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The sorption and reduction of nitrogen oxides by 12-tungstophosphoric acid and its ammonium salt

R. Bélanger, J.B. Moffat*

Department of Chemistry and the Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

Abstract

Nitrogen dioxide is removed from the gas phase by 12-tungstophosphoric (HPW), 12-tungstosilicic and 12-molybdophosphoric acids, with the two solid acids containing tungsten sorbing significantly larger quantities of NO_2 than that containing molybdenum, indicating the dependence on acidic strength. NO_2 interacts with the water contained on and in HPW to form HNO_3 which desorbs. On depletion of the water additional NO_2 remains held on HPW as HNO_2^+.

In contrast the ammonium salt of HPW reduces NO_2 to N_2 , NO and N_2O at an optimal temperature of 175°C for the reduction to N_2. The interaction process occurs between NO_2 and the reductant NH_3 while it is bound as NH_4^+ on the solid. Thus NH_3 is not lost to the gas phase during the reduction process, and ammonia slip is effectively eliminated. The ammonium salt can be regenerated by exposure of HPW to gaseous NH_3 or by precipitation from aqueous solution.

Keywords: Nitrogen oxides; Sorption; Reduction; 12-tungstophosphoric acid

1. Introduction

Nitrogen oxides and the reduction of their emissions have been the focus of numerous catalytic studies in the last several decades [1,2]. In spite of these efforts the emissions of NO_x, while subject to some diminution since 1992, are projected to increase in the first decade of the next century and reach as high as 25 million tons by 2010 [1]. While catalysts based on titanium and vanadium with ammonia as the reductant continue to be employed in stationary applications zeolite solids, particularly H-ZSM-5 and its metal ion-exchanged analogue have attracted considerable attention in the last decade [3]. More recently the recognition of the environmental disadvantages of the use of ammonia as a reductant and the associated problem of ammonia slip has led to a deluge of publications investigating the use of hydrocarbons as reductants with the aforementioned zeolites. The catalysts based on ZSM-5 appear, however, to be economically unattractive, at least at the present stage of development [4]. Since the reductants themselves may be, and generally are, atmospheric pollutants, the substitution of less disadvantageous gases has also been investigated [5]. Unfortunately, however, the ideal solid catalyst producing high conversions of NO_x and virtually complete selectivity to N_2, inexpensive, conveniently regeneratable and requiring

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*Corresponding author. Tel.: +1 519 8884567x2502; e-mail: jbmoffat@uwaterloo.ca

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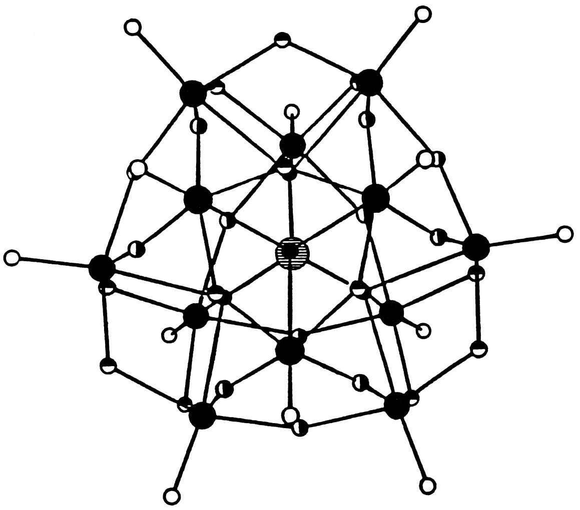

Fig. 1. Heteropoly anion of Keggin structure: (⊜) central atom; (●) Peripheral metal atoms; (•) oxygen atoms attached to central atoms; (◓) oxygen atoms interconnecting peripheral metal atoms; (○) terminal oxygen atoms.

either no reductant or one which is not a pollutant, has not yet been found.

The interaction of NO_x with heteropoly oxometalates is of current interest in this laboratory and the present report is intended to summarize and update the results obtained to this date.

The heteropoly oxometalates of interest are those with Keggin structure. These are ionic solids with discrete cations and anions, in contrast with the network structure frequently found with zeolites. The anions are large (approximately 10 Å in diameter) structures with, in the present context, either phosphorus or silicon at their centres, which are bonded tetrahedrally to four oxygen atoms (Fig. 1). Twelve octahedra, with oxygen atoms at their vertices and, in the present work, molybdenum or tungsten at their approximate centres, surround the central tetrahedron and share oxygen atoms with each other and with the latter. Since the anions are packed structures entry of atoms or molecules is not possible.

