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Interaction of NO and NO_2 on 12-tungstophosphoric acid

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On exposure of the solid 12-tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$ (HPW)) to NO_2 at 150°C NO_2 is sorbed, while HNO_3 is produced. NO_2 is found to penetrate into the bulk structure whose reaction occurs with the water hydrogen-bonded to the protons to produce HNO_3. The NO_2 retained on the catalyst is stoichiometrically equivalent to the total number of protons on and in the solid. This, together with infrared spectra, suggests that NO_2 is associating (1/1) with the protons, producing a nitronium salt of the solid acid. Although insignificant quantities of NO are taken up by HPW, after exposure to NO_2, approximately stoichiometric quantities of NO are sorbed and the infrared spectra show the presence of N_2O_3.

Keywords: nitrogen oxides; 12-tungstophosphoric acid

1. Introduction

The elimination of nitrogen oxides through the application of catalytic processes is attracting considerable attention, in large measure as a consequence of the disadvantageous presence of these gases in the environment (see for example various papers in ref. [1]). While a variety of methods has been examined for the conversion of nitrogen oxides, the preponderance of the work to date has been concerned with catalytic reduction [1,2]. However, the demonstration that direct catalytic decomposition of NO is possible on Cu-ZSM-5 catalysts [3] has led to further studies by a number of workers [1,4] and most recently further evaluations of the reaction mechanism [5] and preparative effects [6] have been provided.

Although the results of many studies of the adsorption and reaction of nitrogen oxides have been published, in contrast relatively few studies of the adsorption of nitrogen oxides have been reported, although Addison and Barrer published the results of an early study [7] and most recently Sachtler and coworkers have reported on the co-adsorption of NO and NO_2 [8].

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The present work is concerned with the adsorption and reaction of NO and NO_2 on 12-tungstophosphoric acid. Although metal–oxygen cluster compounds (MOCC) (also called heteropoly oxometalates) are found in a wide variety of forms [9,10], those of Keggin structure are of particular interest in heterogeneous catalysis [11]. These are ionic solids with discrete cations and anions, the latter having large approximately spherical structures with a central atom, in the present work phosphorus, bonded tetrahedrally to four oxygen atoms and surrounded by twelve octahedra with oxygen atoms at their vertices and, a peripheral metal atom (in the present work, tungsten) at their approximate centers. Oxygen atoms bond the peripheral metal atoms to each other and to the central atom. A terminal oxygen atom protrudes from each of the octahedra.

X-ray and neutron diffraction studies have shown that 12-tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$, abbreviated as HPW) has a cubic Pn3m structure with each proton being hydrogen bonded to as many as four water molecules which are, in turn, hydrogen-bonded to the terminal oxygen atoms of the anion [12].

Although these solids have a number of interesting properties, their sorption and acidic characteristics are of particular relevance to the present report. Photoacoustic (PAS) FTIR studies have shown that polar compounds such as ammonia, pyridine and methanol are capable of penetrating from the vapour phase into the bulk structure of the solids, that is, between the cations and anions [13–15]. In addition, microcalorimetric measurements have shown that the differential heat adsorption of ammonia on 12-tungstophosphoric acid is in the range expected for a solid superacid [16].

2. Experimental

The catalyst, HPW, purchased from BDH chemicals and nitrogen dioxide (99%) obtained from Matheson were both used as received. Nitric oxide (98.9%), obtained from Linde, was passed through a trap at dry ice–acetone temperatures before use. The catalyst was pretreated at the desired temperature in a flow of helium (60 ml/min) for 45 min.

Aliquots (0.075 g) of HPW were loaded into a 4 mm i.d. quartz reactor connected to a gas chromatograph (Shimadzu GC-9A) equipped with a 4 mm o.d. ×30 cm long stainless steel column packed with molecular sieve 5A 60/80 mesh preconditioned at 300°C for 3 h. The temperature of the column was kept at 30°C for the analysis of O_2, N_2, and NO. NO_2 was determined volumetrically after condensation at dry ice–acetone temperatures in a trap placed between the outlet of the reactor and the gas chromatograph. Prior to the injection of NO_2 pulses (17 μmol NO_2/pulse), the reactor was heated to the reaction temperature of 150°C for 15 min in a 15 ml/min flow of helium. Each pulse of NO_2 was injected at the hand of the reactor, in the helium flow, with a gas sampling valve (Whitey).

