Effect of surface modification due to superacid species in controlling the sensitivity and selectivity of SnO_2 gas sensors

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Abstract

The sensitivity and selectivity of SnO_2 gas sensors are found to be affected by the presence of sulphate species on the surface due to the formation of superacidic sites. The potential advantages of this new method of selectivity control of SnO_2 gas sensors are described with respect to the sensing of carbon monoxide, ammonia, ethanol, acetone and LPG. Although an increase in sensitivity is observed in the range 3–60 ppm for a few of these gases, these modified materials show a slow loss of activity upon exposure to humidity. The evidence obtained from instrumental techniques such as XRD, TG–DTA, SEM, IR and TDS indicate that these superacid species exert considerable influence on the sensitivity by modulating the adsorption characteristics along with microstructural changes.

Keywords: Gas sensors; Superacid species; Tin oxide

1. Introduction

There is a great deal of contemporary concern about developing good chemical sensors for combustible and dangerous gases, such as CO, hydrocarbons, ethanol, etc., due to their prominent role in safety, industrial process monitoring and pollution control. Although various methods are available to detect such flammable and toxic gases, the one involving electrical conductivity changes of semiconducting materials by adsorption and, possibly, surface reaction is considered to be advantageous due to its simplicity and ease of miniaturization [1–3].

Among the various semiconducting oxide materials, tin oxide has been extensively studied due to its prominent role in the detection of various gases [4–6]. The SnO_2 surface is a useful and versatile system for numerous and wide-ranging applications in sensors, catalysis, heat mirrors, transparent electrodes for solar cells, opto-electronic devices, etc. [7,8]. The chemical and physical properties of the hydroxyl groups on SnO_2 surfaces are largely responsible for the widespread use of these materials and the credentials of tin oxide-based sensors include high sensitivity at moderate operation temperature, thermal and structural stability, fast response, possibility of heat cleaning and long life.

Although tin oxide sensors have been reported to detect alcohols [9], carbon monoxide [10], ammonia [11], hydrogen [12], hydrogen sulfide [13], nitrogen oxides [14] and other gases, monitoring of specific gases is difficult due to poor selectivity. Also, competitive and co-operative adsorption of gases on the surface can cause long-term drifts, thus affecting the reliability [15].

To overcome this limitation, a great deal of effort has been exerted over the past decade to improve the selectivity by adopting various strategies, such as modifying the surface states and catalytic properties of the tin oxide by noble metal additives [16]. In general, the sensitivity and selectivity have been found to depend on the characteristics of the surface of the SnO_2, temperature of operation, dopant materials and catalyst materials or promoters [17–19]. Modification of tin oxide by doping with noble metals, rare earth metals and other metal oxides [20–22] has been found to be successful to some extent, although the desired level of selectivity is yet to be reached. In addition, selectivity control by temperature programming, use of filters and masks, etc., would adversely alter the response time and sensitivity. For example, the presence of a carbon filter has been found to almost double the response time (from 6–8 min to 12–15 min) for CO sensors [23].

Apart from the dopants, the method of preparation of these oxide materials is shown to play an important role in the gas-sensing properties [24]. A key parameter

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for understanding the details of this is to study the oxide surface in terms of its distribution of acidic and basic sites and the determination of their strength. In this context, the enhanced sensitivity of sulfated SnO_2 is not surprising, as surface modification of oxides such as SnO_2 is well known to generate superacid species [25,26]. Despite this significance, the role of superacid species in determining the selectivity is not yet understood. In addition, the enhancement of sensitivity due to aliovalent doping of SnO_2 can to some extent be considered as a result of a pattern of substitution that involves both an acid–base effect (a change in the concentration of the ionic defects) and/or a redox effect (a change in the concentration of electronic defects).

