



FT-IR surface study of nanosized ceramic materials used as gas sensors

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Abstract

In gas sensing materials, the key part is played by the surface. Therefore, in nanosized powders for which the surface can compete with the bulk, the chemical composition of the surface has to be systematically controlled. To this end Fourier transform infrared (FT-IR) spectrometry is a powerful technique provided a specific vacuum cell is attached to the spectrometer. The effect of the temperature and surrounding atmosphere on the adsorbed species is clearly demonstrated for Al_2O_3 and TiO_2 nanosized powders. Special attention is paid to water molecules and carbonate groups which are by far the most probable surface contaminants. Then the response of the titania surface to oxygen, carbon dioxide and carbon monoxide is investigated under various conditions. Based on these FT-IR spectroscopic results which clearly demonstrated the relevance of the method for gas–surface interaction analysis, a preliminary reaction mechanism for CO adsorption on titania is proposed.

Keywords: Gas sensor; Fourier transform infrared spectrometry; Nanosized ceramic material

1. Introduction

Because of unsaturation or strain, all surfaces react with the surrounding atmosphere in order to reach the maximum entropy. This phenomenon is of critical importance for nanosized powders. Indeed, due to the high surface to bulk ratio, the surface species can compete with the bulk. Now it is widely recognized that the surface plays a key role in metal oxide-based gas sensors [1]. Therefore, the characterization of the surface species is critically needed to ensure a perfect reproducibility of the sensor response. This can be easily done by FT-IR spectrometry even though this technique is more commonly used as a characterization tool for bulk materials. Indeed, in highly disperse systems the chemical bonds located in the first atomic layer contribute in a non-negligible way to the absorption spectrum simply because of their concentration with respect to one of the bonds inside the bulk. It is of critical importance to characterize the surface independently from the bulk. Indeed, all interactions occurring at the contact of various media with solid surfaces cannot be properly understood without a careful determination of the nature of the surface. On this surface, chemical species and adsorption centers which do not exist inside the bulk are responsible for these interac-

tions [2]. On another hand, FT-IR spectrometry provides data on the nature of the bonds formed between adsorbed molecules and the surface. The vibrational spectrum contains information on the perturbed molecules in contact with the solid surfaces. In return, the perturbations of the molecules caused by the adsorption provide information about the adsorption centers on the surface. However in metal oxide-based gas sensors, the interaction between the sensor surface and the gas to be detected must be weak for reversibility purposes. For this reason, the corresponding effects in the infrared spectra are sometimes hardly visible. Despite these difficulties, FT-IR surface spectrometry turns to be again [3] a very powerful technique for studying the complete in situ gas–surface interactions.

2. Experimental conditions

The infrared absorption spectra were recorded using a Nicolet 5DX FT-IR spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ range with a 4 cm^{-1} resolution. For the surface analysis, a specially designed vacuum cell was used [4]. This cell allowed us to run in situ experiments at any temperature from room temperature to 870 K under the atmosphere, a vacuum or controlled pressures of various gases. The

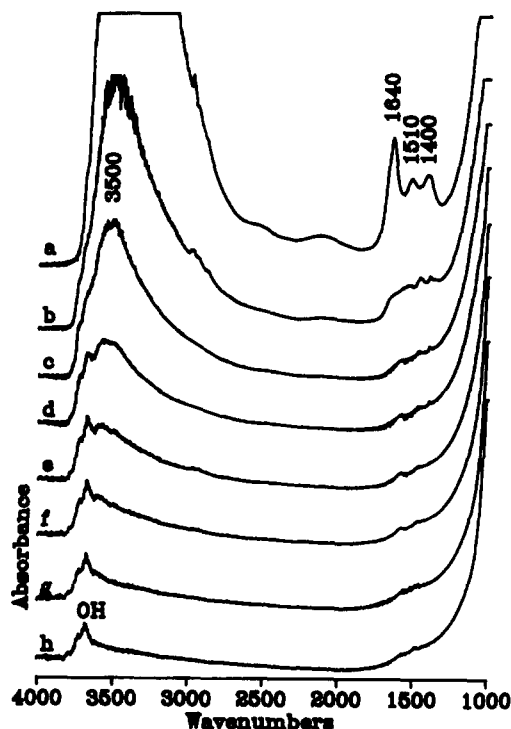


Fig. 1. FT-IR spectra of an alumina pellet at different steps of the activation: (a) room temperature (RT) under atmosphere; (b) RT under vacuum; (c) 370 K; (d) 470 K; (e) 570 K; (f) 670 K; (g) 770 K; (h) 870 K.

