Journal of Thermal Analysis, Vol. 38 (1992) 1835-1845

ENERGETIC PROPERTIES OF NiO SURFACE EXAMINED BY HEAT-OF-ADSORPTION MEASUREMENT

*T. Matsuda, H. Taguchi and M. Nagao**

RESEARCH LABORATORY FOR SURFACE SCIENCE, FACULTY OF SCIENCE,
OKAYAMA UNIVERSITY, 3-1-1 TSUSHIMA-NAKA, OKAYAMA 700, JAPAN

Heat of adsorption and isotherm of water vapor on NiO samples were measured simultaneously at 301 K to examine the energetic properties of the surface. They revealed that NiO has a relatively uniform surface. The heat of adsorption ranging 80–90 $kJ \cdot mol^{-1}$ indicates the production of surface hydroxyl groups on the (100) plane of NiO. It is relatively small compared with that of other metal oxides, which suggests a weak nature of the Ni^{2+} ion sites for chemisorption of water. It is suspected that half of the surface Ni^{2+} ions are covered with hydroxyl groups and the remainings act as relatively strong physisorption sites for water molecules.

Keywords: energetic properties, heat of adsorption, NiO surface

Introduction

Investigation of surface properties of solids, in particular, the energetic properties, is a very important research subject in the fields covering surface physics, surface chemistry, electronic engineering, and heterogeneous catalysis. It is possible to estimate the surface energy for single crystals, because the surface has a well-defined structure and chemical composition. In the case of powdered solids, however, it is difficult because of insufficient information about the structure, composition, and electronic state of the surface. Therefore, an experimental determination is necessary to know the energetic properties. Adsorption studies using various gases or vapors often give us useful information about the surface properties of powder samples.

---

* To whom all correspondence should be addressed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Heat of adsorption, which gives us interaction energy between solid surfaces and adsorbed species, is the most important quantity for powder surfaces [1, 2]. Along this line, direct measurements of heat of adsorption have been carried out for many systems [3–5].

In a series of our adsorption studies of water on metal-oxide surfaces, an adsorption anomaly was found for a fully hydroxylated surface of ZnO [6–8]; the adsorption isotherm of water vapor exhibited a step in the moderate relative-pressure region, and it was interpreted in terms of a two-dimensional condensation of water. The presence of energetically homogeneous sites was responsible for such a phenomenon, and the adsorption model was established for the $ZnO-H_2O$ system [8, 9].

In the present study, the adsorption calorimetry was applied to estimate the interaction energy of NiO surface with water molecules. It is shown that the surface of NiO is uniform in both structural and energetical points of view.

Experimental

Materials and pretreatment

NiO was obtained by thermal decomposition at 673 K of $Ni(CO_3)_2\cdot 2Ni(OH)_2\cdot 4H_2O$ (guaranteed grade, Nakarai Chemicals). Two kinds of NiO samples were prepared by calcining the starting material in a stream of oxygen at 723 K for 6 h and at 973 K for 10 h, respectively, and then they were washed thoroughly with distilled water. Hereafter, these samples are denoted as NiO(I) and NiO(II), respectively.

The NiO sample was placed in a sample cell of the adsorption calorimeter and degassed for 4 h under a pressure of 1.3 mPa at temperatures of 298, 473, 723, and 873 K.

Adsorption calorimeter

The adsorption calorimeter used was an adiabatic type with quadruplex walls [10]. It consists of four parts, i.e., the heat-detecting system, the adiabatic control system, the calibration system, and the measuring system for adsorption amount. Figure 1 shows the main part of the calorimeter. The cylindrical sample cell (inner volume of about 20 cm^3) is made of copper, and both inside and outside of the cell are gold-plated to promote a radiation efficiency of heat as well as to keep a mechanical strength during the heat treatment under a reduced pressure. After placing the sample in the cell, the flange is fastened with bolts to the upper lid through a metal gasket in order to keep it air-tight. The bottom of the cell is deeply concaved so as to accomodate a heater for calibration. The sample cell is connected to the vacuum line and the adsorption measuring system through a

