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Variation of the surface properties of nickel oxide upon heat treatment evidenced by temperature programmed desorption and inverse gas chromatography studies

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The surface properties (dispersive component γ_S^d of surface energy and surface nanomorphology) of nickel oxide samples submitted to heat treatments up to 550 °C were examined by temperature programmed desorption (TPD) and inverse gas chromatography (IGC) methods. It is shown that the variation of γ_S^d is complex, first increasing as the temperature reaches about 300 °C, then decreasing and going again through a maximum, of lower amplitude, for a treatment temperature of about 600 °C. These variations follow closely the TPD curves that relate the rate of H_2O and, in a much lesser extend of CO_2 releases as the heat treatment temperature augments. The surface nanomorphology changes also during this treatment. The NiO surface becomes very interactive when treated around 250 °C. The determination of the adsorption energy distribution curves (energetic heterogeneity) clearly demonstrates the change in surface properties and development of the population of high adsorption energy sites. Rehydration of the sample treated at 300 °C was not possible under our experimental conditions. *© 2000 Kluwer Academic Publishers*

1. Introduction

The surface properties of nickel oxide have been examined using a series of modern physical methods [1] both for fundamental and practical reasons (catalysis). However, to our knowledge, there are no papers where surface properties are analyzed in terms of surface energy characteristics. The present work is an attempt to fulfill this gap. Since years, we developed in our Laboratory Inverse Gas Chromatography (IGC) approaches to measure surface energy of divided solids such as silica [2], iron oxides [3], carbon blacks [4], etc. The difficulties that we encountered were rather of fundamental nature, whereas the measurement of the retention time or volume of a chosen molecular probe (solute injected in the GC column containing the solid of interest) is often easy to measure using conventional GC equipment that is available in almost every chemistry laboratory. The main problem indeed is to extract from a single chromatographic peak information that has the physical meaning it is supposed to have, for instance: the surface energy of the solid. By surface energy, we understand its physical interaction potential. In principle, by choosing molecular probes having a known interaction capacity such as alkanes for the evaluation of the London interaction potential (for London or dispersive component of surface energy) or polar probes (for the polar component of surface energy), it should be possible to evaluate the solid's surface energy. Yet, this is far from being evident! In reality, the solid's surface is very complex having adsorption sites of different energies, having sites that may not be statistically distributed all over the surface, having geometric irregularities of molecular dimensions capable to restrict the access (size exclusion effects) of the GC probes. In other words, the actual surface of a solid is usually very heterogeneous and the definition of its surface energy, by a single value appears to be not realistic.

IGC may be performed under two experimental conditions: IGC at infinite dilution or at finite concentration conditions. In the first case, a very limited amount of molecular probes is injected. Consequently, it is assumed that the molecules adsorbed on the solid's surface will not ⟨⟨see⟩⟩ each other. In other terms, complication stemming from lateral interactions of adsorbed molecules may be neglected and only true adsorbate/adsorbent interactions will occur. Thus, the information they will deliver will be typically local. Moreover, that sites that are going to be unraveled will correspond to the most active sites (sites with the highest adsorption energies). It follows then that IGC at infinite dilution conditions will essentially be a remarkable method to qualitatively detect surface events, like those arising when submitting the sample to a heat treatment for instance. Heat treatment will definitely

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alter the surface chemistry and possibly also the surface nanomorphology due to reorganization or surface chemical relaxation processes that strongly influence the adsorption of the molecular probes used for IGC. A major advantage of IGC, over more sophisticated physical methods, is that IGC is a true surface analysis method. Now by its own, IGC is generally not capable to identify the origins of the changes that follow a surface treatment. The same is true for analytical chromatography that will allow to separate, but not to identify the constituents of a complex mix without previous standardization. Nevertheless, IGC at infinite dilution is a unique method of detection as will be seen below.