powder to be analyzed was slightly pressed into a grid-supported pellet and placed inside the cell. The weight of powder needed for such surface analysis may vary from 20 to 100 mg. In some cases the powders were activated. Activation consists of heating the sample under a dynamic vacuum. This treatment results in a clean surface, i.e. a surface free from physisorbed and weakly chemisorbed species. In contrast to studies for catalytic purposes which require a secondary vacuum, we performed experiments under a primary vacuum, that is 10^{-2} mbar. The alumina powder was oxide C from Degussa with a BET area of $100 \text{ m}^2 \text{ g}^{-1}$. The titanium oxide was manufactured by Aldrich. It was mainly anatase and its BET area was $10 \text{ m}^2 \text{ g}^{-1}$. All gases (oxygen, carbon dioxide and carbon monoxide) from Air Liquide were used without further purification.

3. Surface chemical modifications under thermal treatment

3.1. Alumina

The evolution of the alumina surface during a thermal treatment was compared as a function of the surrounding atmosphere. At first, activation, i.e. heating under a dynamic vacuum, was performed (Fig. 1), then the sample was heated under ambient atmosphere (Fig. 2). It must be

noted that below 1000 cm^{-1} the vibrational modes of the bulk are very intense due to the large amount of powder. In the activation process, the first two spectra (Fig. 1a,b) are recorded at room temperature, one under atmosphere and the other one after evacuation. The striking difference is the decrease of the very broad band centered around 3300 cm^{-1} and of the band at 1640 cm^{-1} . These bands correspond to the stretching and bending vibrational modes, respectively, of water molecules physisorbed on the alumina surface and easily removed [5]. When the temperature increases (Fig. 1c–g), the remaining broad band at 3500 cm^{-1} starts to decrease and completely vanishes at 870 K. This band is assigned to hydrogen bonded hydroxyl groups on the surface [5]. At 870 K, the hydrogen bonds no longer exist and only free hydroxyl groups remain. Different types of surface hydroxyl groups are responsible for the various components of this band in the 3700 cm^{-1} region (Fig. 1h) [6,7]. Moreover, the two bands at 1510 cm^{-1} and 1400 cm^{-1} appearing in the spectrum of the raw alumina (Fig. 1a) strongly decrease after pumping and then completely disappear after subsequent heating. Both bands are assigned to the vibrational modes of CO_2^- carboxylate groups slightly bound to the acidic Al^{3+} surface sites. The surface partly recovers when the

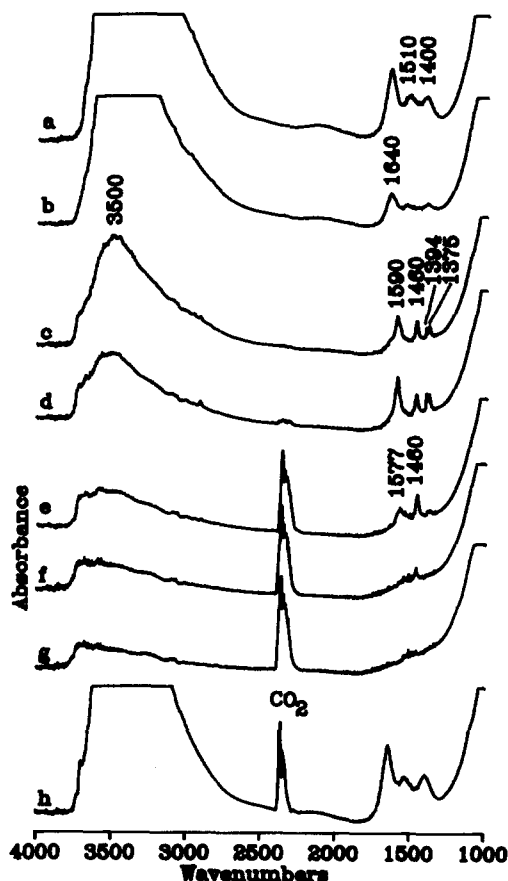


Fig. 2. FT-IR spectra of an alumina pellet heated at different temperatures under atmosphere: (a) RT; (b) 370 K; (c) 470 K; (d) 570 K; (e) 670 K; (f) 770 K; (g) 870 K; (h) cooled to RT.

