

Mesoporous catalytic filters for semiconductor gas sensors

A. Cabot^{a,*}, J. Arbiol^a, A. Cornet^a, J.R. Morante^a, Fanglin Chen^b, Meilin Liu^b

^a*Enginyeria i Materials Electrònics, Departament d'Electrònica, Universitat de Barcelona, c/Martí i Franquès 1, PO Box 4500, Barcelona 08028, Spain*

^b*School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA*

Abstract

An effective way to improve sensor selectivity and stability is the use of catalytic filters to block interfering and poisoning gas molecules from reaching the sensor surface. Mesoporous silica with high resistivity and high surface areas are ideally suited as a base material for this application. When impregnated with proper catalysts, mesoporous silica has a great potential to eliminate responses to undesired gases even of thin-film and/or micro-machined sensors. In this paper, we report our initial results on thick film SnO₂-based gas sensors covered with a catalytic filter consisting of Pd and Pt loaded mesoporous silica. Results indicate that selective oxidation of CO in the catalytic filter leads to the elimination of CO interference to a CH₄ sensor with no perceptible deterioration in sensing performance.

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1. Introduction

While semiconductor gas sensors exhibit high sensitivity (small change in gas composition causes dramatic change in resistance), their stability and selectivity still remain unsatisfactory for many applications. In general, electrical properties of semiconducting sensing elements are influenced not only by the gaseous species to be detected but also by other gas molecules in the sample gas mixture, especially those having similar physico-chemical properties as the target gas. Moreover, undesired gas molecules may be irreversibly adsorbed on the oxide surface, leading to sensor response drift.

Selectivity enhancement is usually achieved by the following three approaches: an improvement of the sensing material properties, the adaptation of the sensor working conditions to the target gas and the assembly of different sensors on arrays involving posterior signal treatments. The improvement of the sensing material properties and optimisation of the working conditions mainly take profit of the different activation energy of the gas reaction on the sensing element surface [1–3]. In micro-machined substrates a modulation of the temperature is also considered in order to obtain a more

complete set of data for the different target/interfering gases. The same technique is used to prevent poisoning by cyclic cleaning of the oxide surface at higher temperature than that of operation. Gas sensor arrays allow a much more complete sketch of the atmosphere composition to be built by means of a larger amount of parameters, which require more or less complicated signal treatments ideally incorporated in the same chip [4].

Another effective way of improving selectivity is to take advantage of selective gas diffusion process by using filters [1,5–10]. In this way, influence of interfering gases can be avoided by blocking these species from reaching sensor surface. While filters may improve selectivity and stability of semiconductor gas sensors, it may lower the sensor detection limit [9].

Until now, the most used filters are passive membranes having different diffusion parameters according to the adsorption affinity of the gas molecules on the sieve material and the pore-molecule size relationship. These kind of adsorbent filters may become saturated for large interfering gas concentrations if no mechanism of gas reaction or desorption are anticipated [10].

Selective catalytic reaction mechanism in the filtering membrane are expected to overcome these limitations, by means of catalytic conversion of the interfering species into innocuous molecules. Catalytic sieves have

*Corresponding author. Tel.: +34-934-021-090; fax: +34-934-021-148.

E-mail address: acabot@el.ub.es (A. Cabot).

already been employed in the form of dielectric oxides, thin metal layers or of dispersed catalytic elements on oxide semiconductor materials. The use of high resistive oxides without the distribution of highly active catalytic elements requires high operation temperatures, which may not always fit the most appropriate conditions to optimise the sensor response to the target gas. Low catalytic activity will also require fabrication of thick enough filters to eliminate the interfering gases, which could lead to longer response times.

Metallic membranes are reported to show exceptional selectivity properties [11]. Nevertheless, on the one hand, in semiconductor devices this may short circuit the system or influence the base sensor resistance if not correctly electrically isolated from the film. Furthermore, metal atoms may diffuse and consequently affect the stability of the device [5,8]. On the other hand, catalytic properties of the noble metals are not fully exploited in such a continuous structure; however, as extensively reported in catalytic literature, a high dispersion of supported active phases would increase its catalytic efficiency [12].

