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Highly selective sensor to CH_4 in presence of CO and ethanol using $LaCoO_3$ perovskite filter with Pt/SnO_2

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Abstract

In the present study, $LaCoO_3$ perovskite was used as an active filter to suppress the sensitivity of a Pt/SnO_2 sensor to CO and C_2H_5OH. A sol–gel procedure was used for the preparation of SnO_2 fine powder, which was impregnated with hexachloroplatinic acid to obtain 1.0 wt% Pt on SnO_2. The $LaCoO_3$ perovskite fine powder was prepared by citrate method, using nitrate precursors of La and Co. $LaCoO_3$ is an effective oxidation catalyst for oxidation of both carbon monoxide and ethanol at temperatures lower than 250 °C. However, the catalyst does not convert methane at temperatures as high as 400 °C. The Pt/SnO_2 is highly sensitive to ethanol and shows a significant sensitivity to CO. The perovskite filter eliminates the sensitivity of the sensor to CO and C_2H_5OH, making the sensor highly selective to methane in the presence of CO and ethanol in air.

Keywords: Methane selective; Sensor; Active filter; $LaCoO_3$; Perovskite

1. Introduction

Low cost tin oxide based gas sensors are widely used for detection of CH_4, the main constituent of natural gas, carbon monoxide, the major poisonous pollutant of incomplete combustion of hydrocarbon fuels, and ethanol. Tin oxide is an n-type semiconductor material, which, at typical working temperatures, i.e., 200–450 °C, adsorbs gas-phase oxygen in the form of oxygen anion species such as O_2^- and/or O^- which in turn creates an electron-depleted zone. Therefore, its resistance decreases in the presence of reducing gases such as methane and carbon monoxide. Variation of the resistance of the film due to the chemical reaction serves as sensing signal. As compared to the other metallic oxides, tin oxide has lower working temperature, thus requires lower heating power for its proper performance [1].

Sensitivity of the SnO_2 sensors to CH_4 and CO is usually enhanced by adding proper amounts of noble metals such as Pt and Pd [2,3]. However, due to the similar reducing character, cross sensitivity between CO, CH_4 and other components like ethanol is one of the major problems of the sensors, giving a lack of selectivity [4]. In general, SnO_2-based gas sensors show good sensitivity but poor selectivity if pure sensor materials are used.

To achieve better selectivity with SnO_2-based sensors, different techniques like optimizing the doping, the operating temperature, or the substrate geometry have been used in the past. Ceria is used to increase selectivity of the SnO_2-based sensors to CO in presence of methane and other light hydrocarbons [2]. Filters have also been utilized to reduce the sensitivity to interfering gases [5].

Filters may be classified in two different categories, chemical and physical filters. Physical filters act as physical barriers for the undesired gases. Chemical filters, however, play catalytic role and enhance the reaction to interfering gases. Both types of filters could be either external or built-in in the sensing layer [1]. The $LaCoO_3$ perovskite is an effective oxidation catalyst for removing pollutant gases such as carbon monoxide and unburned hydrocarbons. Depending upon the reaction temperature, it could oxidize the CO and ethanol while leaves methane intact. Since methane is the most stable hydrocarbon and its catalytic combustion usually takes place at high temperatures [6,7].

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In the present study, $LaCoO_3$ perovskite is used as an external chemical filter for elimination of the sensor sensitivity to CO and C_2H_5OH. The perovskite filter could pass methane while CO and ethanol are oxidized to CO_2.

2. Experimental

A sol–gel procedure was employed for the preparation of SnO_2 fine powder, which was then dried and calcined at 450 °C in air for 2 h. The powder was impregnated with proper amounts of hexachloroplatinic acid solution to give 1.0 wt% Pt on SnO_2. A homogeneous paste of the resulting material was applied onto an alumina ceramic tube with previously deposited gold contacts with 1.5 mm spacing. After sintering at 600 °C for 2 h, the sample was ready for tests of performance.

In order to prepare $LaCoO_3$ perovskite sample, $La(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ precursors and citric acid were used. Initially stoichiometric amounts of lanthanum nitrate and cobalt nitrate were dissolved in water, and then citric acid was added to the solution which followed by heating and stirring at 90 °C for 5 h to form a concentrated solution. As the concentrated solution was aged at 60 °C for 18 h, a dark purple gel with a high viscosity was obtained. The perovskite was formed by heating the gel in air at 300 °C for 1 h, at 500 °C for 5 h, and finally at 800 °C for five more hours. The heating rate in all steps was 5 °C/min. The sample was characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM).

