

EXAFS analysis for CuCr₂O₄ Spinel Nanoparticles: A Recyclable Heterogeneous Catalyst for One Pot Hydroxylation of BenzeneRajaram Bal^{1*} and Takehiko Sasaki²¹Catalytic Conversion & Processes Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, India²Department of Complexity Science and Engineering, School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

1 Introduction

Copper chromium mixed oxides with a spinel structure had been recognized as an important class of bi-metallic oxides that act as a versatile catalyst. The hydrothermal route is one of the most efficient methods to obtain well-defined nanoparticles with controlled morphologies and recently, we have reported the preparation of copper nanoclusters supported on nanocrystalline chromium oxide in hydrothermal synthesis method [1].

Herein we report the EXAFS analysis of CuCr₂O₄ spinel nanoparticles prepared by hydrothermal synthesis method. This preparation method is simple, reproducible and produces high yield (98%) and can be prepared in a large scale (upto 20 g). Furthermore, the catalyst prepared in this process is devoid of leaching properties due to its extremely stable spinel phase. The catalyst was highly active for selective oxidation of benzene to phenol with H₂O₂. The reusability of the catalyst was tested by conducting same experiments with the spent catalyst and it was found that the catalyst did not show any significant activity loss even after 5 reuses [2].

2 Experiment

Extended X-ray absorption fine structure spectroscopy (EXAFS) measurements of Cu-K edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF). The measurement was made at transition mode and spectra were taken at BL-9C. The electron storage ring was operated at 2.5 GeV and 450 mA, synchrotron radiation from the storage ring was monochromatized by a Si (111) channel cut crystal. Ionized chamber, which were used as detectors for incident X-ray (I₀) and transmitted X-ray (I), were filled with N₂ mixture gas, respectively. The angle of the monochromators was calibrated with Cu foil. The EXAFS raw data were analyzed with UWXAFS analysis package including background subtraction program AUTOBK and curve fitting program FEFFIT. The amplitude reducing factor, S₀² was fixed at 1.0. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code. ATOMS were used to obtain FEFF input code for crystalline materials.

3 Results and Discussion

Cu K-edge extended X-ray absorption fine structure (EXAFS) analysis of the catalyst supports the formation

of CuCr₂O₄ spinel and the spinel structure remains unchanged during the catalysis. Detailed structural parameters of the curve fitting results are summarized in Table 1. The EXAFS spectrum analyzed as the superposition of the crystal phase of CuCr₂O₄ and the dual CuO phase. The small coordination number 2.5 for the CuO phase indicates that the CuO phase corresponds to the surface layer of oxidized Cu on CuCr₂O₄ crystal or the monatomically dispersed CuO on the CuCr₂O₄ crystal phase. From Cu2p XPS spectra, tetrahedrally coordinated Cu and the octahedrally coordinated Cu are assigned to the CuCr₂O₄ phase and the surface CuO phase, respectively. The coordination number for CuO was found to be smaller than the value 4-6 in the present study, because it is minor phase as compared to the CuCr₂O₄. Essentially the same results were obtained for both fresh and spent catalysts in agreement with the reusability of catalysts.

Table 1. Summary of the EXAFS fitting results for fresh CuCr₂O₄ catalyst

Catalyst	Path	R(10 ⁻¹ nm)	CN	DW (10 ⁻⁵ nm ²)
fresh ^a CuCr ₂ O ₄	Cu-O	1.938±0.037	2.5±	2.9±1.1
			0.4	
	Cu-O	1.885±0.025	4	13.1
	Cu-O	3.139	4	17.1
	Cu-Cr	3.243	4	7.3

^a Fresh Catalyst: Δk (10nm⁻¹) = 3-14, ΔR (10nm⁻¹) = 1.0-3.6, ΔE_0 (eV) = -12.4±1, R_f (%) = 2.57;

References

- [1] B. Sarkar, P. Prajapati, R. Tiwari, R. Tiwari, S. Ghosh, S. S. Acharyya, C. Pendem, R. K. Singha, L. N. S. Konathala, J. Kumar, T. Sasaki and R. Bal, *Green Chem.*, 2012, **14**, 2600–2606.
[2] S. S. Acharyya, S. Ghosh, S. Adak, T. Sasaki and R. Bal, *Cat. Sci. & Tech.*, in press.

* raja@iip.res.in