It is well known that metal oxides such as zirconia, tin oxide, iron oxide and titanium oxide become highly acidic when treated with sulfates, phosphates and some liquid superacids such as $HF-SbF_5$, CF_3COOH, etc. [27]. Such solid superacid materials with an acid strength of up to $H_0 = -16.04$ (H_0 is the Hammett acidity function) are known to be good catalysts for a variety of specific reactions, such as isomerization of alkanes, alkylation of benzene, cumene cracking, etc. [28–30]. The modification of an SnO_2 surface by various superacid species to control the selectivity of gas sensors hence seems to offer important advantages over other methods. More significantly, the insights obtained from such a study will be helpful for understanding the 'much discussed' relationship between sensors and catalysts [31,32]. The primary objective of the present study is to investigate the role of superacid species in increasing the sensitivity and selectivity of various gaseous molecules on an SnO_2 surface.

2. Experimental

2.1. Sample preparation

Tin (IV) hydroxide was prepared by adding an excess of ammonium hydroxide to an aqueous solution of stannous chloride with constant stirring. The resultant precipitate was washed well with deionized water to remove chloride ions and dried at 110 °C for 12 h. The dry hydroxide powder thus obtained was divided into several parts, equilibrated with a known amount of various concentrations of sulfuric acid and evaporated to dryness to yield appropriate surface coverages. The dry powder was subsequently calcined at 500 °C for 4 h. The tin and sulfur contents were determined by the XRF technique.

2.2. Characterization methods

The powder X-ray diffraction patterns of the prepared samples were recorded in a Rigaku (model D/Max, III

VC, Japan) X-ray diffractometer using Cu $K\alpha$ radiation. The phase identification and crystallinity of the samples were subsequently carried out. The TG–DTA analyses of the samples were performed on a TG–DTA instrument (model 92, Setaram, France). The thermograms of the samples under nitrogen atmosphere were recorded at a heating rate of 10 K min^{-1}. Surface-area measurements were done by adsorption of nitrogen at liquid-nitrogen temperature in a dynamic flow instrument (Omnisorp 100 CX, USA). The particle-size distribution of the sample was measured using a micron photosizer (SKC-300, Seishan, Japan) instrument. SEM photographs were taken in a Joel (model 550) instrument. The acid strength distribution of the samples was estimated by non-aqueous titration with n-butylamine using Hammett indicators [33].

2.3. Measurement of gas-sensing properties

The experimental apparatus for measuring the gas sensitivity is similar to that described earlier [34]. In brief, the calcined powders were made into pellets of 1 cm diameter, 2 mm thickness and sintered at 500 °C for 3 h, subsequently polished and electrodes formed on both the sides by applying silver paste followed by drying under an IR lamp for sensitivity measurements. The test gas with different concentrations was mixed with dry air and passed into the chamber at a constant flow rate. A constant-potential source was connected across the sensor and the change in the current was recorded to monitor the change in resistivity in the presence of test gas. The sensitivity of the sensor is expressed as the ratio of the change in resistance of the sensor in the presence of gas to the original resistance at that temperature and for a specific concentration. The test gases used were carbon monoxide, ammonia, ethanol, acetone and LPG.

3. Results and discussion

3.1. Structural changes

Fig. 1 shows the powder X-ray diffraction patterns of pure and surface modified SnO_2, where the changes due to surface modification in sample crystallinity can easily be observed. A gradual incorporation of sulfate ion decreases the intensity of all the peaks with concomitant broadening. This type of inhomogeneous broadening may be due to surface precipitation. The degree of crystallinity of the sulfated SnO_2 is lower in comparison with that of pure SnO_2 (Fig. 1, curves a–c). The extreme case of sulfation (d) demonstrates a slow evolution of the prominent sulfate peaks; as the new phase evolves, the intensity of the original SnO_2 peaks becomes larger. Indeed, the sensitivity is also poor for
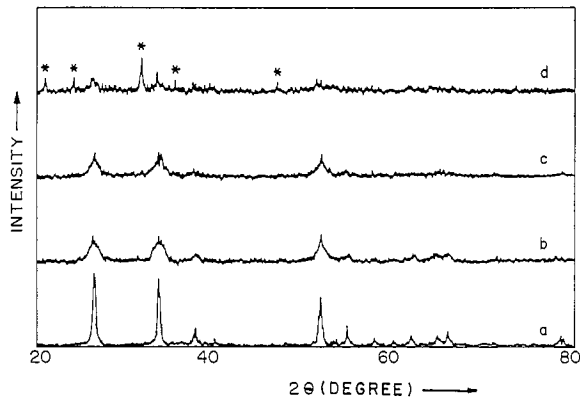
Fig. 1. Powder X-ray diffraction patterns of pure SnO_2 (a) and SnO_2 treated with 1N (b), 2N (c) and 4N (d) sulfuric acid respectively; an asterisk indicates the evolution of bulk sulphate species.

such samples where bulk sulfate formation can be observed in these XRD patterns. Similar changes have been observed for other superacids during catalytic studies of sulfated SnO_2 [35], ZrO_2 [36] and Fe_2O_3 [26].

