Title: GAS SENSOR AND GAS-SENSITIVE METAL OXIDE POWDER

Abstract: Gas sensor comprising a substrate, at least one detector electrode, a gas-sensitive portion comprising at least one metal oxide, said gas-sensitive portion being in contact with said at least one detector electrode, characterized in that said gas-sensitive portion has a total pore volume (V₆) higher than 0.010 ml/g. The gas sensor of the present invention is able to detect gases at low concentrations (i.e. lower than or equal to 5 ppm), both when working at low temperatures (i.e. at temperatures of from 100°C to 250°C) and at high temperatures (i.e. at temperatures higher than 250°C). Moreover, said gas sensor shows an improved life-time.
GAS SENSOR AND GAS-SENSITIVE METAL OXIDE POWDER

The present invention relates to a gas sensor, to a gas-sensitive metal oxide powder, to a method for producing said gas-sensitive metal oxide powder, as well as to an use of said gas sensor for detecting the presence of gases.

Sensors are utilized in a variety of applications to determine the presence of gases, e.g. reducing gases such as hydrogen, carbon monoxide, ammonia, methane, alcohols. For example, ammonia sensors are being used in several applications such as food technology, chemical plants, medical diagnosis, and environmental protection.

In recent years, there has been a growing interest in the reduction of air pollutant gases emitted during combustion processes in order to reduce environmental pollution and preserve the ecosystem (see, for example, N. Yamazoe et al., “Sensors and Actuators”, B 20 (1994), pg. 95-102).

In particular, nitrogen oxides (NO and NO₂: NOₓ), released from automobiles and chemical plants, have been one of the main causes of acid rain, photochemical smog, and the production of ozone.

In the case of environmental monitoring, the threshold limit values (TLVs) for NO₂ gas and NO gas is 3 ppm and 25 ppm, respectively (see, for example, N.O. Korolkoff, “Solid State Technology”, 32 (1989), pg. 49-64).

Accordingly, an NOₓ sensor is required to have a high sensitivity that can correspond to such low threshold limit values (TLVs).

Tungsten trioxide (WO₃) is considered to be one of the best candidates among NOₓ-sensing materials (see, for example, M. Akiyama et al., “Chemical Letters” (1991), pg. 1611-1614).

Typically, gas sensors comprise a gas-sensitive portion, usually in the form of a film, in conjunction with a substrate and electrodes, the chemical/electrical responses of said gas-sensitive portion being subjected to changes by adsorption, desorption of a gas, or the like. Measurements of said chemical/electrical responses provide the concentration of the gas.
For example, C. Cantalini et al., “Sensors and Actuators”, B 31 (1996), pg. 81-87 disclose a thin film (i.e. thickness lower than 3 μm) of tungsten trioxide (WO$_3$) prepared by high vacuum thermal evaporation from tungsten trioxide (WO$_3$) powder and thermal annealing. Said thin film is said to show good sensitivity to NO$_2$ gas in the concentration range of from 0.5 ppm to 5 ppm, at a temperature lower than or equal to 400°C.

G. Sberveglieri et al., “Sensors and Actuators”, B 26-27 (1995), pg. 89-92 disclose the preparation of a thin film of tungsten trioxide (WO$_3$) by reactive sputtering onto an alumina substrate. Said thin film is said to show good sensitivity to low NO$_x$ concentrations (i.e. in the range of from 1 ppm to 10 ppm), at a temperature lower than or equal to 400°C. A response peak is said to be at 400°C.

US Patent 7,017,389 discloses a sensor for detecting gases including a substrate, electrodes and a thin film metal oxide. A method for selecting the metal oxide to be utilized in the sensors which are highly selective for a specific gas, and a method for determining the presence of a specific gas in a gaseous mixture, are also provided. The abovementioned sensor is said to be useful in any environment or for any application where the detection of a specific gas, e.g., ammonia or nitrogen dioxide, is required. Moreover, said sensor is said to be useful in both the qualification and quantification of a specific gas in a gaseous mixture sample. Furthermore, said sensor is said to be especially beneficial for use in automotive processes, such as those involving SCR, and biosensors.

Rossinyol et al., “Sensors and Actuators”, B 109 (2005), pg. 57-63, discloses a method for synthesizing mesoporous oxides using a template system to increase their surface area. The abovementioned mesoporous oxides are said to be useful in the field of semiconductor gas sensors.

Additional methods for synthesizing tungsten trioxide powders have also been disclosed, for example, by Guidi et al., “Sensors and Actuators”, B 100 (2004), pg. 277-282, wherein it has been shown that the proper choice of
solvents allows fine tuning of the shape and dimension of the grains, or by Blo et al, “Sensors and Actuators”, B 103 (2004), pg. 213-218, wherein tungsten precursors has been dissolved in an alcohol solution to give the tungsten trioxide powder. The abovementioned tungsten trioxide powders are said to be useful in the field of gas sensors.

