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# Surface Area and Pore Structure of Nickel Oxide

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Phase and structural changes accompanying the thermal dehydration of crystalline $Ni(OH)_2$ were followed by differential thermal analysis, thermogravimetric analysis, and X-ray diffraction techniques. The isothermal dehydration of the hydroxide was studied at various temperatures in air and *in vacuo*. Adsorption isotherms of nitrogen, carbon tetrachloride, and cyclohexane were measured on the hydroxide and its dehydration products formed in air at temperatures ranging from 35–500°C, and *in vacuo* at 250°C. Application of the BET theory reveals that the surface area of the oxide decreases with the increase of the size of the adsorbate molecule. Carbon tetrachloride seems to be reduced on the oxide formed *in vacuo* (deoxygenated). Nitrogen adsorption isotherms were investigated by the $t$ method. Pore volume distributions were calculated from desorption isotherms of nitrogen.

## INTRODUCTION

Stoichiometric nickel oxide is difficult to prepare; hence it presents an interesting example of metal oxide catalysts. The thermal treatment of nickel hydroxide in air produces an oxide containing excess oxygen both in the lattice and chemisorbed on the surface. This excess oxygen is accompanied by the creation of $Ni^{3+}$, which is black, according to:

$$2O^{2-} + 2Ni^{2+} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons 2Ni^{3+} + 3O^{2-} + c,$$

where $c$ is cationic vacancy. When the decomposition of the hydroxide is effected *in vacuo*, metallic nickel and excess oxygen coexist in the lattice of the formed oxide (*1, 2*).

For most of surface studies carried out on nickel oxide prepared in air, the adsorbent was heated at elevated temperatures thus avoiding the uptake of oxygen (*3*). Alternatively, Teichner *et al.* (*4*) made a vast study on the oxide prepared *in vacuo* in connection with the catalytic oxidation of carbon monoxide.

Reviewing some applications of electrical conductivity measurements to the investigations of catalytic processes on semiconducting oxides, Bielanski (*5*) made it clear that the presence of oxygen on the surface of nickel oxide promotes the oxidation of carbon monoxide as well as the dehydrogenation of isopropyl alcohol.

The present work dealt with a study of the texture of nickel oxide prepared by the thermal decomposition of the corresponding hydroxide both in air and *in vacuo*, through adsorption measurements of nitrogen as well as some nonpolar organic vapors with different molecular cross-sectional area. Phase and structural changes accompanying the dehydration of the parent hydroxide were followed by DTA, TGA, and X-ray analysis. In addition, the isothermal dehydration of the hydroxide was investigated in air and *in vacuo* at various temperatures.

## EXPERIMENTAL METHODS

### *Apparatus and Technique*

Differential thermal analysis of the parent material was obtained with an automatically recording instrument. Thermogravimetric analysis was determined with an automatically recording thermobalance as described by Gordon and Campbell (*6*). The isothermal dehydration of the hydroxide in air was followed also with the thermobalance with the incorporation of a device to keep the temperature constant arbitrarily all over the experiment. The temperature of the furnace was first raised to the required temperature and the specimen was then shock-heated by lowering the furnace to surround it. To follow isothermal dehydration *in vacuo,* a stainless steel spring balance (*7*) was used (sensitivity 17.8 cm/g) in series with a rotary oil pump. X-Ray diffraction patterns were obtained with a Philips (114.23-mm diam) Debye-Scherrer powder camera using Ni-filtered Cu radiation. Adsorption–desorption isotherms of carbon tetrachloride and cyclohexane at 35°C, and of nitrogen at −195°C were determined with the aid of a conventional gas adsorption apparatus.

### *Materials*

Nickel hydroxide was prepared (*8*) by treating nickel nitrate solution with an excess of ammonium hydroxide, followed by steam distillation until the precipitate was ammonia free. After drying over $P_2O_5$, the product had the composition $NiO \cdot 1.058H_2O$ corresponding to 20.13% water content as compared with 19.43% for $Ni(OH)_2$. Dehydration of the parent material was done in air for 5 hr at 200, 250, 300, 400, and 500°C, and *in vacuo* for 15 hr at 250°C. Nitrogen, carbon tetrachloride, and cyclohexane were purified by standard methods.