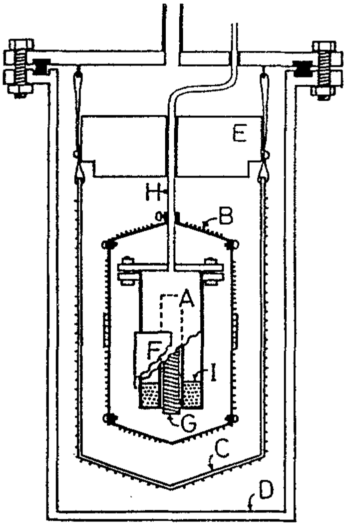

Fig. 1 Adsorption calorimeter; *A*, sample cell; *B*, inter shield; *C*, outer shield; *D*, calorimeter container; *E*, block (copper, 3 kg); *F*, thermistor sleeve; *G*, calibration heater; *H*, gas inlet tube (stainless steel); *I*, sample

stainless tube. The temperature of the shields surrounding the sample cell is controlled adiabatically in reference to that of the cell: the temperature difference between the cell and the inner shield and between the inner shield and the outer shield is detected by thermopiles (chromel-constantan). The temperature was actually maintained within ±1 mK.

The heat released in adsorption process was measured with a Wheatstone-bridge energized at a.c. (23 Hz) 0.1 V. Five thermistors of bead type connected in series (25 kΩ at 273 K) for detecting the heat are attached to the outside of the sample cell.

Water-vapor adsorption

Adsorption of water vapor was carried out volumetrically at 301 K using a conventional adsorption apparatus which was connected to the sample cell of the calorimeter. Either an MKS Baratron pressure gage or an oil-manometer was used to measure the equilibrium vapor pressure. Simultaneous measurements of adsorption isotherm and adsorption heat were performed for the NiO sample which had been pretreated at each temperature as described above. Here, this adsorption process is designated as the first adsorption. After this measurement, the sample was exposed to the saturated water vapor at 301 K for 10 h to complete hydroxylation. The sample was then evacuated at 301 K for 4 h under a reduced pressure of 1.3 mPa. The adsorption of water vapor (here, designated as the second adsorption) was carried out on this fully hydroxylated sample at 301 K.

Krypton adsorption

Adsorption of krypton is often useful to evaluate structural uniformity of powder samples [11]. In the present study, the krypton adsorption on the NiO samples was also performed at 77 K to check the surface uniformity.

Surface area and water content

The specific surface area of the samples was obtained by BET method from adsorption of nitrogen at 77 K, where the cross-sectional area of a nitrogen molecule is assumed to be 0.162 nm^2. The water content was determined volumetrically by successive-ignition-loss method [12].

Results

Electron micrographs of the NiO samples are shown in Fig. 2. A cubic structure can clearly be recognized for both samples of NiO(I) and NiO(II). The particle size of NiO(I) seems to be fairly uniform (about 40 nm in average), which is in good agreement with that estimated from the specific surface area by assuming that the NiO particle has a well-developed cubic structure. On the other hand, the average particle size for NiO(II) sample is about 150 nm. In this case, the possibility of aggregation and sintering is suspected since this sample was subjected to the calcination at higher temperature.