The perovskite powder prepared was placed in front of the sensor located in a glass holder immersed in a molten salts bath. A stirrer was used to obtain a uniform temperature along the testing chamber. A PID temperature controller adjusted the salt bath temperature. Due to the high heat capacity of the salt bath, the bath temperature could be adjusted within ±1 °C accuracy. Mass flow controllers (Unit Instruments, Inc.) were used to regulate the flow from the gas cylinders. Data acquisition was performed by means of an A/D board (Fig. 1). The tested gases were 2.8 mol% CH_4, 1000 ppm CO and 800 ppm ethanol in air flow. The gases could be diluted with another flow of air to reach lower gas concentrations. The sensitivity of the sensor was measured in a wide range of the gases concentrations and at temperatures range from 250 to 450 °C. The sensitivity is defined as the ratio of the sensor resistance in air (R_a) to that in the presence of the gas (R_g).

To test the catalytic activity of the $LaCoO_3$ filter, flows of 2.8 mol% CH_4, 1000 ppm CO, and 800 ppm ethanol in air were passed over the catalyst at different temperatures. A CP-3800 Varian gas chromatograph was used to analyze the reactor effluent gases containing CO, CO_2, methane, and/or ethanol.

3. Results and discussion

XRD patterns for both Pt/SnO_2 and $LaCoO_3$ are presented in Fig. 2. Both patterns indicate crystalline phases of SnO_2 and $LaCoO_3$ were formed under the heat treatments used. However, due to the small amount of Pt, i.e., 1.0 wt%, it could not be detected by XRD. The SEM micrograph representing the morphology of the Pt/SnO_2 and perovskite is presented in Fig. 3. This figure demonstrates that the perovskite particles have a porous and uniform structure with an average size of about 250 nm.

Fig. 4 presents the sensitivity of Pt/SnO_2 sensor to 1000 ppm CO, 800 ppm ethanol and 2.8 mol% CH_4 in air with respect to temperature without active filter. For the all temperatures, the sensor sensitivity to ethanol is higher than those for CO and CH_4 especially at lower temperatures. By increasing temperature, the sensor sensitivity to ethanol declines sharply, while its sensitivity to CH_4 rises steadily. The sensitivity to CO seems to be almost indifferent with respect to the temperature range used for this set of experiments.

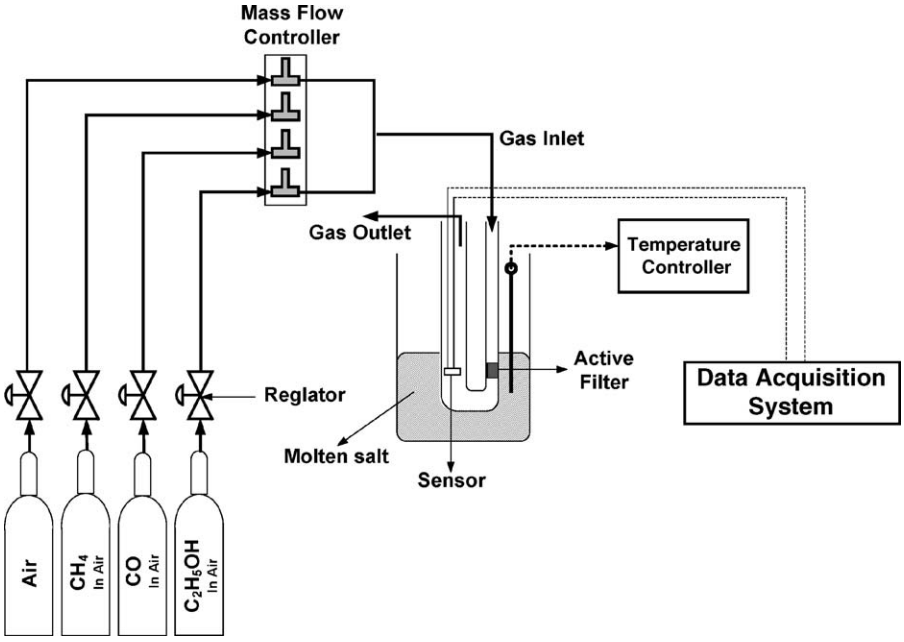

Fig. 1. Schematic diagram of the experimental setup used for measuring the sensitivity of the sensors.

