JOURNAL OF CATALYSIS 17, 230–237 (1970)

The Effects of Additives in Ferric Oxide Catalysts

II. N_2O Decomposition and Methanol Conversion to Formaldehyde over Mg-Doped Ferric Oxide

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Received September 12, 1969

Nitrous oxide decomposition was studied over pure and Mg-doped ferric oxide catalysts which were either in the "as prepared" state or had been used previously to catalyze the conversion of methanol to formaldehyde. Catalysts in both conditions showed the same pattern of activation energy (E) changes with variation in Mg content, viz,, additions of 0.01–0.03% Mg (increasing p-character) decreased E compared with the pure oxide but further additions caused E to increase sharply at 0.1% Mg (by ~10 kcal/mole for "as prepared" catalysts with E then returning to approximately the value for the pure oxide). Results are discussed with special reference to the change in E accompanying the onset of phase-separation (at ~0.1–0.2% Mg) yielding a composite surface where islands of magnesium ferrite (E for pure ferrite $=47$ kcal/mole) are relatively inactive compared with large areas of almost pure hematite.

Selectivity to formaldehyde in methanol conversion was least (~20%) over pure ferric oxide, increasing to a maximum (~60%) at ~0.2% Mg, beyond which selectivity decreased to ~35% over catalysts with 1.0–2.0% Mg; selectivity was inversely proportional to activity (rate of methanol removal). Different Mg incorporation temperatures for 0.3% Mg catalysts produced either very active catalysts or catalysts showing selectivities >80%. Comparison of the variation with Mg-content of activation energies for N_2O decomposition and activities/selectivities in methanol conversion enabled distinctions to be made between the effects of charge carriers and incipient phase-separation in the latter reaction.

INTRODUCTION

It was shown in Pt. I (*1*) that incorporation of Mg^{2+} into high-purity ferric oxide forms a corresponding number of p-carriers up to a limit at ~0.1–0.2 at. % Mg, beyond which the spinel phase, magnesium ferrite, appears. The catalytic reactions carried out over these ferric oxide-based catalysts, the decomposition of nitrous oxide and the conversion of methanol to formaldehyde, were chosen for the following reasons.

It is well established both from activity patterns over a series of different oxides (*2*) and from doping experiments (*3*) that the rate of N_2O decomposition is enhanced by increasing p-character. It is not the present intention merely to provide a further example of this correlation or to reinterpret it in terms of some localized model. Instead, the N_2O decomposition reaction is used to demonstrate that sufficient p-carriers can be introduced into n-type ferric oxide to bring about significant changes in catalytic activity. Further, the response of ferric oxide catalysts to the onset of phase-separation at higher Mg contents can be explored with this comparatively simple reaction.

It was also of interest to examine the catalytic properties of p-type ferric oxide for a more complex reaction, where both the selectivity as well as the activity may be modified, viz., the selective conversion of methanol to formaldehyde. However, spinel-formation may be an important feature of some mixed oxide catalysts involved in methanol synthesis (*4*, *5*). Therefore, the response of N_2O decomposition to the onset of phase-separation, in addition to catalyst characterization by electrical measurements and electron probe microanalysis, should be helpful in discussing the extent to which carrier type and the spinel structure are involved in the conversion of methanol to formaldehyde.

EXPERIMENTAL METHODS

Catalysts were prepared and characterized as described in Pt. I (*1*). Catalyst performance was measured in a flow system using a tubular glass reactor (1.5 cm diameter) charged with a fixed number and weight of catalyst particles when studying methanol conversion, or with a known weight during nitrous oxide decomposition. One thermocouple (bare) was inserted directly into the catalyst bed and a second was in a glass pocket running through the center of the reactor. A 10-cm bed of silica fragments was placed on top of the catalyst charge (2.5 cm deep) to improve preheating of the reactant gases.

