Effects of nanoadditives on stability of Pt/SnO₂ as a sensing material for detection of CO

Sahar Vahdatifar, Abbas Ali Khodadadi, Yadollah Mortazavi

Abstract

The effects of dopants and annealing temperature on the long-term stability of SnO₂-based gas sensors for detection of CO were investigated by doping Pt/SnO₂ nanoparticles with MoO₃, CeO₂, Sm₂O₃ and SiO₂. The sensing materials including pure SnO₂ and SnO₂ doped with 5.0 and 10.0 wt% of nanoadditives were synthesized by a sol-gel method, then they were impregnated with 1.0 wt% platinum. Accelerated stability tests were performed by exposing the fresh powders and the fabricated sensors to air with 30% relative humidity at 600 °C for 15 days. Gas sensing measurements to 100 ppm CO at 250 °C were carried out on the fabricated sensors on the 5th, 9th, 12th and 15th days in addition to the fresh point. MoO₃, CeO₂ and SiO₂ additives were found to be effective in stabilizing the performance of Pt/SnO₂ sensor, while Sm₂O₃ did not have the same effect. Increasing the annealing temperature, in the synthesis process, led to a decrease in sensitivity decline during the exposure period.

1. Introduction

SnO₂ is known as a wide-band-gap semiconductor that presents interesting optical and electronic properties [1]. Gas sensors based on tin oxide have been extensively studied and SnO₂ nanoparticles are supposed to be the most promising material for gas-sensing devices [2]. The typical measurement technique for metal oxide sensors is involved with the conductance/resistance of the sensing material. SnO₂ as a nonstoichiometric oxide has oxygen vacancies which can react with the O₂ molecules and generate different chemisorbed oxygen species in the forms of O₂⁻, O⁻ or O²⁻, depending upon operating temperature. This leads to the electron transfer from the conduction band, which consequently declines the conductance of the sensing layer. A reducing gas can react with the adsorbed oxygen species and release their electrons into the conduction band. This electron transfer leads to a decrease in the sensor’s resistance, which in turn generates electrical signals [3,4].

Generally, the resistance of SnO₂-based sensors steadily increase during long-term operation or exploitation to the surrounding atmosphere due to the influence of ambient parameters such as temperature and humidity. Consequently, their sensitivity declines with time and instability occurs, as a result of the nonstoichiometric conduction mechanism [5–8].

Despite the significance of stability in the development of gas sensors for markets, only limited studies have been devoted to the investigation of the stability issues. Numerous efforts have been devoted to improving sensitivity and selectivity of gas sensors, but without achieving an acceptable level of stability, improvements in these features of the gas sensors are not adequate [9].

According to the published reports, instability in the performance of the metal oxide gas sensors is mainly attributed to: (1) structural transformations, e.g. the grains growth without a change in porosity, which typically takes place through a surface diffusion mechanism at lower temperatures or evaporation-condensation mechanism at higher regions, (2) phase transformation, (3) poisoning, and (4) bulk diffusion, in addition to the change of humidity and temperature [10,11].

Considering that thermal sintering, i.e. grain growth, of tin oxide as the sensing layer is accompanied by the change in its catalytic and electrical properties, structural changes could lead to instability of gas sensors. Different approaches may be used for the stability improvement, such as utilization of thermally and chemically stable materials, optimization of the composition of the gas-sensing materials, avoiding the use of gas-sensing materials with an extremely small grain size and controlling size and shape of the grains [10,12]. Addition of small amount of various metal oxides can stabilize the microstructure of SnO₂ by separation of the connected SnO₂ grains. The fine oxide particles incorporated into
SnO₂ prevent the growth of “neck” between the adjacent grains during the sintering process and stabilize the crystallites size [13]. Sm, Ba, P, Mo, W, Ca, Sr, Cr and In nanoparticles were found to be the most effective crystallite growth inhibitors for SnO₂ [14–17]. It has been proposed that the stabilization effects of minor additives likely to be related to suppression of the surface diffusion, below 900 °C. However, the growth inhibition mechanism by most additives still remains unproved.

On the other hand, variations in the reactivity of the sensing materials toward the sensing reaction is another reason of the sensitivity drifts during the sensors lifetime. This was observed through the addition of rhenium and vanadium to SnO₂ sensor which resulted in excellent stability to H₂. The stabilizing effect of these dopants was mostly attributed to the reduction in the variations of hydrogen oxidation reactivity [18].

Moreover, it should be noted that there is the possibility of phase transformation as a consequence of dopants segregation at the grain surface during exploitation processes, especially at the concentrations close to the solubility limit, which changes the metal oxide properties. Based on these discussions, it may be inferred that the properties of semiconducting metal oxides with a low doping concentration remains more stable [10].

Various attempts have been made in order to enhance the stability of gas sensors. Recently, Pavelko et al. [19] studied the role of impurities in the long term stability of SnO₂-based sensors. Ozaki et al. [9] demonstrated that modification of SnO₂-based sensors by dipping treatment in sulfuric acid significantly improves the stability of these sensors for CO detection as a result of the blockage in hydroxyl groups activities.

Some researchers show that impregnation of platinum group metals (platinum and/or ruthenium) decreases the sensors sensitivity to variations in temperature and humidity [20]. In the case of Pt/SnO₂, the instability problem also can be partly resolved by introducing additional components to stabilize the position of noble metal clusters towards sintering by reinforcing metal-supported interactions.

In this work, we used the accelerated stability tests to study the effect of dopants and annealing temperature on stabilizing the performance of Pt/SnO₂ gas sensors for detection of CO.

2. Experimental

2.1. Synthesis of the sensing materials

The sensing materials in this study, i.e. pure and doped SnO₂ were synthesized using a sol-gel method, in which SnCl₄ was dissolved in isopropyl alcohol to obtain a 0.1 M solution. 5.0 and 10.0 wt% MoO₃, CeO₂, Sm₂O₃ and SiO₂ were doped by utilizing Mo₇(NH₄)₆O₂·4H₂O, Ce(NO₃)₃, Sm(NO₃)₃, C₄H₂O₂Si·(TEOS), respectively, as precursors. The required pH (7) of the final solution was adjusted by controlling addition of liquid ammonia solution.

