

OUTGASING AND CO₂ GASIFICATION OF POTASSIUM CARBONATE/CARBON; INFLUENCE OF CATALYST CONTENT

by

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Abstract. The dependency of the K₂CO₃ catalyzed CO₂ gasification on the catalyst content, studied by reactivity and outgasing measurements, revealed that: The catalyst is most effective between 5-15 wt%, the activation energy remains unaltered. The catalyst is present in highly dispersed K₂CO₃ species and at high loadings as bulk carbonate.

Introduction

The K₂CO₃ catalysed gasification of carbon is still a subject of intensive research directed to the understanding of the mechanism of the reaction, and especially the role of the catalyst. A catalyst can enhance reaction rates in several ways. In this case the potassium might¹

- increase the number of active sites
- increase the concentration of reaction intermediates
- accelerate rates of elementary processes by decreasing activation energies, providing alternative pathways.

Reactivity and outgasing results are presented for the K-catalysed CO₂ gasification of carbon using different K₂CO₃ loadings.

The results are discussed within the framework of possible catalytic mechanisms mentioned above.

Experimental

The carbon substrate, an acid washed activated peat char (norit RX extra), was loaded with K₂CO₃ (Merck, CP) by pore volume impregnation resulting in 1, 2, 5, 10, 15, 20, 25 and 30 wt% K₂CO₃ on C.

Samples containing about 360 mg carbon were gasified in 100 μmol/s CO₂ at 1.5 bar by temperature cycling (10 K/min) between 700 and 1000 K². The second and further cycles yielded identical results. The advantage of this technique is the low carbon burn-off during an experiment.

After gasification the samples were cooled in CO₂ to 473 K after which a helium flow (100 μmol/s) replaced the CO₂ flow. Heating at a constant rate (10 K/min) to 1250 K and analysing the product gases (GC) yielded the outgasing pattern.

Results

In figure 1 the results of the temperature programmed activity measurements are presented. The reaction rate is normalised to the amount of carbon initially present.

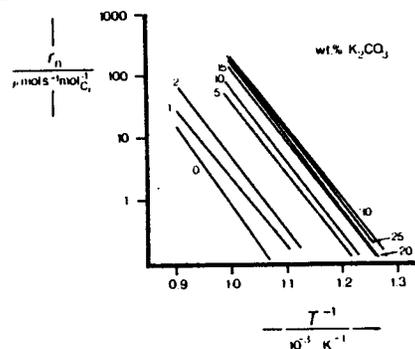


Figure 1. Normalised reaction rates for the CO₂ gasification of activated carbon as a function of 1/T for different wt% K₂CO₃ containing samples. (CO₂ flow 100 μmol/s, 360 mg C, P_{CO₂} = 1.5 bar).

Table 1. Apparent pre-exponential factors, activation energies and normalised reaction rates (at 1000 K) for different wt% K₂CO₃ containing activated carbons in the catalysed CO₂-gasification.

wt% K ₂ CO ₃	k_0 10 ⁶ mol/s mol C _i	E _a kJ/mol	r _i (1000 K) μmol/s mol C _i
0	3	241	0.85
1	0.28	211	2.8
2	1.3	218	5.6
5	6.9	215	40
10	17	217	75
15	30.5	217	143
20	39	221	161
25	27	214	190
30	28	214	203

Table 1 lists the apparent pre-exponential factor k_0 ($\mu\text{mol/s mol C}_1$) and apparent activation energy, E_a (kJ/mol). The reaction rate increases with catalyst content, whereas E_a remains constant within the experimental accuracy, viz. $216 \text{ kJ/mol} \pm 15$. This is comparable with previous results² at one loading. For comparison the reaction rate at 1000 K is included in table 1 and plotted in figure 2 as a function of the initial K/C ratio.

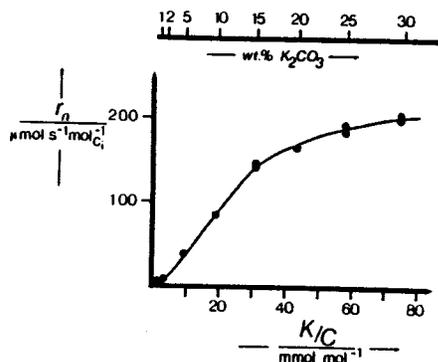


Figure 2. Normalised reaction rates at 1000 K versus the initial K/C ratio (from Fig. 1).

