

Uncatalysed and MoO₃-Catalysed Carbon-Oxygen Reaction: A Kinetic Study

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A kinetic study was made of the reaction of activated carbon with oxygen, uncatalysed and catalysed by MoO₃, using a microbalance to record the loss of weight as a function of time. Orders and activation energies were measured. MoO₃ was found to be a moderate catalyst for this reaction. The effect of loading on reactivity is linear for low loadings and shows saturation above 2.5 wt%. It is proposed that this type of reaction, involving three phases and two interfaces, can be explained by surface catalysis at the gas/catalyst interface with continuous diffusion of carbon atoms through the catalyst. © 1990 Academic Press, Inc.

INTRODUCTION

Many studies have been devoted to the carbon-oxygen reaction and the role of impurities as catalysts for this reaction is well known (1, 2). Many types of catalysts have been added and their effect studied. Work with Mo and MoO₃ has been reported by several authors (3-6).

On graphite, MoO₃ was found to form small particles (60 to 100 nm in diameter) at 600 to 800 K and to operate by pitting and channelling (4). Some kinetic information is available from work using etch decoration/TEM (6) and thermogravimetric analysis (5). Recent developments in the use of carbon-supported molybdenum catalysts led us to make a comprehensive kinetic study of carbon gasification reactions catalysed by this metal. In a previous paper we reported the results of CO₂ gasification (7). In the present work we report a study of MoO₃-doped active carbon gasification by oxygen. A study of the uncatalysed reaction is included. This was made for comparison purposes.

EXPERIMENTAL

The kinetic experiments were conducted isothermally in a C.I. Electronics microbal-

ance with continuous recording of changes in weight. Charcoal of 605 m² g⁻¹ specific surface and a porous volume of 0.48 cm³ g⁻¹ was used (BDH, Product no. 33034). The charcoal was ground to an average radius of 3 μm to minimize internal mass transport limitations. Details of the geometry of the crucible and flow pattern around the sample are shown in Fig. 1. A constant flow rate of 3.5 cm³ s⁻¹ was used throughout this work, after testing for mass transfer limitations at 650°C using air. At higher temperatures the effect of mass transfer may occur, as is well documented in the following results.

The catalyst was MoO₃ obtained by calcination of ammonium molybdate at 600°C for 6 h. The catalyst was used in a percentage of 2.5 by weight and mixed with the activated carbon in a mortar. This percentage was selected after "loading" experiments were performed, as reported below. The purity of the gases was N₂, 99.99%; O₂, 99.5%; air, 99.95%. After mixing, the gases were passed through a molecular sieve to remove water. Total pressure used was always 1 atm (0.1 MPa) and the O₂ partial pressure varied from 1 atm down to 6.9 × 10⁻³ atm.

The present work is based on ca. 90 independent experiments conducted isothermally. An approximately constant rate of

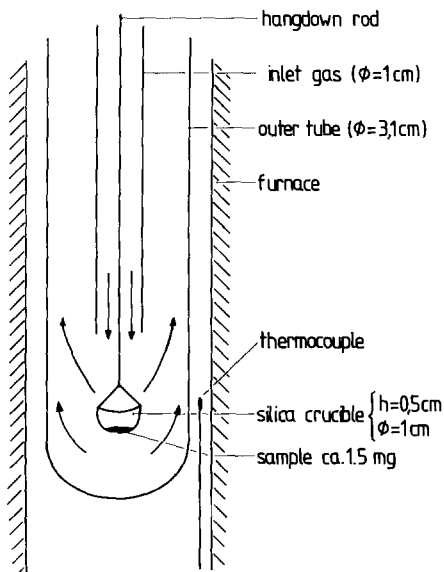


FIG. 1. Details of the geometry and flow pattern.

burnoff was generally observed up to ca. 50% burnoff. The information about the rate in the first 2 min was lost, due to transient conditions. The rate at 20% burnoff was used in the various plots and in calculating activation energies and orders of reaction.

RESULTS

Similarly to a previous work in which CO_2 was the reactant gas, we conducted preliminary stability experiments to check the loss of weight of carbon, of MoO_3 alone, and of the 2.5 wt% mixture in both air and N_2 atmospheres (7). The experiments were made at 700°C , a temperature on the higher side of the range to be explored. The results are shown in Table 1. It can be seen that MoO_3 sublimes slowly at this temperature. When mixed with carbon, however, no sublimation is detected (column 1). In columns 2 and 3 the loss of weight for the uncatalysed and the catalysed carbon combustion can be compared and it is found that the loss of catalyst plays no measurable part in it.