The methanol/air mixture was obtained by passing compressed air from a cylinder (150 ml/min) through a molecular sieve trap into a saturator packed with gauze rings and containing AnalaR methanol thermostated at 22°C. The product gases were analyzed by gas chromatography, sampling directly from the outlet of the reactor through a heated valve. The column used (2 m) was 10% Ethofat (Armour Hess Chemicals) on Columnpak T (Fisher Scientific Company), at 115°C with helium carrier gas which gave a reasonably good separation of methanol, water and formaldehyde detected by thermal conductivity. Methanol and water sensitivities were found using the vapor pressure data. Formaldehyde was released by heating paraformaldehyde and peak areas compared with the concentrations collected in solutions of hydroxylamine hydrochloride or sodium sulfite.

Nitrous oxide (British Oxygen—medical grade) was passed continuously through a molecular sieve trap into the reactor at flow rates of ~5 ml/min. Using a Porapak column at 75°C, good separation of the nitrous oxide peak from the combined $N_2 + O_2$ (products) peak was achieved.

RESULTS

Nitrous Oxide Decomposition

Nitrous oxide decomposition was studied over pure and Mg-doped ferric oxide catalysts where either (a) the catalyst samples were in the "as prepared" state, or (b) the catalyst samples had been used previously in studying the conversion of methanol to formaldehyde. Before all experiments, the catalysts were subjected to an argon flush. 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. The rate equation obtained for a first-order reaction was:

$$\frac{8kSV_0a^2}{V_i^2} = 18a^2 \ln\left(\frac{a}{a-x}\right) - 10ax - x^2 \quad (1)$$

$$= \frac{8SV_0a^2A}{V_i^2} \exp(-E/RT), \quad (2)$$

where k is the rate constant, S is the surface area, V_0 is the reaction volume, V_i is the flow rate, a and $(a - x)$ are proportional to the initial and final N_2O peak heights; A, E, R, and T are the usual terms of the Arrhenius equation.

The right-hand side of Eq. (1), $f(x)$, was plotted as the logarithm against reciprocal temperature yielding satisfactory linear plots (Fig. 1). The corresponding equation for second-order kinetics, when used to represent the data, gave less satisfactory results.

Figure 1 also compares rates observed when the temperature was lowered (square symbols) with observations made with rising temperature (circles), showing that no irreversible changes occurred during reaction. Observed values of $f(x)$ were adjusted to standard flow rate, 5 ml/min, and standard catalyst charge, 10 g, using Eq. (1), assuming reaction volume proportional to the latter. Surface areas of these cata-

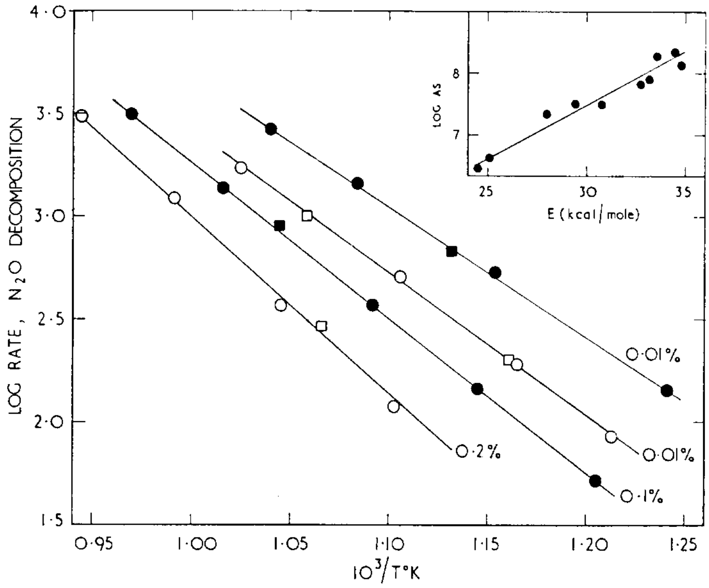

FIG. 1. Arrhenius plots for N_2O decomposition over Mg-doped ferric oxide catalysts, (% Mg indicated), "as prepared" (●, ■); after use in methanol conversion (○, □). Inset shows compensation effect for "as prepared" catalysts.

lysts, fired at 1300°C, were very small, values of ~0.02 m^2/g being observed; it has been shown (*6*) for ferric oxide samples with 0–0.3% Ca that the surface areas only varied by a factor of 2 from 0.17 to 0.08 m^2/g. In the present work, values of log (AS) calculated from the above equations were plotted as a function of activation energy, E, demonstrating a "compensation effect" if S may be assumed constant (Fig. 1, inset).

