \rightleftharpoons H_2 + Ce$							1	
17	$k_{17}, k_{-17}$	$CO^* + H_2O-Ce \rightleftharpoons CO_2^* + H_2-Ce$							1	
18	$k_{18}, k_{-18}$	$CO^* + H_2O + Ce \rightleftharpoons H_2COO-Ce + *$								1
19	$k_{19}, k_{-19}$	$H_2COO-Ce + * \rightleftharpoons H_2 + CO_2^* + Ce$								1

energies and pre-exponentials. The parameters with a low norm value are those with a large 95% confidence interval. By removing one by one the parameters from rate-equation (3), starting with the lowest norm value, the condition number of the Jacobian matrix will be consequently reduced as the number of linear dependent columns is equally reduced. In this way, the least influential parameters are eliminated first. The condition number is given as:

$$C(J_k) = \|J_k\| \cdot \|J_k^{-1}\|. \quad (4)$$

The decrease of the condition number with the number of parameters that are removed is shown in Fig. 4. It can be seen that

the decrease of the condition number is most significant after the removal of the first two parameters and then again after an additional three. Removing more than four parameters does not change the condition number any longer. Another consequence of eliminating a number of parameters from the rate-equation is that the quality of the fit will be reduced. The quality of the fit can be measured in terms of the residual sum of squares. To determine the right number of parameters to be eliminated from the rate-equation, a statistical “additional sum of squares”  $F$ -test can be calculated (Draper and Smith, 1981):

$$F = \frac{SS(\beta_1) - SS(\beta_1, \beta_2)}{s^2 df(\beta_2)}, \quad (5)$$

Table 2

Rate equations corresponding to the reaction sequences listed in Table 1

Reaction path	Equation	Number of parameters
1	$r_{CO} = N_S \frac{k_{13} K_{CO} k_{14} K_{H_2O} P_{H_2O} P_{CO} (1-\beta)}{k_{14} K_{CO} P_{CO} + k_{-13} K_{H_2} P_{H_2} + k_{13} K_{H_2O} P_{H_2O} + k_{-14} K_{CO_2} P_{CO_2}}$	8
2	$r_{CO} = N_S \frac{k_6 K_{CO} K_{H_2O} P_{H_2O} P_{CO} (1-\beta)}{(1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O} + K_{CO_2} P_{CO_2})^2}$	10
3	$r_{CO} = N_S \frac{k_7 K_{H_2O} K_{CO} P_{H_2O} P_{CO} (1-\beta)}{(1 + K_{CO} P_{CO} + \sqrt{k_5 P_{H_2} + K_{H_2O} P_{H_2O} + K_{CO_2} P_{CO_2}})^2}$	10
4	$r_{CO} = N_S \frac{k_{11} K_{H_2O} P_{H_2O} P_{CO} (1-\beta)}{1 + K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}}$	6
5	$r_{CO} = N_S \frac{k_{12} K_{CO} P_{H_2O} P_{CO} (1-\beta)}{1 + K_{CO} P_{CO} + K_{CO_2} P_{CO_2}}$	6
6	$r_{CO} = N_S \frac{k_9 k_{10} K_{CO} P_{H_2O} P_{CO} (1-\beta)}{1 + K_{CO} P_{CO} + \frac{k_9 K_{CO}}{k_{-9} + k_{10}} P_{CO} P_{H_2O} + \frac{k_{-10} K_{H_2}}{k_{-9} + k_{10}} P_{H_2} P_{CO_2} + K_{H_2} P_{H_2}}$	8
7	$r_{CO} = N_S \frac{k_{17} K_{CO} K_{15} P_{H_2O} P_{CO} (1-\beta)}{(1 + K_{CO} P_{CO} + K_{CO_2} P_{CO_2})(1 + K_{16} P_{H_2} + K_{15} P_{H_2O})}$	10
8	$r_{CO} = N_S \frac{k_{18} k_{19} K_{CO} P_{H_2O} P_{CO} (1-\beta)}{k_{-18} + k_{19} + k_{18} K_{CO} P_{CO} P_{H_2O} + k_{-19} K_{CO_2} P_{H_2} P_{CO_2}}$	10

