Manganese doped sol-gel materials with catalytic properties

M. CRISAN, M. RĂILEANU, S. PREDA, M. ZAHARESCU, A. M. VĂLEAN, E. J. POPOVICI,
V. S. TEODORESCU, V. MATEJČ, J. MRAZK
Institute of Physical Chemistry “Ilie Murgulescu”, Romanian Academy, 202 Splaiul Independenței
P.O. Box 12-194, 060021, Bucharest, Romania
**“Raluca Ripan” Institute for Research in Chemistry, 30 Făntânele, 400429 Cluj-Napoca, Romania
†National Institute of Materials Physics, PO Box MG7, 76900, Bucharest, Măgurele, Romania
‡Institute of Radio Engineering and Electronics, AS CR Chaberska 57, 182 51 Prague 8, Czech Republic

In the present study manganese doped alumina and silica gels and thin films deposited on different substrates (refractory metals, silicon wafers) were obtained by the alkoxide and aqueous routes of the sol-gel method. The characterization of the films was realized by X-ray diffraction (XRD), and spectroellipsometry (SE) methods. The un-supported gels (obtained by the gelation of the solutions used for the film deposition) were characterized by DTA/TG analysis, IR spectroscopy, transmission electron-microscopy and electron diffraction (TEM and SAED) and BET method (adsorption of krypton at temperature of liquid nitrogen) for surface area and pores volume determination. The sol-gel materials were tested as catalysts for the ozone decomposition.

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1. Introduction

Unlike the silica (silium dioxide), which is a natural compound, alumina (aluminum oxide) does not occur in nature. Different chemical processes allow obtaining aluminas with high surface areas, which make them active compounds, suitable for being used as adsorbents, catalysts, and desiccants. These reactive aluminas are generally prepared by the hydrothermal transformation of aluminum hydroxides and alumina gels.

The sol-gel process represents an established method to synthesize nanoporous oxide materials and thin films, including in the alumina and silica systems [1-4]. Among the well-known advantages of the sol-gel method, it must be mentioned the possibility to obtain coatings with specific controlled porosity. This is of crucial importance for the properties that must be obtained for catalytic applications.

Ceramic and metallic honeycombs are of great importance as catalytic substrates in processes that aim at the ecosystem protection e.g. ozone decomposition or control of the waste gases from the intern combustion engines. For an increased functionality of the substrate, the honeycomb surface has to be coated with a highly porous adsorbing layer based on alumina, silica or alumina-silica [5]. Because ozone is toxic to the human organism, there is a continuous demand for efficient catalysts in the decomposition of residual ozone from various processes such as cellulose bleaching or water ozonation [6]. Manganese oxide is well known for its high catalytic activity for ozone decomposition [7]. Either honeycomb or classic type, the manganese based catalysts are usually prepared by impregnation method, from pre-formed alumina/silica substrate.

Despite the large number of studies concerning sol-gel aluminas and silicas, literature data regarding the obtaining of films doped with manganese for catalytic applications have not been noticed. Gouvea et al. [8] has used the MnO as additive for α-Al_{2}O_{3}, in order to accelerate sintering rate and grain growth. Ocaha et al. [9] has referred to Mn(II)-doped alumina with important application in the field of ceramic pigments. Castro and Gouveia [10] have studied the effect of manganese ions introduced in alumina synthesized by Pechini’s route. They established that Mn^{2+} ions produce the decrease of the transition temperature of γ- to α-alumina. Regarding the sol-gel silica films doped with various transition metals, for Mn^{2+} only one reference was found [11].

The literature data of the last few years confirm that there are some attempts in order to prepare aqueous (colloidal) sol-gel films. Unfortunately, they refer only to oxide systems with optical [12-16], electro-optical [17,18] or magneto-optical, respectively magnetic properties [19]. Being less expensive and less toxic than the alkoxide route of the sol-gel method, the aqueous (colloidal) route has presented a great interest for our group.