After aging of the samples at room temperature for 24h, the as-synthesized powders were dried at 100 °C and subsequently calcined in air for 4h at two different temperatures, i.e. 700 and 850 °C. The obtained pure and doped SnO₂ samples were then impregnated with the required amount of an aqueous solution of hexachloroplatonic acid to attain 1.0 wt% Pt samples. A paste of the sample was applied onto an alumina substrate with the previously deposited two gold contacts with 1 mm spacing and annealed at 600 °C for 2h. The gas sensors were fabricated in thick films, about 40 μm thickness, and sintered at 700 °C for 2h.

The SnO₂ nanoparticles prepared with different dopants and concentrations at different calcination temperatures, are denoted as d-c-T in which d is the type of dopant, c refers to the concentration of dopant and T indicates calcinations temperature, respectively.

2.2. Characterization of the sensing materials

X-ray Diffraction (XRD) characterization was carried out only for the sensing materials calcined at 700 °C. The crystallite structures and average crystallite size were determined by X-ray powder diffraction with a Philips-Xpert diffractometer using Cu Ka radiation (λ = 1.5406Å), in the 2θ range of 10–90° and at a scanning rate of 0.02 °/min. XRD analyses were utilized in order to determine the phases of the sensing materials before and after the stability tests. The average crystallite sizes of the materials, dₜₐₘₜ, were calculated based on line broadening of the (1 1 0) diffraction peak of SnO₂ using Scherer’s equation.

The specific surface area measurements by Brunauer–Emmet–Teller (BET) method were carried out for all the sensing materials. The BET method employs nitrogen adsorption after evacuating the samples at 300 °C for 1h (degassing of the samples), using a Quantachrome CHEMBET-3000 apparatus. The average particle sizes, dₛₑᵗ, were obtained from BET surface area using Eq. (1).

\[
dₛₑᵗ = \frac{6000}{dₜₐₘₜ}
\]

where ρ is the density of the sensing material and Sₜₑₘₜ is the specific surface area measured by BET method.

In addition, Transmission electron microscopy (TEM) images of the fresh and aged Pt/SnO₂-700 samples were taken using a CM 120 FEG TEM Philipps CM120 apparatus.

2.3. Gas sensing and long-term stability measurements

To study the performance of sensors in the presence of CO at various compositions and different temperatures, a testing setup was used. The experimental setup consisted of the mass flow controllers (Unit Instrument Inc.), which are used to adjust the flow rates to achieve the desired concentration in the gas mixture passing through the sensor holders, i.e. a glass U-tube reactor, the sensor in a glass holder connected to an electrical circuit using platinum wires, a PID temperature controller, and a data acquisition system for continuous monitoring of the sensor response. CO and zero air were mixed with different flow rates to adjust the concentration of the gases passing over the sensors. Response of the sensor is defined as its resistance in air divided by that in the gas, i.e., Rgas/Rair. Both the Rair and the Rgas applied to this equation are measured when they do not change with longer exposure time.

In order to investigate the long term stability, the fabricated sensors and powder of the sensing materials were exposed to zero air with the flow rate of 30–40 cc/min and about 30% RH (based on room temperature) at 600 °C for maximum of 15 days. The sensing materials before and after the exploitation period are denoted as “fresh sample” and “aged sample”, respectively. The gas sensing measurements were carried out on fresh sensors and the sensors exposed to the mentioned conditions for 5, 9, 12 and 15 days. These measurements were done to 100 ppm CO at 250 °C, i.e. the optimum operating temperature for all the sensing materials. The 5th day is considered as zero point which means that the measured response at this point is the reference of time stability.

All the stability experiments were carried out using a Thermolyne 21100 tubular furnace, which was equipped with a air flow inlet and outlet. The inlet air with the flow rate of 30–40 cc/min at room temperature passed through the water bubbler immersed in a water chamber at room temperature. The length of the bubbler was long enough to ensure the desired humidity, confirmed by a humidity sensor.
3. Results and discussion

3.1. Samples characterization

The sensing materials were characterized by XRD and BET specific surface area prior and after the stability tests in order to monitor the morphological and structural changes and follow the stability performance. Based on the X-ray spectra presented in Figs. 1–5, all the prominent peaks of fresh and aged samples correspond to the (1 1 0), (1 0 1) and (2 1 1) crystal lattice planes and all other smaller peaks coincide with the corresponding peaks of the cassiterite structure of SnO₂, which have been indexed on the basis of JCPDS files at Table 1.

No peak corresponding to the dopants phase was detected for both fresh and aged samples doped with MoO₃, CeO₂, Sm₂O₃ and SiO₂, which is probably due to their either amorphous phase or too small crystallites size of dopants to be detected by XRD. As long as the additives are dispersed finely, no peak corresponding to the additives is detected by XRD, even at temperatures as high as 700 °C [11]. In the case of MoO₃-doped samples no detection of the
Table 1
BET specific surface area, \( d_{\text{BET}} \) and \( d_{\text{SBD}} \) of fresh and aged samples (before and after the stability tests in humid air at 600 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>JCPS file No</th>
<th>BET specific surface areaa</th>
<th>( d_{\text{BET}} )b</th>
<th>( d_{\text{SBD}} )c</th>
<th>( d_{\text{BET}} )d</th>
<th>( d_{\text{SBD}} )e</th>
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<td>66.0</td>
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<td>8</td>
<td>107.3</td>
<td>23.1</td>
<td>6</td>
<td>143.1</td>
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<tr>
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<td>01-077-0447</td>
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<td>44.7</td>
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<td>19</td>
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<tr>
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<td>70</td>
<td>12.3</td>
<td>-</td>
<td>66</td>
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</table>

a Specific surface area: (m\(^2\)/g) ± 5%.
b Average particle size: (nm) ± 5%.
c Average crystallite size: (nm) ± 10%.

Dopant phase, may also be attributed the formation of SnO\(_2\)-MoO\(_3\) solid solution by diffusion of Mo into the SnO\(_2\) lattice. According to some authors, the limit of Mo solubility in SnO\(_2\) is about 10 wt% and above this concentration, excess Mo starts to segregate and consequently leads to the formation of MoO\(_3\) aggregates which can be detected by XRD [21,22]. Moreover, a small displacement of SnO\(_2\) diffraction peaks caused by the addition of 10.0 wt% CeO\(_2\), suggests the formation of a solid solution [23].

