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In situ IR and temperature programmed desorption-mass spectrometry study of NO absorption and decomposition by silica supported 12-tungstophosphoric acid

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Abstract

Silica supported 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$ or HPW), as well as unsupported HPW, were examined for NO absorption and temperature programmed desorption by in situ diffuse reflectance infrared spectroscopy and TPD-MS. The SiO_2 supported samples contained HPW at 2, 4, and 8 wt% W loading levels. X-ray powder diffraction for determination of HPW lattice parameter and crystal size, solid state proton NMR, and ex situ IR were also employed to characterize these catalysts. The results indicate a strong interaction between HPW and the surface hydroxyl groups of the silica support, leading to the formation of an entirely different secondary structure than observed in bulk HPW. In this secondary structure, water is proposed to be present at H_3O^+ rather than $H_5O_2^+$ as in unsupported HPW. This structure is more compact than that of bulk HPW leading to a shrinkage of the lattice parameter by approximately 0.5 Å but still accommodating a substantial fraction of the original water. Proton NMR supports the proposal that H_3O^+ is present and indicates that silica supported HPW is a much weaker Brønsted acid than unsupported HPW. NO is absorbed via the same mechanism by both unsupported and supported HPW to produce NOH^+ species, although ν(N–O) bands in the IR are shifted to slightly different wave number in the supported samples. The rate of NO uptake is much lower for the supported catalysts, which may be explained by the much lower acid strength of these materials. Upon temperature programming to 723 K (50 K/min) more than 50% of the absorbed NO decomposes yielding nitrogen and nitrous oxide as the only reaction products. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Polyoxometalate; Hetesopoly acid; Nitric oxide; Absorption; Decomposition; In-situ IR; TPD-MS

1. Introduction

The nitrogen oxides (NO and NO_2, or NO_x) are important pollutants formed in all combustion processes. NO_x participates in chemical reactions leading to the production of photochemical smog [1]. While other species are required for these reactions to occur, NO_x can often be the limiting species [2]. These photochemical reactions produce ozone, polynuclear aromatic compounds, nitric and nitrous acids, and particulate nitrates. Secondary particulate from NO_x emissions accounts for a significant fraction of the environmental particulate in many US cities. Nitrogen oxides are responsible for 25–35% of the acidity of rain. The development of more efficient and envir-

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onmentally benign approaches to combustion requires that new technologies for removal of NO_x from combustion flue gases be developed. Here we describe materials that exhibit the unusual property of NO decomposition during rapid heating in the presence of oxygen and water vapor.

The reaction $2NO\rightarrow N_2+O_2$ is highly thermodynamically favored at temperatures below about 1000°C but proceeds very slowly on the large number of catalysts that have been explored to date [3,4]. While supported noble metal and perovskite catalysts have received much recent attention in the literature, the most active (and most studied) NO decomposition catalysts are Cu-exchanged zeolites, especially Cu-ZSM-5 [4,5]. Reaction rates on Cu-ZSM-5 are too low for practical application. Furthermore, the catalyst is reversibly poisoned by oxygen [6] water vapor, and SO_2 requiring regeneration at high temperatures [5]. Finally, a number of investigators have shown that above 600°C the zeolite matrix undergoes irreversible hydrothermal decomposition resulting in elimination of the catalytically active sites [4,7,8]. In spite of these limitations, an understanding of the reaction mechanism on Cu-ZSM-5 is still worthwhile.

Various proposals regarding the reaction mechanism over Cu-ZSM-5 have been reviewed by Shelef [4]. The first supposes that a pair of Cu^{2+} ions loses an oxygen ion (O^{2-}) upon heating to produce a pair of Cu^+. The Cu^+ adsorb a pair of NO molecules, which they reduce to form NO^- anions. The anions then decompose yielding N_2 and O_2 and restoring the Cu^+ adsorption sites. This mechanism has been criticized because anion formation is a thermodynamically uphill process and the anion would not be stable at catalyst operating temperatures. A second mechanism notes that donation of the electron in the anti-bonding orbital of NO is favored if there is an accepting orbital at the chemisorption site. Such an orbital exists in Cu^{2+} (d^9) but not in Cu^+ (d^{10}). Thus the cupric ions are proposed to be the active sites which chemisorb NO. The *gem*-dinitrosyl (NO^-) observed in IR studies is proposed to be these neutral NO species chemisorbed via donation of their lone pairs. The dinitrosyl rearranges to desorb as N_2 and O_2. Vaylon and Hall [9] have elaborated on this mechanism. They present evidence for extralattice (non-zeolite framework) oxygen bound to Cu^{2+}. They propose that NO chemisorbs on this site to form a surface bound NO_2 species. A second NO molecule then chemisorbs on the same site forming a species similar to a dinitrosyl. This dinitrosyl then decomposes yielding N_2, O_2, and regenerating the extralattice oxygen site. More detailed descriptions are available in the cited literature. However, these mechanisms all involve activation of NO as NO^-, neutral NO or NO_2. As shown elsewhere [10–12] and below, IR spectra of the interaction of NO with tungstophosphoric acid suggest an entirely different protonated reaction intermediate. No evidence for a dinitrosyl species is observed.

The heteropoly acids (HPA) are unique catalytic materials in that they are very strong acids and most importantly absorb polar molecules into their bulk structure. The primary structural unit of HPA is the heteropoly anion. These can be viewed as forming from condensation of six or more oxoanions (of W, Mo, or V, for example) around the oxoanion of a heteroatom. For tungstophosphoric acid ($H_3PW_{12}O_{40}$ or HPW):

$$12WO_4^{2-}+HPO_4^{2-}+23H^+\rightarrow (PW_{12}O_{40})^{3-}+12H_2O \tag{1}$$

The structure of this anion is known as the Keggin structure. The synthesis and structure of a wide variety of heteropoly compounds has been extensively reviewed ([13], for example). The most poorly understood aspect of heteropoly compound structure is how the heteropoly anions are linked together in the solid state to form the so-called secondary structure. HPA are typically hydrated in the presence of water. The hydration water can be replaced by polar molecules such as alcohols, ethers, or amines, which become protonated; or the protons can be replaced by metal ions and other cations. The lattice parameter changes depending upon the number of sorbed molecules per anion, the size of these molecules, and how they are bonded to the heteropoly anions. Because of the flexible nature of the secondary structure it has been referred to as a "pseudoliquid phase" [14].

