Promoting effects of metals for NO reduction over potassium doped carbon

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Received 23 April 1991; accepted 15 August 1991

Reduction of NO to N_2O or N_2 was studied over activated carbons using thermal desorption technique. The addition of other metals such as Zn, Cu, Fe, Ni, Sn, Mn or Ce, to potassium doped carbon remarkably enhanced direct NO reduction or NO reduction by carbon. The high activity might be ascribed to the synergism between potassium-metal on the carbon surface.

Keywords: NO reduction; potassium doped carbon

1. Introduction

Reduction of NO in exhaust gases is considered critical in order to improve overall air quality. New methods for NO reduction have been attempted. Okuhara and Tanaka [1,2] first attempted NO reduction by carbon and found a remarkable enhancement of the NO reduction over carbon doped by alkaline metal. Kapteijn et al. [3] have also reported the same result on the reactivity of alkali-doped carbon. Over those alkali-doped carbons, the activity for NO reduction is still low below 250 ° C.

In this paper, we report new catalyst systems which were created by addition of transition metals to potassium doped activated carbon and have high activity for NO reduction even below 200 ° C.

2. Experimental

The metal-doped carbons were prepared by an impregnation method. At first, the activated carbons with a surface area of 500 $m^2 \cdot g^{-1}$ (Nakarai) were immersed in an aqueous solution of potassium carbonate, followed by overnight

drying at 100 °C. The other metal such as Ce, Cu, Zn, Mn, Sn, Ni, or Fe was further doped on the activated carbon with potassium using an aqueous solution of carboxylate salt and then the sample was dried at 100 °C overnight. Finally, the sample was calcined at 500 °C under 760 Torr of nitrogen gas. All of the doped metal contents in the carbon used were 7 wt%, as revealed by atomic absorption spectroscopy. The catalyst was termed 7 wt% K-7 wt% M-activated carbon, where M is a doped metal.

The behavior of NO over metal doped carbons was investigated by the thermal desorption (TD) method in a conventional vacuum system [1,2]. After evacuating the system at 500 °C under 10^{-5} Torr *, the samples (each 0.1 g) were exposed to 10 Torr of ^{15}NO for 0.5 hours at room temperature, followed by further evacuation for 0.5 hours. TD was subsequently carried out with a heating rate of 9 °C.min^{-1}. The desorbed species were analyzed by Mass Spectrometer (Hitachi RMU-6). ^{15}NO (99.3% ^{15}N, Hikari kogyo Co. LTD) was used to distinguish between N_2O and CO_2, and between N_2 and CO. ^{15}NO was carefully purified by the freeze-pump-thaw technique.

No water desorption was observed in the measurement region.

3. Results and discussion

Fig. 1 shows the typical TD spectra from the NO adsorbed 7 wt% K-activated carbon. The adsorbed NO is desorbed above 200 °C as the major desorbed species, NO followed by N_2 and a small amount of N_2O. The evolution of CO_2 is observed above 400 °C. The results are similar to those from the 3.5 wt% K-doped high purity carbon studied by Okuhara and Tanaka [1,2] except that the ratio of desorbed N_2/NO and N_2O/NO increases in the present results. The distinct NO reduction has not occurred on the present activated carbon and the Ce, Cu, Zn, Mn, Sn, Ni, or Fe doped activated carbon.

Fig. 2 shows the TD spectra from the NO adsorbed 7 wt% K-7 wt% Zn-activated carbon. The spectra reveal that adsorbed NO is mainly desorbed as N_2 around 200–350 °C and N_2O around 160 °C. The desorbed NO, however, is appreciably small, indicating that the addition of zinc to potassium-doped activated carbon is effective to the NO reduction to N_2 and N_2O. Similar effects were observed by the addition of other metal element such as Cu, Ni, Fe, Sn, Mn, or Ce. The relative effect for N_2 formation was derived as follows; Ce, Cu, Zn, Mn, Sn > Ni, Fe.

From isotope labeling experiments using ^{15}NO and $N_2{}^{18}O$, Okuhara and Tanaka reported that the adsorbed NO molecule is transformed to several adsorbed species such as N_2O(a), NO_2(a), and $(NO)_2$(a) around room temperature over potassium-doped carbon. N_2O(a) is desorbed without decomposition

* 1 Torr = 133 Pa.