According to the XRD patterns of fresh Pt/SnO\(_2\) samples, shown in Fig. 1(b and c), there is one set of the diffraction peaks at 39.89° and 46.3° corresponding to Pt cubic crystallites, which have been indexed on the basis of JCPS file No. 01-087-064090. Since the platinum atoms need to get enough energy to move across the tin oxide surface and find other platinum atoms to form metallic clusters, the observation of Pt diffraction peaks demonstrates the sufficiency and remarkable effect of 700 and 850 °C calcination temperatures to form metallic platinum clusters [24]. In fact, contrary to palladium which has the tendency to diffuse toward the bulk, platinum locates on the surface and dry impregnation is considered as the most effective method to deposit impregnated Pt particles on surface of the SnO\(_2\) grains without any diffusion into the SnO\(_2\) lattice [23].

However, no peak corresponding to Pt crystallites is detected after stability test, which could be regarded as a consequence of the platinum oxidation upon exposure to hot air. Moreover, no observable peak characterizing PtO or PtO\(_2\) was detected as a result of the amorphous or too fine particles and/or overlapping the corresponding SnO\(_2\) peaks which are sharper and more intense. There is also another justification proposing that some of platinum are evaporated gradually during the thermal treatment and its concentration decreases to the level that could not be detected by XRD [24–27].

Based on the X-ray spectra presented in Figs. 2–5, no peak attributing to platinum was detected in the case of samples doped with MoO\(_3\), CeO\(_2\), Sm\(_2\)O\(_3\) and SiO\(_2\). The absence of diffraction peaks corresponding to Pt particles on SnO\(_2\)-based grains has also been reported by other researchers, specifically in the case of CeO\(_2\)-doped samples [23,28]. This behavior may be ascribed to the strong interaction between the dopant and platinum, which keeps Pt particles highly dispersed and leads to the formation of very small clusters that cannot be identified by XRD.

In addition to the mentioned phenomenon, it has been also proposed that platinum is mainly present as Pt\(^{2+}\) and Pt\(^{4+}\) on the fresh and aged Pt/ceria-based supports due to strong Pt/oxide-support interaction while it exists as Pt\(^{0}\) on the supports having weak interaction, such as Pt/Al\(_2\)O\(_3\) [28].

Table 1 indicates that 1.0 wt% Pt addition reduced the SnO\(_2\) surface area which could be related to the high calcination temperatures. Generally, the presence of noble metals and some metal oxides between SnO\(_2\) particles prevent their coalescence during thermal treatments, and decrease SnO\(_2\) particle size [24,25,29]. According to some authors’ findings, this influence of Pt is appeared in the certain range of temperature and concentration [26,29]. The incorporation of noble metals prior to the calcination process is more effective in the suppression of the neck size growth between the SnO\(_2\) grains compared to the impregnation method. However, this positive effect in the case of platinum also relies on the concentration and dispersion of Pt to a large extent.

As is evident in Table 1, addition of MoO\(_3\), Sm\(_2\)O\(_3\) and SiO\(_2\) broadened the width of SnO\(_2\) peaks, which was also reported by other authors [21,30–34]. Therefore, according to Scherer’s equation the SnO\(_2\) crystallite size decreased effectively. This significant particle size reduction is explained by the concentration of 10.0 wt% SnO\(_2\) at both calcination temperatures, i.e. 700 and 850 °C.

Increase of SnO\(_2\) surface area caused by the presence of MoO\(_3\) could be related to the substitution of Mo(VI), with smaller ionic radius, for Sn(IV), which in turn resulted in a decrease of the unit cell constant [34,35]. It has been reported that SnO\(_2\)-MoO\(_3\) nanoparticle containing 0 to 12 mol% MoO\(_3\) possesses the highest surface area [21,35].

Addition of 5.0 wt% CeO\(_2\) to Pt/SnO\(_2\) results in the crystallite size reduction. However, an obvious crystallite growth and surface area reduction is observed as the concentration of CeO\(_2\) reached to 10.0 wt%. This behavior has been also observed by other researchers [36].

According to the Scherer’s equation it is estimated that the crystallite size of pure Pt/SnO\(_2\) drastically decreased from 29.2 nm to 11.9 nm and 4.5 nm by the addition of 5.0 and 10.0 wt% SiO\(_2\), respectively. This effect is mostly attributed to the SnO\(_2\)-SiO\(_2\) neck size reduction at low contents while at high SiO\(_2\) contents, SnO\(_2\) sintering is inhibited through the effective separation of the grains by SiO\(_2\) dielectric [32]. According to some reports the reduction in the
unit cell of SnO2–SiO2 lattice can be mainly related to the penetration of Si into SnO2 lattice and the formation of substitutional solid solution that Si4+ with smaller radius substitutes Sn4+ [37].

An increase in the calcination temperature led to the growth of SnO2 particles, which was more pronounced in the case of samples doped with CeO2. Surface area of the sample doped with 5.0 wt% samaria declined about 37.6% as the calcination temperature increased from 700 to 850 °C. However, the corresponding value for the sample containing 10.0 wt% samaria was 41%. The same behavior was observed for the samples doped with MoO3, suggesting that grains with smaller sizes sinter more easily [38].

3.2. Structural stability

According to the spectra presented in Fig. 1(a–c), it may conclude that Pt addition to SnO2 and also calcining the sample at higher temperature, i.e. 850 °C rather than 700 °C, result in a lower crystallite growth of tin oxide in the course of stability test and improved the structural stability of SnO2.

As is observed from Table 1, an increase in the calcination temperature did not significantly change the BET surface area of Pt/SnO2 compared to SnO2, suggesting that the presence of platinum could remarkably stabilize the SnO2 crystallites [29]. Furthermore, considering the surface area reduction for Pt/SnO2 and SnO2 samples during the stability tests, i.e. 8% and 32% respectively, it could be concluded that the presence of Pt improved the structural stability of SnO2 structure and the rise in calcination temperature intensified this effect of platinum. The decline of Pt/SnO2 surface area as a consequence of stability tests may be ascribed to the growth of both Pt and SnO2 particles. This result is consistent with the findings reported in the literatures [26,27,39].