IGC, at finite concentration conditions, provides an overall description of the solid's surface energetic state: the distribution of the surface sites classified according to their adsorption energy of a given probe. The results depend on the chemical nature and on the bulkiness of the chosen probe and hence, the adsorption energy distribution curves should be only considered as finger prints of the solid's surface energetic state. The principle of the IGC method as well as the details of experimental procedures were described in previous papers [5, 6].

2. Experimental

2.1. NiO sample

Nickel oxide was purchased from Aldrich. Its chemical purity is given to be 99.99%.

2.2. I.G.C. measurements

Given the small particle size of the commercial NiO sample, it was necessary to first agglomerate it by compression in an IR die, then to gently crush and to select particles having sizes comprised between 250–400 μm. These particles (about 2.3 g) were then introduced in a stainless steel column, 30 cm long and with an internal diameter of $1/8''$. Before measurement, the surface of NiO was flushed with He, at 120 °C, so as to eliminate physically adsorbed impurities. For IGC under infinite dilution conditions, minor amounts of gaseous solutes were injected so as to approach near zero surface coverage permitting to neglect lateral interactions between adsorbed molecules and the observation of symmetrical GC peaks. All IGC measurements at infinite dilution were made at 104 °C. For IGC under finite concentration conditions, known amounts of liquid probes were injected. Deformed (tailed) peaks were recorded and the peaks' shapes were analyzed using standard methods [7] so as to calculate adsorption isotherms. All IGC measurements at finite concentration were made at 36.5 °C.

2.3. Thermal treatments

Thermal treatments were performed by avoiding the reexposure to air of NiO before analysis either by IGC or by TPD. For IGC purposes, the sample was heated in the GC column under a He flow up to temperatures close to 350 °C. For higher temperature treatments, the GC oven was replaced by a regular tubular oven, the sample being always kept under He. Practically, the temperature was increased at a rate equal to 30 °C/min up to the desired temperature value, and maintained at that temperature for 1 h. Thereafter, the GC column was allowed to cool down to the measuring temperature of 104 °C.

2.4. Temperature programmed desorption (TPD)

During a TPD experiment, the sample was progressively heated at a constant rate and the volatile products that are freed were continuously analysed by mass spectrometry. The volatile products were adsorbed gases or impurities, but also surface groups decomposition products. For a totally pure NiO sample, after outgassing, the sole formation of water, due to the condensation of surface hydroxyl groups, is expected. The amount of freed gases or vapors was estimated through a volumetric method, knowing the volume of the measuring cell and following pressure variations. 50 mg of oxide were necessary for the analysis, the heating rate being equal to 2 K/min.

2.5. Rehydration of thermally treated NiO

In order to verify if it is possible to regenerate the surface structure of a 300 °C heated NiO sample, this sample was cooled under an He flow at room temperature and then exposed to a humidified He flow during 12 hr. Thereafter, the sample was again flushed with He at 104 °C and its γ_S^d was evaluated in the way described below. The whole cycle was repeated twice so as to control the reproducibility of the results.

3. Results

3.1. Dispersive component of surface energy (γ_S^d)

γ_S^d was determined according to the method of Dorris and Gray [8], from the retention times (time it takes for the probe to cross the GC column when pushed by a He flow) of a homologous series of n-alkanes: a long retention time (tr) indicating a high affinity of alkanes for the solid surface. From tr (or V_N, the net retention volume), the variations of standard free energies of adsorption ($\Delta G_a = -RT\,\mathrm{Ln}(V_N)$) were readily obtained. Since ΔG_a vary linearly with the number of C atoms of the n-alkanes, it becomes possible to calculate an incremental value, $\Delta G_a(CH_2)$, corresponding to the free energy of adsorption of a CH_2 group. Then, γ_S^d is obtained by application of the following relation:

$$\gamma_S^D = \frac{1}{4\gamma_{CH_2}}\left(\frac{\Delta G_a(CH_2)}{Na_{CH_2}}\right)^2 \qquad (1)$$

