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The interaction of nitrogen oxides with metal–oxygen cluster compounds (heteropoly oxometalates)

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Abstract

Nitrogen dioxide is sorbed by the solid heteropoly acids, the first sorbates producing HNO_3 while those subsequently taken up remain strongly bound on the acid, up to three NO_2 per heteropoly anion. The sorption of NO_2 is shown to be dependent on the elemental composition of the anions of the solid acids and hence on the acid strengths of these materials. The sorbed NO_2 associates with both the surface and bulk protons to form HNO_2^+ thus demonstrating that NO_2 is capable of penetrating into the crystallographic structure of the solid acid. Prior sorption of NO_2 facilitates the take-up of NO which forms N_2O_3 . 12-tungstophosphoric acid (HPW) supported on silica produces quantitatively different but qualitatively similar results. The microporous ammonium salt of HPW produces markedly different results when exposed to NO_2 with the predominant product being N_2 evidently resulting from the ammonium cation functioning as a source of the reductant ammonia.

Keywords: Metal–oxygen cluster compounds; Heteropoly oxometalates; Nitrogen oxides

1. Introduction

Nitrogen oxides (NO_x) are ubiquitous noxious vapors which have been shown to be responsible for damage to human health either directly through inhalation or indirectly through the formation and deposition of inorganic nitrogen compounds on solids, forests and drainage waters [1–11]. In spite of efforts to reduce the discharge of these gases, the production of nitrogen oxides is projected to increase during the coming decade [12].

The approaches to the problem are twofold: control the quantities of nitrogen oxides pro-

duced or, once formed, trap and convert these to benign alternatives [1]. NO_x may be formed thermally from the oxidation of N_2 contained in the combustion air or from the oxidation of chemically bound nitrogen in fuel. To reduce quantities of NO_x produced in these reactions the combustion process can be modified by use of low- NO_x burners, gas recirculation and/or staged combustion [13–15]. However, to meet current and projected emission standards for NO_x , post combustion removal techniques must frequently be introduced.

Selective catalytic reduction (SCR) is commonly employed for the removal of NO_x from gaseous effluents [1,16–20]. Although vanadia/titania is the most widely employed

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catalyst for this purpose research has recently focussed on zeolitic catalysts, in particular copper-impregnated ZSM-5 (see, for example, Ref. [21]). Unfortunately, however, the activities found with the latter are not yet sufficiently high to warrant commercial implementation [22]. Nevertheless the many reports of studies of these catalysts have provided valuable information on NO_x , its properties and conversion mechanisms, as well as the source of the activity of the zeolitic solids in the related processes.

A portion of the work in this laboratory has been concerned with metal–oxygen cluster compounds (MOCC) (also known as heteropoly oxometalates). Among other projects, the application of photoacoustic (PAS) FTIR to these solids has provided direct evidence for the ability of polar molecules such as ammonia [23], pyridine [24] and methanol [25] to penetrate into the bulk structures, where interaction with the protons takes place. Thus PAS FTIR evidence is found for the formation of the ammonium and pyridinium ions and for a one-to-one association between a given polar species and the protons. Methanol was similarly shown to interact with both the surface and bulk protons, forming its protonated counterpart which was shown to be the first step in the conversion of methanol to hydrocarbons on the MOCC [26].

Studies of the physisorption and chemisorption of molecules on solids are well known to provide considerable information not only on the nature of the interaction of these molecules with the surface but also to elucidate the properties of the sorbent itself. Thus the present work in which the interactions of NO_x with the MOCC are examined provide additional fundamental information on the heteropoly oxometalates and their surface and bulk properties, the dependence of these properties on the composition of the solids and the sites which play the primary role in these interactions. In addition, however, the results presented in the report demonstrate the potential for applicability of these solids to systems of environmental concern. The present report summarizes some of the results of these

studies with NO_x as well as providing information on results not yet published.

2. Experimental

2.1. Materials

12-tungstophosphoric, 12-molybdophosphoric, and 12-tungstosilicic acids (abbreviated as HPW, HPMo, and HSiW, respectively) were obtained from BDH chemicals and used as received. Nitric oxide (98.9%) and dinitrogen tetroxide (99%) were obtained from Linde and Matheson, respectively. Nitric oxide was further purified by passing through a trap held at dry ice–acetone temperature. Nitrogen dioxide was used as received.

Samples of stoichiometric and nonstoichiometric ammonium 12-tungstophosphate were prepared from aqueous solutions of ammonium carbonate and of 12-tungstophosphoric acid. The nonstoichiometric samples contained 15% excess and 15% deficit of the ammonium ion respectively. The salts were first dried on a hot water bath, followed by 24 h under vacuum at room temperature. A separate sample of the stoichiometric ammonium salt was further purified by multiple washing with distilled water.