The results of 7 experiments using different percentages of catalyst (loading) from 0.025 to 10 wt% at 506°C are shown in Fig.

2. It can be observed that for low loading the effect of the catalyst is linear, and can be expressed as $1.0 \times 10^{-3} \text{ s}^{-1} (\text{wt}\% \text{ cat})^{-1}$. The loading curve shows a saturation effect above 2.5 wt%, similar to the case of CO_2 gasification (7).

A comprehensive study of the noncatalytic reaction of carbon and oxygen was made to enable a good comparison with the catalytic one. Figure 3 shows the weight vs time curves as recorded for pure oxygen at 1 atm and various temperatures, from 500 to 710°C . Similar experiments were carried at lower pressures, namely 2.1×10^{-1} , 3.3×10^{-2} , and 6.9×10^{-3} atm. At low pressures, induction periods are observed, followed by constant rate gasification. The rates at 20% burnoff are represented in the Arrhenius plot shown in Fig. 4a. Ignition is only observed with pure oxygen, at ca. 590°C . For lower partial pressures the effect of external mass transfer is dominant above 750°C . Data from Fig. 4a are transposed to a $\ln(\text{rate})/\ln P_{\text{O}_2}$ plot in Fig. 4b, where the orders of reaction at 500 and 750°C are shown.

A similar kinetic study was made for the MoO_3 2.5 wt% catalysed reaction. Figure 5 shows the weight vs time curves as recorded at 500°C and various O_2 partial pressures. Rates at 20% burnoff at various temperatures and under various pressures are represented in the Arrhenius plot shown in Fig. 6. Orders (n) of reaction at 450 , 500 , and 700°C are shown.

DISCUSSION

Kinetics

The uncatalysed and the MoO_3 -catalysed reactions show similar features. Activation energies and orders of reaction are similar. The catalyst lowers the temperature required to achieve a given rate by ca. 75 K. At a given temperature, the rate of the catalysed reaction is ca. 3 to 5 times faster, in the absence of mass transfer limitations. A comparison of the catalysed and uncatalysed reactions is presented in Fig. 7 for two sets of conditions.

TABLE I

Results of the Stability Experiments (Loss of Weight Rate $\times 10^5$ s ⁻¹)				
Gas	N ₂	O ₂ /N ₂	Air	Remarks
O ₂ pressure (atm)	0	0.033	0.21	
MoO ₃	1.5	2.4(b)	8.3(c)	Sublimation
Carbon(C)	0	155	833(d)	Noncatalytic
C + 2.5% MoO ₃	~0(a)	270(e)	1600(e)	Catalytic
C + 20% MoO ₃	~0	—	1610(f)	Catalytic

Notes. (a) MoO₃ does not lose weight when in contact with carbon; (b) with oxygen, loss of weight is more pronounced; (c) the effect of oxygen in the loss of weight is first order; (d) noncatalytic carbon gasification is first order in this case; (e) effect of the catalyst on the rate; (f) saturation effect of increasing MoO₃ load is observed.

Both reactions show ignition points when using pure oxygen. The ignition point is observed at a temperature lower by ca. 55 K for the catalysed reaction, but at similar rates, with values of 2×10^{-3} s⁻¹ just before ignition and 45×10^{-3} s⁻¹ after ignition in both cases. This is to be expected, as the ignition is a result of a combined heat and mass transfer balance, and the sample size and all other variables are kept constant (geometry, flow rate, oxygen pressure).

For the uncatalysed reaction the activation energy observed is 138 ± 8 kJ/mole.

This lies within the range of values reported previously (1).

Activation energies can be strongly affected by mass transfer limitations, being reduced to one-half in the case of pore diffusion limitations and to a very low value when external diffusion controls. This latter case is observed in the present work at temperatures in excess of ca. 650°C. Increasing the flow rate would obviously increase the rates and activation energies in the high tem-

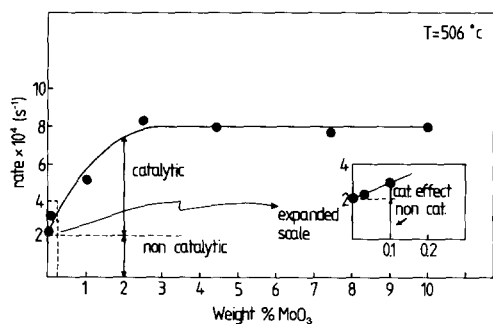


FIG. 2. Effect of catalyst loading on reaction rate.

