

XAFS characterization for  $\text{CoWO}_4@W_{18}\text{O}_{49}$  catalystRajaram Bal<sup>1,\*</sup> and Takehiko Sasaki<sup>2</sup><sup>1</sup> Light Stock Processing Division, CSIR- Indian Institute of Petroleum, Dehradun-248005, India<sup>2</sup> Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8561, Japan

## 1 Introduction

Among the most difficult and significant reactions in the chemical industry is the selective oxidation of cyclohexane in the presence of air to high value-added intermediates such as cyclohexanone and cyclohexanol (the combination is named as 'KA oil,' where 'K' and 'A' represent ketone and alcohol, respectively). For the conversion of cyclohexane to KA oil a  $\text{CoWO}_4@W_{18}\text{O}_{49}$  nano-structured catalyst with abundant oxygen vacancy sites was successfully synthesized via a co-precipitation method. This catalyst selectively oxidized cyclohexane to KA oil in solvent-free conditions, where under optimum conditions, ~24 % cyclohexane conversion with ~93 % KA oil selectivity was achieved. The catalyst was characterized by EXAFS in addition to XRD, TEM, XPS and Raman [1].

## 2 Experiment

$\text{CoWO}_4@W_{18}\text{O}_{49}$  catalysts were prepared by a wet chemical method. Extended X-ray absorption fine structure (EXAFS) measurements at the Co-K edge were carried out in transmission mode at room temperature at the BL9C station of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF). The electron storage ring was operated at 2.5 GeV. A Si(111) channel-cut crystal was used as a monochromator. Ionization chambers for incident X-rays ( $I_0$ ) and transmitted X-rays ( $I$ ) were filled with  $\text{N}_2$ (100%) and 25%Ar/ $\text{N}_2$  gas, respectively. EXAFS data were analyzed and fitted using Athena and Artemis package based on IFFEFFIT program Backscattering amplitude, and phase shift were obtained by FEFF calculation.

## 3 Results and Discussion

Fig. 1 show the observed and fitted data for  $k^3$ -weighted Fourier transforms of Co K-edge for fresh  $\text{CoWO}_4@W_{18}\text{O}_{49}$  catalyst. Since XRD confirmed the  $\text{CoWO}_4$  phase, the cif file for  $\text{CoWO}_4$  was used to obtain the scattering paths from the Co atom as an X-ray absorbing atom for Co K-edge EXAFS fitting procedure. Fitting result was shown in Table 1. The first, second, third, fifth and sixth paths are associated with the CoO bond, while the Co-Co and Co-W bonds were associated with the fourth and seventh paths, respectively. The results of the XRD are consistent with the existence of Co-W species in the fresh catalyst.

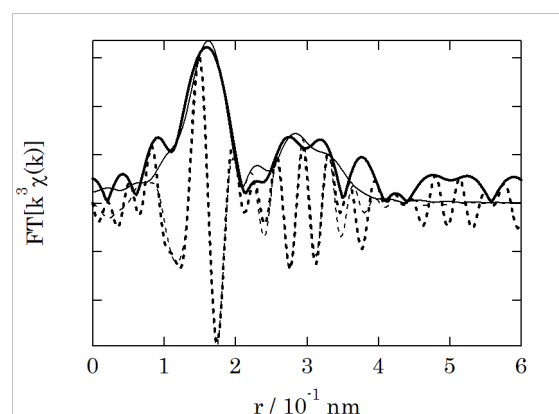


Fig. 1  $k^3$ -weighted Fourier transforms of Co K-edge for fresh  $\text{CoWO}_4@W_{18}\text{O}_{49}$  catalyst. (Amplitude (solid curve) and imaginary part (dotted curve), thick curve (observed) and thin curve (fitted)).

Table 1: Summary of the EXAFS fitting results for the fresh  $\text{CoWO}_4@W_{18}\text{O}_{49}$  catalyst

| Path  | R ( $10^{-1}\text{nm}$ ) | CN        | DW ( $10^{-5}\text{nm}^2$ ) | R <sub>f</sub> (%) |
|-------|--------------------------|-----------|-----------------------------|--------------------|
| Co-O1 | 2.002±0.019              | 2.00±0.44 | 5.9±2.5                     | 2.9                |
| Co-O2 | 2.091±0.019              | 2.00±0.44 |                             |                    |
| Co-O3 | 2.126±0.019              | 2.00±0.44 |                             |                    |
| Co-Co | 3.120±0.019              | 1.90±0.78 |                             |                    |
| Co-O4 | 3.193±0.019              | 2.00±0.44 |                             |                    |
| Co-O5 | 3.369±0.019              | 2.00±0.44 |                             |                    |
| Co-W  | 3.547±0.035              | 2.15±1.46 |                             |                    |

K range 3.0-11.0 ( $10\text{nm}^{-1}$ ), R range 1.0-3.4 ( $10^{-1}\text{nm}$ ),  $\Delta E_0$  -2.5±2.9 (eV).

The sample used for the catalytic reaction was also measured and analyzed in the same way (not shown). The comparison of the FT-EXAFS spectra and the fitting results confirmed that the catalyst phase is retained during the catalytic reaction. These results are in consistent with other characterization methods [1].

## References

[1] S. Bhandari *et al.*, *Journal of Environmental Chemical Engineering*, **11**, 109380 (2023).

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