TEM images of the fresh and aged Pt/SnO2 calcined at 700 °C are presented in Fig. 6. The images reveal the presence of small darker zones with a random dispersion. These nanozones are strongly contrasted in comparison to the surrounding SnO2 and may be attributed to the Pt particles and clusters. According to the TEM analysis of fresh sample, Pt particles are effectively dispersed in SnO2 matrix without being agglomerated. The huge contrasted zones on the images of aged sample indicate the sever sintering of Pt particles during the stability test. It can be concluded that, the interactions between Pt particles and SnO2 as a support were not strong enough to inhibit the agglomeration of Pt under the severe condition of accelerated stability tests.

According to Fig. 2, comparison between the XRD patterns of fresh and aged Mo-doped samples reveals that MoO3 addition suppressed the crystallite growth under the condition of stability tests to a great extent (Table 1), resulting in a negligible reduction of surface area during the long-term stability tests. Thus, the presence of MoO3 significantly enhanced the structural stability of Pt/SnO2. However, increasing the concentration of MoO3 to 10.0 wt% led to finer nanoparticles and larger crystallite growth during the accelerated stability tests, suggesting that smaller grains grow faster and are sintered more severely [38]. The increase in calcination temperature enhanced the structural stability to the extent that the surface area remained almost unchanged after the stability test.

Furthermore, structural stability of Pt/SnO2 has been significantly improved through ceria addition. It was observed that, the crystallite sizes of 5–Ce–700 and 10–Ce–700 remained approximately unchanged following the stability tests. An increase in the concentration of ceria declined the loss of specific surface area and crystallite growth during the accelerated stability tests, which may be attributed firstly to the strong Pt/CeO2-support interaction, leading to the more firmly dispersed platinum particles on the surface and sintering suppression, and secondly to the bigger particles of the samples containing 10.0 wt% CeO2. However, there are other interactions between dopants and tin oxide in addition to Pt/CeO2-support interaction, which depend on various parameters including synthesis conditions [28].

In the case of samples doped with 5.0 and 10.0 wt% samaria, the surface area declined about 8.0% and 5.9%, respectively, during the long term stability tests indicating that as the Sm2O3 concentration rises, the growth inhibiting effect becomes more pronounced. Growth inhibiting effect of samaria may be attributed to its preventive role in the neck growth and particle agglomeration [31]. It is worth mentioning that, the increase in the content of Sm2O3 and calcination temperature improved the structural stability of all the samples doped with samaria and reduced their particle growth during the stability tests.

The particle growth of samples doped with Sm2O3 were comparable with samples containing other dopants, while these samples exhibited the largest amount of crystallite growth during the stability tests. Therefore, Sm2O3 was not as effective as other dopants in preventing the growth of SnO2 crystallites during the stability tests.

It is believed that SiO2 significantly enhances the structural stability of SnO2 particles [32,33]. According to Table 1, it may be concluded that the fine particles obtained through addition of SiO2 up to 10.0 wt% were stable to a large extent, which is confirmed by the surface reduction of about 1.5 to 5 times less than Pt/SnO2 in addition to the negligible changes in XRD patterns upon the stability tests. The grain growth of 5–Si–700 and 10–Si–700 during the stability tests, were about 5.4% and 18.8%, respectively, suggesting that the smaller particles sinter faster. Additionally, as Table 1 reveals, by an increase in the calcination temperature, stability of the microstructure of all samples containing SiO2 have certainly been improved.
3.3. Response and stability of gas sensors

Generally, there are two possible sensing mechanisms to explain the role of metal additives on the sensors' sensitivity including electronic sensitization and chemical sensitization. The latter is the most common mechanism suggested for Pt/SnO2 sensing that focuses on the ability of Pt to adsorb oxygen dissociately and spill it over to the semiconductor oxide [39].

The effect of calcination temperature and different nanaoadditives including MoO3, CeO2, Sm2O3, and SiO2 on stabilizing the performance of SnO2-based sensors, were investigated. The response (R/R0) of all the fabricated sensors to 100 ppm CO at 250 °C, for the fresh sensors and also on the 5th, 8th, 12th and 15th days of stability tests are presented in Table 2. Since the major part of sensitivity drifts during the 15 days of stability tests are observed within the first 5 days, the 5th day is considered as the reference point of investigation.

According to the results in Table 2, Pt presence enhanced the gas response of SnO2 nanoparticles to CO as a result of its catalytic activity in accelerating the sensing reaction and also a raise in the resistance of sensing material which is considered to be due to an increase in the height of intergranular Schottky barrier [29,40,41]. Despite the expectations, this effect of platinum was not striking as a consequence of the high calcination temperature which often reduces the sensitivity of a porous sensor due to sintering and/or ripening [20].

Considering the chemical sensitization mechanism, the response of Pt/SnO2 sensors mainly depends on the platinum dispersion, as the most effective parameter on the activity of supported noble metal catalysts, as well as on the platinum chemical state [29,42]. No generalization can be made for all the platinum supported materials, since platinum in the form of metal (Pt0) or metal oxide (Pt2+−Pt4+), separated nanoparticles (clusters) or solid solution, exhibits different results and responses [39].

MoO3 and CeO2 addition up to 10.0 wt% significantly reduced Pt/SnO2 response to CO, despite the surface area increase. This result in the case of sensors doped with MoO3 is mostly attributed to the presence of Mo(V) which makes the sensing reaction difficult because firstly, the excess amount of Mo(V) on the surface of SnO2 prevents the oxygen reactivity and the formation of active species of O−, and secondly, the oxygen bonding energy with lattice in SnO2-MoO3 is higher than the one in pure SnO2 which prevents the adsorption of target gases [43]. The response enhancement with increase in Mo concentration (see Table 2) may be attributed to additional oxygen sites provided by large increase in the surface area [44].

This response decline in the case of ceria addition, which has been also reported by Khodadadi et al. [45], may be explained through the drastic increase in the catalytic activity of SnO2-CeO2 for CO conversion, i.e.100%, caused by Pt addition [23]. In other words, under this condition CO burns on the surface and the produced CO2 leaves the surface without causing any changes in the bulk, which is an undesirable effect for the sensing reaction. It should be mentioned that the catalytic influence of Pt becomes more dominant by utilizing impregnation method which provides a more effective dispersion of Pt catalysts especially on the surface [24,46].