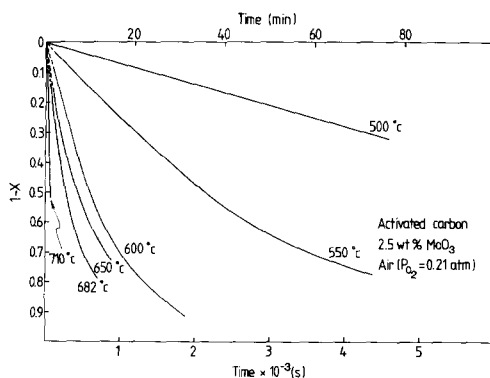


FIG. 3. Uncatalysed reaction runs at 2.1×10^{-1} atm oxygen pressure (air) and various temperatures.

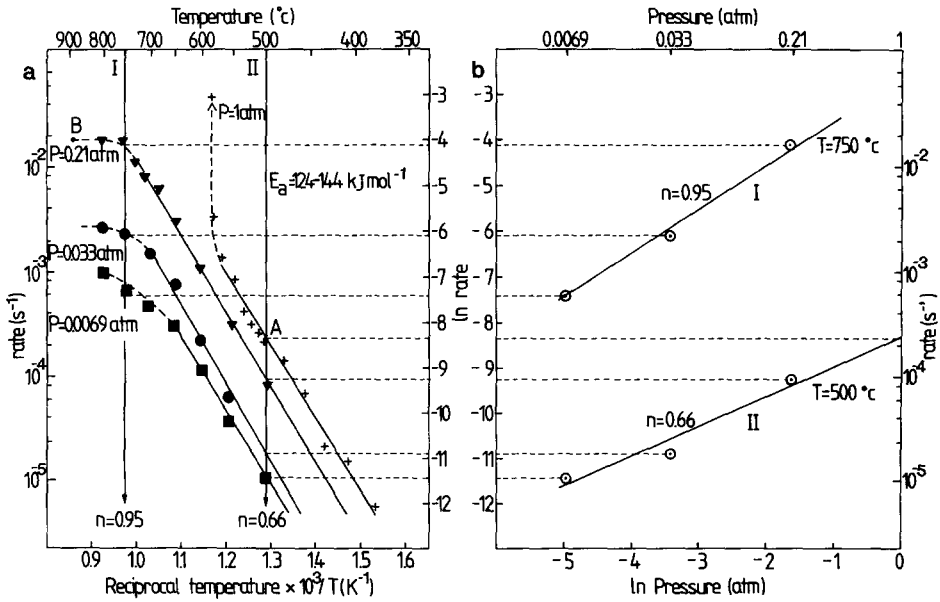


FIG. 4. (a) Arrhenius plot for the uncatalysed reaction. Orders (n) at 500 and 750°C are shown. (b) Rates and orders for the uncatalysed reaction at 500 and 750°C (plot of \ln pressure vs \ln rate).

perature region. However, the flow rates were purposely kept constant throughout the work. At lower temperatures, intrinsic kinetics are measured, this being confirmed by experiments with different amounts of sample and samples of different grain size.

Table 2 summarizes the experiments. On increasing the size 150 times from 3 to 450 μm radius only a small change in rate is observed. The effectiveness factors are 0.9 in the case of the large particles and 1.0 with the smaller size used in the present study. Changing the amount 7 times also shows no appreciable change in the intrinsic rate. The intrinsic activation energy has been found by previous authors to depend on the type of carbon and, for the same carbon, to increase for higher heat treatment temperatures (8). Severe heat treatment possibly removes or levels off the energetically more active sites, decreasing the reactivity. This can derive from changes in the carbon surface structure or in the dispersion of impurities acting as catalysts (2). The value of activation energy observed is similar to the ones reported in recent work on mildly heat treated graphi-

tisable carbons and demineralised chars (2) with values of ca. 130 kJ/mole being reported in both cases. The activation energy calculated from the present work for the MoO_3 -catalysed reaction is somewhat higher: $150 \pm 10 \text{ kJ/mole}$. Small changes in activation energies in carbon gasification due to catalysis have similarly been reported for various reactions (2, 8–10).