The analysis of HNO_3, verified as such with IR spectroscopy, chemical tests, and total nitrogen analysis, was performed with a modified reaction system. The cold trap was replaced by a two-step decomposition system. The first step was used to thermally decompose HNO_3 by passing the effluent of the reactor through a coil held at 700°C. Subsequently the excess NO_2 from the reactor and from the decomposition of HNO_3 was decomposed by passing the gases through copper wool kept at 550°C. The products of the decomposition were predominantly N_2 and NO, and determined as such. The quantity of nitric acid in the gas phase (for each pulse of NO_2) was calculated by difference between the total amount of nitrogen containing compounds (as N) and the quantity of NO_2 found earlier with the volumetric system. The total quantity of nitrogen-containing compounds sorbed by the solid acid was determined, after the desired number of NO_2 pulses had been injected, by flash heating of the catalytic reactor and gas chromatographic analysis of the decomposition products.

Infrared spectra were obtained with a BOMEM MB-100 Michelson infrared spectrophotometer. Each sample was mulled in nujol and placed between two AgBr windows. No evidence was found for the reaction of NO_2 and HPW with the mulling agent, nor the windows. ^1H MAS NMR results were obtained with a Bruker AMX 500 spectrometer. The rotation frequency was set at 10.0 kHz. Each sample was pretreated and exposed to NO_2 as described above and then packed in a sapphire rotor. All spectra recorded were referenced to TMS (tetramethylsilane).

3. Results

The species leaving the reactor held at 150°C, after injection of a pulse of NO_2 are HNO_3 and NO_2, with a portion of the NO_2 remaining on the catalyst. No N_2 was observed under any of the conditions employed in this work. For small quantities of NO_2 virtually all of the gas is either converted to HNO_3 or held on the catalyst. As the cumulative quantity of NO_2 is increased the amount of NO_2 exiting from the reactor increases slowly and finally breaks through at approximately 5 moles of NO_2 per mole of catalyst (fig. 1). Three moles of NO_2, in whatever form, per mole of catalyst, are retained on and in the catalyst, at saturation.

Infrared spectra of HPW taken before and after exposure to NO_2 show that the structure of the anion remains unaltered by the NO_2 (fig. 2 A, B). A set of five or six bands characteristic of the structure can be seen in the 1200–800 cm^{-1} region. Bands at approximately 1080 and 980 cm^{-1} are attributed to the triply degenerate asymmetric stretch of PO_4 and the stretching vibration of the tungsten–terminal oxygen bond [13]. A band at 2264 cm^{-1} characteristic of the nitronium ion is also found after exposure of HPW to NO_2 (fig. 2 C) [17]. In addition, the band for the hydronium ion (H_3O^+) at 1708 cm^{-1} and the broad band at 3200 cm^{-1} due to water decrease significantly after exposure of the acid to NO_2 (fig. 2).

A portion of the NO_2 sorbing on HPW is converted to HNO_3 (fig. 3). As the quantities of NO_2 to which the catalyst is exposed increase the quantities of HNO_3

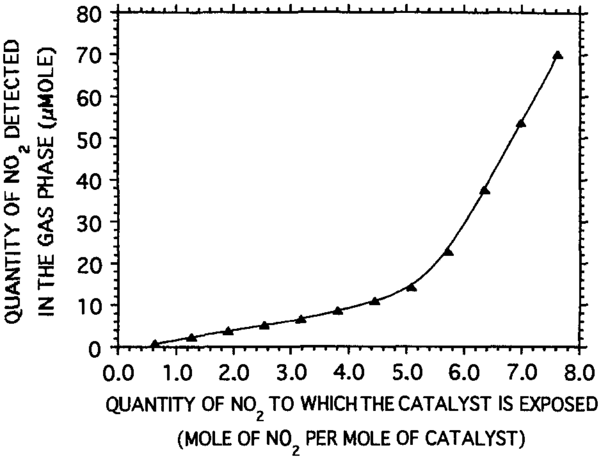

Fig. 1. Quantity of NO_2 detected in the gas phase with increasing amounts of NO_2 to which HPW is exposed at 150°C.