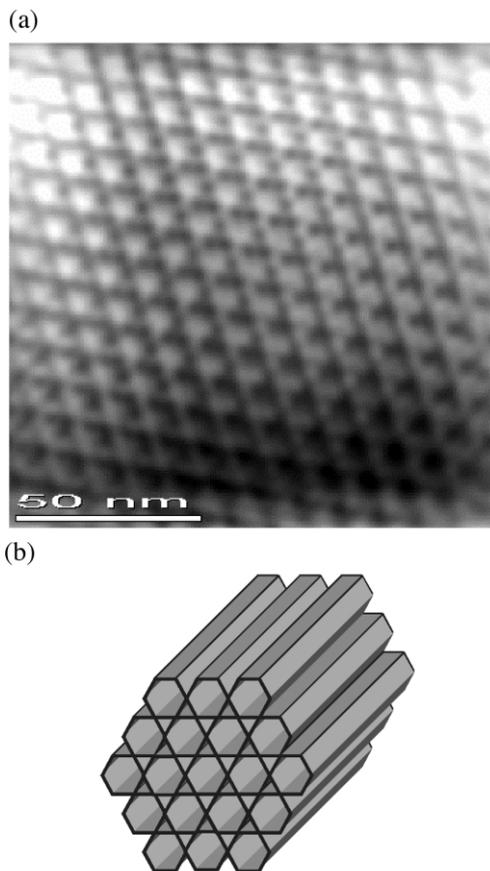


Fig. 1. TEM image illustrating the pores with hexagonal structure (a) and model of the SBA-15 mesoporous silica observed in our samples (b).

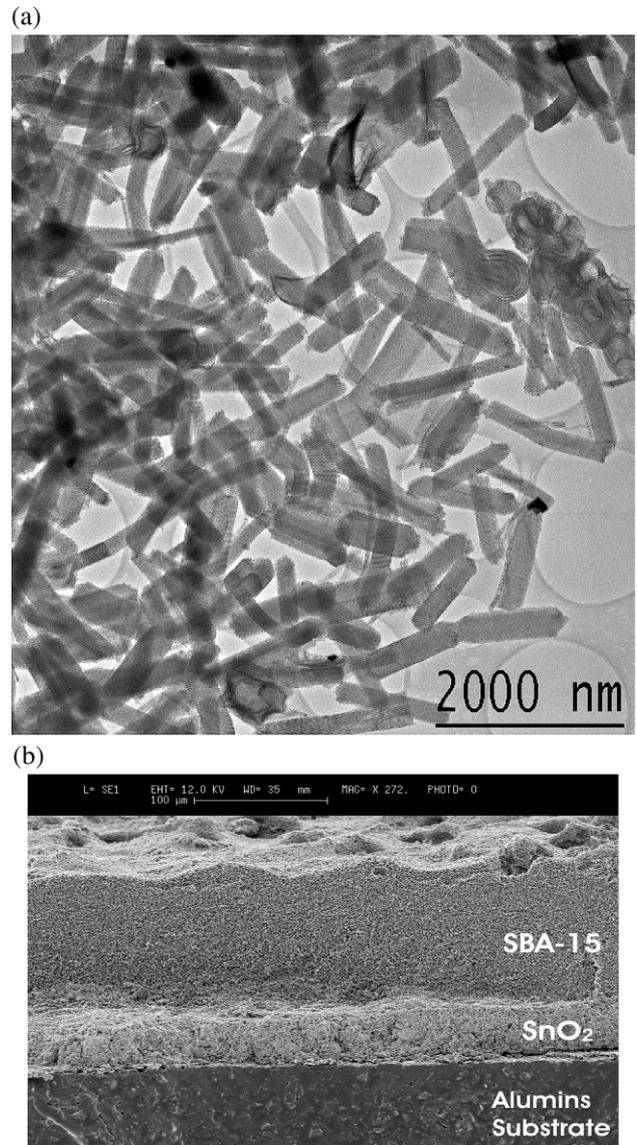


Fig. 2. TEM image of the mesoporous silica powders (a) and a SEM cross-sectional view of a SnO_2 sensor with a mesoporous filter (b).

