Catalysis Letters 20 (1993) 133–139

N_2 formation from NO over metal oxide-dispersed microporous carbon fibers

Jun Imai, Takaomi Suzuki and Katsumi Kaneko [1]

Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

Activated carbon fibers (ACFs) were modified with various kinds of transition metal hydroxides. The surface modified ACFs were characterized by EXAFS. The NO reduction over the surface modified ACFs, which is not poisoned by SO_2, was examined. Almost all NO (80%) was converted to N_2 at 473 K over α-FeOOH-dispersed ACF.

Keywords: NO; N_2; reduction; transition metal oxide; micropore; activated carbon; adsorption

1. Introduction

NO_x emissions from automobiles have become worse in particular at urban areas. Removal of NO_x or its conversion into harmless gases such as N_2 should be desirable. There are recent active studies on NO reduction on various catalysts [1–3]. The catalytic reduction of NO over impregnated carbons has been studied [4–6]. It is also important that activated carbon itself can reduce NO [7].

Activated carbon fiber has a very high specific surface area and a large micropore volume. Vapors can be strongly adsorbed by an enhanced physical adsorption, so-called micropore filling. The fine metal hydroxide dispersed ACF can adsorb a great amount of supercritical NO by chemisorption-assisted micropore filling [8]. Dispersion of fine α-FeOOH particles on ACF is especially effective for the chemisorption-assisted micropore filling of supercritical NO near room temperature [9]. This is because NO molecules are dimerized by the effect of the α-FeOOH fine particles. Disproportionation reaction of NO dimers in the micropores [10] leads to formation of N_2O and NO_2. Coexisting SO_2 has a tendency to accelerate the N_2O formation by consumption of NO_2 [11]. The disproportionation reaction of the NO dimers in the micropores of ACFs is not the catalytic reaction on specific active sites which was observed in the micropores of Y-type zeolites [12,13]. Although the homogeneous disproportionation reaction of the NO

---

[1] To whom correspondence should be addressed.

dimer in the gas phase needs a very high pressure ($\geqslant$200 atm) [14,15], it proceeds easily in the micropore of activated carbons even at a subatmospheric pressure. Heating the coadsorbed NO and SO_2 in the micropores of α-FeOOH dispersed ACF above 423 K gives rise to the decomposition of NO to N_2 [16]. Very recently, it is shown that the NO dimer must be an intermediate in the reaction of NO with carbon to produce N_2 and the surface carbon oxide [17]. Understanding of the relationship between the sort of dispersed oxides and N_2 formation is important for elucidating the reaction mechanism.

2. Experimental

Pitch-based activated carbon fibers were used, as they have oxidation resistive property at high temperatures [18]. Also the ACF preoxidized by HNO_3 (ox-ACF) was used. ACF and ox-ACF were treated under the synthetic conditions of $Cr(OH)_2$, β-MnOOH, α-FeOOH, CoO(OH), $Ni(OH)_2$, and $Cu(OH)_2$ powders; these treated ACF samples were washed with abundant distilled water in order to remove precipitated oxides and they were dried. These samples are designated as $Cr(OH)_2$-ACF, or β-MnOOH-ox-ACF, for example. We measured the Cu and Fe K-edge EXAFS spectra of $Cu(OH)_2$, $Cu(OH)_2$-ACF, α-FeOOH, α-FeOOH-ACF, and α-FeOOH-ox-ACF using the EXAFS facility at BL-7C of the Photon Factory in the National Laboratory for High Energy Physics (Tsukuba, Japan). Surface areas and micropore volumes of these samples were determined from high resolution N_2 adsorption isotherms at 77 K using α_S and Dubinin-Radushkevich (DR) analyses, which are listed in table 1. The NO reduction reaction to N_2 over the surface modified ACFs (250 mg) was measured in a circulation system with an IR spectrometer and a mass spectrometer after preevacuation at 423 K and 1 mPa for 2 h. High purity NO was used after a vacuum distillation. The NO gas (10 kPa) was introduced in the circulation system when the ACF sample was heated at 473 K (some dispersed hydroxides are converted into the oxides during heating). The

Table 1
Adsorption parameters of surface modified ACFs

Sample	Surface area (m^2/g)	Micropore volume (ml/g)
ACF	1340	0.51
α-FeOOH-ACF	1380	0.50
α-FeOOH-ox-ACF	1230	0.44
$Cr(OH)_3$-ACF	1180	0.47
β-MnOOH-ACF	1230	0.47
CoO(OH)-ACF	1210	0.49
$Ni(OH)_2$-ACF	875	0.38
$Cu(OH)_2$-ACF	565	0.31

amounts of N_2O and CO_2 formation were determined using the IR absorption bands. Partial pressures of NO and N_2 were determined by a mass spectrometer. The N_2 yield was determined from the amount of produced N_2 after 6 h. The NO adsorption isotherms were measured at 303 K. The saturated amount of NO adsorption was determined from the Langmuir plot.