In 1994 Yang and Chen [15] reported that the heteropoly acid, tungstophosphoric acid, absorbs NO into its bulk structure at 423 K in the presence of oxygen. Upon temperature programming to 723 K at 100 K/min or greater, nearly 70% of this sorbed NO decomposed to nitrogen. Sorption and decomposition occurred in the presence of water, oxygen, carbon dioxide, and sulfur dioxide. Based on these experiments and additional data published later [10], the authors proposed that the following reaction was occurring upon NO sorption:

$$\begin{aligned}&H_3PW_{12}O_{40}\cdot 6H_2O + 3NO\\&\quad\rightarrow H_3PW_{12}O_{40}\cdot 3NO + 6H_2O \qquad (2)\end{aligned}$$

If the reaction goes to completion, this represents 3.0 wt% NO sorbed by HPW. The bcc lattice constant decreased from 12.2 to 11.7 Å because of this reaction. Moreover, it was proposed that the NO was protonated as NOH^+ in the pseudoliquid phase. The N–O infrared stretching frequency was observed to be 2270 cm^{-1} indicating a considerable weakening of the N–O bond relative to nitrosonium ion NO^+ at 2300 cm^{-1}. The rate of NO uptake was dramatically enhanced in the presence of oxygen and water. Belanger and Moffat [11] have reported on the interaction of pulses of NO_2 in He with tungstophosphoric acid both unsupported and supported on silica at 423 K. Under these conditions NO was not absorbed and these authors observe the same IR band at 2265 cm^{-1} which they propose to be assigned to HNO_2^+.

There is strong evidence that the sorbed NO_x species is protonated. Yang and Chen have shown that exposure of NO saturated HPW to water produces the IR bands characteristic of $H_5O_2^+$, known to be present before NO absorption. Exposure to anhydrous ammonia produces ammonium ion in the HPW secondary structure [10]. These results indicate that the protons have remained in the structure and were not replaced by cationic species such as NO^+ or NO_2^+. Proton NMR data confirm that the protons remain [11,12].

Yang and Chen [10,15] have summarized arguments supporting the NOH^+ assignment. TGA and nitrogen mass balance studies supported the idea that the linkages were NO rather than NO_2. When NO^- or NOH^+ is formed from NO, which exhibits ν(N–O) at 1876 cm^{-1}, an electron is removed from an antibonding orbital, increasing the bond order from 2.5 to 3. From this argument, fully ionized NO^+ would be expected to have a band several hundred wave numbers higher than that of the gas, and in fact, ν(N–O) in free NO^+ is observed at 2300 cm^{-1} [16,17], only 35 cm^{-1} different from the N–O band observed here for NO in HPW. Thus, HPW bound NO^+ molecules represent a weakening of the bond by ca. 35 cm^{-1} with respect to free NO^+, consistent with protonation of the oxygen atom. Furthermore, temperature programmed desorption of the sorbed N–O species at slow heating rates yielded primarily NO. NO_2 and higher molecular weight species were below detection levels. NO_2^+ exhibits an asymmetric stretch at 2350–2375 cm^{-1} and an O–N–O bending vibration at 570 cm^{-1}. This low wave number band was not observed by Yang and Chen [10] or by Herring and McCormick [12]. Evidence for HNO_2^+ includes the facts that NO_2 is readily sorbed by HPW under anaerobic conditions while NO is only sorbed when oxygen is present [11]. Disproportionation and oxidation/reduction reactions occurring on the HPW surface (as opposed to in the secondary structure) have been proposed to explain the sorption of both NO and NO_2 as NOH^+ [12]. Based on these arguments we currently favor the NOH^+ assignment, although a more detailed study is required to resolve this controversy. We have undertaken a detailed in situ IR study of NO sorption by silica supported HPW in the present contribution.

2. Experimental

The silica support was a precipitated, acid washed silica obtained from BDH Chemicals. The surface area of this material was 140 m^2/g. The 12-tungstophosphoric acid was reagent grade from Aldrich. Samples of 2, 4, and 8 wt% tungsten loading (approximately 2.5, 5, and 10 wt% dry tungstophosphoric acid) supported on SiO_2 were prepared by wet impregnation. Samples were dried 24 h under vacuum at 393 K and stored in a dessicator. X-ray powder diffraction (XRD) patterns were obtained using a Rigaku diffractometer and Cu K_α radiation (λ=1.5432 Å). X-ray diffraction results were analyzed by the least squares method of Holland and Redfern [18] to obtain the bcc lattice parameter. Mean crystal size was determined from the most intense X-ray diffraction line width using the Scherrer equation. Surface areas were determined using nitrogen adsorption via the BET method, data were acquired on a Mircromeritics 2100E Accusorb. Solid state proton NMR experiments were carried out on a Chemagnetics CMX Infinity 400 NMR spectrometer by MAS. Samples were spun at 10 kHz in a 5 mm probe under a flow of dry air. Mixtures of O_2 in He and NO in He were purchased from Scott Specialty Gases. Infrared spectra were obtained by diffuse reflectance on a BioRad FTS-40 instrument with a high speed, liquid nitrogen cooled MCT detector and a Harrick diffuse reflectance attachment with a heatable, controlled atmosphere cell (KBr windows). The IR cell was connected to a gas flow system. Exact experimental conditions including temperature, gas composition, and time of exposure are described with the results.

For TPD-MS experiments a Cahn Instruments TG-131 thermogravimetric analyzer coupled to a VG Quadrupoles mass spectrometer were employed. The TGA instrument was used simply as a reactor, mass changes were not recorded. The catalyst sample (0.5 g) was suspended in the quartz pan. The temperature was increased from 298 to 423 K at 10 K/min under 10% O_2 in He, saturated (or nearly so) with water vapor at 298 K in some experiments. At 423 K, 1% NO in He was added producing a gas containing 0.3% NO, 7% O_2, balance He, saturated with water at 298 K, this flow was maintained for 40 min. After turning off the NO, the sample was held for 1 h and then the temperature was ramped at 50 K/min to 773 K and held for 10 min, all under 10% O_2/He saturated with water. The outlet gases from the reactor were continuously analyzed by MS.