In this expression, γ_{CH_2} is the surface energy of a solid entirely made of CH_2 groups, i.e. polyethylene, N is Avogadro's number and a_{CH_2} the cross sectional area of an adsorbed CH_2 group. Fig. 1 displays the variation

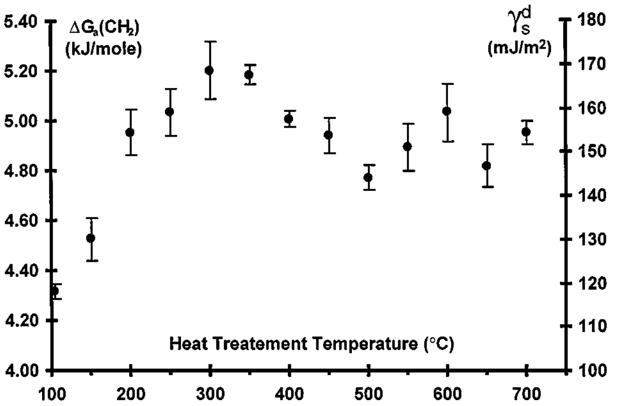

Figure 1 Variation of $\Delta G_a(CH_2)$ and γ_S^d of samples of NiO submitted to increasing heating temperatures.

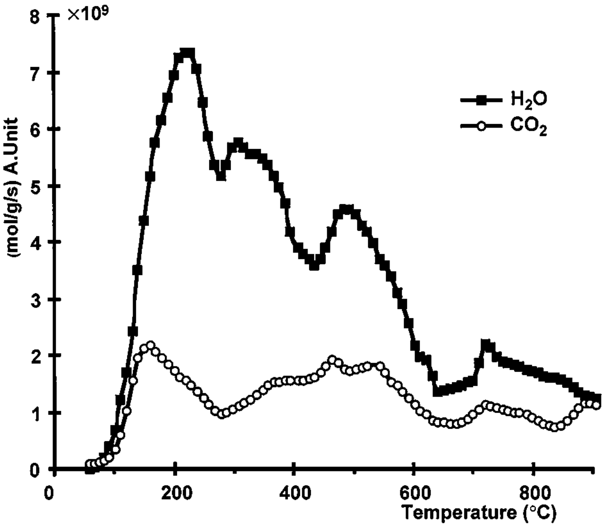

Figure 2 Rates of water and CO_2 evolution when heat treating NiO.

of $\Delta G_a(CH_2)$ and γ_S^d of samples of NiO submitted to increasing heating temperatures.

It is seen that the variations are all, but simple. Variations of γ_S^d result from variations in surface composition, density of atoms or surface groups and polarizability. The departure of water, resulting from the condensation of surface hydroxyl groups, will generated strained, more polarizable surface structures as it was the case when heating silica samples [9]. TPD experiments (Fig. 2) lead to additional information.

The similitude between the curves of Figs 1 and 2 is most striking, at first glance. Maximum are again observed by TPD. The curves are not exactly superimposables: a fact that possibly stems from the unavoidable differences in heating rates of NiO in the GC column or in the TPD instrument. As the temperature approaches 300 °C, the rate of water release suddenly decreases: the dehydroxylation becomes much more difficult since the probability of finding near hydroxyl groups on the NiO surface becomes smaller. But, why should this be a discontinuous process? Possibly because, as it could be demonstrated for silicas, an important surface rearrangement of NiO structures takes place accompanied by a sharp decrease of the polarizability of the newly created structures. There is a second event, of lesser amplitude, occurring in the 600–700 °C temperature range.

