Zeolites

Adsorption Chemistry of Sulfur Dioxide in Hydrated Na–Y Zeolite**

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Na–Y is one of the oldest known synthetic zeolite materials. Like zeolite X, it has the faujasite framework topology. The framework structure of zeolites Na–X and Na–Y extensively was studied by diffraction methods[1a,b] and the positions of exchangeable cations in dehydrated faujasites are well documented.[1c] Positions and occupation numbers of sodium cations in Na–Y dehydrated by evacuation[2a,b] and drying in gas streams[2c] were derived by solid-state NMR spectroscopy. Neutron- and X-ray-diffraction techniques revealed the presence of guest molecules interacting with the sodium ions, which results in a reorganization of the cation distribution.[1a,3a,3b] The presence of water molecules in the structure has a strong impact on position and occupation numbers of sodium atoms.[5,4a,b,c] Exposure of Na–Y zeolite to a gas mixture containing 5–10% water at 250 °C results in a water content of 50–60 water molecules per unit cell.[5] These water molecules interact with the sodium ions of the host to form a complex water–cation structure. The water–sodium arrangement consists of chains of alternating SV and SIII cations, bridged by water molecules. Additional water molecules associated with cations on SII positions stabilize this structure. When nitrogen oxides are present, these can reversibly be inserted into the water–cation net as N_2O_3 (Figure 1), which characterizes Na–Y as an exceptional NO_x storage compound.[5] On Na–Y the NO_x is physisorbed as N_2O_3 that can be conveniently released in a pressure-swing process by using hydrated, inert gas.[5,6] Adsorbents and catalysts for environmental applications have to withstand sulfur oxides. SO_2 is the main sulfur compound in exhaust gas. Even with the stringent regulations on the maximum tolerated sulfur content of diesel and gasoline fuels, the minute concentrations of SO_2 in the exhaust gas still pose problems of poisoning the catalyst within the required lifetimes.[7] When operated in a pressure-swing process for NO_x removal from engine exhaust, Na–Y zeolite is exceptionally resistant to SO_2.[5,6b] The reason for this behavior was not known. Literature on SO_2 adsorption in zeolites is mostly related to the adsorption of pure SO_2.[8] Studies that dealt with SO_2 adsorption in the presence of other relevant gases such as water, carbon dioxide, and NO_x[9] did not provide decisive conclusions as to the position of adsorbed SO_2 molecules in a Na–Y zeolite that had been exposed to exhaust gas. The data suggested a strong dependence on hydration level.

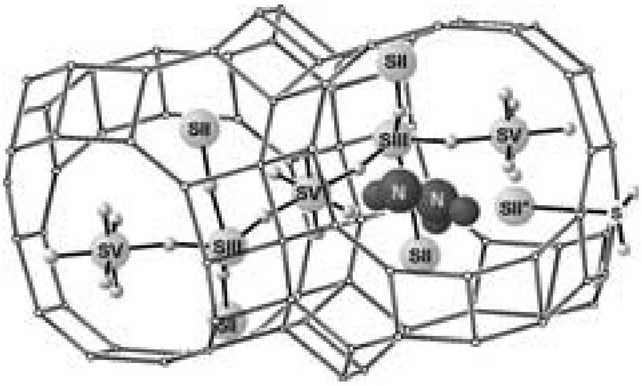

Figure 1. Illustration of the refined structure of SO_2 in Na–Y zeolite in the presence of water and NO_x. For clarity, oxygen atoms of the zeolite framework have been omitted. Sodium cations are labeled SII, SII*, SIII, and SV according to their position. The small spheres are oxygen atoms of water molecules that bridge sodium cations or are from the refined H_2SO_3 molecule. The darkly shaded N_2O_3 molecule has not been refined but has been inserted based on a previous refinement.[5] The figure shows that the presence of H_2SO_3 in the structure does not sterically encumber NO_x adsorption when NO_x is N_2O_3.

We brought an Na–Y zeolite (silicon/aluminum ratio of 2.6) into contact with a gas mixture at 250 °C, quenched it to room temperature, and transferred a small amount into a sealed capillary for transmission XRD studies. Contact of the sample with the atmosphere was carefully avoided. When the zeolite was brought into contact with SO_2 in the absence of water, no strict localization of sulfur dioxide was observed.

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Rietveld refinement of the XRD of this sample resulted in a satisfactory profile fit; only the host framework and the sodium cations were considered. However, an elevated residual electron density in the supercages in front of the six-ring windows was detected. This was in agreement with previous studies of the position of SO_2 in dehydrated faujasite zeolites, in which the preferred occupation of SII* sites by sulfur dioxide was reported.[4c] In the work presented herein, we encountered a different situation when water was present; the refined structure of Na–Y saturated with SO_2 revealed that the sulfur was now located in the six rings of the sodalite cages flanking supercages (Figure 2).[10] A close inspection of the observed and refined electron density in the vicinity of this position revealed two symmetrically independent electron-density maxima within bonding distance to the sulfur atom (Figure 3). One of the two maxima is tripled by the threefold symmetry of the cubic space group of the host. Examination of bond length and angles and the refined occupation numbers led to the identification of this entity as sulfite. One oxygen atom of the sulfite molecule points straight into the supercage, and interacts with a sodium cation on SII*. Of the three symmetrically equivalent positions, only two are occupied and point to O4 atoms of the faujasite six ring. The distance between O4 and the oxygen atoms of the sulfurous acid of 1.93 ± 0.04 Å, and observed electron density between the oxygen atoms indicate hydrogen bonding of both hydroxy groups. In this arrangement the sulfurous acid molecules are not dissociated. Free sulfurous acid is known as an unstable molecule. Its presence in the zeolite can only be explained by its strong interaction with, and stabilization by, the host. The coincidence of observed and theoretical bond lengths and angles of free H_2SO_3 is surprisingly good.[11] The distance from the sulfur atom to the doubly bonded oxygen atom O31, which points into the supercage was determined to be 1.493 Å compared to the theoretical value of 1.496 Å. The distance between hydroxy oxygen atoms (O32 and O33) and sulfur was observed to be 1. 93 ± 0.02 Å compared to theoretical values of 1.690 and 1.695 Å. The bond angles between O33-S-O31 and O32-S-O31 of 103 ± 3° are close to the theoretical value of 107°. The angle between the hydroxyl groups, however, was observed to be larger than calculated, namely, 116° compared to 107°. This discrepancy may be caused by the hydrogen bonding to framework oxygen atom O4, which results in increased negative charge on O32 and O33 and the presence of a repulsive force between these two atoms. In this structure sulfur assumes a typical cation position (SII) in the zeolite framework. In sulfurous acid, the sulfur atom is indeed positively charged, which supports the experimental observations. Another strong support for the identification of H_2SO_3 within the Na–Y structure is the previous observation of the UV adsorption band at 205 nm usually assigned to a hydrogen sulfite species in the investigated sample.[6b,9a,12]

