Catalytic Activities of 12-Molybdophosphoric Acid and Its Salts Supported on Silicon Dioxide for the Reduction of Nitrogen Monoxide

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12-Molybdophosphoric acid and its metal salts, supported on SiO_2 (H_3PA and MPA/SiO_2), were found to exhibit significant activities for the catalytic reduction of nitrogen monoxide with hydrogen or ammonia, the latter reductant being more reactive. The activity orders of the catalysts were as follows, depending on the reductant: $Cu^{2+}>Ag^{+}>Ni^{2+}>Cs^{+}\simeq Co^{2+}\simeq H^{+}$ (hydrogen), $Cu^{2+}>Co^{2+}>H^{+}>Ag^{+}>Ni^{2+}>Cs^{+}$ (ammonia). It is of value to mention also that H_3PA/SiO_2 exhibited ten times many activity when ammonia was applied. The extent of the cation exchange (X) of $Cu_XH_{3-2X}PA/SiO_2$ influenced the catalytic activity differently, depending again on the reductant, although the maximum activity was obtained with both reductants when X was 1.1. Nitrogen monoxide was decomposed by a stoichiometric reaction with the reduced site on $Cu_{1.1}H_{0.8}PA/SiO_2$, especially when the catalyst was reduced with hydrogen, although no oxygen was detected in the product, the initial rate being comparable to that of the reduction with hydrogen. The following rate-equations were obtained with the respective reductants on $Cu_{1.1}H_{0.8}PA/SiO_2$ at 300 °C over the partial pressure range of NO (3.0—10.1 kPa) and reductants (3.0—35.5 kPa): $V=k_{H_2}P_{NO}^{0.8}P_{H_2}^{0.04}$, $V=k_{NH_3}P_{NO}^{0.6}P_{NH_3}^{0.4-−0.7}$. The wide range in the magnitude of powers with respect to the ammonia partial pressure in the latter equation implies the strong adsorption of ammonia on the catalyst. These results suggest that the redox and Langmuir mechanisms are plausible for the reactions with hydrogen and ammonia respectively. An ESR study of the copper and molybdenum ions of the catalyst supports the above mechanisms.

The practical removal or reduction of NO_x in the flue gas has been widely carried out in various industries.[1)] Nevertheless, techniques with higher efficiency are still extensively explored for using various catalytic reactions. The recent increase in coal firing, which tends to exhaust highly contaminated flue gas,[2)] may also force the acceleration of technical development.

In the present study, the catalytic activities of heteropolyphosphoric acid and its metal salts were examined for the reactions of NO-H_2 and NO-NH_3. Since they are well known catalysts for acid-catalyzed and oxidation reactions,[3)] the simultaneons activation of ammonia and nitrogen monoxide can be expected to provide an excellent activity. They are soluble in water or methanol, and can easily be recovered and regenerated when the catalyst is poisoned by fly ashes exhausted from coal. The salt forms may be durable against the alkali metal compounds which are known to poison some metal oxide catalysts severely.[4)]

Experimental

Catalysts. The 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) was purchased from the Nippon Inorganic Colour and Chemical Co. The metal salts were prepared using their corresponding metal carbonates according to the method described in the literature.[5)] The salts or the acid were supported on silica gel (Merck, Kiesel gel 60HR, 350 m²/g) from their methanol solution. The loading level of the salts or the acid was 33.3 wt%. Granules of 28—40 mesh, prepared by molding and crushing, were used for the catalytic reaction.

Reaction Procedure. The reduction of nitrogen monoxide was carried out in a fixed-bed flow reactor (8 mmϕ, Pyrex glass tube) and in a closed-circuration reactor (vol. 800 ml). The reactant gas contained 5 vol% (5.07 kPa) of nitrogen monoxide (Seitetsu Kagaku Co.), plus 10 vol% (10.1 kPa) of ammonia or hydrogen as the reductant. The catalyst weight and the total flow rate in a typical case of the flow reactor were 500 mg and 100 cm³ min⁻¹ (SV: 9200/h) respectively. The same reactant gas was supplied to the circulation reactor, where the circulation rate was 500 ml min^{-1} at a total pressure of 15.2 kPa. The rate dependence on their partial pressures was measured under partial pressures of nitrogen monoxide and reductants varying from 3.0 to 10.1 kPa (3 to 10 vol%) and from 3.0 to 35.5 kPa (3 to 35 vol%) respectively by means of a flow reactor under differential reactor conditions (conversions less than 10%). The gas composition was analyzed before and after the reaction by means of a gas chromatograph with columns packed with Porapak Q (1 m) and Molecular Sieve 13X (2 m).

