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The Distribution of Promoters in Magnetite Catalysts

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The oxides of Ca, Mn, Mg, Ti, Al, Li, and Na readily go into solid solution with Fe_3O_4. It should therefore be possible to prepare magnetite catalysts in which there is a truly homogeneous distribution of promoters. While silica does not appear to dissolve in Fe_3O_4 (and is therefore an ineffective structural promotor) it does inhibit the solution of the more basic promoters. It should be avoided if homogeneous alkali-promoted catalysts are desired. X-Ray line-broadening studies on the reduced magnetites confirm that Al_2O_3 and TiO_2 are superior to MgO as structural promoters while MnO is relatively ineffective. K^+ and Ba^{2+} ions could not be induced to enter into solution in magnetite.

INTRODUCTION

There are two general types of promoters of interest in the preparation of fused magnetite for use, after reduction, as catalysts in the Fischer-Tropsch hydrocarbon synthesis. They are the structural promoters which are added primarily to produce a stable high area catalyst and the chemical promoters which influence the selectivity of the reaction (*1*). The structural promoters are nonreducible metal oxides which are capable of going into solid solution with magnetite and hence are well dispersed throughout the oxide mass. When the magnetite is reduced these promoters precipitate between the metallic iron crystallites and so mechanically prevent to some extent the sintering of neighboring iron crystallites. This stabilization results in high surface area catalysts.

The chemical promoters are the oxides of the alkali metals and their effectiveness increases with the basicity of the oxide (*1*). It is well known that the selectivity shifts towards heavier hydrocarbon production with increasing alkali content (*1*) and it is therefore conceivable that if the distribution of alkali is very heterogeneous, with some particles having a high alkali concentration on their active surfaces while others have little or no alkali present, then the former will produce long-chain hydrocarbon products while the latter will produce lighter products only. This will result in the overall production of an undesirably wide product spectrum. If this picture is correct then a narrower spectrum should result if the alkali were homogeneously distributed. One method of achieving this would be by inducing the alkali ions to enter into true solid solution with the catalyst precursor, magnetite.

For both structural and chemical promoters therefore it seems desirable that the promoter cations dissolve in magnetite. According to Gorter (*2*) metallic ions which have been found in oxidic spinels have Goldschmidt radii that lie between 0.44 and 1.0 Å. The ions Mg^{2+}, Mn^{2+}, Al^{3+}, Ti^{4+}, and Li^+ conform to this requirement. Ca^{2+} and Na^+ ions appear to be borderline cases while K^+, Ba^{2+}, and Si^{4+} ions seem to be well outside this permitted range. The work described in this paper was undertaken to investigate the solubility of the promoter cations in magnetite at high temperatures. Whether or not the promoters had entered into solid solution was estimated from their effect on the lattice parameters of the magnetite. The effectiveness of several of the oxides as structural promoters was compared by X-ray line-broadening studies on the reduced samples.

EXPERIMENTAL

Sample preparation. All the samples were prepared by sintering compressed pellets of intimately mixed oxides. Mixing was done by wet grinding in a mechanical mortar under ethanol, the latter being allowed to evaporate slowly as grinding proceeded. The dried powders were pelletized at 40 tons/sq. inch and sintered in platinum boats in a porcelain pipe. Merck α-Fe_2O_3 (pro analysi) was converted to Fe_3O_4 by heating in a vacuum (1×10^{-4} mm Hg) at 1350°C for 48 hr. Under these conditions (*3*) Fe_2O_3 loses oxygen and is converted to Fe_3O_4 without it being further reduced to FeO. Alternately the Fe_2O_3 pellets were heated in a stream of nitrogen, which contained about 0.01% oxygen, at 1450°C for 2 hr. Both chemical and X-ray analysis showed that the samples contained only Fe_3O_4. The advantage of the above preparation techniques over those in which use is made of mixtures of H_2/H_2O or CO/CO_2 to establish the desired oxygen partial pressure range is that they are more easily controlled experimentally. Samples promoted with MnO, TiO_2, MgO, Al_2O_3, SiO_2, and CaO were prepared as described above directly from the mixtures of the relevant oxides with Fe_2O_3. As heavy losses of the Group I alkali oxides from the samples were found to occur at these high temperatures, samples promoted with Li_2O, Na_2O, K_2O or with mixtures of these oxides were prepared as follows: The alkali carbonates were mixed with Fe_2O_3 to give the composition equivalent to AFe_5O_8 where A is the alkali metal (or metals). The pellets were first fired in air at 700°C for 5 hr, then ground, repelletized, and again fired in air at 1150°C for 2 hr. This material was then mixed with Fe_3O_4, prepared as previously described, and the pellets fired in vacuum at 1150° for 1 hr. A few of the CaO-promoted samples were also prepared in the above manner, i.e., first preparing the compound oxide $CaFe_2O_4$ in air and then vacuum-firing this with Fe_3O_4 at 1150°C. The lattice parameters of these samples were found to be the same as those prepared at the higher temperature of 1450°C. The attempt at promoting magnetite with barium was carried out by sintering a mixture of $BaFe_{12}O_{19}$ and Fe_3O_4 in vacuum at 1150°C.

