

Chemisorption and Interaction of Hydrogen and Oxygen on Ni/SiO₂ Catalysts

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The interaction at room temperature of hydrogen with preadsorbed oxygen on the surface of a Ni/SiO₂ catalyst was studied using volumetric, low-field magnetic, and infrared spectroscopic measurements. Oxygen was adsorbed ($T = 22^\circ\text{C}$) by dissociative chemisorption of O₂ or by decomposition of N₂O according to $\text{N}_2\text{O}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}(\text{ads})$. The chemisorption of O₂ always exceeded the monolayer coverage, which was defined as the amount of hydrogen taken up at 22°C and $P_{\text{H}_2} = 30$ Torr. With N₂O the monolayer coverage could be surpassed with sufficiently large exposures. After admission of hydrogen at room temperature to samples that previously had taken up more than a monolayer of oxygen, a surface reaction that led to formation of physisorbed H₂O proceeded. Adsorption of H₂ and subsequent surface reaction were found to occur only when sites that could dissociate hydrogen molecules were present; on completely oxidized NiO no hydrogen adsorption was observed at 30°C . © 1988 Academic Press, Inc.

INTRODUCTION

Since the classic work of Schuit and De Boer (1) the low-temperature interaction between oxygen and hydrogen on nickel surfaces has been extensively studied. Ponec *et al.* (2–4) investigated the interaction on Ni films at temperatures between 78 and 300 K. Their main conclusion was that hydrogen must be chemisorbed dissociatively on reduced nickel sites prior to reaction with preadsorbed oxygen. Recently De Bokx *et al.* (5) studying the hydrogen–oxygen interaction on a single-crystal Ni(100) surface at temperatures from 150 to 200°C also concluded that hydrogen atoms are required for the reduction reaction to proceed.

More divergence of opinion exists on the nature of the interaction between hydrogen and preadsorbed oxygen on Ni catalysts. Rudajevova and Pour (6) observed that no hydrogen at all was adsorbed on a Ni/Al₂O₃ catalyst having previously taken up oxygen, whereas Slinkin *et al.* (7) reported the

formation of surface hydroxyl groups on a Ni/SiO₂ catalyst under similar conditions. These authors agree with Ponec *et al.* that the amount of H₂ taken up by a sample with preadsorbed oxygen can be larger than the amount adsorbed on an equally large clean surface.

In the present work we have attempted to elucidate the interaction at room temperature between hydrogen and preadsorbed oxygen on a Ni/SiO₂ catalyst. To that end volumetric, magnetic, and infrared spectroscopic measurements were carried out. Oxygen was adsorbed on the Ni surface by either dissociative chemisorption of O₂ or decomposition of nitrous oxide according to $\text{N}_2\text{O}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}(\text{ads})$. During the chemisorption of O₂ and N₂O special attention was paid to the occurrence of bulk oxidation as related to transport of the adsorbing gases through the pores of the catalyst pellets.

EXPERIMENTAL

The catalyst used (prepared by the method of homogeneous deposition–precipitation using urea decomposition at 90°C

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(8) was the same (catalyst "U₄₂") as that described before (e.g., Ref. (9)). The loaded carrier of a nickel-to-silica (Aerosil, 380 m² g⁻¹) weight ratio of 1.0 was dried at 120°C, pressed, and cut into small pieces of dimensions between 1.5 and 2.5 mm. After calcination in N₂ at 350°C, reduction was carried out in a flow of 10% H₂ in Ar at 475°C for at least 80 h (in earlier work (e.g., Ref. (9)) the reduction temperature always was 450°C).

All volumetric experiments were performed at room temperature in a conventional Pyrex high-vacuum apparatus, which has been described by Joziassé (10). The pressure of the adsorbing gas was monitored and recorded by means of a pressure transducer (0–10 Torr differential pressure, Setra Systems). Condensable gases in the system could be removed by a cold trap kept at 77 K connected with the sample cell via a stopcock. All volumetric measurements (H₂, O₂, and N₂O chemisorption) were performed with the same catalyst sample (weight about 0.4 g). Between subsequent experiments the sample always was re-reduced and evacuated.

