10B/2003G264

XAFS characterization of zeolite supported Ir catalysts for hydrogenolysis of cyclohexane

Ryoichi KOJIMA*, Tatsuya GUNJI, Atsushi FUKUOKA, Masaru ICHIKAWA*
Catalysis Research Center, Hokkaido University, N-21 W-10, Kita-ku, Sapporo 001-0021, Japan

Introduction

The formation of C2-C4 hydrocarbons by a selective hydrogenolysis of cyclohexane is considered as the crucial reaction for the petrochemical industry. Some oxide supported noble metal catalysts have been reported previously on the catalytic performance of alkane hydrogenolysis and the mechanism of C-C cleavage of the cyclic alkanes; however, in many cases methane is produced by the complete decomposition and benzene is produced by the dehydrogenation as the main products [1]. Here, we report selective hydrogenolysis of cyclohexane over Ir/HZSM-5 catalyst which exhibited the highest selectivity for C2-C4 hydrocarbons among the noble metal catalysts and the results of XAFS characterization.

Experimental

Noble metal catalysts with 1 wt.% loading were prepared by a conventional impregnation technique. SiO_2 (CARiACT Q-10), γ-Al_2O_3 (Nishio), and HZSM-5 which was obtained by calcination of NH_4-ZSM-5 (Zeolyst, SiO_2 / Al_2O_3 = 40) at 773 K for 5 h were used as materials of supports. $Ir(acac)_3$, $Ru(acac)_3$ (Aldrich), Rh $(acac)_3$ (Strem Chemicals) and $Pt(acac)_2$ (Wako Chemicals) were used as metal precursors. The powder samples put into a U-shaped glass cell were calcined in O_2 flow at 723 K for 2 h and reduced in H_2 flow at 723 K for 2 h. Cyclohexane hydrogenolysis reaction was performed in a fixed-bed flow reactor under 0.1 MPa, at 523-723 K, using reactant gas with molar ratio (H_2 / CH) of 9, and space velocity of 13.6 L / g•h. All the products were analyzed by on-line FID gas chromatograph (Shimazu, GC-14B). XAFS measurements were performed at BL-10B of KEK-PF at room temperature. The data were analyzed using the program of REX2000.

Results and discussion

The reaction profiles for hydrogenolysis of cyclohexane at 623 K over various noble metal catalysts are listed in Table 1. Among noble metal catalysts, Ir/HZSM-5 catalyst showed the highest selectivity toward C2-C4 hydrocarbons (the molar ratio of them = 19.2 %, 44.0 %, and 9.8 %) and the formation of benzene was suppressed effectively. However, in the case of Ir/Al_2O_3 and Ir/SiO_2, a main product was benzene. The selectivity to methylcyclopentane formed by isomerization was lower than that of the Ir/HZSM-5. Then HZSM-5 itself was used for this reaction to investigate its catalytic activity. The conversion over the HZSM-5 was nearly on the same level with that over the Ir/HZSM-5, but C1 and C2 compounds were not formed and C4 was produced more instead of these products. Thus, we proposed the reaction mechanism over Ir/HZSM-5 as follows: At first step, cyclohexane was isomerized to methylcyclopentane on the acid site of HZSM-5. Then cleavage of methylcyclopentane ring occurred and chain C6 species were formed, and then they were decomposed to C3-C4 species on the acid sites. Ir catalyzed a hydrogenolysis reaction forming C2 from longer carbon chain species.

Table 1: Reaction profiles for hydrogenolysis of cyclohexane over various noble metal catalysts

Catalyst	Conversion (%)	Molar selectivity (%)						
		C1	C2	C3	C4	C5-C6	MCP	Aromatics
Ir / Al_2O_3	81.0	—	—	—	—	0.1	0.2	99.7
Ir / SiO_2	52.9	12.6	3.8	0.9	0.7	0.4	0.1	81.6
Ir / HZSM-5	9.1	6.6	19.2	43.9	9.7	4.8	7.7	8.0
Ru / HZSM-5	5.7	74.8	5.7	9.4	3.9	2.0	2.3	1.8
Rh / HZSM-5	51.6	79.6	5.9	0.5	0.8	0.3	0.2	12.8
Pt / HZSM-5	62.7	—	5.0	29.2	6.9	4.2	10.2	44.4
HZSM-5	9.5	—	—	47.4	23.4	8.2	4.3	16.7

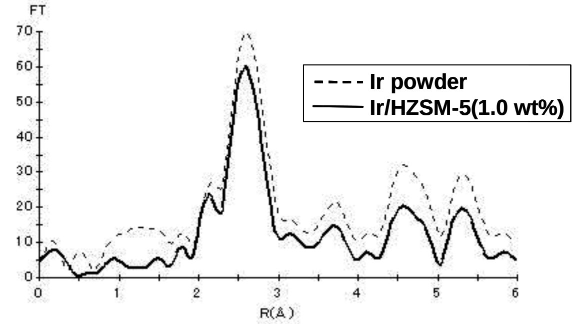

Fig. 1: Fourier- transformed EXAFS spectra at L_{III} edge of Ir powder and Ir/HZSM-5.

Fourier-transformed EXAFS spectra were shown in Figure 1. Ir/HZSM-5 catalyst showed similar spectra with the Ir L_{III} edge adsorption of Ir powder, suggesting the active site of the catalyst is metallic iridium.

Now, we are developing the preparation methods of bimetallic catalysts supported on the HZSM-5, and detailed EXAFS characterization is in progress.

References

[1] F. Locatelli, J-P. Candy, B.Didillon, P. Niccolai, D. Uzio, and J-M. Basset, J. Am. Chem. Soc, 123, 1658 (2001).

* kojima@cat.hokudai.ac.jp