3. Results

3.1. Catalyst characterization

X-ray diffraction data indicate that pure HPW, as received, contains a mixture of hydration states. Drying at 423 K is known to produce the hexahydrate in unsupported HPW [19] and this drying pretreatment was used before acquiring the XRD data used in lattice parameter determination. Calculated lattice parameters, listed in Table 1, do not vary with loading in the supported catalysts. However, the average value of 11.66 Å for the three supported catalysts is substantially smaller than the 12.15 Å we observe for unsupported HPW·6H_2O, and this last value is in good agreement with single crystal neutron diffraction results [19]. This shrinkage of the lattice in the supported catalysts indicates that fewer water molecules are present in the pseudoliquid phase relative to unsupported HPW·6H_2O. This also implies that an entirely different, hydrogen-bound secondary structure is formed in the supported catalysts at 423 K. This secondary structure still contains considerable water, but the water is bound to the protons and Keggin ions in a way that occupies less space. Mean crystal size was unaffected by loading in the range studied and all supported samples had nearly the same surface area, as noted in Table 1. The loadings considered here represent from 0.6, 1.2, and 2.4 theoretical monolayers of Keggin units for the 2%, 4%, and 8% tungsten loading catalysts, respectively. This can be shown by a simple calculation utilizing the fact that typical Keggin ions occupy 14.7 nm^2 [20].

Fig. 1 reports infrared spectra of the W–O and P–O region for unsupported and supported HPW dried at 423 K. For unsupported HPW, ν_{as}(P–O) is evident as a weak band at 1100 cm^{-1} with higher wave number shoulders. The most intense band is ν_{as}(W=O_t) at 1019 cm^{-1}. Two additional tungsten–oxygen stretches are also observed, ν_{as}(W–O_c) at 923 cm^{-1} and ν_{as} (W–O_e) at 861 cm^{-1}. Note that different band positions are obtained if HPW is mixed with KBr because of the formation of the potassium salt [12]. The position of these bands is in part determined by the bonding, or hydrogen bonding, of the Keggin ion to secondary structure species, in this case water. In HPW·6H_2O water is present as $H_5O_2^+$ bound to the terminal oxygen atoms [19]. For the supported mate-

Table 1
Lattice parameters (bcc), mean crystal size, and surface area for supported and unsupported HPW

Sample	Lattice parameter (Å)		Mean crystal size (Å) Room conditions	BET surface area (m^2/g)
	Calcined at 423 K	After NO at 423 K		
2% W/SiO_2	11.67	11.66	321	152
4% W/SiO_2	11.64	11.71	329	148
8% W/SiO_2	11.65	11.71	332	145
Unsupported HPW	12.15	11.78	—	—

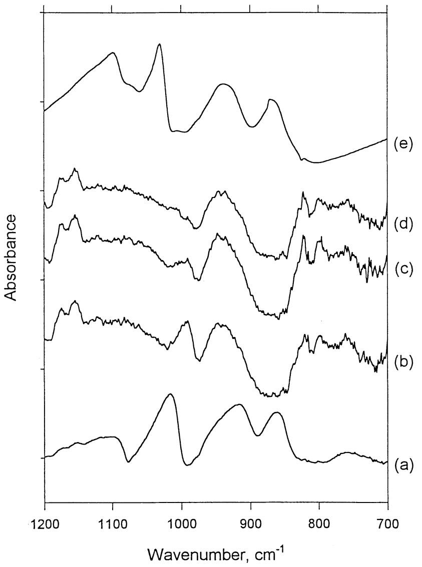

Fig. 1. Diffuse reflectance infrared spectra of (a) HPW·6H_2O, (b) 8% HPW on silica, (c) 4% HPW on silica, (d) 2% HPW on silica, and (e) HPW·<6H_2O prepared by drying at 623 K.

rials, all these infrared bands have shifted relative to the unsupported hexahydrate. Shoulders on the ν_{as}(P–O) envelope have become distinct peaks at 1176 and 1165 cm^{-1}, indicating some distortion of the symmetry of the Keggin ion. The ν_{as}(W=O_t) band has shifted from 1019 to 990 cm^{-1} and its intensity increases with increasing HPW loading. This shift in wave number may indicate that the secondary structure species are interacting more strongly with the terminal oxygen. Unbound ν_{as}(W=O_t) would be observed at 1074 cm^{-1} [12] and if present, is obscured by the broad feature in this region. The ν_{as}(W–O_c) band has shifted to higher wave number, 946 cm^{-1}. The band for ν_{as}(W–O_e) has shifted to lower wave number and split into two bands at approximately 822 and 800 cm^{-1}. For comparison a spectrum of unsupported HPW heated to 623 K is shown in Fig. 1(e). After treatment at this temperature HPW has much less than 6 water molecules per formula unit, and we have proposed that this species is HPW·3H_2O. The ν_{as}(W=O_t) and ν_{as}(W–O_c) (originally at 1019 and 923 cm^{-1}) have both split into two bands at 1074 (weak) and 1031 cm^{-1}, and 1006 (weak) and 940 cm^{-1}, respectively. This spectrum can be interpreted as H_3O^+ bound to O_t and O_c of the Keggin ion leaving some O_t and O_c unbound. The ν_{as}(W=O_t) and ν_{as}(W–O_c) are at significantly different positions than observed for the supported catalysts. Thus, the secondary structure is not simply being desiccated by the silica surface, but forms a new structure with water bonded to the corner and edge oxygen atoms, as well as the terminal oxygens. This results in a more compact structure with smaller lattice parameter, however the present results do not allow a more detailed description of the bonding in this structure. Hydroxyl groups on the silica surface are almost certainly involved in this new structure, as discussed below.

