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Surface Reactivity of NiO: Interaction with Methanol

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The interaction between methanol and a NiO powder sample was studied. The obtained NiO was characterized by means of X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, X-ray diffraction (XRD), and thermal analysis. Chemisorption experiments at atmospheric pressure were studied by means of diffuse reflectance infrared spectroscopy, whereas those carried out under high vacuum (HV) conditions were followed by means of XPS and quadrupolar mass spectrometry (QMS). Methanol interacts mainly molecularly with the NiO powder surface whereas dissociative chemisorption is more evident at higher temperatures. The formation of CO_2 and of formate species is evident at $T \geq 323$ and 423 K, respectively. Under HV conditions formaldehyde forms at higher temperatures.

Introduction

Nickel oxide is a promising material in several fields of applied technology such as in catalysis or in the production of fuel cells.[1,2] For example, this oxide is an important constituent of oxidation catalysts.[3]

Several papers concern the surface reactivity of NiO; usually, the reactivity of specific crystallographic faces (generally (100) or (111)) is considered. The investigation of the interaction with small organic and inorganic molecules, such as methanol,[4−6] formic acid,[7−11] formaldehyde,[12] oxygen,[13,14] nitrogen,[15,16] and carbon oxides,[16] greatly improved the knowledge of the NiO reactivity.

In this paper, we focus on a polycrystalline powder system. As a matter of fact, polycrystalline catalysts usually consist of randomly oriented particles exposing several crystallographic faces. Moreover, powder catalysts can be characterized by a higher density of surface defects. The aim of our work is to understand the reactivity of a NiO powder sample with respect to methanol, and to correlate the obtained results with those reported in the literature.

Further work is in course in our laboratory to characterize the surface acidity of NiO sample powder; in fact, acid/basic surface sites may play an important role in determining the interaction between alcohol and the oxide surface as well as the reaction paths.

Hydroxyl groups, as an example, can influence the mechanism of interaction between CH_3OH and the NiO powder surface;[17,18] moreover, OH groups can stabilize specific crystallographic faces.[18]

This paper is part of a comprehensive work aiming to understand the surface reactivity of Ni and Co oxide based nanocomposite systems. In this contribution NiO is considered, whereas the reactivity of cobalt oxides with respect to methanol was already investigated.[19]

Chemisorptions were carried out both at atmospheric pressure (in inert atmosphere) and under high-vacuum (HV) conditions. In the former case, the reaction was investigated by means of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, whereas X-ray photoelectron spectroscopy (XPS) and quadrupolar mass spectrometry (QMS) have been joined for experiment in HV. It is noteworthy that the acid/basic sites distribution on the powder surface (and then the surface reactivity) can change under different environmental conditions. This has to be considered when trying to

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correlate the obtained results with those deriving from the exposure of single crystal surfaces under a strictly controlled atmosphere. A different surface may be observed in the two cases: as a matter of fact, a less hydroxylated surface is compatible with the HV conditions.

The interaction between alcohols and oxides surfaces is very interesting, and in fact alcohols are important intermediates in several chemical processes. Moreover, the interaction between alcohol and oxide surfaces can help to clarify the relationships between surface acidity and alcohol decomposition mechanisms. Methanol, in particular, is a useful probe because it is a simple organic molecule characterized by a significant acidity. Methanol also can be an interesting combustible for fuel cells.[20]

Experimental Section

Catalyst Preparation. The NiO powder sample was prepared by precipitation from a basic solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Janssen Chimica; 99%). The solution was obtained by dissolving the nitrate in bidistilled water and adding NH_4OH (Carlo Erba; water solution 30%) until the pH value was 8−9. The precipitated $Ni(OH)_2$ was filtered out and washed with bidistilled water until pH = 7 then it was dried at 573 K for 12 h and calcined at different temperatures (ranging from 673 to 973 K) for 30 h. The powder used for the DRIFT analysis was kept in nitrogen flow to eliminate water traces until a stable IR spectrum was obtained. Before exposure in HV, the sample was processed as a pellet (by pressing the powder at ca. 7×10^6 Pa for 10 min) and evacuated at 1×10^{-3} Pa for 12 h.

Reaction Conditions. Methanol (HPLC grade) employed for chemisorption experiments (Sigma-Aldrich; >99.9%) was used without further purification.

The exposure of the pellet to methanol under HV was carried out at temperatures ranging from room temperature (RT) to 773 K, at a total pressure of ca. $4-5 \times 10^{-4}$ Pa. Alcohol vapors were obtained by evaporation under vacuum. The HV reactor, directly connected to the XPS analysis chamber, allows us to work in flow conditions; moreover, volatile products were characterized by means of a quadrupole gas analyzer (European Spectrometry Systems, ESS). Background gas contributions to the spectra were eliminated by subtracting from the spectrum recorded after chemisorption the one obtained just before. Mass spectra assignments were made in reference to the fragmentation patterns.[21,22]

The contribution of the alcohol was subtracted and mass data were analyzed using the method proposed by Ko et al.[23] Desorption patterns were obtained from the mass spectra by plotting the intensities (partial pressures) of the different masses as a function of temperature.

The temperature of the pellet was evaluated by means of a thermocouple directly in contact with the sample holder. To minimize the difference between the temperature of the sample and that of the sample holder, the system was left at the desired temperature for 30 min before the chemisorption experiments.

Table 1. XRD Data (d, nm) Obtained for the NiO Powder Compared to JCPDS Card

NiO (this work)	NiO (Bunsenite)[a]
2.088 (100)	2.088 (100)
2.408 (60)	2.410 (91)
1.476 (40)	1.476 (57)
1.258 (14)	1.259 (16)
1.206 (8)	1.206 (13)

[a] Joint Committe on Powder Diffraction Standards: card number JCPDS 4-835.