According to Table 2, silica addition drastically improved the response of Pt/SnO2 at the concentration of 10.0 wt%, in contrast with CeO2 and MoO3. This enhancement is mostly attributed to the incorporated fine silica particles, which mainly deposits on the necks of SnO2 grains, and consequently decreases the neck size of the SnO2–SiO2 and increases the height of Schottky barrier [32,33].

Since the rare earth metal oxides such as Sm2O3 act as an electron acceptor to SnO2, they promote oxygen adsorption. Additionally, they are mostly situated on the surface of SnO2, therefore, prevent the direct contact of SnO2 nanoparticles with the target gas to some extent. Consequently, the height of Schottky barrier at the Pt/SnO2 grain boundaries and the response increase as a result of Sm2O3 presence [30,36]. Through 5.0 wt% Sm2O3 addition the resistance of Pt/SnO2 reached to its highest value, since this amount of Sm2O3 corresponds to a complete monolayer coverage on the surface of tin oxide, and on the other hand SnO2 particle size drastically reduced, thereby the sensing properties of the sensor significantly enhanced [11,31]. Thus, a proper content of Sm2O3 can improve the sensitivity of the sensor. However, further increase in the concentration of samarium oxide to 10.0 wt% decreased the response, attributing to the suppression of carbon monoxide oxidation and the sensing reaction [31].

It is widely accepted that response of the sensors declines over the time and their resistance increase as a consequence of exposure to surrounding atmosphere and ambient conditions such as humidity and temperature [5,6]. In this work, the effects of these parameters are accelerated under the condition of stability tests.

Response reduction of the SnO2 sensor continued steadily to the end of the period of stability test while the reduction trend slowed down from zero point to final point in the case of Pt/SnO2 sensors (see Table 2). It could be concluded that the response decline for pure tin oxide is suppressed in presence of platinum during the last 10 days of stability test, attributing to the influence of Pt on thermal stability and the achievement of adsorption/desorption equilibrium between oxygen vacancies of SnO2 and the ambient oxygen [42]. Moreover, the resistance increase during the stability tests was more intense for SnO2 compared to Pt/SnO2 and an increase in calcination temperature had an improving effect on the stability of sensors.

Generally, the grain size and dispersion of the noble metals, grain size of the SnO2 crystallities and the concentration of surface hydroxyl groups are the factors that affect the response and stability of gas sensors [41]. In other words the changes in conductivity of Pt/SnO2 during the stability tests are not solely due to the reduction/oxidation interaction of the material with the target gas, which are typically reversible. The large observed changes in conductivity (not reported here) is mainly attributed to the movement of oxygen vacancies into or out of the lattice [14]. Therefore, it may be concluded that the instability of pure SnO2 can be induced by thermal instability and severe structural changes, while the response drifts observed in the case of Pt/SnO2 can be also related to platinum particles growth and reduction in its dispersion as a result of experimental conditions.

It was established that since the growth of noble metal clusters is possible at long exploitations, thus, stabilizing the size of noble metal particles is important in order to achieve stability in the gas sensors [42]. Therefore, stabilizing the size of platinum particles is the best way to improve the stability.

Presence of MoO3 and CeO2 in both concentrations (5.0 and 10.0 wt%) and calcination temperatures (700 and 850 °C) stabilized the performance of Pt/SnO2 gas sensors observed following the 5th day of the stability tests. It is suggested that the major part of structural changes takes place during the first 5 days of the stability tests, however all the doped samples with both of these dopants showed an excellent structural stability. As the results in Table 2 indicate, the response decline during stability tests for Pt/SnO2 sensors doped with ceria and molybdenum oxide reduced with an increase in the concentration of dopants, due to the less agglomeration of samples containing 5.0 wt% of dopants within the stability tests, which had larger particles.

Besides the sintering inhibition effect of ceria, it is suggested that the stability of Pt/SnO2-CeO2 sensors is mostly related to the strong interaction between Pt and CeO2, believed to stabilize the platinum dispersion [26].
Among all the sensors, the ones doped with CeO₂ had the least rise in $R₀$ and $R₅$ during the first 5 days of stability tests and the stabilized value of $R₄$ and $R₅$ stayed almost unchanged to the end of tests.

It is noteworthy that the response of 10-Ce-850 sensor reduced severely from the 8th day of the test to the final point and it became almost insensitive to carbon monoxide, therefore the results of stability tests for this sensor is not discussed.

It should be noted that the incorporation of Sm₂O₃ into SnO₂ lattice did not improve the Pt/SnO₂ stability. Increasing the calcination temperature and samaria concentration only reduced the response drifts during the stability tests, which mainly occurred by the zero point, but did not lead to stabilizing the performance of Pt/SnO₂. As it can be observed in Table 2, the pace of response reduction during the stability tests did not slow down by samarium oxide addition, compared to the undoped Pt/SnO₂ samples. The response decline of the samples doped with samaria excluding 5-Sm-700, continued severely during the stability tests until the sensors became insensitive at the end of stability tests.

There is a noticeable point in the case of samples doped with Sm₂O₃ that, according to the BET results their particle growth was comparable to the samples containing other dopants, while their crystallite growth, observed by XRD measurement, was significantly higher than the other samples. In other words, their crystallite growth during the stability test may be affected more seriously than particle size increase, which was just comparable with crystallite growth value in the case of Pt/SnO₂. Taking into account the instability problem of the Pt/SnO₂-Sm₂O₃ sensors and their intensive response reduction, it may be concluded that the decrease in surface area during the stability tests did not have a crucial role in instability. It should also be pointed out that no second phase was detected after the stability test indicating that instability is not related to the segregation of the dopant phase. However, there is a possibility of the presence of amorphous or too small crystallites which could lead to no detection of the dopant phase.

Stability in the performance of Pt/SnO₂ gas sensors doped with 5.0 and 10.0 wt% silica was observed with the 8th and 12th days of the stability test, respectively. This means that beside the stabilizing effect of SiO₂ on the performance of Pt/SnO₂, an increase in SiO₂ concentration resulted in accelerating the advent of instability.

