

## Reduction of NO<sub>x</sub> over Alkali Metal–Carbon Systems

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Activated carbon-supported alkali metals above 500 K catalyse the reduction of NO<sub>x</sub> by carbon and carbon monoxide in the order: Cs > K > Na; tetraethyl-lead does not poison the catalyst.

Alkali metals are effective catalysts for the gasification of coal and carbon by H<sub>2</sub>O and CO<sub>2</sub>.<sup>1</sup> Moreover, the alkali metal–carbon system catalyses the water gas shift reaction<sup>2</sup> and, as has been demonstrated recently, the methanation of CO.<sup>3</sup> Generally, these reactions can be described as a catalytic oxygen transfer between gaseous molecules or between a gaseous reactant and the carbon. According to this reasoning these systems might also be effective for the reduction of other oxygen-containing compounds such as NO<sub>x</sub>.

Methods to reduce NO<sub>x</sub> in exhaust gases are becoming increasingly important because of the environmental impact of this compound. Many methods are based on noble metal catalysts, since they show high activity at low temperatures.<sup>4</sup> A disadvantage, however, is their price, their sensitivity towards sulphur, and the sintering of the metal at high temperatures. Moreover, a general point of concern is sulphur which is a moderate poison for noble metals and a severe poison for other metals. Cheaper catalysts without these drawbacks would provide a breakthrough. Here we present preliminary results of studies of the applicability of alkali metal–carbon systems for NO<sub>x</sub> reduction.

The catalysts were prepared as reported earlier.<sup>3</sup> The experiments were carried out in a quartz fixed-bed flow reactor, using 360 mg of carbon and a carbon to metal atomic ratio of 51.8:1. The catalysts were activated at 773 K in a stream of helium for 10 min, although this turned out to be unnecessary. The experimental procedure was as follows. After the activation treatment, at one minute intervals NO (11.2 μmol) was injected in a stream of helium flowing continuously through the reactor (60 μmol/s). The outlet of the reactor was connected to a 0.65 m × 1/4" stainless steel

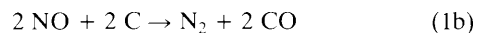
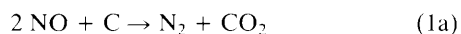
column packed either with Porapak QS or with molecular sieves 13X. The products were separated at room temperature and detected by means of a thermal conductivity cell. The Porapak QS served to separate (O<sub>2</sub>, N<sub>2</sub>, CO, NO) from CO<sub>2</sub> and N<sub>2</sub>O and the molecular sieve 13X to separate O<sub>2</sub>, N<sub>2</sub>, NO, and CO, whilst CO<sub>2</sub> and N<sub>2</sub>O were trapped by the latter column. The measurements were carried out isothermally at different temperatures starting at 773 K and cycling between 773 and 473 K in steps of 100 K.

The results are presented in Table 1. The main products were N<sub>2</sub>, CO, and CO<sub>2</sub>. Between 573 and 673 K N<sub>2</sub>O was also detected. The CO<sub>2</sub>:CO ratio is high at low temperatures and decreases with increasing temperature. Obviously this is governed by thermodynamic considerations. The NO conversion was considered to have reached a steady-state level when the N<sub>2</sub> production was equal to (0.5 CO + CO<sub>2</sub>) formation. At low temperatures the carbon surface is first oxidised resulting in N<sub>2</sub> formation without CO or CO<sub>2</sub> production.

**Table 1.** Steady-state conversions (%) of NO pulses (11.2 μmol) in helium (60 μmol/s) over alkali metal–carbon systems at different temperatures. Amount of carbon, 360 mg; carbon:metal atomic ratio, 51.8:1.

T/K	% Conversion		
	573	673	773
—	0	0	15
Na	5	75	100
K	20	100	100
Cs	80	100	100

The results in Table 1 show that NO can effectively be reduced by alkali metals on a carbon support, thereby consuming the carbon [equations (1)]. The activity increases with atomic number: Na < K < Cs, corresponding with the order for CO<sub>2</sub> gasification<sup>5</sup> and CO methanation.<sup>3</sup> Use of NO<sub>2</sub> instead of NO gave identical results.



For the formation of CO<sub>2</sub> two possibilities suggest themselves: CO<sub>2</sub> might be a primary product or might be formed by reaction (2). To verify this a 1:2 mixture of NO and CO diluted 100:1 with helium was passed over a potassium catalyst at 673 K. The products were analysed by gas chromatography. It was concluded that NO reacted in about equal amounts with the CO and the carbon. The presence of CO lowers the consumption of the carbon support.



Since lead is a serious poison for noble metal catalysts we repeatedly injected tetraethyl-lead (liquid; 10 µl) into the reactor feed. The NO<sub>x</sub> reduction activity did not noticeably change. This demonstrates that this system is far less sensitive to lead poisoning than the conventional catalysts. Further research on this subject, especially with respect to the various components in exhaust gases such as oxygen and sulphur compounds, is in progress.

As far as the authors know only in one other study has the use of carbon as a catalyst support in NO<sub>x</sub> reduction been reported; these catalysts consisted of doped Ni or Co systems.<sup>6</sup> More generally, at high temperatures carbon and coal-char themselves are known to reduce nitrogen oxides.<sup>7,8</sup> The present results show the great potential of the use of carbon in catalysed NO<sub>x</sub> removal.

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