Adsorption Measurements. The adsorption of NO and NH_3 was measured volumetrically with a fixed volume apparatus.

ESR Measurements. The ESR measurements were carried out at room temperature with a JEOL JES-FEIX spectrometer at a modulation frequency of 100 kHz. Mn^{2+} doped in MgO was used as the external standard to determine the g values of the paramagnetic species.

Results

Catalytic Activity for NO Reduction with Hydrogen and Ammonia. The catalytic activities of 12-molybdophosphoric acid and its stoichiometric metal salts supported on silica gel are summarized in Table 1; the reduction of NO was examined with hydrogen as a reductant. All the catalysts showed activity stable enough for more than 12 h and commonly produced nitrogen and dinitrogen monoxide, without any ammonia. The activity and selectivity varied considerably, depending on the kind of metal cation; the following activity order was deduced:

$$Cu^{2+}>Ag^{+}>Ni^{2+}>Cs^{+}\simeq Co^{2+}\simeq H^{+}.$$

The three active catalysts produced considerable amounts of dinitrogen monoxide; its selectivity on the nickel salt was as high as 60%, whereas no dinitrogen monoxide was found over the catalysts of much less

Table 1. Catalytic activities for NO–H_2 reaction over 12-molybdophosphoric acid and its metal salts supported on SiO_2

Catalyst	NO conversion/%	Selectivity (%) N_2	Selectivity (%) N_2O	Rate (mol NO/g min)
H_3PA	2.0	100.0	0.0	8.9×10^{-6}
$Cu_{1.5}PA$	13.0	72.0	28.0	5.8×10^{-5}
$Ni_{1.5}PA$	4.0	40.0	60.0	1.8×10^{-5}
$Co_{1.5}PA$	1.5	0.0	100.0	6.7×10^{-6}
Ag_3PA	9.3	53.1	46.9	4.2×10^{-5}
Cs_3PA	2.4	100.0	0.0	1.1×10^{-5}

Reaction temperature: 300 °C, pretreatment: 300 °C–3 h (in He), catalyst weight: 0.5 g, NO: 5.0%, H_2: 10.0%, He: Carrier: 100 $cm^3 min^{-1}$.

Table 2. Catalytic activities for NO–NH_3 reaction over 12-molybdophosphoric acid and its metal salts supported on SiO_2

Catalyst	NO conversion/%	Selectivity (%) N_2	Selectivity (%) N_2O
H_3PA	21.4	87.4	12.6
$Cu_{1.5}PA$	27.4	77.8	22.2
$Co_{1.5}PA$	24.3	88.7	11.3
$Ni_{1.5}PA$	5.3	65.8	34.2
Ag_3PA	11.2	74.2	25.8
Cs_3PA	6.0	67.9	32.1

Reaction temp: 300 °C, pretreatment: 300 °C–3 h (in He), catalyst weight: 0.5 g, NO: 5.0%, NH_3: 10.0%, He: Carrier: 100 $cm^3 min^{-1}$.

activity except for the cobalt salt.

The catalytic activities using NH_3 as a reductant are shown in Table 2, where the conversion and selectivity were observed 3 h after the reaction had started. Although all the catalysts showed activities higher than those with hydrogen, their activities decreased to *ca.* 80% of the initial value within 3 h and then further gradually to give *ca.* 50% after 20 h. The selectivities, however, stayed constant. The catalytic activities depended considerably on the exchanged cations, although N_2 was always the principal product over all the catalysts, regardless of the cation. The activity order was deduced to be as follows:

$$Cu^{2+} > Co^{2+} > H^{+} > Ag^{+} > Ni^{2+} \simeq Cs^{+}.$$

It must be noted that H^+ and Co^{2+} catalysts showed activities over ten times larger than those observed in the reaction with hydrogen.

