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A Comparative Study of the Adsorption and Reaction of Nitrogen Oxides on 12-Tungstophosphoric, 12-Tungstosilicic, and 12-Molybdophosphoric Acids

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The sorption and conversion of NO and NO_2 on the three heteropoly acids (metal–oxygen cluster compounds), 12-tungstophosphoric (HPW) 12-molybdophosphoric (HPMo), and 12-tungstosilicic (HSiW) acids are investigated and compared. Substantial quantities of NO_2 are taken up by the tungsten-containing acids. In contrast, relatively small amounts of NO_2 are sorbed by HPMo. In the absence of presorbed NO_2 comparatively small quantities of NO are sorbed by any of the three solids. However, HPW and HSiW with presorbed NO_2 sorb substantial quantities of NO. No evidence for reduction of either NO or NO_2 is found. Temperature-programmed desorption, thermal gravimetry, infrared spectroscopy, and X-ray diffraction are employed to provide interpretive data. The results are interpreted as indicative of the formation of HNO_3 from the reaction of NO_2 and water as well as the substitution of the protons by NO_2^+ in establishing a charge balance mechanism.

INTRODUCTION

The deleterious impact of nitrogen oxides on the environment through the production of acid rain and photochemical smog has initiated a flood of research concerned with the elimination, removal, reduction, and decomposition of these materials (1–11). Although the preponderance of the reports pertain to reduction of nitric oxide, there is also considerable interest in the adsorption of NO_x on various substances, for example, carbon (12), Ru/ZnO (13), and zeolites (14).

Work in this laboratory has, for a number of years, been concerned, in part, with the surface and catalytic properties of metal–oxygen cluster compounds (also known as heteropoly oxometalates). Although a variety of stoichiometries and structures are possible, perhaps the most common are those referred to as having Keggin structure (15, 16). These are ionic solids with large, approximately spherical anions (sometimes referred to as Keggin Units, KU) with atoms such as phosphorus or silicon at their centers which are bonded to four oxygen atoms arranged tetrahedrally (Fig. 1). Surrounding the central tetrahedron and sharing oxygen atoms with it and each other are 12 octahedra with a peripheral metal atom such as molybdenum or tungsten at their approximate centers and oxygen atoms at their vertices. These anions may be combined with a variety of cations to produce stoichiometries such as $H_3PW_{12}O_{40} \cdot nH_2O$. The crystallographic structure of 12-tungstophosphoric acid is cubic Pn3m with water molecules hydrogen-bonded to the protons and the terminal oxygen atoms of the anions (17) (Fig. 2).

Although the surface areas of these solid acids are small, earlier photoacoustic FTIR studies in this laboratory have shown that polar molecules are capable of penetrating into the bulk structure, between the cations and anions (18–20). Thus ammonia, pyridine, and methanol have been shown to interact not only with the protons on the surface of 12-tungstophosphoric acid but also with those in the interior of the solid.

Semiempirical quantum mechanical (EXH) calculations have predicted that solid heteropoly acids with anions containing tungsten should have higher acidic strengths than those with molybdenum, while the latter materials are expected to have more labile oxygen atoms than the former (21). Experimental work has provided support for these predictions. For example, 12-tungstophosphoric acid has been found to have activity and selectivity in the conversion of methanol to hydrocarbons (22), while 12-molybdophosphoric acid has been employed as a catalyst in the partial oxidation of methane to methanol (23). Measurements of the adsorption of gaseous and liquid bases (24, 25) and microcalorimetry of ammonia adsorption (26) have also provided information on the acidic strengths of these materials and their dependence on the elemental compositions of the anions.

In view of the current interest in nitrogen oxides it appeared both interesting and worthwhile to study the

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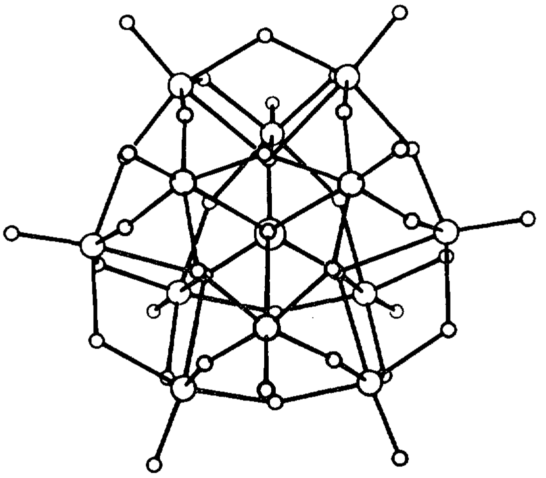

FIG. 1. Anion of Keggin structure (bigger circles: central and peripheral atoms; smaller circles: oxygen atoms).

sorption of these gases on the metal–oxygen cluster compounds with protons as the cations. The present work focuses on the effect of changes in the elemental compositions of the anions. The effect of changes in the central atoms of the anion is examined by comparing the results obtained with 12-tungstophosphoric acid and 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) and that of the peripheral metal atoms from the former and 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$). After this work was completed a paper concerned with the conversion of NO on the former acid has appeared (27).

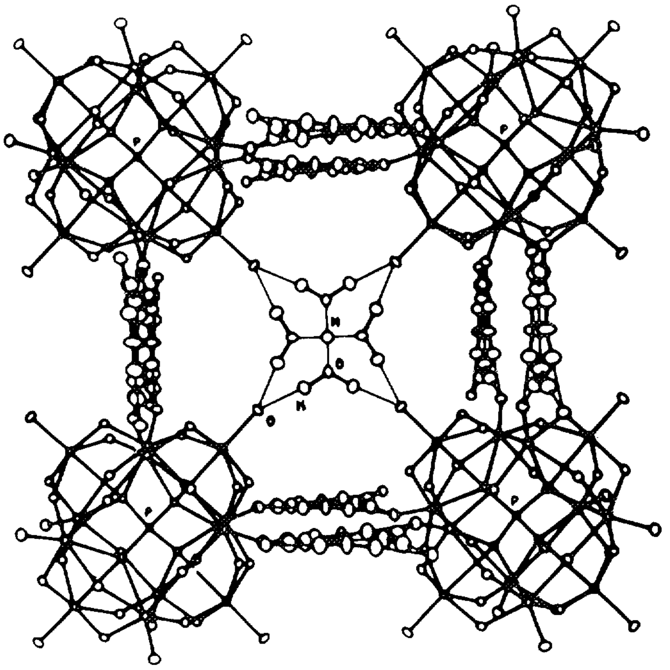

FIG. 2. Crystallographic structure of 12-tungstophosphoric acid showing anions, protons, and water molecules (17).