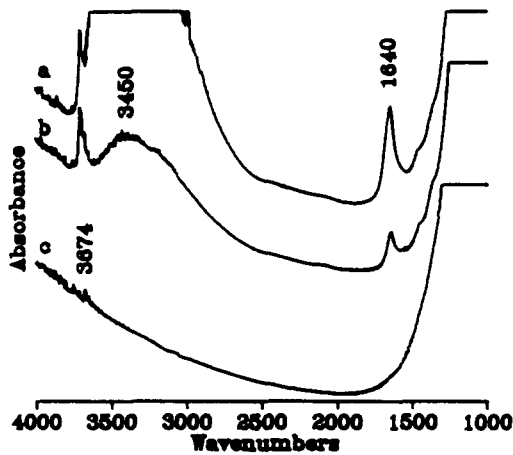


Fig. 3. FT-IR spectra of a titania pellet: (a) RT under atmosphere; (b) RT after evacuation; (c) 670 K under vacuum.

sample is cooled to room temperature and brought back to ambient atmosphere.

The pure alumina powder was then heated under atmosphere (Fig. 2). From 470 K (Fig. 2c), the 1640 cm^{-1} band showing the presence of water molecules no longer exists. Thus, starting from this temperature, the surface is freed from physisorbed water. The surface hydroxyl groups are still hydrogen bonded to each other as indicated by the broad band around 3500 cm^{-1} . But in this case, even at 870 K (Fig. 2g) these hydroxyl groups are not completely freed. Simultaneously, the two bands at 1510 and 1400 cm^{-1} disappear. As previously mentioned, they correspond to the CO_2^- carboxylate groups. As the temperature increases, four new bands appear at 1590, 1460, 1394 and 1375 cm^{-1} (Fig. 2d). Concomitantly, gaseous CO_2 is released (2349 cm^{-1}). At 670 K (Fig. 2e), only two bands remain at 1577 and 1460 cm^{-1} . These latter bands are assigned to monodentate carbonate groups [2,8]. These species are already present on the surface at lower temperatures as proved by the 1460 cm^{-1} band. The other three bands at 1590, 1394 and 1375 cm^{-1} are characteristic of the formate ion. Its formation results from the reaction of carbon monoxide with the highly hydroxylated surface. Indeed a small amount of gaseous CO is released from the surface species between 470 and 570 K, although hardly visible because of a very weak band intensity (2143 cm^{-1}). Finally, above 770 K (Fig.

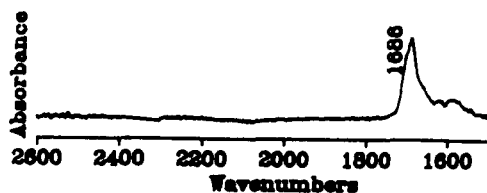


Fig. 4. Oxygen addition (15 mbar, 80 min) at RT on an activated titania pellet: difference between the FT-IR spectra recorded before and after oxygen addition.

2f,g), the surface carbonate species are no longer visible. Only CO_2 appears in the gas phase. The surface recovers when the sample is cooled to room temperature (Fig. 2h).

From this basic study of the alumina surface, it has been demonstrated that alumina substrates used in gas sensors, when heated above 570 K release gaseous CO_2 , CO and water which may contaminate the supported sensing layer.

3.2. Titania

The evolution of titania surface under activation up to 670 K only shows the dehydroxylation process (Fig. 3). A part of molecular water is already removed by pumping at room temperature (Fig. 3a,b). When the temperature increases, the neighboring surface hydroxyl groups condense to form water which is evacuated. At 670 K only a few free hydroxyl groups (Fig. 3c) absorb at 3674 cm^{-1} [9]. The surface quickly recovers when water vapor is added at room temperature. The same dehydroxylation process is observed when the titania sample is heated at 670 K under atmosphere. The surface is completely reversible when cooling it to room temperature under atmosphere. In both cases, no evidence of carbonate groups release has been found.

