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Catalytic Activity of Copper(II) Salt of Heteropolyphosphoric Acid for the Reduction of NO with Its Supporting Active Carbon

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The catalytic activity of a copper(II) salt of polymolybdophosphoric acid ($Cu_{1.1}H_{0.8}PA$) for the reduction of NO with the supporting active carbon into N_2 and N_2O was studied at 400 °C using a fixed bed flow reactor. A considerable activity was observable at a stationary state where the spill-over of oxygen left on the active site of the acid to the carbon surface appeared to be rate-determining. The activity of the salt was much higher than for component oxides produced through its decomposition at higher temperatures. This suggested that the active site was characteristic to the salt (very probably the reduced site in the salt). The reaction mechanism in terms of the reaction paths, the N_2O/N_2 selectivity, and the roles of the supporting active carbon are discussed based on kinetic investigations.

A more efficient removal of the air pollutant, NO_x, has been explored in order to achieve a better environment at less cost.1) The reduction of NO_x with the carbons (Eq. 1)

$$2NO + C \longrightarrow N_2 + CO_2 \qquad (1)$$

can represent such a reaction and should be studied more since active carbon is an inexpensive reductant. Okuhara and Tanaka2) and Inui *et al.*3) have reported on the reactivities of several kinds of active carbons with NO catalyzed by alkali metal salts and complex oxides supported on them.

The present authors have reported on the reduction of NO_x on copper(II) salt of polymolybdophosphoric acid (CuHPA) which gain some reduced sites during preparation.4) If the site oxidized by NO is properly reduced by transferring the left oxygen to the support where it is converted or liberated, the catalytic reduction of NO proceeds on the CuHPA. The soluble CuHPA can be easily recovered and regenerated when the support is greatly consumed.

In this study, the reduction of NO with some kinds of active carbon catalyzed by CuHPA was examined. The carbon can enlarge the effective surface area of CuHPA. The redox interaction of HPA with active carbon has been reported by Izumi *et al.*5) and Baba and Ono.6) The generation or activation of reduced sites by the carbon support can be expected through a catalyst-support interaction. The reactivity of the active carbon for such a reaction may attract other interests since the spill-over is one of the most important mechanisms regarding catalyst-support cooperation, which is a guide-line for the preparation of a better catalyst.

Experimental

Catalysts. 12-Molybdophosphoric acid ($H_3Mo_{12}PO_{40}$) was purchased from Nippon Inorganic Color and Chemical Co. The copper(II) salt in the form of $Cu_{1.1}H_{0.8}PA$ (CuHPA) was prepared using its corresponding metal carbonate according to a method described in the literature.7) CuHPA was supported on to several kinds of active carbons (listed in Table 1 with some of their properties) from its methanol solution. The loading of the $Cu_{1.1}HPA$ was 10—33.3 wt%. Granules of 28—40 mesh (prepared by molding and crushing) were used for the catalytic reaction.

Reaction Procedure. The Reaction of NO or N_2O was carried out in a fixed bed flow reactor (8 mmϕ, Pyrex glass tube). The reactant gas contained 1.0% (1.01 kPa) of NO or 2.7% (2.74 kPA) of N_2O (Seitetsu Kagaku Co.). The catalyst weight and the total flow rate were 1.5—2.5 g and 100 cm^3 min^{-1}, respectively. The gas composition was analyzed by a gas chromatograph using columns packed with Porapak (1 m) and Molecular Sieves 13X(2 m). The partial pressure of NO was varied from 1.0 (1.01 kPa) to 10 vol% (10.1 kPa) to observe the rate dependence on its pressure using a flow reactor under the conditions of the differential reactor.