EXPERIMENTAL

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. The catalysts were preheated in the reactor at the desired pretreatment temperature in a 60 ml/min flow of helium for 45 min.

Procedures

A reactor constructed from 4 mm ID quartz tubing was connected to a Shimadzu GC-9A gas chromatograph equipped with a 4 mm OD × 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 is employed to trap NO_2 which is subsequently measured volumetrically. The reactor was charged with 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 (17 μmol NO_2 or 10 μmol NO; 24°C and 1 atm) was injected into a 15 ml/min flow of helium from a Whitey gas sampling valve. Checks of the initial calibrations of O_2, N_2, NO, and NO_2 were performed periodically.

For the analyses of HNO_3, confirmed as such through IR spectroscopy and various chemical tests, and total nitrogen, 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 NO_2 and HNO_3 will be decomposed completely into NO and N_2. As before, the desired gas pulse (17 μmol NO_2 or 10 μmol NO; 24°C and 1 atm) was introduced into a 15 ml/min flow of helium with a gas sampling valve. The quantities of nitrogen-containing compounds exiting the reactor after each pulse were determined chromatographically and, after the desired number of pulses, the catalyst was flamed in order to desorb any nitrogen-containing material. The quantity of HNO_3 in the gas phase is found by difference between the total amount of nitrogen-containing material in the gas phase after each pulse, and the quantity of NO_2 found earlier with the volumetric system.

For temperature-programmed desorption (TPD) the chromatographic column is replaced by an empty column and the effluent is passed directly over a TCD. The NO_x is, as before, introduced by use of a gas sampling valve. The temperature of the reactor is 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).

For thermogravimetric analysis (TGA) a Cahn electrobalance attached to a standard vacuum system was used. The sample was suspended from the balance in a quartz pan and pumped for 24 hr. The temperature was increased by 50°C and the mass was recorded after 24 hr. The process was repeated up to 600°C.

Surface areas were calculated, using the BET equation, from nitrogen adsorption isotherms obtained at 77 K. The catalysts were evacuated for 15 hr at the desired temperatures prior to the adsorption measurements.

Infrared spectra were obtained with a BOMEM MB-100 Michelson infrared spectrophotometer. The samples were done 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 Cu*kα* radiation. The samples were incorporated in silicone grease.

RESULTS

On contact of nitrogen dioxide with any of the catalysts employed in the present work, a portion of the NO_2 is sorbed into the solid. Some of this NO_2 is converted to O_2, NO, and HNO_3 as is evident from the products emerging from the reactor. The remainder is trapped on the solid. Thus the effluent stream from the reactor consists primarily of NO_2, HNO_3, O_2, and NO. Only insignificant quantities of N_2 were observed under any of the conditions employed in the present work. Multiple pulses of NO_2 were employed to provide information on the capacities and transient behavior of the solids with NO_2. The data will therefore be displayed in two parts. The loss of NO_2 from the gas phase on each of the three catalysts at 150°C after pretreatment at 150°C is reported for a number of pulses (Fig. 3). These data reflect both the NO_2 taken up by the catalyst and that converted to the aforementioned products.

The quantities of NO_2 lost from the gas phase for any given pulse up to the ninth follow the order HPW > HSiW > HPMo, although the values for the first two catalysts and their variation with pulse number are approximately the same. The quantities of NO_2 sorbed or converted with HPW from each pulse are nearly constant at 90% for the first five pulses while with HPMo only 10% of the NO_2 is sorbed and/or converted. After eight pulses a sharp drop in the fraction of NO_2 lost from the gas phase is evident with both HPW and HSiW and the values become almost insignificant after nine pulses.

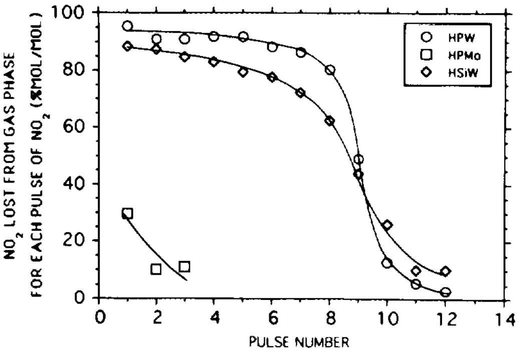

FIG. 3. Losses of NO_2 from the gas phase in a sequence of pulses of NO_2 on HPW, HPMo, and HSiW. Pretreatment and reactor temperature of 150°C. Mass of solid in reactor, 0.075 g; pulse size, 17.0 μmole NO_2.

Exposure of the catalysts after pretreatment at 300°C to pulses of NO_2 at the same temperature produces results remarkably dissimilar to those obtained at 150°C. (Fig. 4). While the fraction of NO_2 sorbed or converted on HPW is relatively large for the first pulse, this quantity diminishes substantially with each successive pulse. In contrast to the results at 150°C, similar results are now found for HSiW and HPMo with both catalysts showing sorption and conversion of NO_2 amounting to 20% or less after the first pulse. All three catalysts show relatively low values of sorption and conversion after two pulses.

