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High-resolution scanning electron microscopy for the characterization of supported metal catalysts

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A scanning electron microscope with a short-focal-length "immersion" lens and sub-nanometer resolution has been used to characterize several oxide-supported metal particle catalysts. Nanometer-sized metal particles in the Pt/TiO_2 and Pd/SiO_2 systems could be imaged with best clarity at the upper end of the operating voltage range (20–30 kV). However, visibility depended upon an adequate yield of secondary electrons relative to the support: small Pt particles on CeO_2 could not be located by secondary electron imaging. Best visibility of the surface topography of the support was obtained at lower accelerating voltages.

Keywords: scanning electron microscopy (SEM); supported metal catalysts; small metal particles

1. Introduction

Oxide-supported metal particles are widely used as heterogeneous catalysts in the petrochemical industry and for environmental control. Information about particle size, shape and distribution, as well as support topography, is essential for reaching a full understanding of the catalyst behavior. Electron microscopy techniques thus continue to be heavily used for catalyst characterization [1–5], in parti-

cular to monitor microstructural changes as a function of treatment conditions. The conventional transmission electron microscope (TEM) can provide high spatial resolution detail on a highly localized scale but the information that can be extracted about particle size and location invariably suffers because of overlapping contrast from the support. Thicker regions of the support cannot be imaged properly because of absorption and multiple scattering of the electron beam. Therefore, any useful information is usually obtained from thin regions. Sample preparation is not a major problem with powder samples which can be easily deposited on "holey" carbon film. However, if the catalyst is in three-dimensional, macroscopic form, such as a bead or a pellet, or present as a washcoat on a monolithic ceramic support, then the preparation of suitable TEM samples can sometimes end up being a daunting task.

The scanning electron microscope (SEM) utilizes a finely focused probe of electrons that is scanned across the specimen while electrons emitted from the surface are used synchronously to form an image of the sample. Observation with the SEM readily provides information about surface topography, for example allowing a three-dimensional visualization of pore structure to be obtained. Ease of sample preparation and convenience of observation over a wide range of magnification represent further benefits of using the instrument. However, while the SEM appears to be a logical choice for studying bulk, unsupported catalysts, characterization of oxide-supported metal particle catalysts with the SEM does not seem to have been reported previously, possibly due to limited SEM resolution or charging of the insulating particle support.

The latest generation of SEMs utilize cold field-emission sources of high brightness with short-focal-length "immersion" lenses for specimen imaging rather than the standard configuration with the specimen located out of the lens field. This geometry enables secondary electron images of surfaces to be obtained with subnanometer resolution [6,7]. Examples of this type of instrument are the Hitachi S-5000 and the Jeol JSM-6000F. These high-resolution SEMs typically provide guaranteed resolutions for test objects ranging from 0.6 nm at 30 kV to 3.0 nm at 1.0 kV. In the present characterization study, we have used an S-5000 operated at accelerating voltages over the range of 2.0–30 kV. Coating of samples to improve secondary electron (SE) yield or to obviate charging effects has been deliberately avoided in order not to cause any modification of catalyst microstructure.

The basic principles of operation of the SEM are now well-established and will not be repeated here [8,9]. It is generally accepted [10] that the best attainable spatial resolution in the secondary electron signal is inevitably limited by the complex interplay of several factors, including the size of the incident electron probe, the (de)localization of the secondary electron excitation process [11], and the Poisson counting statistics of the detection/imaging process. Moreover, differences in SE yield are necessary in order to distinguish between different materials. Operation at higher voltage results in increased gun brightness, in turn giving rise to smaller probe sizes, and hence potentially improved resolution. The interaction volume is,

however, necessarily larger, so that surface detail is likely to be less visible unless the area being imaged is very thin. These general expectations were borne out by our observations of oxide-supported metal particle catalysts described in the following section. We have generally found that it was lack of available contrast that was ultimately limiting the detail visible in the HRSEM images, rather than the probe size or microscope resolution as conventionally defined. Thus, while the shape and habit of nm-sized metal particles could not be discerned, surface topography of the support could often be imaged in great detail.

2. Results

As an example of the types of images of supported metal catalysts that can be recorded with an HRSEM, figs. 1a and 1b show, respectively, low-magnification, and high-magnification, scanning electron micrographs from a Pt/TiO_2 specimen recorded at 30 kV. The TiO_2 support particles, approximately spherical in shape, typically ranged in diameter from about 20 to 100 nm whereas the supported Pt particles, clearly visible as small bright spots in fig. 1b, ranged from about 0.8 up to 14 nm in diameter. It appeared from these and other micrographs that the larger Pt particles were more likely to be located in the vicinity of kinks on the TiO_2 support surface. It was also significant that observations of a similar Pt/CeO_2 catalyst under similar conditions did not reveal any sign of Pt particles although they could be seen in high-resolution TEM profile images [12]. This latter result reinforces the fact that the visibility of metal particles relative to any particular oxide support is dependent upon differences in the SE yields.