Table 1. Reduction of NO CuHPA supported on active carbona)

Support	Area (m^2/g)	NO conv. (%)	Product yield(select.)(%)		
			N_2	N_2O	CO_2
DA	1200	16.7	7.2(45)	8.8(55)	11.6
		1.4b)	1.4(100)	0.0(00)	
SAC	1200	16.2	9.4(58)	6.8(42)	11.7
		1.2b)	0.5(43)	0.7(57)	
BF	210	7.6	6.3(83)	1.3(17)	6.1
		1.3b)	0.6(45)	0.7(55)	
PAN-ACF	595	21.2	18.7(88)	2.5(12)	13.2
		10.5b)	5.6(53)	4.9(47)	
CBc)	560	21.2	15.7(73)	5.8(27)	10.8
		1.4b)	1.4(100)	0.0(00)	
1.7%CuO-3.3% Fe_2O_3/SAC		21.4	21.4(100)	0.0(00)	18.8
0.7%Pt/SACd)		38.0			

a) CuHPA/DA(loading: 33 wt%): 2 g, react. temp: 400 °C, feed: NO 1.0% in He carrier: 100 cm^3·min^{-1}, b) activity of carrier alone(1.33 g), c) carbon black, d) NO: 0.63%, SV: 20000 h^{-1}.3)

Results

Reduction of NO over CuHPA/DA. The reactivity of NO with DA catalyzed by CuHPA (loading 33 wt%) is illustrated in Fig. 1, where the reaction temperature and the amount of carbon used were 400 °C, and 2 g, respectively. NO was reduced into N_2 and N_2O, producing carbon dioxide. Without CuHPA, the reaction rate was very slow, the conversion of NO being as low as 1.4% at the same temperature. The catalytic role of CuHPA is, thus, definite. NO of 1.2×10^{-2} mole was reduced by 3.4×10^{-4} mole of CuHPA within 20 h. The conversion of NO was initially as high as 65% and decreased, gradually, and leveled off at 17% at 6 h on stream.

The conversion after the initial 5 h was much larger than that observed with CuHPA on silica gel, indicating the favorable role of the active carbon. Carbon dioxide produced at this stage was less than expected from the conversion of NO (roughly 3/5), while the production of carbon dioxide at a steady state maintained the oxygen balance.

The yields of N_2 and N_2O at a steady state are compared to the contact time in Fig. 2. Both yields increased monotonously with an increasing contact time. However, a contact time greater than 4.7×10^{-2} min gave more N_2 at the expense of N_2O, suggesting a contribution from the consecutive reaction to the major competitive formation of N_2 and N_2O as described by Eq. 2.

$$\begin{tikzcd} & N_2O \arrow[dr, "\text{minor path}"] & \\ NO \arrow[ur, "\text{major path}"] \arrow[rr, "\text{major path}"'] & & N_2 \end{tikzcd} \qquad (2)$$

The reactivity of DA catalyzed by CuHPA at several reaction temperatures is summarized in Table 2, where the reactivity is described by the stationary conversion observed with the flow reactor. The reactivity increased with an increasing temperature (from 300 to 400 °C), the activation energies for N_2 and N_2O formations being calculated to be 1.23 and 1.83 kJ mol^{-1}, respectively. Although the selectivity of N_2 formation

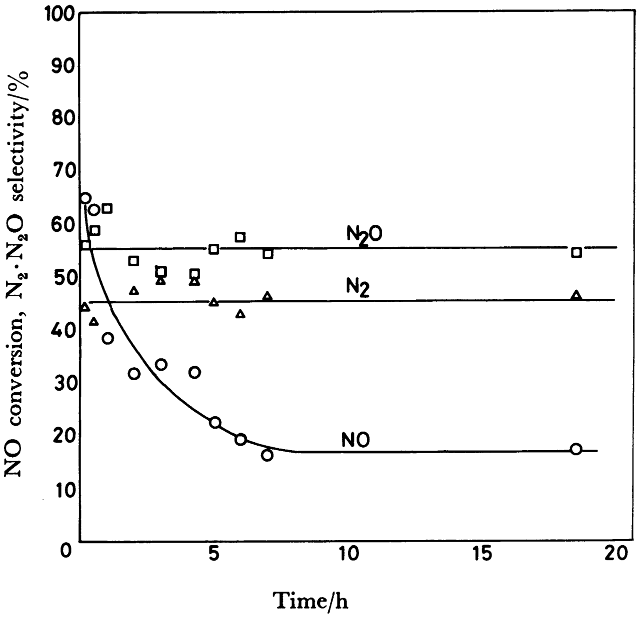

Fig. 1. Reduction of NO over CuHPA supported on DA active carbon.
○: NO conversion
△, □: N_2, N_2O selectivity
CuHPA/DA(loading: 33 wt%): 2 g, react. temp: 400 °C, feed: NO 1.0% in He carrier, 100 cm^3·min^{-1}.