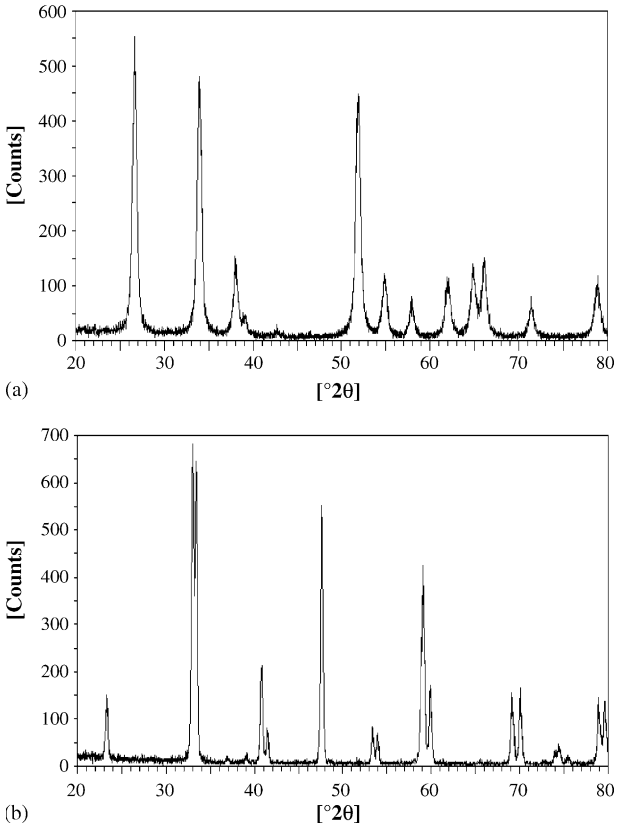

Fig. 2. XRD patterns of (a) Pt/SnO_2 annealed at 600 °C for 2 h and (b) $LaCoO_3$ calcined at 800 °C for 5 h.

Fig. 5 shows the sensor sensitivity of Pt/SnO_2 sensor for the same concentrations of CO, ethanol and CH_4 versus temperature with active filter. The figure clearly demonstrates that the active filter strongly lowers the sensitivity to ethanol and CO. The effect is even more pronounced for ethanol. At 250 °C, the sensor sensitivity to ethanol decreased from 158 to 0.44 with active filter. For all the temperatures, the active filter caused the sensor sensitivity to CO and ethanol decreases to less than 1. In Fig. 5, the sensitivity of the sensor to CO is about 0.9 at 250 °C and decreases with the temperature. However, the sensor sensitivity to methane is about 1.7 at 250 °C and significantly improves as the temperature increases. A three-fold enhancement in the sensor sensitivity to methane is observed, while that

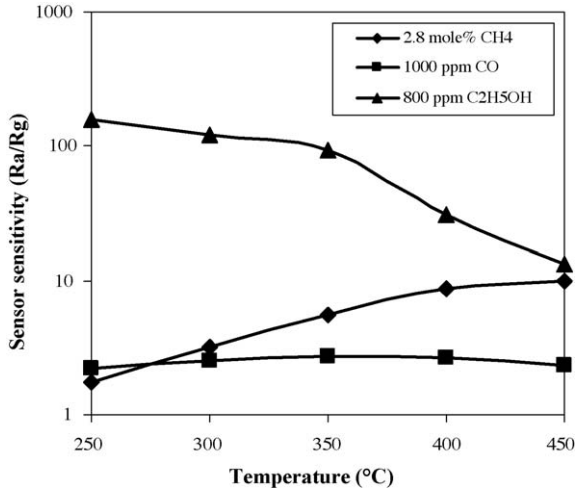

Fig. 4. Sensitivity of Pt/SnO_2 to 1000 ppm CO, 800 ppm ethanol and 2.8 mol% CH_4 in air versus temperature (without the active filter).