3.2. IR spectra

In order to understand the nature of the species on the sulfated SnO_2 surfaces, the IR spectra of these samples were taken with various sulfate coverages (Fig. 2). Comparison of spectral features of pure SnO_2 (curve a) with other cases clearly demonstrates the presence of the unidentate sulfate ions (1040 and 1140 cm^{-1}) attached to Sn [27]. More interestingly, samples treated with higher concentrations of sulfate ions show a decrease in the relative intensities of unidentate sulfate species along with the appearance of peaks corresponding to bidentate sulfate species (988 and 1140 cm^{-1}). Further increase in sulfate concentration shows new bands at 1376 and 1348 cm^{-1} due to bulk sulfate species (Fig. 2, curve d) in agreement with the X-ray diffraction data.

3.3. TG–DTA studies

The changes in the differential thermograms of pure and sulfated stannic hydroxides are presented in Fig. 3. These results are invaluable in deciding the temperature of calcination before sintering the sensor materials to get the desired microstructural control. The strong endothermic peak around 110 °C is due to removal of adsorbed water and the changes at around 300 °C probably correspond to the loss of surface hydroxyl groups [37]. In sharp contrast, the sulfated samples show the endotherm shifted to a higher temperature and the enthalpy of reaction substantially increases. These changes indicate a stabilization of the attached hydroxyl groups so that the surface sulfate holds water much more strongly. The most important information
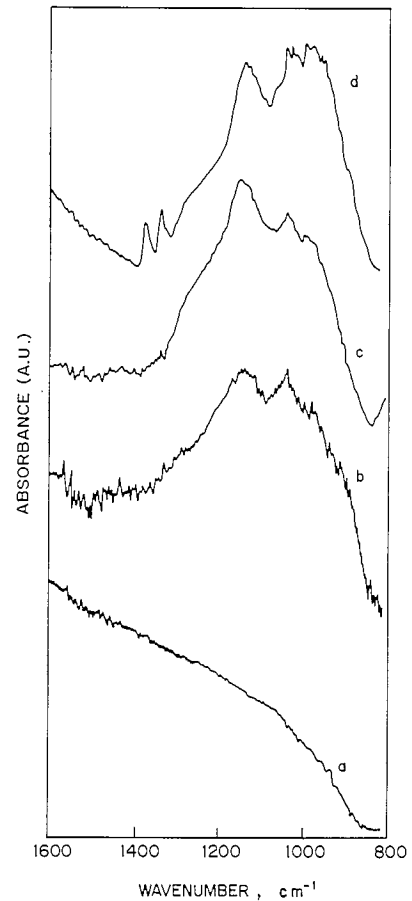

Fig. 2. IR spectra of pure SnO_2 (a) and SnO_2 modified with 1N (b), 2N (c) and 4N (d) sulfuric acid, respectively.
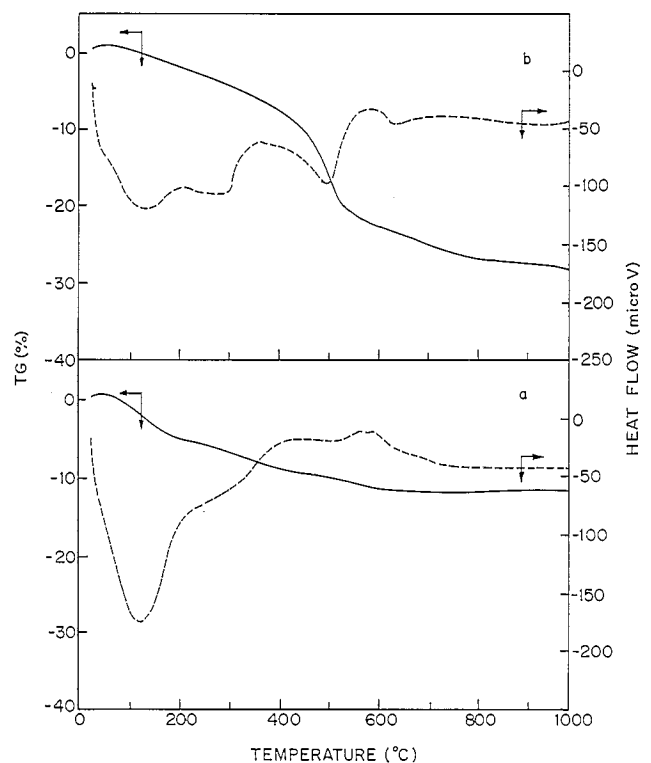