With protons providing the charge balance solid acids are formed. Those with phosphorus in the centre of the anion and tungsten in the peripheral metal

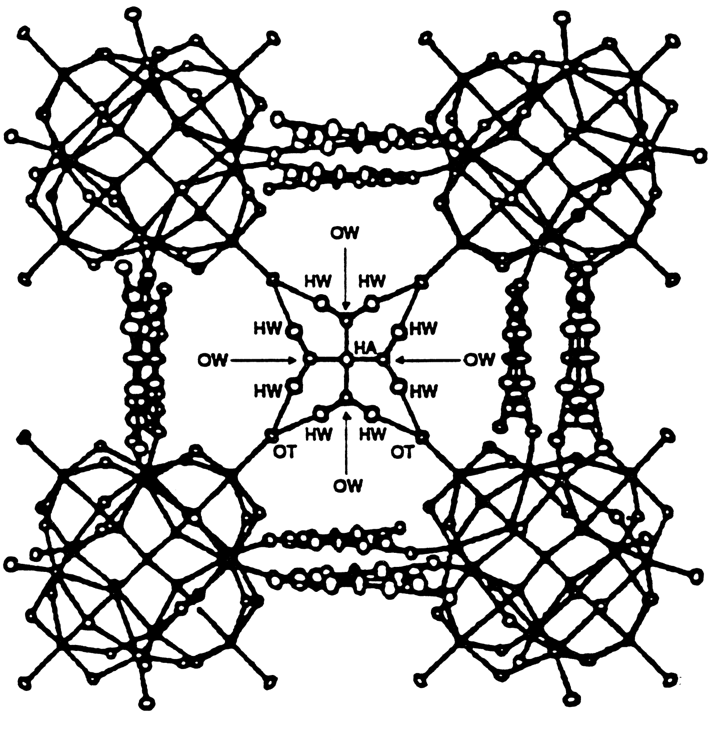

Fig. 2. Cubic structure of 12-tungstophosphoric acid [6].

positions, usually referred to as 12-tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot nH_2O$), have been shown, in the 6-hydrate form, to have a cubic (Pn3m) structure with the protons hydrogen-bonded to water molecules which are, in turn, similarly bonded to the terminal oxygen atoms of the anions (Fig. 2) [6].

Although the solid acids have interstitial voids these are separated from each other by the terminal oxygen atoms and as a consequence the BET N_2 surface areas are less than 10 m^2/g [7].

Substitution of the protons by certain of the monovalent cations, for example those from group 1A of the periodic table, produces solids which have microporous structures as evidenced from the analysis of nitrogen adsorption–desorption isotherms and from Xe NMR measurements [7]. As expected these microporous solids have substantially larger surface areas than the parent acids and pore diameters sufficiently large to permit the entry of a variety of molecules [7].

The present work reports on the use of 12-tungstophosphoric, 12-tungstosilicic and 12-molybdophosphoric acids, and particularly the first, for the removal of NO_x from gaseous streams. The microporous ammonium salt of 12-tungstophosphoric acid has been studied in detail and is shown to be capable of the conversion of NO_2 to N_2 at low temperatures with little or no loss of NH_3.

2. Experimental

2.1. Materials

12-Tungstophosphoric acid was purchased from British Drug Houses, Canada, and was recrystallized before use. Ammonium 12-tungstophosphate was prepared by precipitation from aqueous solutions of the acid and a source of the ammonium cation. The ammonium salt was also prepared by direct reaction of the acid with ammonia. The salts were dried under vacuum at room temperature for at least 24 h. Nitrogen dioxide was purchased (as N_2O_4) from Matheson.

2.2. Equipment and procedure

A 4 mm i.d. × 25 cm quartz reactor with the catalyst held in place by quartz wool was equipped with appropriate stainless steel tubing, open–closed, and flow control gas sampling valves. All lines connecting the reactor to the gas chromatograph (Shimadzu GC-9A) were heated to 130°C. In some experiments a gas chromatograph (HP5890) equipped with a mass selective detector (HP-145 5970) was used as the analytical device.

Powder X-ray diffraction patterns were obtained with a D500 Siemens diffractometer at 40 kV and 30 mA with the CuKα line. Adsorption–desorption isotherms were measured with a standard volumetric system equipped with a suitable pressure transducer. For MAS NMR measurements a Bruker AMX 500 spectrometer with an 11.7 T magnet was employed. Infrared spectra were obtained with a BOMEM MB-100 Michelson infrared spectrometer.

3. Results and discussion

To compare the effect of changes in the composition of the anions on the sorption properties with NO_2, 12-tungstophosphoric, 12-molybdophosphoric and 12-tungstosilicic acids (abbreviated as HPW, HPMo and HSiW, respectively) were selected. The solid acids with tungsten as the peripheral metal of the anion sorbed similar quantities of NO_2 at 150°C while that containing molybdenum took up relatively insignificant amounts of the gas (Fig. 3). Extended Huckel calculations have shown that the magnitude of the charge on the terminal oxygen atoms in the molybdenum-containing anions is significantly higher than that where tungsten is the peripheral metal (Fig. 4). Since the proton is expected to be coulombically interacting with the terminal oxygen atoms, in the absence of water, the protons in the tungsten-containing acids should be more mobile and hence more acidic than those in the molybdenum-containing acid. Thus the results with the three solid acids imply that the acidity plays a role in the sorption of NO_2 with the stronger acids having a higher capacity for the sorption of the gas.