3. Results and discussion

EXAFS spectra of α-FeOOH and $Cu(OH)_2$ dispersed ACFs are compared with α-FeOOH and $Cu(OH)_2$ powder in fig. 1. We used these EXAFS spectra for both qualitative identification and analysis of the dispersion state of the dispersed hydroxides on ACF. Formation of fine α-FeOOH particles was confirmed by comparing EXAFS spectra of α-FeOOH and α-FeOOH-ox-ACF. Detailed examination of ultrafine α-FeOOH formation on cellulose-based ACF was already published elsewhere [19]. Although spectra of $Cu(OH)_2$ and $Cu(OH)_2$ dispersed ACF are not necessarily sufficient, fine $Cu(OH)_2$ particles must be formed. In the case of β-MnOOH dispersed on cellulose-based ACF, a β-MnOOH like substance is formed on the ACF surface; β-MnOOH fine particles are probably formed on

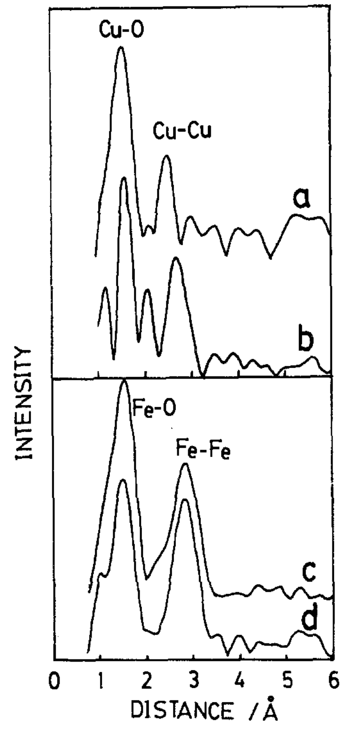

Fig. 1. EXAFS spectra of α-FeOOH and $Cu(OH)_2$ dispersed ACFs compared with α-FeOOH and $Cu(OH)_2$ powder. (a) $Cu(OH)_2$-ACF, (b) $Cu(OH)_2$, (c) α-FeOOH-ox-ACF, (d) α-FeOOH.

the pitch-based ACF. The intensity ratio of the metal–metal coordination to the metal–oxygen one for metal oxide-dispersed ACF is smaller than that for the bulk powder, indicating that very fine metal oxides are dispersed on the ACF surface.

The N_2 adsorption isotherms of ACF samples are of type I, suggesting that they are highly microporous. The surface modification of ACF or ox-ACF with transition metal hydroxides other than $Ni(OH)_2$ and $Cu(OH)_2$ does not seriously change the surface area or the micropore volume. The dispersion treatments with $Ni(OH)_2$ or $Cu(OH)_2$ decrease the surface area of ACF, as shown in table 1. $Ni(OH)_2$ and $Cu(OH)_2$ particles must block the micropores.

Fig. 2 shows the gas phase IR spectral changes over α-FeOOH-ox-ACF at 473 K. The IR absorption by gaseous NO decreases with the reaction time, while the IR absorptions by N_2O and CO_2 increase. The absorption peak of N_2O grows rapidly and stops to increase after 20 min, reaching the equilibrium after 3 h. The CO_2 formation reaction is much slower and reaches the equilibrium after 16 h. The amount of CO_2 produced is about three times of the amount of N_2O produced after 3 h. The amount of N_2O formation over ACF is much less than that over α-FeOOH-ox-ACF. Fig. 3 shows the gas compositional changes determined by the mass filter for ACF and α-FeOOH-ox-ACF. The formation of N_2 over both samples is clearly shown. The N_2 formation reaction over ACF almost finishes within 1 h, while the NO decomposition and N_2 formation over α-FeOOH-ox-ACF continues even after 6 h. The amounts of NO decomposition and N_2 formation over α-FeOOH-ox-ACF were much larger than those over ACF; NO of about 80% was decomposed into N_2 over α-FeOOH-ox-ACF after 16 h. Thus, the dispersion of α-FeOOH on the surface of ACF enhances the NO decomposition and N_2 formation. Consequently, this is probably due to the high NO adsorptivity of