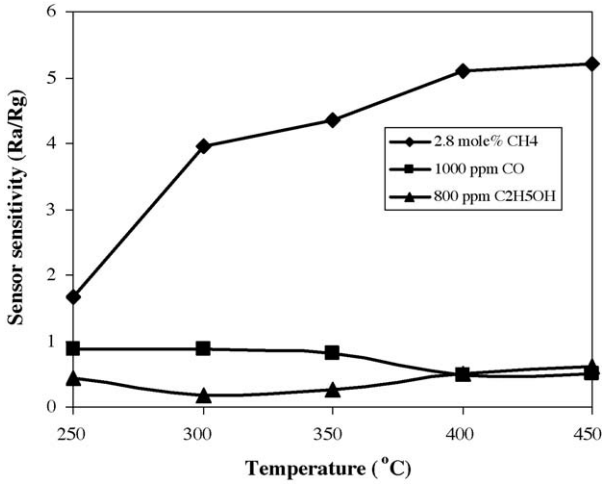

Fig. 5. Sensitivity of Pt/SnO_2 to 1000 ppm CO, 800 ppm ethanol and 2.8 mol% CH_4 in air versus temperature (with the active filter).

of CO is lowered to a half, as the temperature increases from 250 to 450 °C.

Fig. 6 shows the results of catalytic activity of the $LaCoO_3$ filter, for 2.8 mol% CH_4, 1000 ppm CO, and 800 ppm ethanol in

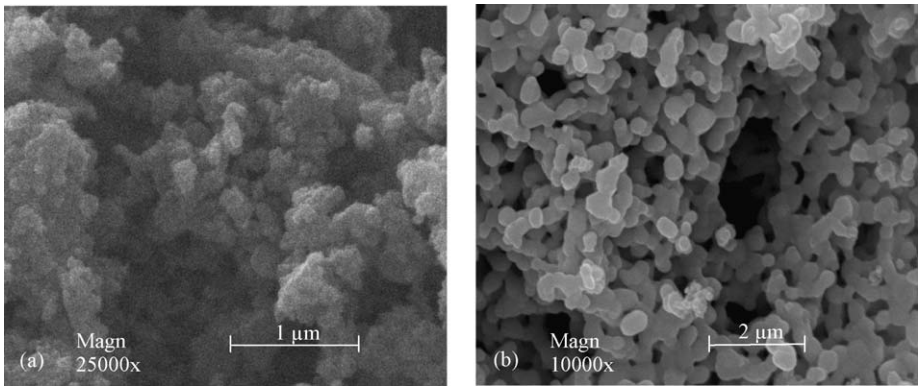

Fig. 3. SEM micrographs of (a) Pt/SnO_2 sensor and (b) $LaCoO_3$ perovskite.

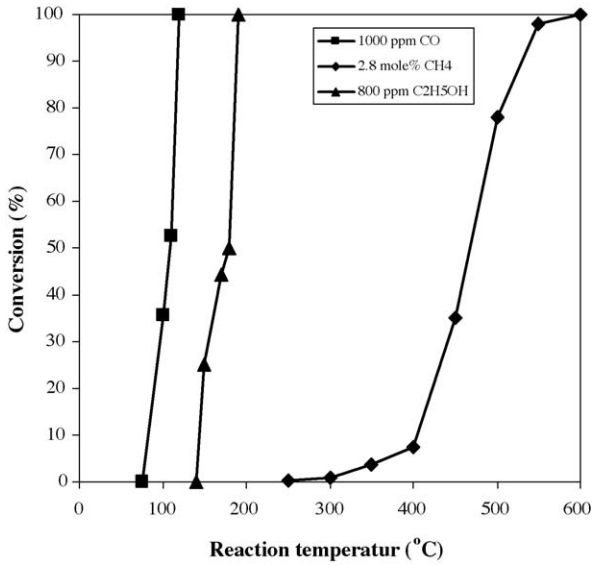

Fig. 6. Variation of conversion of 1000 ppm CO, 800 ppm ethanol and 2.8 mol% CH_4 in air on $LaCoO_3$ perovskite filter with temperature.