The remainder of this report will focus on HPW and its ammonium salt.

NO_2 is adsorbed on HPW at 25°C (Fig. 5). The adsorption–desorption isotherm shows that approximately 3 molecules of NO_2 per anion remain held on the solid, after evacuation, corresponding to 1 molecule of NO_2 per proton. Since the surface area of HPW

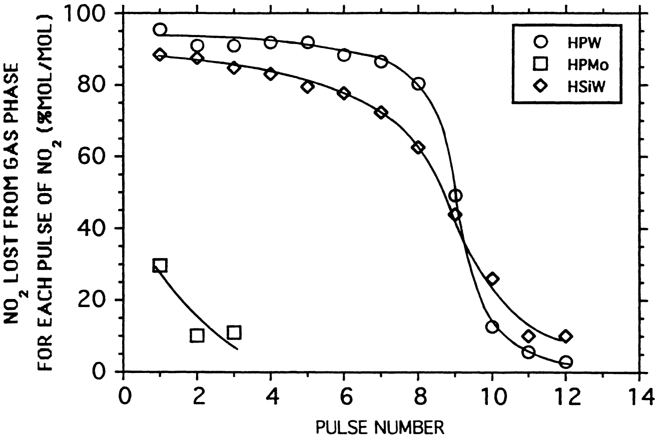

Fig. 3. Nitrogen dioxide removed from the gas phase in a sequence of pulses of NO_2 on HPW, HPMo and HSiW. Pretreatment and reactor temperature 150°C, mass of solid in reactor 0.075 g, and pulse size 17.0 µmol NO_2.

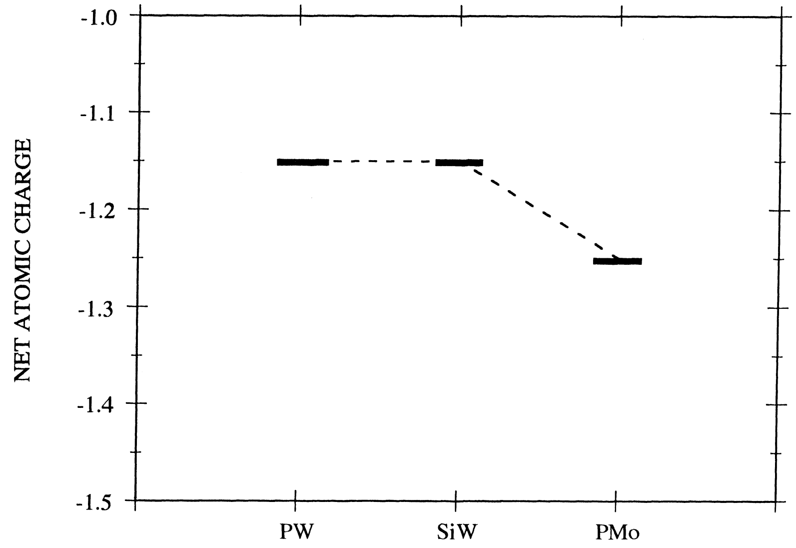

Fig. 4. Magnitude of the charge on the terminal oxygen atoms of the anions PW, SiW and PMo as obtained from EXH calculations.

is less than 10 m^2/g the protons are predominantly in the bulk of the solid and not on the surface. Thus NO_2 is apparently penetrating into the bulk, between the protons and anions. Previous photoacoustic FTIR studies with HPW exposed to aliquots of gaseous ammonia, pyridine and methanol at room temperature have provided direct evidence for the penetration of these molecules into the bulk of the structure [8–10].

Temperature-programmed desorption experiments on HPW before and after exposure to 1,2,4 and 7 pulses of NO_2 at 150°C show two major peaks, one at approximately 300°C resulting from the desorption of molecularly bound water [11] (Fig. 6). Another peak at 500–550°C has been attributed to the associative desorption of water resulting from the extraction of terminal oxygen by protons [11]. With HPW previously exposed to NO_2, the higher temperature water peak is overlapped with one resulting from the desorption of NO_2 and the lower temperature water peak diminishes in intensity, as a result of the reaction of