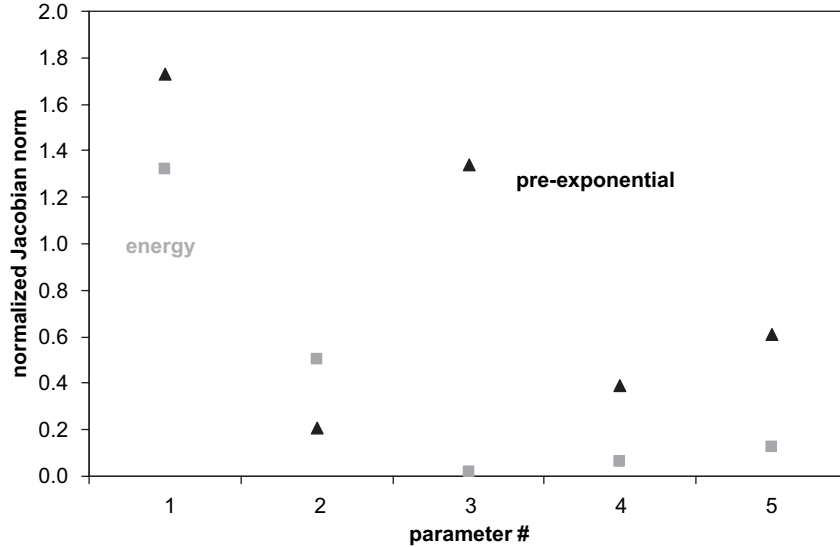


Fig. 3. The norm of the Jacobian matrix for each parameter in rate-equation (3).

where  $SS(\beta_1)$  is the residual sum of squares without parameter  $\beta_2$  and  $SS(\beta_1, \beta_2)$  the residual sum of squares with all parameters;  $df(\beta_2)$  is the degree of freedom from removing one parameter, hence it is equal to one.  $s^2$  is the variance for  $n$  experiments and  $p$  parameters. The calculated  $F$ -value needs to be larger than the tabulated one at a 95% level  $F(0.95, 1, n-p)$ . In Fig. 5 the change in the residual sum of squares is plotted as a function of the number of removed parameters. The dotted horizontal line corresponds to the threshold level of the sum of squares, calculated with Eq. (5), above which removal of an additional parameter is no longer justified statistically. It can be seen that removal of the first three parameters does not change the quality of the fit. By eliminating the fourth parameter, the change in the sum of squares is larger than the tabulated  $F$ -value, even after a re-optimization. Thus, the simplified

rate-equation contains seven parameters that are properly estimated with a correct 95% confidence interval. In this example, the three parameters that have been eliminated are three adsorption enthalpies for water, hydrogen and carbon dioxide. Apparently, the sorption of these components is not very strong or the temperature domain is too limited to estimate these parameters correctly.

This procedure has been applied to all rate-equations listed in Table 2. Table 3 summarizes the number of estimated parameters and the residual sums of squares for the different rate-equations. As follows from Table 3, rate-equation (3) describes the data most adequately for the Cu/Zn/Al catalyst and rate-equation (1) for the Cu/Ce/Al catalyst. The differences with a certain number of other models are rather small.

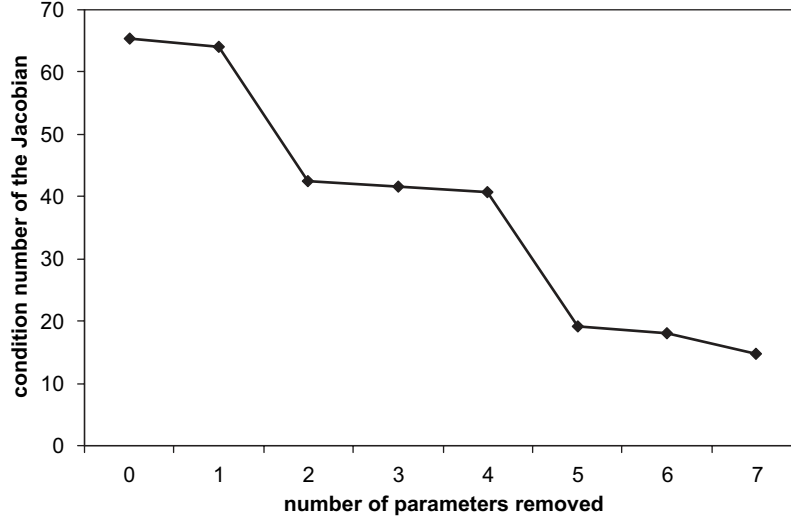


Fig. 4. Condition number of the Jacobian matrix as a function of the number of parameters removed from rate-equation (3).

