

## A KINETIC MECHANISM OF THE WATER-GAS-SHIFT REACTION OVER $K_2CO_3$ /CARBON

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### Abstract

Kinetic data of the alkali catalysed WGS reaction can be described by a two step oxygen-exchange mechanism and an additional  $CO_2$ -chemisorption step. The Water-Gas-Shift reaction rate is dependent on both the partial pressure of the reducing and the oxidizing agent. In the presence of  $CO_2$  in the gas phase reactivity is low, or decreases significantly if  $CO_2$  is added to a  $CO, H_2O$  mixture.

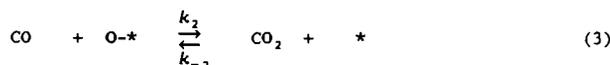
### Introduction

The Water-Gas-Shift reaction (1) is not only of importance for hydrogen production on industrial scale, but also as a side reaction in steam gasification.



Many investigators have studied the kinetics of the WGS reaction over iron, copper, chromium and cobalt-molybdenum catalysts [1-8], but few studies have been made on the role of the WGS reaction in alkali catalysed steam gasification [9-13]. In this study results are presented of a kinetic study on the WGS reaction catalysed by  $K_2CO_3$ /activated carbon at temperatures (650-950 K) where gasification and methanation do not occur.

The kinetics of the WGS reaction have been described [9] as a set of two oxygen-exchange reactions (2),(3), similar to the oxidation-reduction cycle in the mechanism for alkali catalysed gasification in  $CO_2$  and  $H_2O$ .

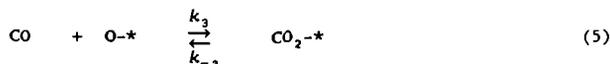


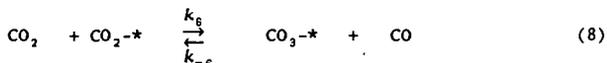
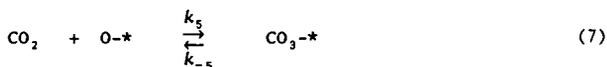
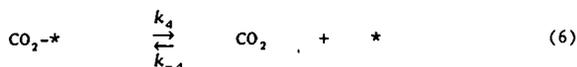
Hüttiger et al. [9] have studied the  $CO, H_2O$  oxygen-exchange rate. Their kinetic data are fitted by a power-law rate equation (4) assuming differential reactor behaviour. They concluded that addition of  $H_2$  to the feed does not affect the oxygen-exchange rate, addition of  $CO_2$  was not investigated.

$$r = k pCO^{0.6} pH_2O^{0.4} \quad (4)$$

Based upon substantial evidence [11,14-16] Cerfontain et al. [14] have proposed an extended model for describing oxygen-exchange in  $CO, CO_2$  mixtures: a  $CO, CO_2$  oxygen-exchange (8), preceded by a  $CO_2$ -chemisorption step. This  $CO_2$ -chemisorption is nearly temperature and pressure independent and  $CO_2$  easily exchanges with gas phase  $CO_2$ . Furthermore the amount of chemisorbed  $CO_2$  per amount of metal initially present correlated with the oxygen-exchange rate.

It is plausible that in the presence of  $CO_2$  in the gas phase,  $CO_2$ -chemisorption in the alkali-metal cluster also plays a role in the alkali catalysed WGS reaction. The two step model (2),(3) is therefore extended with additional chemisorption steps (5),(6),(7) and other routes for  $CO, CO_2$  exchange (5),(6) or (6),(7),(8).





A possible mechanism for CO, CO<sub>2</sub> oxygen-exchange, in which a CO<sub>2</sub>-\* intermediate is present, is a combination of steps (5) and (6). In order to establish a kinetic model of the alkali catalysed WGS reaction the influence of catalyst loading, partial pressures of reactants and products on the forward- (H<sub>2</sub>O + CO →) and backward- (CO<sub>2</sub> + H<sub>2</sub> →) oxygen exchange rate have been studied.

