

## REDUCTION OF NO<sub>x</sub> OVER CARBON SUPPORTED CATALYSTS

Freek Kapteijn, Alexander J.C. Mierop and Jacob A. Moulijn  
Institute of Chemical Technology, University of Amsterdam  
Nieuwe Achtergracht 166, 1018 WV Amsterdam  
The Netherlands

These investigations were financially supported by the Project Office for Energy Research (PEO).

**Abstract.** NO<sub>x</sub> reduction can be achieved by carbon supported catalysts. The activity order of the studied active phases is Ni > Co > K and between the alkali metals Cs > K > Na at comparable loadings. Compared with conventional supports, carbon seems very promising. The only drawback, consumption of the carbon itself is dependent on the carbon nature and reaction conditions.

### Introduction

The pollution by nitrogen oxides, formed by combustion processes, is a severe environmental problem. One of the possibilities to lower NO emission is the catalytic treatment of exhaust gases by selective or non-selective reduction. Three-way catalysts for vehicles have been developed to satisfy the requirements of high activity at low temperature, and resistance towards sintering and sulfur poisoning. In specific applications not all these requirements have to be fulfilled, e.g. in stationary co-generation engines, and cheaper catalysts can be applied.

Results are presented here for the NO<sub>x</sub> reduction using carbon supported catalysts of alkali metals, Ni and Co. They will be compared with analogous systems with conventional supports.

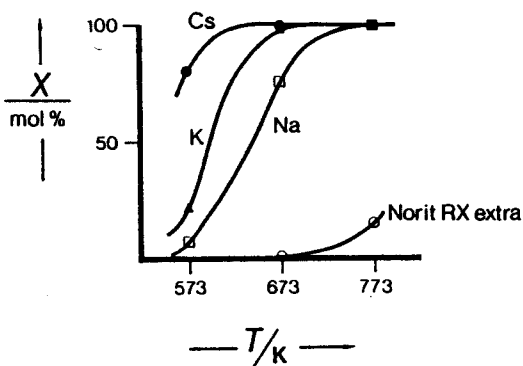


Figure 1. Steady state conversion of NO pulses over alkali metal containing activated carbon at different temperatures. Metal to carbon ratio 51.8. NO pulse 11.2  $\mu\text{mol/s}$ , amount of carbon 360 mg.

### Experimental

The active phases were applied by pore volume impregnation with an aqueous solution of the alkali carbonate or the nitrate (Co, Ni), followed by drying at 383 K. NO<sub>x</sub> reduction reactivity measurements were carried out in a quartz fixed bed flow reactor, either continuously or in pulse mode. Gasflow mixtures were obtained by mass flow controllers. Products were analysed by gaschromatography (molsieve 13X column in series with a Porapak QS column).

### Results

Figure 1 represents comparison of the activity of the alkali metal for NO reduction by the carbon at different temperatures. The activity of the alkali metals increases periodically: Na < K < Cs. The use of NO<sub>2</sub> and N<sub>2</sub>O gave analogous results.

Figure 2 compares the carbon consumption during the NO reduction in a NO/CO mixture for different wt% K<sub>2</sub>CO<sub>3</sub> and a Ni and Co sample at a M/C ratio comparable to 5 wt% K<sub>2</sub>CO<sub>3</sub>. Increasing the K<sub>2</sub>CO<sub>3</sub> loading decreases the carbon consumption, the NO reacts more selective with CO. Ni exhibits the least carbon consumption of all samples. The observed NO reduction activity was Ni > Co > K. Addition of 15 wt% of the

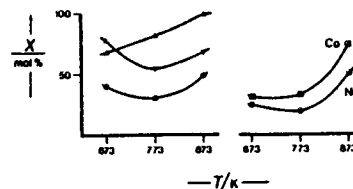


Figure 2. Fraction of NO reduction by reaction with the carbon in a CO/NO/He mixture at different temperatures. Left: K<sub>2</sub>CO<sub>3</sub> 5 wt%  $\Delta$ ; 15 wt%  $\nabla$ ; 30 wt%  $\bullet$ . Right: Co  $\square$ ; Ni  $\circ$ . C/M ratio 108. NO conversion 100%; 700 ppm NO, 1500 ppm CO, balance He.

product  $\text{CO}_2$  to the gas mixture decreased the activity of the  $\text{K}_2\text{CO}_3$  samples by a factor 3.