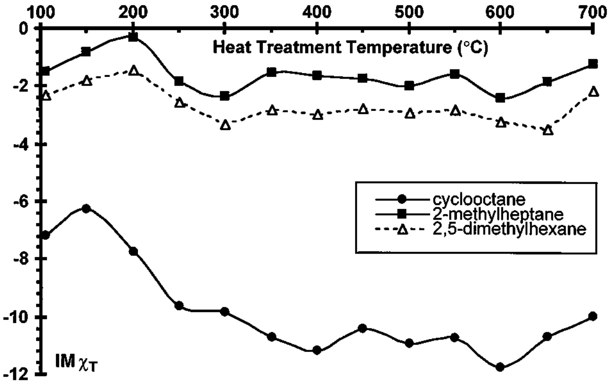

Figure 3 Variation of the nanomorphology of NiO samples upon heat treatment.

In that interval, the loss of water or of CO_2 becomes negligible. Similar observations were made on hematite samples and were attributed to surface restructuration or surface relaxation phenomen favored by thermal agitation. Such an event would possibly lead to a variation of the surface nanorugosity that may also be investigated by IGC.

3.2. Surface nanomorphology

A simple method to verify if a solid surface is flat on the molecular layer (or at least on the level of the probing molecule) is to compare the adsorption behaviors of linear and bulky alkanes isomers on a flat reference surface and on the surface of interest [10]. More recently, we [11] developed a more elaborated method that takes into account the geometry of the probe molecule. This method is based on the use of topology indices, often applied in chemistry for the establishment of quantitative structure-properties relationships, and that may be readily calculated for the probes employed for IGC determinations. Fig. 3 demonstrates the application of these concepts to NiO. The physical meaning of the $IM\chi_T$ parameter is based on the differences of accessibility of molecules having the same topology indices such as *n*-alkanes and their branched isomers.

Cyclooctane appears as amost sensitive molecular probe for the testing of nanomorphology variations occurring in the 200–300 °C and 550–650 °C temperature ranges. This curve exhibits 2 maxima in for temperatures very close to those exhibited by the curves relating γ_S^d and rate of water release to heat treatment temperatures. We may conclude that the NiO surface alterations, induced by temperature, generate modifications of the surface nanomorphology: local increase of roughness due to chemical rearangements, at lower temperature, and possibly structural rearrangement (surface relaxation) at higher temperature.

3.3. Specific interaction parameter (I_{SP})

Heat treatments of NiO significantly alter the surface chemistry of NiO and also its physical interaction potential as seen previously with *n*-alkanes. *n*-alkanes are indicative of London or non specific type of interaction. Polar probes will give additional information on

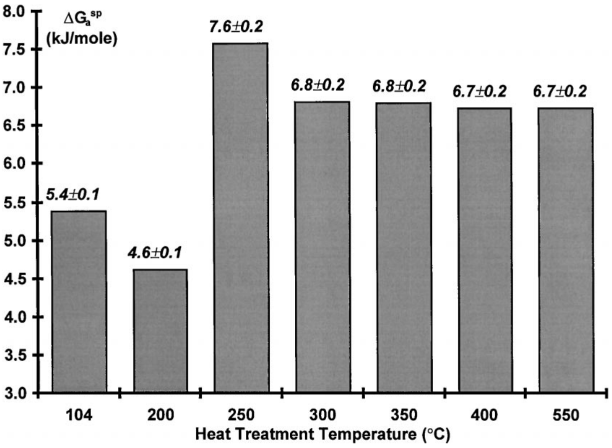

Figure 4 Specific interaction parameters I_{SP} measured with benzene on heat treated NiO samples.

the acid-base (in the Lewis sense) of the NiO surface. A specific interaction parameter (I_{SP}) was proposed in earlier papers [12]. It is obtained by subtracting, from the total ΔG of interaction of the polar probe, the contribution of the London interaction. In the practice, the n-alkane line is plotted as for the γ_S^d determination. The representative point of a given polar probe is always located above that line and the departure from the alkane line defines I_{SP}. NiO is known for its catalytic properties that are enhanced by heat treatments and consequently, only IGC probes that do not undergo catalytic alterations may be used to test the acid-base characteristics of the NiO samples. Benzene that possesses limited acid-base properties allowed to evidence the modifications generated by heat treatment (Fig. 4).

