DOI: 10.1002/ange.201205636

Nitrogen-Oxide Adsorption

Entropy-Driven Chemisorption of NO_x on Phosphotungstic Acid**

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Phosphotungstic acid ($H_3PW_{12}O_{40}$ or HPW), a Keggin-type heteropolyacid, has been proposed as an alternative to barium-based NO_x adsorbents.[1] HPW exhibits a high storage capacity (around 38 mg NO_x/g) and was also found to be sulfur-resistant. Curiously, desorption of the stored NO_x can be achieved by cooling.[2] Adsorptive separation usually is exothermic and driven by changes in enthalpy.[3] Only rare examples of adsorption processes driven by changes in entropy have been reported, and these mostly deal with adsorption of alkanes on zeolites.[4,5] Herein, we show using a complementary set of advanced experimental and theoretical techniques that the adsorption of NO_x on HPW is driven by changes in entropy. A detailed investigation of the adsorption mechanism with in situ XRD, neutron diffraction, and density functional theory (DFT) calculations on the free energy was conducted.

The nature of the adsorbed NO_x species and the exact adsorption site on HPW is still a point of discussion. Previous studies have used FTIR spectroscopy to determine the mode of NO_x adsorption. Chen and Yang[1d] claimed the adsorbed NO_x to be in the $(NOH)^+$ state, while Belanger and Moffat[1c] suggested a HNO_2^+ species. According to the latter authors, N_2O_3 sorption can take place when NO is adsorbed on previously NO_2-saturated HPW. Hodjati et al.[1b] proposed a $[H^+(NO_2^-,NO^+)]$ complex. In a previous study, we investigated the potential of a broad range of heteropolyacids for NO_x adsorption.[2] In a typical experiment, a gas mixture composed of at least NO, NO_2, and water was fed over a fixed bed of heteropolyacid adsorbent (Supporting Information, Figure S1). The onset of NO_x adsorption is at about 120 °C. Desorption is achieved by cooling of the saturated adsorbent to 80 °C. During NO_x uptake, equal amounts of NO and NO_2 are taken up, and during regeneration equal amounts of NO and NO_2 are released.

X-ray diffraction patterns of the HPW heteropolyacid were recorded at ambient and at elevated temperatures (105, 150, and 200 °C; Supporting Information, Figure S2). The patterns in absence of NO_x in the gas mixture are all identical, with a lattice constant of 12.15 Å that is typical of HPA hexahydrate crystals. Heating of the samples to the desired reaction temperature in a 5 % O_2 and 3 % H_2O atmosphere caused no change of the lattice constant. This is in accordance with earlier TGA and FTIR observations, and the observation that HPW hexahydrate is the active phase for NO_x adsorption.[2] ^{31}P MAS NMR spectroscopy also indicated the Keggin ion remains intact (Supporting Information, Figure S4). However, in absence of water in the gas stream, the lattice constant has been observed[6] to decrease to 11.78 Å already at a temperature of 170 °C. Marosi et al.[6] attributed this shrinking to the formation of a HPW trihydrate. Fournier et al.[7] however, did not mention significant changes in the X-ray diffraction pattern in this temperature region. Most probably the presence of water in the gas stream extends the presence of the HPW hexahydrate to higher temperatures, as already observed by thermogravimetric measurements.[2] But the addition of NO_x to the gas stream led to significant changes in the diffraction patterns: the lattice constant significantly decreases at temperatures as low as 150 °C. The resulting unit cell with a lattice constant of 11.78 Å corresponds remarkably to the value reported by Marosi et al.[6] for the trihydrate. Cooling of the NO_x saturated sample to 80 °C in a water-containing gas stream led to recovery of the original lattice constant of the starting compound (12.15 Å). Similar crystal changes were found with the silicotungstic acid (HSiW), which is also capable of NO and NO_2 co-adsorption.[2]

Ex situ XRD measurements performed at Hasylab/Hamburg were used for Rietveld refinement and Fourier analyses performed with the GSAS software package (Figure 1). Synchrotron measurements allowed verification of space groups and the location of heavy elements in the structure.