In each preparation a sintered pellet was put aside for microscopic inspection of a polished section. The remaining pellets were crushed until all particles were smaller than 75 μ and the actual promoter contents determined by chemical analysis.

Lattice parameters. Lattice parameter determinations were carried out with a 114.6-mm diameter Debye-Scherrer powder camera using Co $K\alpha$ radiation. The sizes of the cubic unit cells (a_0) of the spinels were obtained by the technique of extrapolating ($\cos^2 \theta/\sin \theta + \cos^2 \theta/\theta$) against a_0 as described by Klug and Alexander (*4*).

Line-broadening. The powdered samples were reduced in hydrogen at 390°C for times varying from 22 to 100 hr depending on the type of sample. The reduced samples were mounted in wax and the profiles of the (110) reflections of α-Fe were traced with the goniometer of the X-ray unit. Rotating sample holders were used. The linewidth was taken as the total peak area divided by the maximum peak height.

RESULTS

X-Ray analysis of the samples promoted with the oxides of Ca, Mn, Ti, Mg, Al, and Li showed that only one crystalline phase, namely spinel, was present. As a check, polished sections of the samples promoted with MgO and with CaO were microscopically investigated. They appeared to be homogeneous, confirming the presence of only one phase. All samples in which silica was present showed only one phase by X-rays but microscopic investigation revealed that two phases were present in all these cases. The second phase, presumably silica or alkali silicates, was evidently X-ray amorphous. In the Na_2O-promoted magnetite series both X-rays and microscopic investigations showed that up to 8 cation % Na^+ only one phase (spinel) was present, whereas above this figure two phases were present. From the X-ray diffraction pattern this second phase was identified as β-$NaFeO_2$.

It is of interest to record that in the preparation of the alkali ferrites by sintering the oxides in air at 1150°C as described in the experimental section, the lithium and the mixed lithium-sodium ferrite samples yielded compounds with the spinel structure only. In contrast, X-ray analysis showed that in the case of the "sodium ferrite" samples the crystalline phases present were α-Fe_2O_3 together with other unidentified material. On evacuation at 1150°C, however, a spinel phase was formed together with some β-$NaFeO_2$ while the unidentified phase(s) mentioned above disappeared. It appears therefore that in the case of sodium ferrite the presence of oxygen in the gas phase inhibits the formation of the spinel phase while this does not occur in the case of the lithium or mixed lithium-sodium ferrites. All attempts to make a compound having the composition KFe_5O_8 and with a spinel structure failed.

TABLE 1
IONIC RADII (Å)

Ion	Pauling	Goldschmidt
Fe^{3+}	0.64	0.67
Fe^{2+}	0.76	0.83
Li^+	0.60	0.78
Na^+	0.95	0.98
K^+	1.33	1.33
Ba^{2+}	1.35	1.43
Mg^{2+}	0.65	0.78
Ca^{2+}	0.99	1.06
Mn^{2+}	0.80	0.91
Al^{3+}	0.50	0.57
Ti^{4+}	0.68	0.67
Si^{4+}	0.41	0.39

The results of the spinel unit-cell-size determinations are shown in Figs. 1 and 3. A shift in the lattice dimensions with increasing promoter cation concentration is taken as evidence that the cations have entered into solid solution with the magnetite. The direction of the shift is dependent on the size of the promoter cation. For convenience the relevant cation radii are listed in Table 1. The results for the