The purpose of our work was to prepare manganese containing alumina and silica coatings and powders using both routes of the sol-gel method: the alkoxide and the aqueous (colloidal) one. The prepared powders were tested as catalysts for the ozone decomposition process.
2. Experimental

The Mn$^{2+}$-doped alumina coatings and powders were obtained by one step co-gelation of both cations, using the alkoxide route of the sol-gel process. Aluminum isopropoxide [Al(O-iC$_3$H$_7$)] from Merck was used as Al$_2$O$_3$ source, H$_2$O as solvent, CH$_3$COOH as catalyst, and Mn(NO$_3$)$_2$·4H$_2$O as Mn$^{2+}$ source. The presence of the catalyst is necessary in order to ensure the formation of o xo and acetate bidentate bridges that are essential for obtaining of polymer chains, suitable for the films formation. The solution composition, expressed in molar ratios, was: H$_2$O/Al(O-iC$_3$H$_7$)$_2$ = 100; CH$_3$COOH/Al(O-iC$_3$H$_7$)$_2$ = 1.55; Mn$^{2+}$/Al(O-iC$_3$H$_7$)$_2$ = 0.07. The pH was 3.

The Mn$^{2+}$-doped silica coatings and powders were obtained using the aqueous (colloidal) route of the sol-gel method. The SiO$_2$ source was a sodium silicate solution from Merck, which was destabilised with a mineral acid (HNO$_3$ - 25 wt. %) in order to produce the gelation. The aqueous sol-gel route being used for the first time in such kind of applications, a preliminary study of the gelation parameters was realized, in order to establish the best conditions, imposing the choosing of certain "pairs" of parameters.

In order to obtain stable solutions at high SiO$_2$ concentrations (between 3-14 %) an alkaline pH (pH > 9.5) is required. Or, it is well known the fact that solutions of Mn$^{2+}$ salts oxidize in an alkaline (even neutral) pH, leading to the MnO$_2$ precipitate. In order to ensure acidic conditions for synthesis, the sodium silicate solution diluted to a 2% SiO$_2$ concentration and the 5.5 value of pH were chosen.

In order to enhance the adherence of the films and their porosity (after the thermal treatment), a quantity of dimethylsulphoxide (DMS) was added to the reaction mixture. The molar ratio Si:DMS was of 1:0.1.

The Mn(NO$_3$)$_2$: 4H$_2$O was also introduced in the reaction mixture as Mn$^{2+}$ source.

The weight percentage of Mn$^{2+}$ related to Al$_2$O$_3$, respectively SiO$_2$ was of 7%. At 20 °C (the gelation temperature of both unsupported gels), alumina-doped material has gelled in 24 hours, while silica-doped one, in only 2.5 hours.

All films were realised by dipping, using an extraction speed of 5 cm/min. Based on DTA/TG analysis of the unsupported gels, the thermal treatment at 500°C, for one hour was chosen for the films densification. The rate of heating was of 1 °C/min. The used supports were: silica wafer and metal (refractory alloy).

The films were characterised by: X-ray diffraction (XRD), using a Scintag XDS 2000 Diffractometer and Spectroellipsometry (SE), using a spectral ellipsometer Sentech SE 850.

The unsupported gels (resulted by the gelation of the solutions used for film depositions) were characterized by DTA/TG analysis (using a MOM Derivatograph OD 103 with a heating rate of 5 °C/min up to 1000 °C).

The initial gels as well as the powders obtained after thermal treatment were characterized by IR spectroscopy, using a Carl Zeiss Jena Specord 75 Spectrophotometer in 4000-400 cm$^{-1}$ range. TEM and SAED with a Jeol 2000CX equipment with a working tension of 200 kV and by the BET method (adsorption of krypton at temperature of liquid nitrogen) from textural point of view.