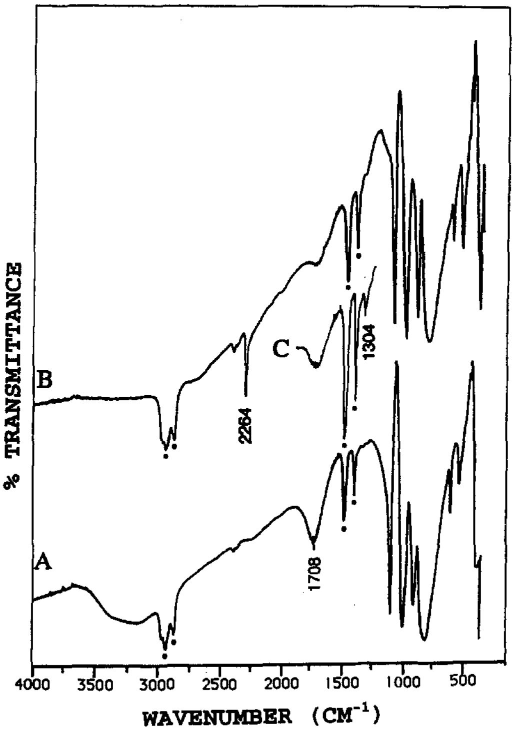

Fig. 2. Infrared spectra of HPW, before (A), after (B) exposure to NO_2 and after exposure to NO and NO_2 (C).

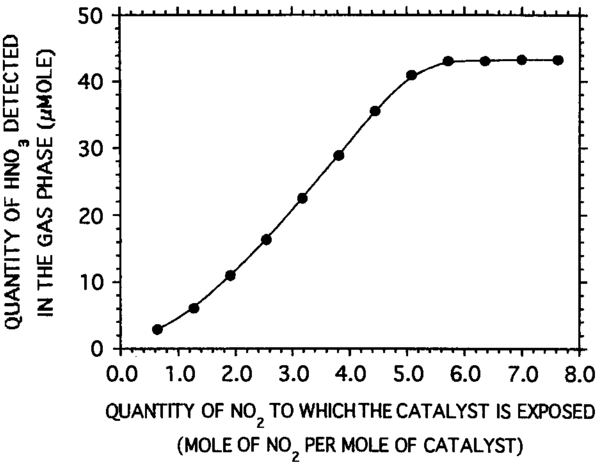

Fig. 3. Quantity of HNO_3 detected in the gas phase with increasing amounts of NO_2 to which HPW is exposed at 150°C.

produced increase and reach a plateau at approximately 5 moles of NO_2 per catalyst. Further additions of NO_2 produce little or no additional HNO_3. In contrast to the observation with NO_2 little or no NO is taken up by HPW at 150°C. However, after exposure of HPW to NO_2 the solid acid is found to sorb NO with a stoichiometry of approximately one NO/NO_2 (mole/mole). In addition a band at 1304 cm^{-1}, attributed to N_2O_3 appears in the infrared spectra (fig. 2 C) [17].

The quantities of water and nitrogen dioxide which are desorbed at 300 and 500°C, respectively, are shown in fig. 4 for various quantities of NO_2 to which the solid had been exposed at 150°C. In the absence of NO_2 the water hydrogen-bonded

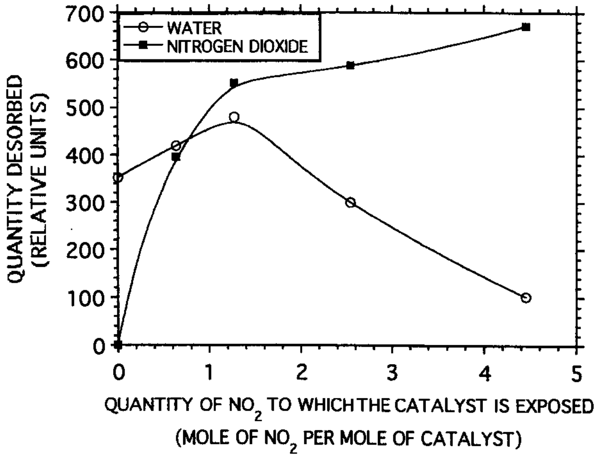

Fig. 4. H_2O and NO_2 desorbed at 300 and 500°C, respectively for increasing quantities of sorbed NO_2.

to the protons and terminal oxygen atoms of the anion is desorbed at approximately 300°C. As the quantity of NO_2 to which the catalyst is exposed at 150°C increases the quantity of water desorbed at 300°C increases, passes through a maximum and decreases. The quantity of NO_2 desorbing at 500°C increases sharply with increase in the NO_2 to which the catalyst is exposed and, at approximately the same value of the dosage of NO_2 as observed for the maximum with water undergoes a reaction in the ratio of desorption with NO_2 dosing.

The ^1H MAS NMR spectra of HPW before and after exposure to NO_2 provide strong evidence for the retention of the protons on the solid acid after contact with nitrogen dioxide (fig. 5).