The quantity of NO_2 lost from the gas phase, as stated above, is representative of the quantity sorbed on the solid acids plus any products of reaction or decomposi-

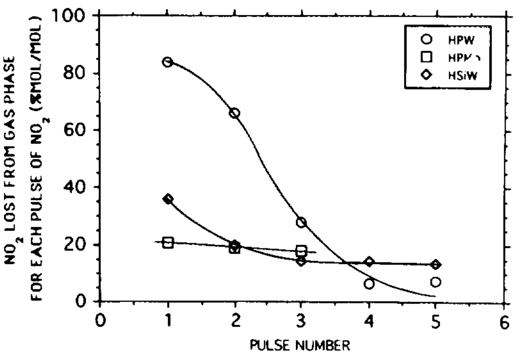

FIG. 4. Losses of NO_2 from the gas phase in a sequence of pulses of NO_2 on HPW, HPMo, and HSiW. Pretreatment and reactor temperature of 300°C. Mass of solid in reactor, 0.075 g; pulse size, 17.0 μmole NO_2.

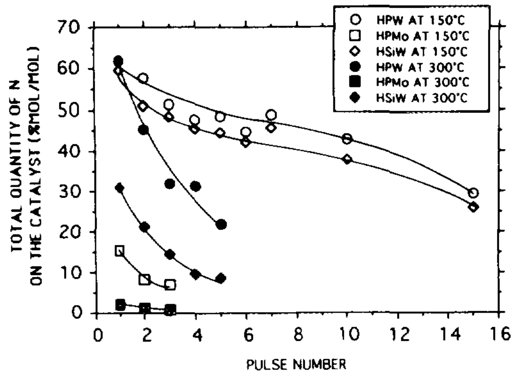

FIG. 5. Total amount of nitrogen compounds on HPW, HPMo, and HSiW (total sorption of NO_2). Pretreatment and reactor temperature of (empty) 150°C; and (filled) 300°C. Each datum is obtained on a fresh sample. Mass of solid in reactor, 0.075 g; pulse size, 17.0 μmole NO_2.

TABLE 1
Sorption of NO_2 on HPW

Temperature[a] (°C)	Total Sorbed[b] (μmol N)
25	4.53
150[c]	6.04
150	10.53
300	10.51
400	3.91
500	0.46
600	0.11

[a] Pretreatment and sorption temperature.

[b] Quantity of N-containing materials remaining on catalyst after exposure of catalyst (0.075 g) to pulse of 17.00 μmol NO_2 (in helium flow 60 ml/min at temperature shown).

[c] This sample of HPW was pretreated at 400°C in helium flow (60 ml/min) prior to the injection of NO_2 at 150°C.

tion exiting from the reactor. The quantities of nitrogen-containing materials, expressed as moles N per moles NO_2 in each pulse, are shown in Fig. 5. For all the solid acids studied in the present work, the fraction of nitrogen remaining on the solids (in whatever form) at 150°C is maximum at the first pulse. As before, the two tungsten-containing acids behave similarly and show a markedly higher retention than HPMo. As observed with the quantities of NO_2 lost from the gas phase, the retention on the catalyst decreases comparatively little for the first seven pulses, following which the changes are more substantial. Although the retention on HPW at 300°C with the first pulse is similar to that on the same catalyst at 150°C, in general, the quantities of NO_2 retained at 300°C are lower with all the solids.

The quantity of NO_2 retained on HPW from the first pulse at various temperatures increases from 25°C, reaches a maximum in the range from 150–300°C, and decreases to small values at 500–600°C (Table 1). For a pretreatment temperature of 400°C and sorption at 150°C, the retention is substantially lower than that observed after both pretreatment and sorption at 150°C.

The maximum quantities of N-containing species held on the catalyst after exposure to repeated pulses of NO_2 at 150°C expressed as the number of NO_2 molecules per anion are, for HPW and HSiW equal to approximately 3, not too dissimilar from the number of protons, 3 and 4, respectively per anion (Table 2). However, after pretreatment and exposure to NO_2 at 300°C these numbers are considerably reduced. The values obtained for HPMo are vanishingly small at both temperatures.

The predominant gaseous products emerging from the catalyst during exposure to a pulse of NO_2 are HNO_3 and O_2, together with the NO_2 not sorbed. With HPW pretreated at 150°C and exposed to NO_2 at the same temperature, the fraction of the NO_2 converted to HNO_3 increases monotonically with the number of pulses up to seven and then decreases markedly, while that with HSiW increases up to three pulses and then begins to decrease (Fig. 6). With both catalysts the HNO_3 vanishes from the effluent after 10 pulses. With HPMo the fraction of NO_2 converted to HNO_3 is relatively small and is reduced significantly after one pulse. After pretreatment at 300°C and exposure to NO_2 at the same temperature the quantity of HNO_3 produced with HPW passes through a maximum during the second pulse and vanishes after four pulses (not shown). With HSiW and HPMo at this temperature the conversion of NO_2 to HNO_3 is very small for each pulse of NO_2. The quantities of oxygen found in the gas phase after exposure of the catalyst to various pulses of NO_2 are less than 1 and 10% at 150 and 300°C, respectively, for HPW and HSiW and vanishingly small for HPMo at either temperature (not shown).

TABLE 2
Maximum Quantity of Sorbed NO_2[a]

	150°C[b]	300°C[b]
HPW	2.9	0.8
HPMo	0.1	0.0
HSiW	2.5	0.3

[a] NO_2 per anion.

[b] Pretreatment (Helium 1 hr) and sorption temperatures.

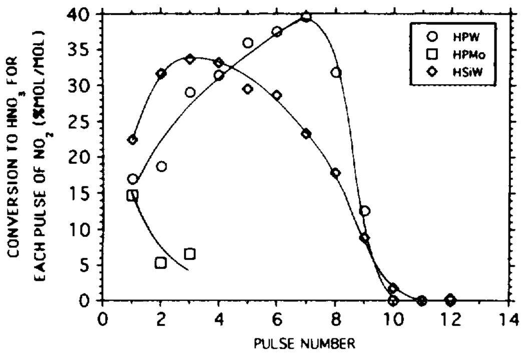

FIG. 6. Conversion of NO_2 to HNO_3 in a sequence of pulses of NO_2 on HPW, HPMo, and HSiW. Pretreatment and reactor temperature of 150°C. Mass of solid in reactor, 0.075 g; pulse size, 17.0 μmole NO_2.