The exposure of NiO powder sample to methanol in the FTIR equipment was done by using the Spectra-Tech. Inc. COLLECTOR apparatus for diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy fitted with a high-temperature high-pressure (HTHP) chamber. The HTHP chamber was filled with nitrogen vapors flowing through a bubbler containing the alcohol. QMS spectra revealed that the methanol/nitrogen partial pressures ratio is always around 0.1 ± 0.01.

DRIFT Measurements. IR spectra were obtained by means of a Bruker IFS 66 spectrometer working in diffuse reflectance mode and are displayed in Kubelka−Munk units.[24,25] The resolution of the spectra was 4 cm^{-1}. The sample temperature was measured through a thermocouple inserted into the sample holder directly in contact with the powder.

XPS Measurements. XP spectra were recorded using a Perkin-Elmer PHI 5600 ci spectrometer with standard Al−Kα source (1486.6 eV) working at 350 W. The working pressure was less than 1×10^{-8} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected in the range 0−1350 eV (187.85 eV pass energy, 0.4 eV step, 0.05 $s \cdot step^{-1}$). Detailed spectra were recorded for the following regions: C 1s, O 1s, Ni 2p (11.75 eV pass energy, 0.1 eV step, 0.1 $s \cdot step^{-1}$); valence band spectra were also recorded (5.85 eV pass energy, 0.05 eV step, 0.1 $s \cdot step^{-1}$). The standard deviation in the BE values of the XPS line is 0.10 eV. The atomic percentage, after a Shirley type background subtraction,[26] was evaluated using the PHI sensitivity factors.[27] To account for charging problems, the C 1s peak was considered to be located at 285.0 eV and the peak BE differences were evaluated.

Thermal Analysis and XRD. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a controlled atmosphere using the simultaneous differential techniques (SDT) 2960 of TA Instruments. Thermograms were recorded at 4 and 10 °C min^{-1} heating rates in air and in nitrogen flow. The covered temperature ranges from RT to 1273 K.

XRD patterns were obtained with a Philips diffractometer with Bragg−Brentano geometry using Cu Kα radiation (40 kV, 40 mA, $\lambda = 0.154$ nm).

Results

Catalyst Characterization. The catalyst powder was characterized by means of XRD, XP, and DRIFT spectroscopies as well as thermal analysis.

The XRD pattern (Table 1) of the sample treated at 973 K coincides with that of cubic Bunsenite,[28] and the average crystallite diameter is about 42 nm.[29]

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Table 2. XPS Peak Positions (BE in eV) Obtained for the NiO Powder as a Function of the Calcination Temperature Compared with Literature Values

sample (calcination temperature/K)	Ni $2p_{3/2}$	multiplet splitting	shake-up Ni $2p_{3/2}$	Ni $2p_{1/2}$	shake-up Ni $2p_{1/2}$
573	855.6		862.8	874.2	880.9
673	853.3	854.9	860.8	871.9	879.1
773	853.8	855.4	860.9	872.3	879.3
873	853.9	855.4	861.0	872.5	879.6
973	854.4	855.9	861.5	873.1	880.1
$Ni(OH)_2$	855.6[a]				
NiO	853.3−854.6[a,b]	856.1[b]	861.7[b]		

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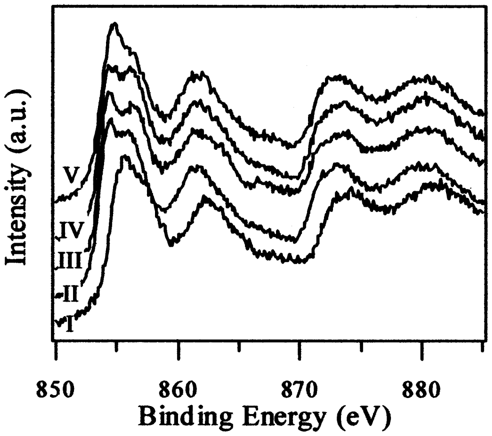

Figure 1. Ni 2p XP spectra obtained on the NiO powder, after heat treatments at (I) 573 K, (II) 973 K, and upon exposure of the powder calcined at 973 K to methanol at (III) RT, (IV) 423 K, and (V) 773 K. (The spectra are normalized with respect to their maximum value).

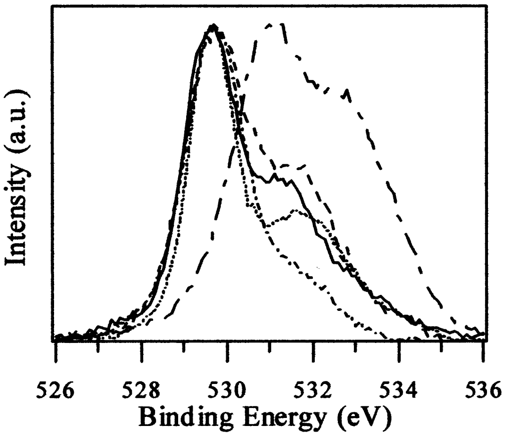

Figure 2. O 1s XP spectra obtained on the NiO powder, after heat treatments at (— —) 573 K, (—) 973 K, and upon exposure of the powder calcined at 973 K to methanol at (•••) RT, (- - -) 423 K, and (-•-•-•-) 773 K. (The spectra are normalized with respect to their maximum value).

The XP Ni $2p_{3/2}$ and $2p_{1/2}$ peak positions observed for the powder samples heated at increasing temperatures are summarized in Table 2 as well as the shake-up and multiplet splitting contributions; and the spectra are shown in Figure 1.