The Effects of the Extents of Cation Exchange on the Catalytic Activity. The catalytic activities of the acid exchanged with Cu^{2+} at variable levels (defined as $M_XH_{3-2X}PA$, where the exchange levels of X were 0.5, 1.1, and 1.5), with hydrogen and ammonia as the reductants, are shown in Fig. 1. When hydrogen was used, the conversion of NO increased proportionally with the increase in X until X was 1.1. The acid and $Cu_{0.5}H_2PA$ produced nitrogen almost exclusively, whereas the more copper(II)-ion-exchanged one produced dinitrogen monoxide with about a 30% selectivity, in addition to the principal product of nitrogen.

The activity in the reduction with NH_3 depended more markedly on the exchange level, showing a bell-shaped correlation against X where $Cu_{1.1}H_{0.8}PA$ showed the highest activity, whereas the selectivity was almost constant at all exchange levels.

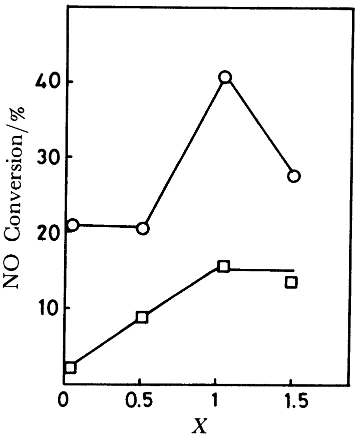

Fig. 1. The effects of the extent of cation exchange (X) on the catalytic activity of $Cu_XH_{3-2X}PA/SiO_2$. Catalyst: 0.5 g, NO and reductant: 5% and 10% in He, total flow rate: 100 $cm^3 min^{-1}$, reaction temp: 300 °C, □: NO–H_2, ○: NO–NH_3.

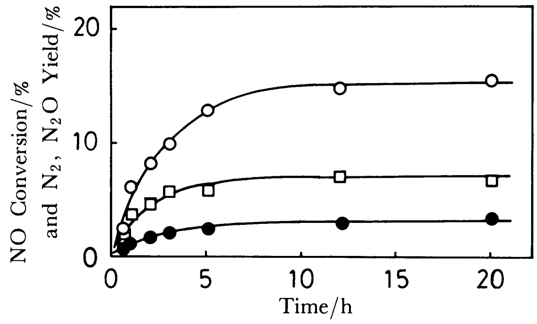

Fig. 2. Decomposition reaction of NO over $Cu_{1.1}H_{0.8}PA/SiO_2$ using a closed circulation reactor. Catalyst: 1.0 g, P_{NO}=40.3 kPa, reaction temp: 300 °C. ○: NO conversion, ●: N_2 yield, □: N_2O yield.

Decomposition Reaction of NO over $Cu_{1.1}H_{0.8}PA/SiO_2$. The decomposition of NO was found to proceed over $Cu_{1.1}H_{0.8}PA/SiO_2$ at 300 °C. Its reaction profile, as observed in a closed circulation reactor (P_{NO} = 40.3 kPa, catalyst = 1 g), is shown in Fig. 2. The reaction proceeded slowly but steadily to produce nitrogen and dinitrogen monoxide, and terminated at 10 h after the reaction started. At the end of the reaction, the reacted NO amounted to one molecule per Keggin unit of the catalyst. It must be noted that no oxygen was detected in the gas phase throughout the reaction.

The activity of reduced $Cu_{1.1}H_{0.8}PA/SiO_2$ (under a hydrogen flow at 300 °C for 20 h) observed with a flow reactor is shown in Fig. 3, where the reaction temperature, the amounts of catalyst, the partial pressure of NO, and the total flow rate were 300 °C, 0.5 g, 1.057% (1.1 kPa) in helium, and 50 cm³ min⁻¹ (SV 4600/h) respectively. Although the conversion was very high at the early stage of the reaction (70% at 30 min), it decreased sharply to *ca.* 2% after 5 h and terminated after 10 h. The total amounts of decomposed NO reached 12 molecules per Keggin unit. Nitrogen was the principal product at the early stage of the reaction; however, the amount of dinitrogen monoxide increased, reaching *ca.* 40% at 1 h and then gradually decreasing with the reaction time. The reaction in the later stage was very similar to that over the unreduced catalyst.