### Experimental

WGS experiments were performed in a Fixed-Bed flow reactor described in detail elsewhere [17,18]. Basically it consists of a gas mixing section, an oven ( $T_{\text{max}} = 1273 \text{ K}$ ,  $P_{\text{max}} = 2.5 \text{ MPa}$ ) containing the carbon sample in a quartz tube (I.D. = 3 - 7 mm) and a gas chromatograph (HP 5190 A) for product analysis (dual column, He carrier, TCD detection). All experiments were performed in a ceramic (0.2-1.6 MPa) or quartz (0.15 MPa) reactor.

The activated carbon used in this study is Norit RX1 Extra, an acid washed, steam activated peat char with a high specific surface area (1100 m<sup>2</sup>.g<sup>-1</sup> (CO<sub>2</sub>(DR), 273 K), 1500 m<sup>2</sup>.g<sup>-1</sup> (N<sub>2</sub>(BET), 77 K), particle size 0.25-0.6 mm, 3 wt% ash). Addition of catalyst was performed by pore volume impregnation with an aqueous M<sub>2</sub>CO<sub>3</sub> (M=Na,K,Cs) solution. The catalyst loading is expressed as a molar M/C ratio.

A reproducible sample for each WGS experiment was obtained by drying *in situ* ( $T = 473 \text{ K}$ , He) followed by isothermal gasification ( $T = 1000 \text{ K}$ ,  $P_t = 0.15 \text{ MPa}$ ,  $F_t = 140 \mu\text{mol.s}^{-1}$ ,  $p\text{H}_2\text{O}$  or  $p\text{CO}_2 = 0.05 \text{ MPa}$ , balance He) to a steady gasification level (20-30 wt% burn-off). Subsequently the sample is cooled to 673 K and a WGS experiment is started. The WGS oxygen-exchange rate  $r_{\text{OX}}$  is measured in a temperature cycle (673-950(833)-673 K), in which temperature is varied stepwise, and expressed as ( $\mu\text{mol oxygen exchanged}$ )/( $\mu\text{mol carbon initially present}$ )<sup>-1</sup>.s<sup>-1</sup>. The oxygen exchange rate of a particular reactant mixture is referred to as  $r_{\text{OX}}$  (reactant molecules), e.g. the forward shift as  $r_{\text{OX}}(\text{CO}, \text{H}_2\text{O})$ .

CO, H<sub>2</sub>O oxygen-exchange experiments were performed with a feed consisting of CO, H<sub>2</sub>O and a balance of helium in which the reactant ratio in the feed ( $q = (p\text{CO}/p\text{H}_2\text{O})_{\text{feed}}$ ) was varied from 0.15 to 5.0 ( $P_t = 0.15 \text{ MPa}$ ,  $F_t = 140 \mu\text{mol.s}^{-1}$ ).

CO<sub>2</sub>, H<sub>2</sub> oxygen-exchange experiments were performed with variation of total pressure (0.15-1.6 MPa) and reactant ratio ( $q' = (p\text{H}_2/p\text{CO}_2)_{\text{feed}} = 0.14 - 7.0$ ).

For each  $q$  and  $q'$  value a fresh sample was used. Inhibition effects of products on oxygen-exchange rates were studied by (partially) replacing the helium in the feed ( $P_t = 0.15 \text{ MPa}$ ) by a product.

### Results

In figure 1 WGS rate data ( $r_{\text{OX}}(\text{CO}, \text{H}_2\text{O})$ ) and CO<sub>2</sub>- and H<sub>2</sub>O-gasification data ( $r_p$ ) are shown. Clearly in all three cases the same dependency on the K/C ratio is observed. The carbon itself hardly showed any oxygen-exchange reactivity. It is found that  $r_{\text{OX}}(\text{CO}, \text{H}_2\text{O})$  is dependent on both the partial pressure of the reducing and the oxidizing agent. As shown in figure 2 addition of H<sub>2</sub> to a feed, containing CO and H<sub>2</sub>O, does not affect the measured CO conversion, whereas CO<sub>2</sub> strongly inhibits.

$r_{\text{OX}}(\text{H}_2, \text{CO}_2)$  is predominantly dependent on the H<sub>2</sub> partial pressure. Figure 3 shows that with increasing  $p\text{H}_2$  ( $q'$  constant; open vs. closed symbols)  $r_{\text{OX}}(\text{H}_2, \text{CO}_2)$  increases. With increasing  $p\text{CO}_2$  ( $p\text{H}_2$  constant; open and closed symbols) a decrease in  $r_{\text{OX}}(\text{H}_2, \text{CO}_2)$  is observed. From figure 4 it can be seen that addition of H<sub>2</sub>O decreases the measured CO<sub>2</sub> conversion significantly,

whereas addition of CO only has a small effect.