After desorption, the space group and position of the Keggin ions suggested the presence of the hexahydrate similar as found for the reference sample before NO_x adsorption. As the space group $Pn\bar{3}m$ was found, lattice constants at 25 °C and −265 °C were refined to 12.252 Å and

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[**] S.H. acknowledges FWO-Vlaanderen (Research Foundation Flanders) for a research grant. This work is supported by long-term structural funding by the Flemish Government (Methusalem Funding) and the Belgian government (IAP/PAI funding). V.V.S. and L.J. acknowledge the Research Board of the Ghent University (BOF) and V.V.S. is grateful to the European Research Council for funding (FP7 (2007-2013) ERC grant 240483). The computational resources for the DFT calculations were provided by Ghent University (Stevin Supercomputer Infrastructure). Dr. Clemens Ritter (ILL/Grenoble) and Dr. Manuel Hinterstein (Hasylab/Hamburg) are acknowledged for their assistance with the neutron and X-ray diffraction experiments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205636.

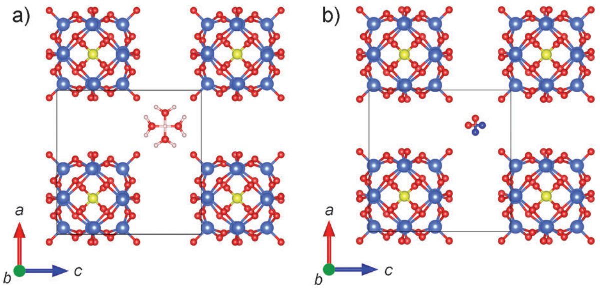

Figure 1. a) Refined structure of HPA hexahydrate (P yellow, W light blue, O red, H pink, N small dark blue spheres). Both possible orientations of the $H_5O_2^+$ species shown. b) Refined structure HPW with NO^+. Two of the possible four positions of guest molecules are shown.

12.177 Å, respectively. Keggin ions were found centered on 0.75 0.75 0.75, while residual electron density was observed around 0.75 0.25 0.75, where, according to the literature, a $H_5O_2^+$ species is located.[8] After NO_x adsorption a significantly smaller lattice constant was observed (11.697 Å at −265 °C), but the space group was retained. No assignment of the species trapped between the heavy Keggin units was attempted, although some electron density was observed on typical cation positions in the structure around 0.75 0.25 0.75. This position has been reported to often be occupied by cations in dehydrated Keggin salts, such as $K_3PW_{12}O_{40}$.[9] The synchrotron results were used as starting parameters for refinement of the neutron diffraction data collected on deuterated samples. The lattice constants obtained from synchrotron diffraction were fixed during refinement, and instead, the wavelength was left free to optimize. As already hinted at by synchrotron diffraction, the starting material clearly was identical to the structure of the hexahydrate as described in literature.[8] After desorption of the NO_x species trapped in the material, the same structure was found. In the structures a disorder of the orientation of the central phosphorous–oxygen tetrahedron was observed. After adsorption, the material contracted with the Keggin units in the same crystallographic positions as before, in agreement with synchrotron experiments. In the space between four terminal oxygen atoms of four Keggin units, a linear species with bonding distance of 1.14 Å was observed. FTIR spectra[2] and the observed bond length allowed identification of this species as a NO^+ moiety. An occupation of 92 % of this adsorption site by NO^+ was freely refined (Figure 1). Although NO_x adsorption was performed in presence of water, no evidence of any water present in the structure was found, which also was in agreement with previously performed FTIR investigations.[2] Owing to the symmetry of the space group, four equivalent positions of NO^+ rotated by 90° were possible (Figure 1). A test refinement in the space group $P4_2/nnm$ with reduced symmetry resulted in no improvement of the refinement quality. A similar disorder of the orientation of the central phosphate tetrahedron in the Keggin ions as observed for the hexahydrates was found during refinement. Using the refined structure as input for the refinement of the synchrotron data resulted in excellent refinement quality, so that soundness of the proposed structure and adsorbed species can be assumed.

