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Note

ELECTRON MICROSCOPIC AND DIFFRACTION STUDIES ON Fe(III)–Al(III) MIXED OXYHYDROXIDE/OXIDES

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During the course of our investigation on the catalytic and solid state (structural, electrical, thermal and magnetic) properties of iron–aluminum mixed oxides [1–4], we observed that the mixed oxides containing 20–100 mole % of alumina were amorphous to X-rays. It was also reported that alumina doped lepidocrocite or goethite was not detected by X-ray diffraction, probably due to limited crystal development [5–7]. Further, Mössbauer spectroscopic studies revealed that these specimens exhibited superparamagnetic behavior at room temperature [4]. This behavior was explained on the assumption of particle size or cluster or solid solution. In order to substantiate this, electron microscopic and diffraction studies were carried out and these results are reported here.

An electron microscope EM6(AEI,UK) was used to measure the particle size and to obtain electron diffraction patterns of the mixed oxide catalysts prepared by the coprecipitation technique [2]. The mole % of alumina in the different samples S8–S12 are 20, 40, 60, 80 and 100%, respectively. The instrument was operated at suitable magnification to measure the particle sizes. The resolution obtained in this instrument was 10 Å. The electron diffraction patterns were observed for these materials using 75 kV accelerating voltage. The d values were calculated using the equation.

$$d_{hkl} = \lambda D/2R$$

where λ is the wavelength (0.039 Å) of the electron beam, R is the radius of the diffraction ring and D is the focal length. This equation is derived from the Bragg equation for smaller angles.

Powdered samples were dispersed in *n*-butyl alcohol and subjected to vigorous shaking for an hour using an ultrasonic vibrator and a drop of the suspension was put on a carbon film placed on a copper grid. It was dried for 30 min and the resulting specimen was used for microscopic as well as diffraction studies.

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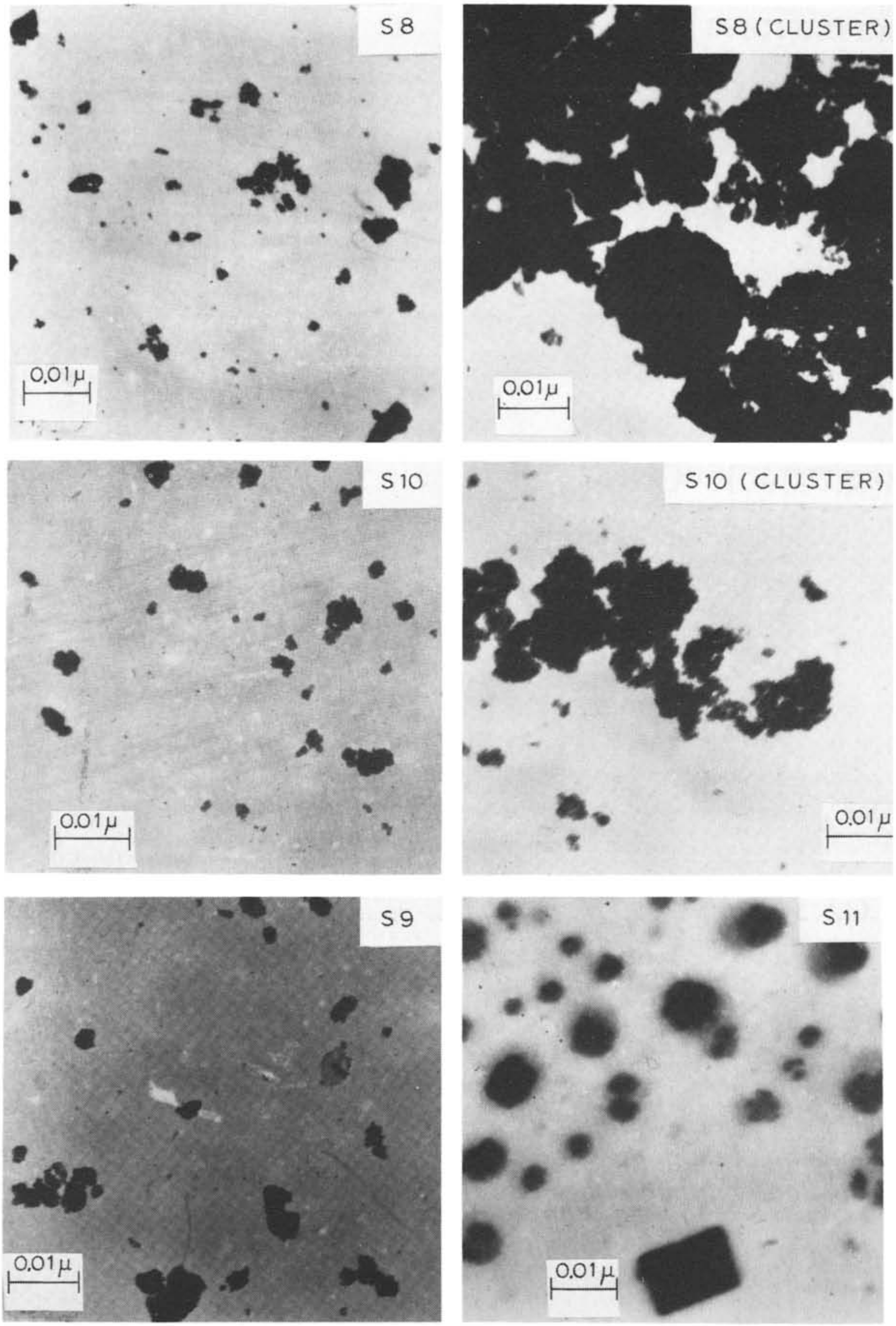

