Thermochimica Acta, 114 (1987) 139–144
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ADSORPTION OF NITROGEN AND WATER VAPOUR ONTO GOETHITE SURFACES

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SUMMARY

The interaction of nitrogen and water vapour with surfaces of goethite have been studied using volumetric adsorption technique. BET areas for nitrogen and water are 72 m^2g^{-1} and 45 m^2g^{-1}, respectively. Hysteresis behaviour differs markedly. Analysis of the isosteric heat of adsorption shows that nitrogen is physisorbed while water initially reacts with reactive (dehydroxylated) sites.

INTRODUCTION

Various methods of vapour adsorption have been applied for the characterization of samples of microcrystalline goethite (α-FeOOH). Mostly these methods aim at a characterization of the surface in terms of a specific surface area and space volume and size distribution of the pores (e.g. refs. 1-4). However, only few studies have been reported aiming at the thermodynamic parameters of the vapour/solid interaction (ref. 5).

In the present work the adsorption of nitrogen and water vapour onto synthetic goethite has been studied at different temperatures. In as much as hydroxyl groups and Lewis acid sites have been found on surfaces of goethite (ref. 6), it is expected that the two gasses will behave differently.

METHODS

Sample preparation

Synthetic goethite was grown from a partially neutralized iron nitrate solution (OH/Fe=2.0) by aging at room temperature for 450 days. Details of the synthesis are similar to sample 1 in ref. 7.

Sample characterization

Powder x-ray diffraction of the sample revealed only the presence of goethite. Transmission electron micrographs showed the presence of aggregates of closely packed lath-shaped particles. Measurements on a few singly lying particles indicate sizes of approx. 80x20x6 nm^3 (Fig. 1).

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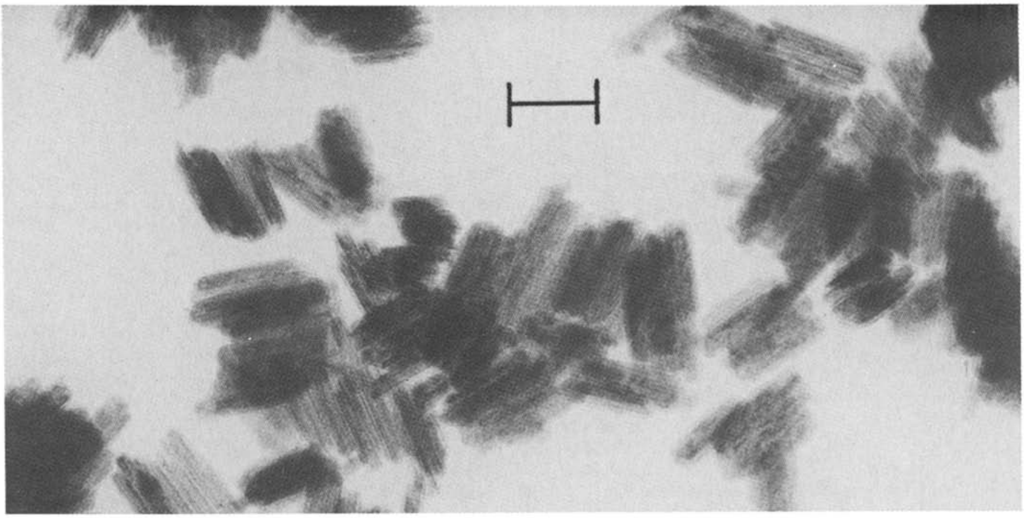

Fig. 1. Electron micrograph of goethite. Scale bar is 50 nm.

Vapour isotherms

Vapour isotherms were obtained using an all metal volumetric ultrahigh vacuum apparatus with a graded seal Pyrex glass sample vessel. The residual pressure of the system was approx. 10^{-7} Pa. Equilibrium pressures were measured by capacitance manometry. Further details on the apparatus are given in ref. 8. The dead space was determined using helium gas at 77.62 K and 273.15 K. Nitrogen and helium were of 99.9992% and 99.9996% purity, respectively, and water was doubly bulp-to-bulp destilled in the ultrahigh vacuum vessel. Prior to adsorption the sample was degassed to the residual pressure by pumping overnight at room temperature. During experiments the sample was held within ±0.10 K in a thermostat. Equilibrium times for water were long (several hours) whereas equilibrium pressures for nitrogen were obtained within minutes. Sample weights were typically 0.5 g.

