Catalysis Today 157 (2010) 131–136

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Simple approach to prepare mesoporous silica supported mixed-oxide nanoparticles by *in situ* autocombustion procedure

D. Sellam[a,b], M. Bonne[a], S. Arrii-Clacens[a], G. Lafaye[a], N. Bion[a], S. Tezkratt[b], S. Royer[a,*], P. Marécot[a], D. Duprez[a]

[a] *Université de Poitiers, LACCO UMR 6503 CNRS, 40 avenue du recteur Pineau, 86022 Poitiers, France*
[b] *LCAGC, Hasnaoua 1, Université Mouloud Mammeri, Tizi Ouzou 15000, Algeria*

ARTICLE INFO

Article history:
Available online 14 April 2010

Keywords:
Autocombustion
Perovskite
Mesoporous
Nanoparticles
Oxygen mobility

ABSTRACT

$LaCoO_3$-based nanocomposites were prepared by an *in situ* autocombustion procedure of a glycine–nitrate complex in mesoporous silica supports. For this purpose, two silica supports with different pore sizes (3.0 nm for the HMS-type silica; 8.2 nm for the SBA15-type silica) were prepared. The final materials were characterized using XRD, TEM, N_2-sorption and reactivities evaluated using oxygen isotopic exchange (OIE). One interesting point is the limited pore plugging, due to the low particle size obtained, when synthesis is specifically performed in large pore silica support (SBA15), as suggested by the limited pore volume decrease with respect to the HMS-based system. TEM coupled with EDXS analyses suggest the formation of crystalline mixed-oxide nanoparticles which have been observed with a cobalt to lanthanum ratio always close to 1. These nanoparticles exhibit high oxygen exchange capacity (1.2–2.3 times higher exchange capacities after 60 min of reaction), albeit a lower initial rate of exchange compared to the bulk reference sample (due to residual carbonate exchange). At the light of these results, it has been concluded that this method is efficient for producing nanocrystalline particles dispersed in silica pore structure.

1. Introduction

During the past 40 years, a growing attention from the catalysis community has been paid on perovskite-type mixed-oxides, of general formula ABO_3. Indeed, the pioneer works from Libby [1] and Voorhoeve et al. [2,3] evidenced a high activity of perovskites in oxidation reaction. In some rare cases, perovskites were found to exhibit catalytic activities comparable to noble-metal based catalysts [4]. Hence, these purely oxidic solids were logically proposed as potential candidates for the substitution of expensive and non thermally stable noble-metal oxidation catalysts [5], and were successfully introduced in three-way catalyst formulation by Dahaïtsu Motors [6]. Among the wide range of compositions that can be achieved (perovskite structure can be achieved when the tolerance factor defined as a function of the component ionic radii lies between 0.75 and 1), only a few are reported to be active. According to the literature, systems with lanthanum in A position, and cobalt or manganese in B position, are the most studied perovskite systems in gas phase oxidation reactions [7–9]. Recently, many successful attempts to use perovskite in other redox heterogeneous catalytic reaction than oxidation [10–15] were reported. In parallel with this extensive use of mixed-oxides in heterogeneous catalysis, much more efficient synthesis procedures were developed in order to obtain nanocrystalline perovskites presenting higher surface areas. Best results were obtained using autocombustion [16,17], reactive grinding (or mechanosynthesis) [18,19], and more recently nanocasting [20,21]. Unfortunately, such procedures always lead to polycrystalline solids having crystal size ranging from 10 nm to 15 nm. One of the other alternative proposed in literature consists in stabilizing nanocrystals on a support, such as mesostructured silica [22–29]. In addition to the increase of surface area due to the limited size of the clusters, we can expect an additional increase in catalytic activity for redox reaction due to the increase in oxygen mobility as already observed on bulk perovskite [30]. Unfortunately, most of the studies reported the formation of perovskite nanocrystals close to the silica pore size thus leading to a significant pore clogging.

