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Application of Scanning Electron Microscopy to the Study of the Morphology of Multicomponent Catalyst Systems

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The morphology of multicomponent catalyst systems was investigated with the aid of the scanning electron microscope (SEM). The catalysts which were studied consisted of alumina, complex aluminates, and a mixture of both. These materials are used in the reduction of sulphur dioxide by methane to sulphur. Direct observations with the scanning electron microscope permitted the study of the effects of various thermal treatments on changes in the morphology with respect to pore geometry, topography and to both particle size and shape. It is shown that changes in the catalyst morphology – as resolvable by the SEM – are related to changes in catalytic activity.

1. Introduction

The rate of a reaction involving heterogeneous catalysis is a measure of the activity of the catalyst [1]. While chemisorption phenomena, surface area, pore volume, pore size distribution and surface topography affect activity, Taylor has proposed [2] that certain "active sites", representing a small fraction of the total surface area, are responsible for catalytic activity. Numerous studies carried out to identify these active sites [3-7] have been concerned with crystal structure and with morphological features such as lattice defects, dislocations, and surface steps. Employing transmission electron microscopy, electron and X-ray diffraction, these studies, carried out on highly pure materials, preferably well-defined single crystals, have shown that catalytic activity can be correlated with surface morphology. Although parallel studies on complex systems such as polycrystalline, multicomponent catalysts of the type frequently employed in technical processes have not been carried out, we may assume that here too there is a direct relationship between surface morphology and catalytic activity. Studies employing indirect methods, mostly those based on adsorption phenomena have been carried out on these complex systems and show in many cases a direct relationship between surface area, pore size, and pore volume on the one hand, and catalytic activity on the other.

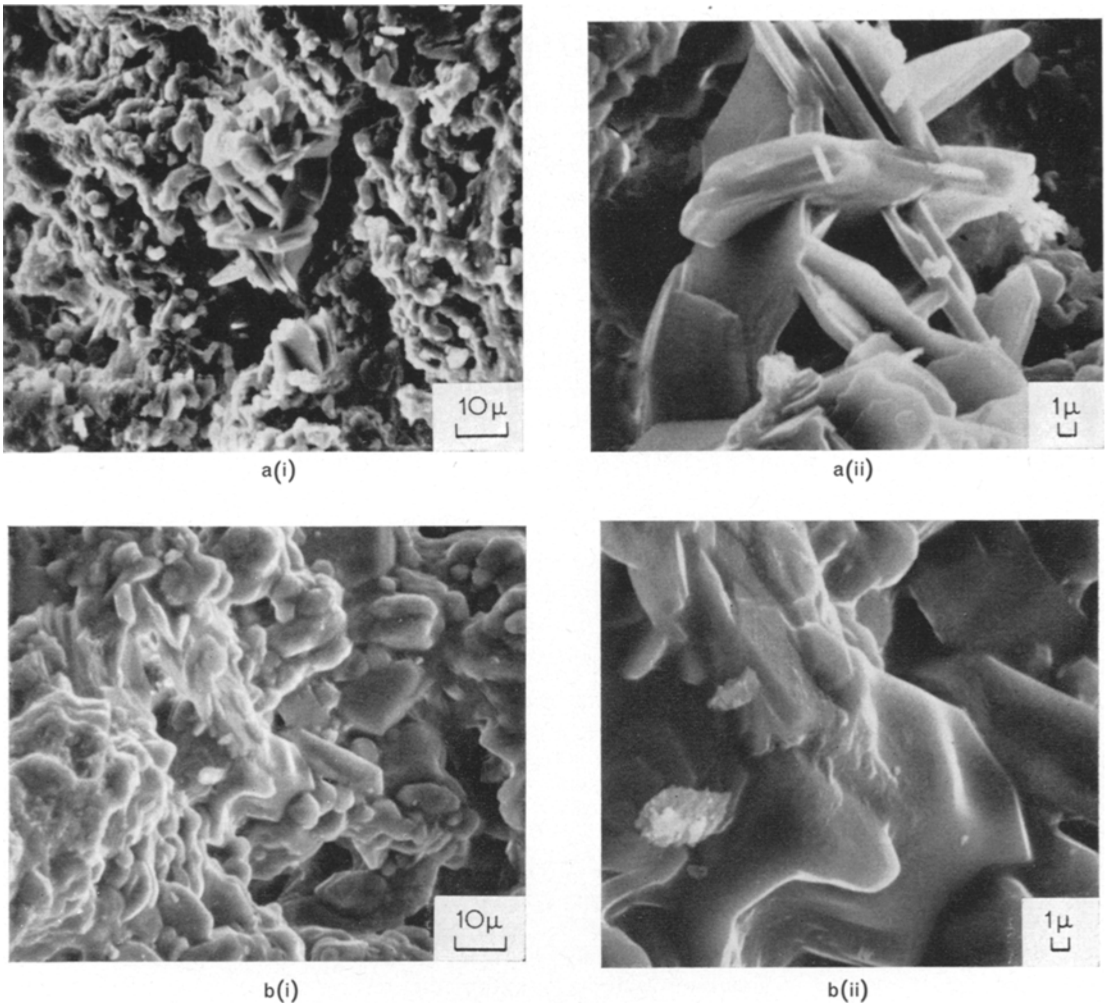
The scanning electron microscope (SEM), which has recently become available, permits a direct examination of the surfaces of complex catalyst systems. Using scanning electron microscopy, the effects of processing conditions on surface morphology can conveniently be studied and predictions on the performance of a catalyst made, if one accepts the premise that there exists a direct relationship between changes in the microstructure of catalyst surfaces and changes in the morphology resolvable with the SEM.