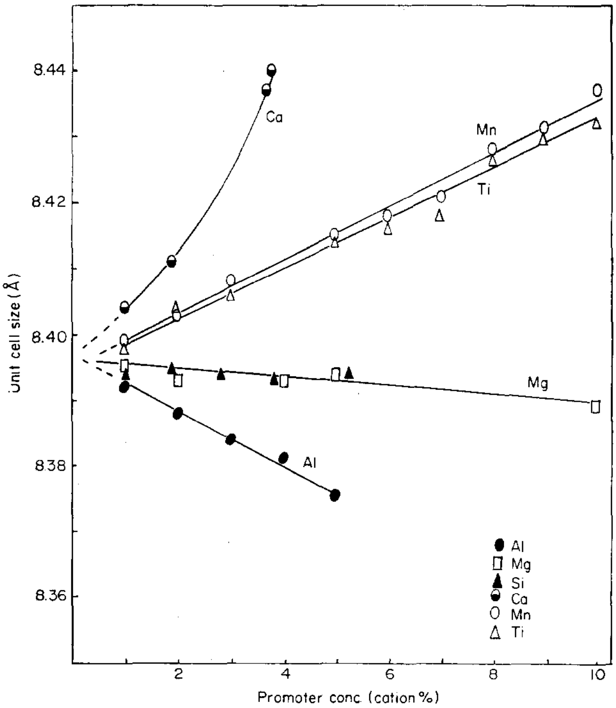

FIG. 1. The size of the unit cell of magnetite as a function of the promoter concentration.

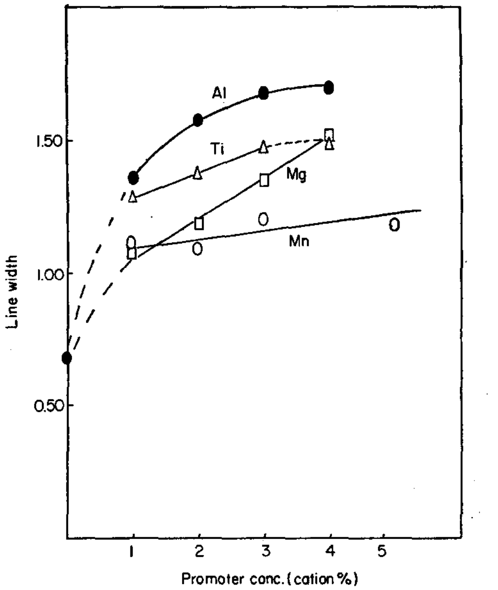

FIG. 2. The X-ray line-broadening (in arbitary units) as a function of promoter concentration. Symbols as in Fig. 1.

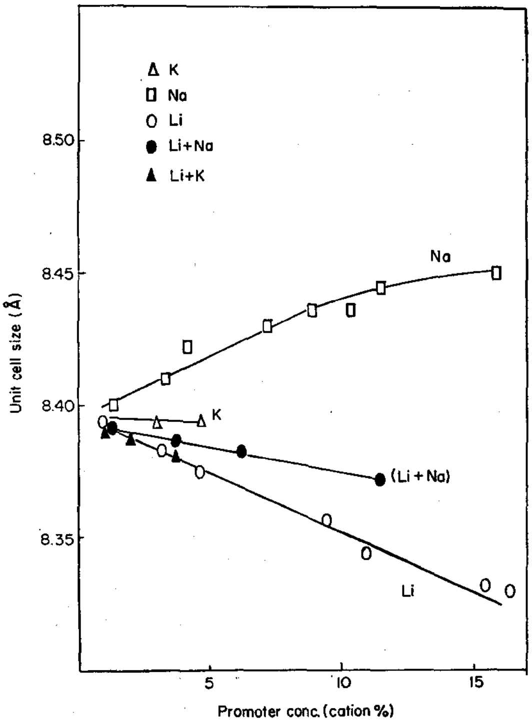

FIG. 3. The size of the unit cell of magnetite as a function of the total alkali cation concentration. The doubly promoted samples were prepared by sintering Fe_3O_4 with the ferrites $Li_{0.7}Na_{0.3}Fe_5O_8$ and "$Li_{0.7}K_{0.3}Fe_5O_8$," respectively.

additives normally considered as structural promoters, as well as those for SiO_2, are given in Fig. 1.