Adsorption–desorption measurements for NO (not shown) on HPW at room temperature produced isotherms displaying an absence of reversibility similar to that observed with zeolites some years ago (28).

In comparison with the quantity of NO_2 sorbed and/or reacted on HPW that of NO is minimal (Fig. 7). The data reported in Fig. 7 are expressed in terms of the increase in the number of moles of atomic nitrogen found on the solid as a result of exposure to a flow of NO as a function of the quantity of NO_2 previously taken up by the solid. In the absence of previously sorbed NO_2 the sorption of NO is almost insignificant. However, after prior sorption of NO_2 the quantity of NO taken up increases, passes through a maximum, and decreases. The maximum quantities of NO taken up by the solid are approximately equal to those of NO_2.

The sorption of NO on HPW containing previously sorbed NO_2 increases with temperature, reaching a maximum at approximately 150°C, and decreases as the temperature continues to increase, ultimately becoming insignificant at 360°C.

The TPD patterns for HPW, pretreated for 1 hr at 150°C in a flow of helium (60 ml/min), display two peaks, one at approximately 300°C and the other at 500°C, both produced by water, the former resulting from the evolution of water molecules hydrogen-bonded to the protons and anionic oxygen atoms, the latter from water resulting from the extraction of the latter by the former (Fig. 8A) (29). After exposure to NO at 30°C for 5 min, little or no change was observed in the TPD peaks (Fig. 8B). However, after exposure to NO_2 at 30°C for 5 min, a shoulder due to the evolution of water is now evident at approximately 200°C and the peak at 500°C has increased and shifted to a somewhat higher temperature (Fig. 8C). It should also be noted that the 300°C peak has slightly diminished. The 500°C peak is now found to result from the desorption of both water and NO_2. Finally, the catalyst was exposed to NO_2 at 30°C for 5 min and subse-

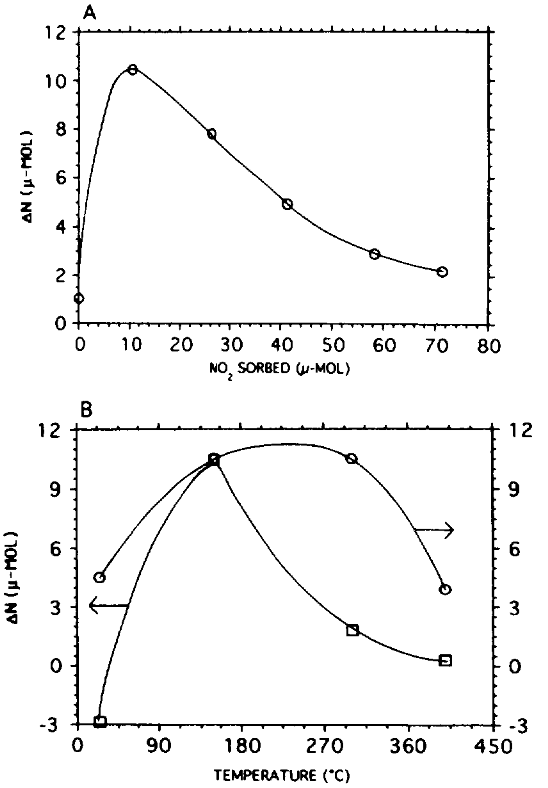

FIG. 7. Sorption of NO on NO_2-exposed HPW; (A) as a function of the quantity of NO_2 sorbed previously, and (B) as a function of pretreatment and reactor temperature when 1 pulse of NO_2 was previously injected. Each point is from a fresh sample. Four pulses of NO (10 μmole each) were injected prior to determination of total nitrogen on the catalyst. Mass in reactor, 0.075 g.

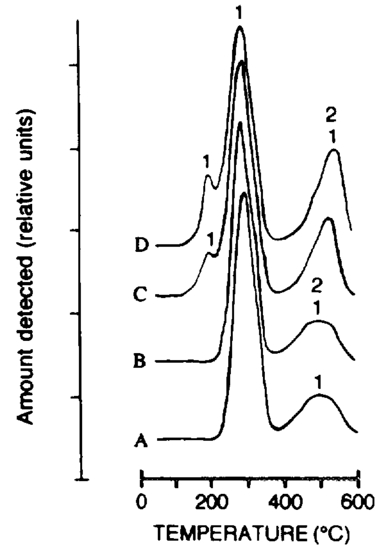

FIG. 8. TPD of HPW pretreated in helium at 150°C for 1 hr and exposed to flow of (A) helium at 30°C; (B) NO at 30°C; (C) NO_2 at 30°C; and (D) first NO_2 at 30°C and then with NO at 30°C. Helium flow rate, 45.0 ml/min; temperature rate, 60°C/min; mass of solid in reactor, 0.150 g; sorbing gas flow rate, 30 ml/min at 1 atm. 1, H_2O; 2, NO_2.

quently to NO at 30°C for 5 min (Fig. 8D). The low-temperature (≈150°C) peak has increased in magnitude, the 300°C peak has decreased still further, and the highest-temperature peak has further increased in magnitude and shifted to a higher temperature.

The effect of exposing HPW pretreated in helium at 150°C for 1 hr to various numbers of pulses of NO_2 at 150°C can be seen in the TPD patterns of Fig. 9. As the number of pulses of NO_2 increases from one to seven, the shoulder at 150–200°C due to water increases and then decreases, while the peak at 300°C due to water continuously decreases. The highest temperature peak shows a monotonic increase both in size and in desorption temperature up to and including four pulses of NO_2 but the position and size of this peak after seven pulses is similar to that after four pulses.

TPD of HSiW shows somewhat similar results to those found with HPW but with some differences. As with HPW, the peak due to water appearing at approximately 300°C decreases in size with increasing number of pulses of NO_2, while that at 500°C increases (Fig. 10). An additional small shoulder due to the desorption of water is evident on the 500°C peak. This has previously been seen with HSiW not exposed to NO_2 (29).