The main variations in surface properties appear in the 100–500 °C temperature range, following the water elimination: physically adsorbed water and water accompanying the condensation of hydroxyl groups. An optimal interaction value of benzene is recorded after a 250 °C treatment and thereafter the acid-base properties do no longer change significantly. The question of the reversibility of the NiO surface alteration may be checked by trying to rehydrate the surface using wapor vapor and determining γ_S^d (Table I).

It is seen that under our experimental conditions, the regeneration of the surface state of a 300 °C treated NiO sample is not possible.

3.4. Surface energetic heterogeneity

As pointed out earlier, IGC at infinite dilution conditions is mainly a qualitative yet most sensitive method to follow surface modifications of chemical and or morphological origins. On the contrary, IGC at finite concentration conditions will deliver a more comprehensive description of the NiO energetic surface properties. This is based on the interpretation of adsorption isotherms calculated from the GC peak [13, 14]. From the isotherms, standard values such as specific surface area (S) and BET constants C (in relation with the enthalpy of interaction during the monolayer formation) may be extracted (Table II).

TABLE I Rehydratation of a 300 °C treated NiO sample and control by γ_S^d determinations at 104 °C

Treatment Temperature	γ_S^d (mJ/m^2) before rehydration	γ_S^d (mJ/m^2) 1st rehydration	γ_S^d (mJ/m^2) 2nd rehydration
104°C	118 ± 2	155 ± 4	154 ± 3
300°C	164 ± 4	163 ± 3	166 ± 3

TABLE II Surface areas and BET constants calculated from n-octane adsorption isotherms (36.5 °C) on NiO samples

Treatment Temperature	S_{BET} (m^2/g)	C_{BET}
104°C	2.4 ± 0.3	6.5 ± 1.0
200°C	2.6 ± 0.2	11.2 ± 1.3
300°C	1.9 ± 0.2	10.6 ± 0,6

In comparison, the area determined by nitrogen adsorption is 1.9 ± 0.2 m^2/g. It is also interesting to note the important increase of the C value after a 200 °C heating of NiO, in agreement with our earlier IGC results.

Surface heterogeneity may have several origions: chemical, structural, presence of impurities, etc. All these will influence the number and nature of adsorption sites. Theories are now well established for the calculation of the energetic adsorption sites distributions [13, 14]. Without going into details, it is supposed that the surface of NiO may be spliced in regions containing sites of given adsorption energy. The actual global isotherm may then be considered as resulting from the contribution of local isotherms, each of them corresponding to a given region or a fixed value of the adsorption energy. Conversely, from the global isotherm it should be possible to evaluate the sites according to their capacity of interaction (adsorption energy) with the GC probes. Obviously, the adsorption energy distribution function will depend on the selected probe (interaction potential and bulkiness). As an example, Fig. 5 relates the number of sites, expressed as μmol/g, to their individual interaction energy with 2,2,4-trimethylpentane on NiO samples treated at increasing temperatures.

On the non treated sample, 3 familes of adsorption sites may be identified. IGC by itself is unable to

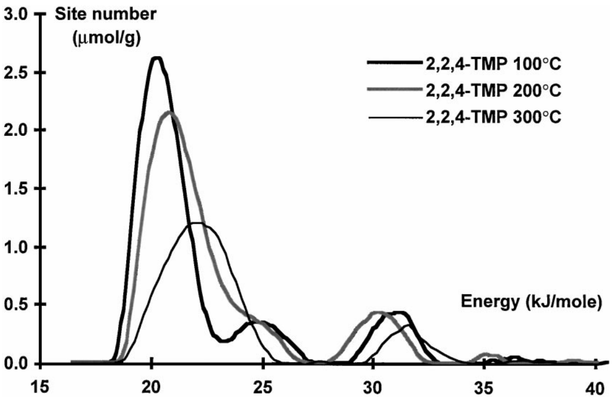

Figure 5 Adsorption energy distributions functions of 2,2,4-trimethylpentane on NiO treated at different temperatures. (From isotherms measured at 50 °C.)