Because the decomposition of nitrous oxide, according to N₂O(g) → N₂(g) + O(ads), does not bring about a change of pressure, a special procedure was utilized to study this reaction. A dose of N₂O was admitted to the sample cell and after 2 min the pressure was measured. From the pressure drop observed the amount of nondissociatively adsorbed nitrous oxide, (N₂O)_{nda}, was calculated. After 2 min the remaining gaseous N₂O was condensed into the cold trap. From the pressure thus obtained, which is due to molecular nitrogen, the amount of dissociatively chemisorbed nitrous oxide, (N₂O)_{da}, was determined. Next the system was evacuated again, the connection between the cold trap and the sample cell was closed, and a new dose of N₂O was admitted.

The equipment and procedures applied in the low-field magnetic measurements ($H = 66$ Oe; 1 Oe = 79.58 A m⁻¹) and in the

infrared spectroscopic experiments have been described before (11). All magnetic measurements were performed at 30°C; the infrared spectra were recorded at room temperature. In the infrared experiments a Ni catalyst with a lower nickel content (about 40 wt% Ni) was used, which previously has been described as catalyst U₄₂ (IR) (11). Prior to the magnetic and the infrared spectroscopic measurements the catalyst samples were pretreated in the same way as that of the sample utilized in the volumetric measurements. Hydrogen and oxygen were dehydrated before use over a molecular sieve (Linde, type 4A); moreover, hydrogen was deoxygenated by a Baker Deoxo catalyst (Pd/alumina). Nitrous oxide (99.99%), which was obtained from l'Air Liquide, was used without further purification.

RESULTS

Adsorption of Hydrogen

Small doses of hydrogen were admitted to the freshly reduced and evacuated catalyst sample at room temperature. In Fig. 1 it can be seen that the volume chemisorbed, V_a , was about 32 ml STP H₂(g Ni)⁻¹ at a hydrogen pressure of 30 Torr (1 Torr = 133.3 N m⁻²). The surface coverage attained at this value of V_a was defined as the monolayer coverage. For a detailed de-

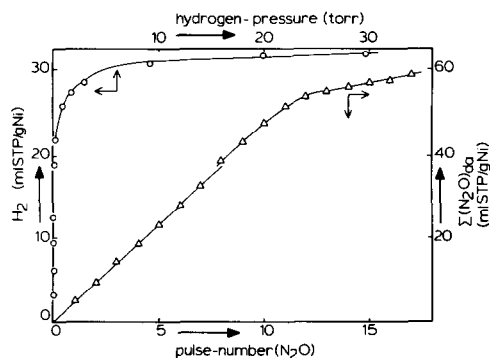


FIG. 1. Comparison of the integral amount of dissociatively chemisorbed N₂O and the amount of adsorbed H₂, both at 30°C on the same sample of Ni/SiO₂.

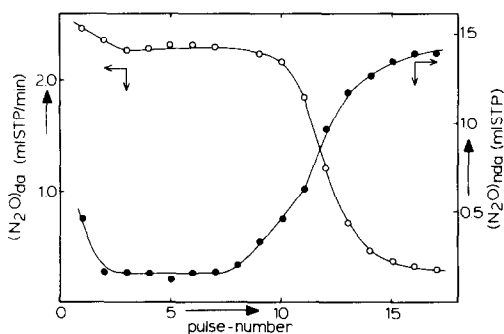


FIG. 2. Rate of the dissociative reaction of N₂O, as well as the amount of nondissociatively adsorbed N₂O, as a function of the dose number (both expressed per gram of nickel). (N₂O)_{da} dissociated, (N₂O)_{nda} not dissociated nitrous oxide.

scription of H₂ chemisorption on Ni/SiO₂ catalysts we refer to a previous paper (12).

