

Structural Analysis of Alkaline-Ion-Doped La-Mg Binary Oxide Catalysts by Means of La K-edge XAFS for Characterization of Highly Active OCM Species

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It is well known that Li-doped MgO is typical catalyst for oxidative coupling of methane (OCM). Rare-earth oxides such as Sm_2O_3 and La_2O_3 also show high OCM selectivity in the OCM reaction. We have presented that Li-doped Mg-La binary oxide containing 25 mol% La show higher OCM activity than Li-MgO or La_2O_3 . To examine the local structure of active La species, La K-edge XAFS was applied.

La-Mg binary oxides were prepared by co-precipitation method by using $\text{Mg}(\text{OH})_2$ and $\text{La}(\text{OH})_3$, followed by calcination at 873 K. Li-doped samples were prepared by impregnation of each oxide with LiNO_3 or Li_2SO_4 aqueous solution, and then dried overnight and calcined at 873 K. La K-edge XAFS spectra were measured at BL01B1 of SPring-8 with 1.2 mrad mirror and Si(311) double-crystal monochromator.

FT-EXAFS of the samples before and after the OCM reaction are shown in figure 1. In case of La_2O_3 (a) before reaction, two peaks due to La-O (at 1.9 Å) and La-La (3.8 Å) are definitely seen. For La_2O_3 -MgO containing 25 mol% La (b), the intensity of La-O and La-La peaks becomes higher and lower than those of La_2O_3 , respectively. In addition, the FT-EXAFS of La_2O_3 -MgO is almost similar to that of $\text{La}_2\text{CO}_3(\text{OH})_2$. This suggests the existence of dispersed La species with hydroxycarbonate-like species. FT-EXAFS of Li/ La_2O_3 -MgO prepared from LiNO_3 (c) suggests the existence of La_2O_3 -like species.

However, Li/ La_2O_3 -MgO prepared from Li_2SO_4 (d) is different from La_2O_3 and sample (c). It is likely that unique La species such as coexistence of La_2O_3 -like and dispersed species are formed in sample (d). After the OCM reaction, the FT-EXAFS profiles of all the samples are similar to that of $\text{La}_2\text{CO}_3(\text{OH})_2$, although La-O peak of sample (d) shows low intensity than that of other samples. It is suggested that La species in sample (d) are less hydrated by water vapor produced during OCM reaction than other samples.

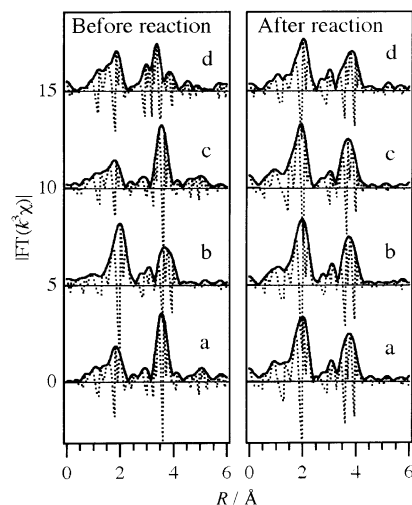


Fig. 1 FT-EXAFS of La-based catalysts. La_2O_3 (a), La_2O_3 -MgO with 25mol% La (b), Li(2.5wt%)/ La_2O_3 -MgO prepared from LiNO_3 (c) or Li_2SO_4 (d). FT-EXAFS of these samples before (left) and after (right) OCM reaction at 1023 K for 6 h are shown.

XAFS study of Sn in PtSn/carbon catalysts. Effect of the carbon support on the state and structure of tin species

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In order to understand the catalytic properties of bimetallic PtSn catalysts, a structural study from an atomic point of view is very useful. Such a study could reveal the presence of alloyed particles or some other species formed by Pt and Sn which can be strongly affected by the interaction with the support. In this work we study the state of tin in bimetallic PtSn catalysts supported on two carbon materials of very different properties: activated carbon (AC) and carbon black (CB). The two metals were introduced either in two steps successive impregnation (SI) or simultaneously (coimpregnation (CI)). The Sn/carbon catalysts were also analysed. All catalysts have been previously reduced in H_2 flow at 350 °C for 5 hours. The Sn K-edge absorption spectra were recorded in the transmission mode. Fourier transformation was performed on k^3 -weighted EXAFS oscillations in the range of 3-12 Å⁻¹.

Figures 1 and 2 show the Fourier transform of Sn K-edge for the references and catalysts investigated in this study. Figure 2a includes the data for monometallic Sn/carbon catalysts and Figure 2b for the bimetallic samples. The results obtained indicate an important effect of the support in the state of tin in Sn/carbon samples. On the CB, tin is partially reduced to the metallic state while on the AC, the peak for reduced Sn does not appear and the metallic element seems to be coordinated by oxygen atoms. In the case of the bimetallic catalysts, however, the differences between the samples are minor. All the spectra are characterised by a peak centered at about 1.6 Å⁻¹ (without phase shift correction) that can be assigned

to Sn-O bonds in a structure similar to that of SnO_2 or SnO (see Figure 1). These data indicate that tin in the bimetallic catalysts shows a very similar state, independently of the carbon support and the preparation procedure. It seems that the interaction with platinum is more important than the interaction with the support in determining the structure and the state of tin.

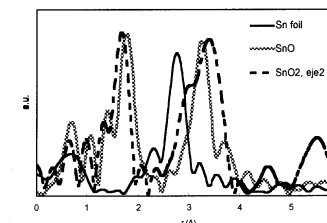


Figure 1. FT of Sn K-edge for the references

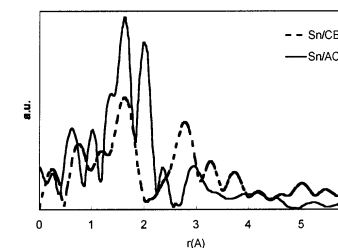


Figure 2a. FT of Sn K-edge of monometallic Sn/carbon samples

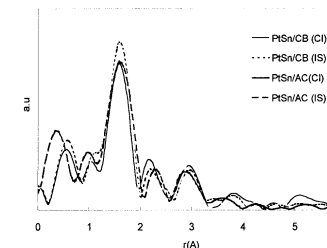


Figure 2b. FT of Sn K-edge of bimetallic samples