Surface Segregation and Consequent SO_2 Sensor Response in SnO_2−NiO

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Many studies have been carried out concerning the development of SO_2 sensors to detect and avoid its health prejudicial effects. However, there is still a lack of reliable, high-speed-response sensors that work at room temperature. In this work, the segregation of Ni in the SnO_2−NiO system is used to obtain a rapid SO_2 sensor response. Segregation and its structure consequences were studied by electron dispersive spectroscopy, infrared spectroscopy, and high-resolution transmission electron microscopy in nanopowders of SnO_2−NiO with different compositions prepared by a polymeric precursor method. The sensor activity of SnO_2−1 mol % Ni was studied and a linear calibration curve was formed with a maximum limit response of 32 ppm SO_2.

Introduction

The presence of additives in SnO_2-based powders and films has been described to play important roles in the sensitivity, selectivity, and response time of this kind of material to a number of pollutant gases.[1−6] Different hypotheses have been proposed to describe the influence of each additive in modifying the common feature of pure SnO_2 sensors to have poor selectivity with dual response to oxiding and reducing gases. As a consensus, the location of the ionic additives on the surface of SnO_2 grains is observed to drastically change the sensor response, specially when dealing with nanoparticles where surface atoms account for almost 30% of the total.

The location of the additive on the matrix oxide structure has been a matter of discussions and contradictions when dealing with Ni-doped SnO_2.[2,7,8] Since the ionic radius of Ni^{2+} is close to that of Sn^{4+}, it has been proposed that Ni atoms are most likely to be located in Sn positions in the crystallite bulk. This has been the base for explaining the impact of Ni on Ni-doped SnO_2 sensors properties, i.e., Ni would give rise to a barrier mechanism of conduction in SnO_2, probably caused by the decrease of the Fermi level as a result of the compensation of intrinsic donor $V_{o''}$ and impurity acceptor $Ni_{Sn''}$ centers, modifying the sensor properties.

However, evidence of surface segregation of this additive onto the surface of SnO_2 has been recently reported.[8] This discredits the hypothesis of barrier mechanism of conduction influencing the sensor properties and gives rise to one based on the possible formation of p(NiO)−n(SnO_2) junctions in surface and grain boundaries. Surface excess, however, has only been detected indirectly on the basis of the absence of X-ray diffraction peak dislocations or any second phase peaks for powders containing even 40 mol % Ni. A complete study of this system with definitive conclusions about ion locations is still lacking and is one of the objectives of the present work.

In addition to this objective, the sensor activity of SnO_2 films containing Ni obtained using the Pechini method is also addressed.[9] Common pollution gases such as CO, C_2H_5-OH, CH_4, and H_2S have already been applied in sensitivity tests of Ni-doped SnO_2. The best results are associated with the reducing gases.[7] However, the response time is always higher than 240 min even at high temperatures under dynamic conditions, restricting the applicability of these devices. In this work we observed that Ni segregation plays a fundamental role in SnO_2 sensor properties, increasing the sensitivity to SO_2 and speeding the responding time to a few minutes in a reversible reaction.

Experimental Procedure

SnO_2−Fe_2O_3 nanopowders have been prepared on the basis of the Pechini method.[9,10] The process can be briefly described as

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follows: (a) The cationic precursors were introduced into a ethylene glycol (20.6 wt %) and citric acid (47.7 wt %) solution. $Sn_2(C_6O_7H_4)\cdot H_2O$ (tin citrate prepared from $SnCl_2\cdot 2H_2O$; Synth P.A.) and $Fe(NO_3)_3\cdot 9H_2O$ (Synth P.A.) were used as the precursors, and HNO_3 was added to the system to promote the solubilization of the citrate. The amounts of precursors were calculated to achieve the desired molar concentrations. (b) The prepared solution was heated to 180−200 °C to promote polyesterification, i.e., polymerization between citric acid and ethylene glycol giving rise to a polymer chain with sites available to react with the present ions. These sites randomly react with tin or iron ions. (c) The obtained liquid precursor was thermally treated at 450 °C for 4 h and a dry carbon rich powder was obtained. After grinding, the powder was treated for 15 h at 500 °C to guarantee total carbon elimination and an energetically stable distribution of the additives and particle size.[11,12]

To determine the lattice parameters, XRD was carried out using 0.02° θ with 10 s of exposition time and using an internal Si standard in Philips X′Pert MPD equipment, using Cu Kα radiation (λ = 1.5406 Å). Infrared spectroscopy was carried out using a diffuse reflectance (DRIFT) apparatus in Magna 560 Nicolet equipment. Powders of SnO_2 containing different amounts of Ni were studied under open-atmosphere conditions after drying the samples at 70 °C for 2 h.