Adsorption of Nitrous Oxide

The dissociative chemisorption of nitrous oxide was studied with the same catalyst sample as that used in the above experiment on hydrogen adsorption. The sample was exposed to subsequent doses of N₂O; the exposure time was always 2 min and the volume admitted per dose amounted to 10.2 ml STP (g Ni)⁻¹. The integral amount of nitrous oxide dissociated, Σ(N₂O)_{da}, is represented in Fig. 1 as a function of the dose number. Up to about 75% of a monolayer, Σ(N₂O)_{da} linearly increased, which indicates a constant rate of reaction. A discontinuity is apparent at the eighth dose. The exposure time of this dose was 4 min instead of the usual 2 min, thus causing an increased extent of reaction. In Fig. 2 the rate of reaction is plotted versus the dose number. After a rather fast reaction of the first and second doses, the rate of oxygen chemisorption was found to be constant from the third to the tenth dose. Subsequently the rate of the reaction dropped. Σ(N₂O)_{da} gradually approached 60 ml STP (g Ni)⁻¹, which is close to the monolayer coverage as found by the dissociative chemisorption of hydrogen (32 ml STP (g Ni)⁻¹). When the size of the nitrous oxide

doses or the reaction time with the catalyst sample was increased, the monolayer coverage could be exceeded. In an experiment we continued the measurements up to a value of V_a of about 80 ml STP (N₂O)_{da}(g Ni)⁻¹. In Fig. 2 the amount of nitrous oxide which was molecularly adsorbed per dose (N₂O)_{nda} is also plotted versus the dose number. At the first dose this amount was found to be larger than that at subsequent doses. When the monolayer coverage was approached, (N₂O)_{nda} started to increase.

Adsorption of Oxygen

The catalyst sample was also exposed to doses of molecular oxygen. Three experiments were performed in which the average volume of the oxygen dose was varied: 1.4, 2.8, and 4.2 (or 9.5) ml STP (g Ni)⁻¹. In each experiment the "sorption time," defined as the time required for the complete uptake of the dose, was measured. In Fig. 3 this time is plotted as a function of the volume of oxygen taken up. At small surface coverages the sorption time of all doses was very small. Up to about a coverage of a monolayer the sorption times of the smallest and medium sized doses followed the same curve. However, the sorption time of the smallest doses increased more steeply at or slightly above the monolayer

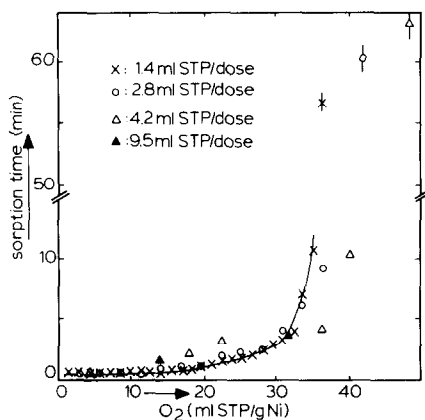


FIG. 3. Sorption time of differently sized oxygen doses as a function of the integral amount of oxygen taken up. In one experiment (Δ, ▲) doses of 4.2 and 9.5 ml STP (g Ni)⁻¹ were utilized.

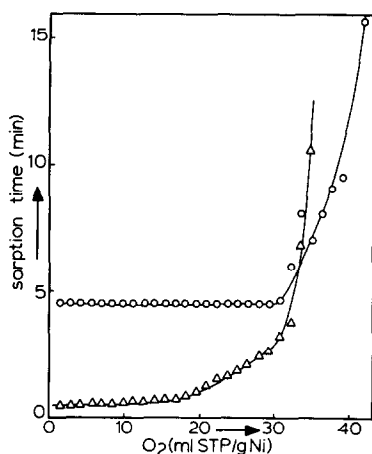


Fig. 4. Sorption time of oxygen doses of 1.4 ml STP (g Ni)⁻¹ as a function of the integral amount of oxygen taken up. Δ, *In vacuo*. ○, With 2 Torr of He.

coverage. The sorption time of the largest doses was always slightly above the curve; it started to increase strongly only after markedly more than a monolayer had been adsorbed. The admission of oxygen was stopped when the sorption time had increased to about 1 h. The integral volume of oxygen taken up in the experiment with the smallest doses was 36.4 ml STP (g Ni)⁻¹, with the medium-sized doses 42 ml STP (g Ni)⁻¹, and with the largest doses 48.3 ml STP (g Ni)⁻¹.