4. Surface chemical modifications caused by gas addition

4.1. Titania subjected to oxygen at room temperature

Molecular oxygen was added at room temperature on a titania activated sample. The difference between the spectra recorded before and after oxygen addition (Fig. 4) presents only one positive band at 1686 cm^{-1} meaning that new species are formed. No negative band is visible indicating that no species disappear. The absorption frequency at 1686 cm^{-1} is clearly higher than that of the molecular oxygen vibration observed at 1555 cm^{-1} by Raman spectroscopy [10]. It is assigned to uncharged molecular oxygen whose polarization is modified by the solid surface [2,11]. Indeed, this interaction between oxygen and the titania surface is weak since adsorbed oxygen is eliminated by pumping at room temperature.

4.2. Titania subjected to carbon dioxide at room temperature

The adsorption of CO_2 at room temperature on the titania activated surface is very fast (Fig. 5a,b). No absorption band corresponding to the gaseous phase is visible. On the contrary, the very intense band at 2348 cm^{-1} is assigned to CO_2 molecules linearly physisorbed on metal cations [12]. On the difference spectrum 5b – 5a (Fig. 5c) positive bands corresponding to the formation of new species are located in the 1700–1300 cm^{-1} region. They

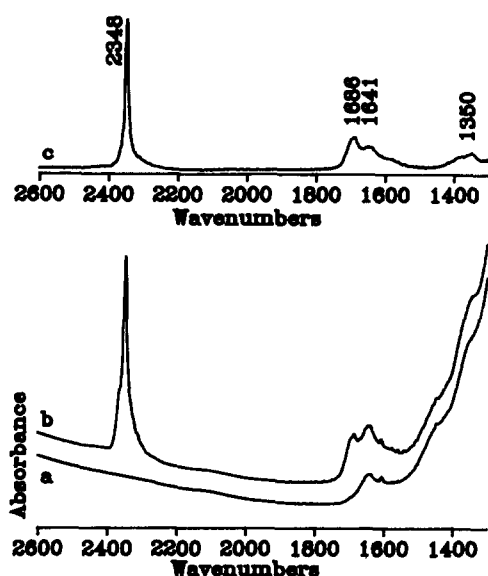


Fig. 5. Carbon dioxide addition at RT on an activated titania pellet. FT-IR spectra: (a) before CO₂ addition; (b) after CO₂ addition (10 mbar, 15 min); (c) difference spectrum (b) – (a).

disappear by pumping at room temperature. These bands are assigned to carboxylate species linked to metal cations either with different geometries or on different sites [8,13]. Carbonate groups could also form on the surface and their corresponding absorption frequencies would also be located in the 1700–1300 cm⁻¹ region. However, the low stability of the species formed on the titania surface suggests weak interactions which definitely rule out carbonate group formation [8].

4.3. Titania subjected to carbon monoxide at room temperature

Like CO₂, carbon monoxide adsorbs quickly at room temperature on the activated titania surface (Fig. 6). A spectrum was recorded after a 1-min contact (Fig. 6b) and another one after 1-h contact (Fig. 6c). The difference spectra between two subsequent steps of the experiment are reported in Fig. 6d,e. The positive bands correspond to appearing species whereas the negative bands correspond to disappearing species between the two subsequent steps under consideration. After the first minute (Fig. 6d), in addition to the band centered at 2143 cm⁻¹ corresponding to the gaseous CO phase [10] and the band characteristic of gaseous CO₂ centered at 2349 cm⁻¹ [10], a broad band has its maximum absorption located at 2044 cm⁻¹. Between 1 and 60 min contact (Fig. 6e), the intensities of these bands decrease while, concurrently, two bands appear at around 1680 and 1370 cm⁻¹.

