High-Throughput Materials Characterization Using Synchrotron Radiation

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Introduction

Combinatorial chemistry refers to highly efficient methodologies for conducting exploratory and developmental research. The characteristic features of the combinatorial approach include: (1) a design to efficiently cover an experimental space; (2) miniaturization of scale to enable one to practically perform hundreds or thousands of experiments; (3) automation to enable one to physically perform hundreds or thousands of experiments; (4) parallel processing of the samples, which leads to the greatest time savings in the experimental procedure; (5) a high-throughput assay to quickly measure the property of interest for each sample; and (6) assembling a visualization or interpretation of the experiment. UOP has a combinatorial chemistry research program in the areas of catalysis and new-materials synthesis. It was believed that the high-intensity, tunable x-ray source at the Advanced Photon Source could greatly impact the area of high-throughput assays. The results presented here are those from a proof-of-principle experiment involving combined powder x-ray diffraction (XRD)(structural information), x-ray fluorescence (XRF)(element identification/concentration), and x-ray absorption near edge structure (XANES)(oxidation state information) on materials and catalysts generated in the combinatorial chemistry program.

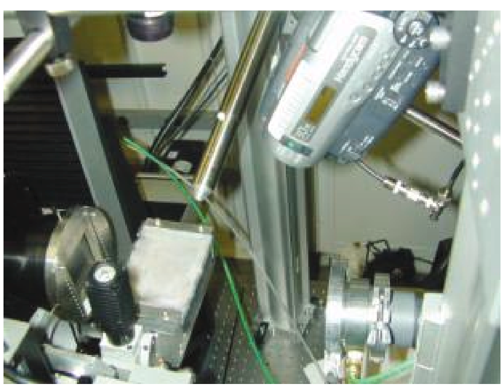

FIG. 1. Experimental arrangement in 33-ID-D.

Results and Discussion

The experimental arrangement that was used for the experiment is shown in Fig. 1. A 2D CCD detector was used to collect the powder diffraction data. X-ray patterns were collected with 1s exposures using a photon energy of 12 keV. Over the course of a typical 4 h experiment, more than 1000 high-quality XRD patterns were collected, and most of that time was spent moving between samples and changing sample arrays! Figure 2 shows a typical ring pattern that was obtained from a mixed Cu-Zn-V oxide sample in a 48-well synthesis plate, and the conversion of the ring pattern to the more familiar 2-dimensional powder XRD format. It is this pattern that is used in search-match routines for phase identification. Element identification/concentration was used to probe the elemental composition of several combinatorially synthesized arrays. The data shown in Fig. 3 are representative of that obtained from an array containing a Cu-Zn-V-O synthesis mixture. In this experiment variables such as the relative amounts of Cu and Zn were varied in a combinatorial manner to map out the phase space for this particular mixed-metal vanadate. The XRF spectra were collected in 1 min using a single-element Ge detector. The s/n is such that an acquisition time of 0.1 min could have been used, and clearly if a 13-element detector had

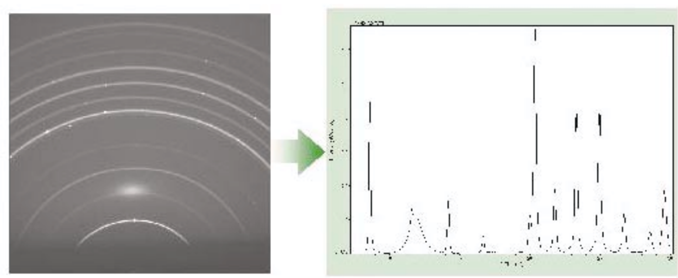

FIG. 2. Pattern collected in 1s from a mixed Cu-Zn vanadate.

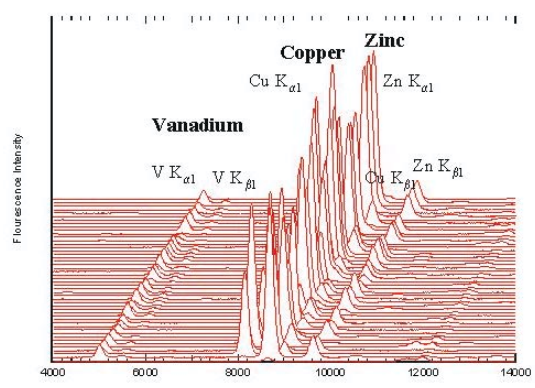

FIG. 3. Raw XRF spectra collected from a 48-well array containing mixed Cu-Zn vanadates.

been used this time could have been further shortened. The quantitative XRF data collected in this experiment were in excellent agreement with individual bulk analyses determined elsewhere.

The last part of the feasibility experiment involved collecting XANES spectra. Figure 4 shows the Mn K-edge XANES spectra from eight wells in a synthesis array. In this experiment some novel manganese phosphates were synthesized, and it was likely that the Mn was present in a range of oxidation states. The data

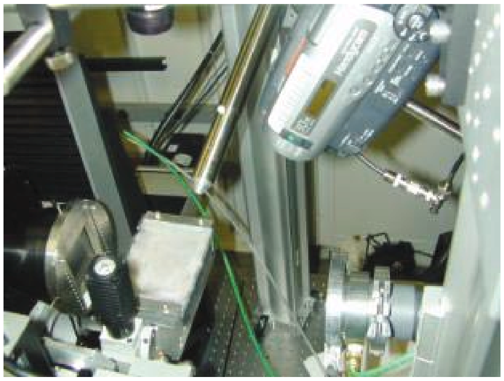

FIG. 4. Mn K-edge XANES spectra from Mn phosphate array.

shown in Fig. 4 indicate that the Mn oxidation state falls in a range of 3-4.

The data from this proof-of-principle experiment clearly show the utility of using synchrotron radiation to rapidly assay combinatorially-synthesized materials using XRD, XRF, and XANES.

Acknowledgment

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