## RESULTS

### *1. Structural and Phase Changes Accompanying Thermal Dehydration*

DTA of the parent material exhibits one sharp endothermic peak located at 320°C. TGA showed that dehydration occurs sharply at a very limited range of temperature whereby nearly 75% of the total water content is driven out. The rate of dehydration reaches its maximum at 305°C. These results indicate the behavior of a typical crystalline material (*9*). X-Ray diffraction patterns were obtained for the parent material and its dehydration products formed in air. Comparison with the ASTM cards (*10*), shows that the parent material is nickel hydroxide. Heating in air at 200°C for 5 hr does not change the water content, viz., 20.13%, and all the lines which give the characteristic *d* spacings of the hydroxide still remain clear. At 250°C, the water content falls to 12.52% and more lines, which correspond to a moderate conversion to the oxide, appear. Finally at and above 300°C, we get only a pattern of the oxide.

### *2. Isothermal Decomposition of* $Ni(OH)_2$

The isothermal dehydration of the hydroxide was carried out at 225, 250, 275, and 300°C in air and at 225, 240, 250, and 275°C *in vacuo*. The results are in general agreement with Mampel's theory (*11*). Over the decay period which corresponds to 80–90% of the complete reaction, decomposition can be represented by the equation:

$$(w/w_0)^{1/3} = -kt + a, \qquad (1)$$

where $w_0$ = initial mass of reactant, $w$ = mass at time $t$. Equation (1) can be alternatively written as:

$$1 - (1 - \alpha)^{1/3} = kt + b, \qquad (2)$$

where $\alpha$ (decomposition fraction) = $(1 - w/w_0)$. On differentiation of (1) gives

$$-dw/dt = k_0 w^{2/3}, \qquad (3)$$

where $k_0$ (velocity constant) = $3kw_0^{1/3}$; $k$, $a$, and $b$ are constants. The decomposition curves ($\alpha$ vs. $t$) are of the usual sigmoid type, where the early acceleratory region is convex to the time axis. This region is generally limited to 15% of the total in air decomposition. The results of the isothermal dehydration of the hydroxide are shown in Fig. 1. By plotting $(w/w_0)^{1/3}$ against $t$, a straight line is obtained, the slope of which gives $k$. The values of $k$ are given in Table 1. Since $k_0 = 3kw_0^{1/3}$, $k$ may be substituted for $k_0$ in an Arrhenius equation, giving

$$d \log_e k/(1/T) = -E/R. \qquad (4)$$

By plotting $\log_{10}k$ against the reciprocal of the absolute temperature, $1/T$, for each set of experiments, the points fall satisfactorily on a straight line, and from the slopes the apparent energy of activation thus obtained

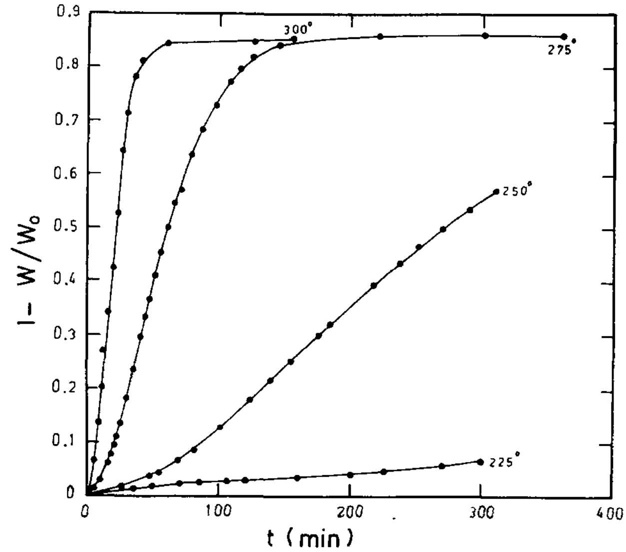

FIG. 1. Isothermal decomposition of nickel hydroxide in air.

is 45.14 for dehydration performed in air ($E_1$) and 28.32 kcal mole$^{-1}$ for that carried out under vacuum ($E_2$). Marcellini, using the same starting material (*12*), gave a value of 25.01 kcal mole$^{-1}$ for ($E_2$). It is worth mentioning that the same kinetic treatment was adopted for the decomposition of $Mg(OH)_2$ (*13*).