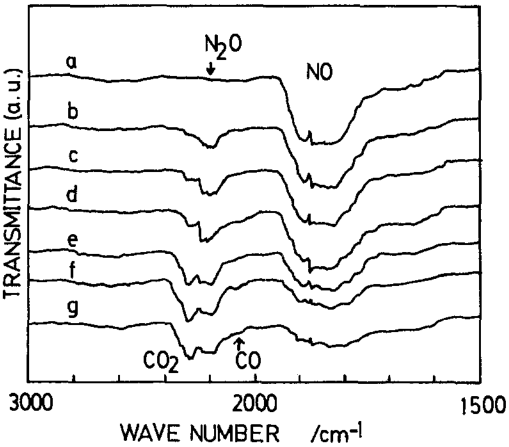

Fig. 2. The gas phase IR spectral changes over α-FeOOH-ox-ACF at 473 K. (a) Before reaction, (b) 20 min, (c) 40 min, (d) 1 h, (e) 3 h, (f) 8 h, (g) 16 h.

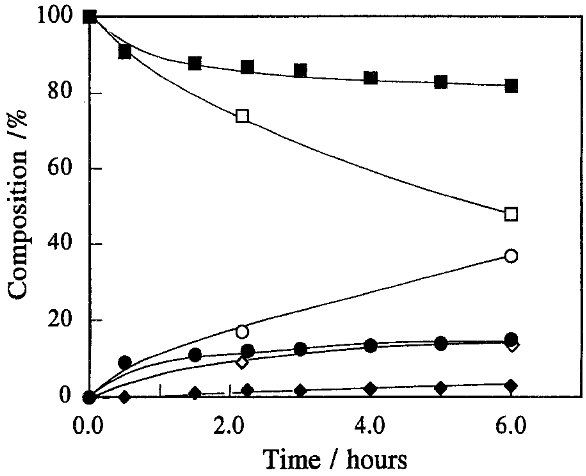

Fig. 3. The gas compositional changes during N_2 formation over ACF and α-FeOOH-ox-ACF. Open symbol: α-FeOOH-ox-ACF, closed symbol: ACF, (□) NO, (○) N_2, (◇) CO_2 (N_2O).

α-FeOOH-ox-ACF even at high temperature [20]. The observed mass number of 44 of longer reaction time is probably ascribed to CO_2 on the basis of the IR data.

The gas phase compositional changes over $Cr(OH)_3$-, β-MnOOH-, CoO(OH)-, $Ni(OH)_2$-, and $Cu(OH)_2$-ACFs were also examined. Both NO decomposition and N_2 formation over these surface modified ACFs do not differ from those over ACF. These results show that dispersion of α-FeOOH is especially important for the enhancement of the NO decomposition. The N_2O formed by the disproportionation reaction of the NO dimer in the micropore can be converted into N_2. On the other hand, NO_2 which is another product of the disproportionation reaction of the NO dimer can also react with carbon to produce NO above 343 K [21]. N_2O was produced at the initial stage of the reaction even at 473 K. Therefore, the main reaction path of the N_2 formation must be caused by the disproportionation reaction. The amount of the dimer in the micropore can be associated with the N_2 yield. It is difficult to determine the amount of the dimer adsorbed during reaction at 473 K; the relationship between the N_2 yield (%) after 16 h and the saturated amount of NO adsorption of various surface modified ACFs at 303 K is shown in fig. 4. The saturated amount of NO adsorption at 303 K must be a scale of the NO dimer at the reaction conditions. The relationships between the N_2 yield and the saturated amount of NO adsorption are divided into two groups: (Fe, Cu) group and (Cr, Mn, Co, Ni) group. In the case of α-FeOOH and $Cu(OH)_2$ dispersed samples, the N_2 yield tends to increase with the amount of NO adsorption. Consequently, the N_2 formation over these ACF samples should be related to the decomposition of N_2O from the disproportionation reaction of the dimerized NO at 473 K. Also CO_2 is evolved in the case of α-FeOOH dispersed ACF, as shown in fig. 3. According to the mechanism by Teng and Suuberg [17], the NO dimer is converted to N_2 and the surface oxides. A part of surface oxide probably can be de-

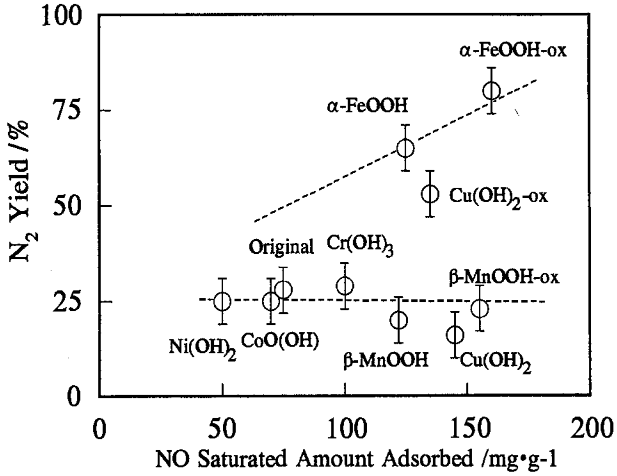

Fig. 4. Relationship between N_2 yield at 473 K and NO saturated amount adsorbed at 303 K.