The adsorption of CO is rather a complex interaction. The CO molecule has one σ orbital and a doubly degenerate π orbital, a free pair of unshared electrons on both atoms and strongly antibonding σ and π orbitals. When

CO is adsorbed on a Lewis acid site, a covalent bond is usually formed between the lone pair of the carbon atom and the electron acceptor. The stability is ensured by a back-donation interaction between the d-orbitals of the metal and the antibonding orbitals of CO. This transfer of charge from metal to CO considerably reduces the strength of the CO bond, thus the $\nu(\text{CO})$ frequency shifts towards lower wavenumbers with respect to the gas phase frequency [2].

This band at 2044 cm⁻¹ presents a complex structure [14], proving that several types of acidic sites are involved. However, these interactions are not stable since, after 1 h, most of these adsorbed molecules have transformed into other species (Fig. 6e). Indeed, the first obvious transformation is the oxidation of CO into carbon dioxide as revealed by the bands centered at 2348 cm⁻¹ [15,16]. As previously seen, these CO₂ molecules are then strongly perturbed by the surface sites and give rise to CO₂⁻ carboxylate species whose two characteristic absorption bands are located in the 1700–1580 cm⁻¹ and 1350–1200 cm⁻¹ regions. Similarly, the broadness of these bands suggests that several types of carboxylate species may be generated [8]. All these species disappear by pumping at 370 K, proving that they are weakly bound to the surface.

4.4. Titania subjected to carbon monoxide at 670 K

The same experiment as above was performed but this time the titania sample was kept at 670 K (Fig. 7). The

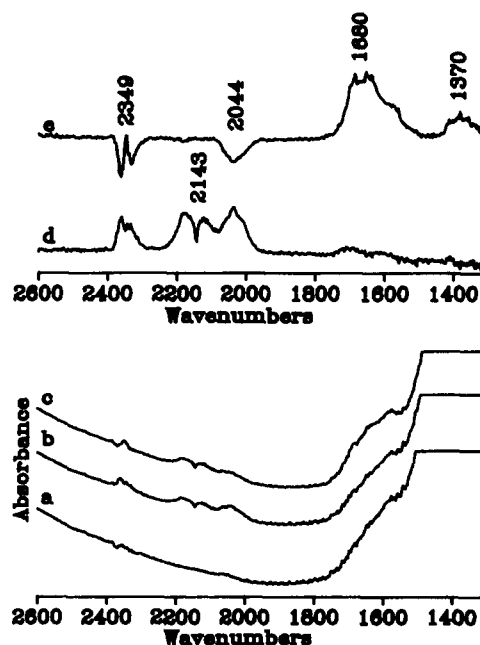


Fig. 6. Carbon monoxide addition at RT on an activated titania pellet. FT-IR spectra: (a) before CO addition; (b) 1 min after CO addition (20 mbar); (c) 1 h after CO addition; (d) difference spectrum (b) – (a); (e) difference spectrum (c) – (b).

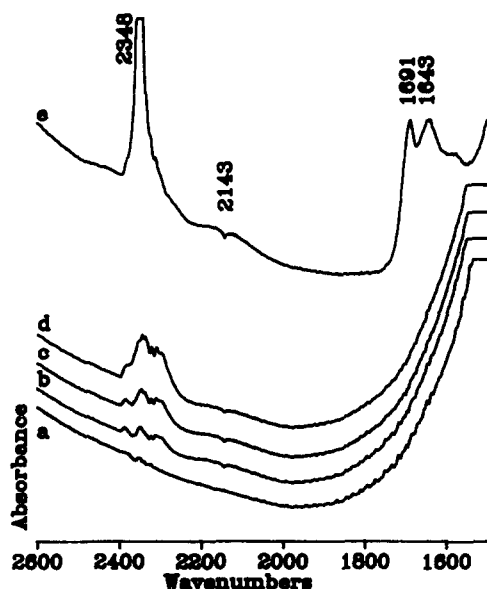


Fig. 7. Carbon monoxide addition at 670 K on an activated titania pellet. FT-IR spectra: (a) before CO addition (670 K); (b) 1 min after CO addition (20 mbar, 670 K); (c) 10 min after CO addition; (d) 25 min after CO addition; (e) cooled to RT.

