One pot synthesis of supported perovskytes to induce synergy effects in catalytic VOCs combustion

Sonia Gil[1*], Mélissandre Richard[3], Jose A. Diaz[2], Fabien Can[3], Nicolas Bion[3], Laurence Retailleau, Anne Giroir-Fendler[1]

[1]*Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France.*

[3]*Université de Poitiers, CNRS UMR 7285, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP) 4 rue Michel Brunet 86073 Poitiers Cedex 9 – France*

**corresponding author: sonia.gil@ircelyon.univ-lyon1.fr.*

Introduction

Environmental protection standards with respect to air pollutants such as volatile organic compounds (VOCs) are becoming increasingly stringent [1]. Also, even at low concentrations, VOCs can adversely affect biological systems and create major dysfunctions. Various technologies exist for eliminating VOCs: either (i) recovery processes that allow VOC reclamation, such as adsorption, absorption or separation; or (ii) destruction processes such as thermal or catalytic oxidation. This last method presents numerous advantages when the VOCs are present in very low quantities and when research is constantly devoted to the formulation of inexpensive catalytic systems that are effective at low temperature. The literature is an abundant source of basic research studies that have made it possible to understand the factors that govern catalytic properties [2]. Above and beyond the intrinsic properties of the elements of the periodic table, the combination of different phases can induce synergy effects that can activate these reactions at lower temperatures. Direct syntheses of active phases on supports that facilitate the migration of surface oxygen can significantly increase the exchange kinetics at the surface of these solid catalysts. Perspectives in this direction will allow the discovery of new catalysts for the special case of the complete oxidation of organic compound. Therefore, the aim of this work was to develop supported perovskites over different oxides and mixed oxides supports with different conductive properties, in order to compare their catalytic performance in the toluene total oxidation.

Materials and Methods

Perovskites $LaMnO_3$ (denoted LM) were prepared by the citrate route as already described [3]. The total oxidation of toluene was performed with 250 mg of catalyst placed over quartz wool in a U-type reactor. The reactant mixture containing 1000 ppm C_7H_8, 21% O_2 and He as carrier gas (GHSV=30000 h^{-1}) was introduced at room temperature followed by a ramp of 2°C min^{-1} up to 400°C. After this treatment, all catalysts were tested during the cooling ramp. The temperature-programmed and isothermal oxygen isotopic exchange (TPOIE and IOIE respectively) experiments were performed in a closed recycling setup with 20 mg of catalyst, as already described elsewhere [4]. The variation of $^{18}O_2$, $^{18}O^{16}O$, $^{16}O_2$ isotopes concentrations as a function of time- were continuously monitored by mass spectrometry. The curves allowed determine the initial rate of exchange (R_e), the atomic fraction of ^{18}O in the gas-phase (α_g) and the number of O atoms exchanged (N_e).

Results and Discussion

HR-TEM images (not shown) confirmed the synthesis of the $LaMnO_3$ on the support surface, also observed by the homogenous La:Mn ratio determined by ICP and XPS, as summarized in **Table 1**.

Table 1. Characterization results and catalytic performances of the supported perovskytes

Catalyst	Supported LM, SSA (m^2g^{-1})	XPS	ICP	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	R_e at 450°C (10^{+20} at/g/min)
$LaMnO_3$ (LM)	n.a.	n.a.	n.a.	290	345	0.2
LM/TiO_2	33	1.7	1.0	220	310	1.6
LM/YSZ	13	1.2	1.1	238	253	4.6

Catalytic results in a model VOC reaction, total oxidation of toluene (**Table 1)**, showed a clear improvement in the catalytic performance in presence of ionic or electronically conductive supports, such as YSZ and TiO_2 respectively. These results could be attributed to perovskite-support interactions. YSZ as catalyst support induces some interactions between oxygen vacancies and perovskite particles. The interaction of TiO_2 could change their reducibility. In order to better understand these phenomena, isotopic exchange experiments have been performed. **Figure 1** shows that the exchange activity of supported perovskites was higher than that observed for the bulk $LaMnO_3$ sample. Thus, LM/YSZ and the bulk perovskite presented similar trends, but the former is shifted to lower temperatures (below 550°C). This behavior is attributed to a decrease of the $LaMnO_3$ crystallites size when they were supported on YSZ. It resulted in a higher perovskite exposed surface area, leading to a higher R_e value obtained at 450°C in IOIE experiments. The improvement of the exchange activity of the LM/TiO_2 catalyst is attributed to the modification of the exchange mechanism, i.e., $^{16}O_2$ molecules appeared at the beginning of the reaction. Such a behavior could suggest a synergy effect between $LaMnO_3$ and TiO_2, which allowed the activation of the dioxygen molecules in the form of diatomic adsorbed species. Comparison between N_e values and the total number of O atoms present in $LaMnO_3$ confirmed that O atoms of TiO_2 support facilitate the migration of surface oxygen.

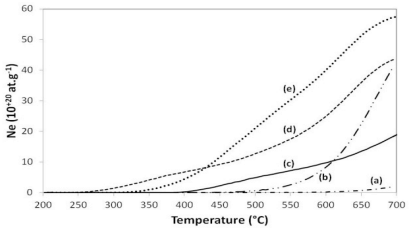

Figure 1. Evolution of N_e during the TPOIE experiments: (a) TiO_2, (b) YSZ, (c) LM+SiC, (d) LM/YSZ and (e) LM/TiO_2.

Significance

The one-pot preparation of supported $LaMnO_3$ was shown herein to be fast, efficient and successful to obtain supported perovskites. This perovskite phase appeared to interact with TiO_2 and YSZ supports in such a way that modified the catalytic oxidation of toluene, led to higher catalytic activity with the supported materials than that obtained with unsupported perovskite. This behavior could be attributed either to a greater dispersion of $LaMnO_3$ on an YSZ support or to an activation of the TiO_2 support.

References

1.a) D1999/13/CE European Council (March 11, 1999) b) D1882/2003 European Council (September 29, 2003) ; c) D 2004/42/CE European Council (April 21, 2004).

2. a) Spivey J.J., *Ind. Eng. Chem. Res*. **1987**, 26, 2165, b) Reddy B.M., Khan A., *Catal. Rev.* **2005**, 47, 257, c) Liotta L.F., *Applied Catal. B: Environ.* **2010**, 100, 403.

3. Zhang C., Guo Y., Lu G., Boreave A., Retailleau L., Baylet A., Giroir-Fendler A., Appl. Catal. B: Environ. **2014**, 148, 490.

4. Martin D., Duprez D., *J. Phys. Chem.* **1996**, 100, 9429.