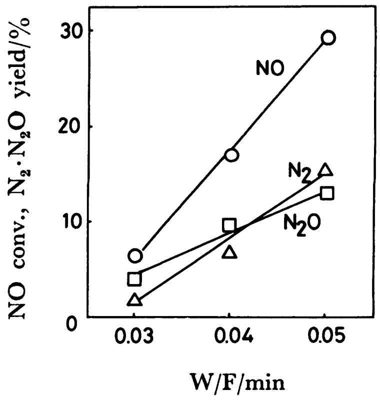

Fig. 2. Dependence of NO conversion on the contact time.
○: NO conversion
△, □: N_2, N_2O yield
CuHPA/DA(loading: 33 wt%), feed: NO 1.0% in He carrier, 100 cm^3·min^{-1}.

TABLE 2. DEPENDENCE OF NO CONVERSION ON THE REACTION TEMPERATURE[a)]

React. temp (°C)	NO conv. (%)	Product yield(select.)(%)		
		N_2	N_2O	CO_2
300	1.7	0.3 (17)	1.4 (83)	0.8
350	3.5	1.3 (38)	2.2 (62)	2.3
400	17	7.7 (45)	9.3 (55)	11.6
450	14	10.5 (75)	3.5 (25)	11.9
500	68	67 (98)	1 (2)	32
400[b)]	2.6	1.4 (51)	1.2 (49)	0.9
NO-H_2 React.[c)]	16.5	10.7 (65)	5.8 (35)	—

a) CuHPA/DA(loading: 33 wt%) 2 g, react. temp: 400 °C, feed: NO 1.0% in He carrier, 100 cm^3·min^{-1}, b) after the reaction at 500 °C for 28 h, c) CuHPA/DA (loading: 33 wt%) 0.5 g, react. temp: 300 °C, feed: NO 5%(H_2 5%) in He carrier, 100 cm^3·min^{-1}.

increased rather sharply with a rising reaction temperature, more N_2O was always produced than N_2 at these temperatures. Even if the consecutive conversion of N_2O was taken into account at a high conversion, the higher temperature appears favorable for the formation of N_2. It is very interesting that the reaction temperature of 450 °C provided a smaller conversion than that observed at 400 °C. More N_2 was produced at this temperature in spite of the smaller conversion than that at 400 °C. A higher temperature (500 °C) allow a high conversion (68%) almost exclusively into N_2. After a reaction at 500 °C for 28 h (where 22% of the carbon was consumed), the conversion became as low 3% at 400 °C. The level of the conversion was much lower than that of the same carbon at the same temperature without experiencing 500 °C. It was also noted that slightly more N_2 was produced in spite of the very low conversion. A significant change in the catalyst nature is suggested.

The reactivities of NO at different partial pressures is illustrated in Fig. 3. The reaction rates into N_2 and N_2O are plotted separately. In order to eliminate the influence of a consecutive contribution, the conversions were kept below 10%. Both reaction orders in NO to produce N_2 and N_2O were *ca.* 0.5.

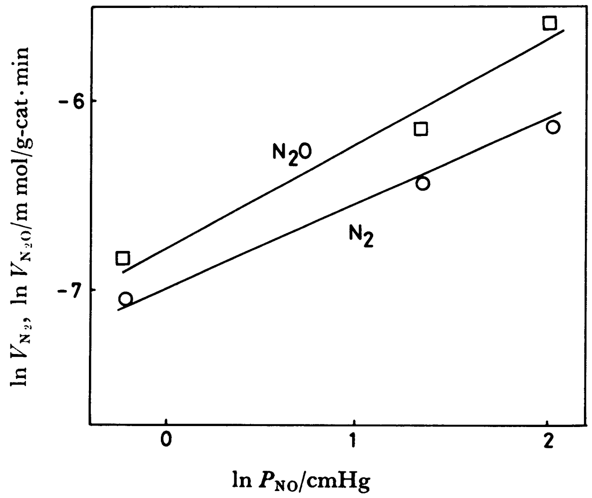

Fig. 3. The reactivity of NO of different partial pressures.
○, □: N_2, N_2O reaction rate,
CuHPA/DA(loading: 33 wt%): 2 g, react. temp: 400 °C, feed(He carrier): 100 cm³·min⁻¹.