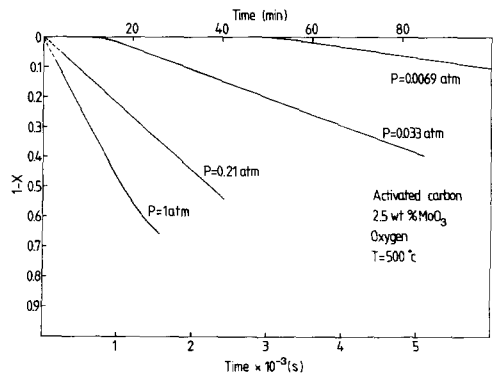


FIG. 5. Catalysed reaction runs (2.5 wt% MoO_3) at 500°C and various pressures.

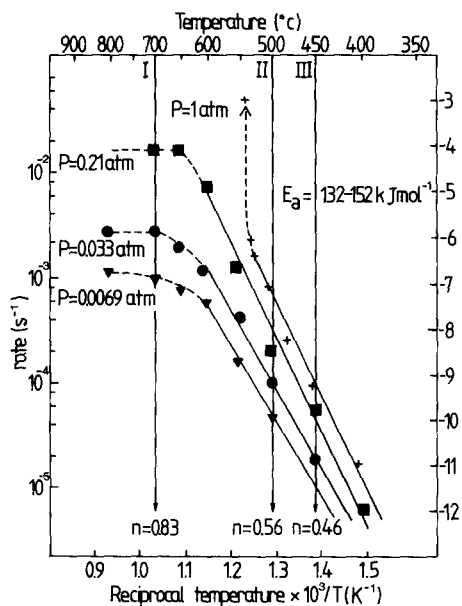


FIG. 6. Arrhenius plot for the 2.5 wt% MoO₃ catalysed reaction. Orders (*n*) at 450, 500, and 700°C are shown.

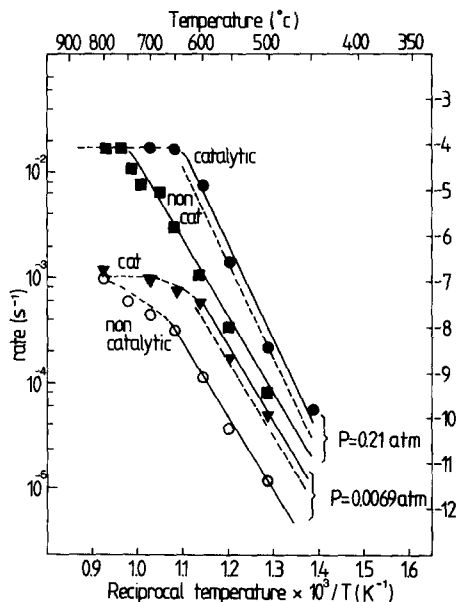


FIG. 7. Arrhenius plot comparing catalysed and uncatalysed reactions at 2.1×10^{-1} atm (air) and 6.9×10^{-3} atm oxygen pressure.

Few authors report detailed measurements of orders of reaction. Values of zero and one have been reported (1). We find the order to be close to one for the external mass transfer limited region, at high temperatures, as should be expected, and close to 0.5 for the intrinsic kinetics. Similar orders have been reported by Marsh and co-workers (8) both for uncatalysed and metal-catalysed reactions. A consistent half order should be expected in two cases: (a) Zero order intrinsic kinetics combined with pore diffusion limitations; and (b) Langmuir-Hinshelwood kinetics involving dis-

sociative adsorption when oxygen adsorption is very low (adsorption term negligible). The former alternative seems to be excluded in the present case, so the second interpretation is favoured. Again, a similar behaviour is observed both in the uncatalysed and the MoO₃-catalysed reactions.

The occurrence of external mass transfer limitations can be compared with values predicted by correlations available (11). The oxygen partial pressure near the surface P_s can be calculated from the value of the bulk value P_b . For the uncatalysed reaction, for example, we find at 506°C and $P_b = 1$ atm,

TABLE 2

Results of Experiments to Confirm that Mass Transfer Limitations are Absent (Uncatalysed System)

P _{O₂} (atm)	0.21		1			
Temperature (°C)	550		500			
Size (μm)	3	450	3			
Amount (mg)	1.2		1.0	2.9	3.1	7.2
Rate (s ⁻¹ × 10 ⁴)	3.30	2.94	2.16	1.79	2.03	1.93

$P_b - P_s = 1.5 \times 10^{-3}$ atm ≈ 0 (point A in Fig. 4a). Under external mass transfer limitations (point B in Fig. 4a), 800°C and $P_b = 2.1 \times 10^{-1}$ atm, $P_s = 1 \times 10^{-1}$ atm. This is an acceptable value. In fact $P_b - P_s \approx 2 \times 10^{-1}$ atm should be expected, but the correlation used can only give a rough indication, as it does. In fact it applies to fixed beds and has been adapted for the present case. Also, the reaction is exothermic, and the correlation used assumes isothermal conditions.