## *3. Nonstoichiometric Composition of the Oxide*

The method of Bunsen-Rupp (*14*) and its modification (*15*) were used for the determination of excess oxygen and excess metallic nickel ($Ni^0$), respectively. The results are shown in Table 2. Excess oxygen is detected for the sample prepared in air at 250°C, corresponding to partial decomposition of the hydroxide; then it reaches its maximum value for the sample at 300°C, and then decreases at higher temperatures of preparation where the oxide gradually becomes inactive due to a process of sintering.

TABLE 1
VALUES OF *k* (velocity constant) FOR THE ISOTHERMAL DEHYDRATION OF $Ni(OH)_2$

| In air | | *In vacuo* | |
|---|---|---|---|
| Temp (°C) | $k \times 10^{-3}$ min$^{-1}$ | Temp (°C) | $k \times 10^{-3}$ min$^{-1}$ |
| 225 | $0.07_4$ | 225 | 0.50 |
| 250 | 0.99 | 240 | 1.78 |
| 275 | 4.38 | 250 | 5.84 |
| 300 | 13.34 | 275 | 9.76 |

TABLE 2
NONSTOICHIOMETRY OF NICKEL OXIDE

| Heat treatment (°C) | Excess oxygen atom% mole NiO | $Ni^0$% mole NiO$^a$ |
|---|---|---|
| 250 *in vacuo* | — | 0.033 |
| 250 in air | 0.211 | — |
| 300 | 1.526 | — |
| 400 | 0.925 | — |
| 500 | 0.220 | — |

$^a$ % $Ni^0$ refers to the difference ($2Ni^{3+} - Ni^0$).

## *3. Adsorption Measurements*

**A. Nickel oxide prepared in air.** Results of experiments on the adsorption of nitrogen at —195°C on the parent material and its dehydration products formed in air are shown in Fig. 2. The isotherms for the parent hydroxide and its product formed at 200°C are very similar and belong to Type II of Brunauer's classification (*16*). The isotherms on the products formed at 250, 300, and 400°C have a peculiar shape.

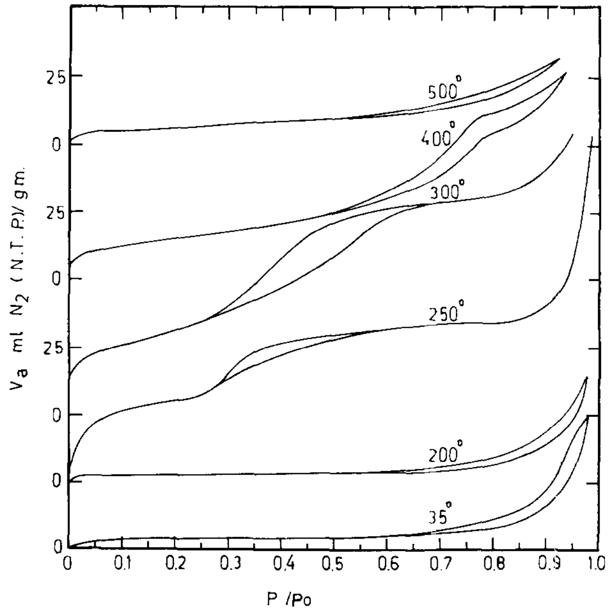

Fig. 2. Sorption isotherms of nitrogen on nickel hydroxide and its dehydration products formed in air.

Thus the isotherm starts as Type II then it passes through an inflection point and then rises again with increase of relative vapor pressure. The inflection point lies at higher relative pressure the more the temperature of decomposition increases. Such a form of isotherm is observed by Lippens (*17*) in the adsorption of nitrogen on some of dehydration products of bayerite. At 500°C, we get an isotherm of Type II. In Fig. 2, desorption isotherms form definite hysteresis loops of Type A with little of Type E of De Boer's classification (*18*).