2. Experimental

This paper is concerned with a scanning electron microscope study of the morphology of a catalyst system used in the reduction of sulphur dioxide by methane to sulphur. The reaction proceeds according to the following equation:

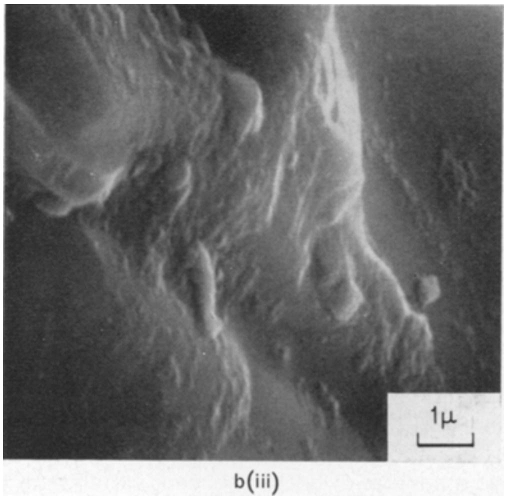
$$2SO_2 + CH_4 \rightarrow 2S + 2H_2O + CO_2 \quad (1)$$

Our work was mainly concerned with the effects of various thermal treatments on the surface morphology of the catalyst and the resulting changes in catalytic activity. The catalysts used in this study were alumina, complex aluminates and a mixture of both. The main variables in the treatment of the catalysts were temperature and time. The activity of the catalyst is expressed as



a(i) a(ii)

b(i) b(ii)



b(iii)

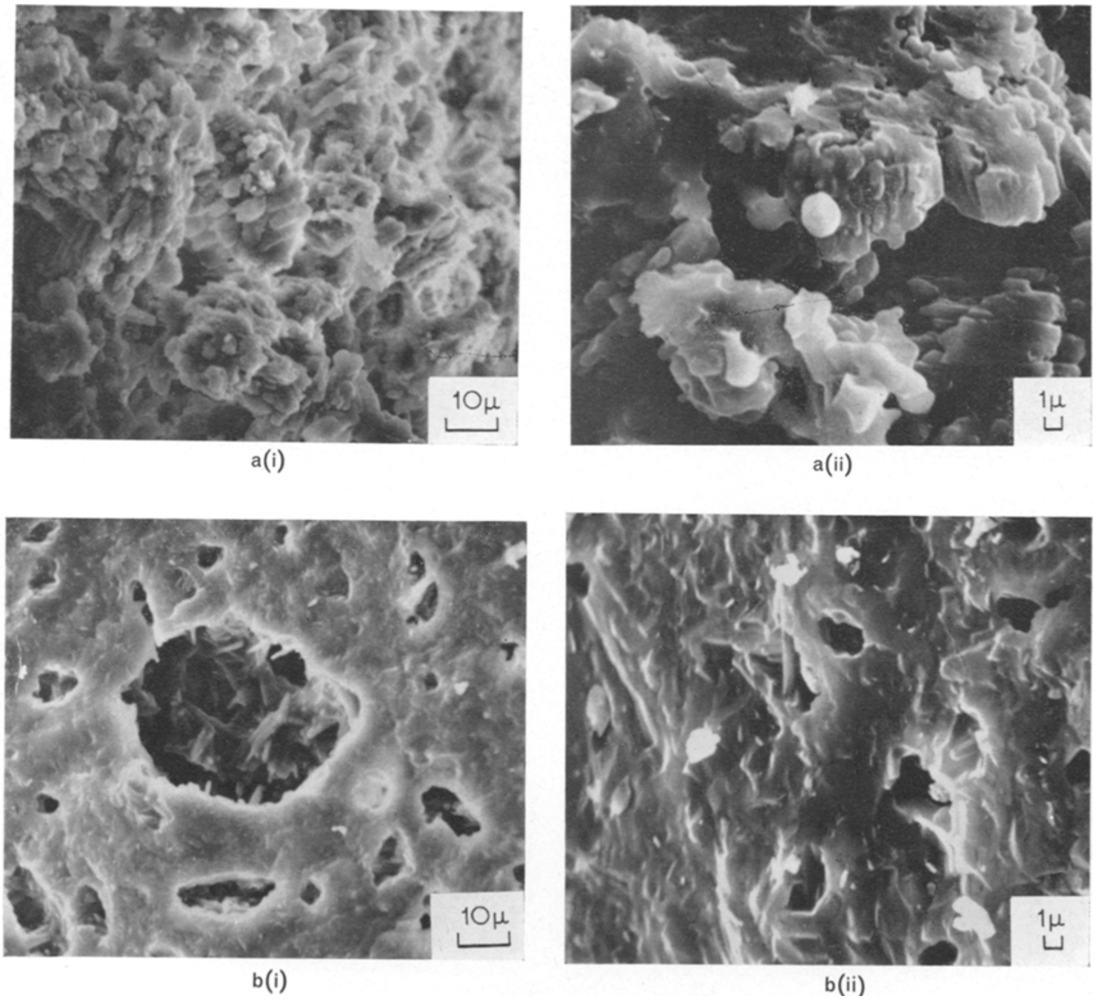
Figure 1 (a) Alumina/complex aluminates, 1300° C, 24 h. (b) Alumina/complex aluminates, 1300° C, 168 h.

