NOTE

Characterization of Oxide Catalysts by Electron Probe Microanalysis

Electron probe microanalysis (EPMA) appears to be an attractive technique for characterizing oxide catalysts with respect to the distribution of promoters, the separation of new phases from solid solutions and the homogeneity of catalyst preparation (1–4). It has been shown previously (4) that high-purity α-Fe_2O_3 doped with 0.2 at.% Mg or more precipitates the spinel phase, magnesium ferrite, identified by EPMA. The limit of Mg solubility in Fe_2O_3 could also be sensitively determined by the appearance of anomalies in the electrical properties, dc conductivities and Seebeck voltages (4, 5). Abrupt changes in catalytic properties (6), i.e., activation energies for N_2O decomposition and selectivity in the conversion of methanol to formaldehyde, were associated with the onset of phase separation. Now, it is known that Ni and Ca also have very limited solubilities in Fe_2O_3. Therefore, it would seem that these systems provide an opportunity to check the precision with which catalyst performance can be correlated with the subjective characterization of the catalyst by EPMA. In contrast, Ti has a greater solubility than Ni or Ca, and 2% Ti-doped Fe_2O_3 samples should show no inhomogeneity with respect to Ti-distribution when examined by EPMA, if the catalyst preparation technique has been satisfactory.

EXPERIMENTAL METHODS

Catalysts were prepared from the same high-purity ferric oxide (Johnson Matthey and Co. Ltd.), used in the previous work (4, 6) and contained only the following impurities: Ag, Cu < 1; Mg, 1; Mn, Ni, 2; Si, 10 ppm. The procedure for incorporating magnesium, pelleting and producing the catalyst charge for the reactor has been described in detail elsewhere (4). In the present work, nickel or calcium were introduced from standard dilute solutions containing the nitrates, and titanyl oxalate solutions were used to prepare Ti-doped ferric oxide. In the final incorporation stage, pellets were fired in air at 1300°C for 15 hr (unless stated otherwise) and allowed to cool slowly in the furnace.

Specimens of oxide catalyst for electron probe microanalysis were set in a plastic block and polished to a flat surface before examination in a "Geoscan" (Cambridge Scientific Instruments Ltd.) for variations in Fe, Ni, Ca or Ti content, as appropriate. Rates for N_2O decomposition were measured in a flow system using a tubular silica reactor charged with a known weight of catalyst. The design of the reactor and analysis of reaction products have been described previously (6).

RESULTS AND DISCUSSION

Electron Probe Microanalysis

No inhomogeneity was detected by electron probe microanalysis in samples containing 2 at.% Ti but some samples of ferric oxide doped with Ni or Ca exhibited regions (Fig. 1) of higher Ni or Ca content than their surroundings. Inhomogeneities were detected at the 0.1% Ni level and above but not at 0.01 or 0.05% Ni, whereas they were found down to 0.03% Ca. Table 1 shows the quantitative analysis of some
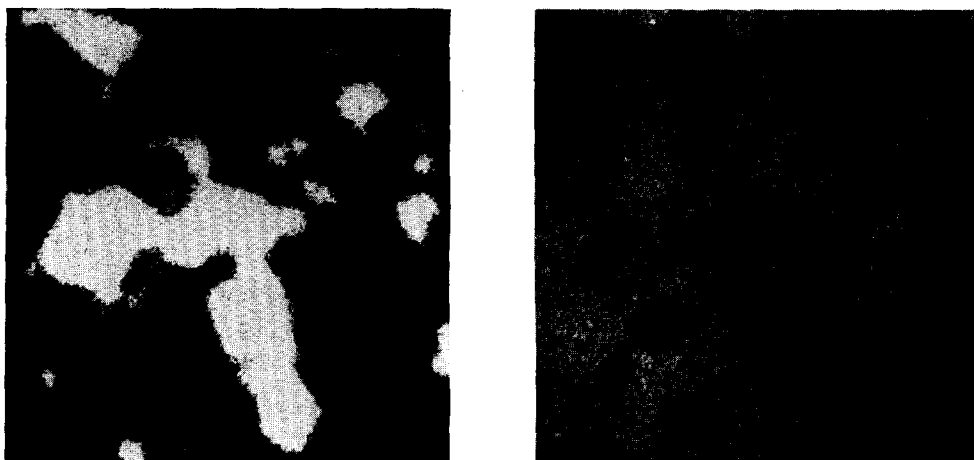
FIG. 1. Electron probe microanalysis of Fe_2O_3 doped with 2 at.% Ni showing inhomogeneities as enhanced Ni content, bright areas (left), and depleted Fe content, grey areas (right). Magnification, 1000×.

of these inhomogeneous regions; count rates due to iron and nickel or iron and calcium are compared with standard samples of nickel and calcium ferrite. Triplicate sets of counts were taken and the average is recorded; counts were taken on the standard before and after counts on the corresponding catalyst sample and the range of count rates is indicated. Areas 1 and 2 in the Ca-doped sample were separate places on a large inhomogeneous region, while areas 3, 4 and 5 were much smaller areas. Correction of the data to provide exact compositions presents some difficulties, e.g., the Fe K_α signal from small inhomogeneities is enhanced by radiation from the neighboring ferric oxide. A computer program making corrections for atomic number effect, absorption, etc., gave the compositions shown for Fe and Ca in the sample with 0.3% Ca. Nevertheless, a satisfactory identification of the regions of interest as nickel ferrite or calcium ferrite may be made, using this method based on the preparation of standard compounds.