Ni−OH bonds are evident on the surface of the sample treated at 573 K, as demonstrated by the comparison with literature data (Table 2). In contrast, Ni $2p_{3/2}$ and $2p_{1/2}$ (as well as multiplet splitting and shake-up) peak positions for the samples heated at higher temperatures are consistent with literature data for NiO.

For the sample treated at 573 K, O 1s peak (Figure 2) fitting procedure shows two contributions at 530.9 and 532.9 eV, respectively. The peak at 530.9 eV is due to Ni−OH bonds;[30] the other band agrees with the presence of a different kind of Ni−OH bond (or of chemisorbed water). The contribution at 532.9 eV can also suggest the presence of peroxo/superoxo species; as a matter of fact, several authors observed these species on different oxide surfaces.[31−33] Moreover, the separation between the O 1s contribution at higher BE and the O 2p level[34,35] agrees with the expected value for O_2^{2-} species (527.5−528 eV).[36] A new peak at about 529.0−529.6 eV, attributed to Ni−O bonds,[37,38] is evident in the O 1s XP spectra after heat treatments at temperatures higher than 573 K. The contribution at higher BE (532.9 eV), in contrast, almost disappears. The high BE tail of the O 1s peak suggests that OH groups are still present on the NiO sample surface after the heat treatment at 973 K. O/Ni atomic ratio is 1.6 in the sample heated a 573 K and 1.0 in the samples treated at higher temperatures (673−973 K).

DRIFT spectra of NiO powder samples treated at different temperatures (573, 873, and 973 K) are reported in Figure 3. All the IR spectra show the signals due to the Ni−O bonds at wavenumbers lower than 650 cm^{-1}. The inspection of the spectral regions of OH stretching and bending (Figure 3a and b, respectively) reveals, in the sample calcined at 573 K, a broad band between 3200 and 3750 cm^{-1} attributed to the presence of water molecules chemisorbed on the sample surface.[39] Consistently, a peak at 1636 cm^{-1}, due to the O−H bending of water, is evident. In the NiO powder samples heated at 573 K, the contributions attributed to molecularly chemisorbed water, decrease and new peaks at 3619 and 3685 cm^{-1} suggest the presence of H-bonded and isolated hydroxyl.

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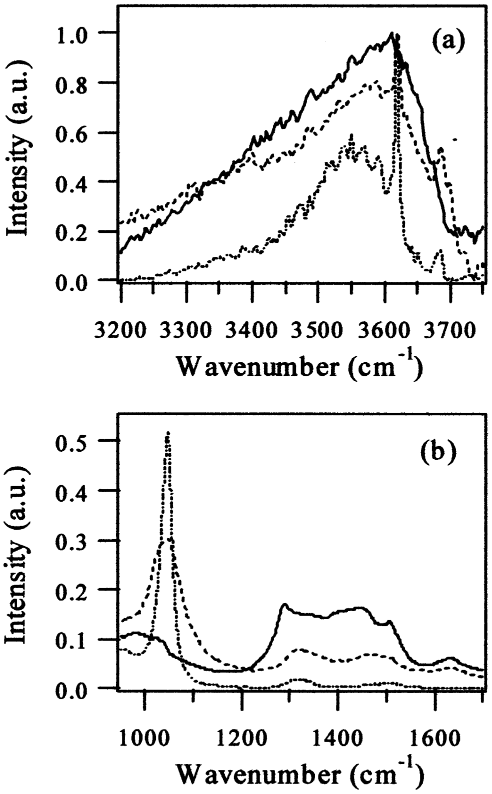

Figure 3. DRIFT spectra of the NiO powder obtained after heat treatment at (—) 573, (- - -) 873, and (···) 973 K: (a) O−H stretching region; (b) region from 950 to 1700 cm^{-1}.

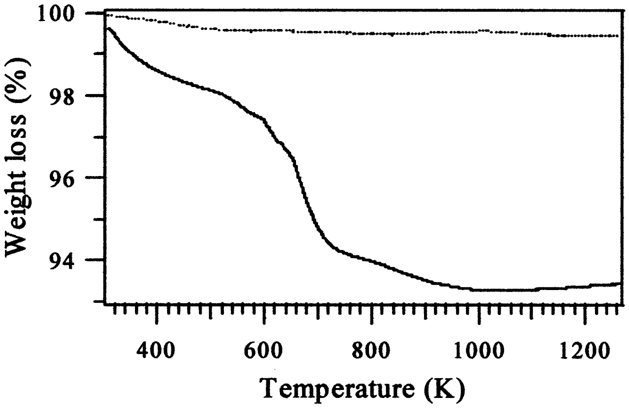

Figure 4. Thermal analysis (weight loss) spectra (4 °C/min) obtained on the NiO powder heated at (—) 573 and (···) 973 K in N_2 flow.

O−H stretching frequencies in NiO samples were studied by Kondo et al.[40] as a function of the coordination number of the oxygen atom. Mono- and dicoordinated OH groups can form on the (100) planes; three-coordinated OH groups may form on Ni atoms of the (111) planes or as a consequence of chemisorption of hydrogen on the oxygen atoms of the (111) planes. On these author's opinion, the adsorption of hydrogen on the steps and edge oxygen atoms causes the formation of tri- and tetracoordinated OH groups, whereas the interaction of hydrogen with the oxygen atoms of the (100) planes originates pentacoordinated OH groups. The stretching frequencies of the O−H bonds decrease with the coordination number, from 3735 cm^{-1} (monocoordination) to 3630 cm^{-1} (penta-coordination).[40]

In accordance with this work, the OH stretching frequency observed in our NiO powder sample (3685 cm^{-1}) should correspond to three-coordinated species.