Fig. 3. Thermogravimetric and DTA profiles of pure SnO_2 (a) and SnO_2 modified with 1N sulfuric acid (b).

that can be obtained from this Figure is the enhanced stability of sulfated SnO_2 at relatively high temperature. This, together with the presence of surface hydroxyl groups, can be seen to play a major role in deciding the sensitivity and selectivity of the samples. Information regarding the stability of these materials after calcination can also be obtained from the TG–DTA profiles, which indicate no loss of weight after 800 °C. This is further confirmed by the thermal desorption spectra, as shown in Fig. 4. The degradation observed around 764 °C corresponds to the oxidative loss of sulfur. These results demonstrate the stability of the superacid species on SnO_2 surfaces during sensing operations (300 °C) as well as during heat cleaning at slightly higher temperature (400 °C).

A comparison of the SEM micrographs of the various samples is shown in Fig. 5. This indicates the effect of sulfation on the texture and morphology. In the case of pure SnO_2, we can see the highly homogeneous and uniform distribution of particles with an average size of about 0.6 μm. Relatively smaller particles appear in the sulfated samples, which is in agreement with the particle size derived from XRD peak broadening (ranging from 60 to 80 Å) and an increase in intensity of the peak at 1140 cm^{-1} with the sulphur content in IR spectra. Furthermore, the average size of crystallites from these micrographs also matches well with that obtained from a particle-size analyser (micron photosizer).

3.4. Microstructural changes

Fig. 6 depicts the surface area and the volume of nitrogen adsorbed on five samples as a function of the sulphur content. As the concentration of sulphur is increased, the surface area also increases. For pure SnO_2 the surface area is found to be about 19 m^2 g^{-1}, whereas for sulfated tin oxide, the surface area increased
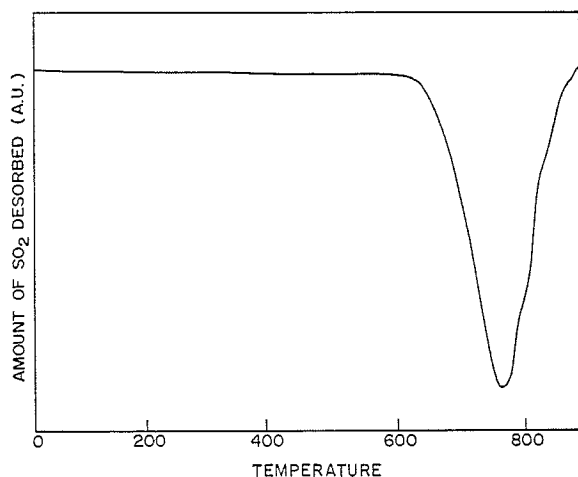
Fig. 4. Thermal desorption spectra of SnO_2 modified with 1N sulfuric acid.

from 50 to 175 m^2 g^{-1}, showing a linear trend. This trend is in good agreement with the value reported by Nakatani et al. [25,26]. Thus the role of surface sulfate species in increasing the surface area may be one of several factors that give higher sensitivity and selectivity.