spectra were recorded 1 min (Fig. 7b), 10 min (Fig. 7c) and 25 min (Fig. 7d) after CO addition. The absorption corresponding to gaseous CO is located at 2143 cm^{-1} while the formation of gaseous CO_2 at 2349 cm^{-1} increases with time. No other species is detected. Indeed, the relatively high temperature prevents the adsorption of CO_2 which occurs at room temperature as just mentioned. When the titania sample is cooled to room temperature under this CO/CO_2 atmosphere, the adsorption becomes

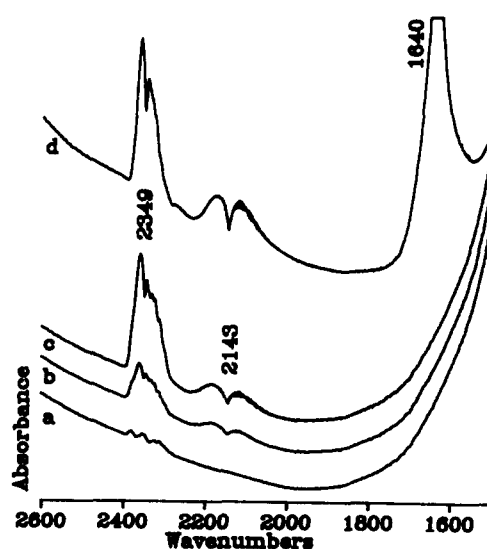


Fig. 8. Carbon monoxide addition at 670 K on a titania pellet. FT-IR spectra: (a) before CO addition (670 K, atmosphere); (b) 15 min after addition of 20 mbar of CO to the atmosphere; (c) 45 min after CO addition; (d) cooled to RT under CO/CO_2 containing atmosphere.

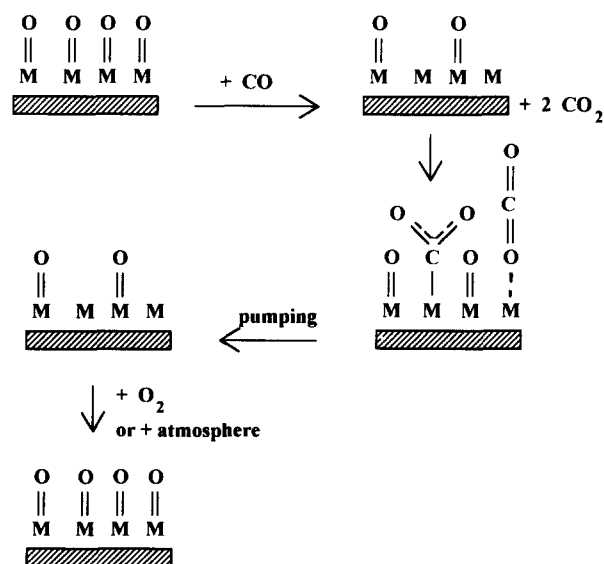
possible. This translates into a strong and sharp band at 2348 cm^{-1} assigned to the CO_2 molecule linearly physisorbed on metal cations as seen before, and both groups of bands corresponding to carboxylate species (Fig. 7e). A quick evacuation removes all physisorbed CO_2 along with carboxylate species and remaining gaseous CO.

4.5. Titania subjected to carbon monoxide/air mixture at 670 K

The TiO_2 sample was heated at 670 K under atmosphere. Then 10 mbar of CO was added to that atmosphere (Fig. 8). The spectrum was recorded 15 min (Fig. 8b) after CO addition. CO and CO_2 gaseous phases were visible. The intensity of the CO_2 bands clearly increases with time. After 45 min contact (Fig. 8c), the sample was cooled to room temperature under the CO/CO_2 containing atmosphere (Fig. 8d). Gaseous CO and CO_2 phases were still visible. As previously mentioned, molecular water present in the atmosphere links again to the surface hydroxyl groups through hydrogen bonds. Neither carboxylate nor other species were detected. Therefore the surrounding atmosphere prevents CO_2 from adsorbing as carboxylate groups.