The effects of the chemical promoters, the alkalis, are illustrated in Fig. 3. The influence of silica on the parameters of samples promoted with Na_2O or CaO is demonstrated in Figs. 4 and 5. The numbers in the abscissa of Fig. 4 gives the "order" of the silicates, if formed, i.e., the value of n for the silicates $CaO \cdot (SiO_2)_n$ or $Na_2O \cdot (SiO_2)_n$. In these two series of samples the Na and Ca contents were maintained constant at 5.4 and 3.7 cation %, respectively, while the silica contents were progressively increased.

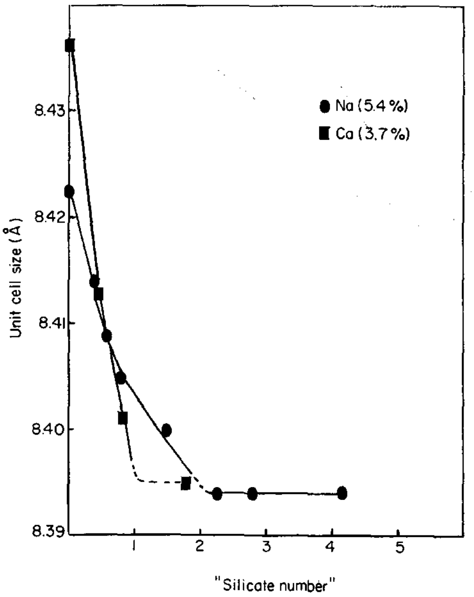

FIG. 4. The size of the unit cell of magnetite promoted with fixed amounts of either Ca^{2+} or Na^+ ions as a function of the "silicate number" n in $CaO \cdot (SiO_2)_n$ or $Na_2O \cdot (SiO_2)_n$.

The effect of structural promoters on the X-ray linewidths of the reduced samples is shown in Fig. 2. As identical experimental conditions were used in all the cases, instrumental broadening was a constant throughout and changes in linewidths were taken as indicating only changes in iron crystallite size (*5*). The broader the lines the smaller the crystallites, i.e., the higher the surface area, and therefore the more effective the structural promoter.

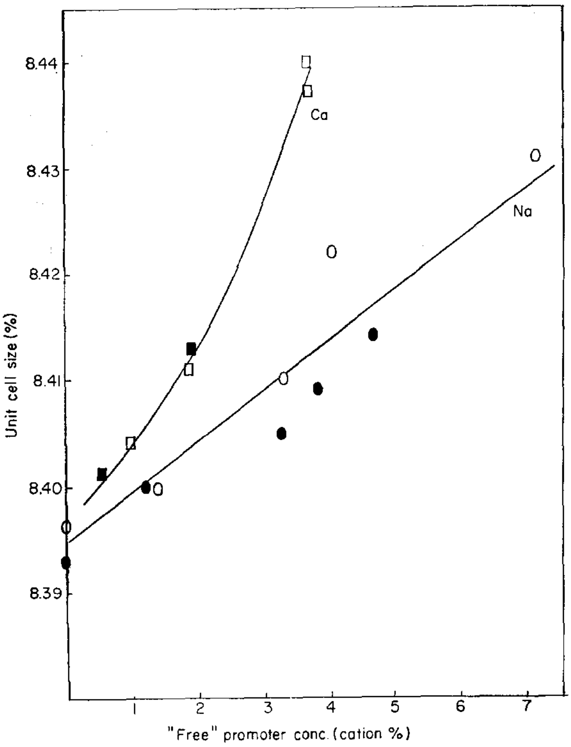

FIG. 5. The size of the unit cell of magnetite as a function of the "free" Ca^{2+} or Na^+ ion concentration. Filled characters are for samples containing silica, open characters for samples with no silica present.