3.5. Gas-sensing characteristics

However, apart from the microstructural parameters, other intrinsic properties such as acid strength and acidity distribution will also affect the sensing properties. Such data are represented in Fig. 7, where the variation of gas sensitivity with different amounts of surface coverage of sulfates in SnO_2 is illustrated. The sensitivity is maximum for vapours of fluids like acetone and ethanol and gases like LPG, CO, etc., while it steadily decreases with further increase in sulphur content. For ammonia, the response is different, as maximum sensitivity is observed at a higher sulphur content. This may be partly ascribed to the strong basic nature of ammonia, which requires very acidic sites for equilibration. In all cases, maximum sensitivity was not observed for the sample with the highest surface area. Thus the role of microstructural control as shown in the correlation of the surface area with enhanced sensitivity appears not to be the decisive factor. On the other hand, control of surface sites by doping is more important as the presence of various superacid species is prone to play a major role in deciding the fate of adsorbed gases.

One of the important parameters for the practical application of these sensor materials is the response time for a particular gaseous species [38]. Fig. 8 shows the response time for representative gases. In all the cases the response is quite fast and in the presence of gas, a steady state value is obtained within 300 s. In addition, heat treatment for desorbing the species to get the original value of the resistance is not essential, as the original value is regained within 7–8 min. Another attractive feature of these materials is that considerable sensitivity is obtained even under very low concentrations of gaseous species (3 ppm). For example, Fig. 9 clearly indicates the increase in sensitivity (for some representative gases) with gas concentration, although there is considerable scattering, probably due to inadequate temperature control.

Fig. 10 shows the effect of temperature on the sensitivity for ethanol and ammonia on the surface of pure SnO_2 and sulfated SnO_2. The most significant result is that if ammonia interferes with the ethanol response, it can be eliminated completely by a trace of sulfate superacid species on the SnO_2 surface even if both gases are present simultaneously. The 50% sensitivity obtained for ammonia on pure SnO_2 gradually disappears as a result of sulphate incorporation, thus increasing the selectivity for ethanol sensing. Unfor-
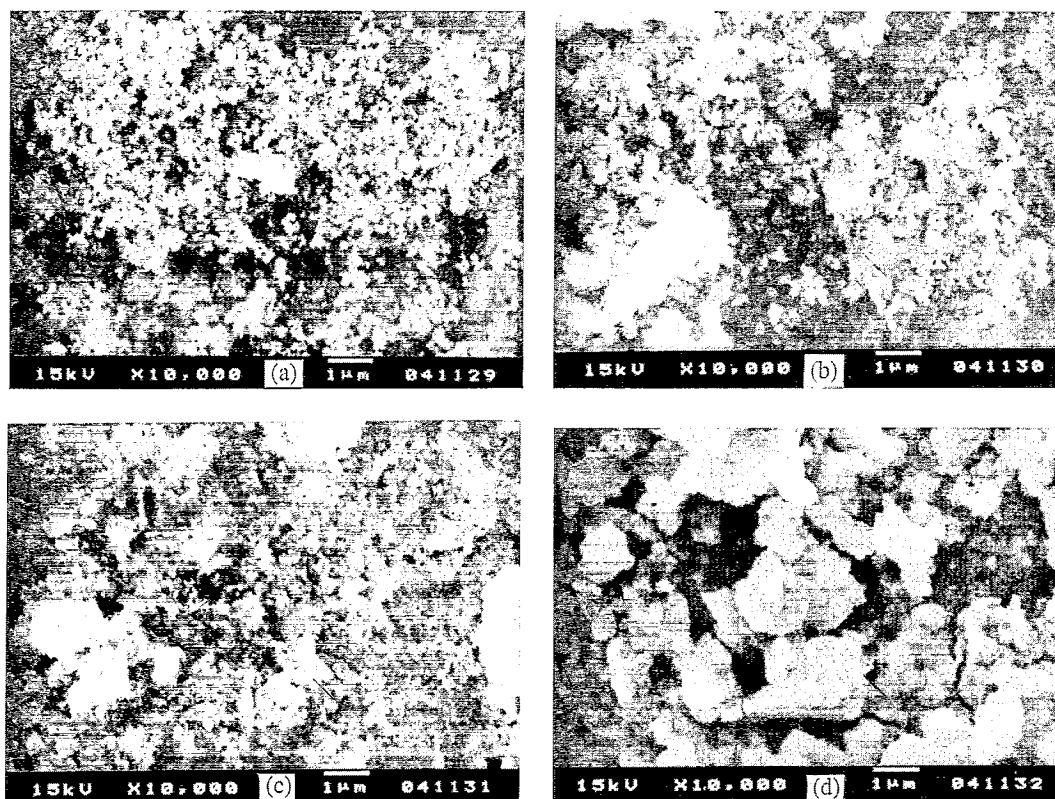
Fig. 5. Scanning electron micrographs of pure SnO$_2$ (a) and SnO$_2$ modified with 1N (b), 2N (c) and 4N (d) sulfuric acid, respectively.
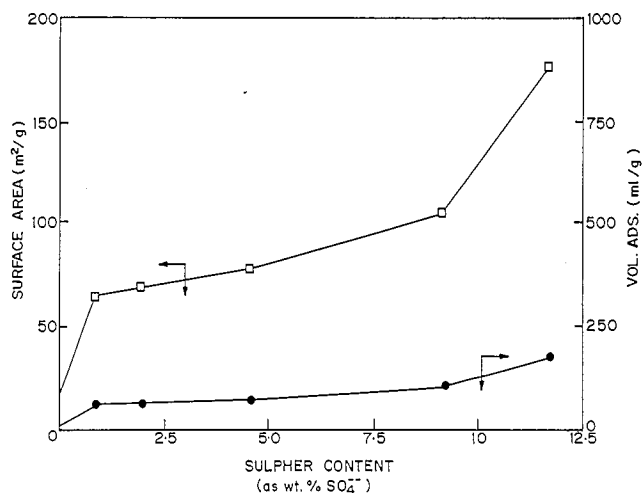

