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EXAFS analysis for Au/La_2O_3 catalysts active for Selective Esterification of Methacrolein to Methyl Methacrylate with Molecular Oxygen

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1 Introduction

Esterification is one of the most important organic synthetic routes from small scale laboratories to industries because of esters' versatility and requirements. Recently we have synthesized Au/La_2O_3 catalysts with controlled sizes and shapes using CTAB (cetyltrimethylammonium bromide) as surfactant and have found that these novel catalysts are highly active and selective for esterification of methacrolein to methyl methacrylate [1]. In this study coordination states of Au for fresh and spent catalysts were examined by Au-L_{III} edge EXAFS.

2 Experiment

Au/La_2O_3 catalysts were prepared by a surfactant assisted hydrothermal method by adapting our own synthesis method. Catalytic performance and characterization with XRD, SEM, TEM and XPS were reported elsewhere [1]. EXAFS measurements of Au-L_{III} edge were carried out at KEK-IMMS-PF BL9C.

3 Results and Discussion

The local structure around Au atoms of the fresh and the spent Au/La_2O_3 catalyst was determined by Au L_{III} edge EXAFS. Fig. 1 shows the k^3-weighted Fourier transform of Au L_{III}-edge EXAFS spectra of the fresh and the spent Au/La_2O_3 catalysts. Table 1 lists the structural parameters of EXAFS fitting results. The Au-Au bond distances in the fresh and the spent catalyst are 0.2863 and 0.2846 nm, respectively. The absence of the Au-O bond is indicative of Au(0) states in both forms of catalysts. The present results are in agreement with XRD and XPS results [1].

Table 1: Summary of the EXAFS fitting results for the 2% Au/La_2O_3 catalysts[a]

	Path	R (10^{-1} nm)	CN	DW (10^{-5} nm^2)	ΔE_0 (eV)	R_f (%)
Fresh	Au-Au	2.863±0.007	7.0±1.0	7.0±0.9	2.8±1.4	1.56
Spent	Au-Au	2.846±0.007	6.6±0.9	6.6±0.8	2.8±1.4	1.68

[a] Fitting was conducted in the range Δk: 3–12 (10^{-1} nm) and ΔR: 1.0–3.2 (10^{-1} nm). Amplitude reducing factor $S_0^2 = 0.74$

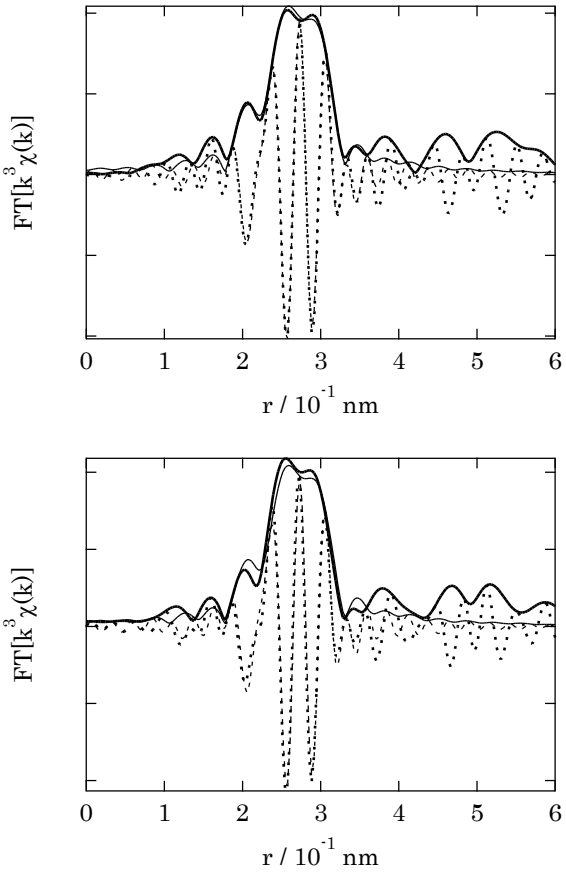

Fig. 1: k^3-weighted Fourier transform (amplitude (solid curve) and imaginary part (dotted curve)) of Au L_{III}-edge EXAFS spectra of (Upper panel) the fresh catalyst and (Lower panel) the spent catalyst.

In summary, Au L_{III}-edge EXAFS measurements confirmed the Au-Au bond distance and Au(0) states for both fresh and spent Au/La_2O_3 catalysts active for esterification of methacrolein to methyl methacrylate.

References

[1] B. Paul *et al.*, *ACS Sustainable Chem. Eng.* **7**, 3982 (2019).

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