However, the gas sensors above disclosed may shows some drawbacks.

In particular, the Applicant has noticed that the gas sensors above disclosed may not have a good sensitivity for the gas to be detected, in particular when low gas concentrations such as, for example, lower than or equal to 5 ppm, has to be detected.

Moreover, the Applicant has noticed that the gas sensors above disclosed may not be able to maintain a good sensitivity when working at high temperatures such as, for example, at temperatures higher than 250°C.

Furthermore, the Applicant has noticed that, in the case of a thin film such as, for example, of a film having a thickness lower than or equal to 3 μm, the life-time of the gas sensors may be remarkably reduced.

The Applicant has faced the problem of providing a gas sensor having a good sensitivity to low gas concentrations (i.e. gas concentrations lower than or equal to 5 ppm), both when working at low temperatures (i.e. at temperatures of from 100°C to 250°C) and at high temperatures (i.e. at temperatures higher than 250°C).

The Applicant has now found that a gas sensor comprising a gas-sensitive portion having a high total pore volume (\(V_t\)) (i.e. a total pore volume higher than 0.010 mL/g) is endowed with good sensing properties, namely it is able to detect gases at low concentrations (i.e. lower than or equal to 5 ppm), both when working at low temperatures (i.e. at temperatures of from 100°C to 250°C) and at high temperatures (i.e. at temperatures higher than 250°C). In particular, said gas-sensor shows improved sensing properties when working at low temperatures (i.e. at temperatures of from 100°C to
250°C). Furthermore, said gas sensor shows an improved life-time.

In a first aspect, the present invention relates to a gas sensor comprising a substrate, at least one detector electrode, a gas-sensitive portion comprising at least one metal oxide, said gas-sensitive portion being in contact with said at least one detector electrode, characterized in that said gas-sensitive portion has a total pore volume ($V_p$) higher than 0.010 mL/g.

According to one preferred embodiment, the substrate of the gas sensors of the present invention may be any material suitable for use in a gas sensor, such as Si/SiO$_2$, SiC, GaN, Al$_2$O$_3$, or mixtures thereof. In one preferred embodiment, the substrate comprises aluminium oxide.

As disclosed above, the gas sensors of the present invention is provided with at least one detector electrode placed between the substrate and in communication with the gas-sensitive portion, and the gas-sensitive portion may be arranged so as to be capable of being contacted with a gas or gaseous mixture to be detected. Said detector electrode may be made of any material suitable for use in sensors, such as gold, silver, tungsten, chromium, titanium, or mixtures thereof. Preferably, a gold detector electrode is used in the gas sensors of the present invention.

According to one preferred embodiment, said at least one metal oxide may be selected, for example, from: tungsten trioxide (WO$_3$), titanium dioxide (TiO$_2$), molybdenum trioxide (MoO$_3$), vanadium pentoxide (V$_2$O$_5$), zirconium dioxide (ZrO$_2$), niobium pentoxide (Nb$_2$O$_5$), iridium dioxide (Ir$_2$O$_2$), tantalum dioxide (Ta$_2$O$_5$), perovskite compounds selected from the group of LaFeO$_3$, SmFeO$_3$, or mixtures thereof. Tungsten trioxide (WO$_3$) is particularly preferred.

The gas sensors of the present invention are resistive gas detectors that rapidly detect, within seconds, low concentrations (i.e. lower than or equal to 5 ppm) of specific gases with reduced interference from other gases, both when working at low temperatures (i.e. at temperatures of from 100°C to 250°C) and at high temperatures (i.e. at temperatures higher than 250°C).
For the purpose of the present description and of the claims which follow, except where otherwise indicated, all numbers expressing amounts, quantities, percentages, and so forth, are to be understood as being modified in all instances by the term "about". Also, all ranges include any combination of the maximum and minimum points disclosed and include any intermediate ranges therein, which may or may not be specifically enumerated herein.

The gas sensor according to the present invention may be configured to detect the presence of various gases as well as of their vapours.

Gases and their vapours which may be detected by the gas sensors in accordance with the present invention may be nitrogen-lacking reducing gases, such as hydrogen, carbon monoxide, alcohols (such as ethanol), hydrocarbons (such as methane and propylene); nitrogen-containing reducing gases, such as ammonia and amines, and oxidizing gases, such as oxygen, nitrogen monoxide, nitrogen dioxide, and the like. Preferably, the gas which may be detected by the gas sensors in accordance with the present invention is nitrogen monoxide (NO), or nitrogen dioxide (NO₂).

