NANOSIZED GOLD AS A PROMOTER FOR HYDROCARBON PARTIAL OXIDATION IN PEROVSKITE COMPOSITES

P. L. Antonucci¹, S. Barison², M. Battagliarin², E. M. Bauer³, C. Bellitto³, S. Candamano¹, S. Daolio², M. Fabrizio², E. Miorin³, G. Righini³, V. Modafferi¹

¹Department of Mechanics and Materials, University of Reggio Calabria
Località Feo di Vito, 89100 Reggio Calabria, Italy
²CNR - Institute for Energetics and Interphases
Corso Stati Uniti, 4, 35127 Padova, Italy
³CNR - Institute of Structure of Matter, Area della Ricerca di Roma 1
Via Salaria km 29,300, 00016 Monterotondo Scalo (Roma), Italy

ABSTRACT

La₁₋ₓSrₓMnO₃ has been studied as anodic material for propane reforming. With this goal, nanostructured La₁₋ₓSrₓMnO₃ (x=0.40) perovskite powder was synthesized by a modified Pechini process. We have attempted to improve the catalytic performance of these materials by synthesizing nanosized Au/La₁₋ₓSrₓMnO₃ composites, and investigating the gold-promoting effect for hydrocarbon reforming. The structural characterization identified single-phase perovskite powders and the morphological investigations verified the nanocrystalline powders structure and the presence of a homogeneous dispersion of gold nanoparticles in composites. Catalytic tests revealed high propane conversions when LSM was used in partial oxidation conditions. Moreover, a slight increase in propane conversion was detected when Au/LSM composites were tested under the same conditions, and structural characterization showed higher powder stability in the presence of gold. Analyses of powder morphology and carbon deposition after catalytic tests are discussed.

INTRODUCTION

In the case of hydrocarbon-fuelled SOFCs, a fuel processing system is required that converts hydrocarbons into a mixture of hydrogen and carbon monoxide before feeding it to SOFC stacks. Direct hydrocarbon fuel cells have been developed using SOFCs at intermediate temperatures (i.e., 500–800°C). This eliminates the need for fuel processing reactions before being fed to the stacks. Usually, the anodic catalysts used in SOFCs are based on nickel, especially when the fuel is pure H₂. However, hydrocarbon fuels (e.g., propane) cause severe carbon deposition and hence rapid deactivation of the catalyst (1,2). Therefore, the search for new anodic materials to avoid carbon deposition is one of the key issues in this field. With this target, a perovskite compound, La₉₅Sr₀₄₅MnO₃, has been studied as anodic material in this work. Moreover, considering that several noble metals show excellent catalytic activity for hydrocarbon reforming (3), nanosized gold has been tested as a promoter of the catalytic performance of the perovskite anodic material.
Among solid oxides exploited to prepare efficient fuel cells, La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} manganites have been widely studied and used as cathodes (4) because of their good electronic conductivity at the working temperatures, good stability, and compatibility with other cell components. However, the variation of manganite stoichiometry can sensibly modify its physical properties, and, in particular, the La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (x \approx 0.4) perovskite features higher electrical conductivity and lower interface resistance (5). La\textsubscript{0.6}Sr\textsubscript{0.4}MnO\textsubscript{3} has already been demonstrated to be, among all La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} perovskites, a more active catalyst for hydrocarbon oxidation at low temperatures because of the significant presence of surface oxygen vacancies and therefore of the possibility of oxygen adsorption on its surface (6). Moreover it has been observed that gold promoted CH\textsubscript{4} oxidation and reforming over Au/MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts (7). In fact, the catalytic performance of gold is significantly adjustable by controlling particle size and by careful selection of the metal oxide substrate (8,9). For this purpose, nanosized Au/La\textsubscript{0.5}Sr\textsubscript{0.4}MnO\textsubscript{3} perovskite composites have been synthesized in this work. La\textsubscript{0.5}Sr\textsubscript{0.4}MnO\textsubscript{3} perovskite powders were prepared by a modified Pechini sol-gel synthesis (10), and an ultrasound-driven process were chosen for gold nanoparticle deposition (11,12).