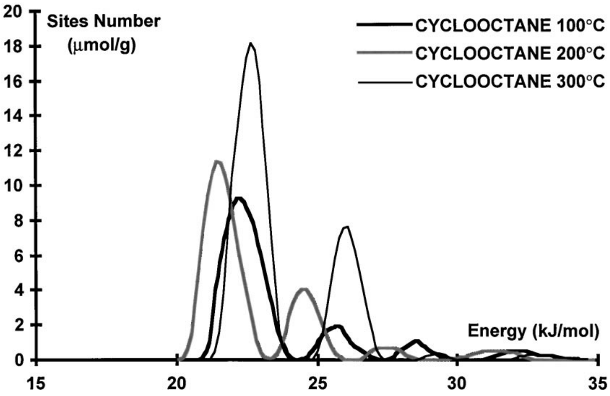

Figure 6 Adsorption energy distributions functions of cyclooctane on NiO treated at different temperatures. (From isotherms measured at 50 °C.)

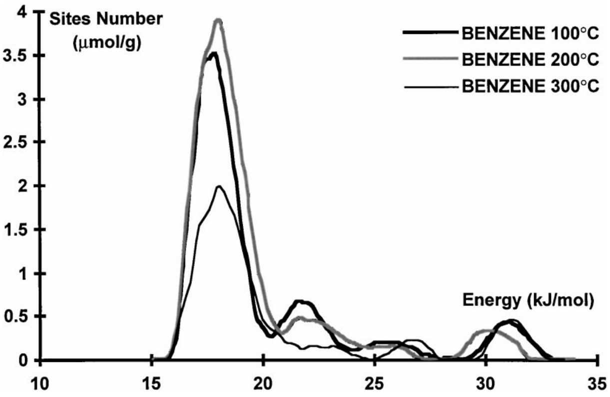

Figure 7 Adsorption energy distribution functions of benzene on NiO treated at different temperatures. (From isotherms measured at 50 °C.)

disclose the origin of these families. Additional methods such as a controlled surface modification as we showed recently [15] will allow to come closer to an answer. Sites of high adsorption energy are also present on this sample's surface. Upon heat treatment up to 300 °C, the surface state of NiO changes. Only 2 families remain with a shift, towards higher energies, of the family corresponding to the lower energies of adsorption. These tendencies were also observed with *n*-octane and become even more apparent on the curves recorded with cyclooctane (Fig. 6).

The curve relative to benzene (Fig. 7) is in global agreement with the others, but some differences show up.

There is no significant shift of the family corresponding to the lowest energies of benzene adsorption, yet the number of sites changes with the temperature of treatment: increasing slightly when going from a heat treatment temperature of 100 to 200 °C, and then decreasing significantly when treating at 300 °C. At this temperature, the family of intermediate adsorption energies is displaced to higher values. One may speculate about the nature of the families in comparison to what has been demonstrated [15] for silica samples: region rich NiO-NiO links (first family), region rich in hydroxyl groups (second family) and region corresponding to structural defects with sizes comparable to the one of the molecular IGC probe.

4. Conclusion

Thermal treatments of NiO destroys the hydrated surface layer possibly formed during a long term aging process of the native particles in the atmosphere. After treatment at 300 °C, the restoring of the initial surface state becomes impossible under mild rehydration conditions. The surface of this oxide is very heterogeneous due to the existence of adsorption sites that can be classified into families. IGC provides a convenient and an interesting way to evidence and quantify these families, yet in a comparative manner: the indication resembling a fingerprint of the studied surface.

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