### Discussion

The WGS reaction, like  $^{12}\text{CO}$ ,  $^{13}\text{CO}_2$  [14] and  $\text{D}_2, \text{H}_2\text{O}$  [19] oxygen-exchange, takes place in the alkali-metal-oxide clusters present on the carbon surface. Furthermore oxygen-exchange rates exhibit the same dependency on the K/C ratio as gasification reactions. In contrast to reported  $\text{D}_2, \text{H}_2\text{O}$  and  $^{12}\text{CO}, ^{13}\text{CO}_2$  oxygen-exchange rates,  $r_{\text{ox}}(\text{CO}, \text{H}_2\text{O})$  is dependent on both the partial pressure of the reducing and the oxidizing agent. With a two step oxygen-exchange mechanism (2),(3), kinetic data from  $\text{CO}, \text{H}_2\text{O}$  exchange experiments could be adequately described. However addition of  $\text{CO}_2$  to the  $\text{CO}, \text{H}_2\text{O}$  reactant mixture and the  $\text{CO}_2, \text{H}_2$  exchange data showed a poor correlation with this model. This is probably caused by a strong  $\text{CO}_2$ -chemisorption under these conditions.

Therefore the kinetic model for best describing the WGS reaction consists of a  $\text{CO}, \text{CO}_2$  oxygen exchange via a chemisorbed  $\text{CO}_2$  intermediate (steps 5 and 6), whereas the  $\text{H}_2, \text{H}_2\text{O}$  exchange is believed to proceed via (2).

Direct proof for the existence of  $\text{CO}_2$ -chemisorption is obtained from thermogravimetric experiments [20] with catalyst/carbon (M=Na,K,Cs) samples. Introduction of  $\text{CO}_2$  at 650 K to a gas phase containing  $\text{CO}, \text{H}_2\text{O}$  or  $\text{H}_2, \text{H}_2\text{O}$  shows an instantaneous weight increase. If the total weight gain is ascribed to  $\text{CO}_2$ -chemisorption in the alkali metal cluster (pure carbon shows no weight change), this corresponds to a  $\text{CO}_2/\text{M}$  ratio of approximately 0.3 for all three alkali metals investigated. Removing  $\text{CO}_2$  from the gas phase only shows a slow isothermal (650 K) desorption rate. The chemisorbed  $\text{CO}_2$  can be completely removed on heating in argon to 850 K.

Mims and Pabst [11] have studied the oxygen-exchange rate in various mixtures and observed a rate order which is in good agreement with this study:  $r_{\text{ox}}(\text{D}_2, \text{H}_2\text{O}) \gg r_{\text{ox}}(\text{H}_2, \text{O}, \text{CO}) > r_{\text{ox}}(\text{CO}_2, \text{H}_2) > r_{\text{ox}}(\text{CO}, \text{CO}_2)$

All oxygen-exchange rates (especially  $\text{D}_2, \text{H}_2\text{O}$ ) are several orders of magnitude higher than the matching gasification rates. Addition of  $\text{CO}_2$  to a  $\text{D}_2, \text{H}_2\text{O}$  mixture suppresses the oxygen-exchange rate to a level similar to that of  $\text{CO}_2, \text{H}_2$  exchange. This difference in oxygen-exchange reactivity can be explained by a different state of the alkali cluster, depending on the amount of CO and/or  $\text{CO}_2$  which is present in the gas phase. From this and other studies [9,11,14,19] a summary of the order and pressure dependencies of oxygen-exchange rates can be made (table 1).

At present more work is in progress on determination of the rate parameters by modeling the whole data set,  $\text{CO}, \text{H}_2\text{O}$ ,  $\text{CO}_2, \text{H}_2$  and product inhibition data, taking  $\text{CO}_2$  chemisorption into account.