RESULTS AND DISCUSSION

The adsorption isotherms of nitrogen onto goethite at 77.58 K and 87.50 K are shown in Figs. 2 and 3, respectively. The inflexion point observed at high relative pressure in Fig. 2 indicates that the isotherm is a mixture of a Type II and Type IV isotherm in the BET classification (ref. 9). The desorption hysteresis in Fig. 2 at high relative pressures indicates the presence of open-ended cylindrical macropores. Multiple runs have shown the nitrogen

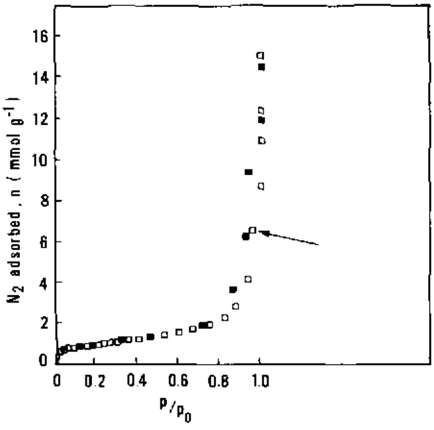

Fig. 2. Adsorption isotherm of nitrogen onto goethite at 77.58 K. □: adsorption, ■: desorption. The arrow indicates the position of the inflexion point.

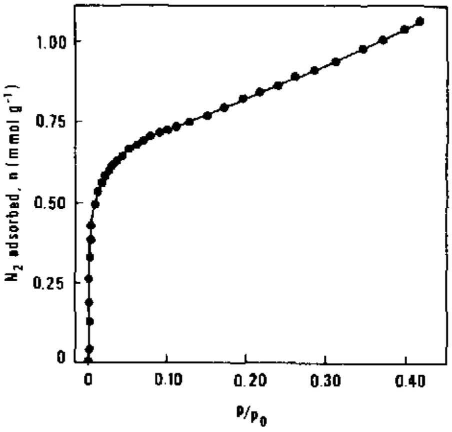

Fig. 3. Adsorption isotherm of nitrogen onto goethite at 87.50 K. ●: adsorption.

adsorption isotherms to be highly reproducible. Type II adsorption isotherms for nitrogen onto goethite have been observed preciously (refs. 2-4).

Using the BET-equation (ref. 9) the specific surface area and c-values for nitrogen adsorption onto goethite have been calculated. Cross-sectional areas of 0.162 nm^2 and 0.169 nm^2 for the nitrogen molecule were used for the calculation at 77.58 K and 87.41 K, respectively. The BET-plot obtained using data from Fig. 2 is shown in Fig. 4; correlation coefficients in the pressure range $0.01 < p/p_0 < 0.30$ are high (0.99994 or better). It is seen that the BET-parameters for nitrogen adsorption (Table 1) are identical at the two temperatures.

The adsorption isotherms for water onto goethite at relative pressures up to approx. 0.9 at 293.13 K and 298.41 K are shown in Figs. 5 and 6, respectively. The water adsorption isotherms are of Type II. Contrary to nitrogen, the water isotherms show hysteresis extending to low relative pressures (Fig. 7). A previous investigation has found the water adsorption to be fully reversible (ref. 5).

Using a cross-sectional area of 0.108 nm^2 for the water molecule the BET parameters for the water adsorption isotherms have been calculated. The BET-plot obtained using data from Fig. 5 is shown in Fig. 4. Correlation coefficents for water adsorption are reasonably (0.9992 in Fig. 4), but consistently smaller then for the nitrogen adsorption isotherms. Although only one experiment was conducted at 298.41 K we conclude that the specific surface area determined by water adsorption is independent of temperature, but the c-value changes with

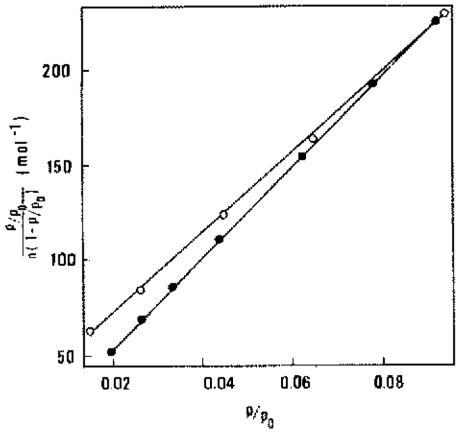

Fig. 4. BET-plots from nitrogen (77.58 K) and water (293.15 K) adsorption. ● :nitrogen, ○ :water.

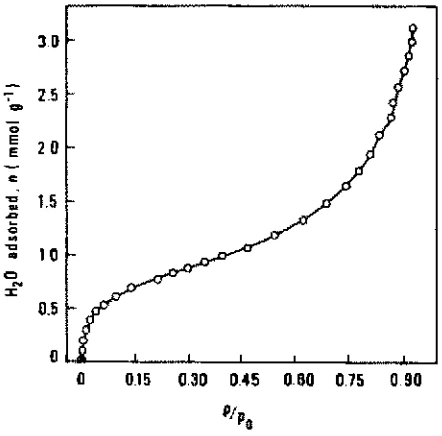

Fig. 5. Adsorption isotherm of water onto goethite at 293.13 K. ○ :adsorption.

TABLE 1

Specific surface area, A, and BET values, c, from BET-plots of nitrogen and water vapour adsorption onto goethite at different adsorption temperatures, T.

	N_2		H_2O	
T (K)	77.58±0.05	87.41±0.05	293.13±0.10	298.41±0.10
A (m^2g^{-1})	73.0±2.0	71.6±2.0	45.0±2.0	47.7
c	260±50	245±40	50±10	150
number of runs	5	4	4	1

temperature (Table 1).

