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Fe_2O_3 Addition Effects on the Ni-MgO Gasification Catalyst

GIULIANO SALVI AND ANNUNZIATA FIUMARA

From the Stazione Sperimentale per i Combustibili—Politecnico di Milano, Milano, Italia

AND

VINCENZO RIGANTI

From the Istituto di Chimica Generale dell'Universita' di Pavia, Pavia, Italia

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Crystallographic techniques were used to study the effects produced by the addition of Fe_2O_3 to the Ni-MgO gasification catalyst, and to understand the reasons for the anomalous behavior of some catalysts. X-Ray diffraction gave a valuable contribution to the knowledge of the phenomena occurring during catalyst life, and enabled a check on the existence of interactions between the active metal (Ni) and the metal of the protective oxide (Fe_2O_3), and a follow up of the course of these reactions in the solid state. These reactions give dispersed Fe-Ni alloys, with little catalytic activity, thus explaining the activity change of the catalyst after a period of use.

INTRODUCTION

A comparative study was made of the behavior of two Ni-supported catalysts, which find application in the manufacturing of town gas by the gasification of hydrocarbons. In the first catalyst, denoted by MSC_6, the Ni was supported on MgO, while in the second one, denoted by MSC_7, the MgO support was first doped with Fe_2O_3 before nickel impregnation.

When iron oxide is added to the support new phases appear, with the result that there is less formation of a solid solution between MgO and NiO than occurs without iron oxide.

The effects produced by the trivalent oxide addition have been followed over a period of time, with different analytic techniques, in order to prove their efficiency.

EXPERIMENTAL

MSC_6 catalyst was prepared by impregnating MgO pellets (previously shaped and fired in air for 48 hr at 1450°C) with 20% aqueous solution of $Ni(NO_3)_2 \cdot 6\ H_2O$. Impregnation in vacuum by barely wetting the MgO support with solution was followed by drying overnight at 120°C and then calcining in air at 400°C for 2–4 hr. The catalyst was reduced *in situ* during the exercise.

The support for MSC_7 catalyst was prepared by mixing MgO powder and Fe_2O_3 powder (both 325 U. S. Sieve) in the weight ratio 9:1, then forming in pellets and firing in air for 48 hr at 1450°C. Impregnation with aqueous $Ni(NO_3)_2$ solution, drying, and calcination were again performed under the same conditions as MSC_6.

The X-ray measurements were performed with a General Electric diffractometer equipped with a scintillation counter, and filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Surface areas were determined by BET apparatus and pore-size distribution by a Carlo Erba porosimeter.

RESULTS

The physical characteristics and the compositions of the two catalysts are reported in the Table 1. Figure 1 shows the percent pore diameter distribution of the same catalysts.

Both magnesium oxide and nickel oxide crystallize in the cubic system, in the same face-centered structure and with very close lattice parameters (MgO, 4.211 Å; NiO, 4.177 Å) (*1*); this makes their identification difficult by diffractometric methods, what ever is the predominant component in the mixture.

TABLE 1
PHYSICAL-CHEMICAL CHARACTERISTICS AND COMPOSITION OF INDUSTRIAL REFORMING CATALYSTS

	MSC_6	MSC_7
Composition		
NiO (wt %)	9.55	7.35
Fe_2O_3 (wt %)	1.65	9.64
SiO_2 (wt %)	1.52	1.35
Al_2O_3 (wt %)	0.54	0.87
MgO (wt %)	86.74	80.79
Shape	Balls	Rings, cylinders
Sizes (mm)	20	25 × 25 × 5
Physical-chemical characteristics		
Bulk density (g/ml)	1.72	1.45
Apparent density (g/ml)	2.39	2.68
Real density (g/ml)	3.24	3.64
Surface area (m^2/g)	—	10.52
Total pore volume (ml/g)	0.110	0.099
Pore volume (by porosimeter) (ml/g)	0.069	0.084

Anyway, in fresh specimens of oxidized MSC_6 and MSC_7 catalysts, nickel oxide can be identified from the asymmetry of peaks 111, 200, and 220 relative to magnesium oxide. Furthermore in MSC_7 catalyst the peaks of an iron compound with a spinel-type structure can be distinguished, and also the much weaker α-Fe_2O_3 peaks, and some impurities (essentially iron and magnesium silicate).

