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INTRAPELLET METAL CRYSTALLITE SIZE DISTRIBUTION IN IMPREGNATED CATALYSTS: NICKEL ON ALUMINA

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Design of intrapellet activity profiles in impregnated catalysts has long been a subject in the field of reaction engineering.[1] While a body of knowledge on the subject has been accumulated, actual catalyst preparation by impregnation has been almost exclusively concerned with the so-called impregnation profiles, i.e., the intrapellet metal concentration profiles. This is mainly due to the difficulty associated with the measurement of local activity as a function of pellet radius. To obtain intrapellet activity profiles, at least one must know the local surface area of the catalyst metal as a function of pellet radius. Or one would seek to obtain a intrapellet metal crystallite size distribution profile if the reaction concerned is structure-sensitive.

Reported here is an attempt to obtain the activity profiles of two Ni/alumina catalysts with different impregnation profiles. For that purpose metal crystallite size distribution was measured as a function of the positions in support pellets. It was found that intrapellet Ni crystallite size distribution is remarkably uniform, regradless of the mode of metal deposition or local level of metal loading.

Experimental

Two Ni/γ-alumina catalysts, one with subsurface impregnation profile (Type III[1,2]) and one with periphery-concentrated profile (hybrid of Types I and II), were examined (samples D-1 and E-4, respectively: see Fig. 2). Their preparation procedures have been reported elsewhere.[3,4] The support pellets used

have *ca.* 4 mm diameter, a BET surface area of 132 m^2/g and a total pore volume of 1.67 cm^3/g. For metal particle size measurement, electron microscopy was employed. Each pellet was sectioned into outer (fractional radius > 0.8) and inner (< 0.8) sections, mortar-ground, suspended in ethanol, and dispersed on a carbon film supported on a copper grid.

Prior to measurement of the Ni crystallite size distribution using a JEOL 7A transmission electron microscope (TEM), crystallite identification was performed by microdiffraction and electron energy loss spectroscopy (ELS) using a VG HB5 scanning transmission electron microscope (STEM). The combination of microdiffraction and ELS in STEM was used since microdiffraction alone was not expected to distinguish the γ-alumina from nickel aluminate unambiguously. Distortion present in microdiffraction due to instrumental problems was corrected by using an unambiguous γ-alumina crystallite as a standard.

Wide-area photographs on the same sample grids examined by STEM were taken by using TEM. From these photographs the metal particle size was measured and its distribution was obtained.

Results and Discussion

Crystallite identification

Using the annular dark field (ADF) imaging in STEM, the presence of intensely electron-scattering particles, mostly in the size range of 2–3 nm, was found. Microdiffraction from these crystallites,[5] after standard indexing, indicated that the crystallites examined were all single crystals of metallic nickel.
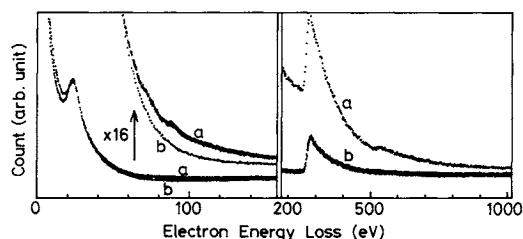
Fig. 1. Electron energy loss spectra from (a) support particle and (b) carbon film substrate.
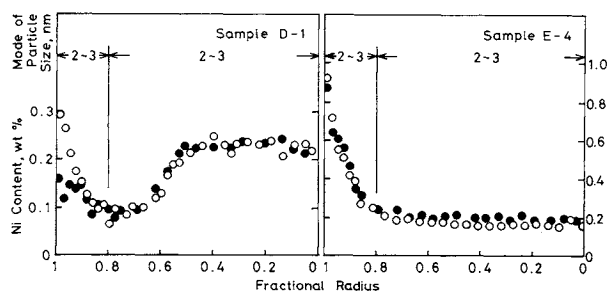

Fig. 2. Intrapellet nickel concentration profiles and intrapellet nickel crystallite size distributions in samples D-1 (left) and E-4 (right). Nickel particle size indicated is the mode of the crystallite size distribution. Open and closed circles for the impregnation profiles indicate non-sectioned and sectioned pellets, respectively, before drying.

No NiO particles were observed.

Alumina substrate particles were also examined by STEM, so as to confirm the presence or absence of nickel aluminate. ELS spectra from non-nickel particles, such as that shown in **Fig. 1**, showed energy-loss peaks attributable to Al_2O_3 and C plasmon losses (23 eV), Al L absorption edges (73 and 87 eV), C K edge (284 eV) and O K edge (523 eV). Peaks attributable to Ni absorption edges M_{III} (66 eV) and L_{III} (854 eV) were not observed in these spectra, indicating the absence of nickel aluminate.

From the above observations it is concluded that almost all the Ni is in the metallic state.

Intrapellet crystallite size distribution

Figure 2 shows intrapellet Ni crystallite size distribution of the two samples, obtained from bright-field TEM photographs, along with their Ni concentration profiles measured by electron-probe microanalyzer (EPMA). Intrapellet crystallite size distribution was remarkably uniform throughout the pellet of both samples: in any position of either sample, particles in the 2–3 nm range constituted over 30% of the population, and those in the 1–4 nm range over 85%. A small population, less than 15% of the particles, was found in the 4–7 nm range.

This result is rather surprising in that the Ni loading and the mode of its deposition are very different at different radial positions in the two samples.[3,4] At fractional radius > 0.8 in sample D-1, Ni is deposited by adsorption during impregnation and

by forced deposition during drying (for detailed discussions see ref. 3). In the other part of sample D-1 the mode of deposition is adsorptive. In sample E-4 the mode of deposition is entirely adsorptive, but the Ni loading varies more than fourfold, from 0.2 to 0.9 wt%.

Such insensitivity of metal crystallite size to its loading is sometimes observed. Dorling et al.[6] report the preparation of Pt/SiO_2, in which platinum particle size remained constant over a 40-fold variation of Pt loading. They explained it by assuming that each pore may contain only one metal particle: increasing the metal loading only increases the number of pores that contain metal particles, and not the size of the particles. Whether this explanation applies to our case remains to be seen.

The consequence of the uniform intrapellet crystallite size distribution is that the activity profiles may parallel the impregnation profiles. In the present samples all Ni is present as metallic Ni, as shown above. Thus the impregnation profiles, which are measured by EPMA and hence do not distinguish chemical states of Ni, are equivalent to the metallic Ni concentration profiles. Given this information, it may be reasonable to consider that the uniform size distribution means weak dependency of metal surface area on local metal loading. Furthermore, as seen above, the Ni size distribution itself does not depend strongly on the local metal loading.

In general, local catalytic activity may be taken to be proportional to local density of active sites if the turnover frequencies (TF) over these sites are constant. Thus the determination of activity profiles must be concerned with two points: local density of active sites and their TF. Density of active sites may depend on various factors, including metal surface area and crystallite size distribution. TF may also depend on various factors, including the extent of metal-support interaction. At the present time measurement of these quantities itself is not well established. Development of techniques which would enable us to measure them as a function of support pellet radius is of importance in order to close the gap between design and preparation of impregnated catalysts.

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