The experiment with the smallest doses was repeated after previous admission of helium to the sample at a pressure of 2 Torr. The results are represented in Fig. 4. In the presence of He the sorption time per dose was larger. Moreover, the helium present raised the volume of oxygen taken up in about 16 min from 37.0 ml STP (g Ni)⁻¹ (interpolated) to 42.0 ml STP (g Ni)⁻¹.

Adsorption of Hydrogen on Preadsorbed Oxygen

Volumetric measurements. Hydrogen doses of 1.4 ml STP (g Ni)⁻¹ were admitted to the catalyst sample which previously had dissociated 76.6 ml STP (g Ni)⁻¹ of N₂O, corresponding to 38.3 ml STP (g Ni)⁻¹ of

O₂. Prior to the admission of H₂ the catalyst had been evacuated to about 10⁻⁶ Torr. It was observed that at equal pressures the amount of hydrogen adsorbed on the "pre-oxidized" sample exceeded the volume chemisorbed on the freshly reduced sample. At an equilibrium pressure of 0.5 Torr, for instance, V(H₂) on the preoxidized sample was found to be 31.0 ml (g Ni)⁻¹ whereas at the same pressure V(H₂) on the clean nickel surface only was 24.2 ml STP (g Ni)⁻¹. At a final pressure of 6 Torr V(H₂) had already increased to a value of 41.0 ml STP (g Ni)⁻¹, which is considerably larger than the monolayer coverage of the freshly reduced sample. Similar results were obtained with catalyst samples which previously had adsorbed oxygen originating from O₂.

Magnetic measurements. Oxygen was added dosewise to the freshly reduced and evacuated superparamagnetic catalyst sample (weight 1.8 g) at 30°C. At the end of the experiment the catalyst had sorbed 40.5 ml STP (g Ni)⁻¹ of oxygen; the relative magnetization, M/M_0 (M is the actual magnetization, M_0 is the magnetization of the freshly reduced and evacuated sample), had decreased to 0.64. After evacuation hydrogen was dosed to the catalyst; the dose size was 11.25 ml STP (g Ni)⁻¹. In Table I the results of three subsequent hydrogen doses are shown. The first H₂ dose was taken up instantaneously with a large heat effect; the temperature of the sample was raised from 30 to 50°C. As can be seen in Table I the relative magnetization, which was measured after the sample had cooled down to 30°C again, increased to 0.71. It was still increasing when the second H₂ dose was admitted. This dose was adsorbed more slowly; the temperature increased only by 0.5°C. After an initial rapid drop the relative magnetization gradually increased to 0.75. The hydrogen of the third dose was chemisorbed very slowly; after 5 h equilibrium had not yet been attained. The effect on the magnetization of the third dose was about equal to that of the second.

TABLE 1

Relative Magnetization of a Catalyst Sample, Which Previously Had Chemisorbed 40.5 ml STP (g Ni)⁻¹ of O₂, after Admission of Subsequent Hydrogen Doses

Pulse number	Amount of H ₂ adsorbed per dose (ml STP (g Ni) ⁻¹)	(M/M ₀) ^a	(M/M ₀) ^b	(M/M ₀) ^c
1	11.25	0.64	0.71	—
2	11.25	0.71	0.64	0.75
3	9.85	0.75	0.65	0.73

^a Relative magnetization prior to the admission of the dose.

^b Relative magnetization immediately after the sample, the temperature of which rose upon the admission of H₂, had cooled down again to 30°C.

^c Relative magnetization after equilibrium had been attained (for the third dose, after 5 h).

Infrared spectroscopic measurements. A small amount of catalyst U₄₂(IR) was pressed into a disk and subsequently reduced. After evacuation the disk was exposed at room temperature to 0.1 Torr O₂ for 30 min. Next the disk was evacuated again and 64.8 Torr of H₂ was admitted, also at room temperature. In the infrared spectrum a shoulder at about 3600 cm⁻¹ in the absorption band with its maximum at 3740 cm⁻¹ was observed (Fig. 5). Moreover, a new band appeared in the spectrum at 1610 cm⁻¹ (Fig. 6). Because in this latter region the silica carrier also shows an absorption band, the spectra in Fig. 6 are corrected for this absorption.