Fig. 6. Variation of surface area and volume of N$_2$ adsorbed for modified SnO$_2$ with various sulfur contents.

Fig. 7. Variation of sensitivity of modified SnO$_2$ with sulfur content for 60 ppm of various gases, namely, carbon monoxide (CO), ammonia (NH$_3$), ethanol (EtOH), LPG and acetone in dry air at 350 °C. The initial resistance of the sample ranged from 18 to 21 kΩ.

tunately, the stability of this modified sensor material is adversely affected by aging, as shown by a slow loss of activity upon continuous exposure to steady or cyclic moderate concentrations of gases and exposure to humidity in the air. For example, gas sensitivity values for 60 ppm ethanol and LPG gases have been observed to decrease by 25% after storing the sulfated SnO$_2$ materials in ambient air for two weeks and also after continuous cycling at operational temperatures. This may be attributed to a gradual loss of sulfate species on the tin oxide surface due to continuous heating.
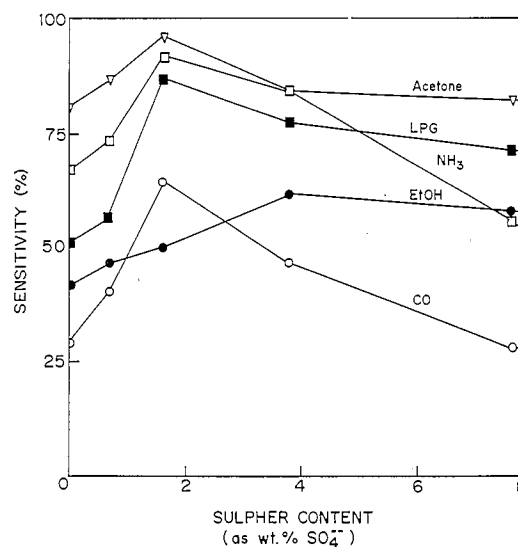
The possibility of further improvement by rejuvenating the surface after a definite cycle is currently being explored.