These experimental observations were confirmed by DFT calculations on the various proposed structures. The calculated cell parameters for HPW hexahydrate were in good agreement with the values derived from the diffractograms. The cell was cubic, and the lattice constants support the diffraction results ($a=b=c=12.36$ Å, $\alpha=\beta=\gamma=90°$). Simulation of NO_x-saturated heteropolyacid also confirmed the experimental results ($a=b=c=11.70$ Å, $\alpha=\beta=\gamma=89.37°$) but the unit cell was no longer cubic. Whereas the XRD refinement localized the NO^+ species along the axes, DFT found them tilted and close, but not exactly on the crystallographic special position in the pores. However, these tilted orientations were not in contradiction with the diffraction results, as XRD averages over space and time, whereas the modeled cell is a representation of only one (infinitely repeated) unit cell at its lowest energy.

Based on the above mentioned structure refinement and earlier experimental evidence,[2] the following reaction mechanism is proposed: NO and NO_2 are adsorbed on the $H_3PW_{12}O_{40}\cdot 6H_2O$ structure in equimolar concentrations in the temperature interval 120–275 °C.[2] On carefully dehydrated HPW, NO_x sorption does not occur. However, NO_x uptake is observed on the heteropolyacid hexahydrate, even in absence of H_2O in the gas mixture.[2] NO and NO_2 can easily form N_2O_3,[5] which can combine with crystal water to HNO_2. This reaction has been observed earlier on dehydrated acidic ZSM-5 zeolites.[10] Strong acids can protonate nitrous acid, and the resulting $H_2NO_2^+$ is in equilibrium with NO^+ and H_2O.[10] Within the HPW hexahydrate, the occluded protonated water clusters serve as protonating agents [Reactions (1) and (2)].

$$2\,(\mathrm{PW}^*\ 3\,H_5O_2^+) + 3\,N_2O_3 \rightarrow 2\,(\mathrm{PW}^*\ 3\,H_3O^+) + 6\,HNO_2 + 3\,H_2O\uparrow \qquad (1)$$

$$2\,(\mathrm{PW}^*\ 3\,H_3O^+) + 6\,HNO_2 \rightarrow 2\,(\mathrm{PW}^*\ 3\,NO^+) + 12\,H_2O\uparrow \qquad (2)$$

The nitrosonium ion balances the negative charge of the heteropolyacid, and water molecules formerly associated to charge balancing protons are released. The absence of water molecules on the NO_x saturated adsorbent is reflected in the structure refinement where no H_2O molecules could be assigned. This mechanism is similar to NO and NO_2 co-adsorption on acid ZSM-5 zeolites, where acid zeolitic protons are exchanged for nitrosonium cations.[11] During NO_x release in humid gas streams, the nitrosonium cation is rapidly hydrolyzed, yielding H^+ and HNO_2.[12] As HNO_2 is unstable, NO and NO_2 are released in the gas phase, as has been observed experimentally.[2]

To obtain mechanistic insight into the driving factors for the NO_x uptake in terms of temperature, free-energy calculations were performed for the adsorption/desorption process (computational details are given in the Supporting Information). The reaction enthalpy at 170 °C (ΔH) for the NO_x chemisorption is positive, yielding a value of +811 kJ per unit cell, indicating that the reaction is enthalpically unfavorable. The overall process is dictated by the free energy