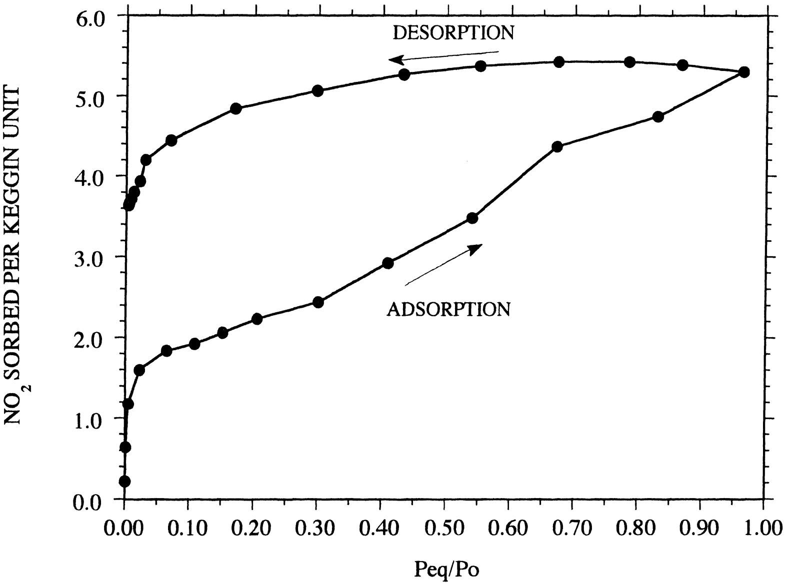

Fig. 5. Adsorption–desorption isotherm of NO_2 on HPW at 25°C. The sample of HPW (0.19 g or 66 μmol) was pretreated in helium at 150°C. The number of molecules of NO_2 is shown per anion of the acid.

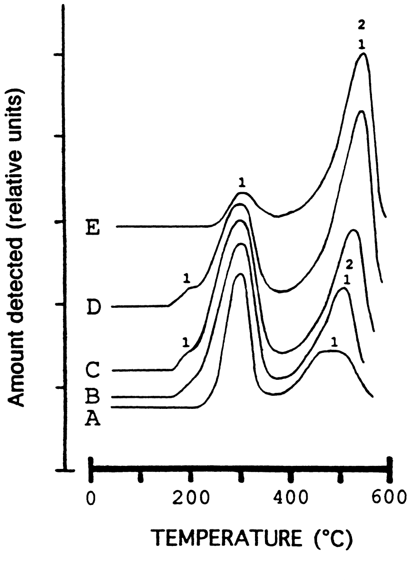

Fig. 6. Temperature-programmed desorption of HPW (A) pretreated in helium at 150°C for 1 h, (B) then exposed at 150°C to 1 pulse of NO_2, (C) 2 pulses of NO_2, (E) 7 pulses of NO_2. Helium flow rate 45.0 ml/min, ramp rate 60°C/min, mass of solid in reactor 0.165 g, and pulse size 17.0 μmol NO_2,. Legend: 1, H_2O; 2, NO_2

NO_2 with water to form nitric acid which desorbs from the solid. After exposure to NO_2 a new band at 2264 cm^{-1} appears in the infrared spectra of HPW and reaches a maximum after pretreatment of the sample at 150°C and saturation with NO_2 at the same temperature (not shown). This band shifted to 2215 cm^{-1} with $^{15}NO_2$ sorbed on HPW. The HMAS NMR spectra of HPW before and after exposure to NO_2 show that the protons are retained on the solid acid after contact with NO_2 while a small downfield displacement of the chemical shift is observed (not shown).

Temperature-programmed reaction experiments on the sodium salt of HPW (NaPW) showed little or no evidence for the sorption or reaction of NO_2 and no infrared absorption band attributable to NO_2 was observed with NaPW.

The protons are evidently playing a crucial role in the interaction of NO_2 with the heteropoly acids. Since the number of NO_2 molecules correlates with the total number of protons the process

$$H^+ + NO_2 \rightarrow [HNO_2]^+ \quad (1)$$

can be visualized. The NO_2 initially displaces (as HNO_3, Eq. (2) and/or 3) the molecular water