4. Discussion

The quantities of NO_2 remaining on the catalyst during the initial exposures to NO_2 demonstrate that NO_2 is penetrating into the bulk structure of the solid acid, that is, between the cations and anions, as found earlier with polar molecules such as those of ammonia. Since the BET N_2 surface area of the solid is less than the 10 m^2/g, insignificant amounts of NO_2 would be expected to adsorb. As noted in the introduction, each proton of HPW may be hydrogen-bonded to as many as four water molecules. On exposure of HPW to NO_2 it is evident that nitrogen dioxide which has penetrated into the bulk structure is interacting with the hydrogen-bonded water contained therein to form HNO_3 which is desorbed from the catalyst.

The stoichiometries by which HNO_3 may be formed from NO_2 and H_2O,

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \tag{1}$$

and

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO\,, \tag{2}$$

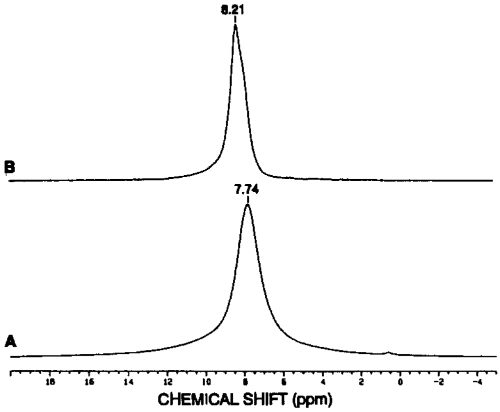

Fig. 5. ^1H MAS NMR of HPW, before (A), and after (B) exposure to NO_2.

each generate a second product and consequently the observation of one or the other of these should provide an interaction of the operative reaction(s). Since traces of NO were seen in the effluent from the reactor it is concluded that reaction (2) is the more probable although, of course, the occurrence of reaction (1) cannot be excluded. Further evidence of the consumption of water contained within the catalyst is found in the decrease of the broad band at 3200 cm^{-1} and the band at 1708 cm^{-1}, the former due to water, the latter to the hydronium ion.

The relatively sharp increase in the amount of NO_2 released to the gas phase, which is observed with increasing quantities of NO_2 to which the catalyst is exposed, occurs at approximately 6 moles NO_2 per mole of catalyst, at which the quantity of HNO_3 released to the gas phase ceases to increase. Since Brown and coworkers [11] found that single crystals of 12-tungstophosphoric acid can be represented as $H_3PW_{12}O_{40}\cdot 6H_2O$, it is clear that the sharp increase in the quantity of NO_2 desorbed and the cessation in the production and release of HNO_3 are coincident with the elimination of water from the structure of HPW. Further, since the infrared spectra characteristic of the anion of Keggin structure are similar before and after exposure of HPW to NO_2, the solid acid evidently suffers no deleterious effects of this interaction.

The band at 2264 cm^{-1} in the infrared spectrum of HPW after exposure to NO_2, which can be attributed to the nitronium ion (NO_2^+) [17], may be interpreted as resulting from one or both of the possibilities. Nitrogen dioxide may disproportionate to form NO_2^+ and NO_2^- [17,18] as

$$2NO_2 \rightleftharpoons NO_2^+ + NO_2^- \qquad (3)$$

The nitrite ion would be expected to interact with the protons of the solid acid to produce HNO_2, while the NO_2^+ substitutes for the protons in balancing the negative charge on the anions. However, it is possible to explain the existence of the infrared band at 2264 cm^{-1} as arising from the association of NO_2 with the acidic protons to form HNO_2^+ as

$$H^+ + NO_2 \rightarrow HNO_2^+ \qquad (4)$$

Although no published infrared spectra for HNO_2^+ are available, it appears reasonable to assume that the perturbation of the electron density in NO_2 by H^+ will be sufficiently small so that the characteristic band for NO_2^+ will be shifted relatively little. The asymmetric stretch for NO_2^+ has been reported as 2375 cm^{-1} [17]. Further, the observation that 3 moles of NO_2 per mole of catalyst and hence per every 3 moles of protons are held on the catalyst provides additional support for the postulated association between the proton and NO_2. Finally, the NMR evidence for the retention of the protons on the catalyst during the process of exposure to NO_2 and production of HNO_3 is also consistent with the postulate. Although not conclusive, the evidence suggests that a nitronium salt has been formed with the 12-tungstophosphate anion, apparently the first time that such a nitronium salt has been prepared from a solid acid and gaseous NO_2. The band attributable to

N_2O_3 which appears on addition of NO to HPW which has previously been exposed to NO_2 may be rationalized as resulting from the association of NO and NO_2 [17,20]. It is interesting to note in this respect that both N_2O_3 and N_2O have been observed to form on zeolites from the disproportionation of NO [7,19,21]. However, no evidence for the formation of N_2O was found in the present work.

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