In fact, NiO exhibits predominantly (111) faces;[15,41] the nonpolar (100) orientation is the energetically favored surface configuration of ionic rock salt materials, because the electrostatic interactions among the surface lattice ions are effectively balanced. In contrast, the NiO (111) faces are considered to be stabilized by hydroxylation.[30] Experimental results of Cappus et al.[17] demonstrated that on NiO (100) hydroxyl groups form exclusively at defect sites. At variance to that, regular sites on NiO (111) strongly interact with OH groups because of the stabilization of the (111) surface. In accordance with literature data the peak observed at 3685 cm^{-1} in the IR spectrum of our NiO powder sample can correspond to tri-coordinated OH groups formed on the (111) surface regular sites or on the (100) surface defects.

The spectral region from 1200 to 1600 cm^{-1} is shown in Figure 3b. Spectra inspection reveals, in the sample treated at 573 K, a broad band between 1250 and 1450 cm^{-1}. Further sample heating causes the intensity decrease of the band and a better resolution of two contributions around 1288 and 1440 cm^{-1}. In the NiO powder samples calcined at higher temperatures two well-defined peaks (attributed to the bending vibration of the O−H groups), are centered at 1480 and 1319 cm^{-1}.

IR data, as a whole, confirm that the NiO powder sample calcined at 573 K is highly hydroxylated;[42] and further heat treatments do not completely remove OH groups. It is noteworthy that heating induces the formation of a new peak at 1048 cm^{-1} that might be due to the formation of peroxo/superoxo-species. As a matter of fact, superoxo-species were already observed on NiO.[43] Moreover, this result agrees with XPS data.

Thermal analysis results are shown in Figure 4; thermal spectra were recorded both in N_2 or in air flow at 4 and 10 °C/min and no differences were observed. Inspection of the spectra reveals a marked water loss ($T \leq 700$ K) in the sample calcined at 573 K. At about 373 K weakly chemisorbed water desorbs; water bonded to Lewis acid sites[44] or due to the condensation of OH groups, desorbs from 540 to 693 K. Accordingly to the XPS and IR data, the weight loss is insignificant in the sample calcined at 973 K.

Reaction with Methanol: Atmospheric Pressure Conditions. DRIFT spectra of NiO powder sample exposed to methanol at temperatures from RT to 523 K, are shown in Figures 5−8, whereas in Table 3 IR data concerning liquid and gas-phase methanol, as well as methoxy species, are reported.

The presence of gas-phase alcohol in the DRIFT spectra obtained after exposure of the NiO powder to

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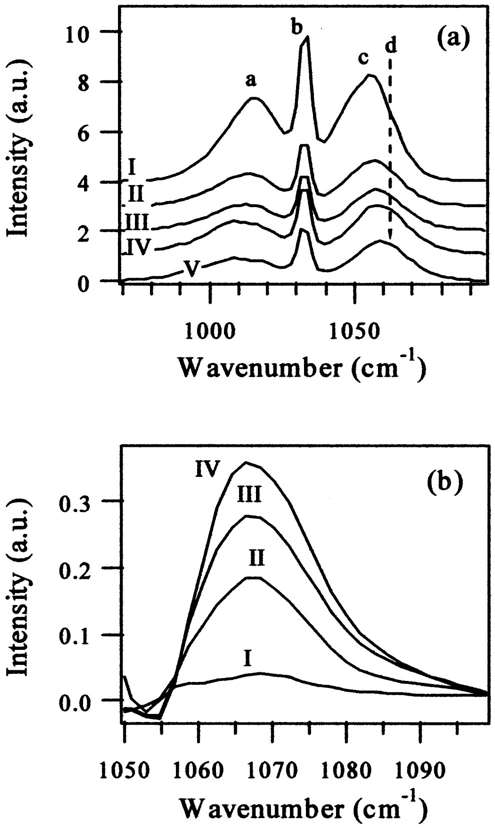

Figure 5. DRIFT spectra (Kubelka–Munk units) obtained after exposure of the NiO powder to methanol at different temperatures: (I) RT, (II) 373 K, (III) 423 K, (IV) 473 K, and (V) 523 K. (a) C–O Stretching region; (b) spectra obtained by subtracting the contribution of gas-phase methanol (the original spectra were normalized before the subtraction).

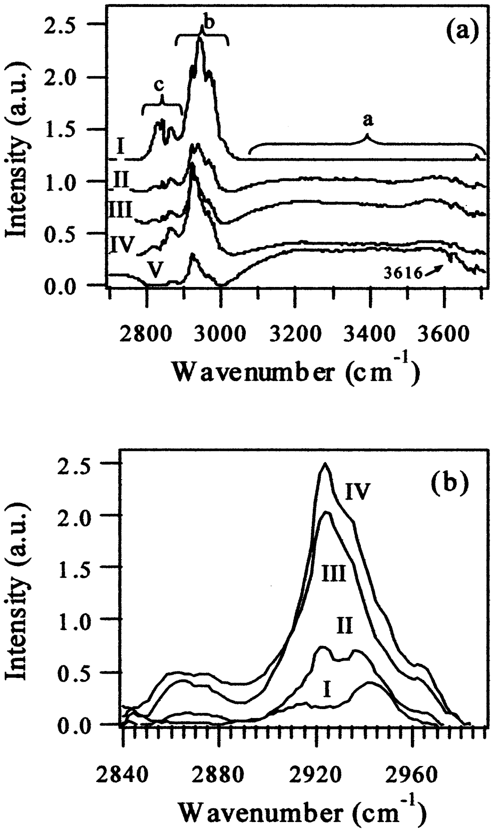

Figure 6. DRIFT spectra (Kubelka–Munk units) obtained after exposure of the NiO powder to methanol at different temperatures: (I) RT, (II) 373 K, (III) 423 K, (IV) 473 K, and (V) 523 K. (a) C–H and O–H Stretching region; (b) spectra obtained by subtracting the contribution of gas-phase methanol (the original spectra were normalized before the subtraction).

methanol at RT, is suggested by the characteristic P, Q, and R rotational branches in the spectral region of C–O stretching (Figure 5a: 1054 (c), 1033 (b), and 1016 (a) cm^{-1}) and is confirmed by the O–H and C–H stretching contributions (Figure 6a, peaks a, b, c). Moving to the spectral region of O–H stretching a weak peak around 3687 cm^{-1}, due to gas-phase methanol (Figure 6a), is the only contribution.