Information on the source of the TPD peaks is available from Fig. 11, which shows the comparative results for all three solid acids pretreated and saturated with NO_2 at 150°C. The numbers found above the curves, representative of each species (see legend), are positioned at the maximum intensity detected for the specific ion. The

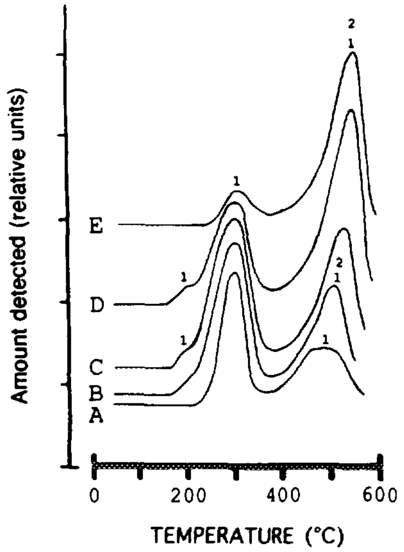

FIG. 9. TPD of HPW pretreated in helium at 150°C for 1 hr, (A), and exposed, at 150°C to (B) 1 pulse of NO_2; (C) 2 pulses of NO_2; (D) 4 pulses of NO_2; and (E) 7 pulses of NO_2. Helium flow rate, 45.0 ml/min; temperature rate, 60°C/min; mass of solid in reactor, 0.165 g; pulse size, 17.0 μmole NO_2. 1, H_2O; 2, NO_2.

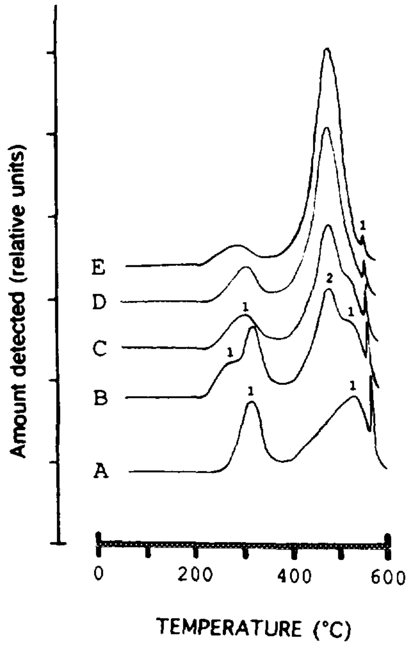

FIG. 10. TPD of HSiW pretreated in helium at 150°C for 1 hr, (A), and exposed, at 150°C to (B) 1 pulse of NO_2; (C) 2 pulses of NO_2; (D) 4 pulses of NO_2; and (E) 7 pulses of NO_2. Helium flow rate, 45.0 ml/min; temperature rate, 60°C/min; mass of solid in reactor, 0.155 g; pulse size, 17.0 μmole NO_2. 1, H_2O; 2, NO_2.

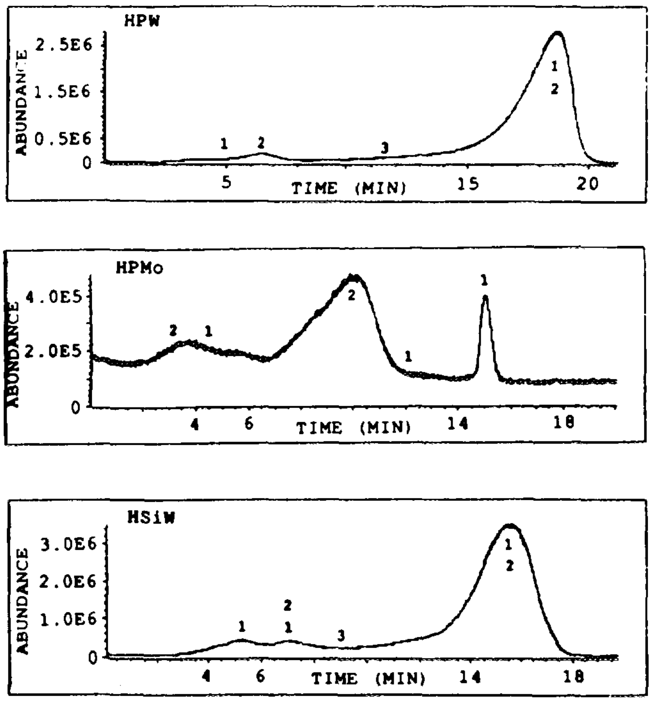

FIG. 11. Total ion TPD–GCMS of HPW, HPMo, and HSiW pretreated (helium flow of 60 ml/min for 45 min) and then exposed to NO_2 (30 ml/min for 5 min) at 150°C. Mass in reactor, 0.15 g; He flow rate, 10 ml/min; temperature range, 30 to 600°C; *dT/dt*, 30°C/min. 1, H_2O; 2, NO_2; and 3, O_2.

presence of a peak attributed to oxygen at 350°C with the two tungsten-containing acids is particularly interesting. Evidently the TPD peak seen in Fig. 10 at approximately 275°C results from the evolution of water and NO_2, while that at 550°C is produced primarily from NO_2 with a trace of water. Furthermore, the third peak for HSiW has completely vanished.

With HPMo, in the absence of NO_x, a similar TPD spectra as observed with HPW and HSiW is seen, but at a temperature of 475°C HPMo begins to decompose. After exposure of HPMo, pretreated at 150°C for 1 hr in a flow of helium (60 ml/min), to NO_2 at 30°C, no definite TPD peak is observed. However, with HPMo pretreated and exposed to NO_2 at 150°C, NO_2 desorbs at 300°C and the water peak at 450°C is not affected by the presence of NO_2.

Supplementary experiments show that HPW sorbs only a small quantity of HNO_3 (i.e., 2.3 μmol/0.078g HPW at 150°C). A TPD of HPW soaked in concentrated HNO_3 shows that HNO_3 desorbs and decomposes with the main water peak (that is, at 300°C) and there is no increase in the intensity of the peak appearing at 500–550°C.