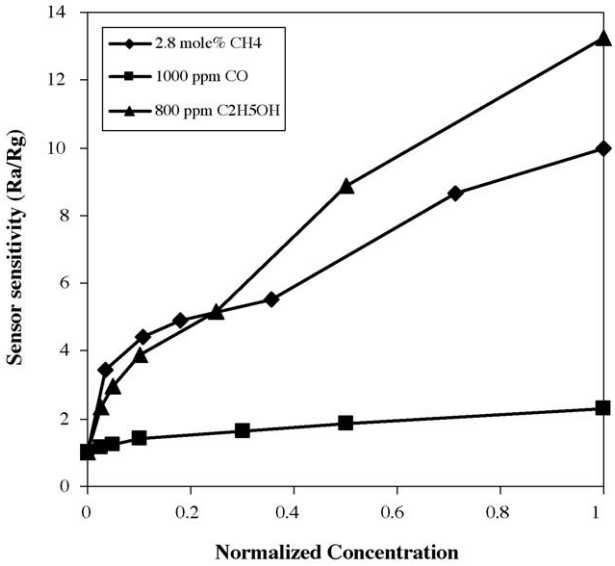

Fig. 7. The Pt/SnO_2 sensitivity with respect to normalized concentration at 450 °C without using active filter. Normalized concentration is defined as the concentration of CO, ethanol and CH_4 divided by 1000 ppm, 800 ppm and 2.8%, respectively.

air. CO and ethanol are completely converted at 120 and 190 °C, respectively, while no significant amount of methane is converted at temperatures below 400 °C. At 450 °C about 35% of methane is converted and the rest passes through the filter and reach the sensor. CO and ethanol are very active molecules that strongly interact with $LaCoO_3$ filter and are combusted to CO_2, at temperatures well below 350 °C, at which the Pt/SnO_2 sensor shows a significant sensitivity to methane (Fig. 4). The CO_2 products of combustion on the filter may have caused a further reduction in the sensitivity of the sensor to CO and ethanol in presence of the filter, as compared to its sensitivity in the absence of the filter (see Fig. 8). This may further enhance the selectivity of the sensor to methane in presence of CO and ethanol, when the active filter is used.

Fig. 7 presents the variation of sensor sensitivity to CO, ethanol and CH_4 with respect to normalized concentration without active filter. The normalized concentration is calculated by dividing the concentration of CO, ethanol and CH_4 to their maximum concentrations of 1000 ppm, 800 ppm and 2.8 mol%, respectively. For all of the three gases sensitivity increases with an increase in the concentration. However, the extent of the variation is different. At 450 °C the sensor sensitivity to the gases at the normalized concentration of 1 were 10, 2.3 and 13.3 for CO, methane and ethanol, respectively.

Fig. 8 displays the effect of active filter on sensitivity of the sensor to CO, ethanol and CH_4 versus normalized concentrations. As methane concentration in the air increases, the sensor shows a sharp increase in its sensitivity to methane and then levels off. At the same time, the sensitivity of CO and ethanol monotonously declines with their concentrations.

Fig. 9 illustrates the selectivity ratios of CH_4 to ethanol and CO. This ratio is the sensitivity of the sensor to 2.8% CH_4 divided by its sensitivity to 800 ppm ethanol and 1000 ppm CO. Thanks to moderate catalytic activity of $LaCoO_3$ perovskite for oxidizing CO and ethanol at temperatures higher than 250 °C. It seems that methane is not significantly combusted at temperatures up to 450 °C. This way the perovskite filter eliminates the sensor sensitivity to CO and ethanol, making the sensor highly selective to methane in presence of CO and ethanol in air.

Fig. 10 displays the sensor sensitivity of binary and ternary mixtures of methane, ethanol and carbon monoxide at maximum concentrations versus temperature without active filter. It is evident that for all of the mixtures, i.e., CH_4–C_2H_5OH, CH_4–CO and CH_4–CO–C_2H_5OH sensitivity declines sharply. This set of experiments was designed to see whether the sensitivity to a mixture is sum of the sensitivities to the components or presence of one gas suppresses or improves the sensitivity to the other gases. Comparing the results presented in Figs. 5 and 10 reveal that the sensitivities are almost additive.