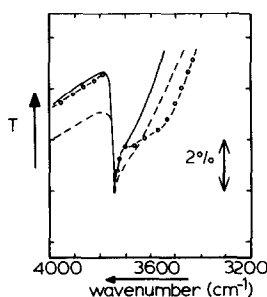


FIG. 5. Broadening of the infrared adsorption band in the O-H stretching region of the spectrum. (—) Freshly reduced and evacuated sample. (---) Sample in 0.1 Torr O₂. (-·-) Sample with preadsorbed oxygen in 64.8 Torr H₂.

DISCUSSION

Adsorption of Hydrogen

The monolayer capacity was determined at a final hydrogen pressure of 30 Torr. In earlier experiments (e.g., Ref. (13)) it was observed that at higher pressures small amounts of hydrogen can be adsorbed additionally. With the pressure gauge used in the present investigation, however, it was impossible to measure pressures above 30 Torr. This implies that the actual monolayer coverage may be at a value of V_a which is slightly above 32 ml STP (g Ni)⁻¹.

Adsorption of Oxygen

Figure 3 shows that the uptake of molecular oxygen eventually exceeded the mono-

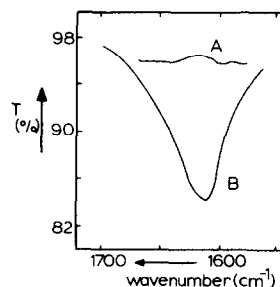


FIG. 6. Infrared spectrum of the catalyst with preadsorbed oxygen prior to (A) and after (B) the admission of 64.8 Torr of H₂. Spectra were corrected for the absorption by the silica carrier.

layer volume, irrespective of the mean dose size. This is to be ascribed to chemisorbed oxygen atoms exchanging places with atoms of the underlying nickel metal. By means of photoelectric measurements Quinn and Roberts (14) have demonstrated that such a place exchange, which results in the onset of bulk oxidation, can proceed on nickel ribbons at 23°C.

It is also evident from Fig. 3 that the amount of O₂ taken up increased with the mean size of the O₂ dose. This is due to a more pronounced bulk oxidation. Bulk oxidation is expected particularly for those Ni particles which are situated near the pore mouths and which are therefore temporarily exposed to oxygen at higher pressures than those of the particles further in the pores. This effect is enhanced when larger O₂ doses, and hence higher pressures, are applied.

Moreover, due to the high heat of adsorption of oxygen on nickel each amount of oxygen adsorbed will cause a local rise of the temperature and, consequently, a more rapid migration of surface oxygen into the bulk. Thus, when the extent of O₂ adsorption increases as a result of larger applied exposures, locally the temperature will rise more pronouncedly leading to further oxygen sorption. So, the effect of increased oxygen exposures is reinforced by the locally higher temperatures induced.

From the above it cannot be derived whether oxidation of the bulk occurs from the first O₂ dose onward or proceeds only after all nickel particles have taken up a monolayer. The sticking probability of oxygen on nickel surfaces is known to be elevated up to the monolayer coverage (15). At higher coverages the sticking probability rapidly drops. When oxygen is admitted to a catalyst sample, it is therefore expected that a monolayer is chemisorbed by all particles before oxidation of the bulk can proceed. This is confirmed by the experiment with small oxygen doses where 2 Torr of He was present. Due to the presence of He the diffusion of oxygen molecules to the

nickel particles is retarded, which leads to the increased sorption times evident from Fig. 4. Accordingly the Ni particles, especially those near the pore mouths, are exposed to O₂ for a longer period than that without He. If the increased exposures result in the oxidation of the bulk before all particles have taken up a monolayer, a gradual increase in the sorption time with the dose number can be predicted. Actually the sorption time did not start to increase before the monolayer coverage had been attained. As is apparent from Fig. 3, however, applying relatively high oxygen pressures does bring about a slight oxidation of subsurface layers before all nickel particles have taken up a monolayer.

