

Electronic Supplementary Information for:

Preparation of Clay-Supported Sn Catalysts and Application to Baeyer-Villiger Oxidation

**Takayoshi Hara, Moriaki Hatakeyama, Arum Kim, Nobuyuki Ichikuni
and Shogo Shimazu***

*Department of Applied Chemistry and Biotechnology, Graduate School of Engineering,
Chiba University / 1-33 Yayoi, Inage, Chiba 263-8522*

E-Mail: shimazu@faculty.chiba-u.jp

Materials

All the organic chemicals were commercial products purchased from Wako Pure Chemical Industry, Ltd. and Tokyo Chemical Industry, Ltd.. Tin(II or IV) compounds including $(\text{CH}_3)_4\text{Sn}$ were also purchased from Wako and Aldrich, Ltd., and used for synthesis and analyses of catalysts without any further purification. Lithium Taeniolite was purchased from Topy Industry Ltd.

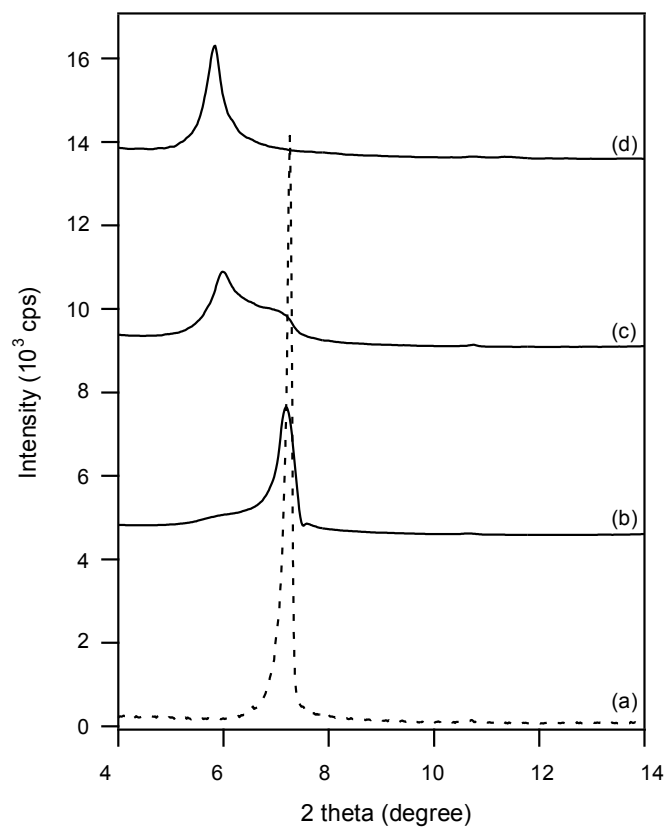


Fig. S1 XRD profiles for (a) Li/TN, (b) Sn(0.19)/TN, (c) Sn(0.40)/TN, and (d) Sn(0.77)/TN.