Table 3. Dependence of NO conversion on the loading level[a)]

Loading (%)	NO conv. (%)	Product yield/%	
		N_2	N_2O
5	3.0	1.9	1.1
		(63)	(37)
8	6.7	4.6	2.1
		(69)	(31)
33.3	16.7	7.2	8.8
		(45)	(55)

a) CuHPA/DA: 2 g, react. temp: 400 °C, feed: NO 1.0%. in He carrier, 100 cm³·min⁻¹.

Table 4. Reduction of N_2O over CuHPA/DA[a)]

Reactant	Inlet gas (%)		Outlet gas (%)		
	N_2O	NO	N_2O	NO	N_2
N_2O	2.70	—	0.00	—	2.70
$NO+N_2O$	2.20	1.01	2.21	0.81	0.09

a) CuHPA/DA: 2 g, react. temp: 400 °C, feed: 100 cm³·min⁻¹ (He carrier).

The stationary rate of NO reduction was proportional to the amount of supported CuHPA until the loading was 33.3% (Table 3). However, the ratio of N_2/N_2O produced decreased with the increasing loading in spite of the increased conversion where a more consecutive conversion of NO may take place. The catalyst density may influence the relative contribution of competitive reaction path which lead to N_2 and N_2O respectively.

The Reactivity of N_2O. The reactivity of N_2O against DA catalyzed by CuHPA (loading: 33.3%) is summarized in Table 4, where N_2O (2.7%) and N_2O–NO (2.2 and 1.0%, respectively) were examined. N_2O was very reactive at 400 °C, allowing its complete conversion into N_2 under similar conditions of NO reduction where the conversion of NO was 17%. The reactivity of N_2O appeared to be very much suppressed when NO was present (Table 4), while the reactivity of NO was almost unchanged by the presence of N_2O to provide an 18% conversion (NO base). To balance the N_2 produced, the conversion of N_2O was calculated to be only 2.3%.

The Reactivities of Several Kinds of Active Carbons Catalyzed by CuHPA. The conversions of several active carbons with and without the catalyst CuHPA are summarized in Table 1, where the loading and the reaction temperature were fixed at 33% and 400 °C, respectively. The reactivities of the active carbons without the catalyst were very low, the conversion being around 1.4% except for an active PAN-fiber. The conversion, when catalyzed, varied from 7.6 to 21%, carbon black showing the highest reactivity. The selectivity was also variable with the carbons, commercial active carbons of DA and SAC showing smaller selectivity for N_2 production than other carbons. The high reactivity and selectivity (to N_2) of active PAN-carbon-fiber without the catalyst needs to be noted. Details on its reactivity will be reported later.

IR Spectrum of CuHPA on DA. The IR spctra of CuHPA on DA before and after the reaction are illustrated in Fig. 4. By supporting on DA, the IR spectrum of CuHPA was slightly changed. Although the bands around 880 and 800 cm⁻¹ somewhat shifted, other major bands were unchanged. The broadening

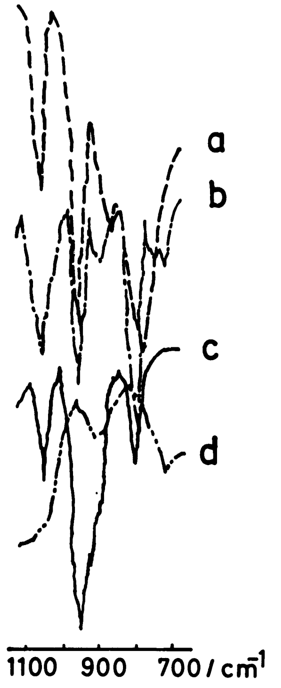

Fig. 4. IR spectra of catalysts after the reaction at several temperature.
a: CuHPA, b: CuHPA/DA, c: CuHPA/DA after the reaction at 400 °C, d: CuHPA/DA after the reaction at 500°C.

of these adsorption bands was observable after the reaction at 400 °C, but still major peaks were unchanged. In contrast, the reaction at 500 °C completely changed the spectrum and the sharp bands observable in the region became very broad or disappeared. The decomposition of CuHPA into component oxides is strongly suggested. The decomposition of CuHPA may take place between 400 and 450 °C.