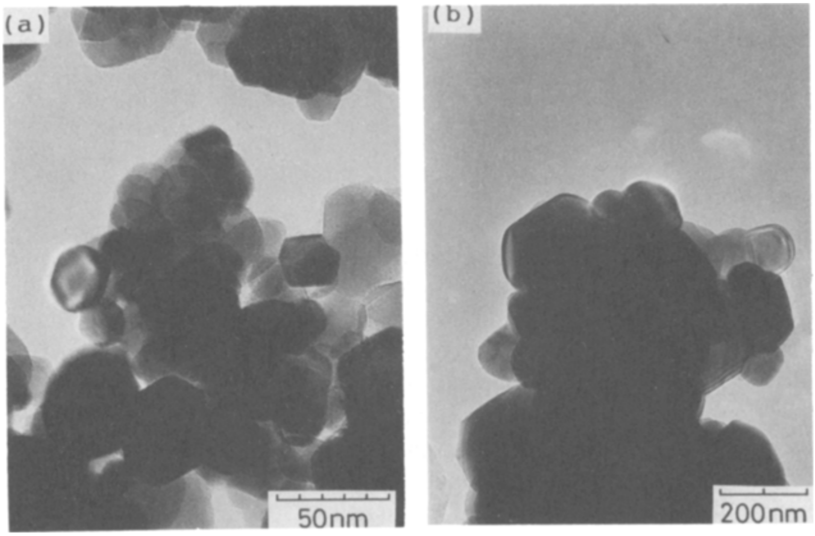

Fig. 2 Electron micrographs of NiO samples: (*a*) NiO(I); (*b*) NiO(II)

Table 1 represents the specific surface area and the surface hydroxyl content (V_h) for NiO(I) and NiO(II) samples treated at various temperatures. The specific surface areas are independent of the pretreatment temperature; ca. 20 m^2g^{-1} for NiO(I) and ca. 2.3 m^2g^{-1} for NiO(II). The surface hydroxyl contents of the NiO(I) and NiO(II) pretreated at 298 K are 13.7 and 10.3 hydroxyl groups nm^{-2}, respectively. By assuming that the (100) plane is predominantly exposed on the NiO surface and that every Ni^{2+} ion on this plane acts as a chemisorption site for water, we obtained that about 60 and 45% of the surface Ni^{2+} ions are covered with hydroxyl groups for the NiO(I) and NiO(II) samples, respectively. The surface hydroxyl groups significantly decreased by the heat treatment at 873 K.

Table 1 Specific surface area and surface hydroxyl content (V_h) for NiO samples

Pretreat. temp./ K	Specific surface area/ m^2g^{-1}		Surface hydroxyl content/ OH's nm^{-2}	
	NiO(I)	Nio(II)	NiO(I)	NiO(II)
298	19.8	2.20	13.7	10.3
473	19.4	2.37	6.01	5.51
723	20.4	2.24	3.22	1.85
873	21.1	2.40	0.57	0.64

Figure 3 shows the adsorption isotherms of krypton for the NiO samples pretreated at 873 K. A step is observed at the relative pressure around 0.25. This step is more distinct for NiO(II) than for NiO(I). The appearance of such step in the adsorption isotherm of krypton suggests high uniformity in surface structure of the NiO sample.

Heat of adsorption and adsorption isotherm of water vapor for the NiO sample pretreated at 723 K are shown in Fig. 4. In this figure V_c corresponds to the endpoint of chemisorption in the first adsorption process and H_L indicates the level of the heat of condensation of water (43.9 kJ·mol^{-1} at 301 K). A peculiar feature is observed in the water vapor adsorption on NiO(I). The amount of adsorbed water increases abruptly in the relative pressure range of 0.15–0.5, giving rise to a step in the isotherm. The position of this step shifts toward a higher pressure range as an increase in the pretreatment temperature of the sample. The initial heat of adsorption gives about 120 kJ·mol^{-1} and then the heats are in 80–90 kJ·mol^{-1} in the chemisorption region, followed by in 50–60 kJ·mol^{-1} in the physisorption region.

The step in the isotherm can hardly be observed for the NiO(II) sample, in contrast to the case of NiO(I). However, the heat-of-adsorption curves for both samples are similar in feature; in the case of NiO(II), the initial heat value is about 105 kJ·mol^{-1}, somewhat lower compared with that for NiO(I). Two plateaus are seen at 85 and 45 kJ·mol^{-1}.