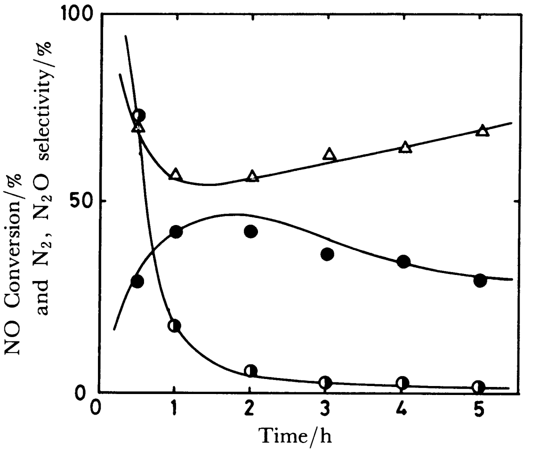

Fig. 3. Time on stream of NO decomposition over $Cu_{1.1}H_{0.8}PA/SiO_2$ reduced with hydrogen.
Catalyst: 0.5 g (reduction conditions: 300 °C, 20 h in H_2), NO: 1.06% in He, total flow rate: 50 cm³ min⁻¹, reaction temp: 300 °C, ◑: NO conversion, △: N_2 yield, ●: N_2O yield.

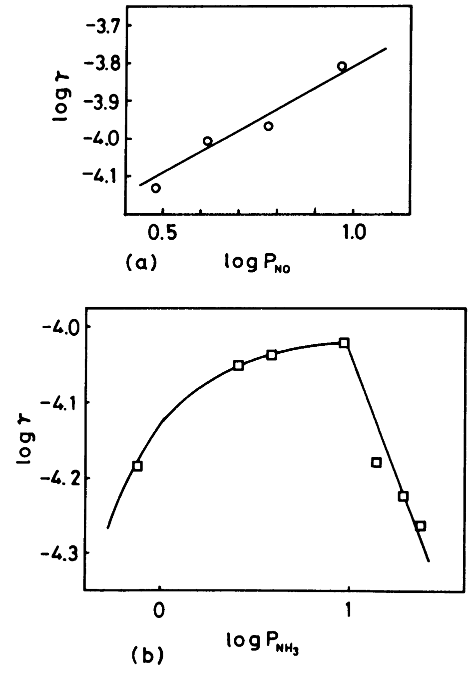

Fig. 4. The partial pressure dependence of NO-NH_3 reaction over $Cu_{1.1}H_{0.8}PA/SiO_2$.
a) Dependence on the partial pressure of NO, b) dependence on the partial pressure of NH_3.

Kinetic Measurements. Some kinetic studies were carried out for the reaction over $Cu_{1.1}H_{0.8}PA/SiO_2$. The logarithmic rates of the NO-H_2 reaction varied linearly with the partial pressures (Fig. 4), providing the following rate equation (Eq. 1):

$$r = k_{H_2}P_{NO}^{0.8}P_{H_2}^{0.04}. \qquad (1)$$

For the NO-NH_3 reaction, a good linear correlation was obtained with NO, providing the order of 0.6 (Fig. 4a). On the other hand, a complex dependence on NH_3 was observed (Fig. 4b). The rate increased rather sharply first while the pressure was below 1.3 kPa, leveling off at *ca.* 5.3 kPa, the order being 0.4 at first and decreasing to zero. Above 10.1 kPa of NH_3 the rate decreased very sharply, providing the order of −0.7. Thus, the rate equation is described by Eq. 2 with a variable order of ammonia:

$$r = k_{NH_3}P_{NO}^{0.6}P_{NH_3}^{0.4--0.7}. \qquad (2)$$

The activation energy for NO disappearance in the NO-NH_3 reaction was calculated to be 91.6 kJ mol⁻¹. The selectivity for N_2 was slightly decreased (85% at 300 °C to 80% at 350 °C); instead, that of N_2O increased.

The adsorption of NO and NH_3 on the H_3PA, $Cu_{0.5}H_2PA$, $Cu_{1.1}H_{0.8}PA$, and $Cu_{1.5}PA$ after pretreatment at 300 °C in He was observed at room temperature and 300 °C respectively. H_3PA adsorbed 0.5 molecule of NO per Keggin unit, whereas the cupric ion exchanged PA adsorbed one molecule per Keggin unit. *Ca.* six molecules of NH_3 were adsorbed at 300 °C on both the acid and the salts, a half of those adsorbed being subsequently desorbed by evacuation at the same temperature.

