

Tin K-edge XAFS study of supported Ir-Sn/SiO₂ bimetallic catalysts for selective propane dehydrogenation

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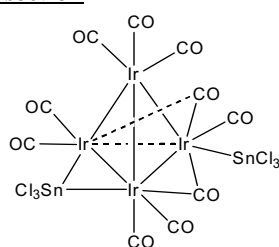
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Introduction

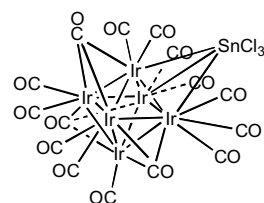
Multi-component catalysts have found widespread usage because the combination of two or more metals lead to increase activity, extend catalyst life, and improve the selectivity. In this work, selective dehydrogenation of propane found for [Ir₄(CO)₁₀(SnCl₃)₂]²⁻ (Scheme 1) supported on amorphous SiO₂ or MCM-41 was interpreted based on the Sn K-edge XANES in comparison with unselective impregnated Ir/SiO₂ and inactive Ir+Sn/SiO₂.

Experimental section

[N(C₂H₅)₄]⁺₂[Ir₄(CO)₁₀(SnCl₃)₂]²⁻ or [N(C₂H₅)₄]⁺[Ir₆(CO)₁₅(SnCl₃)₃]⁻ (Scheme 2) crystal was impregnated on amorphous SiO₂ (specific surface area 290 m²g⁻¹) or MCM-41 (1024 m²g⁻¹) ([Ir₄Sn₂]/oxide, [Ir₆Sn]/oxide). For comparison, IrCl₃ was impregnated on the amorphous SiO₂ followed by the reaction with Sn(*n*-C₄H₉)₄ (Ir+Sn/SiO₂). The Ir content was fixed to 1 wt% in all the catalysts and Ir/Sn ratio was varied between 1 and 6. These incipient samples were reduced in H₂ at 773 K. Sn K-edge XAFS spectra were measured at 290 K at beamline 10B in fluorescence detection mode [1] using Lytle detector.



Scheme 1



Scheme 2

Results and discussion

The Sn K-edge XANES data for Ir+Sn/SiO₂ are depicted in Figure 1f – h. As the Sn amount in catalyst decreased, the absorption edge progressively shifted toward higher energy side. This trend implies that Sn was effective electron donor to Ir and the donation extent per a Sn atom was greater as Sn amount became relatively smaller. When the Ir/Sn ratio was 6, the Sn state was 4+ (Figure 1h, c).

The XANES spectra for [Ir₄Sn₂]/MCM-41 and [Ir₆Sn]/MCM-41 were basically similar to those for Ir+Sn/SiO₂ (Ir/Sn = 2 and 6), respectively (Figure 1e, i, g, and h). The extent of edge energy positive shift was slightly smaller ($\Delta = 0.2 - 0.3$ eV) for supported

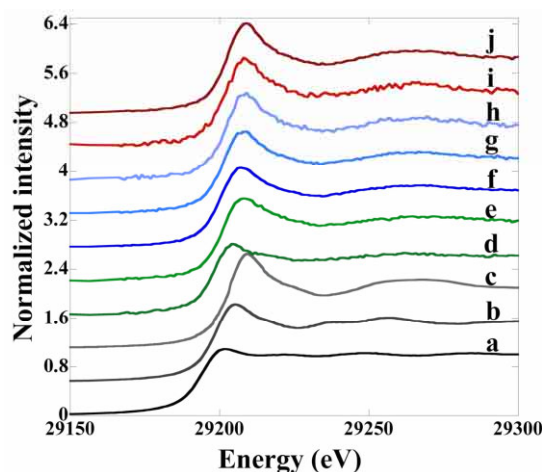


Figure 1. Sn K-edge XANES spectra for Sn metal (a), Sn^{II}O (b), Sn^{IV}O₂ (c), [N(C₂H₅)₄]⁺₂[Ir₄(CO)₁₀(SnCl₃)₂]²⁻ (d), [Ir₄Sn₂]/MCM-41 (e), Ir+Sn/SiO₂ (f – h) (Ir/Sn = 1, 2, and 6, respectively), [Ir₆Sn]/MCM-41 (i), and [Ir₄Sn₂]/SiO₂ (j).

bimetallic cluster on MCM-41 compared for Ir+Sn/SiO₂. This may be due to the difference of average metal particle size: 15Å for supported bimetallic cluster samples and 19Å for Ir+Sn/SiO₂ samples (HR-TEM).

In the dehydrogenation reaction of propane for 18h in 101 kPa at 773 K on [Ir₄Sn₂]/MCM-41 and [Ir₄Sn₂]/SiO₂ catalysts, the selectivity to propene reached as high as 88 – 95% and the conversion decrease compared to Ir/SiO₂ catalyst was acceptable (52 – 58%). The XANES spectrum for [Ir₄Sn₂]/SiO₂ (Figure 1j) even shifted more toward higher energy ($\Delta = 0.25$ eV) compared to Ir+Sn/SiO₂ (Ir/Sn = 6).

To obtain consistent trend of promoter Sn effect on the Ir active site for selective dehydrogenation catalyst, the Sn-Ir bond distance and the coordination number should be analyzed in addition to Sn K-edge XANES above. Sn K-edge EXAFS measurements are in progress at more brilliant PF-AR beamline NW10A from 2006.

References

- [1] Y. Izumi, H. Nagamori, F. Kiyotaki, D. Masih, T. Minato, E. Roisin, J.-P. Candy, H. Tanida, and T. Uruga, *Analytical Chemistry*, **77**(21), 6969 – 6975 (2005); *ibid*, **78**(6), 2075 (2006).

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