Specific surface areas have been deter-

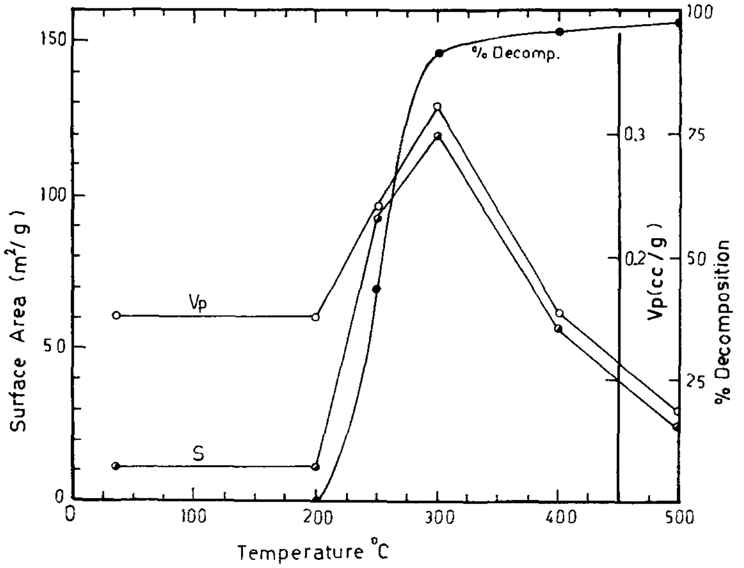

Fig. 3. Variation of surface area, percentage decomposition, and total pore volume with temperature of calcination of nickel hydroxide.

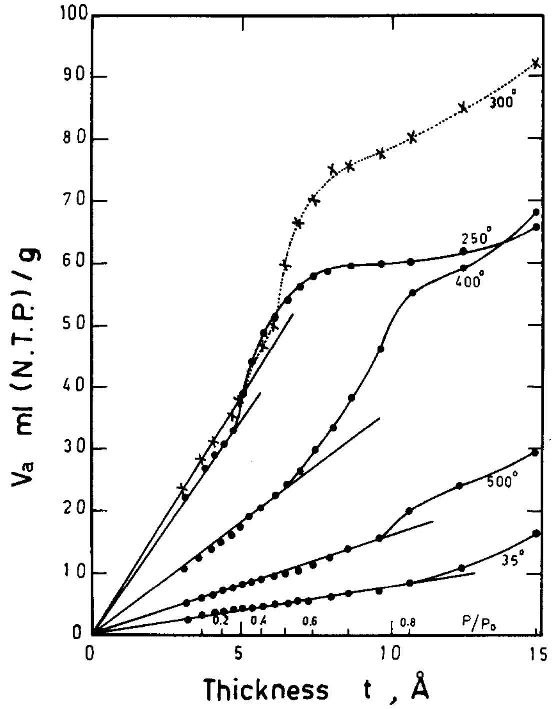

FIG. 4. Volume–thickness curves for nickel hydroxide and its dehydration products.

mined by the BET method using 16.27 Å$^2$ (*19*) for the molecular area of nitrogen. The values obtained are plotted in Fig. 3 as a function of the dehydration temperatures. A maximum is shown at 300°C. As calcination in air for 5 hr up to 500° does not bring about complete dehydration of the parent material, the percentage decomposition at various temperatures of dehydration is also inserted. Total pore volume of the different samples investigated is calculated and the results are also shown in Fig. 3. It does seem that the variation of the total pore volume with temperature of dehydration follows the same trend as that of the specific surface area.

Investigating the nitrogen adsorption isotherms by means of $t$ method, the $t$ curve for aluminum hydroxides and oxides, which is found to be valid for other oxides such as $TiO_2$, $ZrO_2$, and MgO (*20*), is adopted. The experimental values of adsorbed nitrogen were plotted with the aid of the $t$ curve as a function of the $t$ values (Fig. 4). Above certain values of the relative vapor pressure, the volume adsorbed is larger than that corresponding with multilayer adsorption occurring solely. An upward deviation, which is caused by the onset of capillary condensation, was noticed at a relative pressure of 0.80, 0.28, 0.28, 0.50, and 0.75 for the hydroxide (35°) and its decomposition products obtained at 250, 300, 400, and 500°, respectively. It is to be noticed that for samples prepared at 250, 300, and 400°, originally capillary condensation occurs irreversibly, since the first hysteresis phenomena almost take place at the same relative pressure where deviation occurs (cf. Fig. 2). The irreversibility in capillary condensation may be attributed to the presence of fine pores. The shift of the onset of irreversible condensation to higher values of the relative pressure indicates an increase of the minimum pore sizes at higher temperatures (*21*).