EDS and HRTEM images were acquired in a JEM 3010 URP microscope, 300 keV (0.17 nm resolution). For EDS, 3 nm beam size was used, the background obtained for the Cu grid was subtracted. Samples were prepared by milling in an aqueous suspension for 48 h and deagglomerating using an ultrasonic bath. The suspensions were diluted with ethanol and the suspensions were dropped on carbon films (≈5 nm) supported by a Cu grid. Ethanol evaporated in 30 min, and samples were analyzed.

To study the sensor properties of the SnO_2−NiO system, a SnO_2−1 mol % Ni film was prepared on an alumina substrate with interdigitated gold contacts by applying the Pechini method polymeric precursor directly over the substrate (spinning coating at 3000 rpm for 30 s), drying at 70 °C for 24 h, and treating at 450 °C for 4 h. All the experimented films were exposed to dry N_2 for 3 h and then to synthetic air for 3 h for surface cleanness purposes between each experiment. For the SO_2 sensitivity experiments, the films were exposed to nitrogen with 1 vol % SO_2 in a close chamber with constant gas flux passage (∼40 mL min^{-1}). The studies on interferences were carried out in the same apparatus using O_2 diluted in N_2 (88 ppm), C_3H_8 in N_2 (94.4 ppm), and NO_x in N_2 (100 ppm) gases at the same flux. Measurements were carried out after 10 min of exposition. The DRIFT study of the reaction between SnO_2 1 mol % Ni powder and SO_2 was carried out by exposing the sample to a constant N_2 1 vol % SO_2 flux for 5 min and measuring the surface evolution as a function of time under open-atmosphere conditions.

Results and Discussion

The discussion about the location of Ni in the structure of SnO_2 starts with a careful reevaluation of XRD of SnO_2 with different Ni concentrations. Similar data have already been reported previously, but a detailed analysis considering peak dislocations at low concentrations is still lacking.[8] XRD of SnO_2 powders containing increasing amounts of Ni ions showed that for up to 30 mol % Ni all reflection peaks can be assigned to SnO_2 tetragonal phase, and only slight changes were observed in the SnO_2 reflections up to this point.[8] These data were attributed to the segregation of Ni in the structure occurring in this composition range, and the solid solution was disregarded.[13,14] Despite the similarity between Sn^{4+} and Ni^{2+} radius, since the substitution of Sn^{4+} by Ni^{2+} would generate oxygen vacancies to maintain the system neutrality, a distortion in the lattice parameter would be expected. To evaluate a possible solid solution, XRD of powders containing low Ni contents was carried out in more detail to determine lattice parameter distortions. A very slight distortion in the lattice parameters can be observed (Table 1). Since dealing with very small particles, these changes can be attributed to microstrains, inducing lattice compression as previously proposed,[14,15] reinforcing the data reported in the literature that the solid solution must be restricted to the surface of SnO_2 and not distributed throughout the bulk.[8] In fact, some experimental data supports the segregation hypothesis as follows.

Table 1. Lattice Parameters of SnO_2 Powders Containing Different Ni Amounts

samples	*a* (Å)	*c*(Å)	*c*/*a*
SnO_2[a]	4.7367(1)	3.1855(1)	0.6720
SnO_2	4.7315(3)	3.1798(1)	0.6720
0.5 mol % Ni	4.7255(2)	3.1772(5)	0.6723
2.0 mol % Ni	4.7217(1)	3.1789(6)	0.6732
10.0 mol % Ni	4.7194(1)	3.1740(5)	0.6725