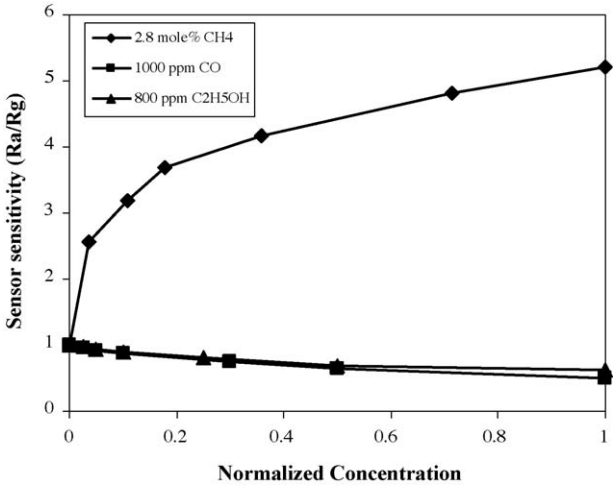

Fig. 8. The Pt/SnO_2 sensitivity to CO, ethanol and CH_4 with respect to normalized concentration at 450 °C, using active filter.

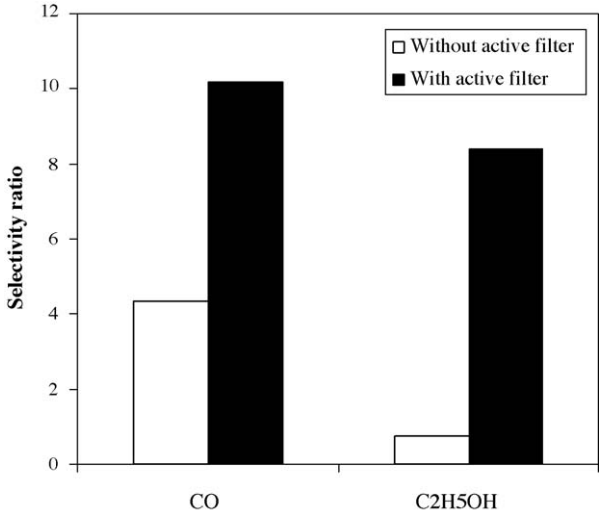

Fig. 9. Selectivity ratios of CH_4 to ethanol and CO for Pt/SnO_2 sensor.

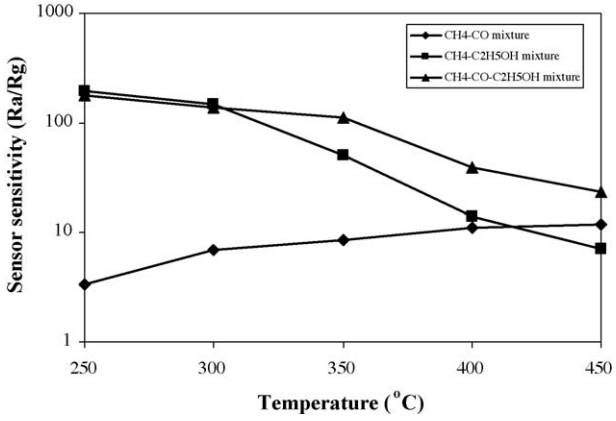

Fig. 10. The Pt/SnO_2 sensitivity to binary and ternary mixtures of CO, ethanol and/or methane with respect to temperature, without using the active filter.

Fig. 11 presents the results of the same set of experiments but with active filter. The results demonstrate that in the presence of active filter the sensitivity to the mixture of CH_4, CO and C_2H_5OH increases sharply with temperature whereas the

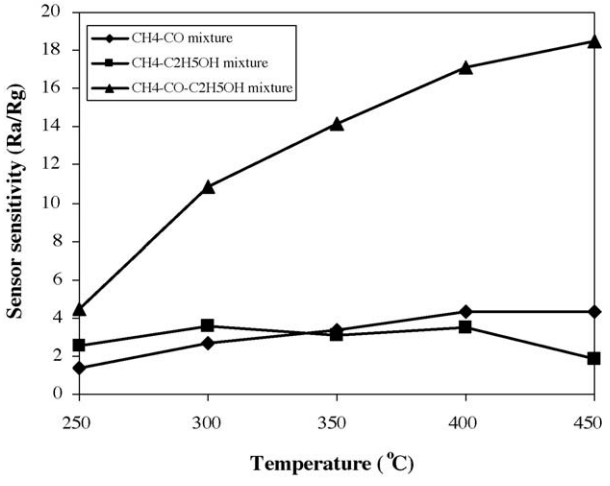

Fig. 11. The Pt/SnO_2 sensitivity to binary and ternary mixtures of CO, ethanol and/or methane with respect to temperature, using with active filter.