According to the results, the stabilizing effect of silica appeared later than those of CeO₂ and MoO₃. This significant difference may be ascribed to the weaker interaction between SiO₂ and Pt, which is required for stabilizing the Pt particles, as the most determinant parameter in the stability in sensing performance of the gas sensors [28].

The amount of response reduction during the accelerated stability tests for 5-Si-700 and 5-Si-850 was approximately equal to 56 and 76%, respectively, while this values for 10-Si-700 and 10-Si-850 were respectively, 71.8 and 91%. Thus, an increase in calcination temperature and in concentration of silica are found to increase the response drift over the stability tests, respectively due to weakening of the Pt-SiO₂ interaction in the case of agglomerated particles and easier sintering in the case of fine particles.

Furthermore, as was mentioned earlier, the most intense part of the response decline belongs to the first 5 days of stability tests. For instance the amount of response reduction of 5-Si-700 at zero point was 50%, while for the rest of the test it reached to just 14%.

### 3.4. The role of dopants in the stability of gas sensors

The type of nanoadditives is one of the most significant parameters in stabilizing the performance of sensors. The effectiveness of additives depends greatly on the dispersion and the way they are present in the SnO₂ lattice, whether in the form of a separate phase or solid solution. For instance, samarium oxide tends to enrich on the surface of SnO₂ grains while molybdenum oxide has a tendency to substitute into SnO₂ structure in the form of solid solution [30,31,34]. The results obtained through the study of the influence of metal oxide additives, including rare earth metal oxides (CeO₂, Sm₂O₃), transition metal oxides (MoO₃) and post transition metal oxides (SiO₂), on the sensors performance and stability are summarized at Table 3.

According to the results, the presence of dopants can influence stability by means of structural modifications, adsorption/desorption processes and electronic effects [12,16]. This key role of additives in the case of Pt/SnO₂-based sensors could arise from their effects on different aspects such as structural stability, stabilizing the Pt-SnO₂ interactions and stabilizing the

#### Table 2

Response ([$R₀/R₅$] ± 3%) of fabricated sensors to 100 ppm CO during the stability tests.

<table>
<thead>
<tr>
<th></th>
<th>Fresh point</th>
<th>The 3rd day</th>
<th>Zero point (the 5th day)</th>
<th>The 8th day</th>
<th>The 12th day</th>
<th>Final point (the 15th day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂-700</td>
<td>108</td>
<td>94.44</td>
<td>74</td>
<td>40.88</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>Pt/SnO₂-700</td>
<td>160</td>
<td>–</td>
<td>35.33</td>
<td>34</td>
<td>–</td>
<td>31</td>
</tr>
<tr>
<td>Pt/SnO₂-850</td>
<td>125.4</td>
<td>–</td>
<td>30</td>
<td>–</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>5-Mo-700</td>
<td>26.88</td>
<td>–</td>
<td>11.5</td>
<td>–</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>5-Ce-700</td>
<td>21.44</td>
<td>–</td>
<td>17.2</td>
<td>17.2</td>
<td>17.7</td>
<td>17.2</td>
</tr>
<tr>
<td>5-Sm-700</td>
<td>215.9</td>
<td>–</td>
<td>41.9</td>
<td>–</td>
<td>26</td>
<td>21</td>
</tr>
<tr>
<td>5-Si-700</td>
<td>98</td>
<td>–</td>
<td>50</td>
<td>44</td>
<td>42.8</td>
<td>42.8</td>
</tr>
<tr>
<td>5-Mo-850</td>
<td>13.2</td>
<td>–</td>
<td>9.5</td>
<td>9.5</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>5-Ce-850</td>
<td>10</td>
<td>–</td>
<td>2.5</td>
<td>2.5</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td>5-Sm-850</td>
<td>18.2</td>
<td>–</td>
<td>6</td>
<td>3.6</td>
<td>2.7</td>
<td>1.6</td>
</tr>
<tr>
<td>5-Si-850</td>
<td>80.8</td>
<td>–</td>
<td>26</td>
<td>22</td>
<td>18.5</td>
<td>18.8</td>
</tr>
<tr>
<td>10-Mo-700</td>
<td>90</td>
<td>–</td>
<td>15.3</td>
<td>15.5</td>
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<td>15.6</td>
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<td>10-Ce-700</td>
<td>14.88</td>
<td>11.5</td>
<td>11.3</td>
<td>11</td>
<td>10.5</td>
<td>11</td>
</tr>
<tr>
<td>10-Sm-700</td>
<td>19.6</td>
<td>–</td>
<td>2.8</td>
<td>2.3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>10-Si-700</td>
<td>208.5</td>
<td>–</td>
<td>61.32</td>
<td>58.8</td>
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<td>58.8</td>
</tr>
<tr>
<td>10-Mo-850</td>
<td>52.38</td>
<td>10.1</td>
<td>10.1</td>
<td>10</td>
<td>10</td>
<td>10.1</td>
</tr>
<tr>
<td>10-Ce-850</td>
<td>5.5</td>
<td>–</td>
<td>3.3</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>10-Sm-850</td>
<td>4.4</td>
<td>2.5</td>
<td>2.4</td>
<td>1.4</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>10-Si-850</td>
<td>198</td>
<td>70</td>
<td>21.8</td>
<td>17.7</td>
<td>17.7</td>
<td>17.7</td>
</tr>
</tbody>
</table>

#### Table 3

The effect of dopants and their concentrations on the stability of Pt/SnO₂ sensing material.

<table>
<thead>
<tr>
<th>Type of dopant</th>
<th>Concentration (wt%)</th>
<th>Stability condition</th>
<th>Start of stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>5, 10</td>
<td>Stable</td>
<td>5th day</td>
</tr>
<tr>
<td>CeO₂</td>
<td>5, 10</td>
<td>Stable</td>
<td>5th day</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>5, 10</td>
<td>Unstable</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>5</td>
<td>Stable</td>
<td>12th day</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>8th day</td>
</tr>
</tbody>
</table>
concentration of the defects, in addition to electronic influences [16,42], which are discussed in the following.

Generally, the gas sensing performance of nanostructured semiconducting materials is affected by porosity, grain size distribution and density of lattice defects [47–49]. Since high temperatures often reduce the response of a porous sensor during their lifetime, mainly due to sintering and/or ripening, therefore, one of the reasons for long-term instability in the performance of the solid-state gas sensors is the change in the structural parameters of the semiconducting metal oxides, i.e. microstructural and morphological changes, as a consequence of insufficient pretreatment [12]. Thus, the materials utilized for design of the gas sensors have to possess high structural stability, in order to suppress the processes of grain growth during exploitation [48].