As defined by IUPAC, mesoporous materials refer to porous inorganic solids or inorganic/organic hybrids with pore diameter in the range of 20–500 Å. Nanostructured mesoporous materials have recently attracted much attention for the development of catalytic applications [12,13]. These base mesoporous materials have often been modified by incorporation of noble metals or metal oxides in order to improve their physical and chemical properties [14–17]. In particular, mesoporous silica has been used as a base material to develop chemical gas sensors [18,19]. Mixtures of mesoporous silica and SnO_2 have also been explored to improve the response of gas sensor [20]. Furthermore, first promising works on the use of typical gas sensing base materials,

such as SnO_2 , in a mesoporous form has recently began to be reported [21–23].

There are mainly three different kinds of mesoporous molecular sieves (MMS) used in catalysis [12]. Among them, hexagonal SBA-15 mesoporous silica has long-range order, large monodispersed mesopores and thick walls, which make it more thermally stable than the other mesoporous structures.

Processes that strongly determine gas transport through microporous and mesoporous materials are sorption and pore diffusion [24,25]. Gas diffusion can be blocked by the inclusion of a large distribution of catalytic elements capable of combusting the interfering gases and thus, preventing them from reaching the sensing material. Large surface area mesoporous silicas are selected since they are also high resistive materials, which would have no significant influence on the electrical conductivity of a parallel sensing layer. This huge potentially catalytic active area on a highly resistive material may also have the potential to filter the interfering gases even in thin film layers and/or in micro-machined devices without affecting sensor resistance [26,27].

In a previous paper, structure of mesoporous SiO_2 and the distributions of Pt and Pd in the SiO_2 frame were reported [28]. In this article, we report our initial results using mesoporous silica as a novel selective filter for gas sensors.

2. Experimental

SBA-15 mesoporous silica was synthesized following the procedure reported by Zhao et al. using Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) [29,30].

Thus, obtained materials were calcined in air at 600°C for 4 h. Pd and Pt additives were introduced by impregnation of the SBA-15 silica with aqueous solution of palladium chloride and ammonium tetrachloroplatinate, followed by slow evaporation of water.

For the electrical characterisation, sensors were fabricated by mixing the powders with an organic binder and then printing the obtained paste onto alumina substrates with Pt electrodes and a heater. A similar procedure was used to obtain a SBA-15 silica paste, which was printed on the top of the SnO_2 layer. Sensor response to CO and CH_4 concentrations in different relative humidity conditions was measured.

Catalytic consumption measurements were carried out in a temperature-controlled reactor. The powders in quantities of 0.1 g were exposed to fluxes of 20 ml/min of the desired gas. Residual gas species were determined using an online IR analyzer. Synthetic air with 1% CO or CH_4 were used as test gases. Prior to each measurement, the sensing material was pretreated overnight in air at 450°C .

3. Results and discussion

The as-synthesized mesoporous silica has a BET surface area of $620\text{ m}^2/\text{g}$ and possesses the well-known SBA-15 structure, as shown in Fig. 1. The obtained material has a hexagonal array of mesopores with a lattice constant of 9.18 nm, and a narrow pore size distribution. The mesopores are arranged in structures grouping a few hundred pores with length up to $2\ \mu\text{m}$ (Fig. 2a).

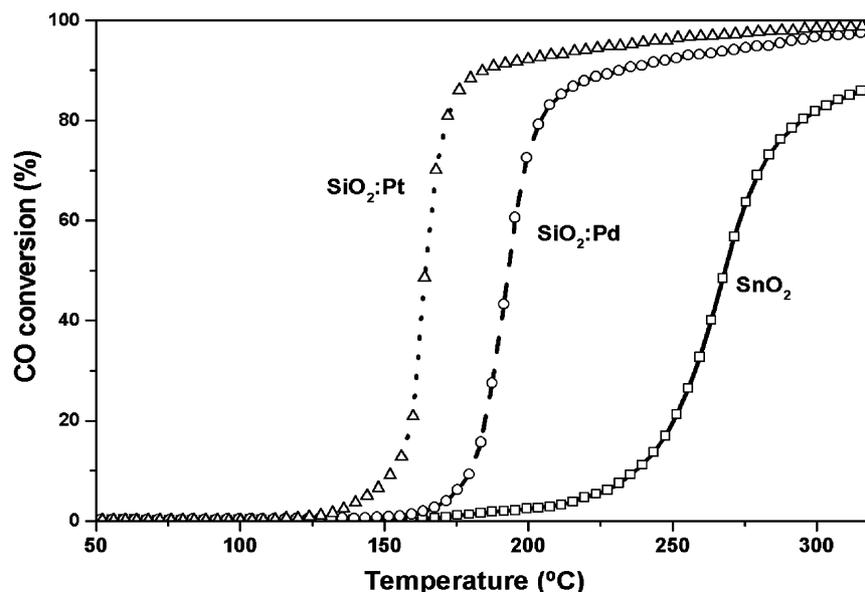


Fig. 3. CO to CO_2 catalytic conversion of the SiO_2 :Pt, SiO_2 :Pd and SnO_2 powders.