The perovskite powders and gold-perovskite composites were analyzed by means of X-ray powder diffraction (XRPD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), BET measurements, and inductively coupled plasma mass spectrometry (ICP-MS) to ascertain chemical composition, crystal structure, and morphology.

Therefore, the catalytic performance of La\textsubscript{0.5}Sr\textsubscript{0.4}MnO\textsubscript{3} (LSM) and Au/LSM composites was tested in propane partial oxidation (POX) reaction conditions. The characterization of the catalysts that were used is discussed.

**EXPERIMENTAL**

**Perovskite Powders Synthesis Procedure**

The polymeric precursors were synthesized starting from a water solution containing stoichiometric quantities of La(NO\textsubscript{3})\textsubscript{3}-6H\textsubscript{2}O (Merck, 99%), Sr(NO\textsubscript{3})\textsubscript{2} (Carlo Erba, 99.5%) and Mn(CH\textsubscript{3}COO)\textsubscript{2}-4H\textsubscript{2}O (Carlo Erba, 99%). The final metal nitrate molar concentration was 0.5 mol L\textsuperscript{-1}. Hence, an aqueous solution containing citric acid and ethylene glycol was added to the metal nitrates solution (citric acid:metal nitrates:ethylene glycol molar ratios = 5:1:4,3). The mixture was stirred at 70°C for 12 hr. Water was then slowly evaporated on a hot plate and the resulting brown gel dried and then heated to 400°C for 2 hr in air to decompose the organic part of the polymeric resin. The resulting spongy precursor powder was ball-milled and the material obtained was finally calcined at 1000°C for 2 hr in air (heating rate 6°/min).

**Gold Nanoparticles Deposition Procedure**

A deposition-precipitation technique was used for the gold nanoparticle synthesis. A gold precursor solution was prepared by dissolving the desired amount (1 wt%) of hydrate HAuCl\textsubscript{4} (Strem Chemicals, 99.9%) in deionized water. In a second step, a few drops of
an ammonia solution (Riedel de Haën, NH$_3$ 33%) were added to a perovskite powder suspension in deionized water until a final pH of 8–9 was reached. The gold precursor solution was then added dropwise under stirring to the LSM suspension. After sonication in an ultrasonic bath (Sintec Srl, 22 kHz) for 15 min, the dispersion was filtered and the sample was washed several times with deionized water, dried at 100°C for 2 h and heated at 300°C for 4 hr in air.

**Powders Characterization**

X-ray powder diffraction patterns were recorded at room temperature using an automated Seifert XRD-3000 diffractometer (flat plate sample, curved graphite single-crystal monochromator [Cu (Kα) $\lambda = 1.542$ Å] with the position sensitive detector) operating in a constant scan mode over the angular range 3 < 2θ < 100°, with steps of 0.02° and 8 s counting time per step. The structural refinements were carried out by the Rietveld method using a GSAS Program suite (13). After fitting of separate reflections, the Warren-Averbach method was used for Fourier analysis of the peaks and calculation of mean crystallite dimensions. The nominal stoichiometries were verified using an ICP–MS (Thermo, model X7). Morphological investigations of fresh catalysts were carried out by scanning electron microscopy (Jeol, model 5600LV) and TEM (Jeol, model JEM 3010). The morphology of used catalysts was inspected by TEM using a Philips CM12 instrument. Specimens were prepared by depositing on carbon-supported films a drop of a suspension obtained by ultrasonic dispersion of the catalysts in isopropyl alcohol. A Carlo Erba CHNS elemental analyzer was used to determine the amount of deposited carbon on the catalysts after reaction.