12-tungstophosphoric acid supported on silica (Cabot Corp) was prepared by impregnation of particles of the latter of 80 mesh or smaller with aqueous solutions of the former, followed by evaporation on a hot water bath and evacuation at room temperature.

All catalyst samples were preheated in the reactor with a flow of helium at the desired temperature and for an appropriate period of time.

2.2. Procedures

A reactor constructed from 4 mm I.D. quartz tubing was connected to a Shimadzu GC-9A gas chromatograph equipped with a 4 mm \times 30 cm MS 5A 60/80 mesh column for analysis of O_2 ,

N_2 and NO. A cold trap (dry ice–acetone) placed between the outlet of the reactor and the gas chromatograph was employed to trap NO_2 which is subsequently measured volumetrically. N_2O was analyzed with the use of a 4 mm by 2.5 m Porapak Q column preconditioned at 200°C for 3 h and held at 40°C during the analysis. The reactor was charged with an aliquot of 0.050 g or 0.075 g of catalyst and heated for 15 min at the desired reaction temperature in a 15 ml/min flow of helium. The reaction system was equipped with suitable flow and temperature measuring devices as well as gas sampling valves. The desired pulse (16.5 μmol NO_2 or 10 μmol NO; 24°C and 1 atm) was injected into a 15 ml/min flow of helium with a Whitey gas sampling valve. Checks of the initial calibrations of O_2 , N_2 , NO, NO_2 and N_2O were performed periodically.

For the analysis of total nitrogen on the catalyst after saturation with NO_x , separate reaction experiments were carried out with a modified reactor system. The effluent from the reactor was passed through a 1 m coil kept at 700°C, subsequently through copper wool at 550°C and finally introduced to the GC. All connecting lines were maintained at 130°C. Under these conditions nitric acid and the oxides of nitrogen are completely decomposed into NO and N_2 . As before, the desired number of gas pulses (16.5 μmol NO_2 or 10 μmol NO; 24°C and 1 atm) were introduced into a 15 ml/min flow of helium with a gas sampling valve until the catalyst was saturated. After the desired number of pulses, the catalyst was flash heated in order to desorb any nitrogen-containing material and the products of decomposition were analyzed chromatographically.

For temperature-programmed desorption (TPD) the chromatographic column was replaced by an empty column and the effluent was passed directly over a TCD. The NO_x was, as before, introduced by use of a gas sampling valve. The temperature of the reactor was ramped linearly with a temperature programmer (Tempstar II, Thermo Electric Instruments, NJ).

In some TPD experiments the effluent was passed to a GC-MS system (HP5890A gas chromatograph, HP5970 MSD).

Surface areas were calculated, using the BET equation, from nitrogen adsorption isotherms obtained at 77 K. Infrared spectra were obtained with a BOMEM MB-100 Michelson infrared spectrophotometer. The samples were prepared with NUJOL mulling agent and placed between AgBr windows. Powder X-ray diffraction patterns were obtained from a Siemens diffractometer (model D500) at 40 kV and 30 mA with CuK radiation. The samples were incorporated in silicone grease. ^1H MAS NMR results were obtained with a Bruker AMX spectrometer. The rotation frequency of the samples was set at 10.0 kHz. Each sample was pretreated and packed in a sapphire rotor. All spectra recorded were referenced to TMS (tetramethylsilane).

3. Results

3.1. The interaction of NO_x with metal–oxygen cluster compounds

3.1.1. 12-tungstophosphoric, 12-tungstosilicic and 12-molybdophosphoric acids

Although all three of the solid acids sorb NO_2 at 150°C, the quantities of NO_2 taken up by 12-tungstophosphoric and 12-tungstosilicic acids exceed those of 12-molybdophosphoric acid (abbreviated as HPW, HSiW and HPMo, respectively) [27–29] (Fig. 1). With the tungsten-containing acids, the quantities of NO_2 removed from the gas phase fall between 80–100% for the first several pulses, but after 8 pulses saturation is evidently occurring.