In figure 3 the effect of oxygen is shown for two carbon samples of different activation level. In a  $\text{O}_2/\text{CO}$  mixture, at 100% oxygen conversion, the oxygen nearly completely reacts with the carbon in case of the highly activated carbon (RX extra), whereas in the case of the least activated carbon the oxygen reacts preferentially with CO at higher temperatures (R 2020). NO, added to the gas mixtures, was also completely converted under the conditions applied. So the reduction took place in a non-selective manner.

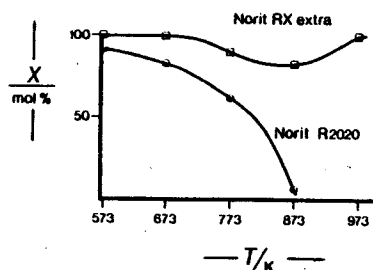


Figure 3. Fraction of  $\text{O}_2$  consumption by reaction with the carbon in a  $\text{CO}/\text{O}_2/\text{He}$  mixture at different temperatures for two activated carbons containing 30 wt%  $\text{K}_2\text{CO}_3$ .  $\text{O}_2$  conversion 100%; 0.8%  $\text{O}_2$ , 1.8%  $\text{CO}$ , balance He.

A comparison of different supports is shown in figure 4 for a Co containing sample at comparable loadings. The NO reduction in a NO/CO mixture is the highest over the C-support, followed by  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Identical results can be obtained for Ni and K.

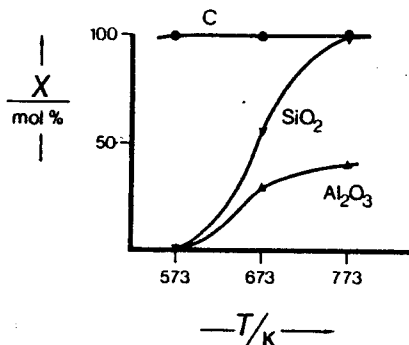
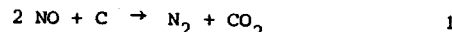


Figure 4. Comparison of NO reduction over different Co containing catalyst supports (20 wt%  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) at different temperatures. Gas mixture: 700 ppm NO, 1500 ppm CO, balance He.

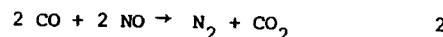
## Discussion and conclusions

Alkali metals are active catalysts for the gasification of carbon<sup>1</sup>, so it is not surprising that they catalyse the reduction of NO according to eq. 1.



which is in fact a gasification reaction too. The same reactivity order is found as for gasification<sup>2</sup>. The difference in activity can be explained by differences in dispersion of the alkali carbonate since it has been concluded that the alkali metals only increase the number of active sites in carbon gasification reactions<sup>3</sup>. The inhibition effect of  $\text{CO}_2$  might be caused by backformation of potassium carbonate, which is sufficiently stable at these relatively low temperatures as compared with gasification conditions.

In exhaust gases CO and  $\text{O}_2$  are present due to incomplete combustion. The CO can be used as reducing agent for NO, thereby reducing the carbon consumption eq. 2.



Apparently at high loading  $\text{K}_2\text{CO}_3$  prevents the attack of the carbon by NO and the selectivity towards NO reduction by CO increases. The Ni shows the highest selectivity.

From figure 3 it is seen that the nature of the carbon is very important, since by a proper choice the carbon consumption can be drastically reduced.

An identical activity order as presented in Fig. 4 is observed for hydrotreating catalysts<sup>4</sup>. The lower activity of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  can be ascribed to the reaction of the support with the active phase, leading to inactive compounds.

From the results presented above, it is obvious that carbon is a promising support for NO reduction due to the high activity.

## References

1. D.W. McKee, Fuel **62** (1983) 170.
2. F. Kapteijn, G. Abbel and J.A. Moulijn, Fuel **63** (1984) 1036.
3. J.P.R. Vissers, Ph.D. Thesis, Technical University Eindhoven, 1984.
4. F. Kapteijn and J.A. Moulijn, contribution NATO/ASI Summerschool on Gasification, Portugal, 1985.