$$2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2 \quad (2)$$

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO \quad (3)$$

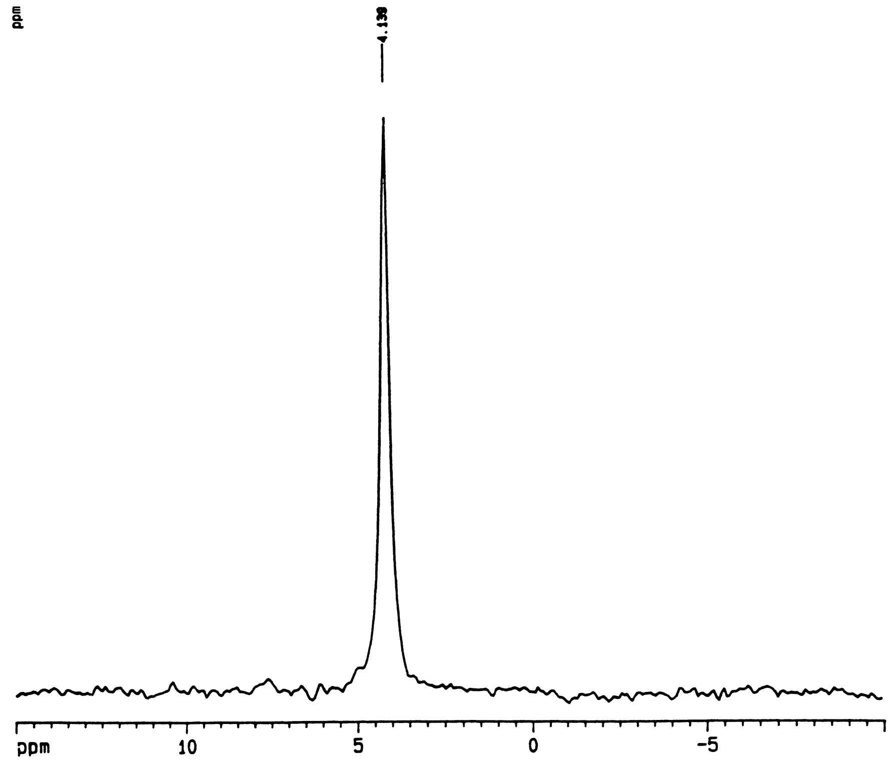

Fig. 7. $^{15}N\{^1H\}$ MAS-NMR of HPW exposed to $^{15}NO_2$ at 150°C.

contained within the solid acid and on consumption of the water the NO2 remains bound on the solid in protonated form. The strength of this binding is reflected in the deviation of the desorption from the adsorption branch in the NO_2 isotherm.

An infrared band ($\nu_2+\nu_3$) for gaseous NO_2 has been reported at 2355 cm^{-1} while the ν_3 (antisymmetric) band in NO_2^+ with inorganic salts has been found in the range 2360–2392 cm^{-1} [12]. The measured isotopic shift found in the present work, 0.978, is in good agreement with that reported in the literature for NO_2 (0.9785) [12].

Proton-decoupling NMR spectra with HPW exposed to $^{15}NO_2$ show one peak at 4.14 ppm confirming that each proton is associated with one NO_2, the latter existing in a monomeric, nonlinear and charged form (Fig. 7). Heteroatom–proton coupling spectra also show a single peak, indicating that the proton is associated with the oxygen atom (Fig. 8).

The proton in HPW may be substituted by the ammonium ion by exposing HPW to gaseous ammonia or by precipitation of the salt from aqueous solution. The latter method produces a high surface area, microporous solid, typically 150–200 m^2/g [7,13].

In contrast to the results with HPW, when NH_4PW is exposed to NO_2, N_2, NO and N_2O are observed (Fig. 9). With increasing temperature the selectivity to N_2 increases while that to NO decreases until at a temperature of approximately 175°C little or no NO is formed and the reduction to N_2 is optimal. At approximately 150°C, N_2O begins to appear but its selectivity remains relatively small until 200°C at which a more substantial increase is seen.

In view of the absence of N_2 in the products seen from the exposure of the parent acid (HPW) to NO_2 the principal benefit from the use of the ammonium salt of HPW appears to result from the presence of the reductant. Such advantages would be lost or at best reduced if the ammonia is lost from the solid at appropriate temperatures for NO_2 reduction. Temperature-programmed desorption experiments with NH_4PW show that the ammonia does not begin to