The results obtained by TGA on HPW (Fig. 12) are similar to those from TPD, but the maxima are shifted to lower temperatures. At room temperature, and upon evacuation, the untreated HPW initially loses 107 mg/g of water (not shown in Fig. 12). On heating from 25 to 50°C approximately 13 mg/g of water is lost (as seen in Fig. 12A). With NO_2-exposed (continuous flow of NO_2 at 30 ml/min and 1 atm) HPW (Fig. 12B) and upon evacuation at 25°C, the weight remains constant. However, increase in the temperature results in a weight loss. For HPW treated with NO_2, the total mass desorbed (combined heat and evacuation) was 40 mg/g of catalyst, which corresponds to 2.5 NO_2/KU (assuming that all desorbing molecules are NO_2, and traces of water molecules, as with TPD–GCMS). A relative maximum in the desorption occurs at 350°C in comparison to 550°C observed in the TPD experiments. For HSiW exposed to NO_2, the weight loss of 46 mg/g of catalyst is equivalent to 2.9 NO_2/KU. As with HPW (treated with NO_2), HSiW did not show any decrease of weight upon evacuation at room temperature. With NO_2-saturated HPMo most of the loss in weight occurs on evacuation at room temperature.

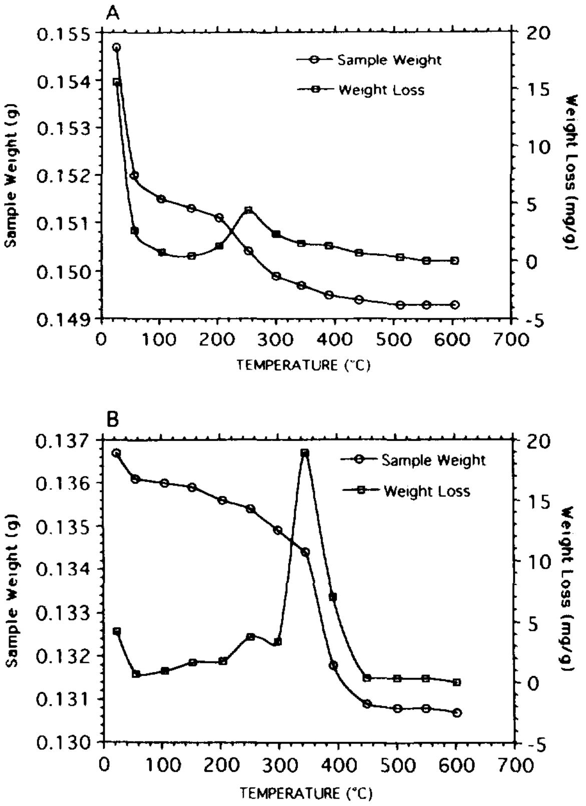

FIG. 12. TGA of (A) HPW as received; and (B) HPW pretreated in helium at 150°C and then exposed to flow of NO_2 (30 ml/min at 1 atm) at 150°C. Mass of acid used: (A) 0.1733 g, (B) 0.1366 g.

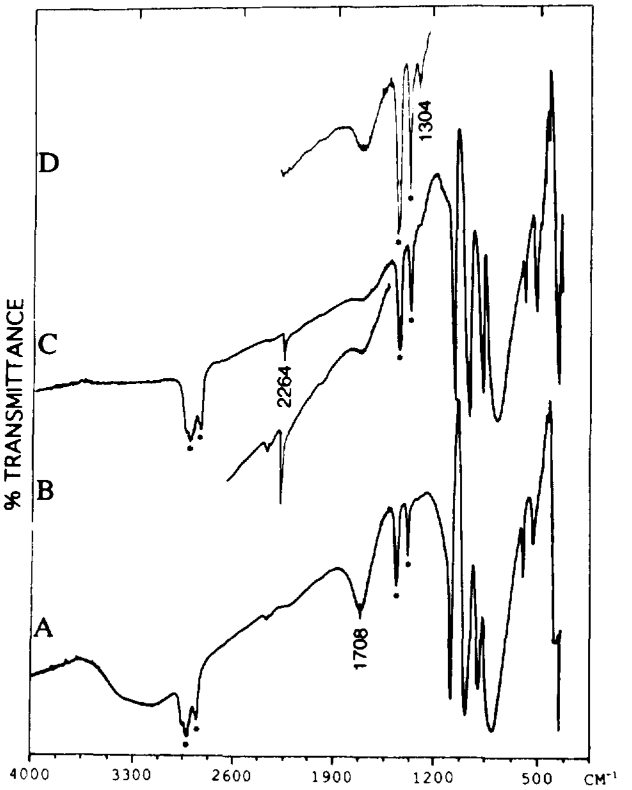

FIG. 13. Infrared spectra of HPW: (A) after pretreatment (200°C, 1 hr) in a flow of helium; (B) after pretreatment (150°C, 1 hr) in a flow of helium and then exposed to flow of NO_2 (30 ml/min at 1 atm) at 150°C; (C) pretreated as in (A) and then exposed to flow of NO_2 (30 ml/min at 1 atm) at 25°C; (D) pretreated as in (B) but after 1 pulse of 17.0 μmole of NO_2 and then 1 pulse of 10.0 μmole of NO at 25°C; * = NUJOL.

