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ABSTRACT

Synchrotron x-ray microscopy techniques have been used to characterize several different types of heterogeneous catalysts. Using a collimator to produce microbeams with a size of less than 10 micrometers, maps of the elemental distributions based on detection of the fluorescent x rays were made, and computed microtomography (CMT) techniques were applied to produce "phase/density contrast" maps. CMT techniques were also used to determine the distribution of a specific major element by making measurements above and below the K-x ray absorption-edge. The measurements were made using bending magnet radiation and, in one case, radiation from a 4T superconducting wiggler at the National Synchrotron Light Source. Examples of applications to the study of polyethylene polymerization particles, fluid catalytic cracking catalysts, and hydrotreating catalysts are given.

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1. Introduction

Owing to the intrinsic complexity of catalytic systems, many different approaches are required to adequately characterize the different types of catalysts now in common use [1]. These include neutron scattering, extended x-ray absorption fine structure (EXAFS), infrared and Raman spectroscopy, electron spin resonance, nuclear magnetic resonance, x-ray photoelectron spectroscopy (XPS), x-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM), electron probe, proton-induced x-ray emission (PIXE), nuclear reaction analysis (NRA), and many others. This paper describes similar industrial applications of the novel synchrotron-based x-ray microscopy (SXRm) which are directed toward the development of a new diagnostic probe for catalysts and other new materials.

The SXRm [2], can make 2-dimensional elemental maps of the major, minor, and trace elements comprising a catalyst with spatial resolutions of about 5-10 micrometers and minimum detection limits of less than 1 part-per-million (ppm) by weight. It is thus suited to complement the use of the electron and proton probes for the study of, for example, the distribution of components in a catalyst particle or to follow the transport of contaminant species in representative particles. Its use is not, however, limited to the production of an image by probing a thin section of a specimen. It can also be used to produce non-destructive maps of the elemental distributions in sections through a pellet by use of the technique of computed microtomography (CMT). CMT maps can be produced either through the measurement of the linear attenuation coefficients or by detection of the fluorescent x rays. In some cases it is possible to map the distribution of particular chemical states using x-ray absorption near-edge spectroscopy (XANES) and to make measurements on in-situ systems.

Three examples of applications of the SXRm for characterization of heterogeneous catalysts are given here: a Cr/SiO₂ heterogeneous catalyst for polyethylene polymerization,

a rare-earth exchanged zeolite fluid catalytic cracking catalyst and a Ni-Mo hydrotreating catalyst for use in the refining of petroleum.

2. Experimental Method

Most of the work was carried out at the X-26 beam line of the National Synchrotron Light Source. The apparatus has been described previously in detail [3]. Microbeams are produced by use of mechanical collimators and measurements of the fluorescent x-rays are made with a Si(Li) x-ray detector or of the linear attenuation coefficient using ion chambers and scintillation detectors. The CMT measurements are made using a first-generation translation-rotation geometry to obtain the data needed for the image reconstruction [4].

The use of fluorescence detection is limited by the escape depth of the fluorescent x rays. The typical values for these depths are shown in fig. 1 for K-x rays from titanium, nickel, molybdenum, and lanthanum and for the L x rays of lanthanum produced in a kaolin matrix. It can be seen that the lighter elements are best suited for observation in thin sections. The higher Z elements can be observed in pellets of moderate size. The detection of rare-earth (RE) elements using the L-x rays is well known to be difficult because of the overlaps with abundant K x rays from the transition elements. Use of high energy x-ray beams to produce K-x rays from the RE elements largely eliminates the overlap problem, at the same time allowing the detailed investigation of larger samples. One such spectrum was obtained for these elements using the X-17 4T superconducting wiggler.

3. Characterization of Polyethylene Polymerization Particles

Polyethylene is produced by the use of a catalyst such as Cr supported on high surface area SiO_2 . In the process of polymerization, the catalyst particles fragment as the polymer forms on the internal surface. The catalyst particles are reduced in size. The rate of continued polymer production depends on this fragmentation, affording access of the

monomer to the active surface. If the fragmentation is slow or incomplete, reaction rates, polymer particle density and, thereby, total polymer yields are reduced. To understand this complex process, it is necessary to follow the fragmentation and spatial distribution of the catalyst particles within the polymer. Measurement of the spatial distribution of catalyst fragments within the growing polymer particles is difficult since conventional sectioning of the pellet will distort the system morphology. The use of SXR in its CMT mode overcomes these difficulties.