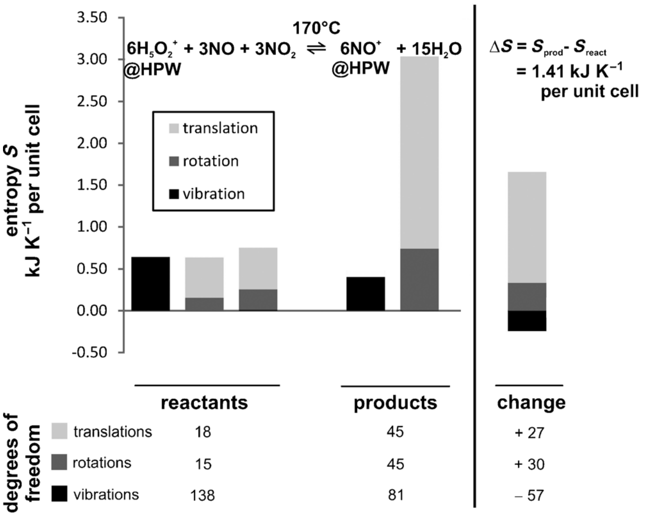

Figure 2. Entropy contributions and the reaction entropy (ΔS) for $6H_5O_2^+ + 3NO + 3NO_2 \rightleftharpoons 6NO^+ + 15H_2O$ in HPW at 170 °C. $\Delta S = S_{prod} - S_{react} = 1.41$ kJ mol^{-1} per unit cell. The loss in vibrational entropy during the reaction is more than compensated by the release of additional translational and rotational degrees of freedom and the entropy associated with these motions.

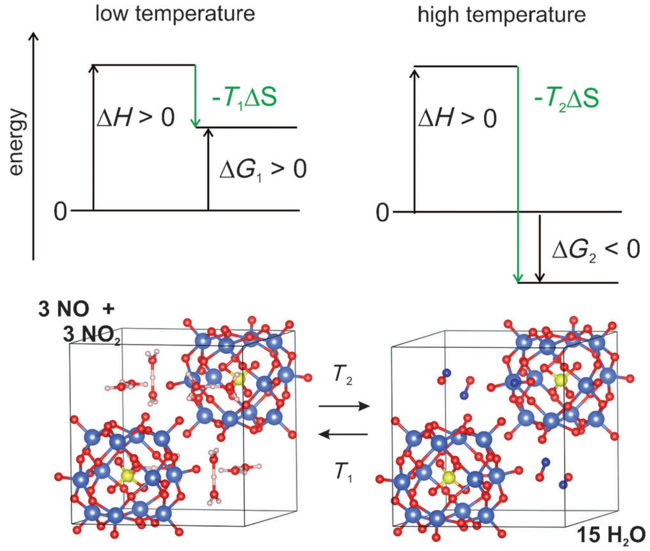

Figure 3. At low temperatures T_1, the reaction free energy ΔG_1 is positive, favoring the existence of the HPW hexahydrate. If however the temperature is high enough, $-T_2\Delta S$ will be sufficiently large to yield a negative reaction free energy ΔG_2 and allow the chemisorption of NO_x.

change, and as a substantial amount of water molecules are released during the reaction, the entropy contribution may be expected to be determining for the adsorption/desorption process. Figure 2 shows the individual entropy contributions for reactants and products and the reaction entropy ($\Delta S = S_{prod} - S_{react}$) at 170 °C, the temperature at which NO_x adsorption occurs experimentally. The separate contributions to the entropy originating from the translational, rotational, and vibrational degrees of freedom are also indicated in Figure 2.

In the reactant state, six hexahydrate ions are located between the Keggin ions, whereas in the product six NO^+ species are trapped between the Keggin ions. Therefore, 57 vibrational degrees of freedom are lost during the reaction, leading to a decrease of the vibrational entropy. The vibrational part is negligible for NO, NO_2, and H_2O, but is significant for the $H_5O_2^+$ and NO^+ moieties in the HPW lattice. This decrease is more than compensated by the release of 15 water molecules, leading to 27 and 30 additional translational and rotational degrees of freedom (detailed information on the various degrees of freedom may be found in the Supporting Information). The translational and rotational entropy per H_2O molecule in the gas phase is lower than per NO_2 or NO molecule, but the increase in the number of gas-phase molecules gives rise to an overall positive translational and rotational entropy change. The overall adsorption of NO^+ species is characterized by an entropy change ΔS of 1.41 kJ/K at 170 °C. The entropy is of course temperature-dependent, but the variations on the given value are small in the temperature range of interest. The same holds for the reaction enthalpy ΔH.

