Simple and green synthesis of $LaMO_3$ perovskites (M= Mn, Fe, Co) by reactive grinding; properties in toluene oxidation reaction

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Abstract: This study presents the optimization of the $LaMO_3$ perovskite (M= Mn, Fe, Co) synthesis using reactive grinding. Reactive grinding presents the advantages to be simple to implement and does not need solvent for synthesis. A two steps procedure, consisting in high energy followed by low energy ball millings, was proposed. Significant increases in surface areas can be obtained, reaching for some samples > 60 m^2 g^{-1}. Redox and catalytic properties in toluene oxidation of materials were evaluated.

Keywords: VOCs total oxidation, reactive grinding, perovskite, nanoparticles.

1. Introduction

Among the different possible technologies to control Volatile Organic compounds (VOCs) emission, the catalytic oxidation process occupy a prominent place with their intrinsic characteristics, including limited energy consumption, a complete and selective elimination of pollutant. Although supported precious metal catalysts show excellent activities for the total oxidation of VOCs at low temperatures, their limited availability and fluctuating costs limit their utilizations. The key issue of environmental catalytic technology is consequently the availability of cheap, environmentally friendly and durable catalysts. Among promising candidates are transition metal containing mixed-oxides. $LaBO_3$ perovskites (B being the transition metal) show interesting catalytic activity and good stability in VOCs oxidation. However their textural and chemical properties are strongly dependent of the synthesis procedure, with low surface areas obtained using conventional preparations in solution mediated synthesis routes (≤ 20 $m^2.g^{-1}$)[1]. Reactive grinding is a common approach in metallurgy for the preparation of nanocrystalline inorganic materials. This technique is flexible, and presents attractive features that are synthesis at low temperature, atmospheric pressure, and without the use of solvents (except water in small amount). Textural properties of materials can be finely tuned by selecting appropriate experimental conditions such as grinding parameters and atmosphere[2]. In this study the reacting grinding approach has been applied to the preparation of $LaBO_3$ materials (B=Mn, Fe, Co). Mn, Fe and Co are the most promising elements from the first row of transition metal, to replace noble metals (Pt, Pd) as active phase for low temperature catalytic reaction in environmental field.

2. Experimental

Perovskite-type mixed transition metal oxides $LaMO_3$ (M=Mn, Fe or Co) were synthesized by solid-state grinding. Firstly, La_2O_3 and M_xO_y precursors were mixed homogeneously in stoichiometric ratio and calcined at 1100°C to obtain the perovskite phase (denoted -*c* material). Secondly, the grinding process of the calcined material consisted in two successive steps: (i) high energy ball milling (*hebm*, for 90 minutes, under static air, in stainless steel equipment) and (ii) low energy milling (*lebm*, different times, wet atmosphere, stainless steel equipment). Prior test, a final step of thermal stabilization (-*s*) was performed at 400°C for 3 hours under static air atmosphere. Physicochemical properties of the obtained $LaMO_3$ materials were evaluated after the different steps of synthesis (XRD, N_2-physisorption, H_2-TPR, ICP-AES, XPS, TEM). Catalytic performances were evaluated in toluene oxidation reaction. Conditions are: 0.2 g of catalyst; 1000 ppm toluene in 20 vol.% O_2 in N_2 at 100 mL.min^{-1}; temperature from 300°C to 150°C with temperature decrease rate of 0.5°C.min^{-1}.

3. Results and discussion

The perovskite phase has been successfully obtained for each composition after the calcination step (-*c* materials). Upon grinding process, significant modifications of the X-ray diffractograms have been observed. After *hebm* step, the crystal phase has been maintained but a significant broadening of the reflections has been observed, according to a decrease of mean crystal domain size (~ 25 nm). Then the *hebm* step ensures the fractioning of microcrystals into nanocrystals but the specific surface areas (SSA) remains low (< 5 m^2.g^{-1}). During *lebm* milling, and whatever step duration, similar $LaMO_3$ diffractograms have been obtained. However this second step of grinding allows the stabilization of higher SSA (for *lebm* of 2 h: 11, 32 and 74 m^2.g^{-1} for $LaMnO_3$, $LaFeO_3$ and $LaCoO_3$, respectively). Increase in surface areas are attributed to the modifications of the nanoparticles assembly in aggregates. ICP-AES analyses pointed out the presence of contaminating iron in $LaMnO_3$ and $LaCoO_3$ perovskites after milling processes. Therefore a compromise between grinding time (responsible for contamination) and final SSA has to be performed to maximize catalytic performances[3]. The investigation of the thermal stabilization shown a slight decrease in SSA until 400°C (Figure 1). At higher temperature the decrease in SSA was much more pronounced. Therefore a temperature of 400°C has been chosen for the stabilization of all perovskites prior to the catalytic tests. The evolution of the toluene conversion into CO_2 as a function of temperature for $LaCoO_3$ materials is shown in Figure 2. The catalytic performances can be ranked as follows: $LaCoO_3$-*c* < $LaCoO_3$-hebm-*s* < $LaCoO_3$-lebm-*s*. Clearly the reactive grinding procedure has a significant impact on the activity of $LaCO_3$. Modifications of catalytic activities are rationalized, not only in terms of textural properties evolution, but also taking into account modification of transition metal redox properties.

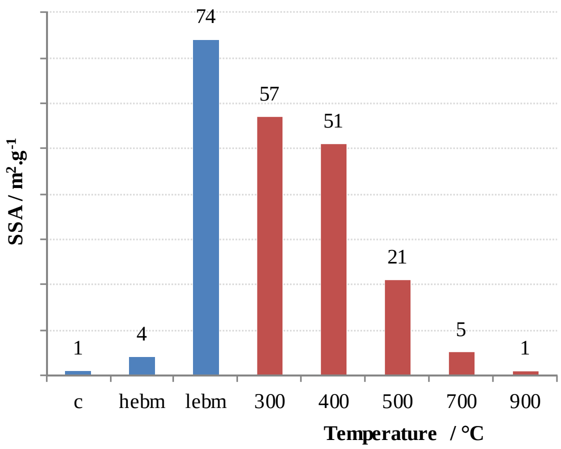

Figure 1. SSA evolution upon grinding processes and temperature of thermal stabilization ($LaCoO_3$-*lebm* samples).

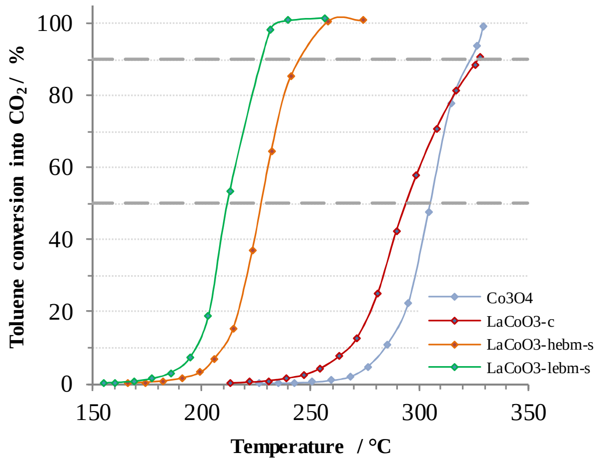

Figure 2. Light-off curves for toluene total oxidation ($LaCoO_3$ samples).

4. Conclusions

Reactive grinding has been proposed as a top-down synthesis approach to produce efficient $LaMO_3$ (M=Mn, Fe or Co) catalysts for VOCs removal. The best catalytic performances in toluene total oxidation have been obtained when using $LaCoO_3$, owing to their improved textural and redox properties after the grinding process and stabilization.

References

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