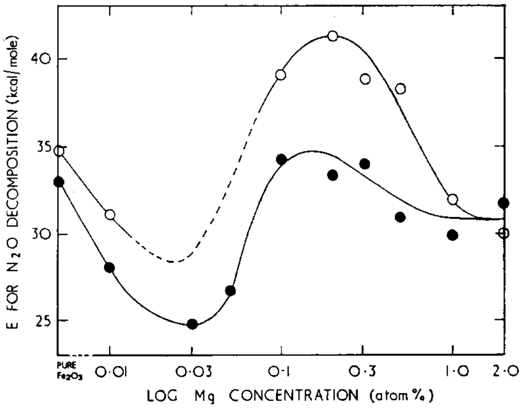

FIG. 2. Variation in activation energy for N_2O decomposition as a function of Mg content in ferric oxide catalysts; "as prepared" catalysts (●); after use in methanol conversion (○).

Figure 2 shows the variation of activation energy with Mg content for "as prepared" catalysts (filled circles) and for catalysts used previously in methanol conversion (open circles). Both types of catalyst show the same activity pattern, but activation energies are higher (except for the 2.0% Mg catalysts) in catalysts after use in methanol conversion. Usually this increase amounted to only a few kilocalories, but in the region 0.1–0.5% Mg the difference increased to ~6 kcal/mole. The pattern of activation energies over "as prepared" catalysts is probably more significant with regard to catalyst characterization.

Addition of 0.01 to 0.03% Mg decreased the activation energy compared with pure ferric oxide (Fig. 2, filled circles) from 33 kcal/mole to 25 kcal/mole at the minimum. Thereafter, further additions of Mg brought about a sharp increase to ~35 kcal/mole at 0.1–0.3% Mg which may represent a maximum, although activation energies then changed little up to 2.0% Mg. Activation energies observed for N_2O decomposition over "as prepared" catalysts with the composition $MgFe_2O_4$ were 46.2 and 48.4 kcal/mole.

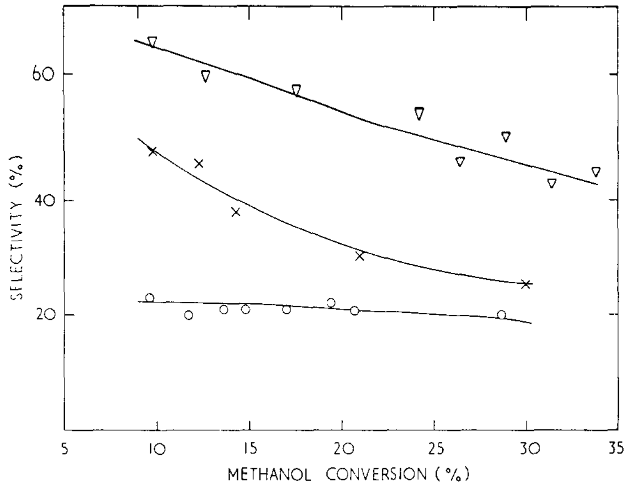

FIG. 3. Observed selectivities (formaldehyde formed/methanol converted) as a function of percentage of methanol conversion for a pure ferric oxide catalyst (○); ferric oxide catalysts with 0.1% Mg (×); with 0.5% Mg, (▽).

