

POSTER

Carbon Oxidation Catalysed by the Eutectic Alloy $\text{MoO}_3/\text{V}_2\text{O}_5$, In Situ X-ray Diffraction versus Kinetics

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INTRODUCTION

Several metal oxides are known to act as catalysts for the oxidation reaction of carbons in oxidizing atmospheres (1). Among them, vanadium pentoxide (2-4) and molybdenum oxide (5, 6) are known to be good catalysts for the air gasification of activated carbon. The catalytic mechanism remains an object of controversy (1, 8) but it is well known that the mobility of the catalyst particles and the wetting of the carbon surface are important factors in determining catalytic activity (9, 10).

McKee et al. (11, 12) measured and compared the kinetic oxidation of carbon catalysed by single pure oxides and their eutectic mixtures. They observed that the catalytic activity of the eutectic salts was much greater than that shown by the equivalent composition of the single oxides, probably due to the fact that the eutectic salt phases have lower melting points and so higher mobility and higher degree of dispersion.

In this work we study the kinetics of the gasification of an activated carbon in the presence of air, catalysed by V_2O_5 , by MoO_3 and by their mixture at the eutectic composition.

EXPERIMENTAL

The kinetic experiments were conducted isothermally in a C. I. Electronics MK II microbalance with continuous recording of change in weight. A constant air flow rate of $4 \text{ cm}^3/\text{s}$ was maintained. *In situ* XRD studies were conducted in a Rigaku D/max III C diffractometer with a $\text{Cu}(\alpha)$ radiation source (40 mV, 30 mA), and a high temperature special chamber. Air and N_2 flowed at a rate of $2.5 \text{ cm}^3/\text{s}$. Details about methods and the apparatus used were given previously (6). A charcoal BDH33033 was used. The eutectic alloy was prepared by fusion of a finely ground salt mixture having a composition (MoO_3 -54.3% wt V_2O_5) corresponding to the eutectic melting temperature, ($T=618^\circ\text{C}$) as obtained from a published phase diagram (13). A weighed amount of the alloy was intimately mixed in a mortar with the powdered char to give an initial catalyst concentration of 6 wt %. We also prepared the mixture of the catalysts by simple physical mixture of the two oxides, in the eutectic proportion, added to carbon in the same proportion of 6 wt %. In order to compare the kinetic results, catalytic gasification measurements were carried out with an equivalent concentration of the single oxide components under the same conditions.

KINETICS RESULTS

The ratio (oxide/carbon) for the single components is the same as the one used in a sample with 6 wt % of the eutectic catalyst (2.7% V_2O_5 and 3.3% MoO_3 , wt %). The activation energies for the systems studied lie between 130-150 KJ. These values are similar to previously published ones (3, 6).

Table 1 compares the relative rates of gasification at 450° , 550° and 575°C for all the systems studied. The mixture exhibits a clearly synergetic effect above 500°C . The rate observed (33) is almost five times the rate expected by the simple addition of the effect of the two catalysts (3+4). Above 575°C external mass diffusion limitations were observed in the case of mixture (faster reaction).

Table 1. Relative rates of gasification.

CATALYST	450°C	550°C	575°C
none	1	1	1
3.3% MoO_3	4	3	3
2.7% V_2O_5	5	4	3
Alloy	5	5	14
Mixture	8	33	33

IN SITU XRD RESULTS

Molybdenum - Previous work (7) showed that the phases present during air gasification were MoO_3 , MoO_2 and some nonstoichiometric oxides ($\text{Mo}_4\text{O}_{11}/\text{Mo}_{17}\text{O}_{24}$). Under N_2 , MoO_3 is reduced to MoO_2 .

Vanadium - Figures 1 and 2 show XRD spectra in N_2 and air respectively. In figure 1 we observe that vanadium pentoxide is reduced by carbon to lower states of oxidation (V_6O_{13} , VO_2 , V_2O_4 and V_2O_3). For carbon gasification in air, only V_2O_5 was detected (figure 2). These were referred by McKee et al. (4) using "ex situ" XRD. The peaks of Pt are due to the XRD sample support, which becomes exposed to the beam as carbon disappears.

Eutectic alloy - Figure 3 shows that MoO_3 and V_2O_5 were reduced. Under reaction conditions, V_2O_5 and MoO_3 were observed but MoO_2 was not detected (figure 4).

Eutectic mixture - Figures 5 and 6 show XRD spectra of experiments with the mixture at eutectic composition. In the first case MoO_3 was reduced to MoO_2 and V_2O_5 was also reduced to V_6O_{13} . Under oxidation conditions only $\text{MoO}_3/\text{MoO}_2$ and V_2O_5 were detected.

DISCUSSION

As shown on table 1 the rates with the alloy, at 450°C and 550°C were similar to the ones observed with the two single oxides. We may compare the kinetic results with XRD data. The presence of MoO_2 was not observed, suggesting that the contact between MoO_3 and carbon is poor and that the active phase is MoO_2 . Above 550°C the oxides may be molten, the catalyst/carbon interaction may be improved, explaining the synergetic effect detected.

CONCLUSIONS

- * The bulk phases observed using MoO_3 and V_2O_5 under carbon gasification by air were $\text{MoO}_3/\text{MoO}_2$ and V_2O_5 .
- * The eutectic mixture exhibits a synergetic effect above 500°C .
- * The catalytic effect observed with the eutectic composition depends on the preparation mode.
- * The mechanism which assumes oxidation-reduction cycles may be interpreted as an event at surface or site level. There is no evidence favouring cycles at bulk level.
- * In situ XRD is a useful tool to understand phase changes and to evaluate catalyst dispersion, and enables a better understanding of the kinetic behaviour.