For a comparison of images recorded at different voltages, figs. 2a and 2b show high-magnification views of a Pd/SiO_2 sample recorded at 2.0 and 20 kV, respectively. The edges of the Pd particles are clearly much better defined in the latter confirming the improved performance at the higher voltage. However, neither image is particularly useful in terms of providing any information about the three-dimensional nature of these particles except for some that are fortuitously protruding beyond the edges of the support. It was also interesting here that charging of the SiO_2 support particles by the incident beam did not create any problems for imaging at either operating voltage.

As a third and final example, figs. 3a and 3b are HRSEM images, recorded at accelerating voltages of 2.0 and 30 kV respectively, showing Ni particles supported on hydrous titanium oxide. For this particular sample, it is immediately clear from comparing the same features present in each of these images that the increased penetration depth of the 30 keV incident electrons has lead to substantial loss of topographical detail about the surface of the support. The three-dimensional nature of the support is much more apparent in the micrograph recorded at lower voltage.

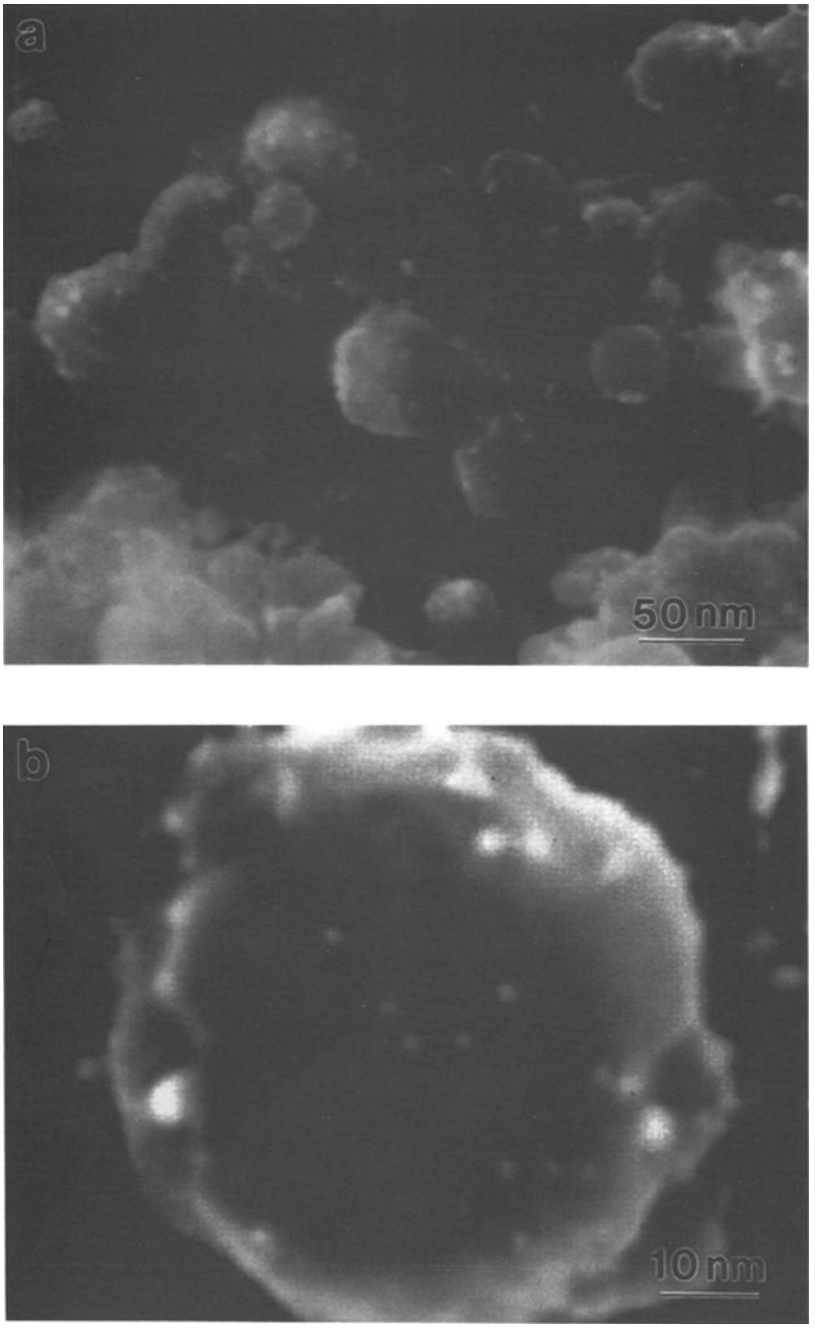

Fig. 1. High-resolution scanning electron micrographs of Pt/TiO_2 catalyst recorded at 30 kV: (a) low magnification; (b) high magnification.