In order to make the materials catalytically active, the mesoporous silica was loaded with Pd and Pt compounds [28]. Films with a thickness in the range between 100 and 150 μm of these Pt and Pd modified SBA-15 structures were deposited over SnO_2 sensing layers. Fig. 2b shows a cross-sectional view of the gas sensor.

The direct deposition of the mesoporous filter layer at the surface of the sensing film was chosen, for its simplicity, in front of the housing of the sensor with an external filter. Moreover, the catalytic filter needs to be heated and therefore, its location on the top of the sensing layer results in a save of power consumption.

Fig. 3 shows CO to CO_2 conversion of the SiO_2 :Pt, SiO_2 :Pd and SnO_2 powders. CO is easily oxidised to CO_2 on the highly catalytic mesoporous layers. The activation energies for CO to CO_2 oxidation for SiO_2 :Pt and SiO_2 :Pd are much lower than that for SnO_2 . Thus, at the temperature which CO would be oxidised to CO_2 in the tin oxide surface, inducing an oxygen coverage variation, the diffusion of this gas would be already impeded by the catalytic filter.

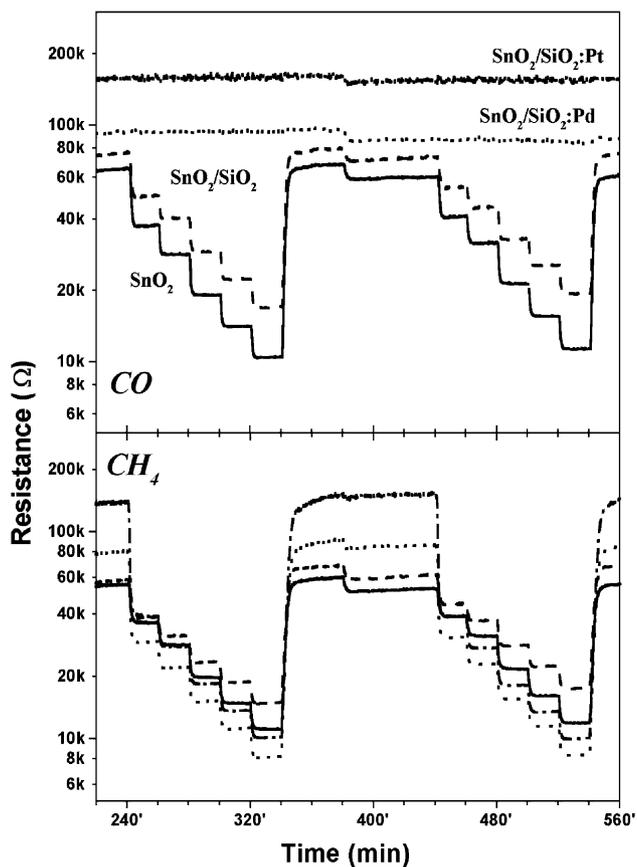


Fig. 4. Transitory resistances of the SnO_2 , $\text{SnO}_2/\text{SiO}_2$, $\text{SnO}_2/\text{SiO}_2$:Pd and $\text{SnO}_2/\text{SiO}_2$:Pt gas sensors when exposed to different concentrations of CO and CH_4 : from 20 to 400 ppm and 200 to 4000 ppm, respectively. Two different relative humidity conditions are considered: 30 and 50%.