Said gas-sensitive portion is capable of exhibiting a response in the form of an increase or a decrease in its electrical property in the presence of the selected gas, while exhibiting little or no response to other gases present in the gaseous mixture sample.

According to one preferred embodiment, said gas-sensitive portion is in the form of a film having a thickness of from 5 μm to 100 μm, more preferably of from 10 μm to 70 μm, still more preferably of from 20 μm to 50 μm.

According to one preferred embodiment, said gas-sensitive portion has a total pore volume (Vₜ) higher than 0.020 mL/g, more preferably higher than 0.030 mL/g, still more preferably higher than 0.040 mL/g. By this way, due to the fact that higher pore volume gas sensors allow an easier passage of the gas to be detected through the gas sensors, it is possible to advantageously
provide gas sensors having a good, and even improved, sensitivity.

According to one preferred embodiment, said gas-sensitive portion has a specific surface area ($S_{\text{BET}}$) higher than 2.0 m$^2$/g, more preferably higher than 3.0 m$^2$/g, still more preferably higher than 4.0 m$^2$/g. Gas sensors having higher specific surface area show a still better sensitivity.

According to the present description and the claims which follow, the total pore volume ($V_t$) and the specific surface area ($S_{\text{BET}}$) have been calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619).

Preferably, the metal oxide powder according to the present description and claims is substantially pure. As used herein, "substantially pure" means that the metal oxide powder lacks any dopant.

The metal oxide powder included in the gas-sensitive portion of the gas sensor according to the present invention is advantageously prepared via a sol-gel process.

Therefore, in a second aspect, the present invention relates to a process for producing a gas-sensitive metal oxide powder, said process comprising the steps of:

a) dissolving a metal oxide precursor in at least one organic solvent in the presence of at least one surfactant;

b) hydrolyzing the dissolved precursor by adding water so as to obtain a metal oxide hydrate gel;

c) drying the obtained metal oxide hydrate gel so as to obtain a xerogel; and

d) thermally treating the obtained xerogel so as to obtain a gas-sensitive metal oxide powder;

wherein in the above step a), said at least one surfactant is present in a molar concentration of from 0.5*10$^{-6}$ M to 5*10$^{-4}$ M, preferably of from 1*10$^{-6}$ M to 3*10$^{-4}$ M and the surfactant/metal oxide precursor are present in a molar ratio of from 1*10$^{-6}$ M to 6*10$^{-4}$ M, preferably of from 4*10$^{-5}$ M to 5*10$^{-4}$ M.
Preferably, said at least one surfactant may be selected from cationic surfactants such as, for example, cetylpyridinium chloride (C$_{21}$H$_{38}$NCl), cetyltrimethylammonium chloride [CH$_3$(CH$_2$)$_{15}$N(CH$_3$)$_3$Cl], cetyltrimethylammonium bromide [CH$_3$(CH$_2$)$_{15}$N(CH$_3$)$_3$Br], or mixtures thereof. Cetylpyridinium chloride (C$_{21}$H$_{38}$NCl) is particularly preferred.

Preferably, the gas-sensitive metal oxide powder obtained with the above described process is a tungsten trioxide (WO$_3$) powder.

According to one preferred embodiment, the metal oxide precursors useful in said dissolving step a) may be selected, for example, from metallorganic precursors such as, for example, metal esters, metal alkoxides, or mixtures thereof; or from inorganic precursors such as, for example, metal nitrates, metal halides, or mixtures thereof. Preferably, the metal oxide precursor may be selected from metal halides such as, for example metal chloride or metal bromide. Metal chloride is particularly preferred. When metal oxide precursors such as, for example, metal halides, are employed, the resulting anions should be removed from the solution, for example by repeated washings, because their presence in the final product could increase the resistivity thereof and decrease the gas sensor sensitivity.

According to one preferred embodiment, the organic solvent useful in said dissolving step a) may be selected, for example, from alcohols such as, for example, ethanol, propanol, butanol, or mixture thereof. Ethanol is particularly preferred.

According to one preferred embodiment, said dissolving step a) is carried out by keeping the metal oxide precursor and the surfactant under stirring, in the organic solvent, for a time sufficient to the salt to dissolve. Preferably, they are kept under stirring at a speed rate of from 100 r.p.m. to 400 r.p.m., more preferably of from 150 r.p.m. to 300 r.p.m., at a temperature of from 10°C to 30°C, more preferably of from 15°C to 25°C, for a time of from 1 min to 100 min, more preferably of from 5 min to 30 min.
According to one preferred embodiment, said hydrolizing step b) is carried out by slowly adding the water to the mixed solution obtained at the end of the dissolving step a), in the amount requested by the stoichiometry of the reaction.