Pore volume distributions have been computed by the method of Barrett *et al.* (*22*) from the desorption isotherms. The dimensions of pores are given by $r = r_k + t$ for cylinderical pores, where $r_k$ is the Kelvin radius and $t$ the thickness of the adsorbed layer. The multilayer thickness built up at various relative vapor pressures is determined from adsorption data on a plane surface where capillary condensation does not take place. Here also the $t$ vs. $p/p_0$ curve for nitrogen adsorption on alumina (*20*) is used. Pore volume distribution curves are shown in Fig. 5. These curves illustrate the effect of temperature of preparation on the distribution of pores of different volumes and on the most probable pore radius. Thus for samples prepared at 250 and 300°, the curves show narrower distribution of pore volumes, and the pores are small having radii less than 30 Å, whereas heating to 400°, or above, leads to much wider distribution of pores. The most probable pore size is not greatly affected by the thermal treatment up to 300°, whereas, for products obtained at higher temperatures, the maximum of the pore volume distribution curve is shifted towards larger radii. The corresponding curves for the hydroxide prepared at 35° or thermally treated at 200° are irregular so that no maximum could be

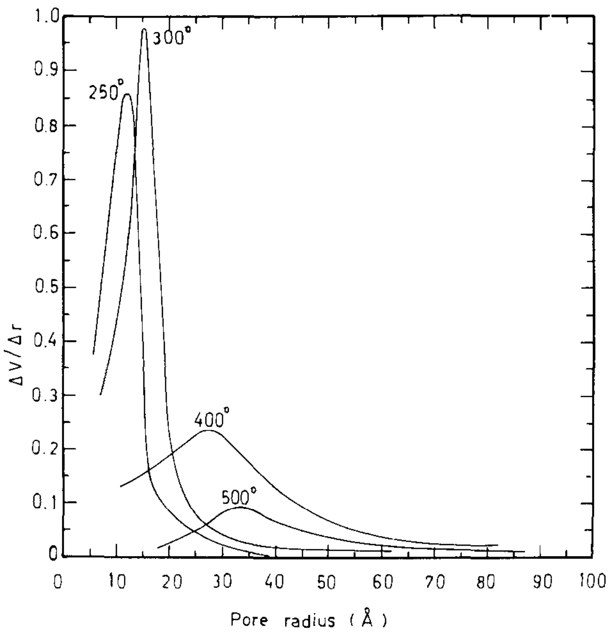

FIG. 5. Pore size distribution for products of dehydration of nickel hydroxide.

confined. This may indicate that the hydroxide has a very broad spectrum of pores.

In order to examine the effect of the size of the adsorbate molecule, adsorption–desorption isotherms of carbon tetrachloride and cyclohexane were measured at 35° on the parent material and its dehydration products. The isotherms of the organic vapors give almost the same picture already described in the case of nitrogen. Specific areas have been determined by the BET method, taking a molecular area of 30 Å$^2$ for carbon tetrachloride *(23)* and 32 Å$^2$ for cyclohexane as a symmetrical molecule *(24)*. The values obtained are given in Table 3, in which are inserted the corresponding values from nitrogen adsorption for comparison. Notice that the surface area of the adsorbents decreases with the increase of the molecular size of the adsorbate.

TABLE 3

SPECIFIC SURFACE AREAS FROM NITROGEN, CARBON TETRACHLORIDE, AND CYCLOHEXANE ADSORPTION ON NICKEL HYDROXIDE AND ITS DEHYDRATION PRODUCTS FORMED IN AIR

| Temperature of dehydration (°C) | $S_{N_2}$ | $S_{CCl_4}$ | $S_{C_6H_{12}}$ (m²/g) |
|---|---|---|---|
| 35 | 11.3 | 10.3 | 10.4 |
| 200 | 10.8 | 10.4 | 9.1 |
| 250 | 92.9 | 53.1 | 49.8 |
| 300 | 119.7 | 83.4 | 81.7 |
| 400 | 56.5 | 36.5 | 34.2 |
| 500 | 24.8 | 14.2 | 12.7 |