### Conclusions

- The WGS oxygen exchange takes place in the alkali-metal-oxide cluster and shows the same rate dependency on the alkali metal loading as gasification reactions.
- The WGS oxygen-exchange is, in contrast to  $\text{D}_2, \text{H}_2\text{O}$  [19] and  $^{12}\text{CO}, ^{13}\text{CO}_2$  [14] oxygen-exchange, dependent on both the partial pressure of the reducing and the oxidizing agent.
- The oxygen-exchange rate in the presence of  $\text{CO}_2$  is low or decreases significantly if  $\text{CO}_2$  is added to a  $\text{CO}, \text{H}_2\text{O}$  mixture.
- In the presence of  $\text{CO}_2$  in the gas phase,  $\text{CO}_2$ -chemisorption in the alkali-metal-oxide cluster takes place.
- Kinetic data of the alkali catalysed WGS reaction can be described by a two step oxygen-exchange mechanism and an additional  $\text{CO}_2$ -chemisorption step

### Acknowledgement

These investigations have been executed within the framework of the Dutch National Coal Research Programme (NOK), which is managed by the Project Office for Energy Research (NOVEM) and financed by the Ministry Of Economic Affairs.

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Table 1 : Order and pressure dependencies of oxygen exchange rates.

order of oxygen-exchange rates	effect on the exchange rate		
	↑	~	↓
D <sub>2</sub> , H <sub>2</sub> O	D <sub>2</sub>	H <sub>2</sub> O	CO <sub>2</sub>
>	CO		
CO, H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub>	CO <sub>2</sub>
>			H <sub>2</sub> O
CO <sub>2</sub> , H <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>
>			
<sup>12</sup> CO, <sup>13</sup> CO <sub>2</sub>	CO	CO <sub>2</sub>	

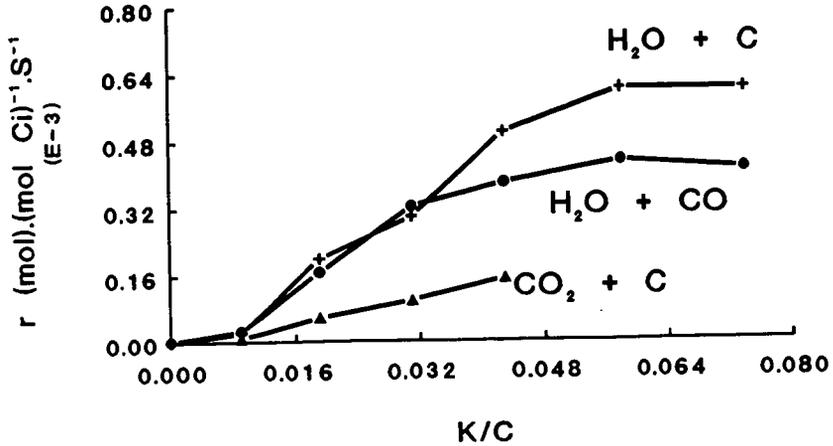


Figure 1 : Steady state reaction rates ( $r_n$ ) for  $\text{CO}_2$  ( $\blacktriangle$ ) and  $\text{H}_2\text{O}$  ( $+$ ) gasification at 1000 K (at 25% burn-off) and  $r_{\text{OX}}$  ( $\bullet$ ) at 833 K (after partial gasification in  $\text{H}_2\text{O}$  at 1000 K to 25% burn-off) as a function of the K/C ratio of the sample.