Preferably, at the end of said hydrolizing step b) and before the beginning of said drying step c), the obtained metal oxide hydrate gel is still kept under stirring at a speed rate of from 100 r.p.m. to 400 r.p.m., more preferably of from 150 r.p.m. to 300 r.p.m., at a temperature of from 10°C to 30°C, more preferably of from 15°C to 25°C, for a time of from 1 min to 30 min, more preferably of from 15 min to 20 min.

According to one preferred embodiment, said drying step c) is carried out by heating the obtained metal oxide hydrate gel at a temperature of from 60°C to 100°C, more preferably of from 70°C to 90°C, for a time of from 10 hours to 25 hours, more preferably of from 15 hours to 20 hours. By this way, the solvent is evaporated and the xerogel related product is obtained.

Preferably, at the end of said drying step c) and before the beginning of said thermally treating step d), the obtained xerogel product may be pulverized in a mortar to obtain a xerogel powder.

According to one preferred embodiment, said thermally treating step d) is carried out by thermally treating the obtained xerogel at a temperature of from 400°C to 1100°C, more preferably of from 550°C to 800°C, for a time of from 1 hour to 6 hours, more preferably of from 2 hours to 5 hours.

Preferably, said thermally treating step d) is carried out in the presence of oxygen current. By this way, the thermal decomposition of the surfactant and the removal of traces of solvent and of crystallization water is greatly improved. In addition, both an improved oxidation of the metal and a crystalline structure of the gas-sensitive metal oxide powder is obtained.

After said thermally treating step d), the obtained gas-sensitive metal oxide powder is cooled to room temperature (23°C). Said cooling may be carried out in air or, preferably, by furnace cooling, applying a cooling rate of
20°C/min to 50°C/min, preferably of from 30°C/min to 40°C/min.

The process of the present invention for producing a gas-sensitive metal oxide powder provides very good yields, higher than 90%, preferably higher than 95%.

The cited above process allows the preparation of a gas-sensitive metal oxide powder having a high total pore volume, feature which allows an easier passage of the gas to be detected through the powder; thus, it is possible to advantageously provide a gas-sensitive metal oxide powder having a good, and even improved, sensitivity.

In a third aspect, the present invention relates to a gas-sensitive metal oxide powder having a total pore volume \( (V_t) \) higher than 0.075 mL/g, more preferably, higher than 0.100 mL/g, still more preferably higher than 0.120 mL/g.

According to one preferred embodiment said gas-sensitive metal oxide powder has a specific surface area \( (S_{BET}) \) higher than 6.0 m\(^2\)/g, more preferably higher than 7.0 m\(^2\)/g, still more preferably higher than 8.0 m\(^2\)/g.

According to the present description and the claims which follow, the total pore volume \( (V_t) \) and the specific surface area \( (S_{BET}) \) have been calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619).

In order to obtain a gas-sensitive portion of the gas sensor according to the present invention, a slurry of the gas-sensitive metal oxide powder obtained as disclosed above may be advantageously prepared.

Preferably, said slurry is prepared by mixing at least one gas-sensitive metal oxide powder obtained as disclosed above with at least one dispersing agent.

Preferably, said mixing is carried out at a temperature of from 10°C to 50°C, preferably of from 20°C to 40°C, for a time of from 10 min to 20 hours, preferably of from 15 min to 5 hours.

Preferably, said slurry further comprises at least one resin.
Preferably, said slurry further comprises at least one glass binder.

Preferably, said at least one dispersing agent may be selected, for example from inert liquids such as, for example, aliphatic alcohols; esters of said alcohols such as, for example, acetates such as, for example, 2-butoxyethoxyethylacetate; terpenes such as, for example, turpentine, α-terpinol; or mixtures thereof. α-Terpineol, 2-butoxyethoxyethylacetate, or mixtures thereof, are particularly preferred.

Preferably, said at least one dispersing agent is present in said slurry in an amount of from 25% to 40% by weight, preferably of from 30% to 35% by weight, with respect to the total weight of the slurry.

Preferably, said at least one resin may be selected, for example, from: cellulose resins such as, for example, methylcellulose, ethylcellulose, or mixtures thereof. Ethylcellulose is particularly preferred.

Preferably, said at least one resin is present in said slurry in an amount of from 1.0% to 4.0% by weight, preferably of from 2.0% to 3.0% by weight, with respect to the total weight of the slurry.

Preferably, said at least one glass binder may be selected, for example, from glass frits, said glass frit comprising at least two metal oxides which may be selected, for example, from: silicon oxides, aluminium oxides, lead oxides, bismuth oxides, boron oxides, phosphate oxides, bismuth oxides, borate oxides. Glass frits comprising a mixture of silicon oxides, aluminum oxides and lead oxides, are particularly preferred.

Preferably, said at least one glass binder is present in said slurry in an amount of from 0.10% to 1.0% by weight, preferably of from 0.15% to 0.30% by weight, with respect to the total weight of the slurry.

