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A Comparison of Techniques for the Examination of Catalyst Particles in the Transmission Electron Microscope

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Four techniques for the preparation of catalyst samples have been used for the determination of particle sizes in the transmission electron microscope: microtomy, grinding by use of a biological tissue grinder, dry crushing and grinding and extraction replication. Two unused catalysts were examined using these techniques and the results are discussed. The microtomy technique allows the geometry–morphology relationship to be studied more realistically but the cost and the non-routine nature of the sample preparation generally prohibit its widespread use. Extraction replication, which has the ability to remove the active element particles from the surface of the catalytic converter, has indicated a much larger range of particle sizes than that encountered when using the other techniques. Active element particles whose sizes range from 10 Å to several microns were observed on the two catalysts studied.

INTRODUCTION

Of increasing importance to the automobile industry is the use of a variety of catalysts for the oxidation of carbon monoxide and unburned hydrocarbons emitted in automobile exhausts. Oxidation catalysts have been manufactured using a high porosity inactive substrate coated with a secondary surface layer called washcoat, on which very high surface area metal or metal oxide particles have been deposited. One of the parameters of prime importance to the catalytic activity is the effective surface area of the active element which is a function of the active element particle size. Most available techniques for particle size measurement are essentially indirect methods such as chemisorption. The only commercially available device which is capable of directly resolving particles on the order of 10 Å in diameter is the transmission electron microscope (TEM). To date, no comparison of analytical techniques for the determination of catalytic particle sizes using the TEM has been found in the literature.

In this paper, four procedures for the preparation of samples for transmission electron microscopy are compared and their relative merits are discussed.

SAMPLE PREPARATION METHODS

1. Microtomy Technique

A portion of the catalyst honeycomb was placed in a polyethylene embedding capsule and covered with 2% benzoyl peroxide catalyzed methyl methacrylate. The catalyst and the embedding liquid were then placed under 350 μm vacuum for 30 min followed by 30 min under 10 μm vacuum. The encapsulated sample was slowly returned to atmospheric pressure and placed in an oven at 50°C for 48 hr to completely polymerize the embedding compound.

The embedded samples were trimmed to reach an area of the catalyst that had not

been disturbed. The samples were cross-sectioned using a diamond knife in an LKB ultramicrotome. These cross sections revealed areas of the catalyst lying in a plane perpendicular to the direction of airflow. The microtomed cross sections were supported on carbon substrates and the embedding material was removed by dissolving it in xylene to ensure sufficient contrast in the electron microscope.

2. Tissue-Grinding Technique

Approximately 0.1 g of catalyst honeycomb was ground to a powder using a mullite mortar and pestle. The ground powder was transferred to a 13 × 100 mm Pyrex tissue grinder with a sufficient volume of absolute ethanol added to cover the ground glass portion of the rod (*1*). The grinding rod was rotated by hand under light pressure for 2–3 min until the fluid was cloudy. The suspension was decanted into a vial and the residue in the tissue grinder was discarded. At this point the maximum particle aggregate size that remained suspended in the decanted liquid was approximately 2–5 μm. The suspension was permitted to stand for approximately 1 min to allow large aggregates to settle before spraying the liquid. A commercially available sprayer [described by Backus and Williams (*2*)] was used to disperse the catalyst suspension prepared as above. The procedure outlined by Backus and Williams was slightly modified in that three separate applications of 0.06 ml of this suspension were made from a distance of 15 cm onto the carbon support film on the microscope grids.

3. Crushing and Grinding Technique

A portion of the catalyst substrate was crushed in a mortar and pestle to a fine powder. The powder was repeatedly sprinkled onto a dry prepared parlodion substrate on microscope grids until a fine haze was observed on the parlodion film. The film was then placed in a vacuum evaporator and coated with approximately 100 Å of evaporated carbon. The sample grids were then placed on bibulous paper soaked in amyl acetate to dissolve the parlodion film prior to examination.

4. Extraction Replication

A cellulose acetate replicating film was softened in acetone and pressed gently onto the active surface of a catalyst honeycomb. After drying, the film was mechanically stripped from the surface and coated with a layer of evaporated carbon. Segments of the coated cellulose acetate film, containing the extracted particles embedded in its surface, were cut with a scalpel into 2 mm^2 pieces and placed in a petri dish filled with acetone to loosen and float the replica from the acetate film. The extraction procedure of the same area was repeated twice more to determine a possible variation of catalyst distribution with the depth of washcoat. These replicas were removed from the acetone after 30 min and placed on microscope grids for examination.