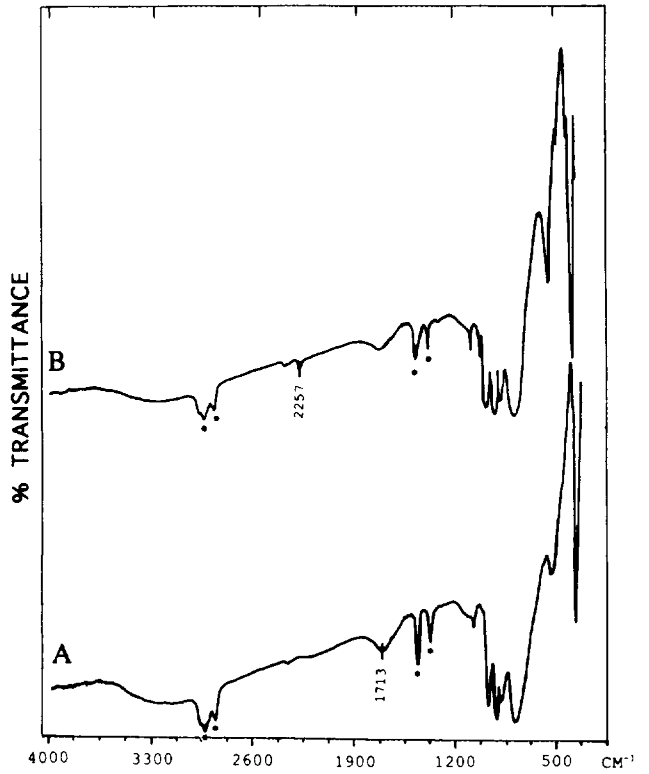

FIG. 14. Infrared spectra of HSiW: (A) after pretreatment (150°C, 1 hr, 60 ml/min) in a flow of helium; (B) after exposition to flow of NO_2 (30 ml/min at 1 atm) at 150°C; * = NUJOL.

The infrared spectra of HPW before and after saturation with NO_2 are shown in Fig. 13. The bands in the region 1200–800 cm^{-1} which are characteristic of the anion of Keggin structure are clearly evident. After exposure of HPW to NO_2, a band at 2264 cm^{-1}, not seen in the presence of NO and the absence of NO_2, is evident in Fig. 13 (B, C). The intensity of this band reaches a maximum after pretreatment of the sample at 150°C and saturation with NO_2 at the same temperature (Fig. 13B). The infrared spectra also show a diminution in the intensity of bands attributed to water and H_3O^+ as NO_2 is sorbed.

When HPW is exposed to NO after saturation with NO_2 at 30°C (Fig. 13D) a band, characteristic of N_2O_3, appears at 1304 cm^{-1}. Similar spectra are found with HSiW (Fig. 14). The molybdenum-containing acid did not show any difference in the infrared spectra.

Powder X-ray diffraction patterns of HPW and HPW treated with NO_2 at 300°C (Fig. 15) show that the crystallographic structure of the solid is retained, although new diffraction bands associated with the presence of NO_2 are evident. The acid was heated to 300°C to remove most of the water molecules which interfere with the diffraction pattern.

The surface areas of HPW, pretreated at 150°C for 1 hr in a flow of helium (60 ml/min), before and after exposure to a continuous flow of NO_2 (30 ml/min at 1 atm), are similar (9.3 m^2/g) indicating that the sorption of NO_2 has little or no influence on the surface of the solid available to N_2.

DISCUSSION

The amount of NO_2 sorbed and converted on the three heteropoly acids is evidently strongly dependent on the composition of the anion, but particularly on the nature of the peripheral metal atom. The two solid acids containing tungsten take up substantially larger quantities of NO_2 than that containing molybdenum. Earlier extended Hückel calculations have predicted that the protonic acidic strengths of the solids containing tungsten would be higher than those containing molybdenum (21) and various experimental methods for the measurement of acidity have provided confirmation of this prediction

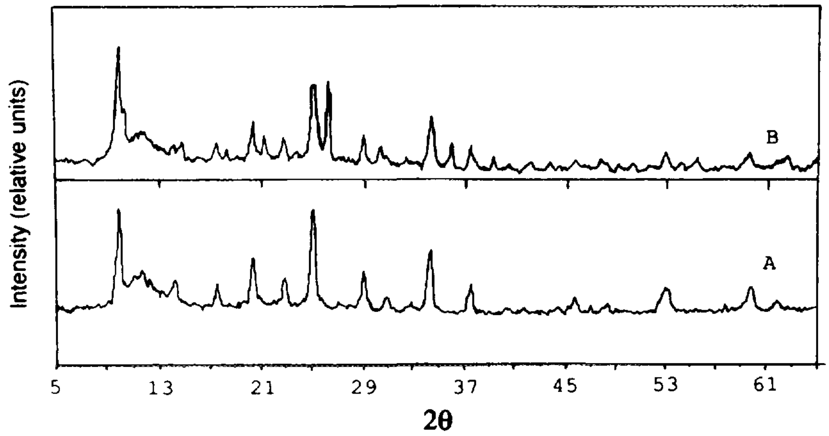

FIG. 15. X-ray diffraction spectra of HPW: (A) after pretreatment (300°C, 1 hr, 60 ml/min) in a flow of helium; (B) after exposure to NO_2 (300°C, 5 hr, 30 ml/min, 1 atm).

(24–26). Thus circumstantial evidence exists for a relationship between the quantity of NO_2 taken up and the Brønsted acidity.

Since the surface areas of these solid acids are small (less than 10 m^2/g), the NO_2 which sorbs and reacts is evidently penetrating, as found with other polar molecules, into the bulk structure of the solid, that is, between the cations and anions. It is of interest to note that the maximum quantity of NO_2 held on the 150°C-pretreated catalyst as NO_2 or other nitrogen-containing molecules corresponds, with HPW and HSiW, to approximately 3 molecules per Keggin unit, while with HPMo the value is only about 0.10. This provides evidence both for the bulk diffusion of NO_2 into the acids and the dependence of the interactive process between NO_2 and the acids on the Brønsted acidic strength of the solids.

The quantity of NO_2 sorbed is strongly dependent on the temperature to which the catalysts have previously been heated. For example, HPW heated to 600°C sorbs relatively small quantities of NO_2. This suggests that the quantity of NO_2 may be related to the protons and/or water which are present on and in the solids. The quantity of water desorbed by the tungsten-containing acids at 300°C clearly decreases with increase in the amount of NO_2 which is sorbed. The desorption at this temperature has previously been shown to be associated with relatively low energies and thus to water existing on and in the solid in hydrogen-bonded form. There are two processes which are consistent with this observation: the hydrogen-bonded water may be displaced by and/or reacts with the added NO_2.