Although it could be established that bulk oxidation proceeds markedly only after most Ni particles have been covered by a monolayer, the distribution of O₂ over the differently sized nickel particles at surface coverages smaller than unity remained obscure. Either the oxygen coverage rises essentially uniformly or particle after particle is taking up a monolayer of oxygen. The latter possibility is the most plausible because of the large sticking probability of O₂. After admission of the initial O₂ doses the gas phase is rapidly depleted by chemisorption by easily accessible particles. Only when these particles are fully covered can the oxygen molecules be expected to penetrate further into the pores. This can be verified experimentally using the low-field magnetic permeameter. In Fig. 7 the initial slopes of the magnetization–volume isotherms for the chemisorption of H₂ and O₂ are represented. Both were measured at 30°C on the same catalyst sample. It can be seen that the slope of the oxygen isotherm is smaller than the slope of the hydrogen isotherm. With an equal distribution of H₂ and O₂ over the Ni particles, however, the slopes of the isotherms are expected to be the same. According to Geus and Nobel (16) the smaller slope of the oxygen isotherm is caused by a more inhomogeneous distribution of oxygen over the crystallites,

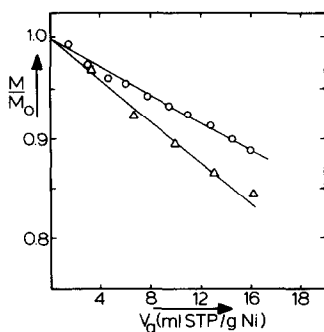


FIG. 7. Initial slopes of the magnetization–volume isotherms for the chemisorption of hydrogen and oxygen at 30°C. ○, O₂ isotherm, △, H₂ isotherm.

compared to that of hydrogen. Our magnetic results are hence in agreement with the conclusion arrived at above, that the surface coverage of oxygen, θ_{O} , is inhomogeneous. Particles situated at the far end of the pores have a smaller θ_{O} than particles at the pore mouths. Martin *et al.* (17) also observed that the slope of the (low-field) magnetization–volume isotherm for the chemisorption of O₂ on Ni/SiO₂ catalysts was smaller than the slope of the H₂ isotherm. The authors ascribe the difference to the preferential adsorption of O₂ on the smallest crystallites. We think that this explanation does not apply to our system. In a previous paper (12) we have reported that due to transport limitations at 30°C the smallest Ni particles in the narrowest pores of the catalyst are hardly attained by hydrogen. It is very unlikely that the O₂ molecules with a much larger sticking probability migrate more easily through the very narrow pores than hydrogen. Hence, a preferential chemisorption of oxygen on the smallest Ni particles can be ruled out with our catalysts that contain a marked fraction of narrow pores (8).

Adsorption of N₂O

Unlike molecular oxygen the dissociative chemisorption of nitrous oxide (N₂O(g) → N₂(g) + O(ads)) leads to a homogeneous distribution of oxygen atoms over the nickel particles (16). Apparently, the trans-

port of N₂O through the pores of the catalyst is faster than the rate of decomposition, which indeed has been reported to be relatively slow (18). As evident from the previous section the homogeneous distribution of N₂O does not prevent the catalyst from taking up more than a monolayer of oxygen during large N₂O exposures. The rate of chemisorption, however, strongly drops at surface coverages above 0.75 (Fig. 2). Since the dissociative adsorption of N₂O does not cease at the monolayer coverage, Rudajevova and Pour (19) correctly state that nitrous oxide is not a suitable adsorbate to determine the specific nickel surface area of Ni catalysts.

After admission of the first N₂O dose the total pressure was found to decrease to a lower value than that after subsequent doses. As has been mentioned in the experimental section, this pressure drop was ascribed to physisorbed nitrous oxide, (N₂O)_{nda}. It is, however, very improbable that (N₂O)_{nda} on the freshly reduced and evacuated catalyst surface (dose number 1, Fig. 2) is larger than that on the slightly oxidized surface (numbers 2 to 8) and then increases again at higher surface coverages of oxygen (dose number > 8). According to Joziassé (10) the large pressure drop after the first N₂O dose is probably due to the adsorption of molecular nitrogen on the nickel surface. He obtained infrared spectroscopic evidence for the adsorption of N₂ molecules on uncontaminated, homogeneously precipitated Ni/SiO₂ catalysts, as was also found by Van Hardeveld and Van Montfoort (20). The amount of nondissociatively adsorbed N₂O started to increase only after θ_{O} had reached a value of 0.65.