As disclosed above, the gas sensor of the present invention is provided with at least one detector electrode. Said at least one detector electrode may be provided on the gas sensor substrate by any suitable method. For example, said at least one detector electrode may be placed on the surface of the gas sensor substrate and, subsequently, the slurry of metal
oxide powder obtained as above reported, may be applied to said at least one detector electrode and said substrate, thereby coating both and adhering said at least one detector electrode to said substrate. Other methods for applying the detector electrode to the substrate include, but are not limited to, lithographic techniques, sputtering, laser processing, photochemical methods, etc.

Said slurry may be applied to said at least one detector electrode by methods known to those skilled in the art which include, but are not limited to, screen printing deposition, ion beam deposition, plasma polymerization of appropriate gases, electron beam polymerization of appropriate monomers, chemical or plasma assisted chemical vapour deposition, e-beam, thermal or laser beam evaporation or sputtering of solid dielectric sources, metallic-organic chemical vapour deposition, laser ablation, excimer laser interactions with appropriate gases at the substrate surface. Screen printing deposition is particularly preferred.

Preferably, after the screen printing deposition has been carried out, the obtained layer of slurry is heated at a temperature higher than or equal to 700°C, preferably of from 750°C to 850°C, for a time of from 20 min to 5 hours, preferably of from 30 min to 2 hours, in air.

The gas sensor of the present invention may further include other means such as, for example, heating means and temperature sensing means.

The present invention will now be illustrated in further detail by means of an illustrative embodiment with reference to the attached Figure 1 which is a view in cross section of a gas sensor made according to the present invention.

In particular, Figure 1 shows a gas sensor 100 comprising six wires for electrical connections 1, a detection electrode 2, a gas-sensitive portion 3 in contact with the detection electrode 2, a substrate 4, a heating means 5 and an electrically insulating layer 6.
In the particular embodiment of Figure 1, the gas-sensitive portion 3 completely covers the detector electrode 2. Alternatively, the gas-sensitive portion 3 may cover only partially the detector electrode 2 (not shown in Figure 1).

According to the present invention, the sensitivity of a gas sensor is defined by means of the following formula:

$$\frac{G_{\text{gas}}}{G_{\text{carrier}}}$$

wherein $G_{\text{carrier}}$ is the conductance of the gas sensor measured in an ambient in which only a reference gas carrier is present, while $G_{\text{gas}}$ is the conductance of the same gas sensor measured in the same ambient of above wherein, in addition to the reference gas carrier, the gas to be detected has been introduced.

The conductance may be detected by directly measuring, for example, the potential difference at the end portions of the gas sensor.

Alternatively, the measurement may be carried out indirectly by incorporating the sensor in a feedback circuit of an oscillator such that the oscillator frequency varies with composition of the gas or gaseous mixture. Gas composition may then be determined using an electronic counter. The signal thus produced may be used to modulate a radio signal and thereby be transmitted over a distance (e.g. by telemetry or as a pulse train along an optical fibre).

The reference gas carrier may be, for example, dry air, or air having an amount of relative humidity ranging from 20% to 80%.

The measurements are generally carried out at temperatures of from 100°C to 700°C, preferably of from 200°C to 400°C.

 Preferably, the gas to be detected is nitrogen monoxide (NO) or nitrogen dioxide (NO$_2$).

More preferably, when the gas to be detected is nitrogen oxide or nitrogen dioxide, the gas sensor comprises a gas-sensitive portion comprising a tungsten trioxide powder.
The present invention will be further illustrated below by means of a number of preparation examples, which are given for purely indicative purposes and without any limitation of this invention.

**EXAMPLE 1**

**Preparation of tungsten trioxide (WO₃) xerogel powder.**

Sample A1 (invention). The synthesis was carried out using a Pyrex reactor type, provided with one cell for the external circulation of water and placed onto a plate of a magnetic stirrer. 35 ml of a 1*10⁻⁴ M ethanol solution of cetylpyridinium chloride (C₂₁H₃₈NCl) surfactant, available from Fluka Catalogue Code No. 52349, was added to the reactor and kept under magnetic stirring, at 200 rpm, maintaining the system at the controlled temperature of 20°C, for 10 min. Then, 3.5 g of tungsten chloride (WCl₆) (molar ratio cetylpiridinium chloride and tungsten chloride: 4*10⁻⁵), available form Aldrich Catalogue Code No. 24191-1, was slowly added to the solution.

