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EXAFS Analysis for Cobalt Oxide and Hydroxide Catalysts for Benzimidazole Derivatives

Murugulla Adharvana Chari[1], Donthabakthuni Shobha[1], Takehiko SASAKI*[1],
[1]Department of Complexity Science and Engineering, School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

Introduction

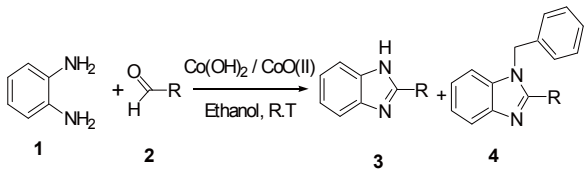
Among the various nitrogen containing heterocycles, benzimidazole derivatives exhibit antiviral, antiulcer, antihypertension and anticancer properties. The benzimidazoles are biologically potent and this moiety is an important pharmacophore in drug discovery and also good intermediate for synthesis of many important organic compounds. Generally, the synthesis of 2-substituted benzimidazoles involves the treatment of 1,2-phenylenediamines either with carboxylic acids or their derivatives (nitriles, imidates or orthoesters), under strongly acidic conditions and some times combined with very high temperatures (i.e.,PPA,180^{0}C) or the use of microwave irradiation. Many nanoporous materials and zeolites have been widely used as heterogeneous catalysts in several organic transformations due to their excellent textural characteristics such as high surface area, large pore volume, uniform pores and high thermal stability. Unfortunately, $Co(OH)_2$ and CoO(II) solid catalysts are not explored much in organic synthesis. These solid catalysts are commercially available, non hazardous, clean, cost effective than other heterogeneous catalysts. In the continuation of our interest on catalytic applications of various heterogeneous catalysts, herein we report for the first time a simple, convenient and efficient method for the synthesis of benzimidazole and its derivatives by condensation of 1,2-phenylenediamines with aldehydes under open oxygen atmospheric conditions at room temperature in ethanol using $Co(OH)_2$ and CoO(II) as reusable solid catalysts. We achieved EXAFS analysis for Co oxides and hydroxides to clarify the reusable activity for benzimidazole derivatives.

Experimental

Measurements of extended X-ray absorption fine structure (Co 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.

Results and Discussion

We have found that Co oxides and hydroxide are active for room temperature synthesis of benzimidazole derivatives. The reaction is represented by the following scheme:



Here molecules denoted as 3 are main products and those designated as 4 are by-products. The optimised quantity of catalyst with respect to reactants was 10 mol%. In the case of $Co(OH)_2$ catalyst, the yields of the final product increases from 75 to 96% and whereas in the case of CoO(II) catalyst, the product yield increases from 71 to 93% with increasing the catalyst weight from 2 mol% to 10 mol%. We also investigated the 10 mol% Co_3O_4(II,III) activity on this synthesis, but the yield 79% was lower than that by $Co(OH)_2$ and CoO(II) solid catalysts. The order of activity was found as $Co(OH)_2$ >CoO(II)> Co_3O_4. It was also found that these catalysts are recyclable up to 4th reuse, where no obvious drop of activity was found. EXAFS analysis was conducted to characterize the used catalysts. Fig. 1 shows the k^3-weighted Co K-edge EXAFS Fourier transforms and curve fitting results for $Co(OH)_2$ sample, which was retrieved after catalytic reaction. In the fitting process of EXAFS functions, the first shell was fitted as the Co-O distance at 0.2088 nm and the second shell was fitted as the Co-Co distance at 0.3196 nm for $Co(OH)_2$ crystal structure. It was confirmed that the crystal structure of $Co(OH)_2$ catalyst was retained after the reaction, in accordance with the reusability of catalyst.

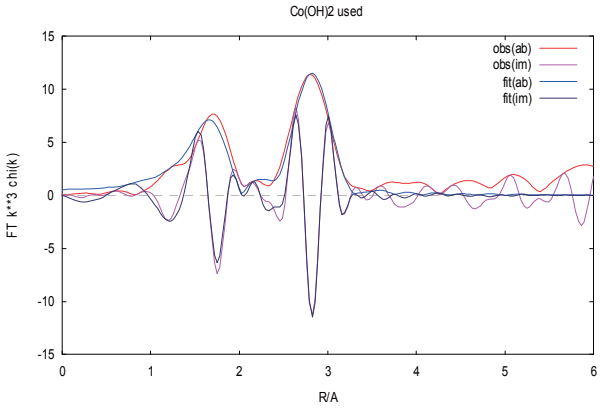


Fig. 1 k^3-weighted Co K-edge EXAFS Fourier transforms and curve fitting results for $Co(OH)_2$ sample after reaction.

* takehiko@k.u-tokyo.ac.jp