The thermodynamic cycle for the NO_x chemisorption is shown in Figure 3. Both the reaction enthalpy and reaction entropy are positive. The NO_x chemisorption will only occur when the reaction free energy is negative. According to our calculations, this will occur at temperatures T_2 that are higher than a given threshold value and for which the entropic contribution to the free energy $-T_2\Delta S$ is able to compensate for the positive values of ΔH (Figure 3). At lower temperatures T_1, the entropic contribution is not large enough, resulting in a positive reaction free energy ΔG_1 and favoring the existence of the HPW hexahydrate. Our calculations predict a threshold temperature for adsorption of 300 °C, which is higher than the experimental value of 170 °C but is acceptable given the various assumptions in the theoretical model.

In conclusion, mechanistic information concerning the adsorption mechanism of NO_x on HPW Keggin-type heteropolyacid was obtained by a variety of ex situ and in situ experimental techniques and theoretical free-energy calculations by means of DFT. Ex situ and in situ synchrotron X-ray diffraction and neutron diffraction the adsorbed state was identified as an NO^+ species trapped between the Keggin ions. Interestingly, the NO_x-saturated adsorbent is devoid of adsorbed water molecules. The free-energy calculations indicated that the adsorption process is entropy-driven, as more gas molecules are released than adsorbed by substitution of $H_5O_2^+$ with NO^+ species. Regeneration of the adsorbent by cooling leads to water adsorption, which triggers the hydrolysis of NO^+ and restoration of the HPW hexahydrate. The apparent co-adsorption and desorption of NO and NO_2 is readily explained by the proposed adsorption mechanism involving formation of unstable HNO_2 and $H_2NO_2^+$ reaction intermediates. The chemisorption of NO_x on an acidic adsorbent is entirely different from the nitrate formation mechanism observed on basic adsorbents, such as barium oxide. The concept of NO_x trap regeneration by cooling may be exploited in new types of exhaust-gas purification systems.

Experimental Section

The HPW heteropolyacid used is commercially available (Fluka). NO_x adsorption and desorption was performed as described elsewhere.[2] For the neutron-diffraction experiments, D_2O instead of H_2O was added to the gas mixture. NO_x concentrations were measured using an internally heated chemiluminescence detector (Eco Physics CLD 700Elht). X-ray diffraction patterns were recorded at the beamline B2 (HASYLAB/DESY Hamburg). As detector the imaging plate OBI detector was used.[13] For the ex situ measurements, powder samples from the NO_x adsorber unit were sealed in 0.5 mm glass capillaries (Hilgenberg) filled under a N_2 atmosphere and transferred to the beamline. The experimental set-up for the in situ measurements consisted of a capillary sample holder (0.7 mm quartz capillaries, Hilgenberg). Neutron diffraction was carried out at the ILL (Grenoble/France) at beamline D2B with a wavelength at 1.6075 Å on deuterated HPW during different stages of NO_x adsorption/desorption cycles. The deuterated material was prepared according to published procedures.[14] CIF files of the refined patterns are available at the Fachinformationszentrum Karlsruhe (CSD number 424920 and 424921). DFT calculations were performed using the periodic DFT code VASP (Vienna Ab Initio Simulation Package).[15] This code uses projector-augmented waves and a plane wave basis set to describe the electron density. All calculations were performed with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.[16] The entropy contributions were calculated using a normal mode analysis and a Partial Hessian Vibrational analysis (PHVA) for the adsorbed species.[17]

Received: July 16, 2012

Keywords: chemisorption · density functional calculations · entropy-driven adsorption · heteropolyacids · nitrogen oxides

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