A broad band around 3000–3615 cm^{-1}, is evident in the IR spectra (Figure 6a, peaks a) after exposure to methanol at higher temperatures (373–423 K). A dip in the broad band, around 3616 cm^{-1}, suggests an Evans hole due to the interaction between a sharp energy level and a broad one. [45–47] Consistently, a narrow peak (due to hydroxyl groups) can be observed at about 3619 cm^{-1} in the NiO powder sample calcined at 973 K (Figure 3a).

The broad band is constituted by two contributions centered around 3560 and 3340 cm^{-1}, attributed to molecularly chemisorbed water[16] and methanol, respectively (see Table 3 and references therein).

In the spectral region of asymmetric C–H stretching (Figure 6a, peaks b), a peak at about 2924 cm^{-1} (asymmetric toward higher wavenumbers) is tentatively attributed to the C–H asymmetric stretching of the methoxy groups.[5] The intensity of this peak grows with the temperature (particularly, from 423 to 473 K) and then decreases abruptly. The contributions due to the gas-phase methanol (2865, 2842, and 2829 cm^{-1}) decrease with temperature, whereas a peak around 2821 cm^{-1}, attributed to the C–H stretching of methoxy groups,[4–6,48] is evident around 423–473 K. Consistently, a shoulder around 1060–1070 cm^{-1} (Figure 5a, shoulder d), due to the C–O stretching vibration of methoxy species, is observed. The peaks attributed to the methoxy groups can be observed easily in the spectrum obtained after exposure to methanol and, successively, to N_2 (Figure 7a and b) or by subtracting the contribution due to the gas-phase methanol (Figures 5b and 6b). In accordance with literature data C–O and C–H stretching contributions are centered at 1080 and 2924 cm^{-1}, respectively.

IR results suggest that methanol interacts molecularly and dissociatively with the NiO powder sample surface; dissociative chemisorption is more evident at higher temperatures (423–473 K).

A weak, double peak at 1550 and 1570 cm^{-1}, attributed to the O–C–O asymmetric stretching of formate species,[7,9] can be observed upon exposure of the NiO powder sample to methanol at about 423 K (Figure 8a). Consistently, formate O–C–O symmetric stretching (1344 cm^{-1}) and C–H bending (1390 cm^{-1}) peaks[10,11] are evident (Figure 8b). IR data suggest the formation

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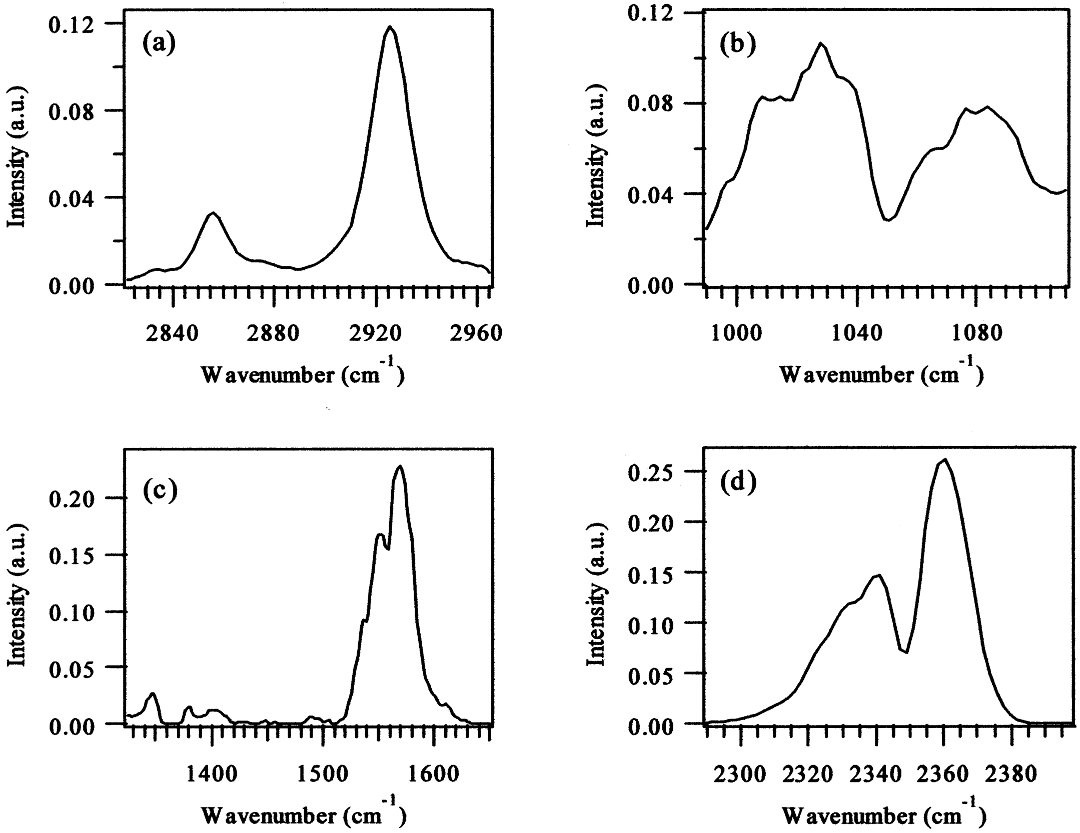