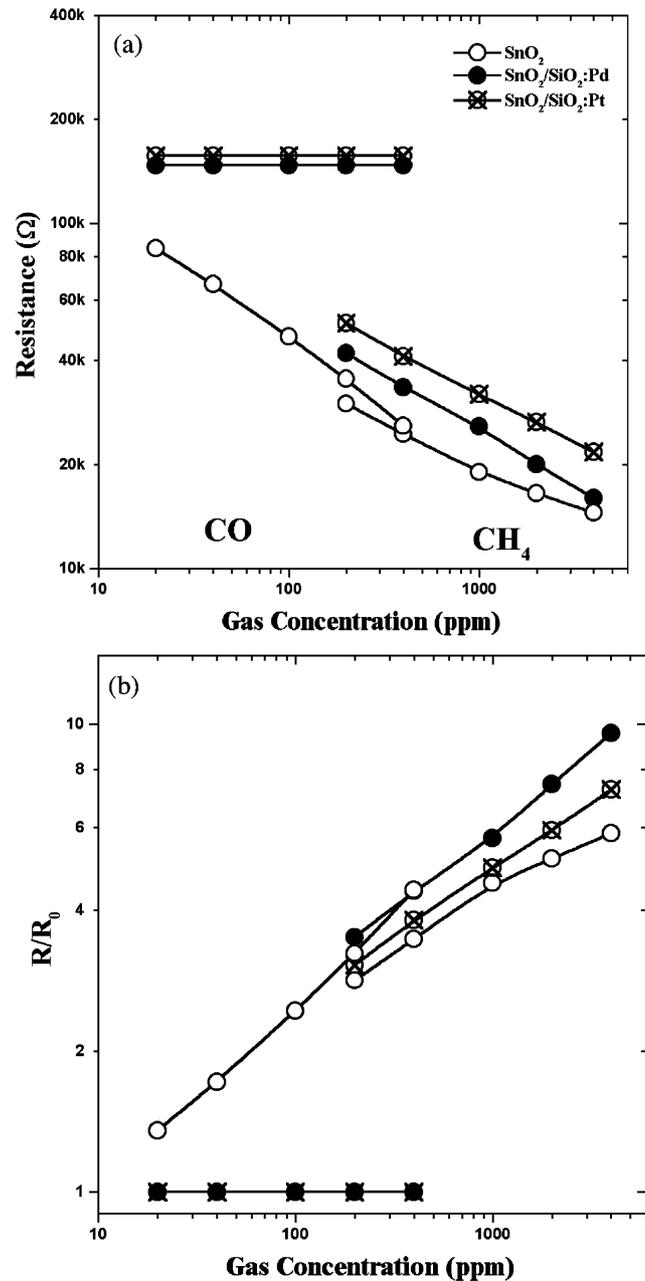


Fig. 5. Resistances and sensor responses of the SnO_2 gas sensors to different concentrations of CO and CH_4 : from 20 to 400 ppm and 200 to 4000 ppm, respectively.

Fig. 4 shows transitory resistance of the SnO_2 material heated at 350 $^{\circ}\text{C}$ with different gas conditions. It is noted that SiO_2 has no observable influence on the CO and CH_4 sensor response. The low density of the silica deposited layer and the well-defined spacious mesoporous channels in the mesoporous filter layer allow efficient diffusion of species involved in the sensing mechanism. Consequently, it does not induce any physical filtering to O_2 , CO and CH_4 , resulting in no slowdown of the sensor response or signal recovery