NMR spectra of these materials (also dried at 423 K) are presented in Fig. 2. Surface hydroxyl groups on the silica support are evident as broad bands at 1.9 and 2.7 ppm. Bronniman et al. [21] have assigned bands at 1.7 and 3.0 ppm in the ^{1}H CRAMPS spectra of silica gell to isolated and hydrogen bound surface silanol groups, respectively. A proton chemical shift of 9.3 ppm is observed for unsupported HPW·6H_2O, in good agreement with the results of Mastikhin and coworkers [19] but somewhat higher than the 7.7 ppm reported by Belanger and Moffat

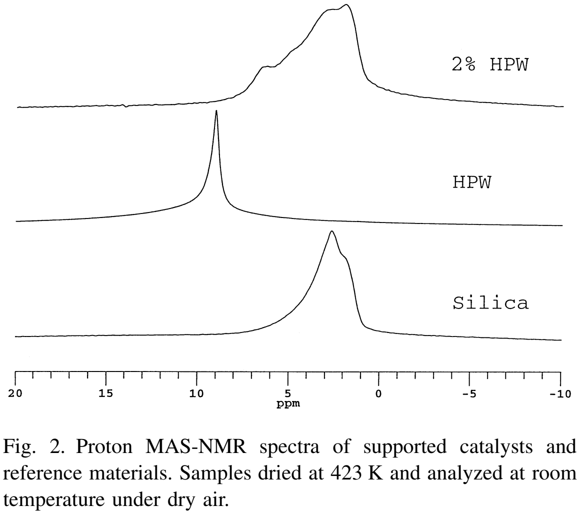

Fig. 2. Proton MAS-NMR spectra of supported catalysts and reference materials. Samples dried at 423 K and analyzed at room temperature under dry air.

[11]. This relatively high value of proton chemical shift is consistent with the strong acidity of this material [22,23]. At 2% loading of HPW on silica, the surface hydroxyl resonance at 2.7 is reduced in intensity relative to that at 1.9 ppm and new peaks are observed at 4.9 and 6.6 ppm. No proton resonance at 9.3 ppm is observed. Clearly the Keggin ion is strongly interacting with the surface hydroxyl groups of silica. This may occur by an exchange reaction leading to the formation of water and replacement of the surface hydroxyl anion by the Keggin anion or through interaction of a protonated hydroxyl group ($-OH_2^+$) with the anion [22,24]. Increasing loading produces further increases in the intensity of the resonance at 4.9 ppm, as also observed by Mastikhin et al. [22], with little or no change in the intensity of other proton resonances. This indicates the formation of a new type of proton, and confirms the conclusion from infrared data that a new secondary structure is formed in silica supported HPW. Mastikhin et al. [22] found that HPW loading of greater than 50% is required for the reappearance of the resonance at 9.3 ppm. Thus, the strong interaction between the support and HPW causes acid strength to be substantially reduced. At the 2% loading the formation of isolated or small clusters of Keggin ions interacting with surface hydroxyl groups can be envisioned, along with the crystals shown to be present by XRD. As loading is increased bulk HPW does not form. Instead a new secondary structure, strongly influenced by the support and the first sorbed Keggin ions is observed.

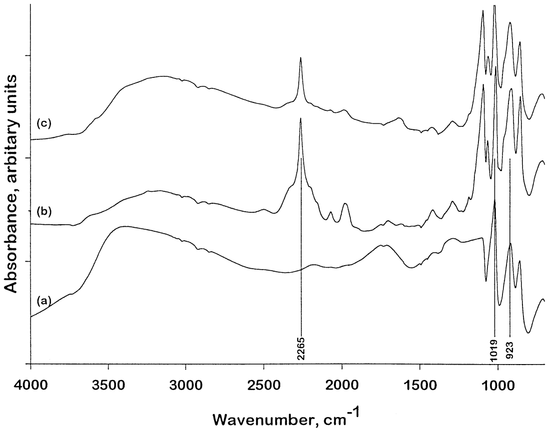

Fig. 3. In situ infrared spectra of HPW at 423 K: (a) under He, (b) under He after exposure to 0.5% NO, 5% O_2, balance He, and (c) after rapid heating to 723 K under He and cooling to 423 K.

3.2. *NO sorption and decomposition by unsupported HPW*

It has been proposed that bulk HPW·3NO is obtained upon exposure to NO (with O_2) at 423 K for an adequate length of time [10,12,15] and this yellow compound is stable in room temperature air for at least several hours. X-ray powder diffraction indicates shrinkage of the lattice to 11.65 Å, as reported previously [10,12] and shown in Table 1. Fig. 3 reports in situ IR spectra of HPW·$6H_2O$ under He/O_2 (a) and He/O_2/NO (b) at 423 K. The most prominent change upon NO sorption is the growth of new bands in the N–O stretching region with maximum absorbance at 2265 cm^{-1}. In agreement with Yang and Chen, we assign the most intense band to ν(N–O) in NOH^+ [10,12,15] as discussed previously. All bands associated with O–H vibrations have shifted or become reduced in intensity. These include the ν_{max}(O–H) band at 3419 cm^{-1} shifting to about 3240 cm^{-1} and loosing about half of its intensity as well as loss of intensity for the δ(O–H) band at 1730 cm^{-1}. The appearance of new bands in the ν(W–O) region suggests that NO is bound to the peripheral oxygen atoms of the Keggin ion. Upon temperature programmed desorption of sorbed NO from HPW the main desorbed product is NO, and a considerable quantity of nitrogen and oxygen are also observed [10,12,15]. Smaller quantities of N_2O and NO_2 are also observed.

We have recently performed a detailed in situ IR study of NO absorption by unsupported HPW [12]. A curve fitting analysis indicates that the ν(N–O) band is composed of a broad band at 2260 cm^{-1} and a narrower band at 2267 cm^{-1}. The presence of water in the pseudoliquid phase was required for NO absorption. Analysis of spectra obtained at different times during NO absorption indicate that NOH^+ is first coordinated by Keggin ions and a water molecule, as shown in Fig. 4 (A observed at 2267 cm^{-1}). Note that the simple structural drawing shows terminal and bridging oxygen atoms of the Keggin ion, the bonding of $H_5O_2^+$ to the Keggin ions is also shown. At longer contact times more water was displaced from the secondary structure and NOH^+ coordinated only by Keggin ions

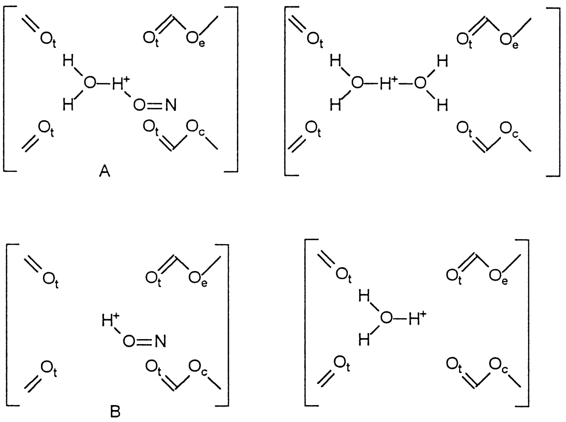

Fig. 4. Sorbed forms of NO and water proposed for supported and unsupported HPW.