The catalytic behaviour of the manganese containing silica and alumina samples was checked out for ozone decomposition process. In this respect, the catalytic activity of the thermally treated powders was evaluated on the basis of the catalytic conversion efficiency for ozone into oxygen. The testing installation contains a catalytic aluminum reactor (Ø = 4 mm) thermostated at 25.0 °C. Ozone was prepared from oxygen, with a generator manufactured by S.C.RAAL S.A. Bistriţa (Romania). Equal amounts of 0.100 mg testing powders, diluted 1:2 with quartz, were disposed on the glass wool bed and analyzed using an O$_3$/O$_2$ gas flow of 15 dm$^3$/h; the initial concentration of ozone was 79.0 – 81.0 mg/dm$^3$. Ozone concentration before and after passing through the catalyst layer was determined with an OZOMAT analyser (ANEROS). The measurements were performed after the stabilization of the system.

3. Results and discussion

In the mentioned experimental conditions, colourless undoped alumina and silica films and gels were obtained. In the presence of manganese, in both cases, a brown-violet colour has been observed. The as deposited films were homogeneous and continuous formed on the substrate. The films showed good adherence to both the Si/SiO$_2$ and refractory metal substrates. By thermal treatment the silica-based coating presented an exfoliation tendency and was not further characterized. A possible explanation, in this case, could consist in the absence of a special treatment of the metallic surface prior to the film deposition, that could ensure a better adhesion of the coating, due to some bonds formed between the substrate and the film [21]. Another possibility to improve the adherence of the silica coating on the metal substrate could be the use of different chelating agents or the increase of DMS concentration into the reaction mixture.

3.1. Films characterisation

The structural and optical properties of the annealed coatings were studied on the alumina based films obtained by deposition on Si wafer (Si/SiO$_2$ - 5000 Å) support.

In the case of manganese-doped alumina coating, the calculated refractive index comparatively with that of the pure Al$_2$O$_3$ film deposited on the same support is presented in Table 1. One may notice that the presence of Mn decreases the refractive index (n) of the film due either to the increase of the absorption coefficient (Fig. 1) or to the decrease of the densification tendency of the films.
Table 1. Refractive index versus wavelength for undoped and doped alumina films.

<table>
<thead>
<tr>
<th>Wavelength (λ) (nm)</th>
<th>Refractive index (n)</th>
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<tbody>
<tr>
<td></td>
<td>undoped-alumina films</td>
</tr>
<tr>
<td>450</td>
<td>1.7770</td>
</tr>
<tr>
<td>550</td>
<td>1.7680</td>
</tr>
<tr>
<td>700</td>
<td>1.7620</td>
</tr>
</tbody>
</table>

Fig. 1 (a and b) presents, for exemplification, the SE results obtained for the Mn-doped alumina coatings.

Fig. 2. The XRD patterns of alumina (a) and manganese-doped alumina films (b).

3.2. Powders characterisation

The results of the structural characterization of the unsupported gels, obtained by IR spectroscopy are presented in Fig. 3 (a and b).

Fig. 3. IR spectra of the manganese-doped alumina (a) and silica (b) gels.
Fig. 3a presents IR characteristic bands for the Mn-doped alumina sample. The characteristic vibrations of condensed AlO₆ octahedra from 570 cm⁻¹ and of the condensed AlO₄ tetrahedra from 780 cm⁻¹ are slightly displaced, probably, due to the formation of Al-O-Mn bonds in the as prepared gel. The IR spectrum of manganese doped silica (Fig. 3b) presents the characteristic vibration bands for the Si-O-Si network. In both cases the presence of Mn could be surely assumed only by the presence of the vibration band of nitrate anion from 1350 cm⁻¹. The structural OH and H₂O vibrations are also present in both cases.

The TEM and SAED results on the manganese doped un-supported gels are presented in the Figs. 4 and 5.

![TEM (a) and SEAD (b) image of the manganese-doped alumina gel.](Image)

![TEM (a) and SEAD (b) image of the manganese-doped silica gel.](Image)

In the case of the Mn doped alumina gel the SAED reflexions correspond clearly to γ-alumina. The sample consists from aggregates of 2-3 microns formed by nanoparticles of lamellar morphology with thickness of about 5 nm and diameter of about 30 nm (Fig. 4a and b).