Fig. 1. Electron micrographs of Fe(III)–Al(III) mixed oxyhydroxide/oxides.

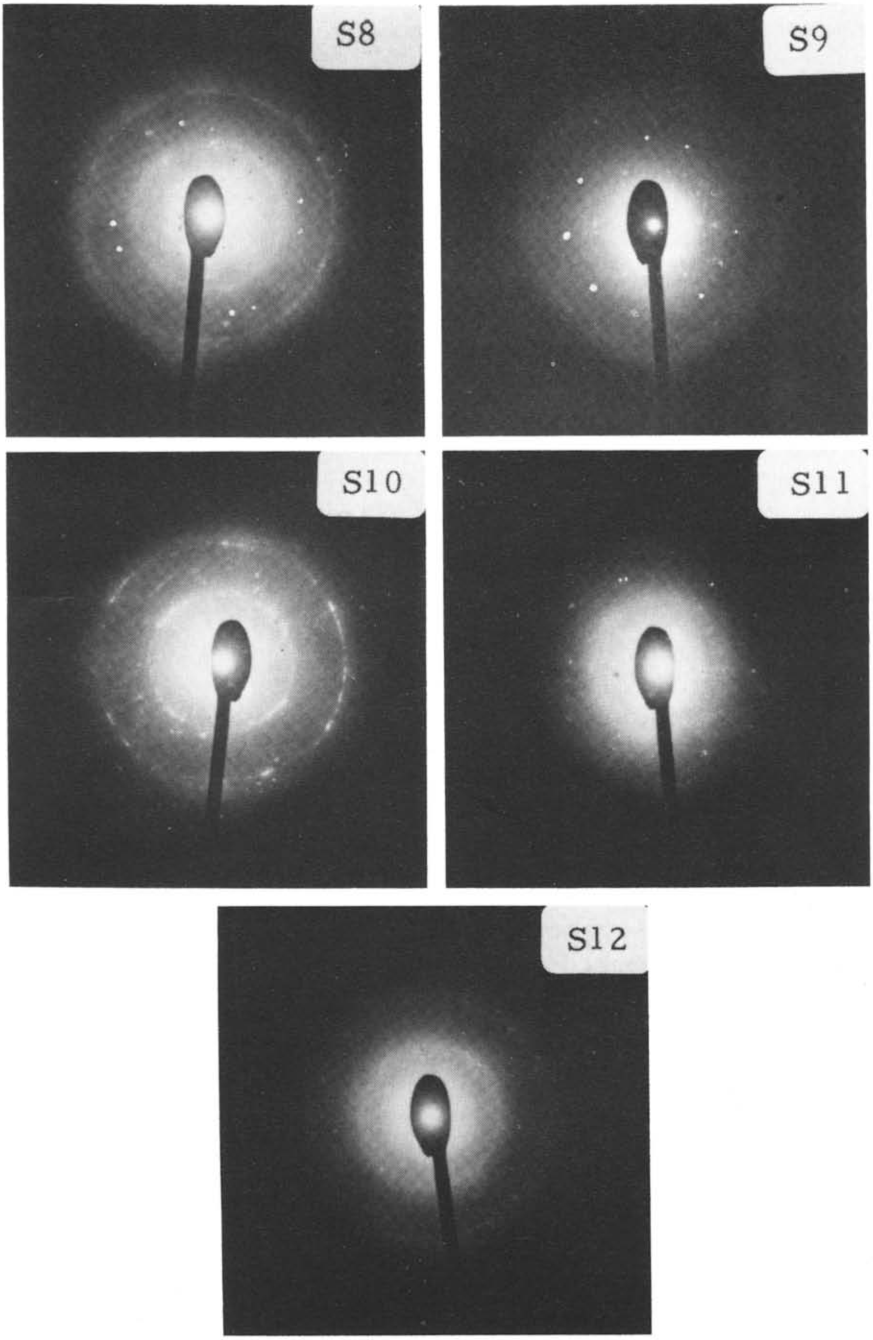

Fig. 2. Electron diffraction patterns of Fe(III)–Al(III) mixed oxyhydroxide/oxides.

Micrographs for the different specimens are given in Fig. 1. Microscopic observation indicates that these were dark brown or red and some of them were very thin flakes. The sizes of the isolated particles were measured and averaged. These results reveal that the samples S8–S12 contain a larger fraction of small particles (< 100 Å) agglomerated together and a smaller fraction of bigger particles.

These materials were initially shown to be amorphous since no lines were observed in X-ray diffraction. No clear electron diffraction patterns were observed for the thicker particles. However, the diffraction patterns were obtained for small and thin flakes, which were transparent to the electron beam. The diffuse rings along with spots are given in Fig. 2. The position of the rings and spots were measured for these patterns. The calculated d values of the samples are compared with the standard d spacings of compounds like α, β and γ forms of FeOOH and AlOOH; α, β, γ and δ forms of Fe_2O_3; α, β, γ, δ, ψ, η and κ forms of Al_2O_3 and $FeAlO_3$ [8]. Although a thorough examination of the diffuse patterns produced by these materials is not attempted, their resemblance to the recorded crystalline phases gives some information about the materials for which X-ray technique is not possible.

These results indicate that $FeAlO_3$/γ-FeOOH (d values 1.48 and 1.17 Å) is present in samples containing 20 and 40 mole% of alumina. γ-Al_2O_3 (d values 1.40 and 1.03 Å) is present in specimens containing 60 and 80 mole%, while $FeAlO_3$ is also present in the latter. In addition to γ-Al_2O_3, γ-Fe/AlOOH (d values 1.45 and 1.31 Å) is also present in S10. Probably these phases (in sample S10) lead to more cluster formation and interaction of zones as reported earlier [3]. Pure alumina (S12) is found to be γ-Al_2O_3. Kundig et al. [9] suggested that the oxide material could exhibit superparamagnetism if they formed clusters and the particle size was $\leqslant 130$ Å. Similar results are observed here too. It is difficult to ascertain which phase causes superparamagnetism. However, these results indicate that the existence of clusters and ultrafine particles may be responsible for the reported magnetic behavior [4].

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