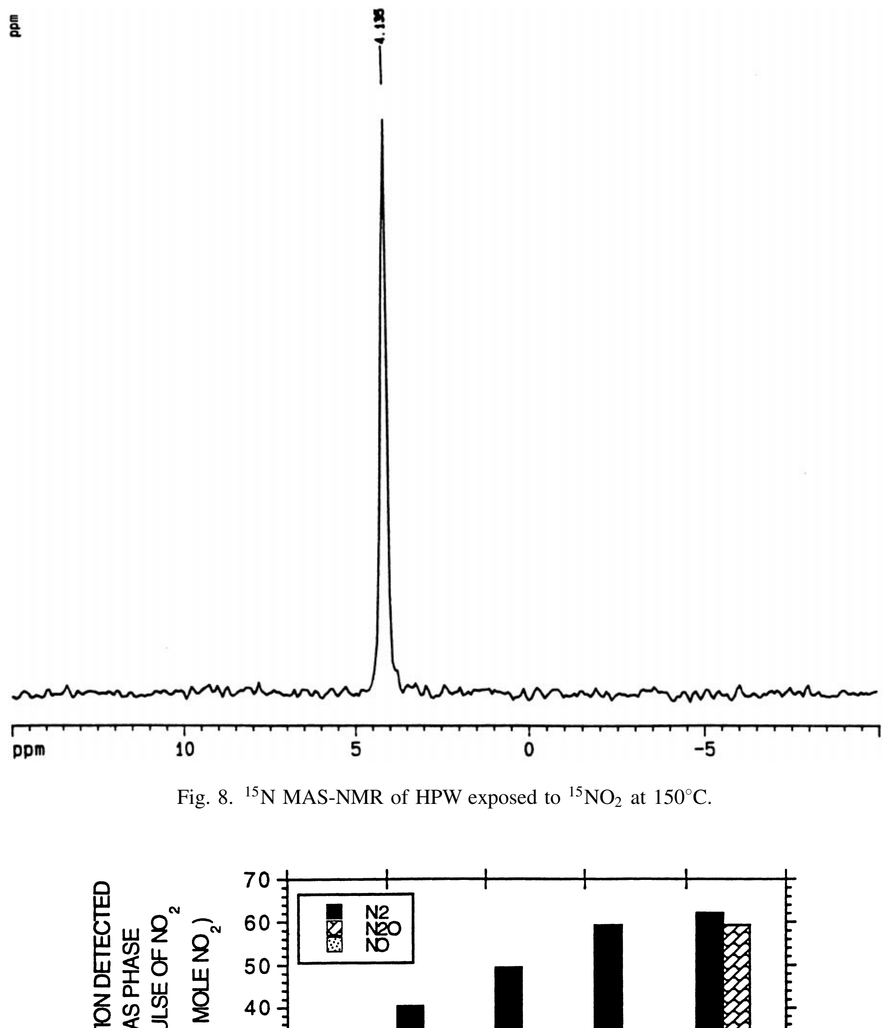

Fig. 8. ^{15}N MAS-NMR of HPW exposed to $^{15}NO_2$ at 150°C.

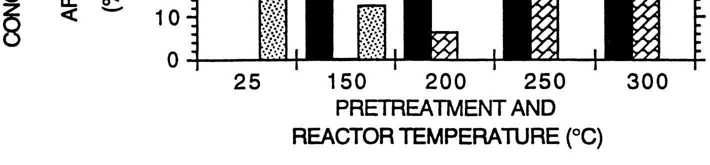

Fig. 9. Quantity of N_2, N_2O and NO found in the effluent of a reactor containing ammonium 12-tungstophosphate after injection of 1 pulse of NO_2 at different temperatures. Mass of solid in reactor 0.075 g, pulse size 17 μmol NO_2, and helium flow 15 ml/min.

desorb until 400°C, well above the optimum reduction temperature, and only small quantities are lost up to 500°C (Fig. 10 A and D). After saturation of NH_4PW with NO and NO_2 at 30°C (Fig. 10 B and C, respectively), the peak at 175°C due to desorbed water has increased markedly, particularly after the introduction of NO_2, indicative of the formation of water during the reduction process. NH_4PW, after pretreatment at 150°C and exposure to NO at the same temperature, displays an enlarged water peak at 175°C in addition