In figure 3 the outgassing patterns are given for the different samples. The CO_2 production patterns ($\mu\text{mol/s mol C}_1$) above 5 wt% K_2CO_3 are nearly identical. For the CO production two evolution peaks can be distinguished. One at high temperatures (1100-1200 K) present in all samples, at higher loadings (above 10 wt% K_2CO_3) hardly perceivable because of the more pronounced CO evolution at lower temperatures (800-1100 K).

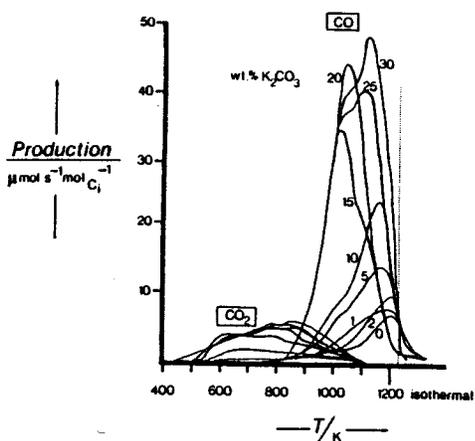


Figure 3. Outgassing patterns in He of activated carbon samples containing different wt% K_2CO_3 , after CO_2 gasification. (He flow $100 \mu\text{mol/s}$; heating rate 10 K/min ; initial sample 360 mg C).

Figure 4 represents the amount of CO and CO_2 released based on the amount of potassium present, which are corrected for the amounts released by the pure carbon. Up to 15 wt% K_2CO_3 the total O/K ratio is about 1.5 and decreases at higher contents. The O/K ratio is about 1 at low contents and decreases also at higher loadings. In the latter results the CO production arises from a different CO evolution region.

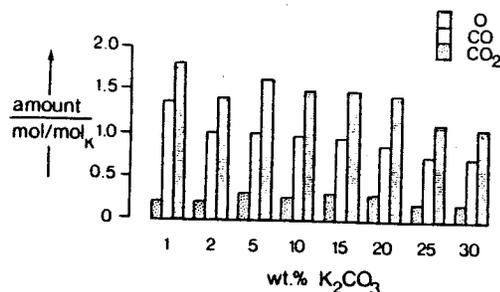


Figure 4. Amounts of CO_2 , CO and total O ($\text{CO} + 2 \text{CO}_2$) released by outgassing in He of K_2CO_3 /activated carbon samples (from Fig. 3).

Discussion

The results presented here are obtained by direct gasification of the samples in CO_2 , since pretreatment effects might disturb this comparison.

The reaction rate versus the K/C ratio shows the S-shaped relation reported by other authors. The deviation from a linear trend is explained by a strong interaction at low loadings resulting in relative low activities and at high loading the surface area limits the dispersion of the catalyst and bulk K_2CO_3 is present, leading to a lower activity per amount of potassium present.

The constant activation energy suggests that only the number of active sites increases with increasing potassium loading and agrees with results of kinetic analyses.

The outgassing results indicate that after gasification and cooling in CO_2 the potassium is present in carbonate-like species up to 15 wt%. At higher loading possibly stable bulk K_2CO_3 crystals are present which cannot be decomposed completely, resulting in lower O/K ratios. The high temperature CO evolution peak up to 10 wt% is ascribed to reduction of OK-species present at the surface². At higher loadings there is also CO production at lower temperatures (CO_2 release followed by gasification). This amount strongly depends, however, on the history of the sample and therefore complicates a correlation with a number of active sites.

In conclusion, these results constitute an extension of results published earlier for the alkali metals and confirm the conclusions proposed there². Increasing the potassium content increases only the number of active sites and doesn't change the apparent activation energy. Outgassing after cooling in CO_2 indicates the presence of highly dispersed carbonate-like species that can be decomposed at high temperature (up to 1200 K); at higher loading (>20 wt% K_2CO_3) possibly bulk K_2CO_3 is present resulting in CO/CO_2 release, and lower reaction rates. No correlation can be found, however, between outgassing results and the fraction of potassium active in gasification. Our results reveal that between 5 and 15 wt% the addition of the potassium is the most effective per potassium atom.

References

1. J.A. Moulijn, M.B. Cerfontain and F. Kapteijn, Fuel 63 (1984) 1043.
2. F. Kapteijn, G. Abbel and J.A. Moulijn, Fuel 63 (1984) 1036.