The NO_2 removed from the gas phase is converted to nitric acid by reaction with the water hydrogen-bonded within the solid acids (Fig. 2). As expected the quantities of HNO_3 increase with increasing amounts of NO_2 , pass through a maximum and decrease as the water contained within the solid becomes depleted. On consumption of the water additional NO_2

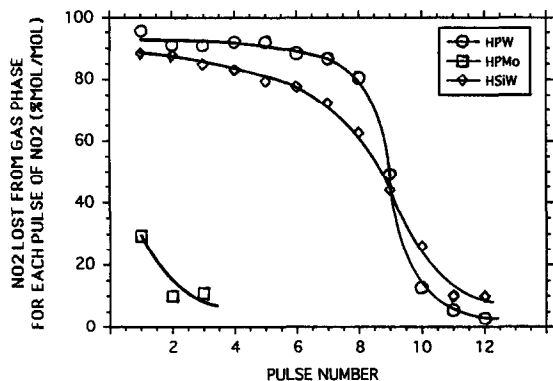


Fig. 1. Nitrogen dioxide (NO_2) removed from the gas phase by HPW, HPMo and HSiW in a sequence of pulses of NO_2 . Pretreatment and reactor temperature: 150°C ; mass of solid: 0.075 g ; NO_2 pulse: $17.0\ \mu\text{mol}$.

remains held within the solid. With HPW at 150°C a maximum of $2.9\ \text{NO}_2$ per anion is retained on the solid suggesting that each NO_2 is interacting with one proton.

In contrast with the observations with NO_2 , only very small quantities of NO are taken up by HPW at 150°C (Fig. 3). However if NO_2 is sorbed on HPW prior to exposure to NO the quantity of the latter which is sorbed increases to a maximum, which corresponds to equimolar amounts of the two oxides, and decreases.

The infrared spectra of HPW show that the structure of the anion remains intact after exposure to NO_2 (Fig. 4). However a new band at

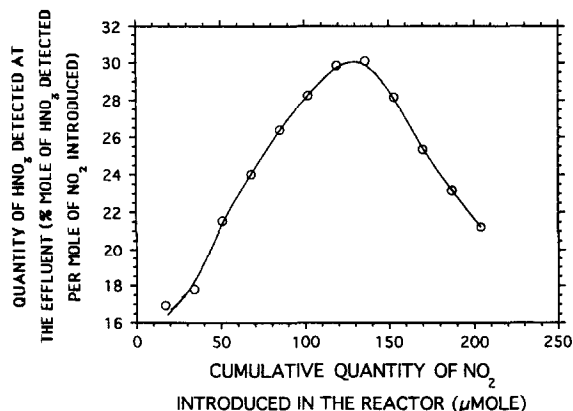


Fig. 2. Quantity of nitric acid (HNO_3) produced from pulses of NO_2 and detected in the effluent from HPW. Reactor temperature: 150°C ; mass of solid: 0.075 g ; NO_2 pulse: $17\ \mu\text{mol}$.

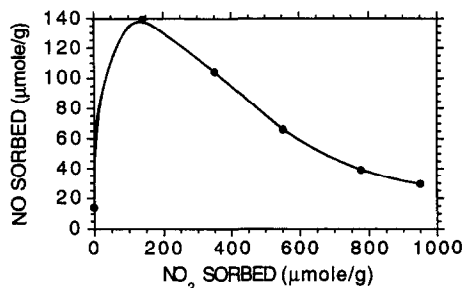


Fig. 3. Nitric oxide (NO) sorbed on HPW containing quantities of previously sorbed nitrogen dioxide. Temperature: 150°C .

2264 cm^{-1} appears in the latter spectrum (Fig. 4B). This band is tentatively attributed to perturbed NO_2^- and in particular to HNO_2^+ . Consistent with the expected consumption of water in the formation of HNO_3 , the two bands at 1708 and 3200 cm^{-1} due to the hydronium ion (H_3O^+) and water [23], respectively, decrease on exposure of HPW to NO_2 . On exposure of

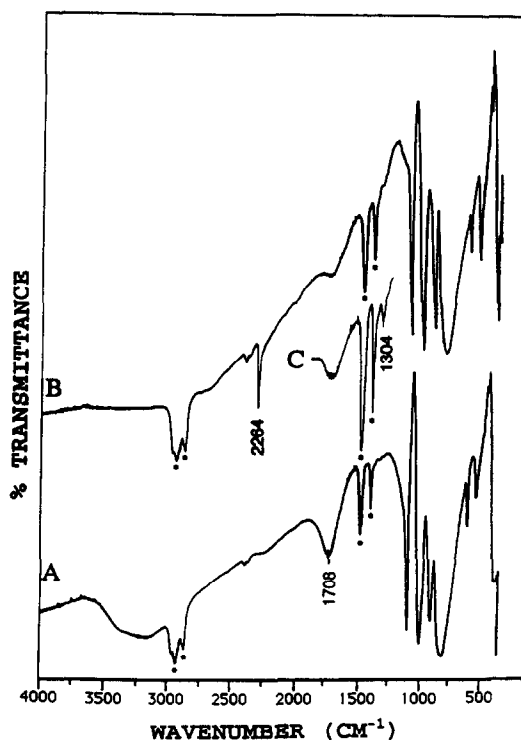


Fig. 4. Infrared spectra of HPW, before (A), after (B) exposure to NO_2 and after exposure to NO and NO_2 (C). Peaks due to the presence of nujol are marked with asterisks.