Methanol Conversion

Catalyst performance was measured in a flow system at atmospheric pressure, using as standard conditions a mixture of 105 torr methanol vapor in air. Information was obtained on the percentage of methanol converted at various temperatures together with the corresponding amounts of formaldehyde produced. The ratio (HCHO formed/CH_3OH converted) is designated as "selectivity" although it is recognized that some formaldehyde initially formed may be re-adsorbed and further converted to carbon dioxide and water.

However, as described below, a Mg-doped catalyst was prepared which produced formaldehyde with "selectivities" of 80–90% at ~470°C, (the highest temperatures required in this series for 10% methanol conversion). This shows, for this catalyst at least, that a flow rate of 150 ml/min was adequate to remove the formaldehyde initially formed from the reaction zone before further significant degradation could occur and, clearly, thermal degradation has not affected any "selectivities" by more than 10%.

In general, catalyst performance was measured over a number of days and selectivities were well maintained. The catalytic activity, expressed in terms of the temperature required for a given percentage of methanol conversion, was rather more variable. Catalysts with 1.0 and 2.0% Mg were initially less active but rapidly attained a reasonably constant activity level. For all other catalysts, temperatures for 10% methanol conversion varied by between ±7°C and ±15°C. This is ascribed to the difficulty of temperature measurement in an exothermic reaction, even

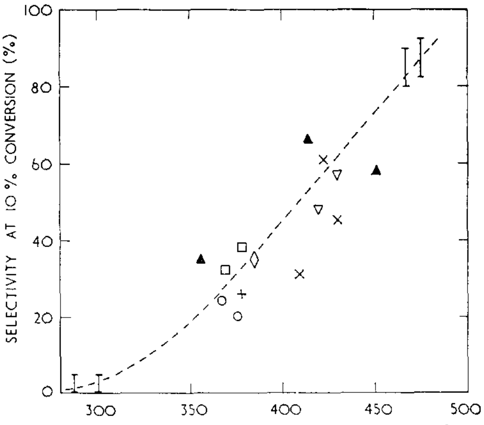

FIG. 4. Relationship between selectivity (formaldehyde formed/methanol converted, at 10% conversion) and activity [temp (°C) for 10% methanol conversion]; pure ferric oxide (○); 0.01% Mg (+); 0.1% Mg, (×); 0.2% Mg (▲); 0.5% Mg (▽); 1.0% Mg (◇); 2.0% Mg (□). Catalysts with 0.3% Mg, fired at 1000°C or refired at 1300°C, low and high selectivities respectively (I).

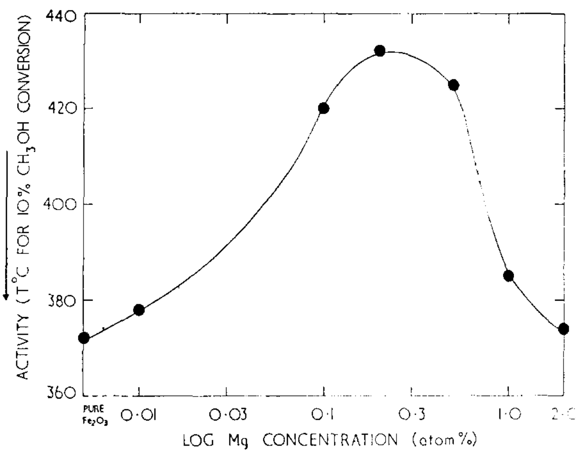

Fig. 5. Variation of activity [temp (°C) for 10% methanol conversion] as a function of Mg content in ferric oxide catalysts.

though a bare thermocouple was inserted in the catalyst bed. However, it is not thought to be due to the development of "hot-spots" because of the reproducible selectivities. Occasionally, "hot-spots" did develop, resulting in a marked decrease in formaldehyde produced, accompanied by a sharp rise in the temperature of the catalyst bed.