ELECTRON MICROSCOPY

Samples prepared using the proceding techniques were examined in a Siemens Elmiskop I TEM at 120 kV and 2 μA beam current and a Philips EM 300 TEM at 100 kV and 15 μA beam current. Qualitative analysis of the sample material *in situ* was made possible by use of a Kevex X-ray energy dispersive analyzer (EDS) and a Northern Scientific NS 750 pulse height analyzer with the Philips EM 300 TEM. With catalyst particles that were much smaller than the size of the electron beam, identification by EDS was precluded because not only the particles but also the washcoat was exposed to the electron beam. However, paying close attention to the morphology of the particles, distinction could be made between the catalyst particles and washcoat. Analysis of

large particles (75 Å or larger) was made by reducing the electron beam diameter to approximately 3000 Å and positioning it in such a way as to illuminate the catalyst particles and the adjacent carbon film. This procedure was found to be very useful when isolated particles of catalyst were extracted during extraction replication. An X-ray spectrum was then obtained to determine the true identity of the material in question. Attempts to use dark-field techniques to identify active element and washcoat as proposed by Fornwalt and Kinoshita (*3*) met with little or no success because the diffraction rings of the active element and the washcoat material were not separable by the objective apertures of the electron microscopes used.

Contrast due to density variations was used to estimate sizes for active element particles smaller than those which could be positively identified by EDS, i.e., particles less than 75 Å or particles intermixed with washcoat. Difficulties arise, however, when multiple scattering from washcoat particles stacked parallel to the specimen plane produce darkened areas which appear as small particles or when washcoat particles are oriented so as to appear dense by virtue of strong diffraction contrast.

In the actual process of evaluation of particle sizes, TEM photographs were made of active element particles and the associated washcoat. Measurements of active element particle sizes were made by micrometer eyepiece from enlarged prints when large numbers of particles were photographed and directly from the plate when few isolated particles were seen. Counts were made of particles measured and the mean value was calculated and reported.

RESULTS AND DISCUSSION

Two unused catalyst samples were examined by the four techniques described and particle size data were obtained for each method of sample preparation. Figure 1 is an electron photomicrograph of a typical area of the catalyst sample prepared using the microtomy technique. The area exhibits the acicular morphology of the less dense washcoat such as at (A) and the more dense spherical shapes of the catalyst particles such as at (B). Figure 2 is a representative electron micrograph of a sample obtained using the tissue-grinding technique. Acicular alumina washcoat and spherical shaped active element particles are visible as in the previous photomicrograph. The difference noted between the microtomed samples and samples prepared using the tissue-grinding technique is the variation in the amounts of alumina and active element. The microtomed samples show a uniformly thin film, whereas the tissue grinding leaves coarse agglomerates requiring more time at the electron microscope to scan about for usable areas. As shown in Fig. 1, the catalyst particles are round objects approximately 40 Å in diameter. Figure 3, typical of a sample obtained using the crushing and grinding technique shows the same structural features as shown in Figs. 1 and 2. The disadvantage of this technique lies in the fact that the agglomerates of washcoat and active element are coarse and do not transmit electrons in sufficient degree to give suitable images. Also, the agglomerates are fewer in number in any particlar grid examined in the TEM, and consequently considerable time is required to acquire a sufficient number of data points. Figures 4A, 4B and 4C show the results obtained when the extraction technique is used to prepare samples. One advantage of this technique is its ability to remove the active element particles from the washcoat. Isolated clusters and massive aggregates are found in Fig. 4A and the smallest particle resolvable is on the order of 10 Å in diameter. Some clusters appear as protrusions on the carbon replica, which fact was observed by tilting the sample in the TEM. The significance of the identifications of the protrusions lies in the fact