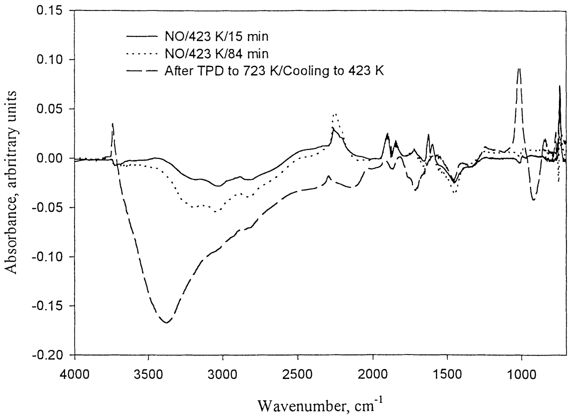

Fig. 5. In situ infrared spectra during NO sorption/TPD on 8% HPW on silica. NO absorption conducted under 0.5% NO, 5% O_2, balance He; TPD performed under He.

forms (B in Fig. 4, observed at 2260 cm^{-1}). The rest of the bands making up the envelope between 2350 and 2150 cm^{-1} are accounted for by bands at 2205 and 2153 cm^{-1} assigned to highly strained δ(O–H), confirmed by deuterium substitution [12]. Water remains in the structure after saturation with NO at 423 K and this water is proposed to exist as H_3O^+, whose bonding to the Keggin ions is shown in Fig. 4.

Fig. 3(c) shows an infrared spectrum of HPW after rapid heating to 723 K to desorb NO. Both ν(N–O) and δ(O–H) bands are reduced in intensity after heating indicating desorption of NO and water. Curve fitting analysis of the ν(N–O) region indicates a much smaller contribution from A at 2267 cm^{-1} relative to B at 2260 cm^{-1}, when compared to the sample before temperature programming.

3.3. *NO sorption and decomposition by silica supported HPW*

X-ray diffraction data indicate that upon exposure to NO the supported materials exhibit a small, perhaps insignificant expansion of the lattice, as noted in Table 1. Fig. 5 reports in situ IR results for NO absorption on the 8% HPW/silica sample. In this figure the spectrum of the starting catalyst sample has been subtracted as the background. Upon NO absorption negative peaks in the ν(O–H) region between about 3300 and 2900 cm^{-1}, as well as for δ(O–H) at 1730 cm^{-1}, indicate loss of water from these structures. New bands with maxima at 2264 and 2250 cm^{-1} appear. These indicate the formation of NOH^+, but at slightly different band positions than observed for unsupported HPW. A shoulder at about 2210 cm^{-1} is assigned to highly strained δ(O–H) by analogy to bulk HPW, although deuterium substitution experiments are necessary to confirm this assignment. The bands of gas phase NO are apparent at 1910, 1875, and 1856 cm^{-1} as these spectra were acquired under gas containing NO. New bands have also appeared at 1627 and 1599 cm^{-1} that can be assigned to adsorbed NO [25], or perhaps to anionic NO_x^{y-} species [26]. Upon rapid heating to 723 K much more water is lost, the original ν(N–O) and associated bands vanish but a new band appears at 2300 cm^{-1}. It is tempting to assign this band to NO^+, as discussed by Chen and Yang [10,16] although a new form of NOH^+ is also possible. Another intriguing possibility is that the 2300 cm^{-1} band is caused by adsorbed N_2. A similar band at 2300–2290 cm^{-1} has been observed for nitrogen adsorption on copper-exchanged zeolites [27,28]. A strong new band is observed at 1017 cm^{-1} indicating a change in the environment of the terminal $\nu_{as}(W{=}O_t)$ from its position at 990 cm^{-1} before NO absorption. Thus it seems likely that the sorbed NO moiety is somehow bonded to the terminal oxygen. Virtually identical results were observed for the 4% HPW/silica sample although peaks were less intense.

Infrared absorbance in the ν(N–O) region at various times of exposure to NO is reported in Fig. 6. At short contact times the 2264 cm^{-1} peak is most intense

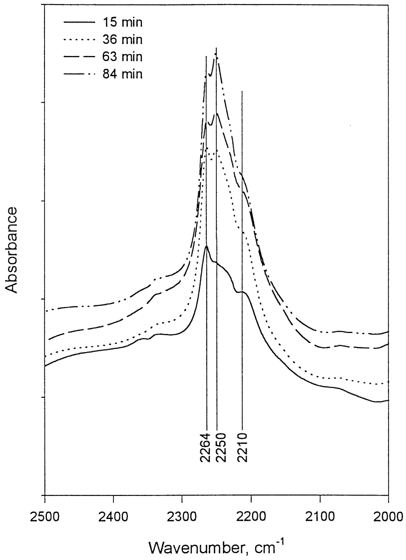

Fig. 6. In situ infrared spectra of 8% HPW/silica at different times of exposure to 0.5% NO, 5% O_2, balance He at 423 K.

suggesting that this species is formed initially. At longer contact time the absorbance maximum at 2250 cm^{-1} becomes most intense. As the spectra in Fig. 5 indicate a loss of water as NO sorption proceeds, the data in Fig. 6 suggest a picture similar to that observed for unsupported HPW. NO is proposed to sorb initially in a hydrated form (A) but converts to a dry form (B) over longer sorption times. For the supported catalysts the pseudoliquid phase structure is much different leading to the observation of ν(N–O) at different wave numbers.