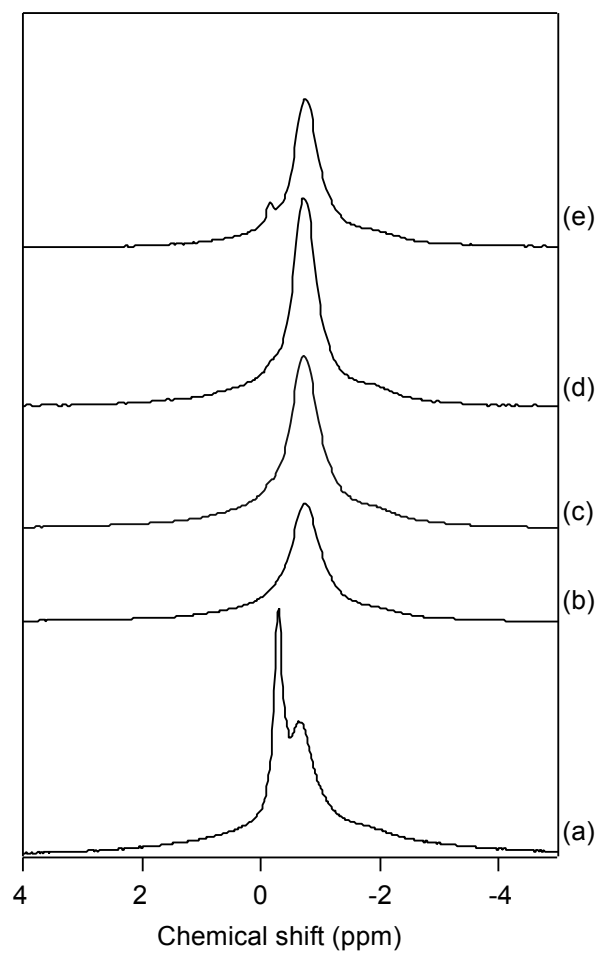


Fig. S2 ^7Li MAS NMR spectra for (a) Li/TN, (b) Na/TN, (c) K/TN, (d) Mg/TN, and (e) Ca/TN.

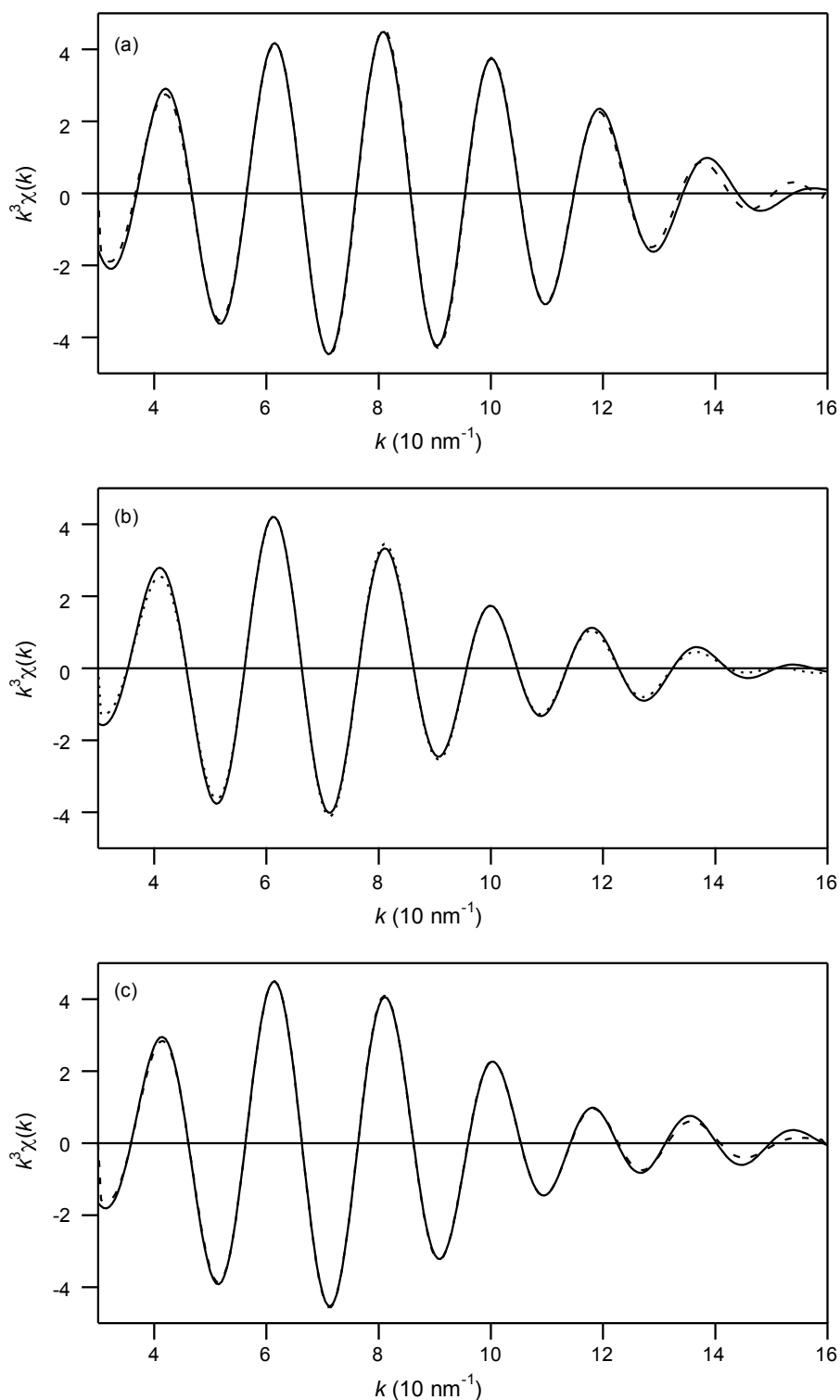
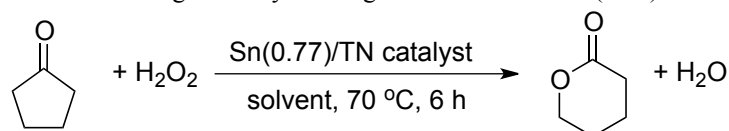