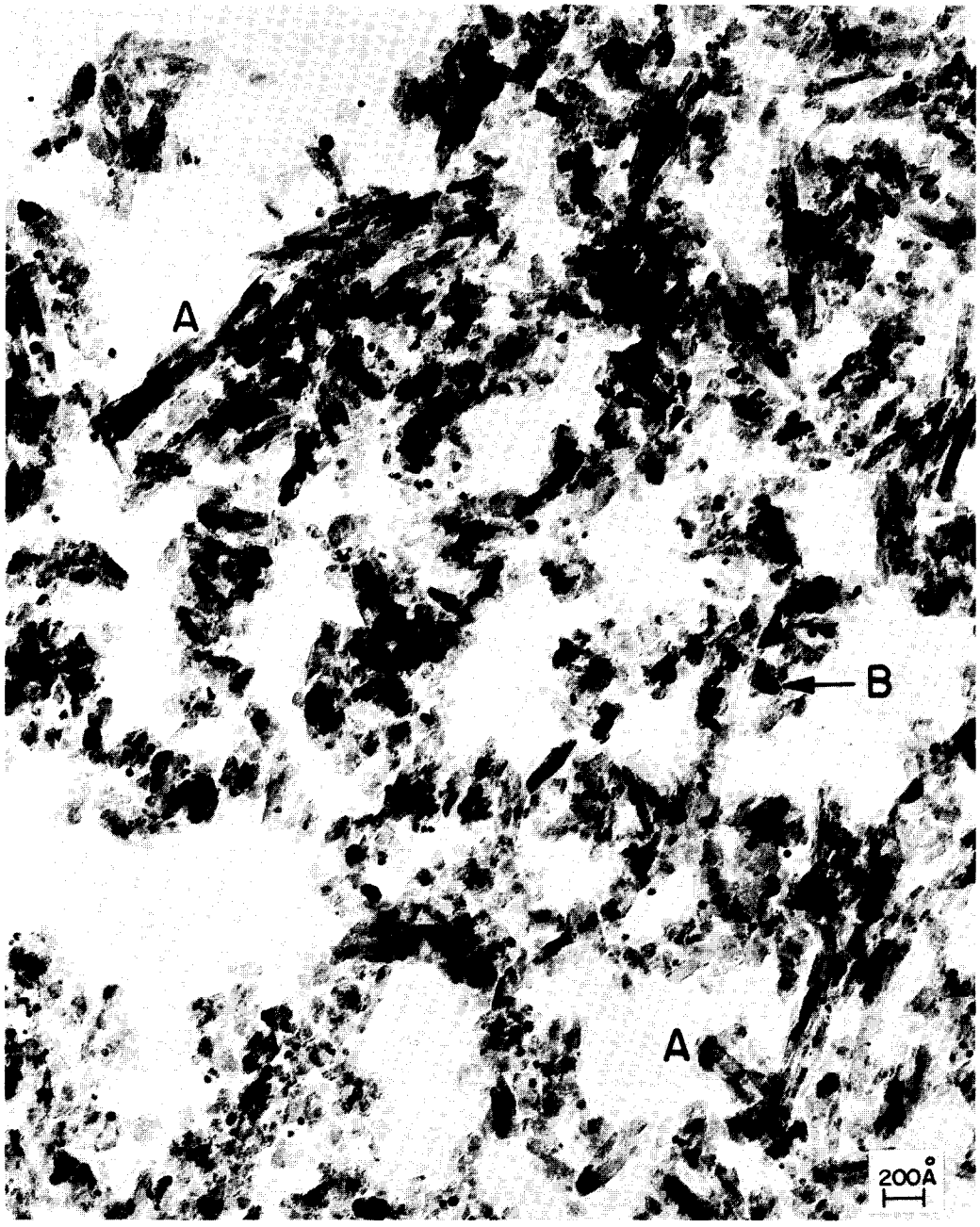

FIG. 1. Sample prepared by microtomy technique showing washcoat and catalyst particles.

that the cellulose acetate film used in the process enables active element particles to be removed from what appear to be deeply recessed crevices or pits on the surface of the washcoat. Figure 4B shows particles which are different in character and larger than those observed in Fig. 4A. Some acicular washcoat can be seen intermingled with the active element, but for the most part, the clusters of material removed are rich in the active element. Figure 4C shows areas similar to that observed in

FIG. 2. Sample prepared by tissue-grinding technique showing washcoat and catalyst particles.

Fig. 4B as well as larger isolated particles of active element which were found to extend into the micron range.

An analysis of the average size of the catalyst particles from the four techniques presented is shown in Table 1. The arithmetic mean particle size obtained using the microtomy and tissue-grinding techniques are similar. The larger mean associated with the samples prepared by the crushing and grinding technique is attributed to the difficulties encountered in seeing smaller

FIG. 3. Sample prepared by crushing and grinding technique showing washcoat and catalyst particles.

particles because of the large overall size of the aggregates obtained and their relative opaqueness to the electron beam. The mean particle size obtained using the extraction replication technique is the largest reported of the three techniques. The large range of particle sizes given by this technique indicates that of the total mass of active element material deposited on the catalyst reactor a portion of that mass is present as large individual particles as much as 1 μm in length. It is interesting to

FIG. 4A. Sample prepared by extraction replication showing isolated clusters and massive aggregates.

note that aggregates of very small particles and the very large particles were not found using any of the preceding three techniques.