Interaction of Hydrogen with Preadsorbed Oxygen

The oxygen-covered catalyst samples were found to take up large quantities of hydrogen, even more than the freshly reduced and evacuated samples. For instance, at 22°C the chemisorption of H₂ on a sample which has chemisorbed 76.6 ml

STP (g Ni)⁻¹ of N₂O exceeds the monolayer coverage already by about 30% at a H₂ pressure as low as 6 Torr. The extent of H₂ adsorption being larger on samples with preadsorbed oxygen was also observed by Ponec *et al.* (4) on Ni films at 298 K and by Slinkin *et al.* (7) on Ni/SiO₂ catalysts at 295 K. The increased H₂ chemisorption indicates that a surface reaction proceeds, the product of which (at least partly) is water. When only surface hydroxyl groups result from the interaction between H(ads) and O(ads), the maximal amount of H₂ taken up cannot be larger than the volume chemisorbed by the bare surface.

The formation of H₂O is also evident from the magnetic measurements of Table 1. The first hydrogen dose, admitted to a catalyst sample after chemisorption of 40.5 ml STP (g Ni)⁻¹ of O₂, is taken up instantaneously with a large heat effect raising the temperature from 30 to 50°C. Apparently the nickel surface is reduced, for the relative magnetization increases from 0.64 to 0.71. During the surface reaction bare nickel is generated, whereupon hydrogen adsorbs very quickly as can be concluded from the initial rapid drop in magnetization after admission of the second and the third dose. Just as with the first dose, after admission of the second and the third dose the reaction subsequently gives rise to an increase in the relative magnetization from 0.64 to 0.75 and from 0.65 to 0.73, respectively. So, the magnetic results support the volumetric results discussed above in that the hydrogen taken up is not only dissociatively adsorbed as such but also consumed in a relatively slow reaction proceeding on the surface of the catalyst.

At least part of the water produced remains physisorbed on the catalyst surface, as is apparent from the infrared data. As is shown in Fig. 5, a broadening at the low-frequency side of the absorption band with its maximum at 3740 cm⁻¹, which is the characteristic wavenumber for the O-H stretching vibration of isolated surface hydroxyl groups on silica (21), was observed.

This broadening can be ascribed to the presence of bridged OH groups and/or physisorbed water (21). Simultaneously with the broadening of the band in the hydroxyl stretching region of the spectrum a new band appeared with its maximal absorbance at 1610 cm⁻¹ (Fig. 6). This band can be unambiguously attributed to the deformation vibration of adsorbed water molecules (21). Thus we have experimental proof for the conclusion from our volumetric and magnetic measurements that at room temperature hydrogen reacts with preadsorbed oxygen to physisorbed water. From Table 1 it can be seen that the rate of the reaction between H(ads) and O(ads) decreased long before all oxygen had been converted into water. Evidently only a fraction of the preadsorbed oxygen is sufficiently reactive to react with H₂ already at 30°C. A relatively small reactivity of preadsorbed oxygen toward hydrogen was also observed by De Bokx *et al.* (5). Studying the interaction between H(ads) and O(ads) on a Ni(100) single-crystal plane, they observed the reaction to occur only at temperatures above 150°C. We feel that the possibility of the reaction proceeding already at low temperatures depends on the presence of active sites for the dissociation of molecular hydrogen. When no bare nickel is present, hydrogen must be dissociated on lattice defects in the "NiO" overlayer (22). On the small, strongly curved catalyst particles the number of defects will be larger than those on the single-crystal (100) surface, thus bringing about the different reaction rate. In a similar way the reactivity of the oxygen chemisorbed by the smaller catalyst particles may differ from the reactivity of O(ads) on the larger particles.