Several models for the distribution of catalyst within the growing polymer have been proposed. In one, a hard core model, the catalyst only fragments progressively from its exterior. The distribution of catalyst fragments within the growing polymer increases toward the center of the catalyst/polymer particle. In a second model, the catalyst fragment spontaneously, and there is a uniform distribution of catalyst throughout the growing polymer. In a third model, the catalyst fragments are moved toward the particle exterior by convection in the solid/molten state. Heretofore, this last perception of the fragmentation process has not been analyzed in detail due to the complexity of the analyses. A combination of models is conceivably such that the actual spatial distribution of catalyst fragments would reflect a combination of these models.

CMT addresses these concerns directly since the catalyst and the polymer can be easily differentiated through differences in their linear x-ray attenuation coefficients and since the spatial resolution of CMT is sufficient to distinguish individual catalyst fragments. By CMT, we are able to determine the actual spatial distribution of catalyst fragments within the growing polymer/catalyst agglomerate. This insight enables us to differentiate between the various solid-state mechanisms of catalyst fragmentation and particle growth, as discussed above.

A typical tomogram obtained with CMT is shown in fig. 2. It can be seen that the fragments are clearly distributed in the surface region of the pellet and that there are a

number of voids in its interior. Work on pellets formed using different production methods show that these conclusions depend on the preparation methods. Tomograms such as the one shown in fig. 2 demonstrate that CMT is an effective tool for the study of polymerization particles. A full description of the results and the implications of CMT/SXRM for gaining a deeper understanding of the polymerization process in this case is given by Conner et al. [5].

4. Characterization of Fluid Catalytic Cracking (FCC) Catalysts

FCC catalysts are widely used in petroleum refining. A common type contains RE-exchanged Y-type zeolite crystallites dispersed in a matrix consisting of a clay such as kaolin along with mixtures of silica and alumina. The composite catalyst is formed into microspheroidal particles approximately 60 to 100 micrometers in diameter. Critical characterization issues include the distribution of the zeolite crystallites, alternatively of the RE in the microsphere and to show the distribution of contaminant metals coming from the petroleum feed stock in sections through the microsphere.

The elemental content of thin sections of several microspheres was determined from detection of the characteristic x rays produced using a filtered white beam of synchrotron radiation. The complex spectrum which results (fig. 3) demonstrates the problems of separating contributions from the transition elements and the RE element when L-x ray detection is used for the latter. A spectrum from an intact microsphere was obtained using a filtered white beam from the X-17 superconducting wiggler. The results, given in fig. 4, demonstrate that the RE contributions are far more reliably analyzed on the basis of K x rays. In addition, use of the higher energy K x rays is expected to allow future applications of CMT in the fluorescence mode to measure the spatial distribution of the RE elements in the catalyst particles.

Measurements were made of the spatial distribution of the elements in a 15 micrometer section of a microsphere using a beam size of 10 micrometers. The results given in fig. 5 show that concentrations of Ni and Fe, which are not readily transported through the catalyst particle are highest at the microsphere surface. Vanadium, which has been demonstrated to be mobile under process conditions, is distributed through the body of the microsphere [6]. These results are supported by parallel investigations using the electron probe. Development of the SXRm for these investigations will yield better detection limits and, ultimately, better definition in elemental distributions.

CMT was also used to measure the linear attenuation coefficients in a section through a catalyst microsphere of a size similar to the one used for production of the thin section. The tomogram is shown in fig. 6. The pixel size is $3\ \mu\text{m} \times 3\ \mu\text{m}$ with a slice thickness of $10\ \mu\text{m}$. The attenuation coefficients are variable within the body of the microsphere. This is attributed to non-homogeneous distribution of the zeolite particles (low attenuation coefficients) within the kaolin/alumina matrix (high attenuation coefficient) of the microsphere. The high attenuation values observed at the periphery of the particle are attributed to the influence of the high Ni and Fe concentrations shown in fig. 5.

The combination of spatially-resolved, elemental maps based on detection of fluorescent x rays with CMT "phase/density contrast" maps based on measurement of linear attenuation coefficients yields information which is complementary to the results that can be obtained with the electron probe. The use of the fluorescence map is valuable in terms of interpreting the results of the linear attenuation coefficient CMT. The next step will be to make CMT measurements using detection of the fluorescent K-x rays from the RE elements. It should ultimately be feasible to measure the distribution of the contaminant metals in the FCC microsphere (Ni, V) as a function of the catalyst particle age as deduced from the nickel concentrations.

5. Characterization of Ni-Mo Hydrotreating Catalyst

An examination of the Ni-Mo hydrotreating catalyst was carried out using measurements of both the fluorescent x rays and the linear attenuation coefficients. A fluorescent spectrum of one of the pellets is shown in fig. 7. The contributions from the high concentrations of Ni and Mo dominate the x-ray spectrum. The use of the filtered white beam is not effective in this case in discriminating the presence of contaminant species with associated characteristic x ray energies less than those of the Ni K x rays. This is not unexpected, but demonstrates that the use of monoenergetic radiation is preferable in this case. Nevertheless, many elements in addition to the Ni and Mo can be observed.