The TEM image of the SiO₂ based sample (Fig. 5a) shows micron size aggregates composed by quasi-amorphous nanoparticles of about 3 to 5 nm in diameter. The SAED pattern (Fig. 5b) presents some diffuse maxima that could not be assigned to any SiO₂ crystalline structure, but fit well to the MnO₂ rutile structure reflections: (111) with 0.31 nm lattice plane distance and (101) with 0.23 nm lattice plane distance.

In this way, the presence of Mn could be directly put in evidence in the silica-based gel.

This can be probably explained by the easy nucleation properties of the rutile structure in a stable amorphous matrix as SiO₂. In the case of alumina-based gel the nucleation of γ-alumina structure will stop probably a second structure nucleation

3.3. Textural and catalytic properties

The specific surface area for both manganese doped gels is presented in the Table 2. As compared to the specific area of the undoped alumina and silica gels, that have 184 m²/g and 177 m²/g, respectively, the doped gels show higher values, due to a higher degree of disorder. This behaviour is usual in the case of polycomponent gels, due to the disorder increase of the network [22].

In order to establish the catalytic properties of the as obtained materials, preliminary tests on the unsupported gels have been accomplished. The catalytic activity of the thermally treated powders was evaluated on the basis of the conversion efficiency for the ozone decomposition process:

\[
\text{O}_3 \xrightarrow{k_1} \frac{3}{2} \text{O}_2
\]

The catalytic conversion efficiency was determined with the formula:

\[
\eta = \frac{(C_o - C)}{C_o} \cdot 100
\]

where C₀ and C are the O₃ concentrations before and after passing through the catalyst layer. The medium value of the conversion efficiency (\(\eta\)) of manganese doped samples was determined in order to be compared with \(\eta\) of the undoped material.

The results of the catalytic tests for the ozone decomposition, together with the textural characteristics of the thermally treated gels are presented in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>(S_{\sigma}(BET)) (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Conversion efficiency* ((\eta)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>362</td>
<td>0.32</td>
<td>6.9</td>
</tr>
<tr>
<td>Silica</td>
<td>210</td>
<td>0.33</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*for 0.10 g Mn-doped samples (gas flow=15 dm³/h; \(C_0\) =79.0 – 81.0 mg/dm³ ozone in oxygen)

Both manganese doped samples are catalytically active and suitable for use in ozone decomposition process. In our experimental conditions, Mn-doped alumina sample is about 3 times more efficient for ozone decomposition process than Mn-doped silica material, probable due to its superior textural properties.
It is worth to mentioning that the undoped alumina and silica powders have negligible catalytic activity for ozone decomposition process.

Some unsolved problems are under evaluation: the establishing of the oxidation state of manganese in films and gels, the improvement of the adherence of the manganese-doped silica films to the metallic supports and the establishing of the catalytic activity of the sol-gel coatings deposited on the refractory alloy support.

4. Conclusions

Either honeycomb or classic type, the manganese based catalysts are usually prepared by impregnation method, from pre-formed alumina/silica substrate. The paper presents our attempts to prepare directly (by coagulation of both cations), by the sol-gel route, manganese containing alumina and silica porous layers deposited onto metallic supports.

Mn-doped alumina and silica coatings have been prepared, using both routes of the sol-gel method: the alkoxyde and the colloidal one.

Textural and catalytic properties determined on the thermally treated powders (unsupported gels) pointed out that both samples show catalytic activity in ozone decomposition process, thus illustrating that Mn-doped materials could be prepared by this synthesis routes.

The results of the performed tests proved that the sol-gel route could be used for the coating of metallic substrates with Mn-doped alumina porous layers in order to manufacture catalytic structures for ozone decomposition process.

References


*Corresponding author: mzaharescu@chimfiz.icf.ro