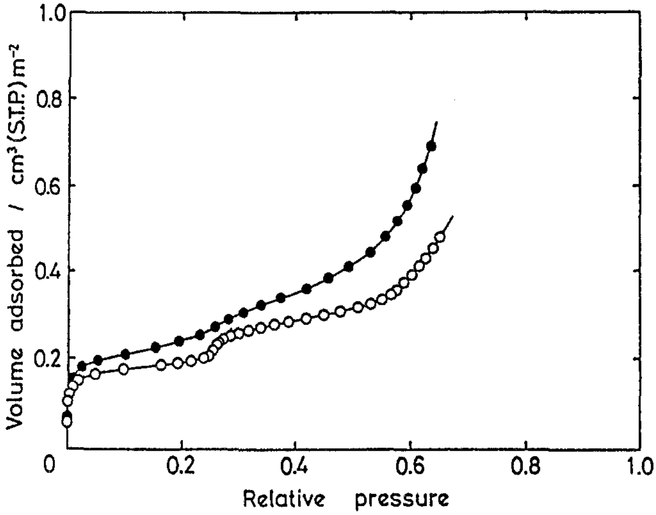

Fig. 3 Adsorption isotherm of krypton on NiO samples at 77 K: ● , NiO(I), o, NiO(II)

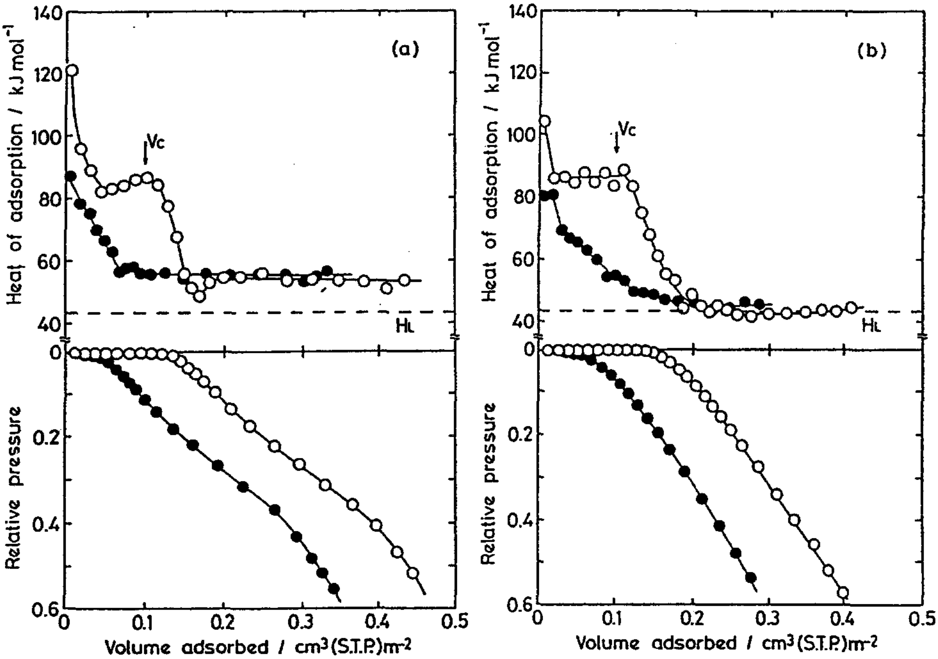

Fig. 4 Heats of adsorption and adsorption isotherms of water vapor at 301 K for NiO samples pretreated at 723 K; (*a*) NiO(I); (*b*) NiO(II). o, first adsorption; ● , second adsorption

Discussion

Surface homogeneity

A distinct feature, appearance of a plateau, in the heat-of-adsorption curve for water strongly suggests energetic uniformity of the NiO surface. The structural homogeneity is also suggested from the TEM observation and krypton adsorption.