Herein, we present the results obtained from the synthesis and characterization of lanthanum cobalt based nanocomposites in silica supports of different porosity. Synthesis is performed using a novel procedure involving impregnation of a glycine complex, followed by a combustion step. Contrary to the conventional impregnation of a citrate gel [22,23], this method allows to obtain highly dispersed particles in a reduced porosity, without segregation of perovskite crystals on the periphery of the mesoporous support [27].

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* Corresponding author. Tel.: +33 (0)5 49 45 34 79; fax: +33 (0)5 49 45 37 41.
E-mail address: sebastien.royer@univ-poitiers.fr (S. Royer).

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doi:10.1016/j.cattod.2010.03.008

2. Experimental

2.1. Synthesis of the mesoporous supports

2.1.1. Synthesis of the HMS support (HMS)

A pure siliceous HMS support is synthesized according to a previous published procedure [31]. Typically, 76 mL of water is added to a solution containing 7.21 g of dodecylamine within 66 mL of absolute ethanol under stirring. After 90 min of dissolution, 26.8 g of TEOS is slowly added to the solution. After ageing, the white solid was recovered by filtration and washing. The solid was then dried at 75 °C for 2 days before being calcined at 600 °C for 6 h (*HMS-c600*).

2.1.2. Synthesis of the SBA-15 support (SBA15)

The SBA15 sample is prepared according to the procedure described by Roggenbuck et al. [32]. To a solution containing 12 g of P123 triblock copolymer in 370 mL of water and 37 mL of concentrated HCl previously heated at 40 °C, 24 g of TEOS is slowly added under stirring. After 6 h of ageing at 40 °C, the milky solution is transferred in an autoclave for hydrothermal treatment at 140 °C during 24 h. The solid is then recovered by filtration and washing. Finally, the solid is dried at 80 °C for one day before being calcined at 600 °C for 4 h (*SBA15-c600*).

2.2. In situ synthesis of the mixed-oxides

Perovskite loading in the composite is fixed at 15 wt.% over HMS and 20 wt.% over SBA15, namely *15LaCo-HMS* and *20LaCo-SBA15* nanocomposites, respectively. Masses of precursors ($La(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$) are adjusted to give after calcination, the desired loading. Corresponding masses of nitrate precursors are dissolved in 20 mL of distilled water, and glycine is added as complexing agent (ratio $(NO_3)^-$/glycine = 1). After mixing of the solution with 1.0 g of support, water is slowly evaporated, and temperature increased up to 300 °C for glycine auto-ignition. Before characterization, solids are calcined at 600 °C (*15LaCo-HMS-c600*) or 620 °C (*20LaCo-SBA15-c620*) for 4 h. Bulk $LaCoO_3$ is prepared as a reference using similar self-combustion conditions ($(NO_3)^-$/glycine ratio = 1).

2.3. Physical characterization

TG–DSC experiment is performed at each step of the synthesis on 20LaCo-SBA15. Signal is recorded between 50 °C and 800 °C under air flowing (total flow rate = 100 mL min^{-1}, temperature increase ramp = 5 °C min^{-1}) on a TA SDT 2960 instrument.

Powder wide-angle and small-angle XRD patterns are collected on a Bruker AXS D5005 X-ray diffractometer, using a Cu Kα radiation (λ = 1.54184 Å) as X-ray source. For small-angle analysis, signal is recorded for 2θ comprised between 0.75° and 5° with a step of 0.01° (step time of 10 s). For wide-angle analysis, signal is recorded for 2θ comprised between 10° and 50° with a step of 0.05° (step time of 2 s).