Figure 7. DRIFT spectra (Kubelka–Munk units) obtained after exposure of the NiO powder to methanol and successively to N_2 at 423 K: (a) C–H stretching region, (b) C–O stretching region, (c) O–C–O stretching region, (d) region from 2280 to 2400 cm^{-1}.

of two nonequivalent bidentate formate species.[8,10,55] Moreover, the presence of formate species can explain the asymmetry (toward higher wavenumbers) observed (Figure 6a) in the peak centered around 2924 cm^{-1}.[8–11] The peaks attributed to formate species can also be observed in the spectra obtained upon exposure of the NiO powder to methanol and successively to N_2 (C–H stretching at 2856 cm^{-1} (Figure 7a) and O–C–O stretching (Figure 7c)).[8,10,55]

CO_2 forms upon exposure to methanol at 373 K (peaks at 2360 and 2341 cm^{-1} in Figure 8c) and grows with temperature. Formate and CO_2 strongly interact with the NiO powder surface and are not removed by nitrogen (Figure 7c and d). Molecularly chemisorbed methanol is also evident after exposure to N_2 (see, as an example, C–O stretching contribution at 1028 cm^{-1} in Figure 7b).

Reaction of NiO with Methanol: HV Conditions. The Ni 2p and O 1s XP spectra of the NiO powder surface recorded before and after exposure to methanol are shown in Figures 1 and 2.

O 1s peak shape shows a significant decrement of the contribution around 532.0 eV (attributed to OH groups) upon exposure to methanol at RT; in contrast, hydroxyl groups increase after exposure at temperatures ≥423 K. The formation of new OH groups on the NiO powder surface suggests a direct dissociation mechanism. The O–H groups contribution decreases after exposure at higher temperatures, probably as a consequence of the heat treatment under HV conditions.

The inspection of the XP Ni 2p peak confirms the increment, after exposure to methanol at 423 K, of a shoulder at 855.9 eV, attributed to Ni–OH bonds (Figure 1 and Table 2).

QMS data obtained upon exposure to methanol are summarized in Figure 9.

Molecularly chemisorbed methanol desorbs at temperatures lower than ca. 423 K, whereas two desorption maxims centered at about 473 and 673 K are attributed to methoxy groups. Traces of CO, H_2O, CO_2, and H_2, as well as of fragmentation and recombination products (CH_3OCH_3) desorb contemporaneously with the molecularly chemisorbed methanol.[22] CO desorbs at 473 K whereas at 673 K the desorption of methoxy groups is accompanied by H_2O, CO_2, and H_2CO. As a whole, QMS results suggest that molecularly chemisorbed methanol desorbs and decomposes at low temperatures. At 473 K the oxidation of the alcohol becomes evident. The desorption patterns of CO, H_2O, CO_2, H_2, and CH_3OCH_3 suggest that the decomposition and oxidation of the alcohol compete with the desorption of methoxy groups, whereas the fragmentation/recombination processes become less significant. Formaldehyde desorbs around 600–700 K.

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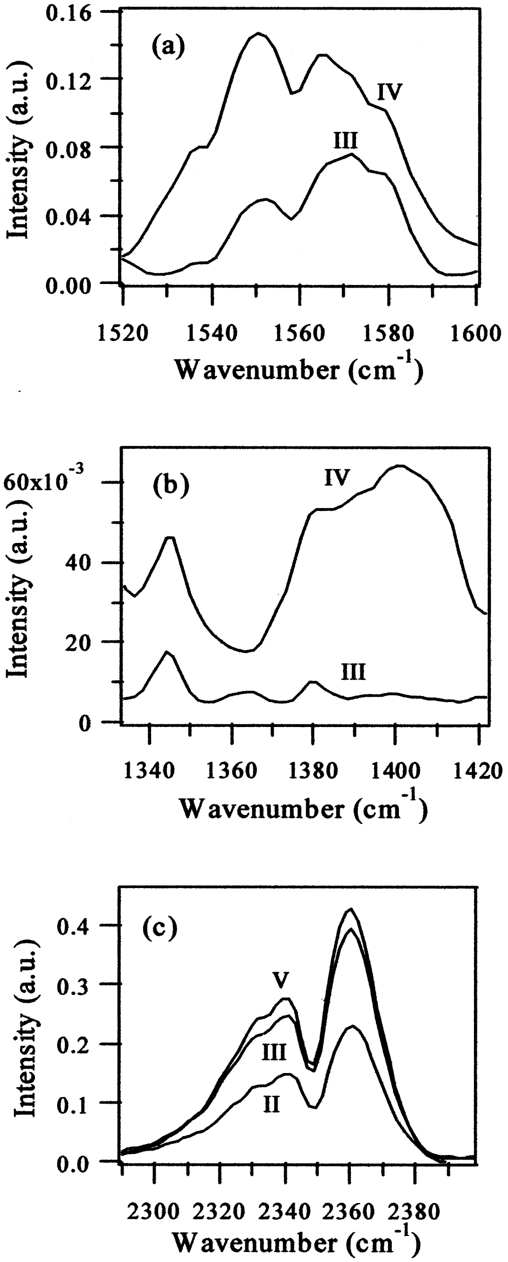

Figure 8. DRIFT spectra (Kubelka−Munk units) obtained after exposure of the NiO powder to methanol at different temperatures: (II) 373 K, (III) 423 K, and (IV) 473 K. (a) Region from 1520 to 1600 cm^{-1}; (b) region from 1334 to 1422 cm^{-1}; and (c) region from 2280 to 2400 cm^{-1}.