4. Conclusions

The modification of SnO$_2$ surfaces with superacid species seems to offer a new way of controlling the
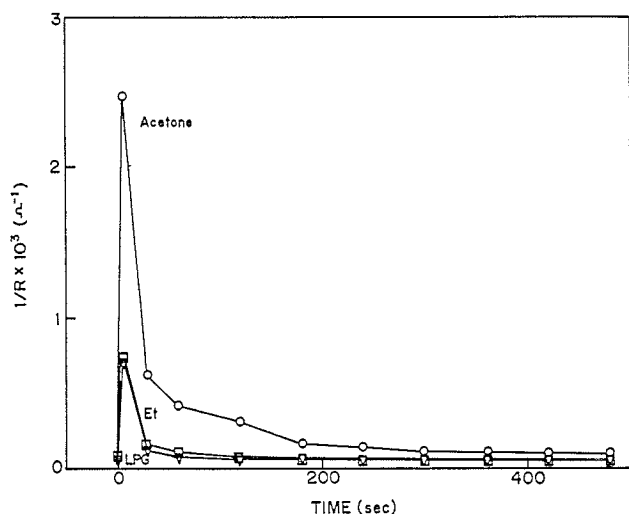
Fig. 8. Relative changes of resistance with time for 60 ppm of various gases, namely, LPG, ethanol (Et) and acetone shown by SnO_2 modified with 1N sulfuric acid at 350 °C.

Fig. 10. Effect of temperature on the sensitivity for 60 ppm ethanol and ammonia in dry air on the surface of pure SnO_2 (Et/SnO_2 and NH_3/SnO_2 respectively) and SnO_2 modified with 1N sulfuric acid (Et/SnO_2/S and NH_3/SnO_2/S, respectively).
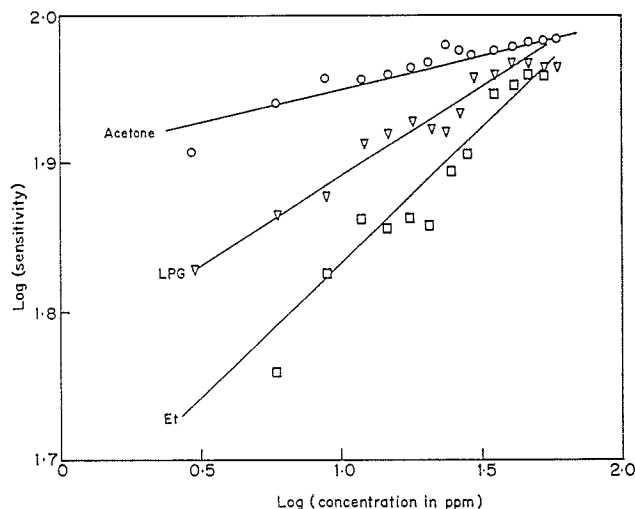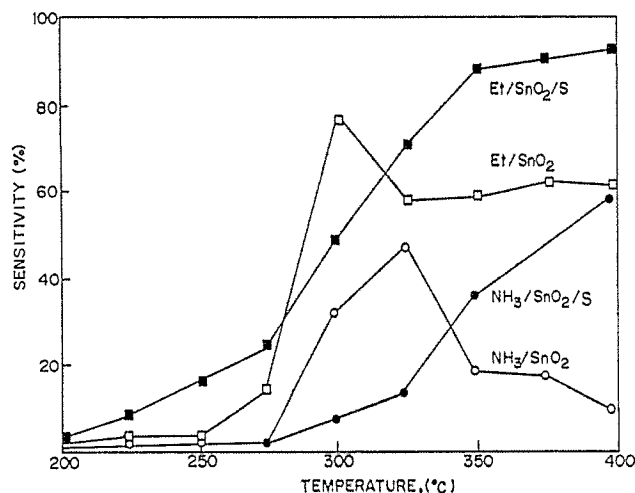

Fig. 9. Effect of gas concentration (in ppm) on sensitivity for ethanol (Et), LPG and acetone at 400 °C for SnO_2 modified with 1N sulfuric acid.

selectivity of SnO_2 gas sensors. Specific surface-modification procedures of SnO_2 using controlled amounts of sulfate species provide enhanced sensitivity towards CO, ethanol, LPG, ammonia and acetone in the range 3–60 ppm. The gas-sensing performance of the surface-modified materials indicates a strong correlation with the nature and extent of superacidic sites. In order to verify the generality of these observations, surface doping of chromates, phosphates and triflic acid is also currently being investigated. These results should further confirm the main observation of enhancement of sensitivity due to superacid species.

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