

Structures analyses of supported ruthenium catalysts under asymmetric hydrogenation reaction

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Introduction

Asymmetric hydrogenation is one of the most widely used, most efficient method to obtain optically active compounds in the fields of fine chemical synthesis. For practical uses in the industry, the reactions with heterogeneous catalysts have advantages due to their easy separation and recycling. In this study, we employed a reaction method introducing chiral ligands to metal oxide supported ruthenium oxide catalysts for asymmetric hydrogenation of olefins. Enantioselective hydrogenation of diethyl itaconate proceeded in 95% ee in the presence of 1 wt% Ru/ZrO₂ with 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) as a chiral ligand. The structures of active species on the catalysts were analyzed by in situ XAFS obtained under the reaction conditions.

Experimental methods

The supported ruthenium catalysts were prepared using an impregnation method following by a calcination at 823 K under air. The typical catalytic reaction is carried out as follows: diethyl itaconate (5 mmol), the catalyst (1.0 mol %), (*S*)-BINAP (1.1 mol %), and methanol (4 mL) as solvent were introduced into a stainless steel autoclave with X-ray windows made of polyetheretherketone. The autoclave was sealed after replacing the residual air with H₂ (3 atm), and then heated at 353 K. In situ Ru K-edge XAFS measurements were performed at the BL14B2 beamline of SPring-8 (Hyogo, Japan) using Si311 double-crystal monochromator. The experiments were conducted in the fluorescence mode using a 19-element Ge solid-state detector. The collection of a XAFS spectrum required approximately 7.5 min.

Results and discussion

The XANES spectrum of the 1 wt% Ru/ZrO₂ catalyst was similar to that of RuO₂ and no pre-edge peak was observed indicating that tetrahedral coordination structure of RuO₂. Only a dominant peak due to Ru–O coordination of RuO₂, which appeared in the range from 0.1 nm to 0.2 nm, was observed in the Fourier transformed function for the 1 wt% Ru/ZrO₂. It has been suggested that octahedral coordinated ruthenium oxides highly dispersed on ZrO₂ showed high activity and enantioselectivity for hydrogenation of diethyl itaconate. Average oxidation state of ruthenium species in the catalyst was determined using correlation between the oxidation states and the edge energy of various standard ruthenium compounds. Under the reaction condition, reductions of the ruthenium species was observed by in situ XAFS spectra. The average oxidation state of the ruthenium species were reduced from +3.3 to +2.4 during the reaction.