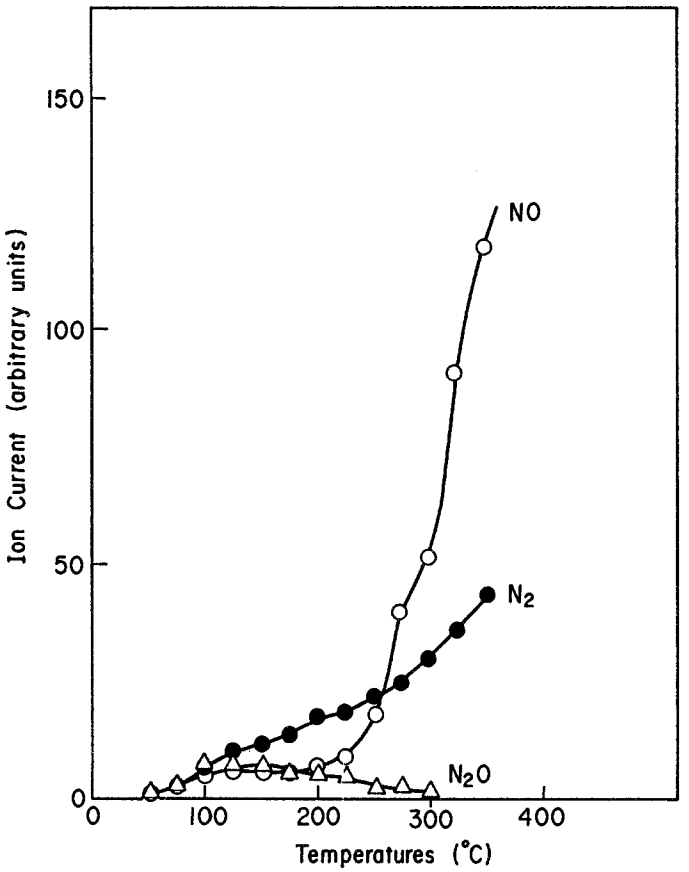

Fig. 1. Typical thermal desorption spectra from NO adsorbed 7 wt% K-activated carbon.

at low temperature $< 130\,^{\circ}C$, $(NO)_2(a)$ decomposes directly around $200\,^{\circ}C$ to produce N_2O or N_2, and $NO_2(a)$ reacts with carbon to form NO, N_2, or CO_2 above $280\,^{\circ}C$.

On the present activated carbon doped with potassium and transition metals, two types of N_2 were desorbed as main products. Hence, the addition of other metals to potassium doped carbon, we suppose, enhances both direct NO reduction to N_2 and NO reduction by carbon.

High activity for NO reduction to N_2 was observed on the potassium doped activated carbon which has high surface area (ca. 1000 $m^2.g^{-1}$) and contained 0.7 wt% Zn as a major impurity. This result indicates that a small amount of zinc (0.7 wt%) can play an important co-operative role in the NO reduction to N_2 on the potassium doped carbon with high surface area. Further addition of Ce to this potassium doped carbon causes N_2 formation at lower temperature. The result suggests that cerium ions act as the effective promoter for the direct NO decomposition. It is noted that a similar effect was also observed by

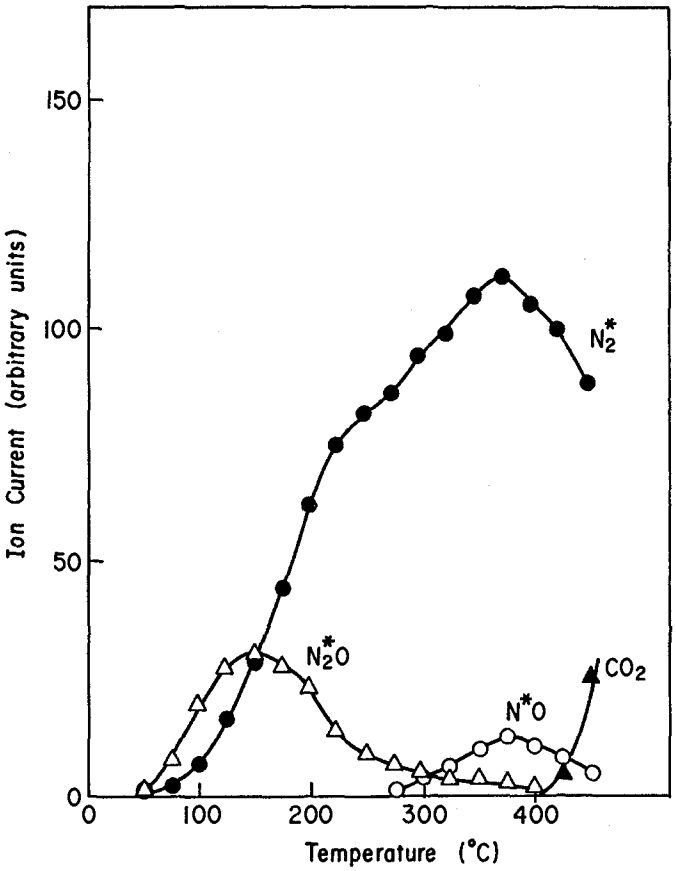

Fig. 2. The thermal desorption spectra NO adsorbed 7 wt% K-7 wt% Zn-activated carbon.

addition of other metal element such as Cu, Ni, Fe, Sn, or Mn, respectively.

In summary, we have demonstrated that reduction of NO to N_2 is possible at relatively low temperatures on activated carbon surfaces. The high activity for direct NO decomposition on the surface and NO reduction by carbon is created for the first time by addition of zinc or other metals with potassium. This enhanced activity also reveals even by addition of small amounts of zinc on the potassium doped carbon with high surface area. It has also been observed that the activity can be further enhanced by further addition of other metals. We suppose that the increase of the activity is ascribed to synergism among metals on the carbon surface.

The effect of potassium as described above is also observed by other alkaline metal such as Li, Na, and Cs.

Further investigations are continuing and results will be published in the future.

References

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