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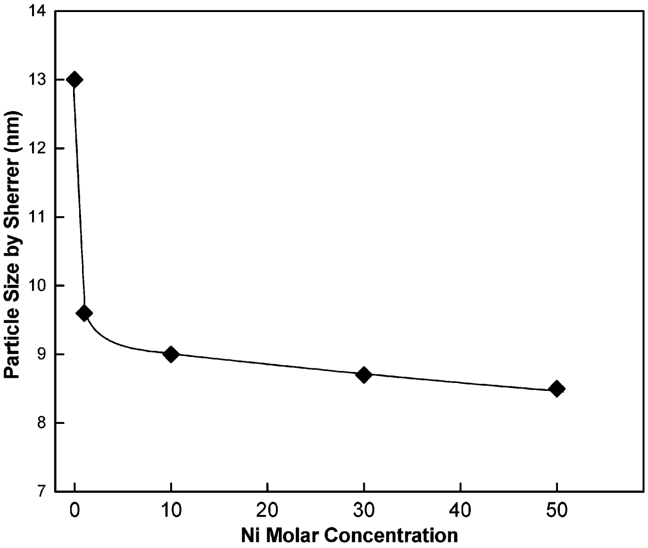

Figure 1. Particle size determined by the Scherrer method of SnO_2 nanopowders with increasing Ni concentration.

Figure 1 shows particles sizes obtained by the Sherrer method applied to XRD of SnO_2 containing different Ni amounts. A particle size decrease is observed up to 10 mol %, beyond which it remains almost constant. These results are consistent with the specific surface area results reported previously for Ni[8] and a number of others additives (Mn,

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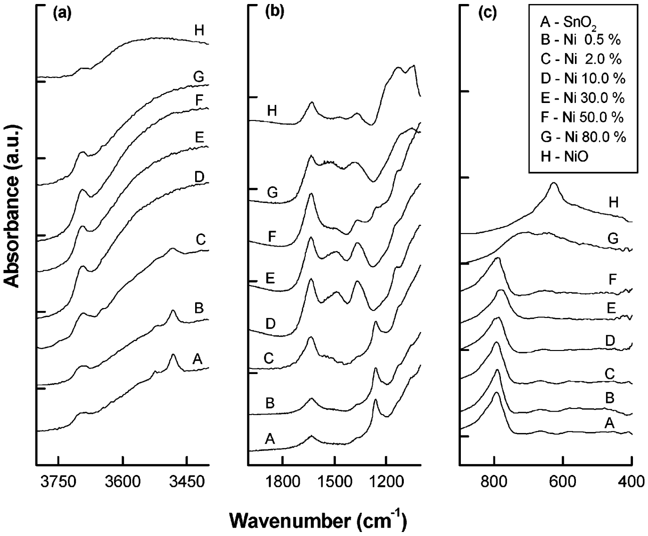

Figure 2. DRIFT spectra of SnO_2 samples containing increasing Ni amounts. Samples were dried at 70 °C for 2 h and measurements were carried out under open-atmosphere conditions.

Ru, Rh, Cu, Mg, and Fe).[2,12,17,18] It is important to note that this behavior is incoherent with a model of solid solution between SnO_2 and Ni ion, i.e., since the Ni ion is a divalent cation, substitution of Sn^{4+} by Ni^{2+} could generate oxygen vacancies that are expected to promote diffusion enhancement and, thereafter, a particle size increase (surface area decrease). Moreover, despite the similar radius, the oxygen vacancies generated after a possible solid solution to maintain the system neutrality are expected to change the lattice parameters, which is hardly observed by XRD.[8] Since no second phase can be observed by XRD experiments until 40 mol %, the increasing effect of the additive in the surface areas can be attributed to a surface excess of Ni ions onto SnO_2 particles surface. Since surface excess can be related to a surface energy reduction and or a barrier to crystal growth diffusion mechanisms, this location of the Ni ions is expected to stabilize smaller particles.[8,12,13]