Specific surface area, pore size distribution and pore volume are obtained from N_2-sorption experiments. A known mass of sample was first heat treated under vacuum at 250 °C. Isotherms are collected on a Micromeritics TRISTAR instrument. The specific surface area, S_{BET}, is calculated from the linear part of the BET plot. The mesopore size distribution is determined from the desorption branch using the Barrett–Joyner–Halenda (BJH) formula. Mesopore volume is determined on the isotherms at $P/P_0 = 0.97$. ΔV_p is the pore volume decrease per weight percent of perovskite in the composite, calculated using the following formula:

$$\Delta V_p = \frac{((V_{p(\text{support})} - V_{p(\text{composite})})/V_{p(\text{support})}) \times 100}{\text{wt.\% perovskite}}$$

The pore structure, as well as the mixed-oxide particle distribution inside the silica grain, is evaluated by TEM coupled with energy dispersive X-ray spectroscopy (EDXS). Micrographs are obtained on a JEOL 2100 instrument (operated at 200 kV with a LaB_6 source and equipped with a Gatan UltraScan camera). Cation homogeneity inside silica, and composition of the crystallized particles are evaluated by EDX spectroscopy. Analysis is repeated on several nanoparticles in order to rach a mean value of mixed-oxide composition.

2.4. Oxygen isotopic exchange reaction $^{18}O/^{16}O$

The oxygen isotopic exchange (OIE) technique is used to evaluate oxygen mobility in the mixed-oxide phase in these novel composites and in the reference bulk perovskite sample. Full description of the exchange test and data treatment can be found elsewhere [27,30], and is only summarized here. The exchange mechanism can be described by the following equation, even if different mechanisms are depicted: $^{18}O_g + ^{16}O_s \rightarrow ^{16}O_g + ^{18}O_s$, where s and g refer to oxygen from the solid and from the gas phase, respectively. For the exchange experiment, an equivalent of 20 mg of perovksite is inserted in a microreactor. Then the sample is heated at its calcination temperature under O_2 (ramp = 10 °C min^{-1}, $Q_{O_2} = 20$ mL min^{-1}), cooled down at 450 °C under O_2 and maintained at the same temperature under dynamic vacuum. Pure $^{18}O_2$ at a pressure of about 56.0 mbar was introduced into the reactor. Partial pressure evolutions in $^{18}O_2$ (mass 36), $^{16}O_2$ (mass 32), and $^{16}O^{18}O$ (mass 34) are followed by mass spectrometry for an experiment time of 60 min. α_g^{60} is the fraction of ^{18}O in the gas phase at 60 min. N_{ex}^{60} corresponds to the number of oxygen atoms exchanged from the solid after 60 min.

3. Results and discussion

3.1. "In situ" formation of the mixed-oxide

As described in the experimental part, a classical autocombustion procedure (LaCo-Bulk) consists in a first step of nitrate precursor dissolution in water followed by complexation with a fuel such as glycine, urea or ammonium nitrate. After complexation, water is slowly evaporated at 100 °C until a viscous gel is obtained, then temperature is increased up to 300 °C for fuel auto-ignition, much less violent in the composites than for the bulk materials. An additional calcination step can be needed for residual carbon elimination (formed by incomplete glycine combustion). The TG–DSC curves obtained for the LaCo-SBA15 sample after each step of the synthesis are presented in Fig. 1a–c. As shown, after a drying step at 100 °C (Fig. 1a), two exothermal peaks occurred at 180 °C and 275 °C on the DSC curve that is ascribed to the combustion process. This later achieves at 300 °C, with no more exothermal process visible above this temperature. After autocombustion at 300 °C, we can observe that glycine combustion is incomplete, and a further decrease of 5 wt.% is observed at 275 °C (Fig. 1b). This weight loss is no more visible on the sample after further calcination at 620 °C, and residual weight loss is mainly attributed to water desorption (at low temperature, <200 °C) and to residual carbon combustion or support dehydration (at higher temperature than the calcination temperature, >620 °C). Overall, this clearly shows that the calcination step is necessary on the composites before their characterization or use as catalyst.

3.2. Pore structure in the nanocomposites

Small-angle X-ray diffraction patterns (supports and derived nanocomposites) are presented in Fig. 2. The HMS-c600 support