Discussion

The interaction mechanism between alcohol molecules and oxide surfaces (Scheme 1) depends strongly on the degree of surface hydroxylation. On a dehydroxylated surface a direct dissociation mechanism (Scheme 1, type I) produces hydroxyl and alkoxy groups, whereas molecular chemisorption (Scheme 1, type II) arises from a Lewis acid/base interaction.[49,50] Three additional modes of chemisorption are possible for a hydroxylated surface: esterification with surface hydroxyl groups (Scheme 1, type III), replacement of molecular water present on the surface (Scheme 1, type IV) and reversible adsorption on the surface hydroxyl or methoxy groups, through hydrogen bonds (Scheme 1, type V).[51]

Table 3. FTIR Data (cm^{-1}) of Vapor and Liquid Methanol and Nickel Methoxide

assignment	gas CH_3OH	liquid CH_3OH[a]	CH_3OH/NiO
C−O str.	1012[a] 1034 vs[a] 1060[a]	1029	1070[c] 1080[d]
O−H bend	1340[b] 1346 m[a]	1420 m br	
CH_3 bend. (a) a″	1430 w[a,b]	1420	
CH_3 bend. (s) a′	1455 m[a,b]	1455 m	1450[d]
CH_3 bend. (a) a′	1477 m[a,b]	1480 sh	
CH_3 str. (s)	2826 2845 s[a] (2844)[b] 2869[a]	2822 s	2823[c]
CH_3 str. (a)	2973 vs[a] (2977)[b]	2934 vs	2936[c] 2920[d]
OH str.	3673[a] 3687 s[a] (3682)[b] 3713[a]	3337 vs br	

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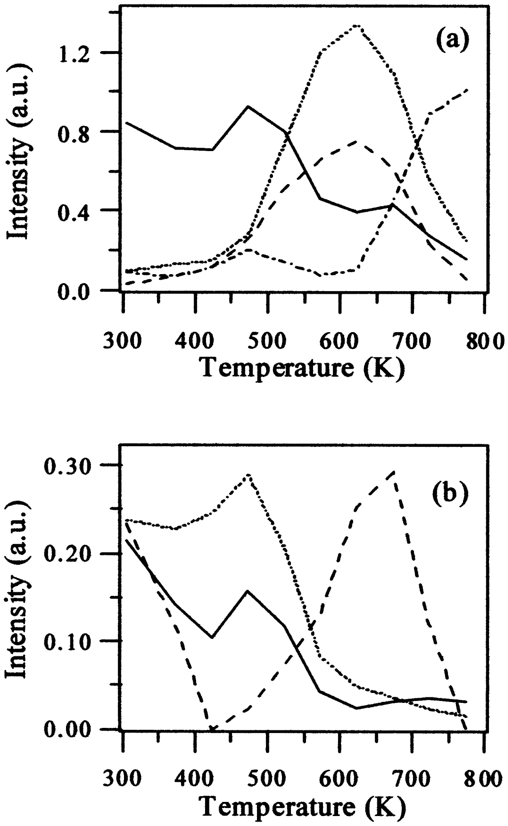
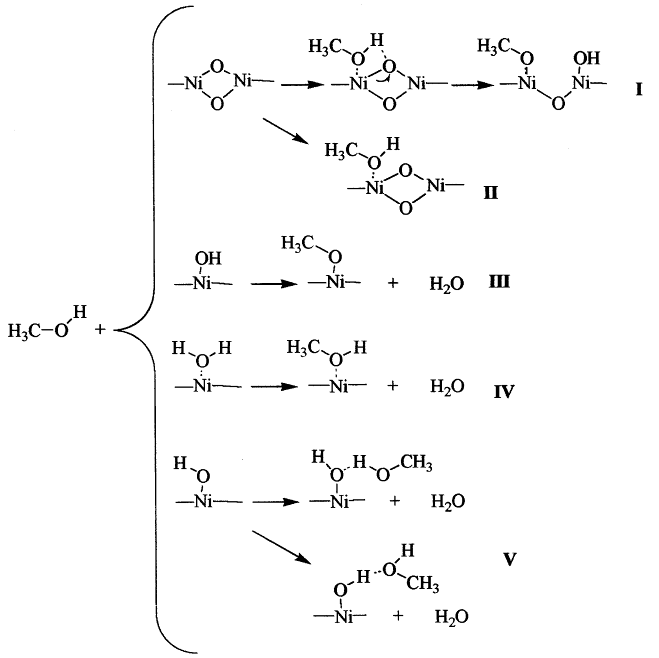


Figure 9. Desorption patterns obtained after exposure of the NiO powder to methanol: (a) (—) CH_3OH, (···) H_2O, (-·-·-·-) CO, (- - -) CO_2 × 3; (b) (—) CH_3CH_2, (···) CH_3OCH_3, (- - -) H_2CO × 7 (CO_2 and H_2CO desorption patterns were multiplied for 3 and 7, respectively).

NiO exhibits predominantly (111) faces,[41] whereas (100) surface can be significant in high sintered nickel oxide samples.[15]

The NiO(111) surface is thought to be unstable because it is polar. Recent studies indicate that the NiO(111) surface can be stabilized by charge rearrangement at the surface and by the presence of oxygen atoms,[52] instead of decomposing in (100) microfacets. In fact, NiO(111) surface resulted to be covered by a nearly

Scheme 1



saturated layer of hydroxyl groups.[53] Our DRIFT results agree with the presence, on the NiO powder surface, of OH groups tri-coordinated to Ni cations. In accordance with literature the tri-coordinated OH groups form principally on the (111) face.