HPW to NO_2 and NO a new band assigned to N_2O_3 [30,31] appears at 1304 cm^{-1} (Fig. 4C).

The ^1H MAS NMR spectra of HPW before and after exposure to NO_2 show small changes in the chemical shift, which may result from the interaction between the proton and NO_2 (Fig. 5). However, the intensities of the peaks are similar indicating that the quantity of protons is relatively undiminished on exposure of HPW to NO_2 at 150°C .

3.1.2. 12-tungstophosphoric acid supported on silica

The effect on the interaction with NO_x of supporting HPW on a high surface area solid has also been studied [32]. Although the support, SiO_2 , itself has activity for the NO_2 conversion process the quantity of NO_2 removed at 150°C from the gas phase increased with the loading of HPW (Fig. 6), reaching a maximum for the pure solid acid. In contrast, the selectivity to N_2 decreases with increase in loading, while that to NO passes through a maximum at approximately 23% HPW/ SiO_2 . It should be noted that studies of other processes on the supported MOCC have found that conversions and/or selectivities pass through maxima as the loading increases, usually at $20(\pm 5)\%$, which has been shown to correspond, at least approxi-

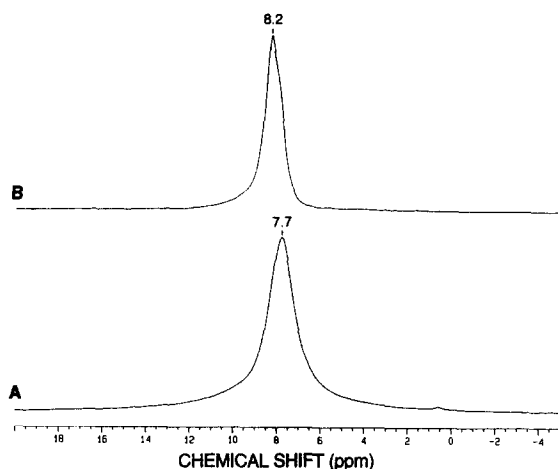


Fig. 5. ^1H MAS NMR of HPW, before (A), and after (B) exposure to NO_2 .

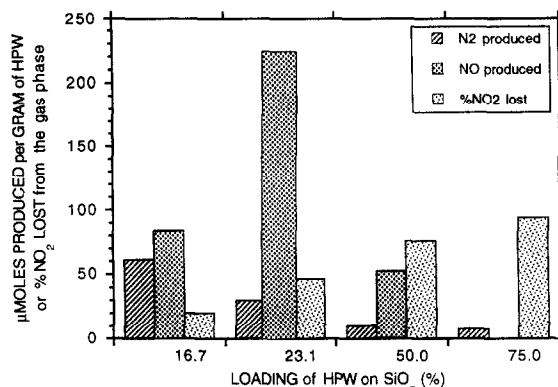


Fig. 6. Removal of NO_2 from gas phase and production of N_2 and NO for various loadings of HPW on SiO_2 . Temperature: 150°C .

mately, to a monolayer of the supported solid acid [33–38]. The increase in the relative amounts of NO_2 removed from the gas phase as the loading of HPW on SiO_2 increases can be interpreted as indicative of the ability of NO_2 to penetrate into the bulk structure of the solid acid, while the decrease in the selectivity to N_2 is consistent with the inability of the unsupported HPW to produce N_2 . In contrast to the observations with pure HPW, no HNO_3 is produced on HPW/ SiO_2 , at least at relatively low loadings, but this is believed to result from the relatively small quantities of water contained on the supported catalysts after the pretreatment.

Treatment of HPW/ SiO_2 with NH_3 prior to exposure to NO_2 produces substantial differences in the behavior of the solid (Fig. 7). At 150°C substantial quantities of N_2 are produced along with smaller amounts of NO on the HPW/ SiO_2 with loading of 10%. With increase in the loading the selectivity to N_2 decreases until at 75% HPW/ SiO_2 that of N_2 and NO are approximately equal.