Evidence for surface Ni is reinforced when observing DRIFT spectra in Figure 2. The DRIFT technique is known to focus the infrared analysis on the surface chemistry of powders being used to characterize oxide surface hydroxyl groups.[19,20] Since these hydroxyls are very sensitive to neighbor atoms, DRIFT appears as a suitable technique to observe surface segregation in oxides. The figure shows SnO_2 characteristic vibration bands for the pure powder at 3480, 3700 (Figure 2a), and 1300 cm^{-1} (Figure 2b) attributed to the oxide surface hydroxyl groups.[21,22] A decrease in the vibration band at 3480 cm^{-1} and a slight increase in the intensity of the band at 3700 cm^{-1} can be observed with increasing additive concentration. Simultaneously, two bands appear near 1450 cm^{-1} that are very similar to those of pure NiO (Figure 2b), indicating a change in the surface chemistry to a similar pure NiO one. At the same time, a decrease in the intensity of the band 1400 cm^{-1} is observed. The results are consistent with the substitution of surface Sn ions by Ni (surface solid solution), causing a change in the hydroxyl groups attached to them. Note that bulk characteristic bands related to metal−oxygen bonds, located at low wavenumbers (900−400 cm^{-1}) in Figure 2c, are almost unaltered up to 30 mol % Ni. This reinforces the idea that bulk bonds are almost unaltered until high concentrations of Ni. Beyond 30 mol %, however, the presence of a trace of Ni−O attributed to bands near 650 cm^{-1} is observed, coherently with XRD data reported previously. Remarkable changes are only observed in 80 mol % Ni sample, where the Sn−O attributed band is dislocated to lower wavenumbers due to the relatively small particles size and Ni surface excess. Also in this sample, the Ni−O band noticeably emerges, confirming the XRD data presented above.

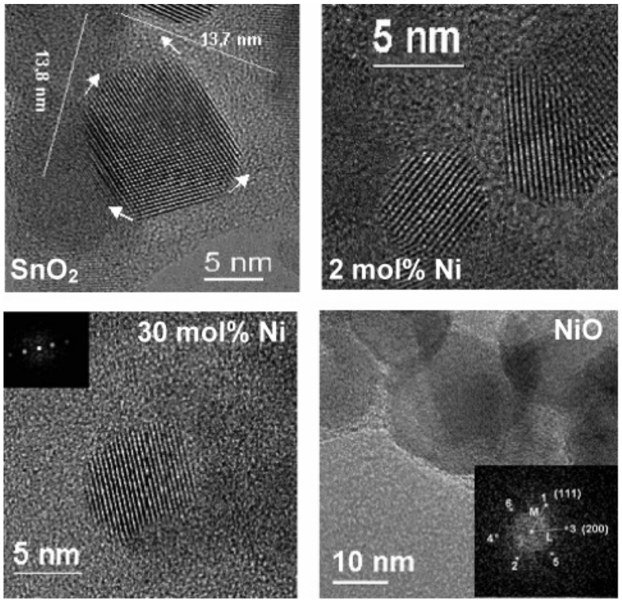

Figure 3. HRTEM of SnO_2, SnO_2 2 mol % Ni, SnO_2 30 mol % Ni, and NiO particles. Samples were prepared in ethanol suspension and dropped on a carbon film supported by a Cu grid. Ordered parts in the figure are SnO_2 particles except for the low right picture, where NiO particles are observed. The unordered parts are due to the supports. Arrows in pure SnO_2 picture represent the particle limits used to determine the average sizes shown. Electron diffraction patterns for particles containing 30 mol % Ni and NiO_2 are also presented.

Segregation of Ni onto the surface of the SnO_2 particles is confirmed when observing EDS results associated with HRTEM presented in Figures 3 and 4. In Figure 3, isolated particles of pure SnO_2, SnO_2 containing 2 and 30 mol % Ni, and pure NiO demonstrate the effect of the additive in controlling the particle sizes. Electron diffraction patterns shown in each picture could show the lattice structure type. The results are consistent with previous XRD,[8] demonstrating SnO_2 tetragonal phase in both 2 and 30 mol % Ni particles and conclusively defining the NiO cubic structure by electron diffraction. The ratio between the distances of the points attributed to both (111) and (200) planes from the center point (1.150) is very similar to that described in the literature to this structure (1.155). Similar results were observed for

