

## XAFS study on local structure of highly-functionalized metal catalysts immobilized on the surface of inorganic crystals

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### Introduction

Apatites and related compounds are of great interest because of their structural stability and their potential ability for cationic and anionic isomorphous substitution [1]. The hexagonal hydroxyapatite (HAP) structure comprises  $\text{Ca}^{2+}$  sites surrounded by  $\text{PO}_4^{3-}$  tetrahedra. The chemical composition of HAP can be modified from the stoichiometric form,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , to the non-stoichiometric form,  $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$ . We have focused on doping the apatite surface with various transition metal cations, which can function as catalytically active centers, via cation exchanged at  $\text{Ca}^{2+}$  sites[2]. Recently, a calcium vanadate apatite (VAp),  $\text{Ca}_{10}(\text{VO}_4)_6(\text{OH})_2$ , was developed by substituting  $\text{VO}_4^{3-}$  for  $\text{PO}_4^{3-}$  in the whole apatite matrix as a nano-structured heterogeneous catalyst for highly efficient carbon-carbon bond forming reactions under aqueous conditions[3]. In this report, local structures of V species in the VAp catalyst were studied by V K-edge XAFS.

### Experimental

The VAp was prepared from an aqueous solution of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_3\text{VO}_4$ , followed by calcinations at  $800^\circ\text{C}$ [3]. Elemental analysis showed the amounts of Ca and V were 35.0 and 26.6 wt%, respectively. X-ray absorption spectra were measured in a transmission mode at the EXAFS facilities of KEK-PF, Tsukuba. Details of data analysis are referred to the reported procedure[4].

### Results and Discussion

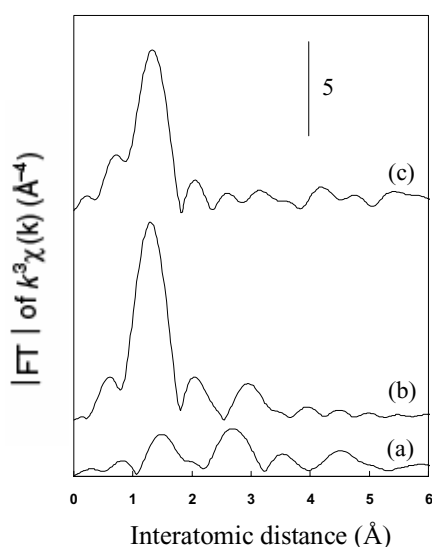
In V K-edge X-ray absorption near edge structure spectra, the VAp showed a strong pre-edge peak comparable to those seen for  $\text{K}_3\text{VO}_4$ . The energy positions of pre-edge peak, of the main absorption edge and of the peak due to *1s-4d* dipole-allowed transition in the VAp were good agreement with those observed for  $\text{K}_3\text{VO}_4$ , respectively.

As depicted in Figure, in the Fourier transforms of  $k^3$ -weighted extended X-ray absorption fine structure data, peaks due to V-O-V bonds in the second coordination sphere, detectable at  $2.8 \text{ \AA}$  for  $\text{V}_2\text{O}_5$ , were not observed for either  $\text{K}_3\text{VO}_4$  or VAp. These results imply that the vanadium species in the VAp catalyst exists in an isolated tetrahedral geometry with an oxidation state of +5. The above conclusion from the V K-edge XAFS measurement is well supported by the results of  $^{51}\text{V}$  NMR, UV-vis, and Raman techniques[3].

The VAp acted as heterogeneous and recyclable catalyst in various types of carbon-carbon bond

formations under aqueous conditions[3]. Correspondingly, stability of the V structures in the recovered VAp catalyst was straightforwardly established by XAFS measurement.

The present preparation method using the character of apatites can provide a powerful protocol to generate a catalytically active and robust metal species within the apatite frameworks.



**Figure:** Fourier-transforms of  $k^3$ -weighted V K-edge EXAFS of (a)  $\text{V}_2\text{O}_5$ , (b)  $\text{K}_3\text{VO}_4$ , and (c) VAp. EXAFS were transformed in the range of  $3.5\text{--}11.0 \text{ \AA}$ . The phase shift was not corrected. The peak at  $1.5 \text{ \AA}$  corresponds to V=O and V-OH shells.

### References

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