**B. Nickel oxide prepared *in vacuo*.** Above 250°, metallic nickel (Ni$^0$) is formed on the dehydration of nickel hydroxide *in vacuo*. Hence we stick for our surface study to this temperature only. The nitrogen adsorption isotherm on the sample prepared at 250° *in vacuo* is of Type II of Brunauer's classification, and on desorption no hysteresis could be observed. The surface area calculated ($S_N$) is 164.1 m$^2$/g. Adsorption of cyclohexane at 35° gives almost the same picture as in the case of nitrogen, and the calculated $S_{C_6H_{12}}$ is 106.7 m$^2$/g. This big difference between the two surface area values may indicate that the surface is microporous. Adsorption of carbon tetrachloride at 35° on this sample gives rather interesting observations: (i) on exposure of $CCl_4$ vapor to the adsorbent, its color changes gradually from yellowish green to black, and (ii) adsorption measurements could be continued above 174 Torr (the saturation pressure of $CCl_4$ at 35°) till 177 Torr. The black color was due to the formation of $Ni^{3+}$ ions. In a separate experiment, the adsorbent was exposed to $CCl_4$ vapor at 35° for enough time, then the adsorption bulb was sealed off and the amount of formed $Ni^{3+}$ was determined with the aid of Bunsen-Rupp method (*14*). A value of 0.318% $Ni^{3+}$ was detected, after comparison with a blank (cf. Table 2). It is important to report that similar experiments were carried out with samples prepared at 300° in air, and no change in the nonstoichiometry of the oxide was detected, indicating that no reaction of $CCl_4$ vapor on the oxygenated oxide (prepared in air) takes place. The fact that adsorption measurements exceeded $p/p_0 = 1$ on the deoxygenated oxide may be attributed to the formation of some relatively more volatile products due to the reduction of $CCl_4$.

## DISCUSSION

Crystalline hydroxides are frequently used as starting materials for the preparation of active solids, because their specific surface areas increase considerably upon heating. Generally dehydration gives rise to pseudomorphosis, and the volume of the solid does not vary much. Meantime, water is expelled during dehydration and space will be created in the porous product.

The isothermal dehydration of nickel hydroxide was found to be in good agreement with Mampel's theory (*11*) which accounts for the kinetics and mechanism of the decomposition of solids. This theory is based on generalizations given by earlier investigators (*13*), who postulated that in the decomposition of solids, the reaction is initiated at certain centers, or nuclei, formed usually on the external surfaces of the solid and in some cases also on the surfaces of cracks and lattice imperfections. The reaction then spreads from these nuclei both along the surface and into the interior of the solid.

From the study of the surface properties of many metal oxides (*25*), it has been shown that during the thermal treatment of the parent crystalline hydroxide, the mechanism which determines the surface area–temperature relationship is governed by three consecutive processes; namely, decomposition, recrystallization, and sintering. The three processes overlap in the neighborhood of a maximum. The results obtained in the present investigation are in good agreement with this picture.

Investigating the nitrogen isotherms on NiO formed in air by means of the *t* method, it was shown that for samples prepared at 250, 300, and 400°, originally capillary condensation occurs irreversibly. It is probable that during the decomposition of the hydroxide narrow pores are formed in which capillary condensation occurs on adsorption (*17*). These narrow pores diminish gradually from the surface with increase of temperature of dehydration, until at 500° we get the usual Brunauer's Type II isotherm. This may explain the shift of the inflection point on the isotherms with rise of temperature of decomposition of the hydroxide.

Following the pore structure changes during dehydration of the hydroxide in air, it has been shown that passing from 250 to 300°, the marked increase in surface area is accompanied by an increase in the total pore volume, while the mean size of pores is not appreciably effected. Above 300°, the loss in surface area is accompanied by a decrease in the total pore volume, while the mean size of pores shows a marked increase with rise of temperature of decomposition.

From the study of the kinetics and mechanism of the isothermal dehydration of the hydroxide, it became evident that the decomposition starts from the surface and moves inwards towards the core of the crystal. During this process, new narrow pores are formed resulting in an increase of both surface area and total pore volume. At 300°, decomposition is nearly complete and almost all the hydroxide hexagonal crystals collapse, and a new orientation is set up from the formed cubic crystallites of the oxide. The process of sintering, which continues above 300°, is responsible for the blocking of narrow pores; and in this way the mean pore radius increases. As the narrow pores possess greater surface area, their blocking leads to a drop in the surface area and in the total pore volume.

From the adsorption of carbon tetrachloride and cyclohexane on NiO prepared in air and compared with that of nitrogen, it is clear that the surface area of the adsorbent decreases with increase of the molecular size of the adsorbate. This fact confirms the microporous nature of the oxide surface and it also indicates that almost all the surface is provided by the walls of the micropores (*25*). Similar behavior was noticed with NiO prepared *in vacuo* at 250°C, with the exception that $CCl_4$ vapor seems to be reduced on this adsorbent as indicated mainly by the formation of black $Ni^{3+}$ ions on exposure of the organic vapor to the oxide. A detailed study of this phenomenon is now in progress.

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