Furthermore, the microstructure of SnO2 could be stabilized by an addition of a small amount of various metal oxides such as MoO3, CeO2 and SiO2 dispersed well on the surface of SnO2, through providing a barrier for surface diffusion, separation of SnO2 grains by growth inhibition of neck size between the grains [10,42] and thus, preventing crystal growth or agglomeration of SnO2 particles during calcination even at high temperatures [11,37]. This structural stability caused by the mentioned dopants in the case of Pt/SnO2 samples could also be attributed to the interactions which stabilize the Pt particles on SnO2 grains [10,42].

Considering the surface area reduction and crystallite growth for SnO2 and Pt/SnO2 samples within the stability tests, it can be inferred that Pt presence enhanced the structural stability of SnO2. The crystallite growth in the case of the sensors doped with 5.0 and 10.0 wt% of different metal oxides increased during the accelerated stability tests in the following order: CeO2 < SiO2 < MoO3 < SnO2. However, the particle growth was evaluated in this order: MoO3 < SiO2 (except 10-Si-700) < Sm2O3 < CeO2 (except 5-Ce-700).

An increase in the concentration of dopants, except for CeO2 and Sm2O3, reduced their restrictive influence on particle growth because it is strongly believed that smaller particles grow faster during the sintering processes [38]. The contrasting behavior observed in the case of samples containing CeO2, could be attributed to the stronger interaction between Pt and SnO2, since ceria at high concentration is widely used as an stabilizing agent for dispersion of the precious metal [28]. In order to draw a conclusion about the extent of effectiveness of the structural stability in stabilizing the sensors performance, behavior of the sensors from the structural and reaction aspects during the stability tests are compared.

Despite the comparable particle growth of the samples doped with 5.0 wt% Sm2O3 and CeO2, these two sensors exhibited quite different behaviors during the stability tests: the sensor containing CeO2 became stable at zero point while response of the sensor doped with Sm2O3 did not reach a stable value until the end of the test, even samaria presence did not suppress the pace of response reduction compared to Pt/SnO2. On the other hand, Sm2O3 was not as effective as the other dopants in improving the thermal stability of SnO2 crystallites size during the stability tests. Additionally the less particle growth of the sensors doped with MoO3 compared to the ones doped with CeO2 did not lead to lower response reduction between the fresh and zero point, the point which they all became stable. However, the crystallite growth in the case of sensors doped with MoO3 was remarkably more than the ones containing different concentrations of CeO2.

These inconsistent results about the particle growth over the period of stability tests with regard to the response decline and stability of various samples, especially in the case of instable sensors doped with samaria, guide us to propose that crystallites stability plays a more effective role on stabilizing the performance of sensors or these results are induced by some other stabilizing parameters except thermal stability.

As it was mentioned before, the response drifts observed in the case of Pt/SnO2 sensors can be related to platinum particles growth and reduction in its dispersion under the condition of stability test along with the agglomeration of SnO2. Since the average particle size of the fabricated sensors is far larger than the depth of depletion layer, thus their resistance and the response mostly depend on the height of potential barrier rather than the SnO2 particles size [12,49,50]. Consequently, this rules out the SnO2 grain growth as a main cause of the long term drift in these sensors. It can be concluded that restriction of the platinum particle growth could play more dominant role in controlling the response and stability.

It is widely accepted that the structural stability is not the only determinant parameter for observing stability in performance of the gas sensors. This means that the effect of some other parameters such as reactivity (chemical reactivity) of the sensing materials toward oxygen and movement of oxygen vacancies into or out of the lattice should be considered simultaneously [14,49].

However, it should be considered that sintering of the particles is mostly accompanied with other microstructural changes such as concentration of the lattice defects which affects the electrical properties [5,16]. Thus, importance of the structural stability is due to dependency of both response and electrical properties on the particle size.

SnO2 is known to be a nonstoichiometric oxide with some oxygen vacancies and electron donor sites. The electron carriers could be produced due to the oxygen vacancies as follows [5]:

$$\text{Sn}^{4+2e^{-}}\rightarrow \text{O}^{2-}$$

(2)

The oxygen vacancies of SnO2 can react with an ambient oxygen at the operating temperature, and the vacancy concentration varies toward an equilibrium status compatible with the ambient oxygen pressure and temperature. Since this equilibrium has an extremely low oxygen partial pressure from a thermodynamic point of view, thus the oxygen vacancies could be diminished through the forward reaction of the following equation:

$$V_{0} + 1/2 \text{O}_{2}(g) \rightarrow \text{O}_{0}$$

(3)

For this reason, the resistance of sensing film keeps increasing with the operating conditions, i.e. temperature and humidity and time which finally become unable to operate. For the improvement of the long-term stability of SnO2-based sensing films, it is required to replace the nonstoichiometric conduction mechanism with another conduction mechanism, such as, the controlled valence mechanism [5].

In the X-doped SnO2 sensors, which Sn sites of the SnO2 crystal lattice are substituted by the dopant ions, the conduction mechanism is dominated by the valence mechanism. This means that the resistance of X-doped SnO2 gas sensors are controlled mainly by the dopant without large contribution of the concentration of oxygen vacancies. Even though the oxygen vacancies of SnO2 react with ambient oxygen gas, this effect is not enough to change the whole resistance of X-doped SnO2 sensor. Consequently, the long-term stability could be obtained.

It was observed that the resistance of all fabricated sensors deviate from its initial values following the stability tests. The amount of resistance increment varied for sensing material doped with different metal oxides, indicating that different metal oxides can restrict the increase of resistance to different extents (not reported here). For instance, the rather higher stability of Pt/SnO2 sensor compared to the pure SnO2 can be related to reaching adsorption/desorption equilibrium faster and suppressing the resistance increase until the end of the period. It can be concluded that some dopants accelerate the rate of resistance increase during the exploitation period to air and the equilibrium condition is achieved more quickly, so they provide the condition to cease the
change in the conductance before the final point, even at the zero point in some cases. As Table 3 shows, the sensors doped with CeO₂ and MoO₃ attained the stability in a shorter period compared to the sensors doped with SiO₂, due to the quicker achievement of equilibrium. Furthermore, an increase in the content of SiO₂ accelerated the advent of stability.