ESR Spectra of $Cu_xH_{3-2x}PA/SiO_2$. The ESR spectra of the orignal $Cu_{1.1}H_{0.8}PA/SiO_2$ and that after the heat-treatment at 300 °C *in vacuo* are illustrated in Fig. 5. The original salt exhibited only an anisotropic signal due to the cupric ion ($g_\perp = 2.222$, $g = 2.071$); however, the heat-treatment decreased its intensity very much, to one-eighth of the original value, because of the formation of Cu^+, and provided an intense signal of Mo^{5+} ($g_\perp = 1.945$, $g = 1.894$). These facts suggest that a considerable reduction takes place during the heat-treatment. The extent of reduction for $Cu_xH_{3-2x}PA/SiO_2$, based on the decrease of Cu^{2+} and the appearance of Mo^{5+}, were estimated thus: $Cu_{1.1}H_{0.8}PA$ (1.8 electron/Keggin unit)$>$$Cu_{0.5}H_2PA$ (1.4 electron/Keggin unit)$\simeq$ $Cu_{1.5}PA$ (1.3 electron/Keggin unit)$>$$H_3PA$ (0.7 electron/Keggin unit).

A similar spectrum was observed in the $Cu_{1.1}H_{0.8}PA$ after the reaction of NO-H_2. The extent of reduction did not change after the NH_3 treatment at 300 °C; however it decreased samewhat after the reaction of NO-NH_3, Mo^{5+} decreasing by *ca.* 10% with the increase in Cu^{2+} (twice the intensity) compared to their respective intensities after the heat-treatment.

Mechanistic Consideration. The heteropoly acid and its transition-metal salts have been well documented to exhibit significant activities in the acid-catalyzed and oxidation reactions.[3] The reduction of

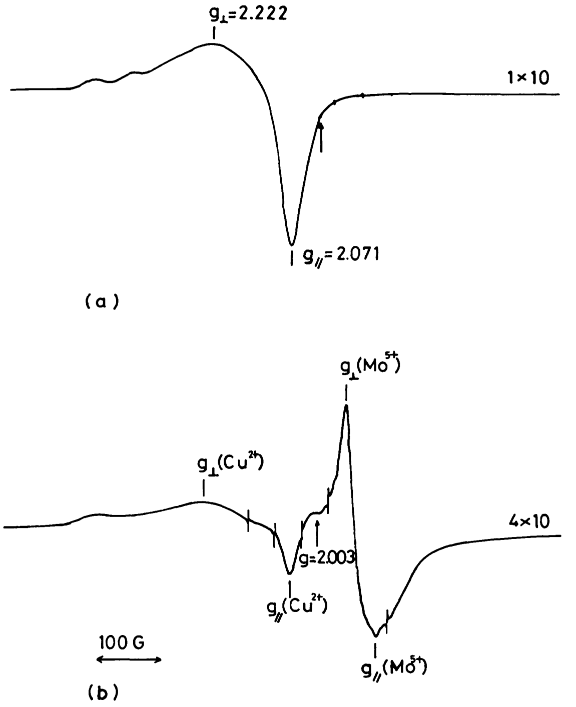

Fig. 5. ESR specra of $Cu_{1.1}H_{0.8}PA/SiO_2$.
a) Original, b) after evacuation at 300 °C.

NO can be listed for one of them, although its activity is not remarkably high. Copper(II) salt supported on silica gel showed the highest activities for the reactions of both $NO-H_2$ and $NO-NH_3$: however, some different features of the catalytic reactions suggest different mechanisms.