Discussion

The catalytic activity of CuHPA in the reduction of NO with active carbon is comparable to those for mixed oxides[8] of copper and iron but much less than that for noble metals[3] supported on active carbon. The former catalyst has been reported to be very active for the NO-NH_3 reaction. An interesting observation is that the activity of CuHPA was much larger than that of its decomposed component oxides produced by heating to above 450 °C. Certain sites characteristic to the heteropoly acid appear to be active in this reaction.

In a previous study,[4] the acid supported on silica gel was reported to reduce NO to a limited extent (3.49×10^{-4} mole NO/mole acid within 20 h). Some reduced sites are induced in the acid during the preparation as ESR suggested. Such a reduced site may also be the active site for the present catalysis. NO is reduced by the site into N_2O and N_2, leaving oxygen. Oxygen, thus produced, may spillover to the carbon to produce carbon dioxide and to regenerate the reduced site in the acid. The high conversion during the initial 7—8 h may be partly due to the reduced sites induced prior to the catalysis, and partly due to the active portions of the carbon probably located in the vicinity of CuHPA. Because some portions of the former sites were irreversibly oxidized by NO, a smaller amount of CO_2 was produced than expected from the amount of consumed NO. The conversion decreased, corresponding to the decreasing number of the sites, to the stationary one, which is determined by the regeneration of the active site through the spill-over mechanism. It may be noted that the product from active carbon was only CO_2. Furusawa *et al.*[9] reported that CO_2 was formed by the reaction of NO with active carbon below 579 °C. The oxidation of active carbon may proceed *via* the formation of an oxygen-containing functionarity to form CO_2.[10,11]

The activity in the present reaction is much smaller than that of the reduction with hydrogen in spite of the similar mechanism.[4] This suggests that the rate of the oxygen spill-over onto the active carbon was inferior to that of the reductive regeneration of the active site. It is noted that similar product distributions were obtained in both reactions on the same support.

The reduction of NO on CuHPA supported on the active carbon proceeds into N_2O and N_2 through both competitive and consecutive paths as described in the Results. In spite of the high reactivity, N_2O remained in the product, suggesting its weaker adsorption to the active site. It can be easily converted into N_2 simply to extend the contact time.

The selectivity in the competitive paths is worth being discussed. The reaction kinetics suggest the dissociative adsorption of NO as the common intermediate for both N_2O and N_2, although the former product may require another NO molecule. Thus, the selectivity is determined by the respective rates of coupling of dissociatively adsorbed nitrogen with another nitrogen (to N_2) and NO (to N_2O), respectively. The superior formation of N_2 on the catalyst of low CuHPA loading even at the lower conversion may suggest the favorable geometry of active site for the N_2 formation. It has been reported that several reduced sites are produced in a unit cell of the heteropoly acid.[12]

The roles of active carbon are the support for the catalyst as well as the reductant. Through these two roles, the carbon influences the activity and selectivity of the present reaction. The reactivity of active carbon may be most influential on a stationary conversion, however the initial conversion, which is due to the reduced sites of CuHPA being induced during the catalyst preparation, is much higher on the active carbon than that on silica gel, suggesting a role of the support in their generation. The redox interaction may attract for the study.[5,6,13] At present, the factors influencing the spill-over are difficult to discuss.

The selectivity is different among the used active carbons, high N_2 formation being noted on the PAN-ACF and the carbon black in spite of their similar conversions to those of the active carbons. Although the removal of N_2O is much easier than NO because of its thermodynamical unstability, such carbons may provide the better catalysts for the conversion of NO to N_2. The support may influence the geometry of the active sites in the supported CuHPA through a magnetic interaction.

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