100% if equation 1 is followed stoichiometrically. The treatment conditions for the catalysts studied and the respective activity ratings are listed in table I.

Examination with the scanning electron micro-

TABLE I Treatment conditions and activity values of catalysts.

Catalysts	Temp. °C	Time h	Activity value ± 0.5%
1. Alumina/complex aluminates	1300	24	93.0
2. Alumina/complex aluminates	1300	168	90.0
3. Alumina	1300	24	92.0
4. Alumina	1600	24	75.0
5. Complex aluminates	1000	3	95.0
6. Complex aluminates	1300	24	90.0



a(i) a(ii)

b(i) b(ii)

Figure 2 (a) Alumina, 1300° C, 24 h. (b) Alumina, 1600° C, 24 h.

scope was carried out on both the outer surface of the catalyst granules and on surfaces exposed by brittle fracture. A thin metal alloy film (Au/Pd) was vapour-deposited onto the surface to render the specimens conductive. Representative scanning electron micrographs were obtained at two different magnifications for each of the specimens studied. The final magnification is shown on each of the figures.

3. Results and Discussion

The results of the microscopical study are shown in figs. 1a to 3b. Fig. 1a shows photomicrographs of a mixture of alumina and complex aluminates that had been exposed to 1300° C for 24 h. This material is characterised by the presence of numerous agglomerates formed by platelets that exhibit sharp edges and corners. Heating the catalyst mixture at the same temperature for a period of 168 h resulted in partial fusion, recrystallisation and grain growth, as shown in fig. 1b. The loss of the characteristic sharp edges and corners of individual platelets and the change of the pore geometry is paralleled by a loss in activity from a value of 93 to 90%. It should be noted that partial fusion had occurred, although the melt temperatures of both the alumina and the complex aluminates are above the treatment temperature. This may be explained by the fact that surface mobility starts at temperatures as low as approximately $T_m/2$ [8]; and in addition, the presence of impurities in these commercial grade materials may act as "flux" and result in a lowering of the melting point of the components.