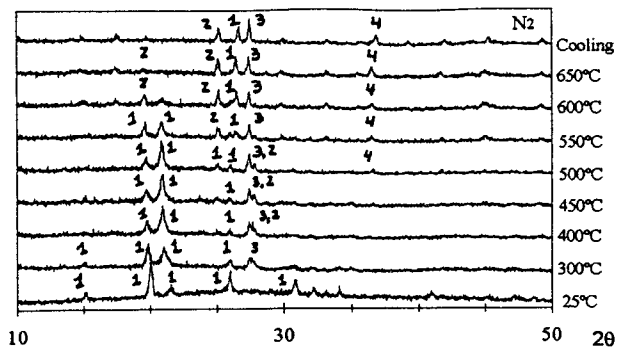


Figure 1. In situ XRD data of Vanadium doped active carbon in N₂. Code 1-V₂O₅ 2-V₆O₁₃ 3-VO₂ 4-V₂O₃ or V₂O₄

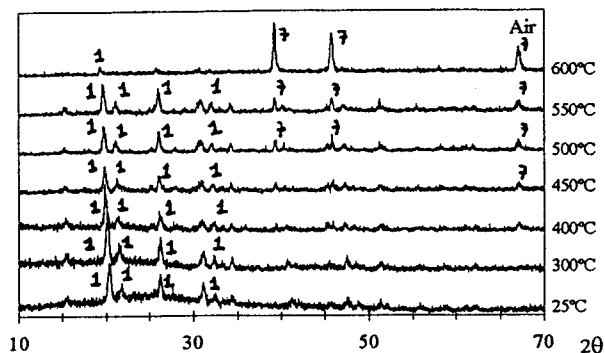


Figure 2. In situ XRD data of Vanadium doped active carbon reacting with air. Code 1-V₂O₅ 7-Pt

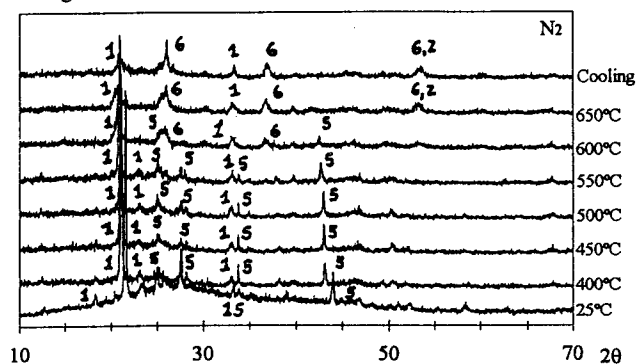


Figure 3. In situ XRD data of alloy doped active carbon in N₂. Code 1-V₂O₅ 2-V₆O₁₃ 5-MoO₃ 6-MoO₂

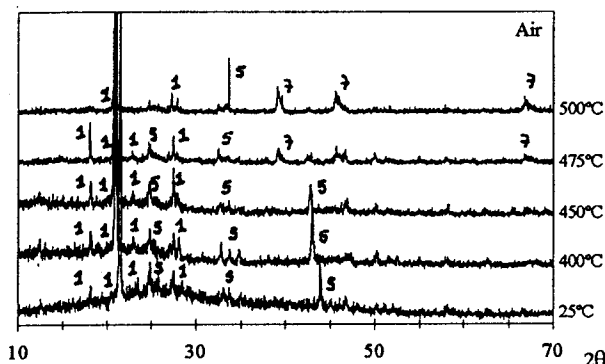


Figure 4. In situ XRD data of alloy doped active carbon reacting with air. Code 1-V₂O₅ 5-MoO₃ 7-Pt

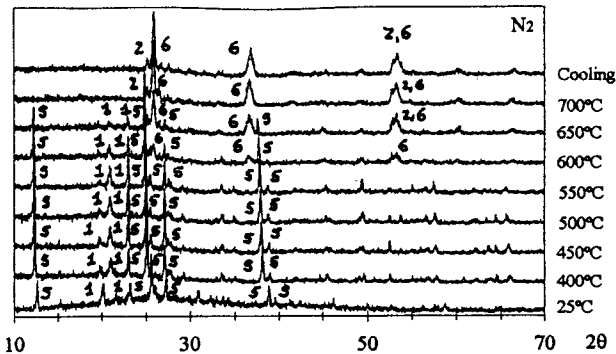


Figure 5. In situ XRD data of mixture doped active carbon in N₂. Code 1-V₂O₅ 2-V₆O₁₃ 5-MoO₃ 6-MoO₂

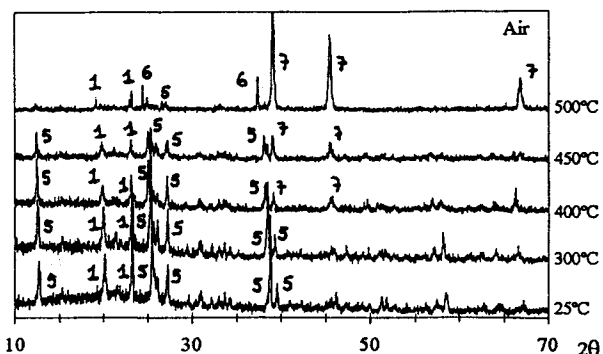


Figure 6. In situ XRD data of mixture doped active carbon reacting with air. Code 1-V₂O₅ 5-MoO₃ 6-MoO₂ 7-Pt

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