

# Cycles Across an Equilibrium: Studies of the Reverse and Forward WGS Reaction over a 2% Pt/CeO<sub>2</sub> Catalyst (Experimental Data and ‘Kinetic Resistance’ Analysis)

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## 1. Introduction

The water-gas shift reaction (WGS), both the reverse one ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ) and forward one ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ), are important reactions. The forward WGS reaction (FWGS) has found a wide application in hydrogen production, ammonia synthesis and hydrotreating of petroleum stocks. Presently, ceria-supported noble catalysts are considered as potential candidates for the next generation of catalysts. In comparison with industrially based Cu-based materials, these catalysts present high low-temperature activity and are less pyrophoric. The reverse WGS reaction (RWGS) can be used in some cases for control of CO<sub>2</sub> – emission.

The goal of this paper is to examine the forward and reverse WGS reactions over 2%Pt/CeO<sub>2</sub> catalyst under steady-state conditions using a procedure which entails adjusting feed gas concentrations to cycle back and forth across the equilibrium line. To our best knowledge, such a procedure has not been used before in WGS studies. Steady-state kinetic data was collected on ‘both sides’ of the equilibrium under varying feed gas compositions (CO and CO<sub>2</sub> concentrations) and temperatures. The obtained data are interpreted using the apparent ‘kinetic resistance’ concept.

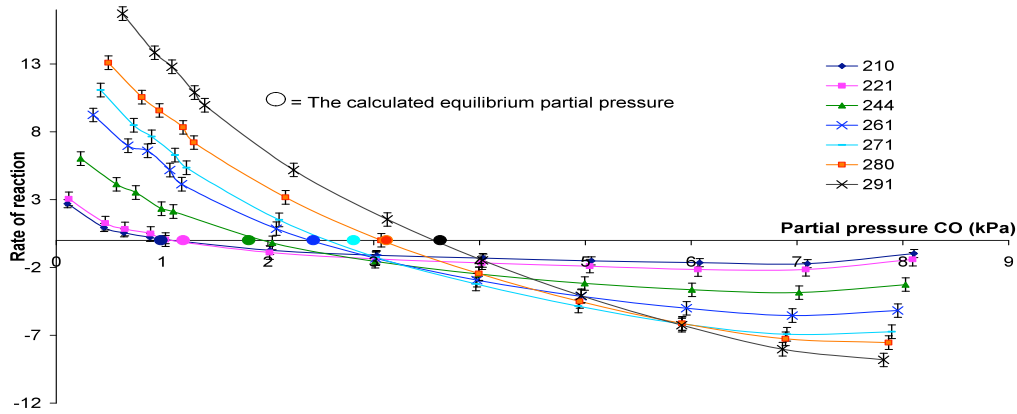
## 2. Experimental

Kinetic experiments were carried out in a plug flow quartz tube microreactor containing 50 mg of 2%Pt/CeO<sub>2</sub>. CO, CO<sub>2</sub> and H<sub>2</sub> were fed to the reactor using Aera mass flow controllers, the water was delivered by means of a water saturator. The partial pressures of H<sub>2</sub>O and H<sub>2</sub> were maintained at 10 and 57.2 kPa respectively. The partial pressures of CO and CO<sub>2</sub> were varied, however, the combined partial pressure of CO and CO<sub>2</sub> was maintained at 32.8 kPa. The reaction was studied at temperatures ranging from 210 to 291 °C. Prior to reaction the catalyst was pre-treated in pure H<sub>2</sub> at 300 °C for 30 min. Analysis of the reactants and products was by means of a GC (Perkin Elmer; Auto System XL ARNEL) fitted with a thermal conductivity detector. Equilibrium calculations were conducted using HSC Chemistry Ver 4.1 software from Outokumpu Research Oy, Finland.

## 3. Results and discussion

Figure 1 shows the reaction rate at different temperatures as a function of the partial pressure of CO. A positive rate of reaction signifies production of CO via the reverse WGS reaction. Conversely, a negative rate of reaction indicates CO consumption via the forward reaction. The equilibrium partial pressure at each

temperature is denoted as a filled circle on the x-axis. As expected the reaction passed from the reverse to the forward reaction with increasing partial pressure of CO. The point at which this occurred closely matched the calculated equilibrium CO partial pressure at each temperature.



**Figure 1.** Reaction rate as a function of reaction temperature and partial pressure of CO

Comparing the reaction rate dependences obtained in different concentration domains , ‘left’ and ‘right’ from the equilibrium point, a difference in kinetic behavior between two studied domains on “both sides of the equilibrium” can be seen.

(a) ‘left’ domain (the reverse WGS-reaction) is characterized by the regular steady-state kinetic dependences on the CO concentration and temperature: rate is growing with the temperature rise and CO concentration decrease.