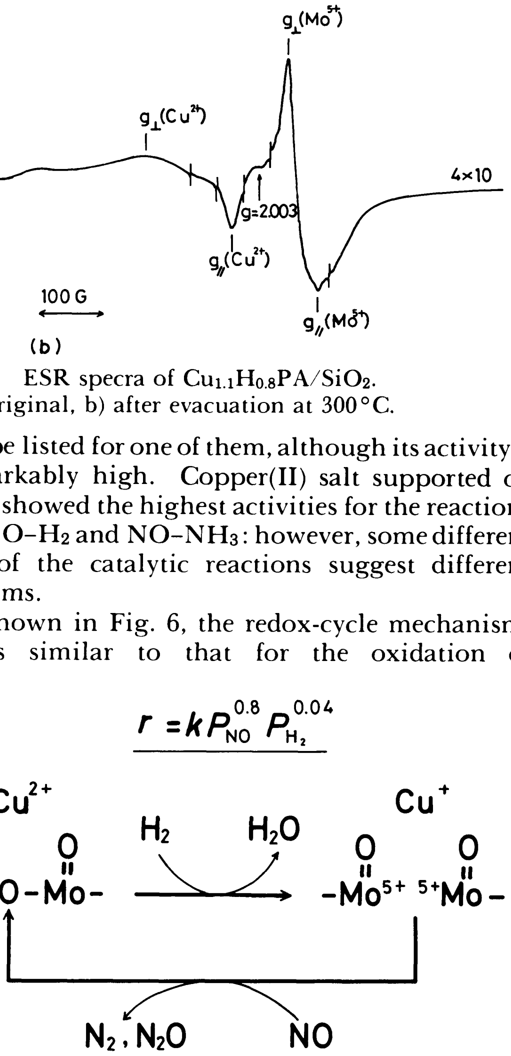

Fig. 6. Mechanism of $NO-H_2$ reaction over $Cu_{1.1}H_{0.8}PA/SiO_2$.

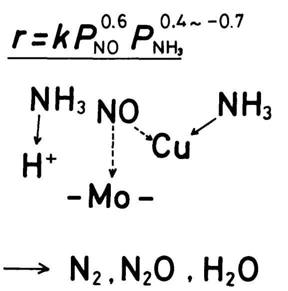

Fig. 7. Mechanism of $NO-NH_3$ reaction over $Cu_{1.1}H_{0.8}PA/SiO_2$.

As is shown in Fig. 6, the redox-cycle mechanism, which is similar to that for the oxidation of methacrolein,[6] is assumed in the $NO-H_2$ reaction over $Cu_{1.1}H_{0.8}PA/SiO_2$, where the reduction of NO by copper(I) or molybdenum(V) ions of the reduced catalyst is rate-determining, judging from the kinetic equation. The rate of NO decomposition over the catalyst reduced by hydrogen at 300 °C is similar to that of NO reduction with hydrogen on the same catalyst when the rates are compared at similar reduction extents of the catalyst (as estimated by ESR measurements after the reaction). The catalytic activity is, thus, influenced by the number of reduced sites[7] and by the activation degree of NO, both of which are themseleves influenced by the cations, the transition metal ions probably being favorable for both factors since they can activate NO as well as hydrogen, the latter of which reduces the catalyst. It may be of value to mention that the most active $Cu_{1.1}H_{0.8}PA$ was revealed by ESR to be the most easily reduced by the heat-treatment. Eguchi *et al.* have also reported that the reduction of the heteropoly acid occurred upon evacuation at 300 °C[8].

The ESR measurements suggest that the decomposition reaction of NO on the $Cu_{1.1}H_{0.8}PA/SiO_2$ may proceed by means of the stoichiometric oxidation of the reduced sites which may be produced during the heat-treatment (*ca.* 1 sites/Keggin unit). The reduction of the catalyst by hydrogen before the reaction enhances the activity; however, the reaction also terminates when the reduced sites are consumed. In the latter case, the possibility that the adsorbed hydrogen atoms[9] contribute the high activity at the early stage of the reaction cannot be excluded. No generation of a reduced site takes place during the reaction under the present conditions.

The $NO-NH_3$ reaction provides some contrasting mechanistic features to the $NO-H_2$ reaction. A plausible mechanism is illustrated in Fig. 7. The acid itself showed a significant activity, but $Cu_{1.5}PA$ was much inferior to $Cu_{1.1}H_{0.8}PA$. The ammonia treatment of $Cu_{1.1}H_{0.8}PA$ after the evacuation at 300 °C causes no change in the ESR spectrum, suggesting that ammonia did not produce the reduced sites. Such results as well as the kinetic equation suggest the participation of NH_3 activation. Thus, the surface reaction between the NO adsorbed on the metal-ion sites and the NH_3 on the acidic sites seems to be rate-determining. $Cu_{1.1}H_{0.8}PA$, which contains proton as well as copper sites suitable for activating both reactants, naturally exhibits the highest activity. In contrast, the lack of any proton site on $Cu_{1.5}PA$ may lose the advantages of NH_3 activation. Excess NH_3 decreases the rate, covering the active sites for NO.

In conclusion, the heteropoly acid and its transition-metal salts were found to exhibit significant activities for the reduction of nitrogen monoxide with hydrogen and ammonia, according to their redox and acidic properties. Although the activities were not markedly high, such origins of activity may be suggestive for the catalyst design.

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