In view of the observations showing that the preponderance of the effluent gases from the catalyst on exposure to NO_2 is HNO_3 the interaction between NO_2 and H_2O appears to play a major role in the overall process. A sequence of pulses of water injected at 150°C on HPW containing previously sorbed NO_2 showed that HNO_3 was desorbed in diminishing quantity with each pulse, while the quantity of NO_2 remaining on the catalyst also decreased with each pulse. The displaced NO_2 was readily replaced by again contacting the catalyst containing the residual NO_2 with additional quantities of NO_2. It is also relevant to note that HPW has a relatively small capacity for HNO_3 with only 2.3 and 3.1 μmol of HNO_3/0.076g HPW sorbed at 150 and 300°C, respectively.

A number of observations provide evidence for the reaction of NO_2 with the water contained within the tungsten-containing solids. The quantities of NO_2 lost from the gas phase at 300°C are considerably smaller than those at 150°C. As noted earlier in this report a variety of observations including both TPD and TGA measurements show that water is lost at temperatures between 200 and 400°C from all three of the solids studied in the present work. HNO_3 is the predominant gaseous product resulting from the exposure of the solids to NO_2. The loss of NO_2 from the gas phase at 150°C remains relatively constant up to seven pulses at which the production of HNO_3 and its desorption into the gas phase reaches a maximum. The TPD peak at approximately 300°C clearly decreases in intensity as the quantity of NO_2 sorbed increases. These observations can be rationalized through the process in which NO_2 reacts with water contained within the solid as represented by one or both of the stoichiometries

$$2\,NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \qquad [1]$$

$$3\,NO_2 + H_2O \rightleftharpoons 2\,HNO_3 + NO, \qquad [2]$$

to produce HNO_3 which is evolved into the gas phase. This is also consistent with the observation that the sorptive capacity of these solids for HNO_3 is very small.

Not all of the NO_2 lost from the gas phase reacts with water to produce HNO_3. Evidently amounts greater than 50% are retained on the catalyst, depending on the conditions, with the maximum quantities found on HPW at temperatures of approximately 300°C. That the maximum quantities of NO_2 retained on the catalyst, after reaction with water, correspond very closely to the number of protons per anion can be interpreted as indicative of an interaction between the protons and NO_2. However, since two IR bands characteristic of the nitronium ion were found in this work at 2264 and 600 cm^{-1} with HPW, a more probable scenario involves the disproportionation of an electron on NO_2 to produce negatively and positively charged NO_2 (9, 10)

$$NO_2 + NO_2 \rightleftharpoons NO_2^+ + NO_2^-. \qquad [3]$$

The positively charged protons may then combine with the negatively charged NO_2^- ion to produce HNO_2.

$$H^+ + NO_2^- \rightleftharpoons HNO_2 \qquad [4]$$

The positively charged NO_2^+ may serve, at least in part, in place of H^+ to counterbalance the negative charge on the anion. Relatively high temperatures will dissociate the nitrous acid and result in the release of the NO_2 from the catalysts.

With the present solids the sorption of significant quantities of NO requires the presence of presorbed NO_2 and the maximum in NO is achieved for an approximately 1/1 ratio of NO/NO_2. The observations are consistent with the formation of N_2O_3 as (30)

$$NO + NO_2 \rightleftharpoons N_2O_3, \qquad [5]$$

a band for which was observed in the infrared spectra at 1304 cm^{-1}. Since the equilibrium in [5] is shifted to NO and NO_2 at higher temperatures, the sorption of NO would be expected to be insignificant at temperatures as high as 360°C, which is indeed observed. Although the disproportionation reaction of NO

$$4\ NO \rightarrow N_2O + N_2O_3$$

is reported to be catalyzed on zeolites at ambient temperature (9, 10, 11, 28), no evidence for the formation of N_2O was found with the present catalysts.

Since the Keggin structure is evidently retained on exposure of the solids to NO and/or NO_2, the properties of the solid acid are presumably retained. As noted earlier, EXH calculations have shown that the protons in the tungsten-containing solid acids are more mobile, and hence have higher acidic strength than those in the solids containing molybdenum. Consequently, the disparity in behavior of these two types of materials with respect to NO_x is apparently due, at least in part, to the differences in the acid strength distributions.

This work has compared the sorbing properties of heteropoly acids for the removal and transformation of nitrogen oxides. Strong evidence for the replacement of the protons by NO_2^+ has been provided and thus for the formation of compounds with stoichiometry $H_x(NO_2)_{n-x}XM_{12}O_{40}$. Further work is now in progress to assess the surface and catalytic properties of these solids. Unfortunately, at least from a practical point of view, no evidence was found for the reduction of either NO or NO_2. However, the abilities of the tungsten-containing heteropoly acids to sorb NO_2, in particular, and NO to a lesser extent, provide a further insight into the unusual properties of these solid acids and their potential for the formation of new and unusual heterogeneous catalysts.

CONCLUSIONS

1. Although NO is not sorbed on any of the present solids, after prior sorption of NO_2 on HPW and HSiW, significant quantities of NO are sorbed.
The previously sorbed NO_2 facilitates the formation of N_2O_3 on addition of NO.
2. Substantial quantities of NO_2 are removed from the gas phase by either HPW or HSiW, but the greater portion of the NO_2 thus removed is converted to HNO_3, which is recovered in the gas phase.
3. The quantity of NO_2 retained on HPW or HSiW at 150°C corresponds, at least approximately, to the total number of protons on and in the solid.
4. Disproportionation of an electron on NO_2 leads to the production of NO_2^- and NO_2^+, the former of which interacts with protons to form HNO_2, while the latter replaces the protons in their charge-balancing capacity.
5. At temperatures of 500–600°C, the aforementioned process is reversed and NO_2 is desorbed from the catalyst.
6. The catalyst HPMo sorbs relatively small quantities of NO_2, and the aforementioned processes observed with the more acidic HPW and HSiW do not occur to any appreciable extent with HPMo.

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