Figure 3 shows the variation in selectivity with the extent of methanol conversion over pure and Mg-doped ferric oxide catalysts. The selectivity of pure ferric oxide remains at ~20% over the conversion range examined, while the better selectivities of the 0.1% and 0.5% Mg-doped catalysts shown decreased with conversion. However, the relative levels of selectivity are maintained and are compared for 10% methanol conversion (Figs. 4 and 6) where selectivities are highest, consistent with their accurate determination.

The selectivity (at 10% conversion) is inversely related to catalytic activity (expressed as temperature for 10% methanol conversion) over almost the widest possible range of selectivity variation, Fig. 4. Activity/selectivity observed for entirely separate catalyst preparations are shown in Fig. 4. In general, there was satisfactory reproducibility, except for catalysts containing 0.1 and 0.2% Mg. As discussed be-

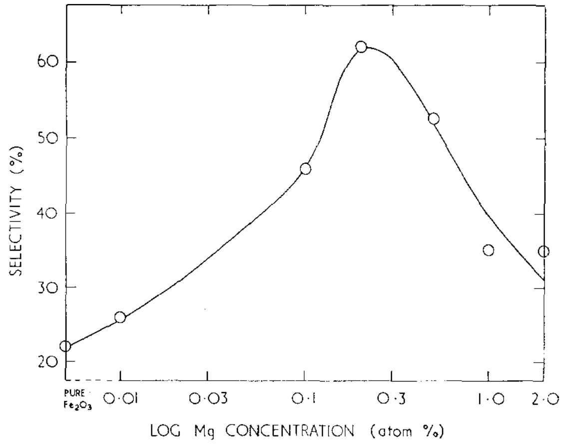

Fig. 6. Variation of selectivity (formaldehyde formed/methanol converted) as a function of Mg content in ferric oxide catalysts.

low, at exactly these Mg contents the samples are subject to critical variations in structure, i.e., separation of the spinel phase.

Figure 4 also shows activity/selectivity observed in catalysts with 0.3% Mg (vertical bars). Four separate catalyst preparations were carried out where the catalysts were fired in pellets at 1000°C instead of 1300°C at the high temperature firing stage [cf. Experimental Methods Pt. I (*1*)]. The pellets were crushed to produce the catalyst charge; in one sample, very good selectivities, $>80\%$, were observed but otherwise the catalysts were very active, (10% conversion at $\sim$300°C and below) with correspondingly low selectivities (see Fig. 4). When these catalysts charges were re-fired at 1300°C, selectivities were enhanced, reaching values in excess of 80%. Firing the most selective catalyst yet again at 1300°C, then reduced the selectivity to $\sim$50%, in keeping with the selectivity expected for this Mg-doping level (see below).

Finally, Figs. 5 and 6 show the variation of activity and selectivity as a function of Mg content. When magnesium is added to pure ferric oxide, the activity is diminished (i.e., T°C for 10% conversion rises) and the selectivity is enhanced, reaching their respective minimum and maximum at approximately 0.2% Mg. Thereafter, further addition of magnesium causes the activity to rise and the selectivity to decrease until in both cases observed values approach those for pure ferric oxide.

DISCUSSION

Comparison of the activity/selectivity observed in methanol conversion (Figs. 5 and 6) with activation energies for N_2O decomposition (Fig. 2, filled circles) show different responses to variation in the Mg content of the catalyst. These differences enable distinctions to be drawn between the role of semiconducting properties (or some equilvalent treatment in terms of a localized model) and effects accompanying the separation of the spinel phase.

N_2O decomposition. As might be anticipated, converting pure ferric oxide (n-type) into a p-type conductor by Mg-doping reduces the activation energy for N_2O decomposition. The generally higher activity of p-type oxides for this reaction has been seen as a consequence of their capacity for oxygen chemisorption involving electron transfer from the catalyst (*2*). The minimum activation energy (25–27 kcal/mole) was observed in catalysts with 0.03–0.05% Mg, compared with 33 kcal/mole for pure ferric oxide ("as prepared" catalysts).