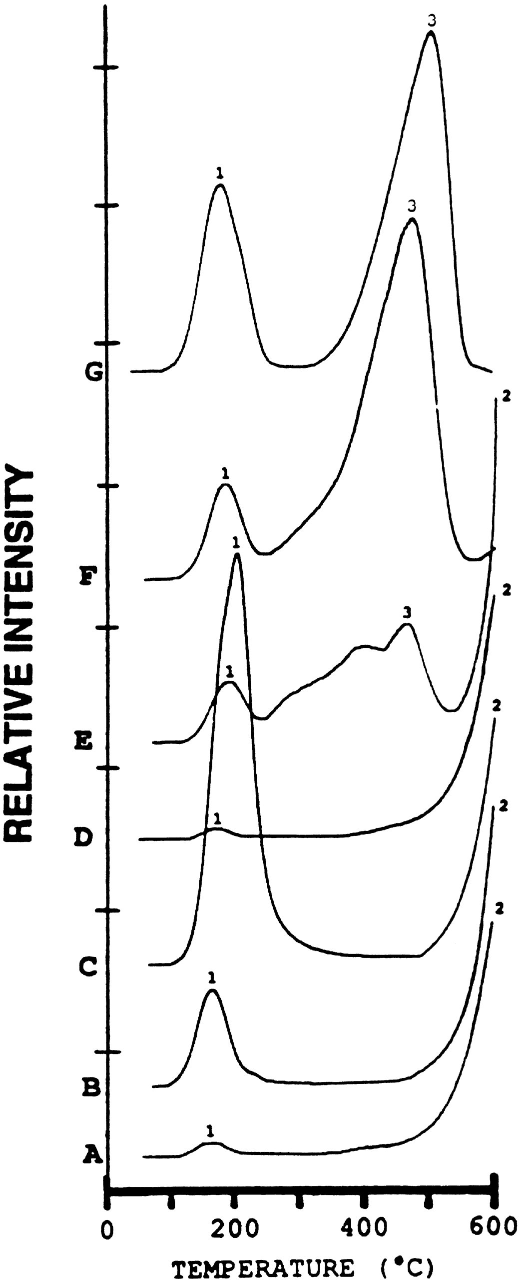

Fig. 10. TPD of NH_4PW (A) pretreated in helium at 30°C for 1 h; then (B) saturated with NO at 30°C for 1 h; (C) same pretreatment as in (A) but saturated with NO_2 at 30°C for 1 h; (D) NH_4PW pretreated at 150°C for 1 h; then (E) saturated with NO at 150°C for 1 h; (F) NH_4PW pretreated at 300°C for 1 h, then saturated with NO at 300°C for 1 h; (G) same pretreatment as in (D) but saturated with NO_2 at 150°C for 1 h. Mass of solid in reactor=0.075 g (38.8 μmol). Pulse size=17 μmol of NO_2. Helium flow rate=45 ml/min. Temperature rate=60°C/min. Legend: 1, H_2O; 2, NH_3; 3, NO_2; 4, N_2O.

to several overlapping peaks at temperatures ranging from 300–500°C (Fig. 10E). In contrast NH_4PW pretreated at 300°C and saturated with NO at the same temperature shows a large peak due to the desorption of NO_2 whose maximum occurs at approximately 475°C (Fig. 10F), while after saturation with NO_2 the latter peak is similar in magnitude but the water peak at 200°C is significantly enlarged (Fig. 10E). The NO_2 which desorbs after saturation with NO probably results from the extraction of anionic oxygen atoms by the NO. It should be noted that any N_2 produced will desorb immediately.

The infrared spectra of NH_4PW shows, as expected, the characteristic infrared bands of the Keggin anion in the 800–1200 cm^{-1} region, as well as bands at 3200 and 142 cm^{-1} attributed to the ammonium ion (Fig. 11A). After exposure to NO_2 at 150°C the former and latter bands remain although somewhat diminished in intensity (Fig. 11B) and, in addition, a small band appears at 2263 cm^{-1}, which is intensified in the spectra of the sample pretreated and exposed to NO_2 at 300°C.

The expected loss of the bound NH_3 can also be seen from ^1H NMR spectra (Fig. 12). For comparison the spectra for HPW before and after saturation with NO_2 are shown in Fig. 12A (1 and 2). Exposure of HPW to NO_2 at 150°C produces an increase in the chemical shift but little or no diminution in the intensity of the protium peaks, indicating that the loss of NO_2, bound as HNO_2^+, does not result in the loss of protons. In contrast the spectra for stoichiometric NH_4PW contains four peaks, the most prominent appearing at 4.85 ppm but after saturation with NO_2 at 300°C only one peak (7.89 ppm) remains, similar to that found with HPW (Fig. 12B, 1 and 2). The oxidation of NH_3 by NO_2 evidently restores the parent acid, HPW.

The product composition from NH_4PW is summarized for three pulses of NO_2 in Table 1. Although not shown, with continued introduction of NO_2, as seen from both the infrared and NMR experiments the NH_3 bound within NH_4PW is depleted and the conversion concomitantly decreases.

As evident from the TPD experiments NO is not reduced at 150°C when injected on NH_4PW. However, after pretreatment of NH_4PW with NO_2 or nitric acid the reduction of NO is facilitated (Table 2).

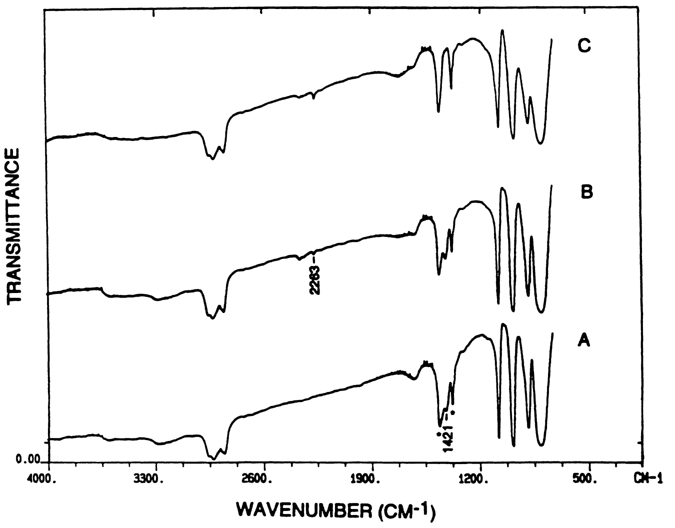

Fig. 11. Infrared spectra of (A) NH_4PW at 25°C, then (B) pretreated and exposed to 20 pulses of NO_2 at 150°C. Same salt as in (A) but (C) pretreated and exposed to 14 pulses of NO_2 at 300°C. *=NUJOL bands.