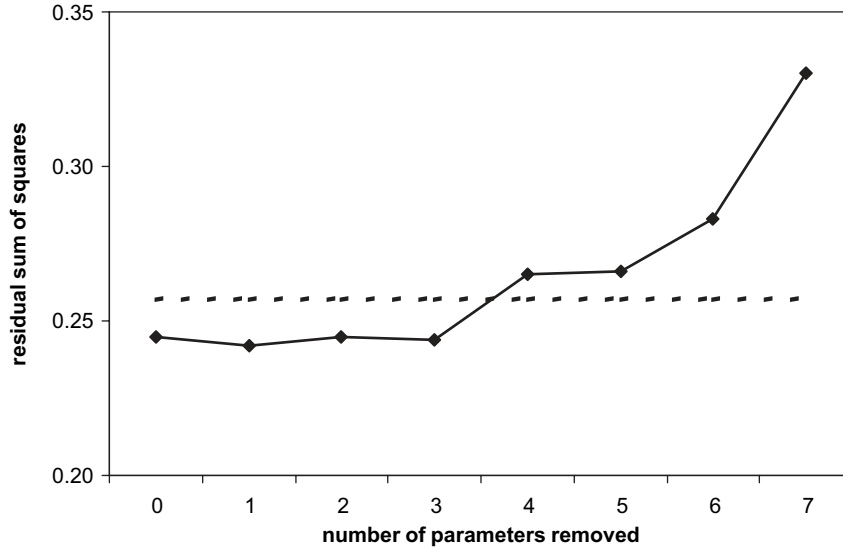


Fig. 5. Residual sum of squares as a function of the number of parameters removed from rate-equation (3). The dashed line represents the threshold value of the additional sum of squares criterion (5).

Table 3  
Residual sum of squares for the data over the Cu/Zn/Al and Cu/Ce/Al catalysts using rate equation (1)–(8)

Rate equation	Number of estimated parameters	Residual sum of squares Cu/Zn/Al	Residual sum of squares Cu/Ce/Al
1	4	0.32	0.24
2	5	0.28	0.48
3	7	0.25	0.47
4	4	0.32	
5	3	0.36	
6	5	0.34	
7	5		0.41
8	4		0.59

Rate-equation (1) describes the data for both catalysts adequately and is based on the two-step redox mechanism:



In order to compare the two catalysts properly, rate-equation (1) has been rearranged into the following form:

$$r_{\text{CO}} = N_S \frac{k_1' \exp\left(-\frac{E_I}{RT}\right) k_1'' \exp\left(-\frac{E_{II}}{RT}\right) P_{\text{H}_2\text{O}} P_{\text{CO}} (1 - \beta_I \beta_{II})}{k_1' \exp\left(-\frac{E_I}{RT}\right) P_{\text{H}_2\text{O}} (1 + \beta_I) + k_1'' \exp\left(-\frac{E_{II}}{RT}\right) P_{\text{CO}} (1 + \beta_{II})} \quad (8)$$

Table 4  
Parameter estimates of rate-equation (8)

Parameter	Cu/Zn/Al	Cu/Ce/Al
$k_1^0$	$1.0 \pm 0.6 \times 10^7$	$2.4 \pm 1.0 \times 10^3$
$E_1$	$79 \pm 20$	$31 \pm 18$
$k_{II}^0$	$9.3 \pm 1.1 \times 10^2$	$1.6 \pm 0.2 \times 10^3$
$E_{II}$	$23 \pm 5$	$26 \pm 9$

where  $\beta_I$  and  $\beta_{II}$  are the analogue expressions of  $\beta$  for reactions (6) and (7). The parameter estimates for  $k_i^0$  and  $E_i$  are listed in Table 4

#### 4. Discussion

There are two reaction mechanisms proposed in the literature, an associative and a redox. In the associative mechanism a surface reaction between CO and H<sub>2</sub>O forms an intermediate species, usually referred to as a formate species. This intermediate species decomposes into H<sub>2</sub> and CO<sub>2</sub> (Van Herwijnen and De Jong, 1980; Shido and Iwasawa, 1993; Grenoble et al., 1981). The redox mechanism consists of the decomposition of water into hydrogen and adsorbed oxygen followed by a reaction between CO and the adsorbed oxygen species into CO<sub>2</sub> (Temkin, 1979; Waugh, 1999; Ovesen et al., 1992; Callaghan et al., 2003).

In the case of the Cu/Ce/Al catalyst the experimental data are most adequately described by rate-equation (1). However, in the case of the Cu/Zn/Al catalyst the kinetic study does not allow to discriminate between the two reaction mechanisms. A large number of the rate-equations describe the data adequately and the difference in the quality of the fit seems to mainly depend on the number of parameters appearing in the final equation. In fact, the form of the rate-equations for the different reaction paths is rather similar. If no parameters are eliminated during the regression analysis, it will result in an identical fit for all models. The procedure for eliminating model parameters, presented here allows to choose the best rate-equation and improves the robustness of the model, but we still believe that the models are too close to conclude on the prevailing reaction mechanism. A microkinetic approach where the rate parameters are taken from independent studies over well-defined Cu surfaces can thus be justified. Several different studies (Temkin, 1979; Waugh, 1999; Ovesen et al., 1992) have shown that the WGS reaction over copper catalyst can be adequately described by a redox mechanism with physical meaningful parameters obtained from either independent experimental studies under well-defined conditions or theoretical calculations. A recent study has shown that this redox mechanism describes the data over a Cu/ceria catalyst as well (Koryabkina et al., 2003). This redox mechanism can be reduced to the well-known two-step mechanism initially proposed by Temkin (1979). Our study is in agreement with the above-mentioned studies as the data over both catalysts are adequately described by the two-step mechanism. Fig. 6 shows a parity graph of the experimental data fitted to rate-equation (8). From this graph it can be concluded that the model describes the data over both catalysts adequately