By a combination of electrical measurements and electron probe microanalysis, it was shown in Pt. I (*1*) with some precision that the limit of solubility occurs at 0.1–0.2% Mg. In good agreement with the location of the Mg content at which phase-separation begins, the activation energy for N_2O decomposition increased sharply to $\sim$35 kcal/mole when the Mg content was increased to 0.1%. Above this Mg content, the activation energy remains comparable to the value for pure ferric oxide, although bulk electrical properties indicate that these catalysts (0.1–2.0% Mg) are predominantly p-type. Hence it would seem that the surfaces of catalysts with 0.1–2.0% Mg are composed of large areas of almost pure hematite. The magnesium may accumulate in islands of magnesium ferrite as suggested by electron probe microanalysis [Pt. I, Fig. 6 (*1*)], removing p-carriers from these areas of hematite surface.

Such composite surfaces would be expected to yield an activation energy for N_2O decomposition appropriate to almost pure hematite, if the activation energy for reaction over the spinel phase was sufficiently high to minimize the contribution to the total observed reaction rate. It was shown, in fact, that the activation energy for N_2O decomposition over the stoichiometric magnesium ferrite is $\sim$47 kcal/mole.

Observations on N_2O decomposition over catalysts previously used in methanol conversion demonstrate that the latter reaction does not produce any serious modification of the catalyst structure, obviating the use of N_2O decomposition for catalyst "characterization." The main difference compared with "as prepared" catalysts occurs at $\sim$0.2% Mg, i.e., activation energies are $\sim$6 kcal/mole higher and this is associated with the larger yields of formaldehyde from catalysts with this Mg content.

CH_3OH conversion. An *apparent correlation* between activity/selectivity in methanol conversion and bulk electrical properties might be developed in the following way. The adsorption of methanol was shown in Pt. I (*1*) to be accompanied by electron transfer to the catalyst which may imply lower methanol coverages on the *p*-type Mg-doped catalysts (*2*) than on the pure *n*-type ferric oxide, leading to the lower rates of conversion observed (Fig. 5). Further, it was shown that there was a satisfactory inverse relationship between activity and selectivity, which is found in various other partial oxidation reactions (*7*).

Pure ferric oxide where the conductivity is low and *n*-type [Pt. I, Figs. 1 and 3 (*1*)] shows relatively high catalytic activity in terms of methanol converted and poor selectivity toward formaldehyde, ~20%. Minimum activity/maximum selectivity, ~60%, occurred with *p*-type catalysts containing 0.2% Mg which exhibited maximum conductivity; these catalysts also had the highest Mg content where the expected Seebeck voltage could still be observed [Pt. I, Fig. 4 (*1*)]. It might also be argued that the *p*-carrier content of the surface layers is only reduced by phase-separation beyond 0.2% Mg, associated with a decrease in bulk conductivity, and activities/selectivities comparable to pure ferric oxide, (Figs. 5 and 6).

It then becomes necessary to search for a mechanism by which phase-separation can be accelerated under N_2O decomposition in catalysts with Mg contents beyond 0.05%. This would explain why "as prepared" catalysts with 0.1, 0.2, and 0.5% Mg resemble pure ferric oxide in N_2O decomposition, whereas they have totally different properties for methanol conversion in comparison with the pure oxide. It is now believed (*8*, *9*) that the formation of $MgFe_2O_4$ takes place predominantly by the exchange of Mg^{2+} and Fe^{2+} ions (only to a minor extent by the exchange of Mg^{2+} and Fe^{3+} ions) and hence the reaction is dependent on the ambient oxygen partial pressure. High oxygen partial pressures will retard the formation of $MgFe_2O_4$ while reducing conditions will increase the rate. The likelihood of oxygen retention by the surface (*10*) would oppose any tendency for phase-separation to be encouraged by N_2O decomposition.

Further, the very satisfactory Arrhenius plots for N_2O decomposition (Fig. 1), with respect to linearity and agreement between rates measured with rising and falling temperatures suggests that phase-separation under reaction conditions, if it had occurred, must have been extremely rapid. Therefore, it would seem that catalysts containing 0.1% Mg or more, when used in methanol conversion, are affected by the existence of spinel initially present in the catalyst.