The plateau of 80–90 kJ·mol^{-1} in the heat curve is ascribed to a dissociative adsorption of water since it is observed only in the chemisorption range of the first adsorption immediately after the pretreatment of the sample. The heat of dissociative adsorption, i.e., the heat of formation of surface hydroxyl groups is considerably lower than those obtained for other metal oxides; 140–150 kJ·mol^{-1} for ZnO, SnO_2, and Cr_2O_3, 120 kJ·mol^{-1} for MgO and TiO_2 (rutile) [13]. It can be deduced that Ni^{2+} ion sites on the NiO surface are less active compared to the cation sites on the other metal oxides.

On the other hand, the second plateau of 50–60 kJ·mol^{-1} is observed in both the first and second adsorptions, and hence this plateau is safely ascribed to physisorption of water. It seems to be caused by the presence of surface hydroxyl groups arranged so as to act as homogeneous sites for water molecules, since the physisorption of water molecules usually occurs on the surface hydroxyl groups through the formation of hydrogen bonding [12].

A large value of the heat of adsorption in the initial stage, 120 kJ·mol^{-1} for NiO(I) and 105 kJ·mol^{-1} for NiO(II), is probably due to heterogeneity of the surface. Some structural defects such as steps, edges, and corners may give such effect because of their enhanced degree of unsaturation.

Adsorption model of water on NiO surface

Using the content of the surface hydroxyl groups and assuming that the (100) plane is predominantly exposed on the NiO particles, it can be estimated that about 50% of the surface Ni^{2+} ions are covered with the hydroxyl groups which have been produced by the dissociative adsorption of water. One of the possible structural models is that the surface hydroxyl groups form a c(2×2) lattice on the (100) plane of NiO (Fig. 5). The formation of such ordered layer may give rise to the plateau of about 80–90 kJ·mol^{-1} in the heat curve. Furthermore, it is presumed that the physisorption of water molecules on this hydroxyls-layer causes the second plateau of 50–60 kJ·mol^{-1}. The formation of c(2×2) lattice structure has also been observed for the adsorption of CO and NO on the NiO surface [14], where the molecules are adsorbed on half of the Ni^{2+} ions on the (100) plane. The argument is that if every Ni^{2+} ion on the (100) plane, where the nearest Ni^{2+}-Ni^{2+} distance is 0.295 nm, acted as an adsorption site, the distance was too short for

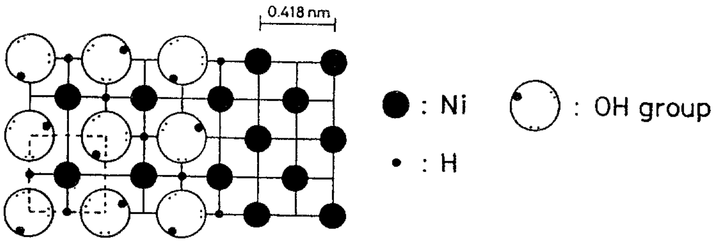

Fig. 5 Adsorption model of water on the (100) plane of NiO

the molecules to be accommodated, which resulted that a 1:1 stoichiometry is unfavored.

The similar consideration may be accepted for the present case of NiO-H_2O system. After half of the Ni^{2+} ions on the (100) plane are covered with hydroxyl groups, water molecules can no longer be adsorbed dissociatively on this plane, resulting in an abrupt decrease in the heat of adsorption. As illustrated in Fig. 5, some of the Ni^{2+} ions still remain uncovered even after the formation of surface-hydroxyl layer (see the area surrounded by broken line), and they have no ability to dissociate further water molecules. Two reasons may be possible for this; first, there is no room to permit dissociative adsorption of water, and secondly the acidity of the Ni^{2+} ions is originally so weak that they cannot dissociate water molecules.