CMT was also used to construct linear attenuation maps of fresh and aged pellets. Both these maps and mechanical measurements showed that the size of the pellet had increased for the used pellet. This expansion results in a concomitant decrease in the attenuation coefficients indicating a redistribution of the Ni-Mo catalyst. The results of the CMT examination of the two particles are shown in fig. 8.

The concentration of molybdenum was high enough so that it was also feasible to produce an image of the molybdenum distribution by measurements above and below the Mo K-x ray absorption edge. In this case a variable energy monoenergetic x-ray beam was produced using a channel-cut silicon monochromator. The tomogram produced as a result of a subtraction of the two images is a direct measurement of the molybdenum concentration in the catalyst. The resulting tomogram is shown in fig. 9.

These results, together with the foregoing, demonstrate that SXRM can be effectively applied to a wide range of heterogeneous catalyst systems. SXRM studies of contaminant species distributions will supplement the use of electron probes. CMT will be effective in studying catalyst inhomogeneity and, in certain cases, specific metals distributions as a function of catalyst age without requiring sectioning of the catalyst.

6. Conclusions

Results of SXRM examination of three different types of catalysts have been presented. It has been shown that SXRM is an effective tool for studies of these materials that addresses questions that are not readily answered using other types of analytical tools. SXRM can be expected to both supplement and complement the use of electron probes in investigations of catalyst deactivation, particularly with respect to determination of contaminant metals distributions. It seems reasonable to expect that SXRM will increasingly be recognized as an important new method for catalyst characterization in the future.

References

- [1]. B. C. Gates, J. R. Katzer, G. C. A. Schuit, eds. Chemistry of Catalytic Processes (McGraw-Hill, New York, 1979); J. M. Thomas and R. M. Lambert, eds. Characterization of Catalysts. (John Wiley, Chichester, 1980).
- [2]. K. W. Jones and B. M. Gordon. Anal. Chem. 61(5) (1989) 341A.
- [3]. K. W. Jones, B. M. Gordon, A. L. Hanson, W. M. Kwiitek, and J. G. Pounds. Ultramicroscopy 24 (1988) 313.
- [4]. P. Spanne and M. L. Rivers. Nucl. Instr. and Meth. B24/25 (1987) 1063.
- [5]. W. C. Conner, S. W. Webb, P. Spanne, and K. W. Jones, Macromolecules, in press.
- [6]. E. L. Kugler and D. P. Leta, J. Catalysis 109 (1988) 337.

Figure Captions

- Figure 1. Yield of characteristic x rays from Ti, V, Ni, Mo, and La is shown as a function of the specimen thickness for a kaolin matrix. The thick target yield is taken as 100%.
- Figure 2. Tomogram showing the distribution of linear attenuation coefficients in a polymer pellet. The bright spots at the periphery represent Si-CrO₂ fragments. The pixel size is 10 μm $\times$ 10 μm with a slice thickness of 5 μm .
- Figure 3. Typical x-ray spectrum for the FCC catalyst pellet obtained with filtered white radiation from the X-26 beam line.
- Figure 4. Typical x-ray spectrum from the FCC catalyst pellet obtained with filtered white radiation from the X-17 superconducting wiggler.
- Figure 5. SXRM map of the elemental distributions in a thin section of FCC catalyst. Heterogeneous distribution of some, but not all, elements is seen.
- Figure 6. CMT tomogram of a 90- μm diameter FCC catalyst pellet. The variations in the linear attenuation coefficients show that the concentration of the zeolite catalyst is not uniform within the particle. The pixel size is 3 μm $\times$ 3 μm with a slice thickness of 10 μm .
- Figure 7. Fluorescent x-ray spectrum for the hydrotreating catalyst obtained using filtered white light from the X-26 beam line. A number of elements can be seen in addition to the peaks from the high concentrations of Ni and Mo.
- Figure 8. Linear attenuation coefficient tomograms of used and unused Ni-Mo hydrotreating pellets. The change in morphology resulting from use is obvious. The pixel size is 5 μm $\times$ 5 μm with a slice thickness of 10 μm .
- Figure 9. Tomogram of the Mo concentrations of a hydrotreating catalyst obtained from subtraction of above and below Mo absorption K-edge tomograms. The pixel size was 10 μm $\times$ 10 μm with a slice thickness of 15 μm .

Figure 1

Figure 3

Figure 4

Figure 5

Figure 7

Figure 8

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