

Tin K-edge XAFS study of supported Ir-Sn/SiO₂ catalysts utilizing brilliant X-ray beam at 29 keV from PF-AR

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Introduction

Selective dehydrogenation of propane was found to proceed on [Ir₄(CO)₁₀(SnCl₃)₂]²⁻ (Scheme 1) supported on SiO₂ gel or MCM-41 [1]. In this report, the role of Sn site is discussed based on the Sn local structure given by Sn K-edge EXAFS.

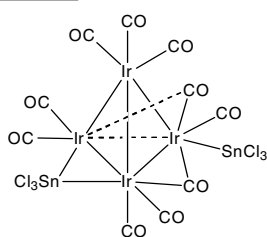
Experimental section

[N(C₂H₅)₄]⁺₂[Ir₄(CO)₁₀(SnCl₃)₂]²⁻ crystal (**1**) (Scheme 1) was impregnated on SiO₂ (290 m²g⁻¹) or MCM-41 (1024 m²g⁻¹) ([Ir₄Sn₂]/support). IrCl₃ was impregnated on the SiO₂ followed by reaction with Sn(*n*-C₄H₉)₄ (Ir_{1.8}+Sn_{1.0}/SiO₂, Ir/Sn atomic ratio 1.8). The Ir content was 1.0 wt% in all catalysts. The incipient samples were heated in H₂ at 773 K. Sn K-edge XAFS spectra were measured at 30 – 290 K at beamline NW10A of PF-AR in transmission mode.

The standard parameters for curve fit were derived from EXAFS spectra for SnO powder and crystal **1** for Sn–O and Sn–Cl bonds, respectively, and theoretically generated from FEFF8.2 for Sn–Ir bond.

Results and discussion

The results of curve-fit analyses were summarized in Table 1. In the data measured at 30 K for crystal **1**, Sn–Ir peak was relatively enhanced compared to data at 290 K. Below, the data at 290 K were mainly compared between catalysts of different supports and preparation routes.



Scheme 1

For [Ir₄Sn₂]/MCM-41 and [Ir₄Sn₂]/SiO₂ catalysts, oxidic Sn and metallic Sn–Ir alloy co-existed based on the presence of Sn–O and Sn–Ir bonds, respectively. The population of Sn–Ir alloy was greater on MCM-41 (*N*(Sn–Ir) = 4.6 – 4.7) versus on SiO₂ (*N*(Sn–Ir) = 1.7 – 2.0).

Oxidic Sn species dominant for Ir_{1.8}+Sn_{1.0}/SiO₂ (*N*(Sn–O) = 6.5 – 6.6) may play no role in propane dehydrogenation because the catalytic results of Ir_{1.8}+Sn_{1.0}/SiO₂ were similar to those of Ir/SiO₂ [1]. The curve fit results for [Ir₄Sn₂]/SiO₂ were intermediate values between [Ir₄Sn₂]/MCM-41 and Ir_{1.8}+Sn_{1.0}/SiO₂ samples (Table 1). Therefore, the catalyst consisted of comparable mixture of oxidic Sn and Ir–Sn alloy. The population of Ir–Sn alloy based on Sn K-edge EXAFS was correlated with the selective dehydrogenation activity.

As-supported [Ir₄Sn₂] cluster on MCM-41 was also analyzed. Two thirds of ligand chlorines dissociated and the Sn atom bonded to either oxygen (*N* = 2.8) or iridium (*N* = 4.7). The cluster **1** seems to react inhomogeneously either with surface oxygen (or hydroxyl) of MCM-41 or to begin to form alloy (growth from smaller [Ir₄Sn₂] core unit to 1.5 nm-particles).

Reference

[1] M. Guidotti, V. Dal Santo, A. Gallo, E. Gianotti, R. Psaro, L. Sordelli, *Catalysis Letters* **112**(1-2), 89 – 95 (2006).

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Table 1. Best-fit results of Sn K-edge EXAFS for supported bimetallic Ir–Sn catalysts

Sample Condition	<i>T</i> (observed)	Sn–O		Sn–Cl		Sn–Ir		Goodness of fit
		<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	
[Ir₄Sn₂]/MCM-41								
As supported	290 K	2.8	2.070	1.2	2.364	2.7	2.584	2464
						2.0	2.847	
Reduced 773 K	290 K	4.6	2.040			4.6	2.865	81370
[Ir₄Sn₂]/SiO₂								
Reduced 773 K	290 K	3.3	2.037			0.8	2.502	9567
						1.2	2.830	
	30 K	2.6	2.034			0.7	2.479	16561
						1.0	2.890	
Ir_{1.8}+Sn_{1.0}/SiO₂								
Reduced 773 K	290 K	2.0	1.997			0.6	2.887	4567
		4.5	2.106					
	30 K	2.0	2.006			1.3	2.853	98986
		4.6	2.131					
Crystal 1								
				(3)	(2.426)	(0.5)	(2.584)	
						(1)	(2.718)	