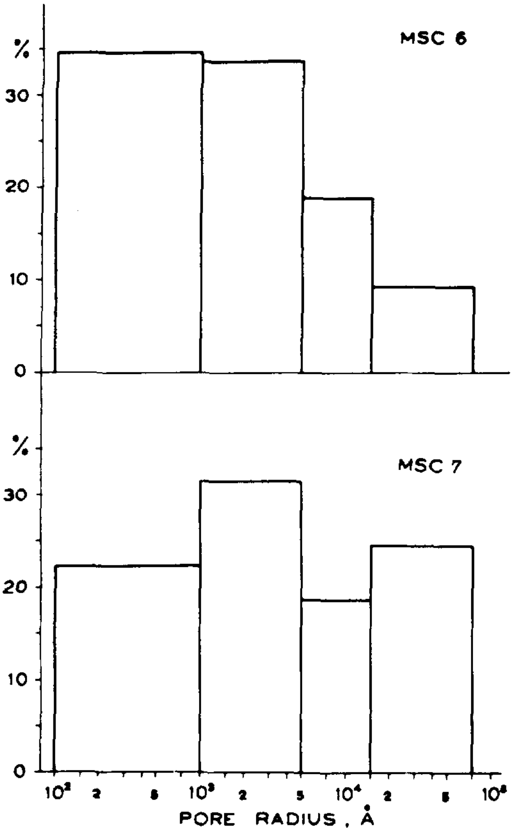

FIG. 1. Pore distribution of the MSC_6 and MSC_7 catalysts.

Owing to the support preparation technique, most of the oxidized iron is probably retained as $MgFe_2O_4$ in solid solution with little magnetite; the identified lattice parameter 8.38 Å is in good accordance with this assumption. These compounds are in fact linked to each other by well-known structural relations (*2*).

In specimens of the MSC_6 catalyst reduced with hydrogen, the presence of metallic nickel is evident, particularly through the strong reflections 111 ($d = 2.034$ Å) and 200 ($d = 1.762$ Å). The latter reflection is not affected by interferences due to the probable presence of iron, while the former is almost overlapped by iron reflection 110 ($d = 2.027$ Å).

In the case of the MSC_7 catalyst, the reduction process with H_2 at 950°C gradually leads, through compounds like $(MgFe_2O_4)_c \cdot (Fe_3O_4)_{1-c}$, to a wüstitic solid solution $(MgO)_x \cdot (FeO)_{1-x}$ and later to

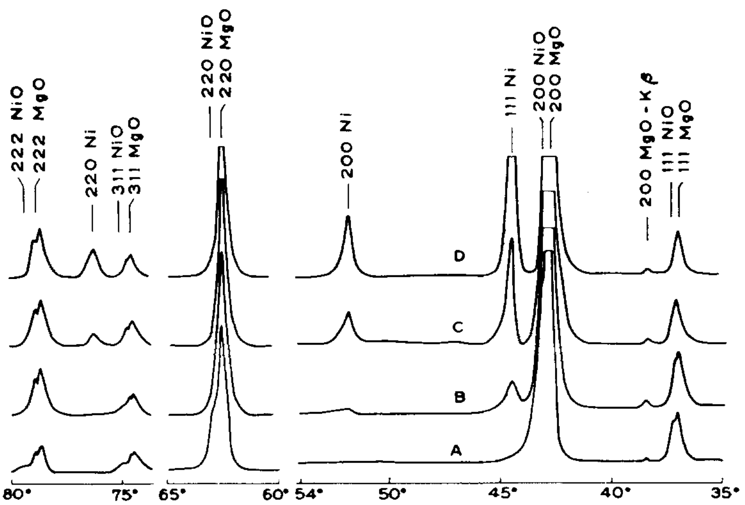

FIG. 2. X-Ray diffractograms of an MSC_6 catalyst subjected to reduction with H_2 at different temperature: A, fresh specimen; B, reduced at 500°C for 3 hr; C, reduced at 800°C for 3 hr; D, reduced at 950°C for 3 hr.

metallic iron (*3*). Again the iron and nickel diffraction peaks can be distinguished, the former by reflection 200 and the latter by reflection 211 ($d = 1.170$ Å), while the stronger reflections (111 for nickel and 110 for iron) are almost overlapping. If in the fresh material iron and magnesium silicate is present, it is not reduced under our experimental conditions, while the spinel is. Sometimes weak reflections due to α-Fe_2O_3 are present too.