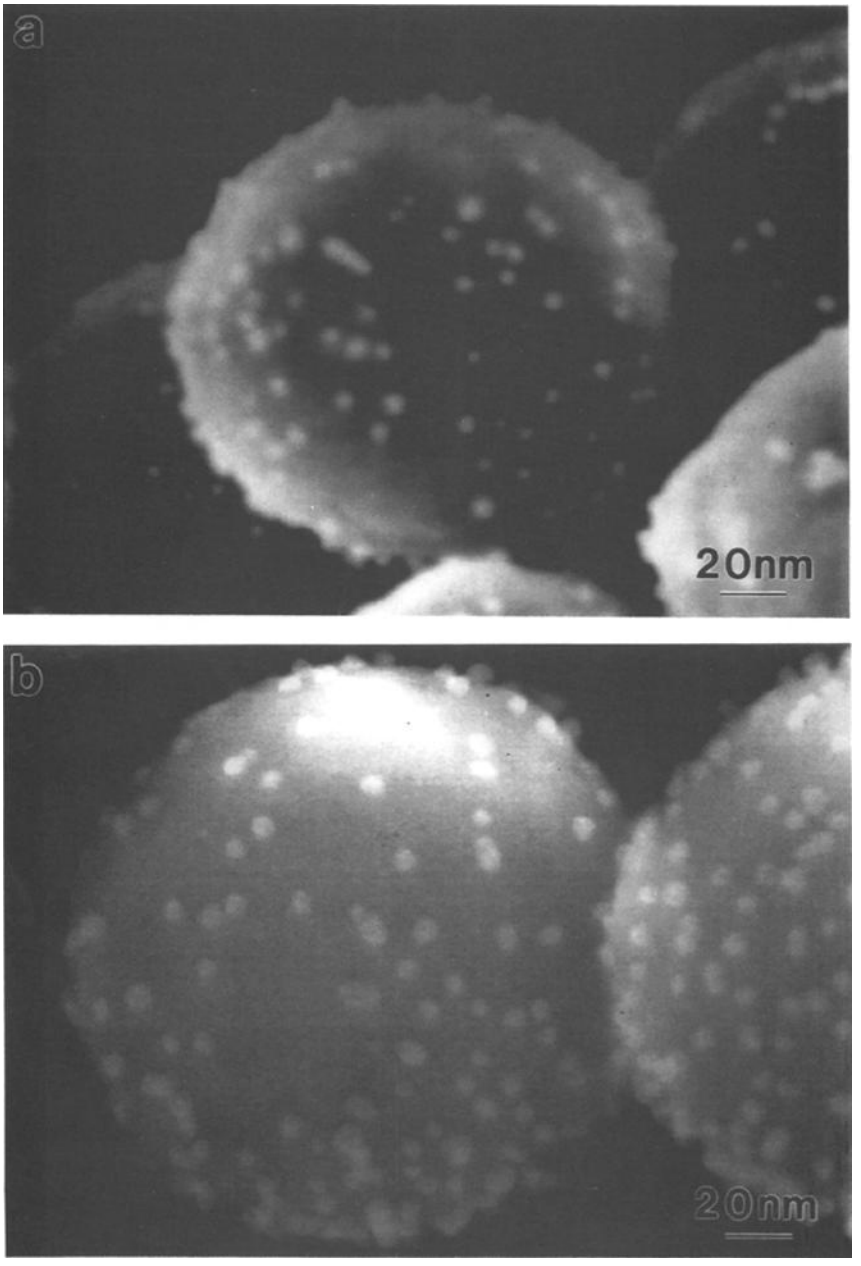

Fig. 2. Specimen of Pd/SiO_2 catalyst: (a) 2.0 kV; (b) 20 kV.