A comparison of the catalysed and uncatalysed rates must take into account that in the former case both mechanisms can be operating in parallel. Thus the rate of the uncatalysed reaction should be deducted from the catalysed one. This is shown in Fig. 7 by the dashed lines. A similar precaution has been taken in the loading curve of Fig. 2. In this case, at low loadings, the effect of the catalyst is linear, as shown in the insert in the figure. It can be expressed as $1.0 \times 10^{-3} \text{ s}^{-1} (\% \text{cat})^{-1}$.

Mechanism

In a gas/solid reaction, such as carbon gasification, a catalyst acts in principle as a third phase. The three-phase situation involves two interfaces: solid/catalyst and gas/catalyst. The mass transfer problems in a three-phase system are more complex than in two-phase systems, such as liquid/liquid reactions, heterogeneous catalysis, or gas/solid noncatalytic reactions.

Experience shows that the carbon/catalyst interaction is important in the catalytic effect (12, 13). In the present study, this interaction is reflected in the stability studies. In fact, at 700°C MoO_3 was found to lose weight at a rate $1.48 \times 10^{-5} \text{ s}^{-1}$ in N_2 (see Table 1, column 1). However, when mixed with carbon, it becomes quite stable, and no sublimation or loss of weight is detected.

Another important clue to the mechanism is the so-called order to carbon, as observed in the weight vs time curves recorded (Fig. 5). A constant slope is observed, which shows that the rate is independent of the

amount of carbon present. It may be concluded that the rate is mainly related to the amount (or the surface) of catalyst present. Assuming that the degree of dispersion of catalyst is not changing appreciably during part of the process (say, up to 50% conversion), we can state, in short: the rate of reaction is zero order with respect to the carbon and first order with respect to the catalyst. A linearity of the weight vs time change, as recorded, can be in some cases observed up to very high conversions (80% and more) (7). To explain this, the reaction can be described by an overall reaction front consisting of all the active catalyst particles moving through the carbon. As long as this reaction front remains constant, the rate remains constant. When the particles begin to coalesce or collide or are left with no reactant, the rate decreases and eventually stops.

It is interesting that a similar zero order kinetics with respect to carbon is observed for the uncatalysed reaction up to ca. 50% conversion. We may suspect that the reaction is in fact first order with respect to the impurities present.

Two conclusions can be drawn from these observations: (a) information obtained in isothermal experiments is important, and is lost in part when programmed temperature procedures are used; and (b) fitting mathematical laws based on assumptions of geometric changes in carbon may be misleading (15). It may be more correct to use rates based simply on the linear part of the curves if observed, as referred to by Walker *et al.* (1).

The importance of the two interfaces in kinetic models involving three phases must be interpreted. The following question should be addressed: where do carbon atoms meet oxygen atoms? If they meet on the carbon surface, the effect of the catalyst is a long distance one, via a spillover mechanism or some other. On the other hand, if carbon and oxygen meet at the catalyst surface, carbon diffusion through the bulk of the catalyst offers the more simple explana-

tion. Although this mechanism of carbon diffusion through the catalyst has only been *proved* for carbon formation on nickel (16) and carbon gasification on a few metals (17), we believe that it could usefully be postulated in many other gas/solid catalytic systems, including the present one.

The work of Baker *et al.* (4) on catalysis of graphite oxidation by MoO₃ and Mo presents important information for the understanding of the mechanism. Unfortunately, it is not easy to compare the information from work at the microscopic level on pure graphite with the present work. The higher activation energy observed (191 kJ/mole) is not surprising, crystalline graphite being well ordered and much less reactive than active carbons. Baker *et al.* (4) observed, in this as well as in many other systems, that catalysis is accompanied by channelling, pitting, or edge recession by the particles, droplets, or liquid catalyst. Thus we do have a three-phase system operating. The progress of the catalytic carbon reaction is observed at the carbon/catalyst interface. If a spillover mechanism was operating, the reaction front would be the carbon/gas interface (18). Diffusion through the bulk of the catalyst must be assumed. Baker *et al.* (4) also observed that particles of different size react at different rates. In the present case, the smaller particles move (and we say, promote reaction) faster. These effects are further evidence in favour of a "catalysis with bulk diffusion" mechanism: if carbon diffusion is rate controlling, diffusion being easier in small particles, they move faster.

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