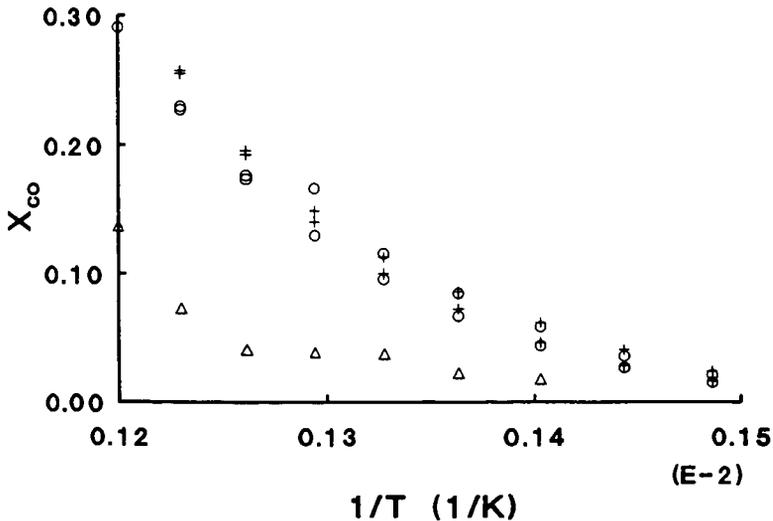


Figure 2 :  $\text{CO}_2/\text{H}_2\text{O}$  oxygen-exchange ( $\circ$ ) over a 10 wt%  $\text{K}_2\text{CO}_3$ /Norit RXI sample. The CO conversion is plotted as a function of  $1/T$  (1/K). Effect of  $\text{CO}_2$  ( $\blacktriangle$ ) and  $\text{H}_2$  ( $+$ ) addition to the feed.

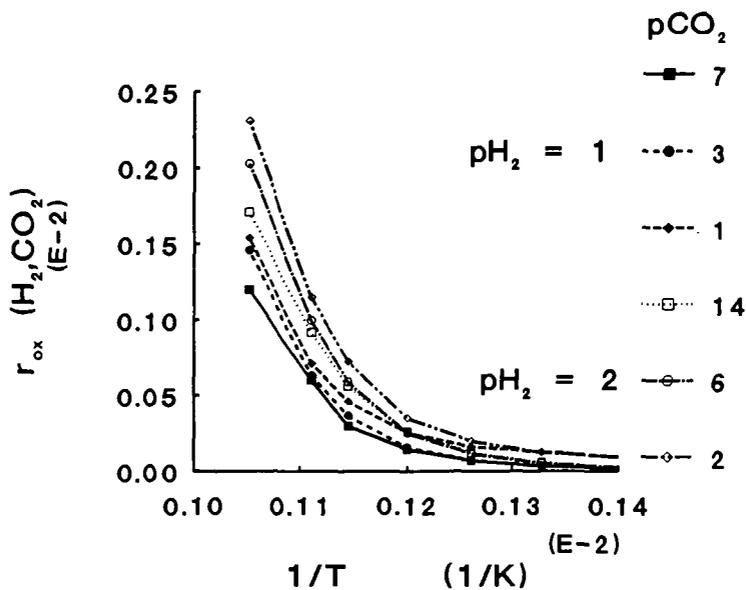


Figure 3 :  $r_{Ox}(H_2, CO_2)$  over a 10 wt%  $K_2CO_3$ /Norit RXI Extra sample as a function of  $1/T$  (1/K) for  $pH_2 = 1$  bar (closed symbols) and  $pH_2 = 2$  bar (open symbols) at different  $H_2/CO_2$  feed ratio.

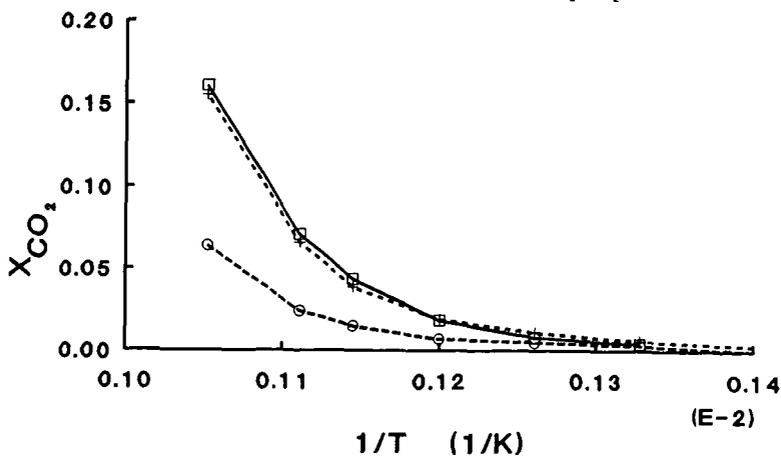


Figure 4 :  $CO_2, H_2$  oxygen exchange ( $\square$ ) over a 10 wt%  $K_2CO_3$ /Norit RXI sample. The  $CO_2$  conversion is plotted as a function of  $1/T$  (1/K). Effect of  $CO$  (+) and  $H_2O$  (O) addition to the feed.