Then, the agitation was maintained for additional 20 minutes, during which salt dissolution occurs, giving the solution a clear yellow color. Subsequently, 0.48 ml of water was added dropwise into the solution. A blue gel formation started to be observed on the reactor walls after 15-20 min; then, after additional 30 min, the complete formation of blue colored tungsten trioxide (WO₃) gel hydrate was obtained. The solution was maintained under stirring, at 200 rpm, for additional 10 min; then, the reactor was placed into a heater at 80°C, for 16 hours till the solvent was evaporated and the xerogel tungsten trioxide isolated. The xerogel tungsten trioxide was pulverized in an agatha small mortar and subsequently placed within a quartz cell, isolated from the outside, into a tubular oven to be thermally treated at the temperature of 650°C, for 4h, in a oxygen current. The desired temperature has been reached approximately in 15 min, starting from ambient temperature and increasing approximately of 40°C each min. The so obtained tungsten trioxide powder A1 showed a clear yellow color. The obtained tungsten trioxide powder was furnace cooled to room temperature (23°C) decreasing
approximately of 35°C/min. The reaction yield was 97%.

The total pore volume (V̂) and the specific surface area (S_{BET}) were calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619). The obtained data are the following:

- total pore volume (V̂): 0.15 mL/g;
- specific surface area (S_{BET}): 9.63 m²/g.

**Sample B1 (reference).** A reference sample of tungsten trioxide powder B1 was prepared according to the same procedure disclosed for preparing invention Sample A1, with the difference that the synthesis was carried out in the absence of the cetylpyridinium chloride (C_{21}H_{33}NCl) surfactant. To this aim, a 2.5×10^{-1} M solution of tungsten chloride WCl₆ was used.

The total pore volume (V̂) and the specific surface area (S_{BET}) were calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619). The obtained data are the following:

- total pore volume (V̂): 0.04 mL/g;
- specific surface area (S_{BET}): 4.95 m²/g.

**EXAMPLE 2**

**Preparation of tungsten trioxide (WO₃) slurry**

**Sample A2 (invention).** A tungsten trioxide slurry A2 was prepared by mixing 66.11 g of Sample A1 (as prepared according to the synthesis previously disclosed in Example 1), 27.85 g of α-terpineol, 3.55 g of 2-butoxyethoxyethylacetate, 2.27 g of ethylcellulose and 0.22 g of a glass frit having a melting point of about 650°C and the following composition: SiO_{2}/A_{2}O_{3}/PbO_{2}.

**Sample B2 (reference).** A reference sample of solid solution of tungsten trioxide B2 was prepared according to the same procedure disclosed for preparing invention Sample A2, with the difference that the
Sample A1 has been replaced by Sample B1, in the same amount.

**EXAMPLE 3**

**Preparation of gas sensor**

*Sample A3 (invention).* A gas sensor according to Fig. 1 was made. In particular, a gas sensor comprising six wires for electrical connections 1, a gold detection electrode 2, a gas-sensitive portion 3 including the tungsten trioxide A2 (as prepared according to Example 2) in contact with a detection electrode 2, a substrate 4 of aluminium oxide, an heating mean (5) and an electrically insulating layer (6) was made.

Said gas-sensitive portion was made by screen printing deposition of the tungsten trioxide slurry obtained as disclosed in Example 2, and further heating at 750°C, for 1 hour, in air. The obtained gas-sensitive portion had a thickness of 30 μm.

The total pore volume \((V_t)\) and the specific surface area \((S_{BET})\) of the gas-sensitive portion were calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619). The obtained data are the following:

- total pore volume \((V_t)\): 0.042 mL/g;
- specific surface area \((S_{BET})\): 43.3 m²/g.

**Sample B3 (reference).** A reference gas sensor B3 was prepared according to the same procedure disclosed for preparing invention Sample A3, with the difference that, in the gas-sensitive portion 3, the tungsten trioxide A2 has been replaced by reference Sample B2. Said gas-sensitive portion has a thickness of 30 μm.

The total pore volume \((V_t)\) and the specific surface area \((S_{BET})\) of the gas-sensitive portion were calculated from the adsorption isotherms following IUPAC recommendations (Sing et al., "Pure and Applied Chemistry", Vol. 57 (1985), pg. 603-619). The obtained data are the following:

- total pore volume \((V_t)\): 0.004 mL/g;
- specific surface area \((S_{BET})\): 1.52 m²/g.
EXAMPLE 4

Gas detection.

The gas sensor according to the present invention (Sample A3) and the reference gas sensor (Sample B3) were subjected to a gas detection.

To this aim, the gas sensor according to the present invention (Sample A3) and the reference gas sensor (Sample B3) were placed in a testing chamber which was connected to a computer which allows to control:

- the heating means 5 in order to heat the gas sensor and to maintain the gas sensor to a desired temperature (i.e. 230°C and 330°C);

- the detection electrode 2 by recording the voltage-drop on a resistor during the gas flowing over the gas sensor (the obtained data were subsequently converted into conductance values and were given in Table 1 and Table 2).

