

# CATALYSED NO AND N<sub>2</sub>O REACTION WITH ACTIVATED CARBON: A KINETIC STUDY VERSUS IN SITU XRD

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## Introduction

The removal of NO<sub>x</sub> from the exhaust streams of various combustion sources is of increasing importance and the subject has been studied in the recent past [1-6, 8].

In a previous study we have observed that oxygen and nitrogen containing groups on the carbon surface promote NO<sub>x</sub> adsorption and carbon reactivity increases [8]. The behaviour of several transition metals as catalysts for C/NO<sub>x</sub> reactions was also briefly studied.

The aim of the present work is to analyse in more detail the behavior of oxygen and nitrogen groups on carbon surface towards NO conversion. Also the behaviour of vanadium and lead as catalysts for NO conversion was studied. The influence of temperature and partial pressure on C/NO and C/N<sub>2</sub>O reactions was studied at isothermal conditions. In situ XRD was carried out to identify the bulk phases present under reaction conditions.

## Experimental

Isothermal kinetics studies were carried out in a thermobalance system (C.I. Electronics MK II Microbalance) with continuous recording of change in weight. The reactant mixture contained 0.5% NO in Ar and 0.5% N<sub>2</sub>O in Ar. The gas flow rate was 200 ml/min. All the samples were previously heated in Ar at 10°C/min to 300°C with a holding time of one hour before introduction of the reaction gases. A charcoal BDH 33033 was used and some samples were treated with HNO<sub>3</sub> at 0.2N (H0.2N) or NH<sub>3</sub> at 400°C (N400). The details of the experimental procedures and sample characterisation were described elsewhere [7]. Catalyst addition was performed by physical mixture using the precursor NH<sub>4</sub>VO<sub>3</sub> and Pb(CH<sub>3</sub>COO)<sub>2</sub>. The metal loading was 5%.

The conversion of NO were determined using a differential reaction. The reactor effluents were analysed by a GC-MS (Fisons MD800), using a GS-Molesieve (30mx0.541mm) column. The experiments involved of heating the sample at 5°/min to 900°C in a NO/He mixture (0.5% NO). The gas flow rate was 200 ml/min. All the samples were previously heated in He at 10°C/min to 300°C with a holding time of one hour.

In situ XRD studies were conducted in a Rigaku D/max IIC Diffractometer with a Cu(α) radiation source (50kV, 30 mA) equipped with a high temperature special chamber. All experiments were carried out at exactly the same experimental conditions as in the thermogravimetric studies.

## Results and Discussion

Fig. 1 shows the Arrhenius plots for C/NO gasification. The presence of oxygen and nitrogen surface groups increase carbon reactivity. For temperatures below 600°C, nitrogen groups promote NO-carbon reactivity. Above 600°C activation energy is reduced to one half, suggesting internal diffusion limitations. The values of kinetic parameters lie within those reported by others [4].

Fig. 2 shows the Arrhenius plot for C/N<sub>2</sub>O gasification. Above 600°C the apparent activation energy increases with temperature (Table 2). There seems to be a change in the mechanism. This behaviour was also observed by Mirasol et al [4] but for the C/NO reaction.

Fig. 3 shows TPR curves for NO conversion. The presence of nitrogen groups increases NO conversion in temperature range of 400-700°C. The amount of CO<sub>2</sub> involved was much higher than the observed with BDH and H0.2N samples.

It is likely that surface groups decompose to leave vacant sites (nascent sites) although the mechanism is not clear. As reported by Tomita et al [3] carbon oxygen surface complexes play an important role in the reaction of NO conversion.

Fig. 4 compares TPR curves for the BDH carbon with those samples containing vanadium and lead. Only lead caused a significant decrease in the temperature required to reach 100% conversion.

In situ XRD obtained in NO (300-850°C) showed that the catalysts precursors are decomposed at 300°C in Ar to give PbO/Pb<sub>3</sub>O<sub>4</sub> and V<sub>6</sub>O<sub>13</sub>/V<sub>2</sub>O<sub>5</sub>. Above 300°C, in an NO atmosphere, only V<sub>2</sub>O<sub>5</sub> was detected but PbO/Pb<sub>3</sub>O<sub>4</sub> were present in the range 300-850°C.

Linares et al showed that, for NO conversion, the reduction temperature of the metal oxide by carbon seems to control catalyst activity [6].

The reduction of V<sub>2</sub>O<sub>5</sub> to V<sub>6</sub>O<sub>13</sub> did not take place suggesting that the ease of the metal oxide reduction by carbon is important for NO conversion reaction.

## Conclusions

- Oxygen and nitrogen groups promote NO conversion.
- Less stable surface groups which decompose to leave "nascent sites", seem to increase NO conversion.
- Lead is better than vanadium as a catalyst for NO conversion and it seems that catalytic activity is related to the ability of catalyst to be reduced by carbon (Pb<sub>3</sub>O<sub>4</sub>/PbO).