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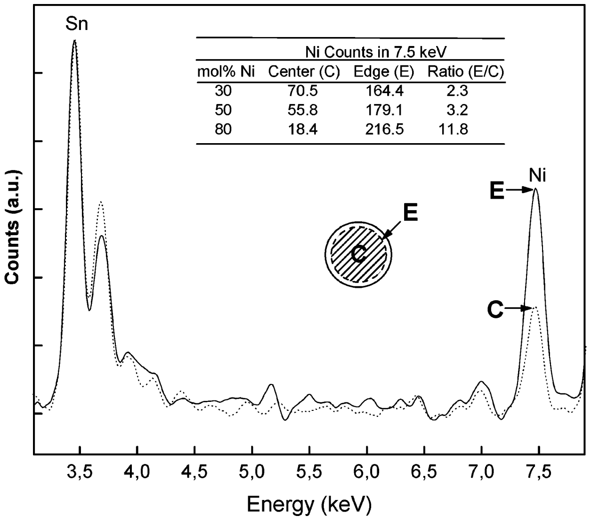

Figure 4. Energy dispersive spectra of SnO_2−30 mol % Ni nanoparticle measured in the particle center (C) and edge (E). The table inside shows the Ni counts for particles containing 30, 50, and 80 mol % Ni at 7.5 keV normalized for the Sn signal intensity.

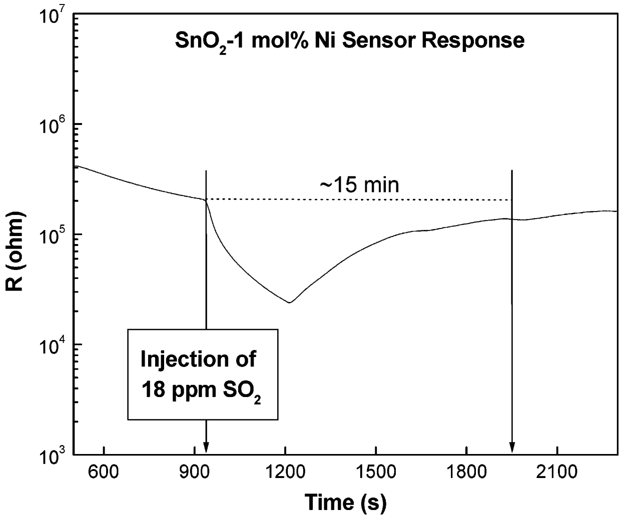

Figure 5. Time dependence of the SnO_2−1 mol % Ni sensor response to 18 ppm SO_2 diluted in dry N_2. The sensor was exposed to N_2 flux for 3 h and then to synthetic air flux for 3 h before injection of SO_2.

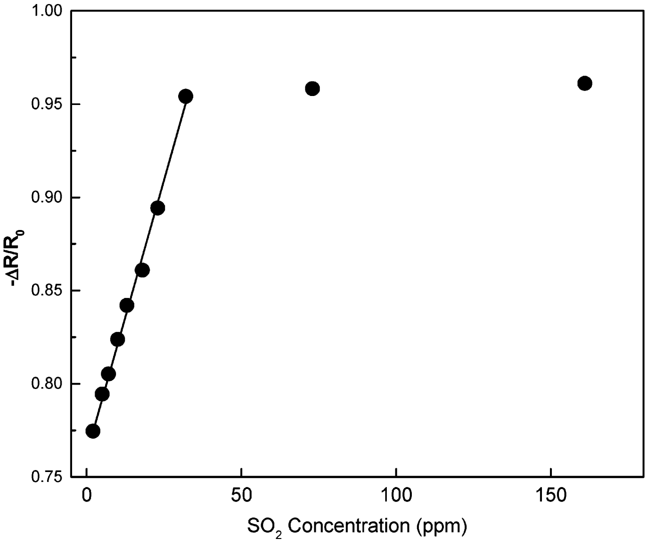

Figure 6. Calibration curve of SnO_2−1 mol % Ni sensor for SO_2 relating the SO_2 content to the electrical response. SO_2 was diluted in dry N_2 to achieve the desired concentrations. The electrical responses were measured after 4.5 min of the injection.

the 50 and 80 mol % Ni samples. By isolating particles containing 30, 50, and 80 mol % Ni and carrying out an EDS analysis, using a 3 nm beam size, the Ni relative concentration in both edge and center of the particles could be determined. Data collected for SnO_2 30 mol % Ni are plotted in Figure 4. Note that the peak attributed to Ni (7.5 keV) is higher at the edges of the particle. Three particles of each type were used to determine the counts presented in the table inside the figure. Similar results are observed for powders containing 50 and 80 mol % Ni, where Ni counts in center (C) and edge (E) is presented as well as the ratios, indicating segregation in all occasions. Note that, as shown in Figure 3 and XRD,[8] all samples used in the EDS study were identified as SnO_2 tetragonal phase.