The rate of NO uptake is significantly different for supported relative to unsupported HPW, as shown in Fig. 7. Here the integrated intensity of the total ν(N–O) band centered at roughly 2265 cm^{-1} is plotted versus time of exposure to NO and O_2. Intensity for the supported sample is much lower as this sample contains only a few percent HPW and is apparently sorbing fewer NO per Keggin ion. For unsupported HPW the reaction is essentially complete in 60 min. For the supported samples, exemplified by the 8% HPW sample in Fig. 7(b), there is an induction period followed by slow formation of the sorbed NO species. The reaction is not complete after even 120 min. Thus, silica supported HPW sorbs NO much more slowly than unsupported HPW.

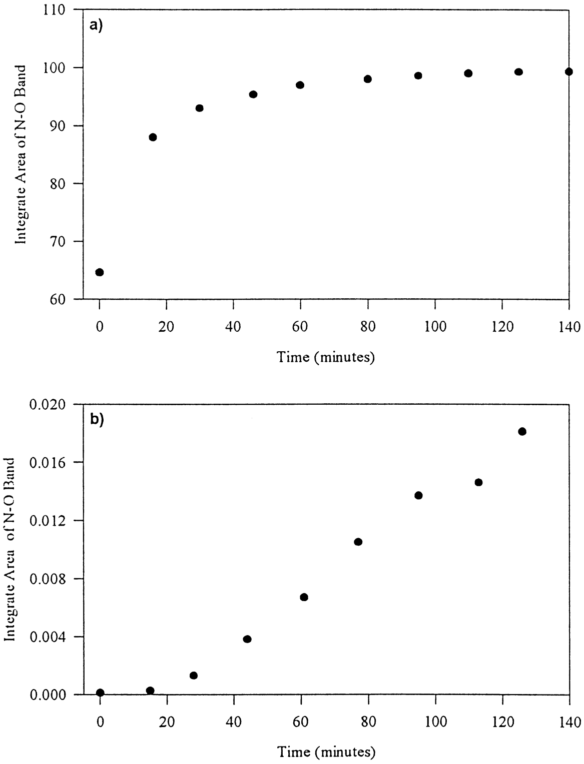

Fig. 7. Integrated area of ν(N–O) band at about 2265 cm^{-1} as a function of time of exposure to NO at 423 K, 0.3% NO, 7% O_2, balance He: (a) unsupported HPW; (b) 8% HPW/SiO_2.

Fig. 8(a) shows an expanded picture of the ν(N–O) region after NO sorption for HPW on silica at three loadings levels. These data suggest that the 2% HPW sample does not absorb a significant amount of NO as no ν(N–O) bands are observed. Calculations indicate that this sample contains only 0.6 of a theoretical monolayer of Keggin ions and all may be strongly interacting with silica surface hydroxyls. Perhaps higher loading and less interaction with the silica surface is required for NO absorption. Note that the weak band near 2345 cm^{-1} is most likely caused by failure to adequately purge CO_2 from the IR instrument. The previously described ν(N–O) bands at 2264 and 2250 cm^{-1} are observed in the higher loading samples. Fig. 8(b) presents spectra of the same samples after rapid heating to 723 K to desorb NO. Essentially no changes are observed for the 2% HPW sample. At 4% and 8% HPW a strong band is observed at 2300 cm^{-1} as well as a weaker feature at

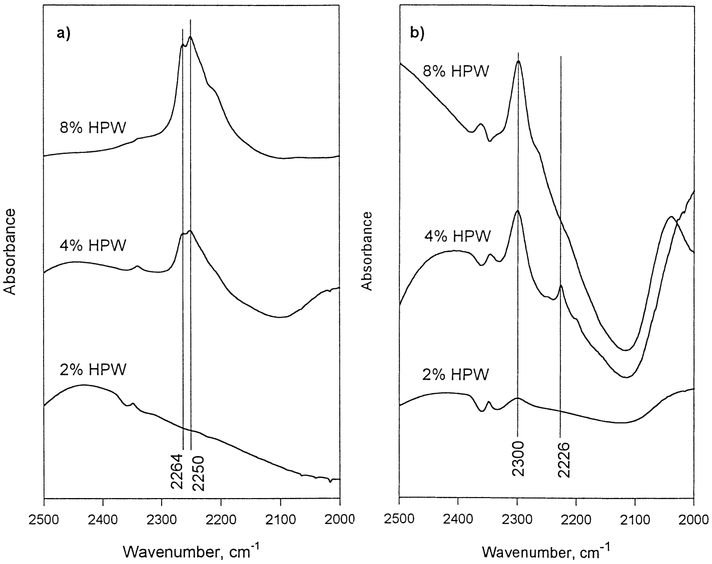

Fig. 8. In situ infrared spectra of the N–O stretch region for silica supported tungstophosphoric acid: (a) after NO absorption for 90 min at 423 K, 0.5% NO, 5% O_2, balance He, and (b) after rapid heating to 723 K and cooling to 423 K under He.

2226 cm^{-1} (shoulder in the 8% HPW sample). In the 8% sample the original band at 2264 cm^{-1} is also present as a shoulder. As noted above, the 2300 cm^{-1} band might be assigned to NO^-, NOH^+, or perhaps chemisorbed N_2. The 2226 cm^{-1} band is very close to the infrared absorption band of gaseous N_2O and may therefore be associated with that or similar species.

TPD-MS results are shown in Fig. 9 for NO, N_2, N_2O, and H_2O. NO_2 and HNO_3 were not observed in any of the desorption experiments. Note that TPD was performed in the presence of 7% O_2 and thus oxygen desorbing from the samples could not be detected. All desorption spectra in each figure are plotted to the same scale, they have been shifted by addition of a constant to produce the stacked plots. The desorption data support the contention that the 2% HPW material does not absorb a detectable quantity of NO as the level of nitrogen containing species desorbing was only slightly above the level of the blank (empty reactor). At higher loading, desorption of NO and other nitrogen containing gases occurs. Background corrected integrated intensities have been used to calculate an NO sorption capacity relative to the 8% HPW sample, which sorbed the most NO. This number is calculated from the sum of desorbed $NO+2N_2O+2N_2$. Sorption capacities, NO conversions (percentage of NO desorbing that is converted to products), and selectivities are listed in Table 2. Nitrogen and nitrous oxide desorption was only slightly above background level for the 2% sample with a selectivity of approximately 50% for each product, no NO was observed to desorb. For the 4%

Table 2
Results of TPD-MS experiments

Sample	NO sorption capacity[a]	Conversion of sorbed NO (%)	N_2 selectivity (%)	N_2O selectivity (%)
2% HPW/SiO_2	<0.1	100	50	50
4% HPW/SiO_2	0.3	90	50	50
8% HPW/SiO_2	1.0	70	80	20

[a] Relative to the 8% HPW sample and based on summation of TPD peak areas for NO, N_2 and N_2O, the only nitrogen containing species desorbed.