3.1.3. Ammonium 12-tungstophosphate

Although the parent acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) has a low surface area and no porous structure the ammonium salt (NH_4PW) can be prepared with high surface area and a microporous structure [39–45]. Earlier work in which both stoichiometric and nonstoichiometric NH_4PW have been

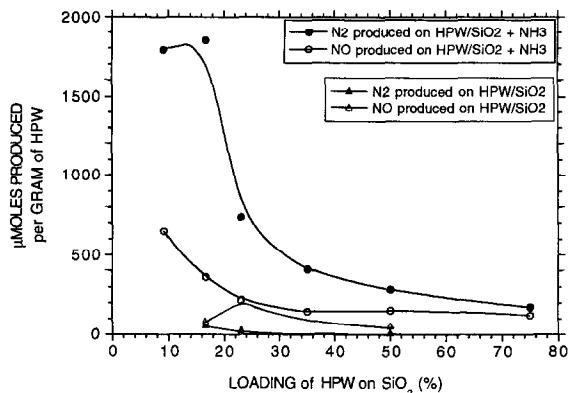


Fig. 7. N_2 , NO and N_2O produced on HPW/ SiO_2 after exposure to one pulse of NO_2 ; N_2 , NO and N_2O produced on fresh aliquots of HPW/ SiO_2 after saturation with NH_3 , followed by exposure to one pulse of NO_2 . Mass of solid: 0.075 g; NO_2 pulse: 17.0 μ mol. Temperature: 150°C.

prepared from aqueous solutions of ammonium carbonate and of HPW has shown that both the surface areas and pore volumes are dependent on the relative quantities of the preparative reagents [45]. However it should be emphasized that photoacoustic (PAS) FTIR studies have shown that NH_4PW synthesized from stoichiometric quantities of the preparative reagents contains significant amounts of residual protons [23].

On exposure of stoichiometric NH_4PW to NO_2 at ambient temperatures NO is produced [46] (Fig. 8). However as the temperature is increased the selectivity to NO decreases and at 150°C the selectivity to N_2 is approximately 40%. As the temperature is further increased

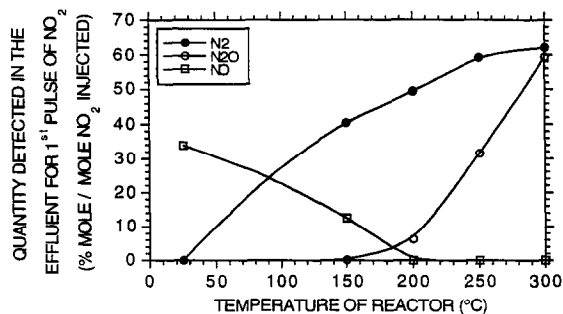


Fig. 8. Concentrations of N_2 , N_2O and NO in the effluent after exposure of NH_4PW to one pulse of NO_2 . Mass of solid: 0.075 g; helium flow: 15 ml/min.

N_2O is seen at 200°C, NO has vanished from the product at 200°C and the selectivity to N_2 continues to increase. At 300°C approximately equal selectivities to N_2 and N_2O are found.

In contrast to the observations with HPW the dominant product with NH_4PW , at least at temperatures between 150 and 250°C, is N_2 . Although NH_4PW differs morphologically from HPW it is expected that the chemical differences, in particular the presence of the ammonium ion, are responsible for the markedly different results on exposure to NO_2 . However, the reduction of NO_2 by NH_3 may occur entirely in the gas phase as a result of desorption of NH_3 from the catalyst or, alternatively, the conversion of NO_2 may result from the interaction of NO_2 with the solid while the NH_3 is retained. Since temperature-programmed desorption experiments show that temperatures of 600°C or higher are required to desorb NH_3 from NH_4PW it is evident that NO_2 interacts with the ammo-

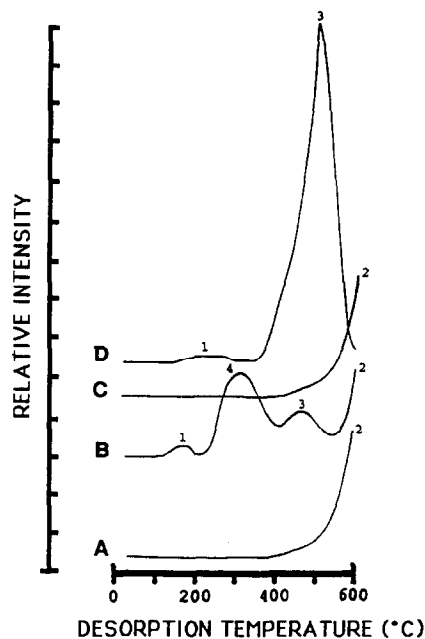


Fig. 9. Temperature-programmed desorption of (A) 0.075 g of NH_4PW pretreated at 150°C; (B) 0.075 g of NH_4PW pretreated as in (A) but exposed to 25 pulses of NO_2 at 150°C; (C) 0.075 g of NH_4PW pretreated at 300°C; (D) 0.075 g of NH_4PW pretreated as in (C) but exposed to 25 pulses of NO_2 at 300°C. Heating rate = 60°C/min, flow rate = 45 ml/min. LEGEND: 1 = H_2O , 2 = NH_3 , 3 = NO_2 , 4 = N_2O .