The segregation of Ni onto SnO_2-based powders has a pronounced effect on the sensor properties of this material, even at low concentrations, since they are highly dependent on the surface composition. A study of SnO_2 containing 1 mol % Ni as SO_2 sensor was carried out in some detail as follows.

SO_2 was chosen as a well-known harmful gas for human health.[1,23−25] In a preliminary analysis of the SnO_2−Ni system sensitivity to SO_2, pellets of both pure SnO_2 and SnO_2 containing 1 mol % Ni were pressed and exposed to 10 mL of SO_2. Both pellets reacted with the gas and $-\Delta R/R_0$ ratios of 0.1672 and 0.1380 were obtained for the pure materials and the doped one, respectively. Despite the higher response of pure SnO_2 to SO_2, it is well-known that the low selectivity, irreversibility, and electrical response absence of this reaction makes it unsuitable for sensor purpose.[2] However, the observed capability of SnO_2 1 mol % Ni to release the absorbed molecule with a measurable and simultaneous resistance modification makes it an interesting material for sensor production.

To evaluate and study this potentiality, in this work we produced a SnO_2−1 mol % Ni film on an alumina substrate by directly applying the Pechini method polymeric precursor by spinner as described in the Experimental Procedures. A film with around a thickness of 180 nm was obtained.

The electrical response of the sensor film exposed to SO_2 is presented in Figure 5. A pure SnO_2 film similarly produced exhibited very low resistance modification under the same conditions. Note that after introducing 18 ppm of SO_2 at 25 °C, the SnO_2−1 mol % Ni film resistance markedly decreases up to about 12% of that under air flux with a total responding time of about only 4.5 min. The system resistance is totally restored after about 15 min under clean air flux. This result suggests that the film is suitable for sensor applications. However, to confirm this applicability, the material should have a rational dependence of the electrical response on the SO_2 content. A so-called calibration curve is therefore presented in Figure 6. Linear dependence is observed up to 32 ppm, beyond which the resistance does not vary, demonstrating the sensor applicability to low SO_2 concentrations. This response limit is assumed to be associated with

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Table 2. Computed Relative Areas of DRIFT Variation Bands at 1355 and 1345 cm^{-1} of SnO_2−1 mol % Ni after Exposition to SO_2

sample	time frame	relative areas
A	after exposition to SO_2 for 10 min	1.026
B	after 2 min under clean atmosphere	0.429
C	after 3 min	0.418
D	after 4 min	0.288
E	after 8 min	0.003
F	after 10 min	0.001

Table 3. Responses of SnO_2−1 mol % Ni Sensor to O_2, C_3H_8, and NO_x in $\Delta R/R_0$ at 25 °C

	$\Delta R/R_o$	
gas	SnO_2[a]	SnO_2−Ni
O_2	0.091	0.072
C_3H_8 (propane)	0.083	<0.001
NO_x	0.010	<0.001

[a] For comparison, the responses of pure SnO_2 films are also reported.

the saturation of the reaction sites onto the surface of the powders. Probably the existence of these reactive sites is a consequence of Ni surface segregation. Therefore, an increase in Ni concentration should increase the sensibility of the sensor, but evaluation of this behavior is an objective of future work.