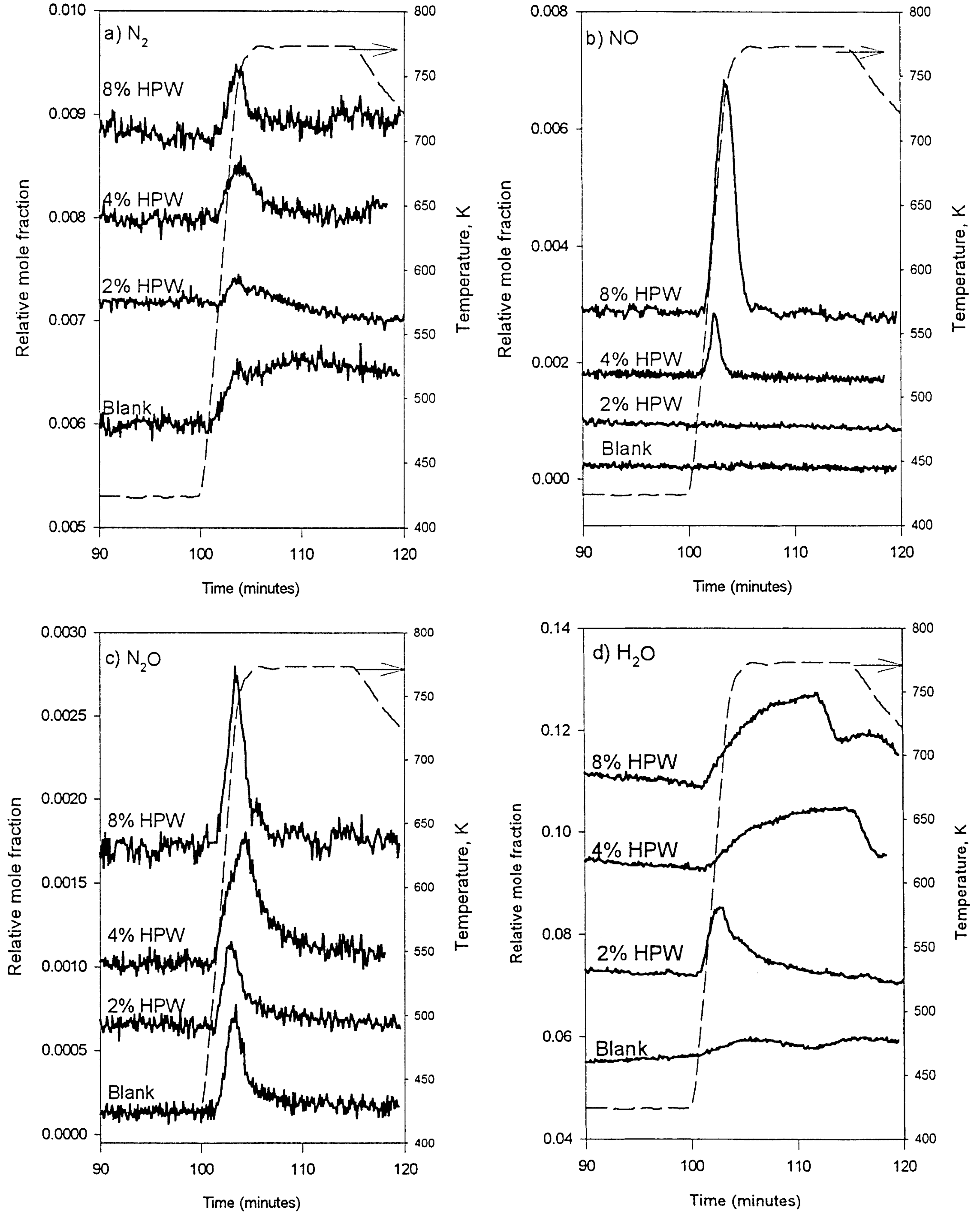

Fig. 9. TPD-MS results after NO absorption at 423 K, 50 K/min: (a) N_2, (b) NO, (c) N_2O, and (d) H_2O. Both absorption and desorption in the presence of 7% O_2, balance He, saturated with water vapor at 298 K.

and 8% samples the conversion of sorbed NO was 90% and 70%, respectively. Note that this is based on the total amount of nitrogen containing gases desorbed, although a small fraction of the sorbed NO remains on the catalyst after TPD (Fig. 5). Nitrogen selectivity was 50% for the 4% sample but was 80% at the 8% HPW loading. Water desorbed at approximately 575 K for the 2% sample, but was desorbed continuously over the temperature ramp for the higher loadings.

4. Discussion

Wu et al. [24] point out that there are three types of adsorbed Keggin ions, isolated, monolayered, and multilayered. Isolated Keggin ions can be viewed as forming via a ligand exchange mechanism with a surface hydroxyl group, M-OH:

$$\text{M-OH}_{(s)} + \text{H}^+_{(aq)} \rightarrow \text{M-OH}^+_{2(s)} \quad (3)$$

$$\text{M-OH}^+_{2(s)} + (\text{HPAn})^{-1}_{(aq)} \rightarrow \text{M(HPAn)}_{(s)} + \text{H}_2\text{O}_{(l)} \quad (4)$$

Or by formation of a surface complex:

$$\text{M-OH}^+_{2(s)} + (\text{HPAn})^{-1}_{(aq)} \rightarrow \text{M-OH}^+_2(\text{HPAn})^{-1}_{(s)} \quad (5)$$