We carried out an additional experiment to demonstrate that active sites for the dissociation of H₂ should be present for the reduction reaction to occur already at room temperature. The catalyst sample of Table 1 was completely oxidized at 400°C for 16 h. The relative magnetization decreased to only 0.02. After evacuation an attempt was

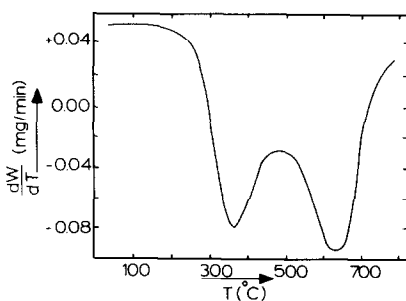


FIG.8. Differential thermal gravimetric (DTG) plot for the reduction of a sample of catalyst U₄₂, previously reduced at 450°C and reoxidized at 440°C. Heating rate 5°C min⁻¹.

made to adsorb hydrogen on this sample at a H₂ pressure of 30 Torr and at 30°C. No hydrogen was taken up and no change in magnetization was measured. This is in agreement with the thermogravimetric experiment represented in Fig. 8. In this figure the temperature-programmed reduction of a catalyst sample, previously reduced at 450°C and reoxidized at 440°C, is shown. The first derivative with time of the weight signal (the "DTG signal") starts to decrease at a temperature as high as 175°C, which indicates the onset of the reduction. Hence "stoichiometric" NiO with only a very small number of lattice defects is not reduced at room temperature.

REFERENCES

- Schuit, G. C. A., and De Boer, N. H., *Recl. Trav. Chim. Pays-Bas* **70**, 1067 (1951).
- Ponec, V., and Knor, Z., *Collect. Czech. Chem. Commun.* **27**, 1443 (1962).
- Ponec, V., Knor, Z., and Cerný, S., in "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 1 p. 353. North-Holland, Amsterdam, 1965.
- Ponec, V., Knor, Z., and Cerný, S., *Discuss. Faraday Soc.* **41**, 149 (1966).
- De Bokx, P. K., Labohm, F., Gijzeman, O. L. J., Bootsma, G. A., and Geus, J. W., *Appl. Surf. Sci.* **5**, 321 (1980).
- Rudajeva, A., and Pour, V., *Collect. Czech. Chem. Commun.* **40**, 597 (1975).
- Slinkin, A. A., Kucherov, A. V., Fedorovskaya, E. A., and Rubinshtein, A. M., *Kinet. Katal.* **18**, 619 (1977).
- Hermans, L. A. M., and Geus, J. W., in "Studies of Surface Science and Catalysis" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), Vol. 3, p. 113. Elsevier, Amsterdam, 1979.
- Kuijpers, E. G. M., Jansen, J. W., Van Dillen, A. J., and Geus, J. W., *J. Catal.* **72**, 75 (1981).
- Joziassé, J., Ph.D. thesis, Utrecht, 1978.
- Kuijpers, E. G. M., Breedijk, A. K., Van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **72**, 210 (1981).
- Kuijpers, E. G. M., Breedijk, A. K., Van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **81**, 429 (1983).
- Kuijpers, E. G. M., Kock, A. J. H. M., Wermer, G. J., and Geus, J. W., *J. Catal.* **88**, 1 (1984).
- Quinn, C. M., and Roberts, M. W., *Trans. Faraday Soc.* **61**, 1775 (1965).
- Holloway, P. H., and Hudson, J. B., *Surf. Sci.* **43**, 123, 141 (1974).
- Geus, J. W., and Nobel, A. P. P., *J. Catal.* **6**, 108 (1966).
- Martin, G. A., De Montgolfier, P., and Imelik, B., *Surf. Sci.* **3**, 675 (1973).
- Dell, R. M., Klemperer, D. F., and Stone, F. S., *J. Phys. Chem.* **60**, 1586 (1956).
- Rudajeva, H., and Pour, V., *Collect. Czech. Chem. Commun.* **40**, 1126 (1975).
- Van Hardeveld, R., and Van Montfoort, A., *Surf. Sci.* **4**, 396 (1966).
- Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York/London, 1966.
- Surrat, G. T., and Kunz, A. B., *Phys. Rev. B* **19**, 2352 (1979).