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EXAFS Analysis for Supported Ru Catalyst Active for Syntheses of Quinoxaline Derivatives

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1 Introduction

Many Heterocyclic compounds are acting as various drugs. Here we synthesized various biologically active substituted heterocyclic compounds such as quinoxalines, benzimidazoles, benzoxazoles and benzothiazoles using novel recyclable silica supported ruthenium catalyst. For the purpose of obtaining reactive and selective catalysts, the selection of metal element and the ligand whch promotes catalytic function of metal atom are very important. In this study we tried to develop multinuclei Ru catalyst using $Ru_3(CO)_{12}$ and 1,3,5-trimethyl-hexahydro- 1,3,5-triazine, which will be referred to as N3 ligand hereafter, as a ligand for stabilization and promotion of complex. N3 ligand possesses the three nitrogen atoms which can interact with mutinucleic Ru catalytic species. Catalytic performance and EXAFS characterization exhibited that the present catalyst was active for syntheses of quinoxaline derivatives.

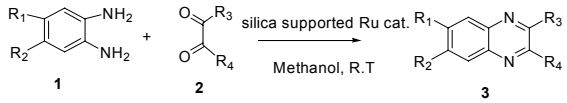
2 Experimental

For the preparation of the catalyst, N3 ligand was reacted with $Ru_3(CO)_{12}$ where reaction was done at 65^0C in toluene. The product was removed from the unreacted starting material with Soxhlet extraction with hexane and subsequent redissolving in methanol with filtration. The resulting dark-brown microcrystalline product was characterized with elemental analysis, IR and NMR ^{1}H and ^{13}C spectroscopy, and EXAFS. In order to prepare solid catalyst for recycles and easy separation of products from the catalyst, the compound was impregnated on silica support from methanol solution. This silica supported Ru catalyst (containing 0.186 mmol/g as Ru) was used for catalytic reactions.

Measurements of extended X-ray absorption fine structure (Ru K-edge EXAFS of each element) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK－IMSS－PF). The EXAFS spectra were analyzed with the UWXAFS package. The curve-fitting analysis was carried out using the FEFFIT program in the R-space.

3 Results and Discussion

We observed the silica supported Ru catalyst with N3 ligand is highly reactive in the synthesis of various biologically active heterocyclic compounds.



R_1 = H,Cl, CH_3
R_2 = H,Cl, NO_2
CH_3
$R_3 = R_4$ = Ph,Furyl, CH_3

Several substituted OPDAs such as chloro, nitro, methyl, dichloro, dimethyl, cyclohexyl and EDA, bisOPDA, were used to get the products in excellent yields as shown in the above scheme. Substituted diamines and various aromatic and aliphatic substituted diketones like benzyl, furyl and 2,3-butadione or diacetal were used to synthesize multifunctionalised quinoxalines and 2,3-dihydropyrazines using the silica supported Ru catalyst. Similarly, the above diamines treated with various substituted aromatic aldehydes to get excellent yields of benzimidazoles. The catalyst was reusable up to 4 times without significant drop of reactivity.

Ru-K edge EXAFS measurements were conducted to characterize the local structure of the supported Ru catalyst. Fig. 1 shows the k^3-weighted Ru K-edge EXAFS Fourier transforms and curve fitting results for $RuN3/SiO_2$ catalyst. Three shells were observed in the spectrum. The first shell corresponds to the overlapped paths of Ru-N and Ru-C. The second shell corresponds to the Ru-(C)-O and the third shell corresponds to the Ru-Ru path. It was found that the multinucleic character of Ru was retained in the present supported Ru catalyst.

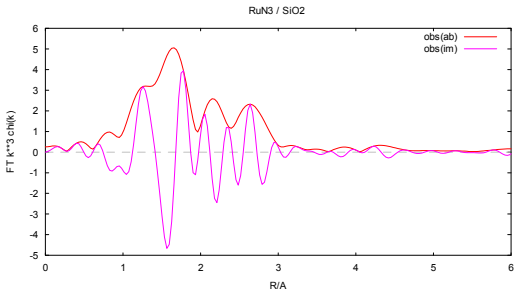


Fig. 1 : k^3-weighted Ru K-edge EXAFS Fourier transforms and curve fitting results for $RuN3/SiO_2$ catalyst.

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