In particular, the gas sensor according to the present invention (Sample A3) and the reference gas sensor (Sample B3) were placed in a testing chamber in the presence of a dry air carrier, at a temperature of 230°C, to detect the presence of a nitrogen dioxide gas at the concentration of 1 ppm. The response of the gas sensors (sensitivity) at the tested gas is defined as $G_{gas}$ to $G_{air}$ ratio, wherein $G_{gas}$ and $G_{air}$ are the conductance in an atmosphere containing nitrogen dioxide and air free from nitrogen dioxide, respectively.

The experiments were repeated by changing the concentrations to 2 ppm and 5 ppm, and then by replacing the dry air carrier with humid air at 50% of relative humidity (RH). The results are set forth in Table 1.

Then, the experiments were repeated by setting the temperature at 330°C. The results are set forth in Table 2.
TABLE 1 - Gas sensor sensitivity at Temperature = 230°C

<table>
<thead>
<tr>
<th>NO₂ ppm</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>1</th>
<th>2</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier</td>
<td>Dry Air</td>
<td>Dry Air</td>
<td>Dry Air</td>
<td>RH=50% Air</td>
<td>RH=50% Air</td>
<td>RH=50% Air</td>
</tr>
<tr>
<td>Sample A3 (invention)</td>
<td>4.54</td>
<td>20.33</td>
<td>51.99</td>
<td>18.61</td>
<td>509.12</td>
<td>1069.68</td>
</tr>
<tr>
<td>Sample B3 (reference)</td>
<td>3.50</td>
<td>16.34</td>
<td>17.93</td>
<td>4.91</td>
<td>94.50</td>
<td>717.45</td>
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</tbody>
</table>

TABLE 2 - Gas sensor sensitivity at Temperature = 330°C

<table>
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<tr>
<th>NO₂ ppm</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>1</th>
<th>2</th>
<th>5</th>
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<td>Carrier</td>
<td>Dry Air</td>
<td>Dry Air</td>
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<td>RH=50% Air</td>
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<td>Sample A3 (invention)</td>
<td>1.84</td>
<td>5.38</td>
<td>28.60</td>
<td>1.69</td>
<td>5.00</td>
<td>22.18</td>
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<td>Sample B3 (reference)</td>
<td>1.50</td>
<td>3.15</td>
<td>14.86</td>
<td>1.49</td>
<td>2.77</td>
<td>9.30</td>
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The gas sensor according to the invention showed to be able to detect nitrogen dioxide with a sensitivity markedly higher, in particular when working at low temperature (i.e. at 230°C), than those provided by the reference samples, whichever was the concentration of gas to be detected and the gas carrier used.
CLAIMS

1. Gas sensor comprising a substrate, at least one detector electrode, a gas-sensitive portion comprising at least one metal oxide, said gas-sensitive portion being in contact with said at least one detector electrode, characterized in that said gas-sensitive portion has a total pore volume ($V_t$) higher than 0.010 mL/g.

2. Gas sensor according to claim 1, wherein the substrate comprises Si/SiO$_2$, SiC, GaN, or Al$_2$O$_3$.

3. Gas sensor according to claim 1 or 2, wherein the at least one detector electrode is made of gold, silver, tungsten, chromium, titanium, or mixtures thereof.

4. Gas sensor according to any preceding claims, wherein the metal oxide is selected from tungsten trioxide (WO$_3$), titanium dioxide (TiO$_2$), molybdenum trioxide (MoO$_3$), vanadium pentoxide (V$_2$O$_5$), zirconium dioxide (ZrO$_2$), niobium pentoxide (Nb$_2$O$_5$), iridium dioxide (Ir$_2$O$_2$), tantalum dioxide (Ta$_2$O$_3$), perovskite compounds selected from the group of LaFeO$_3$, SmFeO$_3$, or mixtures thereof.

5. Gas sensor according to claim 4, wherein the metal oxide is tungsten trioxide (WO$_3$).

6. Gas sensor according to any preceding claims, wherein the gas sensor is a hydrogen, a carbon monoxide, an alcohol, a hydrocarbon, an ammonia, an amine, an oxygen, a nitrogen monoxide (NO), or a nitrogen dioxide (NO$_2$) gas sensor.

7. Gas sensor according to claim 6 wherein, the gas sensor is a nitrogen monoxide (NO), or a nitrogen dioxide (NO$_2$) gas sensor.

8. Gas sensor according to any preceding claims, wherein the total pore volume ($V_t$) is higher than 0.020 mL/g.

9. Gas sensor according to any preceding claims, wherein the gas sensor has a specific surface area ($S_{BET}$) higher than 2.0 m$^2$/g.