(b) In the ‘right’ domain (the forward WGS-reaction), the rate dependence on the temperature has a minimum at some temperature interval. Under the low temperatures the rate dependence on CO concentration is characterized by the minimum as well, although this minimum is not well distinguished (rather to say it is a plateau). Under high temperatures (above 261°C) such a rate minimum is not observed.

The presented data have been interpreted based on general ‘four-term’ kinetic expression obtained recently by Lazman and Yablonsky<sup>1</sup> with no typical simplifications about the limiting step or the ‘vicinity’ of the equilibrium, i.e.

$$R = \frac{k_+ (f_+(c) - K_{eq}^{-1} f_-(c))}{\Sigma(k, c)} N(k, c), \quad (I)$$

The four terms are: (1) the apparent kinetic coefficient  $k_+$ ; (2) the ‘potential term’  $(f_+(c) - K_{eq}^{-1} f_-(c))$  related to the global (overall) reaction (‘driving force’ of irreversible thermodynamics). In our case  $f_+(c) - K_{eq}^{-1} f_-(c) = C_{CO} C_{H_2O} - C_{CO_2} C_{H_2} / K_{eq}$ , where  $C_{CO}$ ,  $C_{H_2O}$ ,  $C_{CO_2}$ ,  $C_{H_2}$  are concentrations of gaseous substances,  $K_{eq}$  is a equilibrium constant; (3) the ‘resistance’ term,  $\Sigma(k, c)$ , denominator of the polynomial type , which reflects complexity of chemical reaction, both its non-elementarity (many- step character) and non-linearity of elementary steps as well; (4) finally, the “fourth term”,  $N(k, c)$ , a polynomial in concentrations and kinetic parameters. This fourth term is generated exclusively by the non-linearity of reaction steps. It is the main distinguishing feature of this equation in comparison with

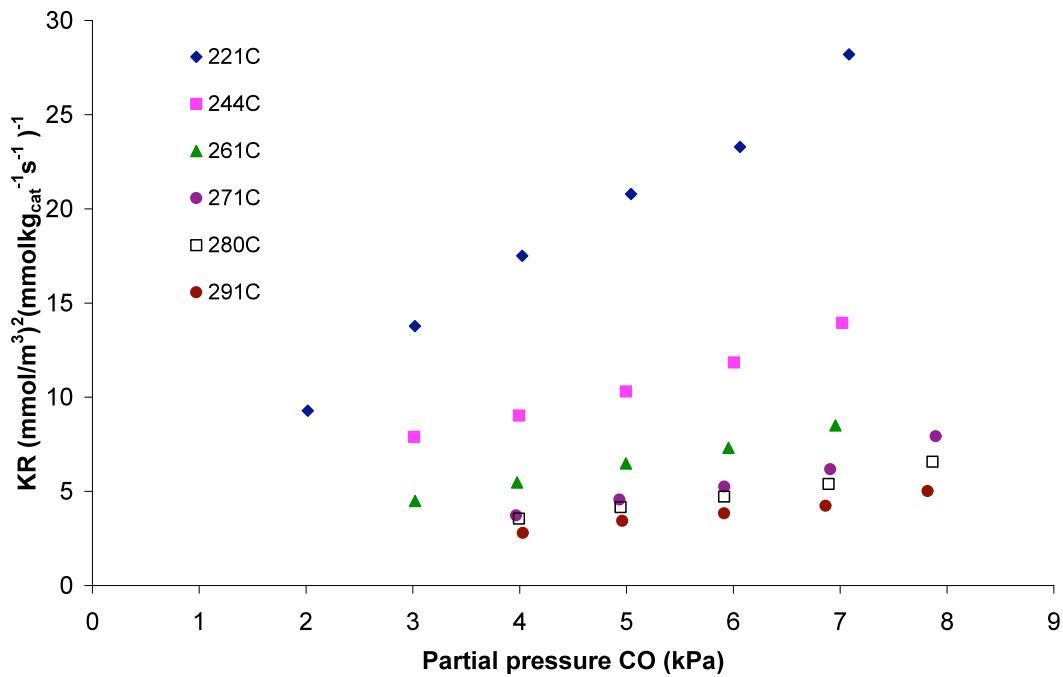
Langmuir-Hinshelwood-Hougen-Watson(LHHW)-equations based on simplifying assumptions. In the absence of non-linear steps the “fourth” term is also absent. The kinetic equation (1) has been presented as follows

$$KR_{app} = (f_+(c) - K_{eq}^{-1} f_-(c)) / R, \quad (2)$$

where  $KR_{app}$  = is the “apparent kinetic resistance”

$$KR_{app} = \Sigma(k, c)_{app} = (\Sigma(k, c)) / (k + N(k, c))$$

The apparent kinetic resistance ( $KR_{app}$ ) was presented as a function of the partial pressure of CO(kPa) at fixed temperatures and a function of the temperature, T, at given partial pressure of CO, see fig.2 and 3.