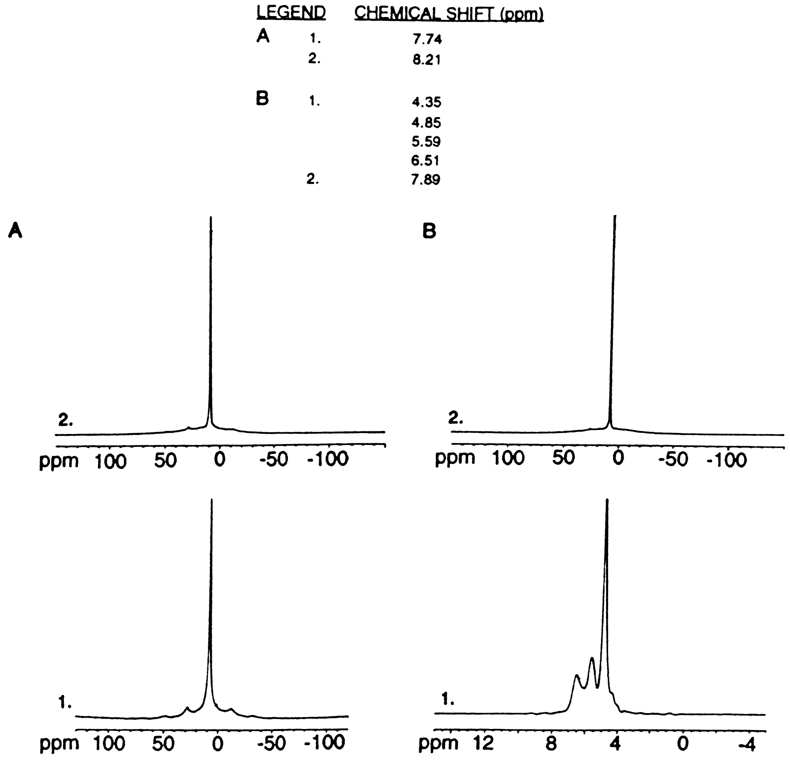

Fig. 12. ^1H MAS NMR of (A): (1) HPW pretreated at 150°C; (2) HPW pretreated and saturated with NO_2 at 150°C; (B): (1) NH_4PW pretreated at 300°C; (2) NH_4PW pretreated and saturated with NO_2 at 300°C.

Table 1
Composition of the Effluent from NO_2 on NH_4PW

Pulse[a] number	N_2	Product composition[b,c,d]	
		NO	NO_2
1	58.0	0.4	0.0
2	56.7	0.0	0.0
3	56.6	0.0	0.0

[a] 1 pulse=17 μmol of NO_2.
[b] 0.500 g NH_4PW.
[c] Reaction temperature 150°C.
[d] Moles N/Moles NO_2 (×100).

Table 2
Reduction of NO on NH_4PW at 150°C

Pretreatment[a]	NO pulse[b] number	N_2[c]	NO[c]
17 μmol NO_2[d]	1	98.4	39.8
	2	9.5	91.8
2 μl HNO_3[e]	1	130.5	0.0
	2	115.8	7.6
	3	57.0	54.1
	4	8.4	87.0

[a] Injection of HNO_3 and NO_2 directly on the NH_4PW contained in the reactor held at 150°C prior to the injection of NO pulses.
[b] 1 pulse=10 μmol of NO.
[c] Mole of nitrogen atoms per mole of NO injected (×100).
[d] 74 mg NH_4PW.
[e] 101 mg NH_4PW.

NH_4PW can be regenerated from its parent acid by precipitation with any ammonium salt from aqueous solution at room temperature or by gas phase regeneration with ammonia at 150°C. Regeneration restores the original reductive properties of the solid and can be repeated indefinitely.

It is clear that NO_2 (and probably NO) are interacting with NH_3 held on the solid as the ammonium ion. Since as noted earlier in this report NO_2 enters the bulk of HPW to interact with both the interior and the surface protons it is expected that a similar entry occurs with NO_2 and NH_4PW. Indeed, the results of the various spectroscopic experiments provide evidence for this. Presumably, however, the interaction between NO_2 and NH_3 is additionally facilitated by the presence of the porous structure in NH_4PW and its consequent high surface area.

Although the participation of the protons in NH_4PW in the reduction process is not fully understood it is apparent that their presence is required to bind NH_3 within the solid. Thus the reduction process is one in which the reactants are effectively NO_2 and NH_4^+. In the absence of the relatively stable binding of NH_3 in NH_4PW the process would become that of two gas phase molecules reacting, rather than a gas phase species interacting with a solid.

Acknowledgements

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