Fig. S3 Curve-fitting of Fourier-filtered EXAFS of (a) Sn(0.77)/TN, (b) Sn(0.40)/TN, and (c) Sn(0.19)/TN catalyst. The solid curve is obtained experimentally, and the dashed curve is the calculated fit.

Table S1 Solvent screening for Baeyer-Villiger oxidation with Sn(0.77)/TN catalyst^a



| Entry | Solvent | Conv. (%) ^b | Yield (%) ^b |
|-------|-------------------------------|------------------------|------------------------|
| 1 | 1,2-dichloroethane | 75 | 70 |
| 2 | <i>n</i> -hexane | 95 | 36 |
| 3 | toluene | 69 | 35 |
| 4 | ethyl acetate | 27 | 22 |
| 5 | acetonitrile | 7 | 5 |
| 6 | 1,4-dioxane | 4 | 3 |
| 7 | tetrahydrofuran | 11 | 2 |
| 8 | <i>N,N</i> -dimethylformamide | 2 | <i>n. d.</i> |
| 9 | dimethylsulfoxide | <i>n. d.</i> | <i>n. d.</i> |
| 10 | water | 5 | 2 |
| 11 | ethanol | 21 | 6 |
| 12 | methanol | 20 | 5 |
| 13 | neat | 97 | 50 |

^a Cyclopentanone (0.5 mmol), Sn(0.77)/TN catalyst (0.05 g), solvent (1.5 mL), 30 wt% H₂O₂ (2 eq. relative to ketone), 70 °C, 6 h

^b Determined by GC using an internal standard technique.

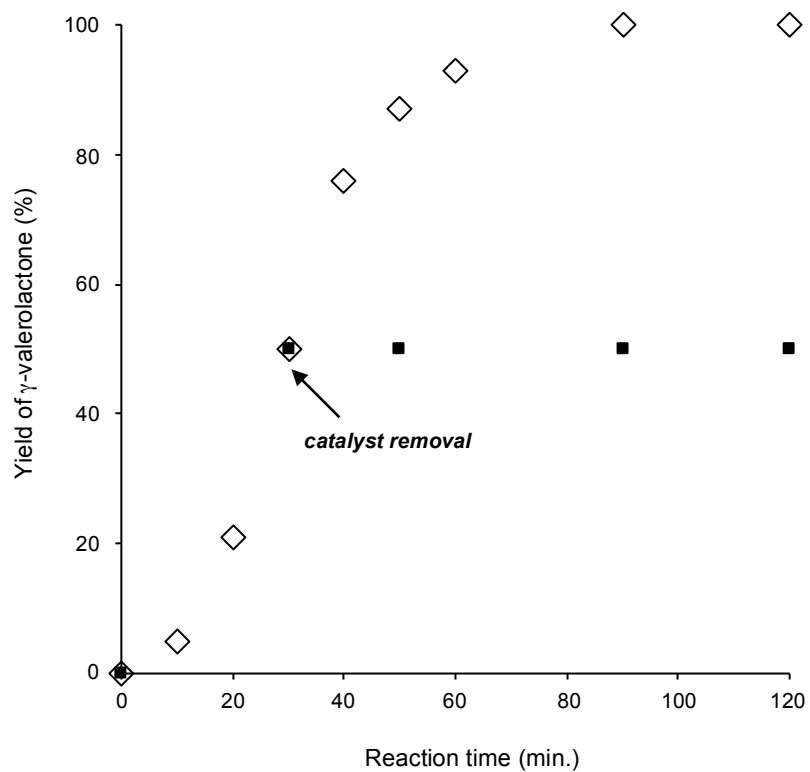


Fig. S4 Effect of removal of the Sn(0.77)/TN catalyst on the Baeyer-Villiger oxidation of cyclopentanone: without removal of catalyst (\diamond) and removal of catalyst (\blacksquare).