Reason for appearance of step

Figure 6 shows the second adsorption isotherms of water vapor for the NiO(I) samples pretreated at various temperatures. The position of the step appearing in the isotherm shifts to a higher pressure as the pretreatment temperature increases. However, the amount of adsorbed water at the end of the step was substantially constant, e.g., 0.22 cm^3(STP)m^{-2} or 5.9 H_2O molecules nm^{-2}, irrespective of the pretreatment temperature. This value corresponds to the amount of water enough to cover the Ni^{2+} ions in the area surrounded by broken lines in Fig. 5. It has been revealed that the step resulting from the two-dimensional condensation of water appears in almost the same relative-pressure region, independent of the pretreatment temperature [8, 15, 16]. Thus, it can be concluded that the step appearing in the adsorption isotherm of water on the NiO surface is caused by an adsorption mode different from the two-dimensional condensation of water. In the case of NiO, the adsorption mechanism leading to the appearance of the step is presumed as follows. The Ni^{2+} ions in the surrounded area by broken lines are just as situated at the bottom of a 'box' framed with surface hydroxyl groups, which results in making impossible to dissociate water molecules owing to a steric hindrance. Consequently, the Ni^{2+} ions are still remained uncoordinated, and hence they act as relatively strong sites for physisorption of water molecules. It may be reasonable to consider that the step in the adsorption isotherm is caused by the process of pushing water molecules into the 'box' and that the heat of adsorption corresponding to this process is 50–60 kJ mol^{-1}.

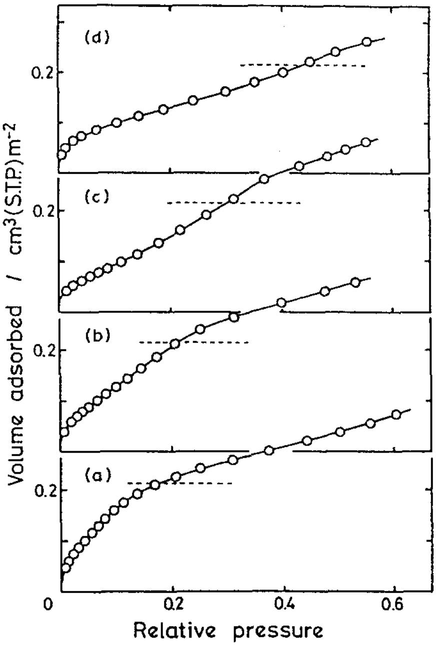

Fig. 6 Second adsorption isotherms of water vapor on NiO(I) samples pretreated at various temperatures; (*a*) 298; (*b*) 473; (*c*) 723; (*d*) 873 K

A question still remains about the shift of the step by the heat treatment of the sample. However, one of the reasons may be found in difficulty in the rehydroxylation of NiO surface. Table 2 shows the amount of chemisorbed water (V_c), the total amount of surface hydroxyl groups (V_c+V_h), and the degree of rehydroxylation for the NiO(I) sample. Here, it is assumed that the full rehydroxylation is accomplished when half of the surface Ni^{2+} ions are covered with hydroxyl groups (11.45 OH's nm^{-2}). The degree of rehydroxylation obviously decreases with increasing temperature of the pretreatment. This means that the surface hydroxyl groups are substituted by water molecules at the sites originally occupied by the hydroxyls. The 'box' formed by Ni^{2+} ion sites becomes more cramped due to a larger van der Waals radius of water molecule, and therefore higher vapor pressures are needed to accommodate further water molecules in it. The shift of the step would be interpreted in this manner.

Table 2 Amount of chemisorbed water (V_c), total amount of surface hydroxyl groups (V_c+V_h*) and degree of rehydroxylation for NiO(I)

Pretreat. temp./ K	Amount of chemisorbed water/ OH's nm^{-2}	Total amount of OH groups/ OH's nm^{-2}	Degree of rehydroxylation/ %
298	–	13.7	120
473	3.01	9.02	79
723	5.39	8.61	75
873	7.48	8.05	70

*V_h is taken from Table 1.

Finally, it is interesting to note that the NiO(II) sample which seems to be more uniform in surface structure gives no appreciable steps in the adsorption isotherm of water. Further investigation will be necessary for this subject.