**Fig. 2** Relationship between the apparent kinetic resistance,  $KR_{app}$ , and partial pressure of CO at different temperatures

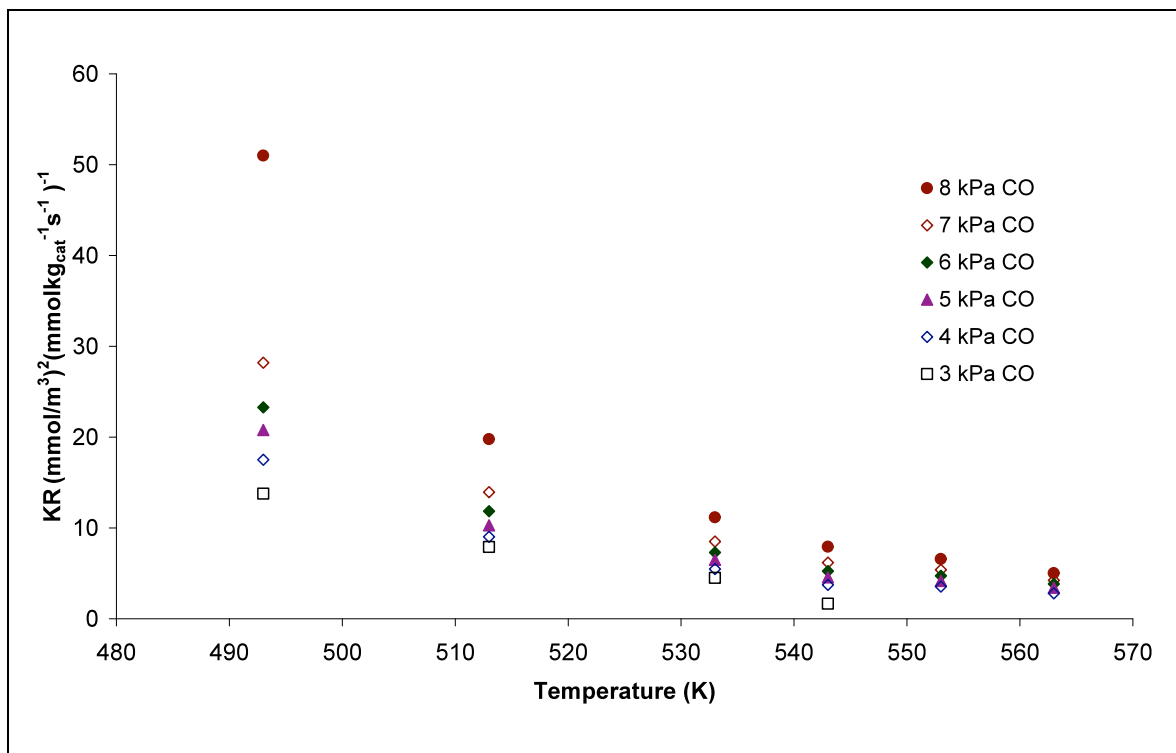


Fig. 3 Relationship between resistance ( $KR_{app}$ ) and temperatures at different partial pressures of CO

The presented concentration and temperature dependences of the apparent kinetic resistance behave in a whole parametric domain of ‘both sides’ of the equilibrium” in a very simple way which is “easy to understand”. The values of the kinetic resistance are increased with the CO concentration and exponentially decreased with the temperature. This behavior is explained within the detailed mechanism by the change of surface composition with the change of controlled parameters. The pressure rise promotes the increase of surface carbon containing concentrations. The temperature rise accelerates desorption of adsorbed species.

An apparent ‘kinetic resistance can be easily approximated by the polynomial regarding gas concentrations (in this case, CO concentration) which parameters depend on the temperature exponentially.

Summing up, we consider that a problem of the search for the description of steady-state kinetic behavior “on both sides of equilibrium” can be solved as follows:

- (a) Knowing the reaction net-rate and its driving force, we calculate the apparent kinetic resistance using Eqn (2)
- (b) Presenting this resistance as a function of concentration(s) and temperature, we approximate it by polynomials in the whole concentration domain on” both sides of the equilibrium”.

The advantage of this procedure is that in many cases the apparent ‘kinetic resistance’ is a linear function regarding its parameters, and procedure based on the  $KR_{app}$  identification is more convenient than the identification of the parameters of non-linear LHHW-models.

### References

1. Lazman M.Z., & Yablonsky G.S. (2008). Overall Reaction Rate Equation of Single-Route Complex Catalytic Reaction in Terms of Hypergeometric Series, *Adv. in Chemical Engineering*, v.34, pp. 47-102