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“EXAFS and XANES studies on supported perovskite catalysts”

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For the 08-01-210 experiment we requested 18 shifts at the beamline Gilda (Italian time) to perform XAS measurements on Mn, Co, Fe and La K edge of  $\text{LaMO}_3/\text{ZrO}_2$  (M = Mn, Co and Fe) supported materials. These shifts were divided into two different runs, the first for the transition metals K edge, and the second for lanthanum K edge. The present report is obviously detailing about the first and most important run, the second being just finished.

### Experimental

XAS measurements were performed at 77 K, in the transmission (for the reference samples) and fluorescence (for the supported samples) mode, at the beamline GILDA, ESRF, Grenoble (France) and were aimed to determine the nature of chemical species supported and disperse on zirconia as XRD technique could not detect too small particles.

$\text{LaMO}_3/\text{ZrO}_2$  materials containing 2, 6 and 12 weight percent of  $\text{LaMO}_3$  (M = Mn, Co and Fe) were measured in addition to some reference compounds, namely pure  $\text{LaMO}_3$  perovskites,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$  and  $\text{Fe}_2\text{O}_3$ . The zirconia oxide (surface area about  $100 \text{ m}^2/\text{g}$ ) and the supported powder samples were prepared in our laboratories; samples were mixed to an appropriate amount of boron nitride (BN) and pressed into pellets.

The XANES part of the experimental signal was obtained by subtracting a linear pre-edge and normalizing to one in correspondence of the first EXAFS oscillation. First derivatives were calculated. The EXAFS signal  $\chi(k)$  was extracted by using the “Autobk” program. Fourier transforms (FTs) for the signal  $k^3\chi(k)$  were calculated in the range  $2.5 < k < 11 \text{ \AA}^{-1}$  by using a Kaiser window. Structural information, for Co and Fe containing materials, was obtained by backtransforming the  $F(R)$  function in the  $0.8 - 4.0 \text{ \AA}$  range. Fits were performed using the theoretical phase and amplitude functions generated by the FEFF8 code. These functions were calibrated using the EXAFS spectra of the reference compounds.

### Results and Discussion

#### Mn containing samples

The profiles analysis of the XANES first derivatives reveals that the sample that markedly resembles to pure  $\text{LaMnO}_3$  perovskite is the most concentrated one (12%). Moreover, particularly in the 2 and 6% samples, the first derivative profiles show some structures both at lower and at higher energy with respect to the maximum that are typical for  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  respectively. Perhaps, in the samples with lower Mn content, manganese oxides can be formed on the surface of the zirconia support, thus inhibiting the formation of the perovskite phase.

For all the samples the FTs show an intense first shell Mn-O peak in the  $R = 0.8 - 2.0 \text{ \AA}$  range, which is evidently broadened towards low R values for the 2 and 6 % samples. Such an evidence could be explained with the presence, in these samples, of different Mn-O bond distances probably due to the presence of various Mn containing phases (perovskite and/or oxides). As to the second

shell features, only in the most concentrated sample the presence of barely intense structures can be noted whose position is equal to that of the second coordination shell (Mn-La, Mn-Mn) in the FT of pure LaMnO<sub>3</sub>. This evidence suggests the formation, in the 12% sample, of a perovskite phase very well dispersed on the zirconia support. In the same sample the presence of a Mn<sub>3</sub>O<sub>4</sub> phase cannot be excluded decisively because the FT for Mn<sub>3</sub>O<sub>4</sub> shows a second shell peak that appears in the same position as for LaMnO<sub>3</sub>. In all the samples, the high degree of dispersion of any phase (perovskite or manganese oxides) supported on the zirconia surface is really testified by the absence (in the 2 and 6% samples) or very low (in the 12% sample) intensity of the second and successive shell structures.

### **Co containing samples**

The profiles analysis of the XANES first derivatives reveals that the sample that markedly resembles to pure LaCoO<sub>3</sub> perovskite is the less concentrated one (2 %). Moreover, particularly in the 6 and 12 % samples, the first derivative profiles show some structures, at lower energy with respect to the maximum, that are typical for Co<sub>3</sub>O<sub>4</sub>. It seems that, with increasing Co content, cobalt oxide can be formed on the surface of the zirconia support, thus inhibiting the formation of the perovskite phase.

This hypothesis was confirmed by the EXAFS analysis. In the FTs, LaCoO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> show a first shell peak in the 1.0 – 2.0 Å range, while the second and third coordination shell structures differ in shape and position. Particularly, Co<sub>3</sub>O<sub>4</sub> reveals two different Co-Co contributions in the range 2.0 – 3.5 Å and an intense peak at about 4.8 Å, while LaCoO<sub>3</sub> presents a single second shell peak at about 3.1 Å, due to both Co-Co and Co-La contributions, and a broad, not very intense, peak at about 5.1 Å. As to the supported samples, the FTs reveal a broadening of the first shell peak, particularly evident for the 6 % sample, which could be due to a heterogeneity for Co-O contributions coming from different cobalt containing phases. However, for the FTs, the greatest differences appear in the 2.0 – 5.0 Å range. The 2 % Co containing material reveals a second shell structure in position typical for LaCoO<sub>3</sub>, while the 6 and 12 % samples show second shell structures which can be attributed both to perovskite and Co<sub>3</sub>O<sub>4</sub>. Best fits, performed by introducing the contributions of Co-O, Co-Co and Co-La confirm this evidence.

### **Fe containing samples**

The profiles analysis of the XANES first derivatives reveals that the samples are really very similar to LaFeO<sub>3</sub> pure perovskite. EXAFS data evidenced that supported phases are really very well dispersed. FTs show a first shell peak in the 0.8 – 2.1 Å range and only for the 12 % sample the presence of very little intense second shell features is revealed. These features can be attributed to perovskite, but the presence of Fe<sub>2</sub>O<sub>3</sub> cannot be decisively excluded. For all the samples best fits confirm the presence of the perovskite phase as the major and most abundant phase.

### **Conclusions**

XAS investigation on LaMO<sub>3</sub>/ZrO<sub>2</sub> supported materials (M = Mn, Co and Fe) gave really interesting results clearly revealing the presence of oxide phases different from perovskite only for Mn and Co containing samples: at lower transition metal loading (2, 6 %) for Mn samples, and higher (6, 12 %) for Co samples.

The greatest degree of particles dispersion on the zirconia surface was shown for Mn and Fe containing materials.