These structures serve as a model for the strong interaction of the Keggin ion with surface hydroxyl groups of the silica support. Anions sorbed or coordinated in this way will have a different symmetry and distribution of electron density than in unsupported HPW. Thus, as loading is increased and clusters form, the arrangement of the Keggin ions and chemistry of the secondary structure will be influenced by the electronic structure of the isolated Keggin ions initially adsorbed. IR and NMR characterization of the supported catalysts examined here indicates significant differences in the secondary structure when compared to unsupported HPW. In particular, tungsten–oxygen and phosphorus–oxygen IR bands have shifted in a way that suggests coordination of the secondary structure water by edge and corner oxygen rather than terminal oxygen as in the bulk solid. Proton NMR data indicate that the highly acidic proton of bulk HPW, observed at 9.3 ppm and assigned to the $H_5O_2^+$ structure, does not exist in the supported samples at the loadings considered here. New resonances are observed at 4.9 and 6.6 ppm. The 6.6 ppm signal has the same intensity in the 2%, 4%, and 8% samples while the 4.9 ppm resonance increases in intensity as loading is increased. Thus the 6.6 ppm resonance is probably associated with the strong interaction of the Keggin ions with the silica surface hydroxyl groups, perhaps via a reaction similar to (5). The 4.9 ppm resonance can be assigned to protons in the secondary structure of clusters of Keggin anions. It is worth noting that 4.9 ppm is within experimental error of the 4.65 ppm resonance observed for pure water. Thus we tentatively propose that this resonance be assigned to H_3O^+ in the secondary structure. This species is smaller than $H_5O_2^+$ and might easily allow the structure to contract by roughly 0.5 Å as observed.

The 2% loading sample contains a high fraction of Keggin anions strongly interacting with the silica surface. These species apparently do not react with NO. The quantity of NO absorbed appears to increase in a non-linear way as HPW loading is increased, which supports the idea that Keggin ions directly interacting with the support do not absorb NO. The reactions of NO with HPW at higher loading are similar to those observed for bulk HPW, but with the formation of species having slightly different vibrational frequencies. Initially a hydrated species with ν(N–O) at 2264 cm^{-1} is observed which we propose is identical to species A in Fig. 4. As NO absorption progresses, water is displaced from the structure and the band at 2250 cm^{-1} grows in intensity. This species is similar to B in Fig. 4 although ν(N–O) is shifted lower by 10 cm^{-1}. The hydrated species A is not shifted significantly as ν(N–O) is interacting with the Keggin ion in a way very similar or identical to that for bulk HPW. For species B, ν(N–O) is more directly coupled to the Keggin ion electronic and vibrational structure producing the wave number shift.

The amount of NO absorbed per Keggin ion was not investigated in this study but appears to be less than absorbed by unsupported HPW. Clearly the rate of NO uptake was much lower for the supported samples. The NO sorption reaction can be viewed as an acid–base reaction, protonation of NO to form NOH^+. Proton NMR data indicate a much lower chemical shift and hence lower Brønsted acid strength for the supported samples. This lower acid strength, perhaps indicative of the presence of H_3O^+ rather than $H_5O_2^+$, explains the slower rate of this protonation reaction. The very slow rate of NO uptake exhibited by HPW supported on silica precludes use of this material, at the loading levels examined here, as a practical NO_x sorbent.

Silica supported HPW, at loadings greater than 4 wt% W, catalyzes reactions of NO under temperature programming conditions. The conversion of sorbed NO observed here was somewhat lower than reported for unsupported HPW at higher heating rate [12]. Increased heating rate is known to increase NO conversion. Nitrogen was a major reaction product, as also observed for unsupported HPW. Significant yields of N_2O have not been observed for unsupported HPW but selectivities to this product as high as 50% were observed here. Li and Armor [29] have reported similar reaction products (NO and N_2O) for temperature programmed desorption of NO from Cu-ZSM-5. They proposed that NO disproportionates and the products undergo decomposition:

$$3NO \rightarrow N_2O + NO_2 \qquad (6)$$

$$N_2O \rightarrow N_2 + O \qquad (7)$$

$$NO_2 \rightarrow NO + O \qquad (8)$$

HPW has been shown to react rapidly with NO_2 [11,12] and the surface of HPW has been shown to catalyze the disproportionation [12]. It is tempting to employ this mechanism to interpret the TPD results reported here. Under this scenario NO undergoes disproportionation during rapid heating. This reaction may occur in the secondary structure or on the surface of HPW. The N_2O produced then decomposes or desorbs. Note that an IR band is observed at $2226\ cm^{-1}$ after NO TPD and can be assigned to sorbed N_2O. As no NO_2 was observed to desorb, it is all decomposed. Oxygen atoms ultimately desorb as O_2. Unsupported HPW is apparently much more active for reaction (7) accounting for the difference in selectivities compared to the supported catalysts.

A number of important questions regarding NO decomposition by HPW remain to be answered. In particular, little is known about how the absorbed NOH^+ species actually reacts to disproportionate or to form nitrogen and oxygen. The global, disproportionation mechanism described above may prove a useful framework for investigating the role of NOH^+ in elementary reaction steps. It is also important to determine if HPW or other heteropoly compounds might be practically applied as NO sorbents/decomposition catalysts. While sorption rates (for unsupported HPW) and capacities appear to be adequate [15], the ability of HPW to retain activity over repeated sorption/desorption cycling under realistic flue gas conditions has yet to be determined.

5. Conclusions

The data indicate that for silica supported HPW in the range 2–8 wt% W a strong interaction with the support dramatically alters the heteropoly acid secondary structure. Keggin ions strongly interacting with the silica surface hydroxyls are proposed and these appear to be completely unreactive with NO. These strongly interacting Keggin anions affect the structure of subsequent layers as loading is increased. This interaction with the support and first sorbed layer of Keggin ions leads to a reduction in HPW acid strength through formation of H_3O^+ rather than the $H_5O_2^+$ observed in the bulk solid. NO absorption producing NOH^+ is observed for these samples but at a much slower rate than observed for unsupported HPW. As observed for bulk HPW, hydrated (A) NOH^+ is formed initially followed by formation of anhydrous NOH^+ (B). TPD of the sorbed NO produced a similar level of conversion as reported for unsupported HPW with formation of both N_2O and N_2.

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