mium salt and the conversion takes place while NH_3 remains as the ammonium cation (Fig. 9A).

Further temperature-programmed desorption studies show that after exposure to NO_2 at 150°C , with further increase in temperature water is desorbed from NH_4PW up to approximately 200°C , N_2O at $200\text{--}400^\circ\text{C}$, NO_2 at $400\text{--}550^\circ\text{C}$ and NH_3 above 550°C (Fig. 9B). After pretreatment of NH_4PW at 300°C and exposure to NO_2 at the same temperature a small broad water peak is seen at 200°C with a considerable desorption of NO_2 at 500°C (Fig. 9D).

Infrared spectra of NH_4PW show the characteristic set of 5–6 bands between $500\text{--}1200\text{ cm}^{-1}$ which is attributed to the presence of the anion with Keggin structure (Fig. 10). The band at 1421 cm^{-1} characteristic of the ammonium ion is, as expected, also present. On exposure of NH_4PW to NO_2 at 300°C these bands are retained, indicating that the structure of the anion is not altered by NO_2 . In addition a small band at 2264 cm^{-1} , which intensifies on further addition of NO_2 , is also seen (Fig. 10C). As noted earlier in this report this band is also observed on the parent acid HPW after saturation with NO_2 and is attributed to HNO_2^+ [30]. Meanwhile, as the band at 2264 cm^{-1} increases, that

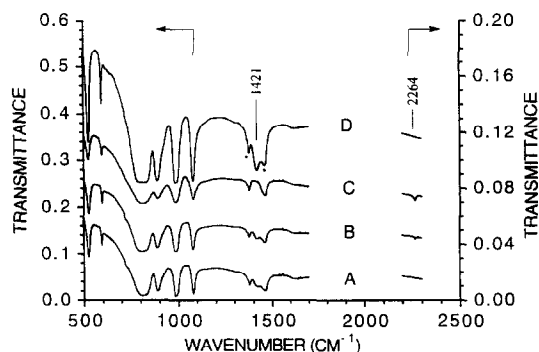
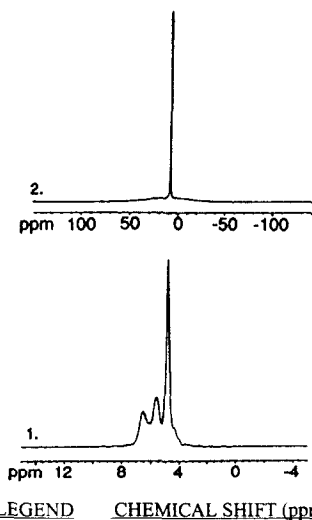


Fig. 10. Infrared spectra of (A) NH_4PW at 25°C , then (B) pretreated and exposed to 20 pulses of NO_2 ($16.5\ \mu\text{moles/pulse}$) at 150°C ; (C) NH_4PW pretreated and exposed to 14 pulses of NO_2 ($16.5\ \mu\text{moles/pulse}$) at 300°C , (D) NH_4PW pretreated and saturated with NO_2 at 300°C , and then saturated with NH_3 at 300°C . Peaks due to nujol are marked with asterisks.



LEGEND	CHEMICAL SHIFT (ppm)
1.	4.4
	4.9
	5.6
	6.5
2.	7.9

Fig. 11. ^1H MAS NMR of 1. NH_4PW pretreated at 300°C , 2. NH_4PW pretreated and saturated with NO_2 at 300°C .

at 1421 cm^{-1} diminishes, as NH_4^+ is converted to H^+ by depletion of NH_3 . It is to be noted, however, that during these processes the structure of the anion is retained. Finally on exposure of the depleted catalyst to NH_3 , the band at 1421 cm^{-1} reappears while that at 2264 cm^{-1} vanishes.

^1H MAS NMR of NH_4PW pretreated at 300°C contains four peaks, the most prominent at 4.85 ppm but, after saturation with NO_2 at 300°C , only one peak remains, appearing at 7.89 ppm , a chemical shift similar to that found with HPW (Fig. 11).