A comparison of the specific surface area as determined by the two gasses (Table 1) shows the water area to be considerably smaller than the nitrogen area. To investigate the gas/solid interaction further we have calculated the isosteric heat of adsorption (Fig. 8) from plots of coverage versus pressure. It is seen that the isosteric heat of adsorption for nitrogen decreases as the coverage approaches the first monolayer, whereafter it increases slightly, the absolute value being close to the heat of liquefaction of nitrogen. Linear extrapolation towards zero coverage indicates a max. of 22.5 kJ mol^{-1}. These results indicate that nitrogen is physisorbed onto the surface. For water, however, the isosteric heat of adsorption is negative at low coverage, approx. nil at the monolayer and approaches the heat of liquefaction at two monolayers. This result indicate that also processes other than chemisorption and physisorption are of importance in the formation of the first water layer whereas the following layers are formed by condensation. We tentatively explain the behaviour of water as due to the surface of goethite being rendered more

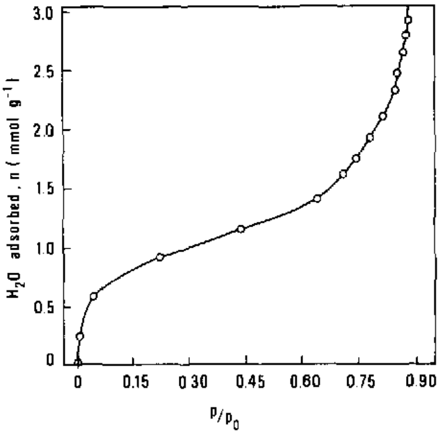

Fig. 6. Adsorption isotherm of water onto goethite at 289.41 K. ○: adsorption.

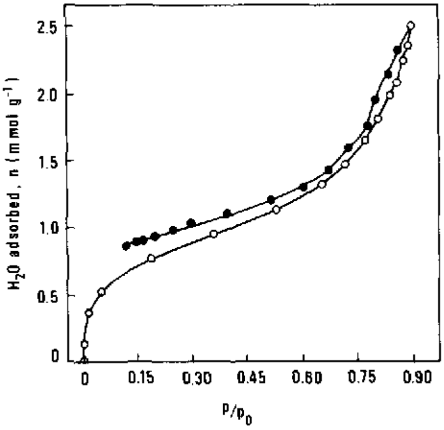

Fig. 7. Adsorption isotherm of water onto goethite at 293.13 K. ○: adsorption, ● : desorption.

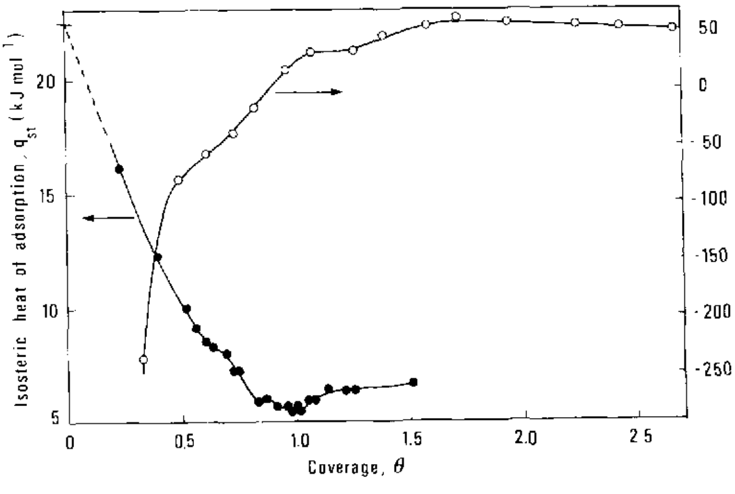

Fig. 8. Isosteric heat of adsorption of nitrogen and water onto goethite as a function of coverage. ● : nitrogen, ○ : water.

reactive for a reaction with water during the outgassing process in the ultrahigh vacuum applied in the present work. The adsorption would then partly be determined by a rehydroxylation of the active sites on the surface and subsequent adsorption onto the fully hydroxylated surface. The very long equilibrium times observed for water may then be due to surface diffusion of the initially reactive water molecules. This also explain the difference in the specific surface area for nitrogen and water: The incoming water molecule reacts with one active site and two hydroxyl groups are formed. The monolayer point for water thus requires a smaller number of molecules of water as expected by comparison with the inert nitrogen molecules. Further, this reaction could also explains the observed hysteresis of the water isotherm (Fig. 7) since the dehydroxylation requires ultrahigh vacuum.

CONCLUSIONS

Nitrogen is physisorbed onto goethite. Water reacts initially with goethite at reactive sites formed during the initial ultrahigh vacuum outgassing. The second and following layers of water are more weakly bound (physisorption).

ACKNOWLEDGEMENTS

The assistance of L.I. Madsen and J.O. Pedersen in acquiring the volumetric data is gratefully acknowledged. Thanks are due to B. Bloch for obtaining the electron micrograph.

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