DISCUSSION

From Fig. 1 it is clear that the majority of the structural promoters have a marked effect on the lattice parameter of magnetite, indicating that solid solution had occurred. The ferrites of Mn, Al, Mg, and Ti are spinels and it was therefore expected that these cations would dissolve in magnetite. $CaO \cdot Fe_2O_3$, however, has an orthorhombic structure but it appears nevertheless that at lower concentrations at least Ca^{2+} ions can enter into solid solution with magnetite. This confirms the findings of Uchida *et al.* (*6*). The Al^{3+} ion is smaller than the Fe^{3+} ion it replaces in the magnetite lattice; as was expected (*7*) the unit cell shrank with the introduction of Al^{3+}. Similarly the Ca^{2+} and Mn^{2+} ions are larger than the Fe^{2+} ion so that an increase in parameter can be expected with Ca^{2+}, being the bigger ion, having the greater effect. If Ti^{4+} replaces Fe^{3+} it is essential for the maintenance of electrical neutrality that an Fe^{3+} ion in the crystal be reduced to an Fe^{2+} ion and this, more than the actual size of the Ti^{4+} ion itself, is probably responsible for the expansion of the unit cell.

Silica, which was not expected to go into solid solution, had little or no effect on the lattice parameter. If it did enter substitutionally as Si^{4+} it should, being smaller, have had a more marked effect than Al^{3+}. Consequently its solubility in magnetite, if anything, was probably less than 1 cation %. This was supported by the microscopic observation that all the SiO_2-promoted samples had a small amount of a second phase present. This insolubility is no doubt the reason why silica was found to be ineffective as a structural promoter (*8*).

For the MgO-promoted samples the direction of the shift in lattice parameter was as expected but the magnitude of the shift was small, especially when the Pauling radii of Fe^{2+} and Mg^{2+} are compared. MgO is known to be a good structural promoter of magnetite and the effect of MgO on the crystallite size of the reduced samples (see Fig. 2) clearly implies that MgO had entered into solid solution in the present series of samples. Curie point determinations (*9*) on these samples supported this. The Curie point decreased as the MgO content increased. Uchida *et al.* (*6*) also reported that magnesia did not cause any changes in the lattice constant of magnetite and they suggest that Mg^{2+} ions do not enter the lattice as substituents of the Fe^{2+} ions but that they occupy empty interstices in the spinel lattice.

From Fig. 2 it can be seen that the size of the iron crystallites of the reduced magnetite samples decreases with increasing promoter content and also that some promoters are more effective than others. The crystallites in the samples promoted with MnO are, for instance, clearly larger than those promoted with Al_2O_3 in spite of the fact that the latter samples had to be reduced for much longer times to attain full reduction. The longer the reduction time the more the iron crystals already formed could be expected to grow. The effectiveness to produce small crystallites increases in the order MnO, MgO, TiO_4, and Al_2O_3. This corresponds exactly to the order deduced from BET surface area measurements on reduced fused magnetites promoted with the above oxides (*8*). It is therefore established that even though MnO and CaO are not reducible by hydrogen and that they both do go into solid solution with magnetite, they are inferior as surface area promoters.

The existence of the spinel $LiFe_5O_8$ and also of those in which up to 40% of the Li^+ ions in the above compound are replaced by Na^+ ions is well known (*10*). More recently the spinel $NaFe_5O_8$ has been reported (*11*, *12*). It was therefore expected that the alkali ions Li^+ and Na^+ would be able to dissolve in magnetite and from the results illustrated in Fig. 3 it is apparent that they did indeed do so under the experimental conditions used in the sample preparation.

In substituting a monovalent cation for say an Fe^{2+} ion in the spinel lattice it is necessary for the maintenance of electrical neutrality that an Fe^{2+} ion be oxidized to an Fe^{3+} ion and this should result in a shrinkage of the lattice. In the case of Li^+ the ion is itself smaller than the Fe^{2+} ion it is replacing. Therefore for these two reasons the parameter of magnetite should decrease with increasing lithium content, as was found experimentally. The Na^+ ion on the other hand is larger than the Fe^{2+} ion. From Fig. 3 it is seen that promotion with Na^+ ions increases the parameters of magnetite and therefore the increase due to the introduction of the large ion predominates over the shrinkage due to the accompanying Fe^{2+} oxidation. As can be expected, the parameters of magnetite promoted with the mixed spinel $Li_{0.7}Na_{0.3}$-Fe_5O_8 lie intermediate between those of the Li^+- and the Na^+-promoted series. If K^+ ions were capable of entering into solid solution with magnetite then the parameters of the latter should exceed those of the Na_2O-promoted series. The results plotted in Fig. 3, however, show that K^+ ions had no apparent effect. The results for the series doubly promoted with "Li-K-ferrite" also lie below the series promoted with the Li-Na-ferrite, whereas they should have been above if K^+ ions did enter into solution. The samples promoted with $BaFe_{12}O_{19}$ also showed no change in magnetite parameter. It appears therefore that it is not possible to introduce large ions such as K^+ or Ba^{2+} into the magnetite lattice.