**Catalytic Activity Measurements**

Catalytic activity was measured at atmospheric pressure in a quartz microreactor (4 mm ID) placed in a ceramic tube furnace, at a space velocity of 60,000 hr$^{-1}$, in the temperature range 600–800°C. The catalyst, placed between quartz wool in the middle of the reactor, was diluted with SiC (SiC/catalyst = 2). The temperature of the catalyst bed was monitored with a thermocouple sheathed in a quartz thermowell inserted into the reactor bed. The gas lines were maintained at approximately 70°C to prevent condensation. Before passing into the gas chromatograph, water was eliminated from the reactor outlet gases by a condenser. Gases were fed with properly calibrated mass flow controllers (Brooks 5850S) after purification by Deoxo Gas Clean Filters (Chrompack) and molecular sieve traps. The gaseous mixture inlet flow was adjusted to obtain the following molar ratios: oxygen to carbon (O/C) = 0.5. The total inlet flow was fixed at 150 cc/min, using nitrogen as balance. Reaction streams were analyzed by gas chromatography (Chrompack 9001 instrument) equipped with a two-column system (13X molecular sieve and Porapack sh 172 columns) and TCD. The catalytic activity results were generally taken 90 min after the setting of the reaction conditions and reproducible data were obtained for registration periods of at least 60 min.

**RESULTS AND DISCUSSION**

The modified Pechini sol-gel process described in this work ensured homogeneous mixing of metallic cations on a molecular level using citric acid and ethylene glycol as
complexation and polymerization agents, respectively. Pure mixed metal oxides can be obtained by this synthetic procedure at lower calcination temperatures than the usual solid state synthesis, and grain growth can often be limited up to a nanosized level. Figure 1 shows the XRD patterns of $\text{La}_{0.59}\text{Sr}_{0.41}\text{MnO}_3$ (LSM) and Au/$\text{La}_{0.59}\text{Sr}_{0.41}\text{MnO}_3$ powders obtained by the above described techniques and calcined at 1000°C.

![Figure 1. XRD patterns of $\text{La}_{0.59}\text{Sr}_{0.41}\text{MnO}_3$ and Au/$\text{La}_{0.59}\text{Sr}_{0.41}\text{MnO}_3$ powders.](image)

The Rietveld refinement ascertained for LSM a pure and single phase perovskite structure and permitted identification of a rhombohedral unit cell with the following unit cell parameters: $a=5.467$ Å and $c=13.343$ Å. BET measurements showed surface area of about 5.3 m$^2$/g after treatment at 1000°C. Structural characterization of the Au/LSM composites allowed to identify weak gold reflection signals indicating a face centered cubic structure ($a=4.075$ Å). Calculations of the mean crystallites dimensions for powders treated at 1000°C were based on size distributions whose modes ranged from 20 to 45 nm, as per the couples of crystallographic planes considered.

ICP-MS analyses verified the powders purity and confirmed the stoichiometry ($\text{La}_{0.59}\text{Sr}_{0.41}\text{MnO}_3$) both by standard addition method and trough calibration curves of the analytes. In the case of gold-perovskite composites obtained from the solutions containing 1 wt% of gold, ICP-MS analyses revealed the presence of gold amounts around $0.7 \pm 0.1$ wt% in the powders.

SEM observations assured that the Pechini process favored the formation of ultra-fine particles. In fact, Figure 2 shows a SEM micrograph recorded for the LSM obtained by the Pechini method and treated at 1000°C, where the presence of small aggregates of nanoparticles was detected.

TEM investigations of the same powders showed the presence of compact agglomerates that maintained the nanocrystalline structure: see, as an example, a TEM micrograph recorded in bright field mode (Figure 3). Calculating the particles diameters from TEM micrographs recorded in dark field mode (where the nanoparticles were highlighted) for powders treated at 1000°C, a size distribution centered around 40–60 nm was estimated, which is comparable to XRD data.
TEM investigations of Au/LSM composites revealed a homogeneous distribution of gold nanoparticles on the manganite powders surface, having dimensions \( \leq 5 \) nm. As an example, TEM micrographs for a Au/La\(_{0.59}\)Sr\(_{0.41}\)MnO\(_3\) composite, with a gold amount around 0.7 wt\%, are reported in Figure 4.
The catalytic activity measurements of the perovskite and gold/perovskite composite were performed by the partial oxidation reaction of propane and an oxygen to carbon ratio (O/C) of 0.5 (oxygen to propane molar ratio = 1.5) was chosen. High conversions were obtained under POX conditions. Table 1 summarizes the products composition percentages for both LSM and Au/LSM at the investigated temperatures. Both catalysts attained nearly 100% conversion already at 600°C.