At 1300°C, up to 3-4% TiO_2 dissolves in Fe_2O_3 (7), forming solid solutions, and thus our samples with 2% Ti should avoid the formation of pseudobrookite as a second phase. The absence of inhomogeneities in our 2% Ti-doped samples confirms that the preparation technique

TABLE 1

ELECTRON PROBE MICROANALYSIS OF INHOMOGENEITIES

		Counts/sec		Composition (wt %)	
Sample	Area	Fe K_α	Ni K_α or Ca K_α	Fe	Ca
Fe_2O_3 + 0.5% Ni		4750	3000		
Fe_2O_3 + 2% Ni	1	4200	3070		
	2	4280	3110		
$Fe_2O_3 \cdot$ NiO (standard)		4860 ± 30	3300 ± 20		
$Fe_2O_3{}^a$ + 0.3% Ca	1	4152	1570	51.6	17.9
	2	4004	1504	49.9	17.2
	3	4450	1222	55.0	13.9
	4	4289	1392	53.0	15.9
	5	4183	1535	51.8	17.6
$Fe_2O_3 \cdot$ CaO (standard)		4182 ± 15	1632 ± 10	$(51.8)^b$	$(18.6)^b$

[a] Fired at 1100°C for 15 hr.

[b] Calculated.

adopted can produce satisfactory incorporation. Hence, for Ca- or Ni-doped samples, the appearance of inhomogeneities indicates that the solubility limit has been exceeded. In comparison, with previous EPMA results for Mg-doping (4), the order of solubility is:

$$Ca \ (0.99 \ \text{Å}) < Ni \ (0.72 \ \text{Å}) < Mg \ (0.65 \ \text{Å}),$$

i.e., solubility increases with decreasing radius of the divalent ion (shown in brackets).

N_2O Decomposition

The decomposition of N_2O was examined over a wide range of conversions, and kinetic equations applicable to a flow system were modified for volume change during reaction as previously (6). Good linear plots were obtained from which the activation energies (E) shown in Fig. 2 were derived. The variation of E with Mg-doping found in previous work (6) is shown for comparison (broken line). The plateau in the Mg-curve at 32.4 kcal/mole represents the mean activation energy observed for N_2O decomposition over six catalysts containing between 0.1 and 2.0% Mg and should be compared with 33.1 kcal/mole for undoped ferric oxide.

Addition of Mg converts pure Fe_2O_3 (n-type) into a p-type semiconductor, and so one interpretation of the initial decrease in E is to be found in the boundary layer approach. However, when the Mg-content is 0.1% or more, E reverts to the value for pure Fe_2O_3, and it would seem that the surfaces of catalysts with >0.1% Mg are composed of large areas of almost pure haematite, with Mg accumulated into "islands" of magnesium ferrite, as suggested by EPMA. (Pure magnesium ferrite has a low activity for this reaction (6) and it was found in the present work that the ferrites of Ni and Ca are also relatively inactive). Not unexpectedly, the reversal in the direction of activation energy change is observed at Mg-contents just *below* that at which EPMA is able to detect the onset of ferrite formation. EPMA detected magnesium ferrite at 0.2 at.% Mg and above, whereas E has reverted to the value for pure Fe_2O_3 at 0.1% Mg.

The same pattern of activation energy variation is again observed for Ni-doping, and again EPMA had detected phase separation above a certain doping level. However, for Ni-doping, the reversal in the direction of activation energy change occurred at Ni-contents *above* that at which
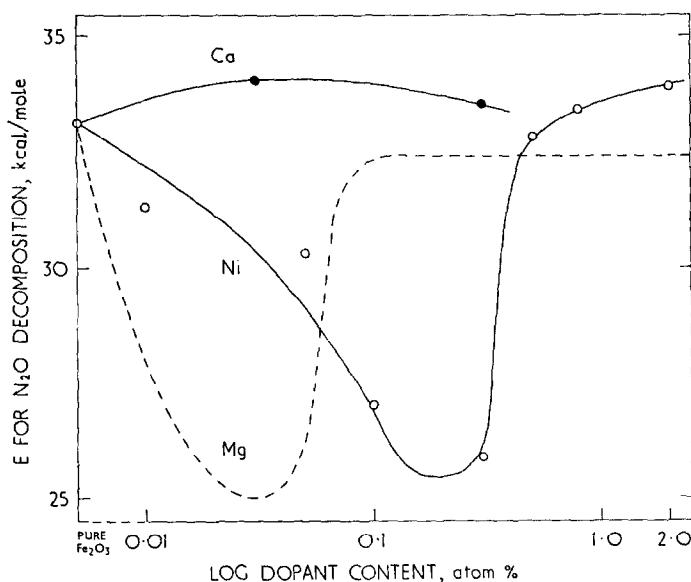

FIG. 2. Variation in activation energy for N_2O decomposition over doped Fe_2O_3 catalysts as a function of Ni-content (○) or Ca-content (●). Broken line shows previous results (6) for Mg-doping.

ferrite was first detected by EPMA. (Inhomogeneities were first detected at the 0.1% Ni doping level). It could be considered that EPMA has detected reasonably well a characteristic of these oxide catalysts which correlates with changes in catalytic properties. Nevertheless, catalysts with Ni-contents between 0.1 and 0.5% Ni, according to catalytic behavior, must possess surfaces still doped with nickel ions which have not accumulated into the "islands" of ferrite. Clearly, a feature of this type is beyond the capacity of the instrument to resolve.

The results of Ca-doping are entirely satisfactory, in that the presence of calcium ferrite was detected by EPMA down to the lowest level examined (0.03% Ca) and no minimum in activation energy is indicated. Hence it is concluded that EPMA has provided a *qualitative* description of these Mg-, Ni- or Ca-doped Fe_2O_3 catalysts around which a plausible explanation of catalytic behavior can be developed.

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