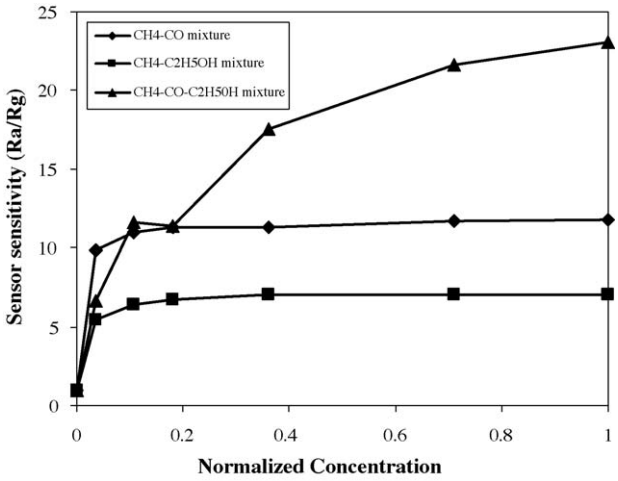

Fig. 12. The Pt/SnO_2 sensitivity to binary and ternary mixtures of CO, ethanol and/or methane with respect to normalized concentration at 450 °C, without using the active filter.

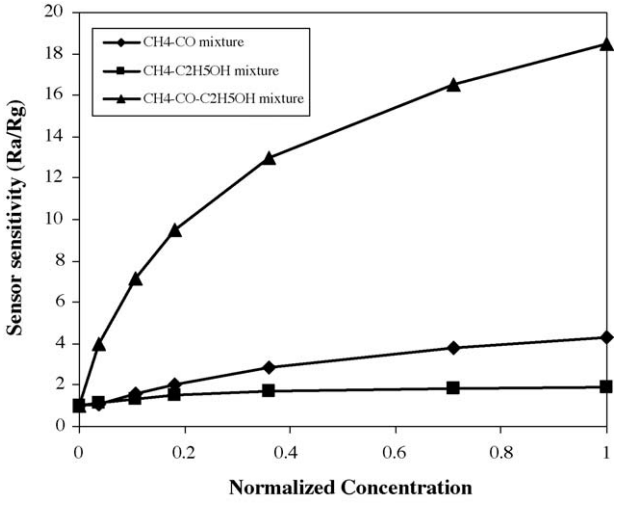

Fig. 13. The Pt/SnO_2 sensitivity to the binary and ternary mixtures of CO, ethanol and/or methane with respect to normalized concentration at 450 °C, using the active filter.

extent of improvements for the binary mixtures of CH_4–CO and CH_4–C_2H_5OH is not so significant. Thus, the improvement in sensitivity of the sensor to methane displayed by the results in Fig. 5 can certainly be attributed to the role played by active filter itself.

Figs. 12 and 13 show the sensor sensitivity to the binary and ternary mixtures of CH_4, CO and C_2H_5OH versus normalized concentrations. These results also indicate that the active filter improves the sensitivity to methane for the whole spectrum of concentrations used in this study.

4. Conclusion

Tin oxide-based gas sensors show high sensitivity, but poor selectivity to pollutant and combustible gases. Using active filter is one of the most promising ways to make the sensors selective to particular gases, in presence of interfering gases.

In the present study, $LaCoO_3$ perovskite is used as an active filter for elimination of the sensor sensitivity to CO and ethanol. Both CO and ethanol are completely removed by the filter at temperatures as low as 190 °C. At 250 °C, the sensor sensitivity to ethanol dramatically decreased from 158 to 0.44 and that to CO declined from 2.2 to 0.9, when active filter is used. Only methane reaches the Pt/SnO_2 sensor at temperatures higher than 190 °C, for which the sensor shows high sensitivity to methane. As a result, $LaCoO_3$ perovskite filter eliminates the sensor sensitivity to CO and ethanol, making the sensor highly selective to methane in presence of CO and ethanol in air.

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Biographies

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