Table 1. Product composition (%) for propane partial oxidation.

| T °C | C₃H₈ | H₂  | CO  | CO₂ | C₂H₄ | CH₄ | O₂  | others |
|------|------|-----|-----|-----|------|-----|-----|--------|
| 600  | 3,26 | 22,87 | 24,10 | 8,67 | 13,17 | 17,46 | 0,00 | 11,43  |
| 700  | 0,14 | 25,47 | 27,30 | 4,37 | 9,68  | 17,07 | 0,00 | 16,70  |
| 800  | 0,00 | 29,80 | 27,70 | 3,70 | 8,80  | 15,30 | 0,00 | 15,30  |

| T °C | C₃H₈ | H₂  | CO  | CO₂ | C₂H₄ | CH₄ | O₂  | others |
|------|------|-----|-----|-----|------|-----|-----|--------|
| 600  | 0,53 | 26,27 | 26,99 | 3,5  | 11,41 | 20,14 | 0   | 11,12  |
| 700  | 0,48 | 25,18 | 26,69 | 2,27 | 13,27 | 20,00 | 0   | 12,18  |
| 800  | 0,38 | 24,08 | 25,26 | 2,82 | 14,72 | 22,31 | 0   | 10,37  |

A nearly equimolar syngas composition (H₂:CO≈1) was obtained in the entire temperature range with the gold catalyst, the rest of the product outlet being mainly methane and ethylene. The LSM sample showed a similar catalytic behavior starting from 700°C; at 600°C a much lower conversion was obtained (about 50%) and the main reaction product was CO₂.

Figure 5 shows the XRD patterns of as prepared LSM and of LSM and Au/LSM catalysts after reactions. The XRD analyses of used catalysts that demonstrated that the single perovskite phase is not stable under partial oxidation conditions. In fact, peaks related to lanthanum oxide (2θ ≈ 26.8, 28.2, 31.2, etc.) were detected. Nevertheless, a higher stability for Au/LSM composites was observed.
The amounts of carbon deposited on the catalysts in the course of the reactions, obtained by CHNS measurements, are reported in Table 2. A small amount of carbon was observed for dry conditions of partial oxidation. However, the content of deposited carbon was considerably lower than that observed for Ni-based catalysts under comparable reaction conditions (2).

Table 2. Carbon content (wt/wt%) of catalysts after partial oxidation.

|        | LSM | Au/LSM |
|--------|-----|--------|
|        | 3.71| 4.38   |

Figure 6 shows TEM micrographs of used Au/LSM composites where carbon deposition was observed (Figure 6a). Moreover, a partial aggregation of LSM grains and gold nanoparticles was observed (Figure 6b), and vaporization of some gold nanoparticles can be supposed. Therefore, the stability of these perovskite composites needs to be increased. Future work will be to synthesize more stable nanosized Au/perovskite composites such as Au/La$_{1-x}$Sr$_x$Cr$_{1-y}$Mn$_y$O$_3$ and catalytic investigations of perovskite materials, which show good performance and stability as anodic catalysts for methane reforming (14).

**CONCLUSIONS**

The present investigation focused on studying La$_{0.59}$Sr$_{0.41}$MnO$_3$ and Au/La$_{0.59}$Sr$_{0.41}$MnO$_3$ composites as anodic materials for hydrocarbon reforming. In particular, the nanostructured Au/La$_{0.59}$Sr$_{0.41}$MnO$_3$ composites gave good results on the propane conversion under partial oxidation conditions. A low carbon deposition was detected, but limited stability Au/LSM composites and, particularly, of LSM powders was confirmed by the characterization of the catalysts after catalytic reactions.

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