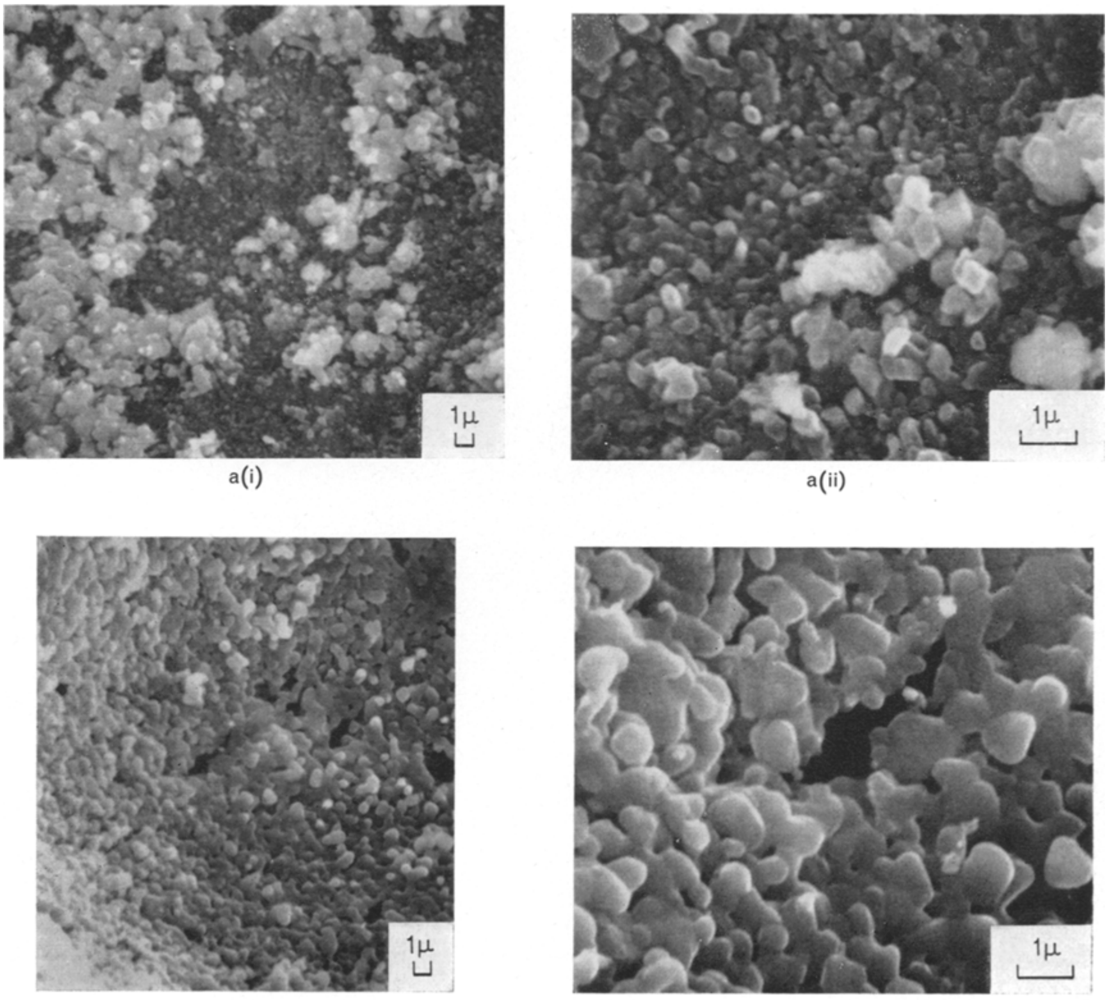
Figs. 2a and b show photomicrographs of alumina that had been exposed to temperatures of 1300 and 1600° C, respectively, for a period of 24 h. A pronounced change in morphology with respect to both shape and size of particles and pore geometry was accompanied by a drop of the activity from 92 to 75%.

The "fused" appearance of large areas, visible in fig. 2b, was not a surface effect but was observed throughout the granules. The presence of these crusts indicates that a large portion of the surface of the remaining or recrystallised particles of the catalyst had become inaccessible.

Figs. 3a and b illustrate the effect of both temperature and time on the morphology of the complex aluminates. Fig. 3a shows the material heated at 1000° C for 3 h. Numerous small individual particles are present and exhibit the typical sharp edges and corners of tabular and equidimensional crystals. Increasing both temperature (1300° C) and time (24 h) of the treatment resulted in rounding of edges and corners of particles, grain growth, and partial fusion, as can be seen in fig. 3b.

4. Conclusion

Inspection of figs. 1a to 3b in combination with the measured values of activity shows that changes in the catalyst morphology with respect to surface topography and pore geometry – as resolvable by the scanning electron microscope – are related to changes in catalytic activity.



a(i) a(ii)

b(i) b(ii)

Figure 3 (a) Complex aluminates, 1000° C, 3 h. (b) Complex aluminates, 1300° C, 24 h.

Although the present limit of resolution of the SEM (~ 300 Å) is not adequate for the identification of dislocations, lattice imperfections and other microstructure characteristics, scanning electron microscopy must be considered an extremely useful tool in the evaluation and characterisation of multiphase, multicomponent catalyst systems.

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