Conclusion

Energetic properties of NiO surface was investigated by measuring the heat of adsorption and adsorption isotherm of water vapor for the samples pretreated at various temperatures.

NiO has a relatively homogeneous surface in energy and the heat of dissociative adsorption leading to a production of surface hydroxyl groups was found to be 80–90 kJ·mol^{-1} on the (100) plane exposed predominantly. These heats are lower compared with those for other metal oxides, which suggests a weak nature of the Ni^{2+} ion sites for chemisorption of water.

About half of the surface Ni^{2+} ions on the (100) plane are covered with surface hydroxyl groups and the remainings do not have enough activity to dissociate water molecules but act as relatively strong physisorption sites with interaction energies of 50–60 kJ·mol^{-1}. The latter adsorption sites seem to be responsible for the appearance of step in the adsorption isotherm of water vapor on NiO surface.

* * *

The authors are grateful for the help of Prof. S. Kittaka of Okayama University of Science in taking electron micrographs. This work was partly supported by Grant-in-Aid for Scientific Research No. 02640348 from the Ministry of Education, Science and Culture of Japanese Government.

References

1 P. C. Gravella, Adv. Catal., 22 (1972) 191.
2 P. C. Gravelle, Catal. Rev. Sci. Eng., 16 (1977) 37.
3 D. N. Furlong, F. Rouquerol, J. Rouquerol and K. S. W. Sing, J. Chem. Soc. Faraday Trans. I, 76 (1980) 774.
4 R. F. Rossi and G. Busca, Coll. Surf., 16 (1985) 95.
5 E. Garrone, B. Fubini, E. E. Platero and A. Zecchina, Langmuir, 5 (1982) 240.
6 T. Morimoto and M. Nagao, Bull. Chem. Soc. Jpn., 43 (1970) 3746.
7 M. Nagao, J. Phys. Chem., 75 (1971) 3822.
8 T. Morimoto and M. Nagao, J. Phys. Chem., 78 (1974) 1116.
9 M. Nagao, K. Yunoki, H. Muraishi and T. Morimoto, J. Phys. Chem., 82 (1978) 1032.
10 M. Nagao, T. Matsuda and N. Ueno, Netsusokutei, 19 (1992) 57.submitted for publication.
11 J. H. Singleton and G. D. Halsey, J. Phys. Chem., 58 (1954) 1011.
12 T. Morimoto, M. Nagao and F. Tokuda, J. Phys. Chem., 73 (1969) 243.
13 M. Nagao and N. Ueno, Abstracts in 6th International Conf. Surface and Colloid Science, Hakone, 1988, p. 233.
14 E. E. Platero, S. Coluccia and A. Zecchina, Langmuir, 1 (1985) 407.
15 T. Morimoto, Y. Yokota and S. Kittaka, J. Phys. Chem., 82 (1978) 1996.
16 S. Kittaka, J. Nishiyama, K. Morishige and T. Morimoto, Coll. Surf., 3 (1981) 51.

Zusammenfassung — Zur Untersuchung der energetischen Eigenschaften der Oberfläche von NiO-Proben wurden bei 301 K simultan die Adsorptionswärme und die Isotherme von Wasserdampf an NiO-Proben ermittelt. Es zeigte sich, daß NiO eine relativ gleichmäßige Oberfläche besitzt. Die Adsorptionswärme mit einem Wert zwischen 80 und 90 kJ·mol^{-1} weist auf die Bildung von Oberflächen-Hydroxylgruppen in der (100) Ebene des NiO hin. Im Vergleich mit der von anderen Metalloxiden ist sie relativ klein, was die Empfindlichkeit der Ni^{2+}-Ionenstellen gegenüber der Chemisorption von Wasser zeigt. Man nimmt an, daß etwa die Hälfte der Ni^{2+}-Ionen an der Oberfläche mit Hydroxylgruppen belegt sind, die restlichen agieren als relativ starke physiosorptive Stellen für Wassermoleküle.