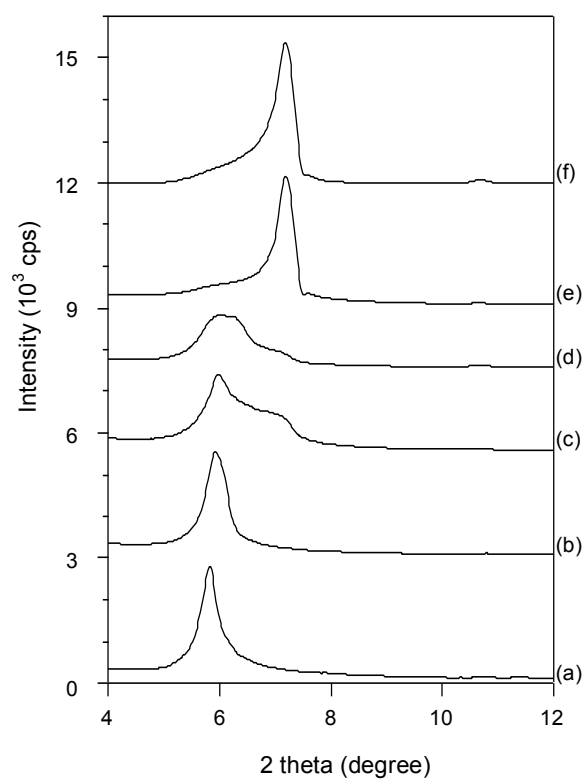


Fig. S5 XRD profiles for (a) recovered Sn(0.77)/TN, (b) fresh Sn(0.77)/TN, (c) recovered Sn(0.40)/TN, (d) fresh Sn(0.40)/TN, (e) recovered Sn(0.19)/TN, and (f) fresh Sn(0.19)/TN catalysts.

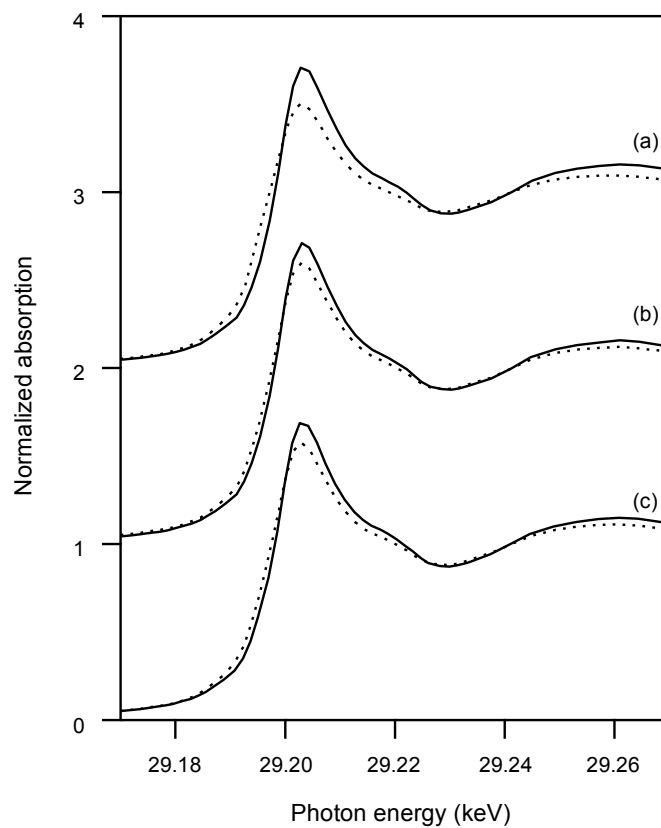


Fig. S6 Sn *K*-edge XANES spectra for (a) Sn(0.77)/TN, (b) Sn(0.40)/TN, and (c) Sn(0.19)/TN catalyst. The solid curves are recovered catalysts, and the dashed curves are fresh catalyst.