DRIFT spectra reveal that water contribution decreases after exposure to methanol at RT: this suggests an associative chemisorption of methanol by replacement of water molecules (Scheme 1, type IV).

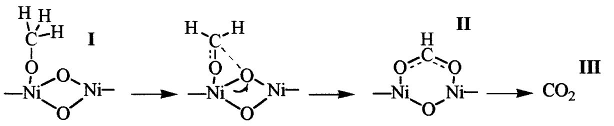
DRIFT spectra recorded upon exposure to methanol at higher temperatures ($T \geq 373$ K), reveal the formation of methoxy groups (2924, 2821, and 1080 cm^{-1}), as well as of molecularly chemisorbed water (3560 and 1636 cm^{-1}). IR data suggest the dissociative chemisorption of methanol (at $T \geq 373-423$ K) by interaction with surface hydroxyl groups (Scheme 1, type III). The direct dissociation mechanism cannot be excluded. Accordingly, QMS spectra show the existence of two nonequivalent methoxy groups whose desorption temperatures are centered around 473 and 673 K, respectively. Moreover, O 1s XP spectra clearly show the increasing presence of OH groups after exposure to methanol at $T \geq 423$ K.

The temperature increment around 373−423 K promotes the condensation of the OH groups, and new acid and basic sites appear on the surface facilitating a direct dissociation mechanism (Scheme 1, type I).

As already observed, IR data are consistent with the presence, on the surface of the NiO powder sample, of tri-coordinated OH groups formed on the (111) surface regular sites or on the (100) surface defects. It is thus probable that the interaction between methanol and hydroxyl groups mainly involves the OH distributed on the (111) surface, whereas less significant should be the interaction with the OH formed on the (100) surface defect sites.

Moreover, literature data demonstrated that the nearly perfect UHV-cleaved NiO(100) surface is completely inert with respect to many organic and inorganic molecules;[5,54,55] Sanders et al.[4] suggested that surface defects are determinant for the alcohol interaction: methanol adsorbs molecularly at regular cation sites and dissociatively with the defect sites. Water behavior is similar.[16]

Scheme 2



DRIFT results and literature data suggest that methanol direct dissociation can involve the defect sites distributed on the NiO powder surface; direct dissociation originates new OH groups by interaction of hydrogen with oxygen atoms on the (100) plane.[40]

The oxidation products form upon exposure of the NiO powder sample to methanol at higher temperatures. Formate is evident at about 423 K, and CO_2 is evident at 373 K. The obtained results are consistent with the following mechanism of methanol oxidation (Scheme 2):[49,50,56−58] methanol reacts with the NiO powder surface to form methoxy groups (Scheme 2, type I). At higher temperatures, the methoxy groups loose hydrogen and mutate to formate species (Scheme 2, type II).

Moving to the HV experiment, the desorption of CO_2 agrees with the formation of formate; formaldehyde is both an intermediate of the oxidation route and a decomposition product of formic acid.

A peak in the desorption path of CO_2 (around 523 K) is consistent with the decomposition of formic acid (Scheme 2, type III). In fact, several authors[7,8] observed, around 520−560 K, the dehydrogenation and the dehydration of formic acid on the NiO(111) surface. There is no evidence, on the contrary, for decomposition of formate on NiO(100) surface to yield CO_2, CO, H_2 and H_2O products.[41]

The comparison with literature results suggests that methanol interacts dissociatively with the OH groups distributed on the NiO (111) surface exposed by the powder sample. Formate originates from the methoxy species and decomposes following both a dehydration and a dehydrogenation path. In a previous paper we suggested that the oxygen deficiency can disfavor the formation of oxidation products on the oxide surface, as observed in Co_3O_4;[19] consistently, in NiO, which exposes an oxygen rich surface, formate formation is easier than in the case of cobalt oxide.

This result is relevant for applications in fuel cells technology. In fact, methanol can be considered a hydrogen source for fuel cells. A particularly pertinent application of methanol-derived hydrogen is the case of motor vehicles. Several data concerning the different methods of storing hydrogen fuel demonstrated that methanol compares very favorably with all the other methods, including cryogenic hydrogen. Furthermore, methanol is greatly safer, simpler, and cheaper to transport than hydrogen. The steam reforming of methanol is a mildly endothermic reaction and occurs at about 523 K on Cu/ZnO catalysts. Our results suggest the

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possibility, with a NiO based catalyst, to operate at lower temperature.[20]

Conclusions

In this paper the interaction between methanol and a NiO polycrystalline powder sample was studied. NiO was prepared by precipitation from an aqueous solution followed by heat treatments. The obtained powder sample was characterized by means of XPS, DRIFT spectroscopy, XRD, and thermal analysis. Experimental results suggest that the prepared sample is a highly hydroxylated NiO powder. Heat treatments at temperatures higher than 573 K cause partial desorption of the hydroxyl groups and the formation of a Bunsenite type structure. The sample calcined at 973 K was chosen for the chemisorption experiments.

IR data obtained upon exposure of the NiO powder sample to methanol suggest that the interaction is mainly molecular at RT, whereas the dissociation of the alcohol is more evident at higher temperatures (423–473 K). Around 373 K the formation of CO_2 is evident. CO_2 increases with temperature, whereas formate species are visible from 423 K. Both formate and CO_2 are strongly bonded to the NiO surface.

The dissociation of methanol is more evident in the HV experiment, probably because of the experimental conditions. Molecularly chemisorbed methanol desorbs from the NiO powder surface at temperatures lower than 423 K, whereas at higher temperatures (473 and 623 K) the desorption of methoxy species is evident. Molecularly chemisorbed methanol desorbs and decomposes with fragmentation and recombination patterns at low temperatures. In contrast, alcohol oxidation is evident at high temperature; formaldehyde desorbs around 623 K.

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