Moreover, various nanoadditives have different impacts on SnO₂ lattice defects and the concentration of these crystallographic defects, which vary under the accelerated stability tests with different pences, even some nanoadditives can stabilize the concentration of defects. Thus, the nanoadditives can also affect on the electrical properties of SnO₂ and Pt/SnO₂ through altering the crystallographic defects.

3.5. The role of calcination temperature in the stability of gas sensors

Calcination temperature is considered as an effective parameter for the sensing materials to reach more thermodynamically stable structures. Utilizing high calcination temperatures can firstly, limit the particle growth during operation of the sensors and secondly, accelerate the response drifts during the long term stability tests. In other words, an increase in calcination temperature affects the sensors stability via structural stability improvement and reduction in the response drifts of the sensors in the course of stability tests. In case of the sensors doped with 5.0 wt% SiO₂ the response reduction during the stability tests decreased from 56.3% to 40% through an increase in calcinations temperature from 700 to 850 °C respectively. The same behavior was observed for 10-Sm-700 and 10-Sm-850 samples, which had 89.8 and 68.1% response reduction, respectively. It could be concluded that this decrease in response reduction is attributed to the stabilizing effect of calcination temperature on particle growth during the stability test, which was changed from 36.0 to 11.6% as a result of an increase in the calcination temperature from 700 to 850 °C.

If SnO₂ contains noble metals and metal oxides, they usually enrich on the surface of SnO₂ in various oxidation states at different annealing temperatures which exhibit different responses to a specific gas. Therefore, calcination temperature can affect on the response of sensing materials containing some of the noble metals and metal oxides as dopants.

Comparison between the calcination temperature as an effective factor on the sensors stability with other factors such as dopants and interactions, led to conclude that calcination temperature has the least effect on the sensors stability. In other words no instable sensor reached to stability by rising the calcination temperature, for instance an increase in the calcination temperature of Sm₂O₃–doped sensors did not lead to stabilizing their performance. However, the stability could be improved to a large extent at higher calcinations temperatures especially in the case of Pt/SnO₂ which showed the least changes in response and resistance at final days of the stability tests.

4. Conclusion

Sensing materials including pure SnO₂ and SnO₂ doped with 5.0 and 10.0 wt% of MoO₃, CeO₂, Sm₂O₃ and SiO₂ were synthesized by a sol–gel method, then they were all impregnated with 1.0 wt% platinum. In order to investigate the long term stability of the fabricated sensors, all the sensors and their corresponding sensing materials in the form of powders were exposed to the condition of the accelerated stability test.

The results also revealed that addition of Pt, MoO₃, CeO₂, and SiO₂ improved the structural stability of SnO₂, while Sm₂O₃ addition did not lead to the same result. The structure of Sm₂O₃ doped samples were thermally stable from the aspect of particle growth, however, their crystallographic growth was measured to be about 50% during the stability tests.

The major part of the response decline for all sensors was observed during the first 5 days of stability tests. Presence of platinum decreased the drift in SnO₂ response during the stability tests on one hand, and on the other hand accelerated the process of reaching to equilibrium. The same accelerating effect was observed especially for the case of CeO₂– and MoO₃–doped sensors which became stable at the zero point. Addition of SiO₂ with 5.0 and 10.0 wt%, stabilized the performance of Pt/SnO₂ sensor, which occurred on 12th and 8th days of the test, respectively.

Since the humidity condition was remained constant within the stability tests, it is suggested that the drift in resistance and response values during the stability tests may be attributed to two main factors, i.e. grain growth of SnO₂ particles, sintering and reduction in the dispersion of Pt particles. Sensitivity of the SnO₂–based sensors utilized in this work with average grain size of larger than the depletion layer, depends on the height of the potential barrier between the grains rather than on the size of SnO₂ particle. However, the effect of particle growth on the other aspects of the sensors such as electrical properties, as a result of the change in the concentration of the lattice defects. Thus, it seems that the interactions between the dopant and the Pt particles, which stabilize the Pt particles on the SnO₂ grains, play a more significant role in stabilizing the performance of the gas sensors and it may be concluded that this 5 days have a remarkable effect on stabilization of the structural properties of metal oxides and also on stabilization of Pt location.

The sensors doped with CeO₂ and MoO₃ attained the stability in a shorter period compared to the sensors doped with SiO₂, due to the quicker achievement of equilibrium. Furthermore, an increase in the content of SiO₂ accelerated the equilibrium of adsorption/desorption and the advent of stability.

It was found that long term stability was also improved by annealing the sensing material at high temperatures. The increase in calcination temperature enhanced the structural stability to the extent that the surface area remained almost unchanged after the stability test.

References


S. Vahdatifar received the B.S. degree in Chemical Engineering from Iran University of Science and Technology, and the M.Sc., degree in Chemical Engineering from University of Tehran, Tehran, Iran. She has been a research assistant at the catalysis and reaction Engineering Laboratory, University of Tehran since 2010. Her research interests include nano-structured materials and metal oxide semiconductor gas-sensors.

A. A. Khodadadi received his M.Sc. in Chemical Engineering from University of Tehran, Tehran, Iran, and his Ph.D. in Catalysis and Reaction Engineering from University of Waterlo, Waterloo, Canada. His research interests include catalysis, reaction engineering, nano-structured materials as applied to nano-particles, carbon nanotubes, plasma-catalytic conversion of natural gas to liquids and chemicals, metal oxide semiconductor gas-sensors, air pollution control using catalytic converters and oxygen sensors using solid electrolytes.

Y. Mortazavi received the B.S. degree in Chemical Engineering from Shiraz, Shiraz, Iran, and the M.Sc., and Ph.D., degrees in Chemical Engineering from University of Waterlo, Waterloo, Canada. He joined University of Tehran, Iran in 1995. His research interests include catalysis and reaction engineering especially in C, chemistry, environmental catalysis, chemical gas-sensors and nano-structured materials. Currently he is the chair of Nanotechnology Department at College of Engineering, University of Tehran, Tehran, Iran.