As can be seen in Fig. 3 the graph of the singly promoted Na^+ series flattens at high Na^+ concentrations. This flattening is associated with the fact that above 8 cation % two crystalline phases appear in these samples (see the Results section). Below 8%, however, only one phase is present. Thus at the lower concentrations which are used in practice it should be possible to manufacture a promoted magnetite catalyst in which the sodium ions are homogeneously distributed.

Figure 4 shows that with increasing silica content at fixed Na^+ or Ca^{2+} ion contents the parameter of the promoted magnetite decreases, which indicates that the amount of Na^+ or Ca^{2+} ions in solid solution decreases. Silica presumably combines with the bases to form a separate phase and so prevents them from entering into solid solution. Such separate phases were microscopically observed in polished sections of these samples. The presence of silica must therefore be avoided if a truly homogeneous alkali-promoted catalyst is desired.

Both curves in Fig. 4 flatten at higher silica contents at parameter values corresponding to that of magnetite promoted with silica only, which is taken to mean that at these high silica contents no Na^+ or Ca^{2+} ions are in solid solution in the magnetite. This latter state appears to occur at "silicate numbers" 1 and 2 for Ca^{2+} and Na^+, respectively; when there is enough silica to form either $CaO \cdot SiO_2$ or $Na_2O \cdot (SiO_2)_2$ no basic ions are present in the magnetite lattice, while at lower silica contents the excess basic ions are free to enter into solid solution. To test this hypothesis the "free" ion concentration was plotted against lattice parameters to see how this compared with the results obtained on the samples which contained no silica. "Free" alkali was taken as equal to the difference between the total alkali cation content and the total Si content. As can be seen in Fig. 5 there is fair agreement between the two sets of results. It appears therefore that under the experimental conditions used in the sample preparation, the silicates 2 $Na_2O \cdot SiO_2$ and $Na_2O \cdot SiO_2$ were not formed. Presumably silica would otherwise have inhibited the solid solution of Na^+ ions in magnetite at much lower "silicate numbers" than 2.

The lattice parameter and the Curie point of a magnetite sample promoted with MgO and SiO_2 to contain 10 cation % of each was found to be identical with the values of a sample promoted only with 10 cation % Mg^{2+}. Silica does not therefore seem capable of preventing MgO from going into solid solution with magnetite. Apparently the less basic the promoter the less likely is silica to prevent it dissolving in magnetite.

REFERENCES

1. ANDERSON, R. B., *Catalysis* 4 (Reinhold, New York, 1956).
2. GORTER, E. W., *Philips Res. Rept.* **9,** 295 (1954).
3. DARKEN, L. S., AND GURRY, R. W., "Physical Chemistry of Metals," p. 351. McGraw-Hill, New York, 1953.
4. KLUG, H. P., AND ALEXANDER, L. E., "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials." Wiley, New York, 1954.
5. NIELSEN, A., "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," p. 165. Jul. Gjellerups Forlag, Copenhagen, 1956.
6. UCHIDA, H., TERAO, I., OGAWA, K., AND OBA, M., *Bull. Chem. Soc. Japan* **37,** 1508 (1964).
7. WESTRIK, R., *J. Chem. Phys.* **21,** 2094 (1953).
8. DRY, M. E., DU PLESSIS, J. A. K., AND LEUTERITZ, G. M., *J. Catalysis* **6,** 194 (1966).
9. FERREIRA, L. C., AND ALBERTS, L., *J. Chem. Phys.* **44,** 2204 (1966).
10. SMIT, J., AND WIJN, H. P. J., "Ferrites," p. 136. Wiley, New York, 1959.
11. THERY, J., AND COLLONGUES, R., *Comp. Rend.* **250,** 1070 (1960).
12. TAKEI, T., AND OKAMOTO, S., *Kagaku Kenkyusho Hokoku* **33,** 53 (1957).