sorbed as CO_2. The observed CO_2 in fig. 3 should be such a desorbed surface oxide. The observed reaction in this work must be the same as studied by Teng and Suuberg [17]. As they do not consider the presence of N_2O, their reaction mechanism may be extended to include the intermediate N_2O. A preliminary experiment on the NO reactivity over α-FeOOH powder showed marked formation of N_2O. The highest N_2 yield over α-FeOOH dispersed ACF probably arises from both the disproportionation reaction and catalytic N_2O formation over the dispersed α-FeOOH itself. However, catalytic activity of iron oxides for N_2O decomposition is not so high, compared with other transition metal oxides [22]. Another important factor must be elucidated.

In another (Cr, Mn, Co, Ni) group, the amount of NO adsorption is independent of the N_2 yield. It is known that p-type oxides such as NiO or CoO have higher N_2O decomposition activity than n-type oxides [22]. There is a possibility that this group has greater N_2O decomposition activity than α-FeOOH. The observed results disagree with this anticipation. Possibly the N_2O decomposition activity of these dispersed p-type oxides should be deactivated by electron transfer from the carbon support. Also these fine oxides should be dispersed on the active sites of ACFs for oxidation reaction to lower the reactivity. Effects of the reaction temperature and the NO pressure on N_2 formation should be examined in order to understand this reaction mechanism.

Acknowledgement

We acknowledge the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

References

[1] Y. Li and W.K. Hall, J. Phys. Chem. 94 (1990) 6145.

[2] F. Okada, A. Satsuma, A. Furuta, A. Miyamoto and T. Hattori, J. Phys. Chem. 95 (1992) 5900.

[3] M. Iwamoto, H. Yahiro, Y. Mine and S. Kagawa, Chem. Lett. (1989) 213.

[4] K.J. Lim and M. Boudart, J. Catal. 105 (1987) 263.

[5] H. Yamasita, A. Tomita, H. Yamada, T. Kyotani and L. R. Radovic, Energy and Fuels, in press.

[6] L. Singoredjo, J. van Wees, F. Kapteijn and A. Moulijn, Catal. Today 7 (1990) 157.

[7] M.S. Shah, J. Chem. Soc. (1929) 2661.

[8] Z. Wang, T. Suzuki, K. Asakura and K. Kaneko, J. Phys. Chem. 96 (1992) 10917.

[9] K. Kaneko and N. Shindo, Carbon 27 (1989) 815.

[10] K. Kaneko, A. Kobayashi, T. Suzuki, S. Ozeki, K. Kakei, N. Kosugi and H. Kuroda, J. Chem. Soc. Faraday Trans. I 84 (1988) 1795.

[11] J. Imai, M. Souma, S. Ozeki, T. Suzuki and K. Kaneko, J. Phys. Chem. 95 (1991) 9955.

[12] C.-C. Chao and J.H. Lunsford, J. Am. Chem. Soc. 93 (1971) 71.

[13] Y. Kanno and H. Imai, Hyoumen Kagaku 11 (1990) 23.

[14] T.P. Melia, J. Inorg. Nucl. Chem. 27 (1965) 95.

[15] S.F. Agnew, B.I. Swanson, L.H. Jones and R.L. Mills, J. Phys. Chem. 89 (1985) 1678.

[16] J. Imai and K. Kaneko, J. Colloid Interf. Sci. 148 (1992) 595.

[17] H. Teng and E.M. Suuberg, J. Phys. Chem., in press.

[18] K. Kaneko and K. Kakei, J. Colloid Interf. Sci. 129 (1989) 583.

[19] K. Kaneko, N. Kosugi and H. Kuroda, J. Chem. Soc. Faraday Trans. I 85 (1989) 869.

[20] K. Kaneko, Colloid Surf. 37 (1989) 115.

[21] A.R. Chughtai, W.F. Welch and D.M. Smith, Carbon 28 (1990) 411.

[22] O.V. Krylov, *Catalysis by Nonmetals*, transl. M.F. Delleo Jr., G. Dembinski, J. Happel and A.H. Weiss (Academic Press, New York, 1970) p. 189.