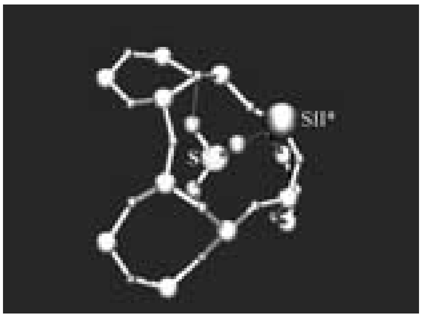

Figure 2. Refined position of the sulfite group in the six ring of hydrated Na–Y. One sulfite O atom is in interaction distance with a sodium ion on the SII* position. The distance from the other two sulfite O atoms to framework oxygen atoms suggest hydrogen bonding.

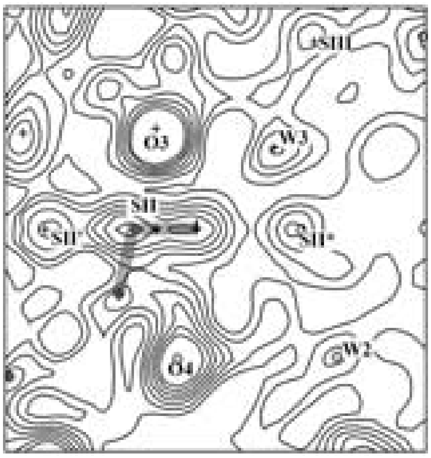

Figure 3. Observed electron density map (mapsize: 10 Å) before last-cycle refinement. Shown is a side-view of the six rings that containing the sulfite group (marked in grey). Water molecules are labeled W, cation sites are labeled SII and SIII* according to their position. Electron density between framework oxygen O4 and oxygen atoms of the sulfite group suggest hydrogen bonding.

The position of the sulfurous acid molecule in the six-ring window of the supercage has only slight influence on the cation and water distribution in the host. The SII* cation, which interacts with the nonprotonated oxygen atom of the sulfurous acid, is shifted by 1.2 Å into the supercage. For the stabilization of the SV–SIII chain of interlinked sodium ions and water molecules, only two of the four possible SII sites per supercage are necessary, which means that theoretically up to two SO_2 molecules per supercage can be adsorbed as H_2SO_3 on the observed site without disturbing the water–cation chain necessary for reversible NO_x adsorption. This theoretical value translates to 80 mg of SO_2 per gram of adsorbent. The shift of the SII cations into the supercage should have, if any, a beneficial influence on the adsorption of N_2O_3, which itself is known to shift the SII cation into the supercage to a position close to the cation position observed in the presence of H_2SO_3. These results show that SO_2 can be adsorbed independently of the water–cation structure, whereas N_2O_3 is incorporated into the water–cation network by replacing three water molecules. Too high loadings of sulfur-dioxides, however, break down the water–cation net either by replacing the two necessary SII cations or by assuming a new position. In any case the adsorption capacity for NO_x should drastically decrease as has been observed previously.[7] This observation explains the experimentally proven advantage of using short adsorption–regeneration cycles to prevent deactivation by sulfur oxides of Na–Y zeolite as a NO_x storage material.[7]

In summary, Na–Y zeolite was brought into contact with sulfur dioxide and water vapor at 250 °C. Rietveld refinement of the XRD patterns of the zeolite revealed the formation of sulfurous acid molecules at a specific site of the Na–Y zeolite cage. This discovery is particularly relevant to environmental catalytic applications that involve faujasite-type zeolites. Na–Y zeolite was recently identified as an effective DeNOx catalyst for exhaust gas after-treatment systems[13] and as a sulfur-tolerant NO_x trap.[5] The sulfur resistance of Na–Y zeolite can now be explained by the reversible formation of sulfurous acid molecules at locations in the zeolite cages remote from the NO_x adsorption sites. This study shows that Rietveld refinement of guest molecules in zeolites can be a powerful tool to elucidate complex molecular interactions inside porous crystalline host materials on an atomic level.

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[10] The powder-diffraction pattern was recorded at room temperature on a D5000 diffractometer in Debye–Scherrer geometry. As the X-ray source served a rotating anode with a Cu target, a Goebel mirror was used to obtain a parallel beam. Residual β-radiation was removed with a Ni filter. A scintillation detector was used to record the data set (4–70° 2Θ, 0.02° steps). The sample was sealed in a capillary (inner diameter 0.7 mm). Rietveld refinement was performed with GSAS (Rp = 1.6 %, Rwp = 2.5 %). Further details on the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; email: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413809.

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