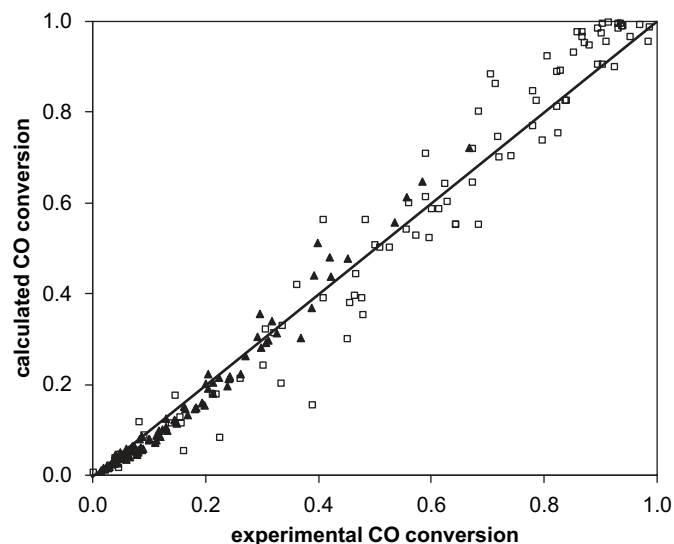


Fig. 6. Parity plot of all experimental data fitted to rate-equation (8). Open squares: Cu/Zn/Al, closed triangles: Cu/Ce/Al.

although some scattering exists for the data over Cu/Zn/Al and the model is slightly biased with respect to the regions of low and high conversions in case of Cu/Ce/Al. To evaluate the accuracy of the model, the model was tested against data that were not included in the regression procedure. Fig. 2 compares the model to these specific data. Although there is more scattering than with the regressed data, the fit is still adequate.

Note that the rate constants obtained from rate-equation (8) are lumped terms of the rate constant with the adsorption rate constants of CO and H<sub>2</sub>O. This makes a careful assessment of the physical meaning of the parameters rather difficult. However, the activation energies of the processes over copper related sites on both Cu/Zn/Al and Cu/Ce/Al can be estimated by assuming typical values for the adsorption enthalpies of carbon monoxide and water on copper surfaces of  $-50$  and  $-44$  kJ/mol, respectively (Ovesen et al., 1992). This leads to activation energies for the carbon monoxide oxidation step of approximately 75 kJ/mol for both catalysts. This is in the range of the values of 64 kJ/mol given by Ovesen et al. (1992) and 80 kJ/mol given by Waugh (1999). The activation energies for the oxidation of CO are rather similar for both catalysts, confirming that the active site for carbon monoxide activation is a reduced copper site for both catalysts. The values of the activation energies for the activation of water strongly depend on the type of catalyst. Using the above value for the adsorption enthalpy of water, an activation energy of 123 kJ/mol is calculated for the dissociation of water over the Cu/Zn/Al catalyst. This value is slightly higher than the 114 kJ/mol given by Ovesen et al. (1992) for the predominant crystal face Cu(1 1 1). Apparently the addition of ceria leads to a lower barrier for the activation of water (31 vs. 79 kJ/mol). As the parameters are lumped this might be a combined effect of adsorption and reaction. Indeed, reduced ceria is known to decompose water into hydrogen in the investigated temperatures range (Otsuka et al., 1983).

The lower activity of the Cu/Ce/Al catalyst compared to the Cu/Zn/Al is thus entirely due to the much lower copper surface area of the former one (2 vs. 12 m<sup>2</sup>/g<sub>cat</sub>).

## 5. Conclusions

A rigorous procedure based on an analysis of the Jacobian matrix has been applied in order to eliminate non-influential parameters from the rate-equations. This improves the estimation of the parameters and leads to a more robust model.

Discrimination between associative and redox mechanisms for the Cu/Zn/Al catalyst based on Langmuir–Hinshelwood type rate-equations was not feasible. The data over both the Cu/Zn/Al and the Cu/Ce/Al catalysts can be adequately described by a two-step redox mechanism with physically meaningful parameters. The role of ceria consists of lowering the activation barrier of water.

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