5. Discussion on CO adsorption

A mechanism of CO adsorption on metal oxides has been described by Davydov [2]. In the present experiments the spectra do not bring evidence of the formation of bridged carbonate species. These latter species may be only intermediate ones with a short lifetime yielding to gaseous CO_2 as soon as they are formed. Indeed, in our experiments, the titania sample was heated to 670 K and therefore, the endothermic decomposition of the surface carbonates may take place fairly rapidly. These results obtained by our specific experimental procedure rather suggest the following scheme:



When the TiO₂ sample is cooled to room temperature, gaseous CO₂ can physisorb on surface metal atoms but a part of these CO₂ molecules also adsorbs in the carboxylate form. Both interactions are eliminated by pumping and the surface recovers after addition of oxygen or air. If the TiO₂ sample is cooled under atmosphere, the presence of both water and oxygen prevents CO₂ from adsorbing on the surface.

6. Conclusion

Surface FT-IR spectrometry proved to be a powerful technique for studying the complete in situ gas–surface interactions occurring in a metal oxide used in gas sensor fabrication. This technique has demonstrated that gas sensor surface reactivity critically depends on the activation conditions, namely the temperature and surrounding atmosphere.

In other words, to ensure a better response reproducibility, a higher sensitivity and selectivity of the gas sensor, the chemical composition of its surface must be carefully controlled and the working conditions clearly defined. Further work on these gas sensors will concentrate on the correlation between the spectroscopic infrared data describing the surface chemical evolution and the macroscopic conductivity measurements depicting the electronic transport.

References

- [1] W. Göpel, J. Hesse and J.N. Zemel (eds.), *Sensors – A Comprehensive Survey, Vol. 7, Chemical Sensors*, Verlag Chemie, Weinheim, 1990.
- [2] A.A. Davydov, *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*, Wiley, New York, 1984.
- [3] J.M. Chovelon, N. Jaffrezic-Renault, P. Clechet, Y. Cros, J.J. Fombon, M.-I. Baraton and P. Quintard, PECVD silicon oxynitride: a new insulator for ISFETs with insulator surface modified by chemical grafting, *Sensors and Actuators, B4* (1991) 385.
- [4] M.-I. Baraton, Infrared and Raman characterization of nanophase ceramic materials, *High Temp. Chem. Proc.*, 3 (1994) 545.
- [5] M.L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, New York, 1967.
- [6] G. Busca, V. Lorenzelli, V. Sanchez Escribano and R. Guidetti, FT-IR study of the surface properties of the spinels NiAl₂O₄ and CoAl₂O₄ in relation to those of transitional aluminas, *J. Catal.*, 131 (1991) 167.
- [7] B.A. Morrow, in J.L.G. Fierro (ed.), *Spectroscopic Characterization of Heterogeneous Catalysts*, Elsevier, Amsterdam, 1990.
- [8] G. Busca and V. Lorenzelli, Infrared spectroscopic identification of species arising from reactive adsorption of carbon oxides on metal oxide surfaces, *Mater. Chem.*, 7 (1982) 89.
- [9] A. Zecchina, S. Coluccia and C. Morterra, Infrared spectra of molecules adsorbed on oxide surfaces, *Appl. Spectrosc. Rev.*, 21 (1985) 259.
- [10] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vols. I and II, D. Van Nostrand, Princeton, NJ, 1963.
- [11] V.D. Sokolovskii, Principles of oxidative catalysis on solid oxides, *Catal. Rev.-Sci. Eng.*, 32 (1990) 1.
- [12] C. Morterra, G. Cerrato and C. Emanuel, End-on surface coordinated (adsorbed) CO₂: a specific ligand for surface Lewis acidic centers, *Mater. Chem. Phys.*, 29 (1991) 447.
- [13] H. Knözinger, Specific poisoning and characterization of catalytically active oxide surfaces, *Adv. Catal.*, 25 (1976) 184.
- [14] E. Garrone, V. Bolis, B. Fubini and C. Morterra, Thermodynamic and spectroscopic characterization of heterogeneity among adsorption sites: CO on anatase at ambient temperature, *Langmuir*, 5 (1989) 892.
- [15] G. Hussain and N. Sheppard, The generation of formate species on the surface of zinc oxide near 200°C from CO with H₂, or from CO alone, as shown by infrared spectroscopy, *Spectrochim. Acta*, 43A (1987) 1631.
- [16] M.I. Zaki and H. Knözinger, Characterization of oxide surfaces by adsorption of carbon monoxide – a low temperature infrared spectroscopy study, *Spectrochim. Acta*, 43A (1987) 1455.