## References

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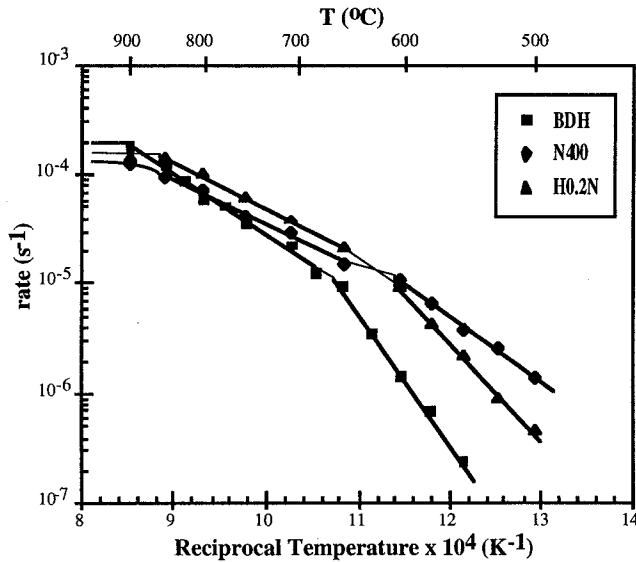


Figure 1. Arrhenius plot for the rate of gasification in NO.

Table 1. Kinetics parameters for C/NO reaction.

sample	Ea (kJ/mol)		Order to NO
	500-600°C	600-850°C	550°C
BDH	225	108	0.5
N400	113	80	0.2
H0.2N	171	82	0.3

Table 2. Kinetics parameters for C/N<sub>2</sub>O reaction.

sample	Ea (kJ/mol)		Order to N <sub>2</sub> O	
	500-600°C	600-850°C	550°C	750°C
BDH	78	196	0.6	1.4
N400	77	181	0.4	1.0
H0.2N	51	144	0.2	0.8

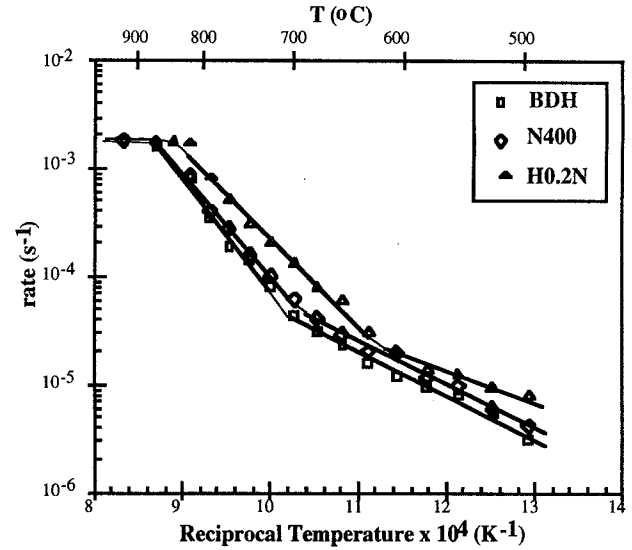


Figure 2. Arrhenius plot for the rate of gasification in N<sub>2</sub>O.

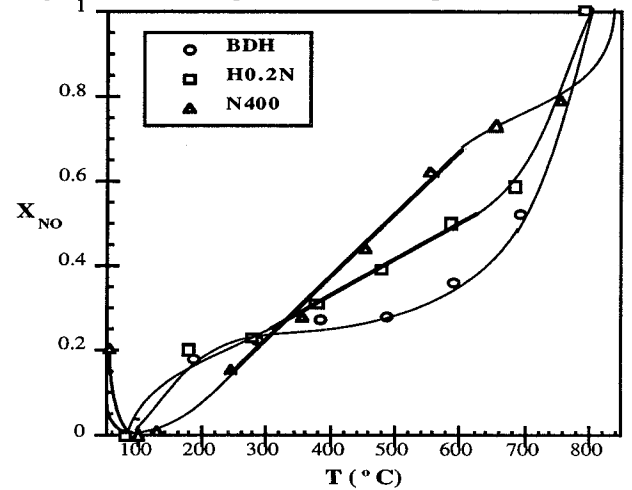


Figure 3. Conversion of NO as a function of temperature for treated samples.

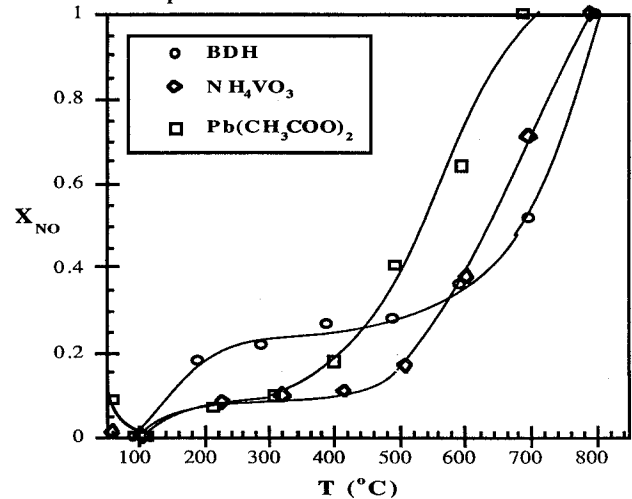


Figure 4. Conversion of NO as a function of temperature for carbon samples containing vanadium and lead.