We take the view that the best test of the effect of carrier type/concentration on methanol conversion should be free from any suspicion of complications arising from phase-separation. Thus, if even the 0.1% Mg catalyst does not fulfill this condition (as discussed above), the best comparison is between the 0.01% Mg catalyst and the pure *n*-type oxide. Although doping with 0.01% Mg produced a clearly *p*-type catalyst [see Pt. I, Fig. 3 (*1*)] with significantly modified activity for N_2O decomposition compared with the pure *n*-type oxide, nevertheless its activity/selectivity for methanol conversion was closely similar to that for the pure oxide. Therefore, the sharp change in activity/selectivity for methanol conversion when the Mg content was increased from 0.01 to 0.1% seems unlikely to be due to the increase in *p*-carrier concentration. This conclusion is supported by the special study on the effects of firing temperature on both the electrical [Pt. I, Table 1 (*1*)] and catalytic properties of catalysts with 0.3% Mg, which also point to the importance of incipient spinel formation.

Catalysts with 0.3% Mg fired at 1000–1100°C showed approximately the expected Seebeck voltages. It is believed that the formation of magnesium ferrite at these firing temperatures should be minimal for the following reasons. As discussed above, oxygen loss is essential for this reaction but below 1150°C it cannot be detected thermogravimetrically in ferric oxide samples with 0.2–1.0% Mg (*11*). Further, only 10% ferric oxide had reacted in an intimate equimolar mixture with magnesium oxide after 10 hr at 1000°C and no reaction was detected with coarser particles (*12*). In contrast, anomalous Seebeck voltages were observed after firing 0.3% Mg catalysts at 1300°C, oxygen loss was appreciable, and complete reaction of an equimolar mixture of $Fe_2O_3 + MgO$ was observed after 1–2 hr.

Thus, catalysts with 0.3% Mg fired at 1000°C appear to have the maximum number of *p*-carriers, arising from Mg^{2+} well distributed in the hematite lattice, whereas after firing at 1300°C, ferrite formation has developed. Although they possess a large number of *p*-carriers, these catalysts fired at 1000°C usually exhibited *virtually no selectivity towards formaldehyde,* accompanied by maximum activity in terms of methanol converted (Fig. 4). In complete contrast, when the catalyst charge was refired at 1300°C, very high selectivities, >80%, and low activities could be observed.

It is concluded that activity/selectivity in methanol conversion over Mg-doped ferric oxides is not related to *p*-carrier concentration but is sensitive to the incipient separation of the spinel phase, i.e., magnesium ferrite. It has been suggested that in methanol synthesis catalysts of zinc oxide–chromia type, zones of contact consisting of zinc chromite are formed which provide a disordered interface which improves catalyst performance (*4*). This spinel is not itself an active catalyst.

Before firing Mg-doped ferric oxide at 1300°C, the material is still inhomogeneous so that where >0.1–0.2% Mg is present, regions of magnesium ferrite are formed [see Pt. I, Fig. 6 (*1*)], once the temperature is raised to 1300°C. However, preliminary firing at 1000°C in pellets produced a good Mg distribution without ferrite formation and hence re-firing the catalyst charge at 1300°C should readily cause oxygen loss from the surfaces of the catalyst particles and a large number of "microregions" of the spinel will be formed.

It is suggested that very high selectivity in the specially-prepared 0.3% Mg catalysts towards formaldehyde production is due to these "microregions" of spinel in contact with the hematite phase. In the same way, the high selectivities of catalysts with ~0.2% Mg, but fired at 1300°C following the standard procedure, where phase-separation was just detectable, may also be due to microregions of spinel. More Mg, 1–2%, well in excess of the limit of solubility, should produce larger regions of spinel which are apparently less effective for producing formaldehyde.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Messrs. R. Griffiths and N. M. Hudson with part of the experimental work.

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