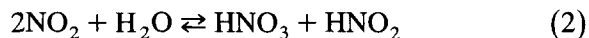
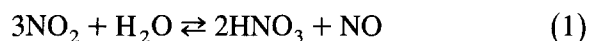
4. Discussion

The disparate observations on exposure of the three heteropoly acids, 12-tungstophosphoric, 12-molybdophosphoric and 12-tungstosilicic to NO_2 suggest a dependence of their sorption capacities on the elemental compositions of the heteropoly anions but, more importantly, a relationship to the proton mobilities and hence acidic strengths.

Extended Hückel calculations have predicted that the magnitude of the charges on the terminal oxygen atoms of the tungsten-containing acids is smaller than that on those anions containing molybdenum and hence the strength of the Coulombic attractive interactions between these oxygen atoms and the protons is smaller with the former as compared with the latter [39,47]. Thus the protons in the tungsten-containing acids are less tightly bound and the acidic strength is higher than that in the acids whose anions contain molybdenum in the peripheral metal positions. Calorimetric measurements [48,49], titrations with Hammett indicators [50] and catalytic studies [51–56] have provided additional evidence for the differences in acidic strength of the tungsten- and molybdenum-containing heteropoly acids. Thus these results imply that the ability of the acids to sorb NO_2 is dependent upon the presence of protons and the acidic strengths of the solid acids.

Since substitution of a cation such as that of sodium virtually eliminates the sorption of NO_2 it is evident that the presence of protons is a necessary condition for the takeup of NO_2 . The observation that up to three NO_2 may be held on HPW and, from the TPD experiments, relatively tightly, demonstrates that NO_2 molecules are capable of penetrating into the bulk structure of the solid acid. Thus no direct dependence of the process on surface area is extant.

The first molecules of NO_2 evidently form HNO_3 which is readily desorbed. Since the water contained within the solid acid is depleted as this process continues, the HNO_3 must be formed from the interaction of NO_2 with H_2O through either or both of the stoichiometries,



Although an unambiguous declaration of the stoichiometry is not possible at this time, since NO is detected Eq. (1) appears to be more probable, although Eq. (2) cannot be excluded.

On depletion of the water contained within the solid acid, up to three molecules of NO_2 per

heteropoly anion remain sorbed, apparently one for each proton. Tentatively this can be interpreted through the formation of HNO_2^+ as



The band at 2264 cm^{-1} in the infrared spectrum of HPW containing sorbed NO_2 can be attributed to an electronically perturbed NO_2 such as could arise from the association of H^+ and NO_2 . Although infrared spectra for gaseous HNO_2^+ are not available in the literature, the asymmetric stretch for the nitronium ion (NO_2^+), reported as 2375 cm^{-1} [30], would be expected to be larger than that for HNO_2^+ .

The inability of NO to penetrate into the bulk structure of HPW contrasts sharply with the observations for NO_2 . The source of such differences is, at this time, unclear. However as noted earlier in this report the observation of a band at 1304 cm^{-1} in the infrared spectra of HPW exposed to NO_2 followed by NO provides evidence for the formation of N_2O_3 [30,31].



Although TPD experiments show that temperatures as high as 550°C are required in order to desorb NO_2 from HPW previously saturated with NO_2 , the sorbed NO_2 can be largely removed by exposure to water vapor at 150°C and consequently, regeneration of the catalyst is possible.

The studies of the effect of supporting HPW on SiO_2 provide a number of interesting results. Earlier work on the silica-supported heteropoly acids with various techniques such as MAS NMR and XPS as well as catalytic studies has shown that a strong interaction arises between the acid and the silica support and has provided information on the dependence of the dispersion on the loading of the catalytic solid. The first report of the application of ^{31}P NMR to such systems appeared in 1990 [57]. In that work ^{31}P NMR spectra of 23 wt% HPMo/SiO_2 samples which had been heated at a number of temperatures for various periods of time showed one relatively broad peak. The samples heated at

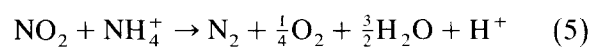
temperatures of 550°C or less showed peaks at positions consistent with the ^{31}P NMR spectra of heteropolymolybdates [58]. Since after use in a methane oxidation test reaction at 570°C for 4 h the position and FWHM of the ^{31}P NMR line are unchanged from those observed for HPMo at lower temperatures, the structure of the heteropoly anion is retained under catalytic operating conditions. For temperatures of 600°C and higher it is clear, however, that the anion is no longer in existence. It is clear, however, that since the decomposition temperature of the unsupported heteropoly acid is usually considered to be several hundred degrees lower, that the interaction between the support and the supported acid is sufficiently strong to provide an enhanced thermal stability of the latter. Further evidence for this stabilization is available from the results of catalytic experiments [34,59]. ^{31}P NMR spectra of HPMo/SiO₂ samples of various loadings which had previously been calcined at 350°C for 2 hours again showed peaks characteristic of bulk HPMo up to and including a loading of 31 wt% HPMo.