Since in all studied cases SO_2 was diluted in dry N_2, one could argue that the observed electrical signals are related to a lowering of the oxygen pressure during the injection of the gas. That is to say, because before the experiments the sensor was exposed to dry air for 3 h and after that the clean air flux to remove SO_2 restored the oxygen pressure, this could have been responsible for the read electrical response of the sensor. This possibility can be, however, disregarded considering interference results presented in Table 3 that also complete the evaluation of the sensors capabilities of SnO_2 1 mol % Ni. Sensor responses to O_2, C_3H_8, and NO_x independently are reported. Very low electrical responses were observed for the tested gases, and especially propane and NO_x showed almost no interferences on the signals. $\Delta R/R_0$ for O_2 was measured as 0.072 in contrast to 0.77 for 2 ppm SO_2 and 0.95 for 32 ppm SO_2. Since all tested gases were also diluted in dry N_2, if the O_2 pressure were responsible for the sensor electrical signal, this would have appeared also in the interference experiments. This reinforces the applicability of this film composition as a SO_2 sensor, with reasonable time response since at room temperature. It should be expected that at higher temperature the time response would significantly decrease.

Infrared spectroscopy using a reflectance apparatus (DRIFT) confirms the reversibility of the reaction between the surface and SO_2, demonstrating the formation of surface sulfur groups that disappear when exposition to SO_2 stops. Figure 7 shows a specific region of the spectrum of SnO_2 containing 1 mol % Ni exposed for 10 min to N_2−1 vol % SO_2 gas flux and its evolution with time as pointed in the figure caption. Similarly to the experiments carried out by Berger et al.,[26] the formation of sulfate or sulfite linked to hydroxyl surface groups is proposed. The peaks presented in the figure are all attributed to sulfate vibrations. Note that after 10 min the band near 1370 cm^{-1} is almost completely vanished. To quantify the infrared spectra evolution, the summations of the areas of the peaks at 1355 and 1345 cm^{-1} were computed and are presented in Table 2. The peak at 1370 cm^{-1} was not considered in this calculation since a SnO_2 hydroxyl vibration band coexists at this wavenumber range. The peak area data confirm sulfur groups that were completely desorbed after 10 min. This is very consistent with the relaxing time determined in Figure 5. In fact, the accuracy of the infrared equipment does not permit one to determine exactly the moment of complete desorption of the molecules, so that the relaxing time determined by DRIFT and resistance measurements do not match.

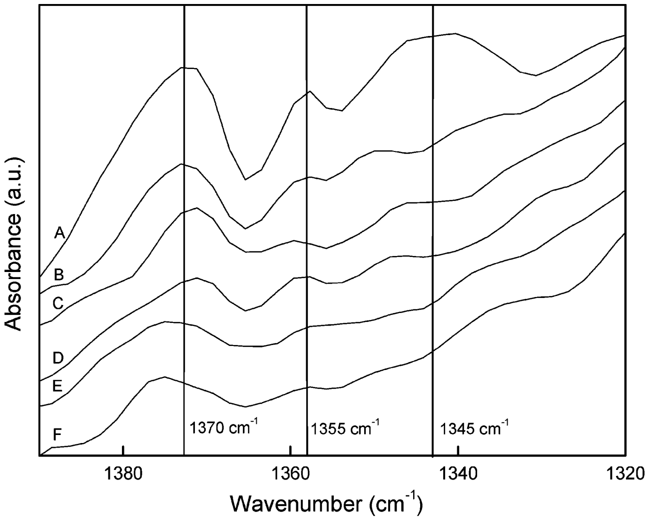

Figure 7. Time evolution of DRIFT spectra of SnO_2−1 mol % Ni exposed to N_2−1 vol % SO_2 flux: (A) after exposition to SO_2 for 10 min, (B) after 2 min under open-atmosphere conditions, (C) after 3 min, (D) 4 min, (E) 8 min, and (F) 10 min.

Conclusions

Segregation of Ni onto the surface of SnO_2 nanopowders was observed by indirect and direct analysis. The segregation showed a strong influence on the powder microstructure and especially on the sensor properties of SnO_2. Response to SO_2 is enhanced in speed and in sensitivity compared to pure SnO_2 behavior with reliability and working at room temperature for SnO_2 containing 1 mol % of Ni films. DRIFT results and sensor measurements showed this composition to have a completely reversible reaction with SO_2 at this temperature with a good electrical response. The calibration curve shows the sensor to be applicable for detecting low SO_2 concentrations (<32 ppm). Studies on O_2, C_3H_8, and NO_x interferences on the sensor response showed low effects, guaranteeing its selectivity.

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