The use of the microtomy technique for catalyst examination allows investigation of the washcoat and support in sections made in various directions, e.g., parallel or perpendicular to the surface. Such sectioning permits examination of particle distributions throughout the washcoat. Embedding of the material in a methacrylate

FIG. 4B. Extraction replication showing discrete catalyst particles much larger than clusters of Fig. 4A.

compound prevents motion of the particles with respect to the support during the microtomy and preserves the relationship of catalyst to the washcoat as well as the location and shape of the pores within the washcoat. A disadvantage of this technique, however, is the damage done to the diamond knife used for the sectioning. About two samples can be microtomed successfully with a diamond knife before resharpening is required at considerable expense and risk of permanent loss of the

FIG. 4C. Extraction replication showing mixture of catalyst particles from 10 Å to 1 μm in size.

knife. Preparation of the catalyst materials for examination by the use of the tissue-grinding and crushing and grinding techniques requires that the sample be initially subjected to severe crushing and grinding before examination in the TEM. Care must be exercised in the selection of material for use as a mortar and pestle since particles resulting from their attrition will be included in the resultant dispersions. The material that is crushed and ground during the use of these two techniques

FIG. 5A. Catalyst particles clusters before beam heating (uncoalesced).

contains the support materials, washcoat and the catalyst particles. In the case considered in this investigation, the catalyst material constitutes approximately 0.4% of the entire mass of the crushed material. When the entire mass is ground and distributed by either technique, large numbers of areas examined in the TEM prove to be either washcoat or support free of catalyst particles. Consequently, many areas must be examined to acquire a sufficient number of particles for a meaningful statistical

FIG. 5B. Catalyst particles after beam heating (coalesced).

analysis and the dangers of not detecting small active element particles is high.

The use of the extraction technique allows the selective examination of the top surface of the washcoat. The cellulose acetate film lifts the upper layer of the washcoat and catalyst particles from the support and in many instances lifts only catalyst particles from the washcoat surfaces. Repeated extraction replication of the same area reveals no change in the particle size or morphology which would be indica-

TABLE 1
CATALYST PARTICLE SIZE DETERMINED BY THE FOUR TECHNIQUES

Sample	Microtomy (Å)	Tissue grinding (Å)	Crushing and grinding (Å)	Extraction replication (Å)	
A	47	47	72	200	Aggregates and clusters, 10 Å–1 μm
B	38	39	72	200	

tive of a layering effect. Because of the ability of the extraction replication technique to selectively remove these particles, the task of particle identification and measurement is greatly simplified.

During early examination of catalyst materials it was observed that clusters of active element could be made to coalesce from aggregates of many small particles to clusters of larger particles when exposed to the heat of the electron beam. An example of this coalescence is shown in Figs. 5A and 5B. Figure 5A shows the aggregates of readily identifiable active element particles when observed at low electron beam intensities. The area was then subjected to an increased electron beam current and its attendant increased heating of the area exposed to the beam. The result of that heating is shown in Fig. 5B where the heating has caused coalescence of the fine particles into larger crystals. As a result of this experiment it is certain that undue exposure of active element particles to high electron beam currents and its attendant heat could cause coalescence of the particles into larger agglomerates. This growth of the particles by the beam heating could destroy the original population distribution of the active element particles and bias the resultant particle size measurements. Proper precautions must therefore be taken to ensure that no alteration of particle size of the active element occurs because of electron beam heating.

CONCLUSIONS

1. Use of microtomy as a technique for the examination of catalyst particles in the TEM allows the examination of the catalyst distribution of the active element throughout the depth of the washcoat while preserving the location of those active elements and the porosity of the washcoat. The cost is prohibitive because of the damage to the knife.

2. Tissue-grinding and crushing and grinding techniques distribute the active elements, washcoat and support material for an average particle size distribution. The severe crushing operation can, however, alter the size of agglomerates and some large particles of catalyst can be lost in the distribution and the settling operations. A large number of distributed particles must be examined to obtain a suitable amount of data for good statistical analysis.

3. The extraction technique examines the active element particles on the honeycomb surface of the catalytic converter and reveals large agglomerates and individual particles not observed by any of the first three techniques discussed. This technique preserves the distribution and locations of the particles from the surface and in a great number of cases the active element particles are freed from the washcoat allowing easy EDS analysis for identification of the active elements present. Furthermore, the large number of particles removed from the surface ensure good statistical measurements.

4. Visual means, subject to focus and contrast effects and where possible, EDS analysis, are relied upon for identification of the active element when using the microtomy, tissue-grinding or crush and grind techniques.

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