Information on the dispersion of the supported species on the silica surface has been obtained from X-ray photoelectron spectroscopy [57]. The Mo_{3d}/Si_{2p} intensity ratio increases linearly with the loading up to approximately 0.04 KU nm⁻² or approximately 10 wt% HPMo, with a slope similar to that of the calculated line for a monolayer dispersion. For this loading range single anions or perhaps small aggregates of these are dispersed on the surface. For higher loadings a change in slope signals the appearance of larger aggregates up to a plateau at 0.10 KU/nm² or approximately 23 wt% HPMo, at which loadings large aggregates are formed. After use in a methane oxidation reaction the curve for the intensity ratio has a similar shape but is shifted to lower values, indicative of the small loss of molybdenum during the reaction. The results of the aforementioned studies show that HPMo can be deposited uniformly on the surface of silica in a highly dispersed form up to a loading of approximately 10 wt% [57]. For load-

ings between this and 25%, aggregates begin to form, while at higher loadings particles of the acid are present. More recently, ^{31}P spin-lattice relaxation measurements have been performed on HPMo/SiO₂ and HPW/SiO₂ [60,61].

Reduction of NO₂ to N₂ and NO occurs on SiO₂ itself at temperatures as low as 150°C, although the conversion does not exceed 30% even at 300°C. With increasing loading the quantities of NO₂ removed from the gas phase increase, as would be expected, while the selectivity to NO decreases. Saturation of HPW/SiO₂ with NH₃ followed by exposure to NO₂ generates significantly increased quantities of N₂, as expected. Although the quantities of NO₂ sorbed by HPW/SiO₂ with relatively low loadings are less than the stoichiometric value of 3 found with HPW itself, nevertheless this value increases with loading providing further evidence for the participation of the bulk structure of HPW in the sorption and conversion of NO₂.

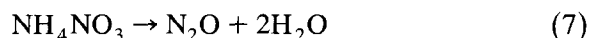
With NH₄PW significantly different results from those observed with HPW and HPW/SiO₂ are obtained with N₂ being the predominant product with the former catalyst. Although the presence of the ammonium cation is undoubtedly the primary contributor to such dissimilarities, the role played by the microporous structure which exists in NH₄PW but not in HPW, cannot be disregarded. Since NH₃ is a well-known reductant of NO_x it is highly probable that the ammonium cation is serving in this function with NH₄PW. As noted earlier in this report the reaction between NH₃ and NO₂ is primarily occurring on and in the catalyst, although of course, the possibility of some contribution from a purely gas phase process cannot be discounted. Thus NO₂, as with HPW, appears to be migrating into the interior of the solid where, in the former, interaction with NH₃, as NH₄⁺, occurs. Studies with $^{15}\text{NO}_2$ provide evidence for a one-to-one interaction between NO₂ and NH₄⁺ as



The protons produced will restore the parent acid HPW and the water produced will hydrogen-bond with these protons, so that ultimately the NH_4PW will be converted to the acidic form. Eqs. (1)–(3) will then be applicable. Both the infrared and ^1H MAS NMR spectra confirm the aforementioned conclusion.

In contrast to the results obtained for HPW with which HNO_3 was observed, no HNO_3 is detected in the effluent from NH_4PW . Any HNO_3 formed as NH_4PW is being converted to HPW may be consumed by reaction with NH_4^+ , $\text{HNO}_3 + \text{NH}_4^+ \rightarrow \text{NH}_4\text{NO}_3 + \text{H}^+$ (6)

The nitrous oxide which is observed to form at temperatures of 200°C and higher may then result from the decomposition of NH_4NO_3



The work reported here provides both fundamental and practical information on the MOCC and the conversion of NO_2 . It is clear that NO_2 , as with other polar molecules, is capable of penetrating into the bulk structure of HPW. Indeed it appears that such a process generates a nitronium salt which is capable of existing stably at room temperature. The use of HPW as a sorbent for NO_2 and the application of NH_4PW for the reduction for NO_2 offer considerable potential for environmental purposes.

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