10. Gas sensor according to claim 9, wherein the gas sensor has a
specific surface area ($S_{\text{BET}}$) higher than 3.0 m$^2$/g.

11. Gas sensor according to any preceding claims, wherein the gas-sensitive portion is in the form of a film having a thickness of from 5 µm to 100 µm.

12. Gas sensor according to claim 11, wherein the gas-sensitive portion is in the form of a film having a thickness of from 10 µm to 70 µm.

13. Process for producing a gas-sensitive metal oxide powder, said process comprising the steps of:
   a) dissolving a metal oxide precursor in at least one organic solvent in the presence of at least one surfactant;
   b) hydrolyzing the dissolved precursor by adding water so as to obtain a metal oxide hydrate gel;
   c) drying the obtained metal oxide hydrate gel so as to obtain a xerogel; and
   d) thermally treating the obtained xerogel so as to obtain a gas-sensitive metal oxide powder;

wherein in the above step a), said at least one surfactant is present in a molar concentration of from $0.5\times10^{-6}$ M to $5\times10^{-4}$ M and the surfactant/metal oxide precursor are present in a molar ratio of from $1\times10^{-5}$ M to $6\times10^{-4}$ M.

14. Process according to claim 13, wherein said at least one surfactant is present in a molar concentration of from $1\times10^{-6}$ M to $3\times10^{-4}$ M.

15. Process according to claim 13 or 14, wherein said surfactant/metal oxide precursor are present in a molar ratio of from $4\times10^{-6}$ M to $5\times10^{-4}$ M.

16. Process according to any claims 13 to 15, wherein said at least one surfactant is a cationic surfactant.

17. Process according to claim 16, wherein said at least one cationic surfactant is cetylpyridinium chloride ($\text{C}_{21}\text{H}_{39}\text{NCl}$), cetyltrimethylammonium chloride [$\text{CH}_{3}(\text{CH}_{2})_{15}\text{N}(\text{CH}_{3})_{3}\text{Cl}$], cetyltrimethylammonium bromide [$\text{CH}_{3}(\text{CH}_{2})_{15}\text{N}(\text{CH}_{3})_{3}\text{Br}$], or mixtures thereof.
18. Process according to any claims 13 to 17, wherein said gas-sensitive metal oxide powder is a tungsten trioxide (WO₃) powder.

19. Process according to any claims 13 to 18, wherein said metal oxide precursor is selected a metal halide precursor.

20. Gas-sensitive metal oxide powder having a total pore volume (Vₚ) higher than 0.075 mL/g.

21. Gas-sensitive metal oxide powder according to claim 20, wherein said gas-sensitive metal oxide powder has a specific surface area (S_BET) higher than 6.0 m²/g.

22. Process for producing a slurry of the gas-sensitive metal oxide powder according to claims 20 or 21 by mixing at least one gas-sensitive metal oxide powder with at least one dispersing agent.

23. Use of a gas sensor according to any of claims 1 to 12 for detecting the presence of gases at temperatures of from 100°C to 250°C.

24. Use of a gas sensor according to any of claims 1 to 12 for detecting the presence of gases at temperatures higher than 250°C.
# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. GO1N27/12 GO1N27/407

According to international Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

GO1N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>GB 1 467 735 A (FORD MOTOR CO) 23 March 1977 (1977-03-23) page 3, line 6 - line 36</td>
<td>1-8,23, 24</td>
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<td>Y</td>
<td>JP 09 113480 A (NGK SPARK PLUG CO) 2 May 1997 (1997-05-02) PAJ ABSTRACT abstract</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claims or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "C" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed

- **"I"** later document published after the international filing date or priority data and not in conflict with the application but cited to understand the principle or theory underlying the invention

- **"X"** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

- **"Y"** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

- **"&"** document member of the same patent family

Date of the actual completion of the international search: 22 August 2007

Date of mailing of the international search report: 07/11/2007

Name and mailing address of the ISA:

European Patent Office, P.B. 5819 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Authorized officer:

Savage, John

Form PCT/ISA/210 (second sheet) (April 2006)
INTERNATIONAL SEARCH REPORT

Box II  Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

   1-12, 23, 24

Remark on Protest:

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2004)
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12, 23, 24

   Gas Sensor with a gas-sensitive portion comprising at least one metal oxide

2. claims: 13-19

   Method of manufacturing a gas-sensitive metal oxide powder

3. claims: 20-22

   Gas-sensitive metal oxide powder with a total pore volume higher than 0.075 mL/g
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<tr>
<td></td>
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<td>AU 7273274 A</td>
<td>25-03-1976</td>
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<td>CA 995482 A1</td>
<td>24-08-1976</td>
</tr>
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<td>JP 50056292 A</td>
<td>16-05-1975</td>
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<td>JP 55033547 B</td>
<td>01-09-1980</td>
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