3. Discussion and conclusion

Our objective has been to evaluate the relative merits and drawbacks of using the high-resolution SEM for supported particle catalysis research. It was immedi-

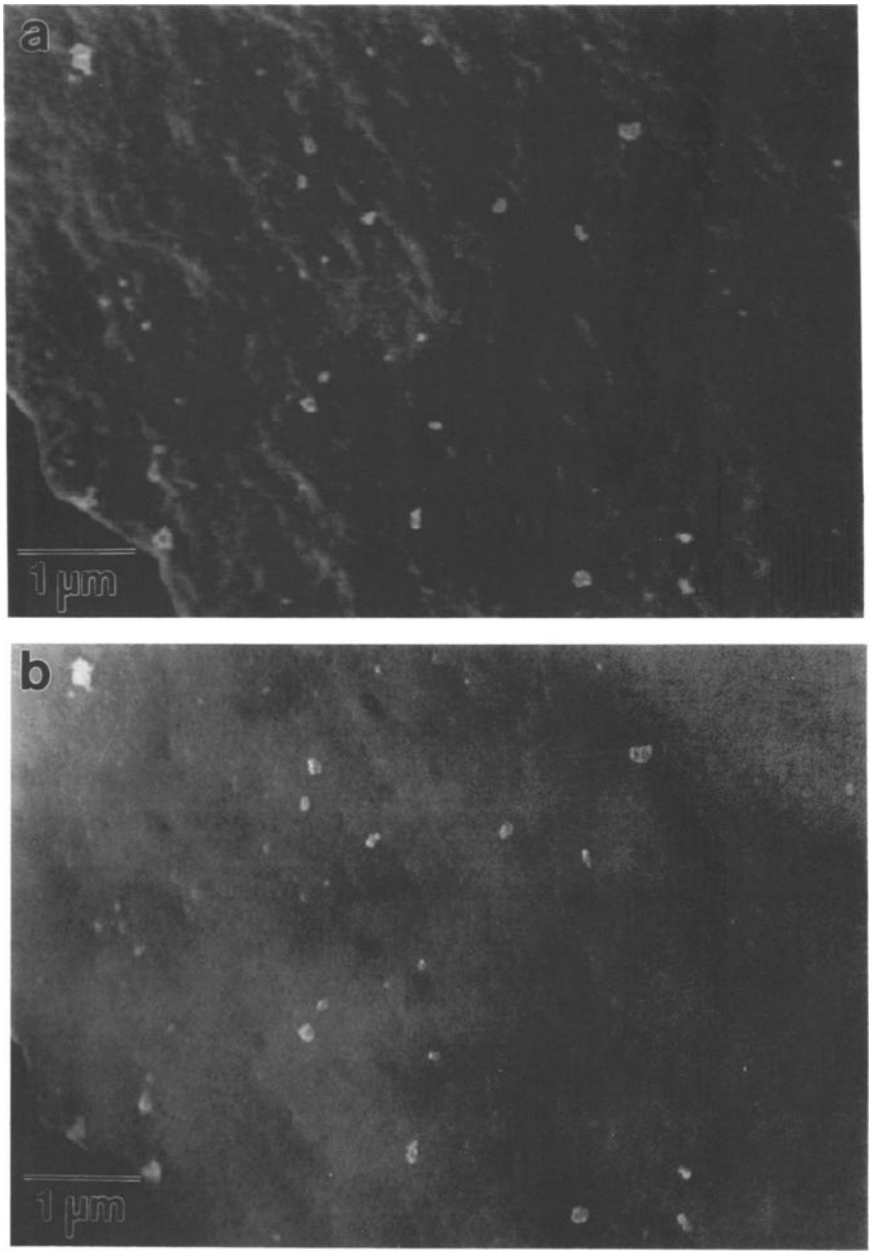

Fig. 3. Specimen of Ni supported on hydrous titanium oxide: (a) 2.0 kV; (b) 30 kV.

ately clear that images obtained with the HRSEM lacked any characteristic features, equivalent to lattice fringes in the conventional TEM, that could serve to facilitate positive identification of small metal crystallites. Moreover, our results

suggest that the detectability of supported particles may be poor when the particles are very small or when they have similar SE yields as their support. On the contrary, sample preparation is comparatively easy, location of areas of interest is rapid and straightforward, and there is no need to restrict examination to thin regions of the support, as with the TEM. Our experience also indicated that application of a surface coating was unnecessary, and no noticeable contamination of the surfaces was apparent during extended periods of observation provided that the samples were handled carefully and kept clean before insertion into the microscope. Relevant and useful information about the surface topography of the oxide support could usually be extracted by imaging at comparatively low accelerating voltage, even though the spatial resolution was then somewhat limited. Improved resolution detail about the size and distribution of the supported particles was, however, usually obtainable by imaging at higher voltage levels, except in some special cases where the relative SE yields of the support and the particles was comparable.

Overall, it can be concluded that the dedicated HRSEM should play an increasingly important role in characterization of oxide-supported metal particle catalysts, particularly since microscope resolution now makes it possible to image nm-sized metal particles. The HRSEM has obvious advantages in terms of its ability to handle macroscopic samples wherein the size distribution of the supported particles and the surface morphology of the support can be readily extracted.

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