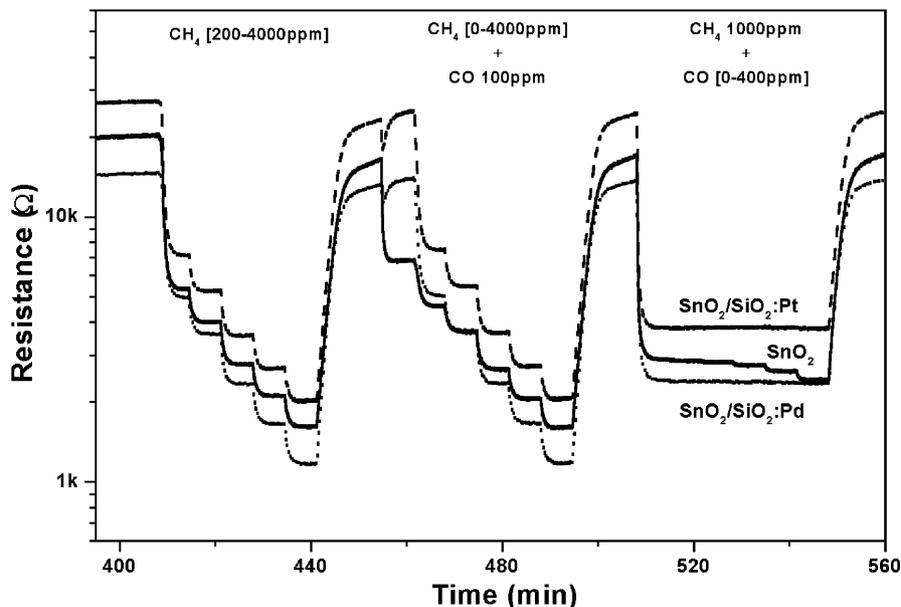


Fig. 6. Transitory resistances of the SnO_2 , $\text{SnO}_2/\text{SiO}_2$, $\text{SnO}_2/\text{SiO}_2:\text{Pd}$ and $\text{SnO}_2/\text{SiO}_2:\text{Pt}$ gas sensors when exposed to different CO and CH_4 mixtures.

speed. $\text{SiO}_2:\text{Pd}$ and $\text{SiO}_2:\text{Pt}$ filters, on the other hand, eliminate response to CO without affecting the response to CH_4 .

Baseline resistance is slightly different for the different sensors with or without a catalytic filter. This resistance difference is associated with resistance dispersion of the base SnO_2 sensor, probably due to small inter-electrode distance or layer thickness differences, together with the possible small temperature discrepancies between sensors. Pt and Pd impregnated mesoporous SiO_2 has a large resistivity, thus having no observable influence on the electrical conductivity of the active sensing layer.

Pt and Pd are shown to have similar characteristics, although $\text{SiO}_2:\text{Pd}$ filter is less effective in the lower range of CH_4 detection. On the other hand, $\text{SiO}_2:\text{Pt}$ filter eliminates CO response in the whole range of temperature where the sensing layer has a response to CH_4 .

As shown in Fig. 5 there is resistance variation as a function of CO and CH_4 concentrations. The relative resistance variation of the sensors with or without the filter layer is also plotted. A similar dependence of the sensor response with the gas concentration is observed, therefore, at this temperature range any decomposition or filter role on the gas sensing mechanism is not mediated.

Fig. 6 shows the responses of the different sensors to CO– CH_4 gas mixture. No observable influence of CO concentration on CH_4 detection is obtained. $\text{SiO}_2:\text{Pt}$ filter clearly decreases humidity influence, although at this step, humidity interference has not been totally eliminated by the catalytic filter layer. Organic solvents,

such as ethanol, are other important interfering gases for semiconductor gas sensors; concretely tin oxide is highly sensitive to these gases. The catalytic filter which is object of this study greatly decreases ethanol interference by its reaction in the filter layer. Nevertheless, ethanol response has not been totally eliminated. It is anticipated that proper selection of one or more catalytic elements in one or more filter layers should improve current model.

Huge surface area and catalytic activity of the filter layers are expected to prevent saturation of the filter and helps stability of the sensor [10]. Moreover, SBA-15 support is reported to have high stability even at relatively high operating temperature [31]. Otherwise, stability problems could arise from the degradation of the catalytic additive particle distribution, by agglomeration, evaporation or diffusion inside the oxide structure of the supported elements. Also a migration of the metal atoms into the sensing material would induce a drift on its electrical and sensing properties. In both the cases such a porous structure should, furthermore, prevent the mobility of the metal atoms if encapsulated inside the structure channels. Nevertheless, long-term stability of the supported catalytic elements needs to be studied.

4. Conclusions

The use of new mesoporous catalytic filters for semiconductor gas sensors have been reported. As an example of its potential applicability, the selective removal of CO has been shown and discussed. It was found that, at appropriate operating temperatures, sen-

sors covered with a layer of Pt/Pd loaded mesoporous silica did not respond to changes in CO concentration when it was exposed to CH₄–CO mixtures, demonstrating a high selectivity to CH₄. The large catalytically active surface area and the high resistivity of the mesoporous SiO₂ make it suitable as an efficient filter to improve the selectivity and stability of gas sensors. Even though the good stability of the supporting mesoporous structures, long time stability measurements of the supported catalytic elements need to be checked.

Acknowledgments

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