In order better to evidence the metals in these masses, reduction must be carried out at high temperature, as the extent of the reduction depends on the temperature (Fig. 2).

In the specimen reduced at 950°C it can be supposed that most of the nickel is present in a reduced form; the quantitative determination of metallic nickel in the presence of nickel oxide, with the bromine method,* has given the results shown in Table 2.

TABLE 2

METALLIC NICKEL CONTENT OF AN MSC_7 SPECIMEN ACCORDING TO THE REDUCTION TEMPERATURE[a]

T (°C)	Ni %
500°	0.6
700°	1.1
800°	1.6
850°	2.8
900°	3.6
950°	4.5

[a] Total Ni = 6.0%; reduction time, 3 hr.

The MSC_6 catalyst shows a progressive loss of activity over a period of time; the nickel chemical proportion in different specimens taken from a plant at different intervals of time (1000 hr; 3000 hr; 7000 hr) reveals an increasingly small quantity of free, and therefore catalytically active nickel. The diffractograms of the same specimens confirm the progressive decrease of free nickel quantity, under the same reduction conditions (Fig. 3), while the diffractograms of the oxidized specimen show reflections that can be related to a solid solution between MgO and NiO.

This solid solution is more difficult to reduce than pure nickel oxide (*4*, *5*); it still shows catalytic activity, though inferior by far to that of metallic nickel. (It is therefore necessary either to raise the reactor temperature or to decrease the hydrocarbon space velocity if the gas characteristics must be maintained constant.)

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* Metallic nickel can be quantitatively determined in the presence of nickel oxide by reacting the specimen with bromine dissolved in methyl alcohol. Only metallic nickel goes into solution; after eliminating bromine in the filtrate, nickel is determined with diacetyldioxime.

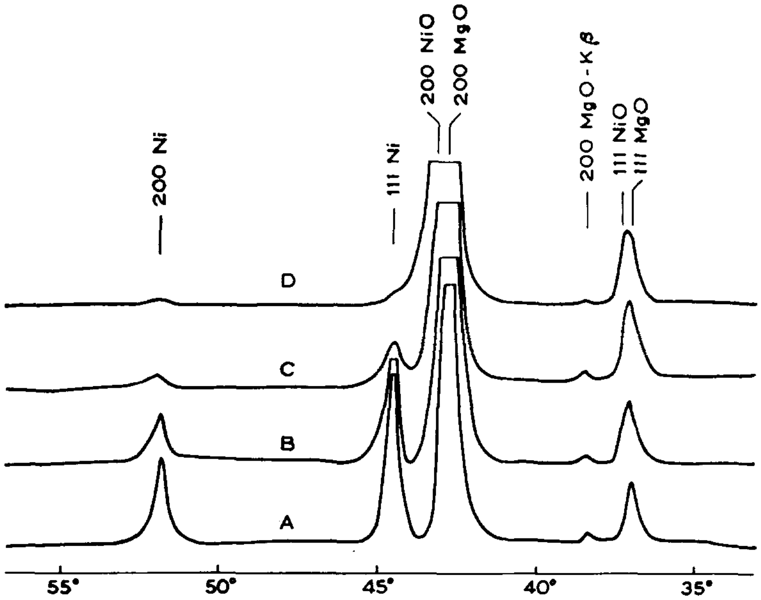

FIG. 3. X-Ray diffractograms of an MSC$_6$ reduced catalyst: A, fresh specimen; B, after 1000 hr industrial processing; C, after 3000 hr industrial processing; D, after 7000 hr industrial processing.

The diffractograms of specimens of an MSC$_7$ catalyst, taken from a cyclic reforming plant at different times (fresh, after 1000 and 5000 processing hours) show a greater resistance of nickel to reaction with the support; this can be noted from the weak variation in shape and height of its characteristic peaks (Fig. 4); the results obtained in an industrial plant are in accordance with the diffractographic results.

In some plants, however, some trouble was encountered with the MSC$_7$ catalyst that, at first, could not be explained, since the composition checked by chemical analysis was found to be perfectly in order: the only difference, as compared with a good material, was the appearance of the nickel peaks in the X-ray diffractograms (in spec-

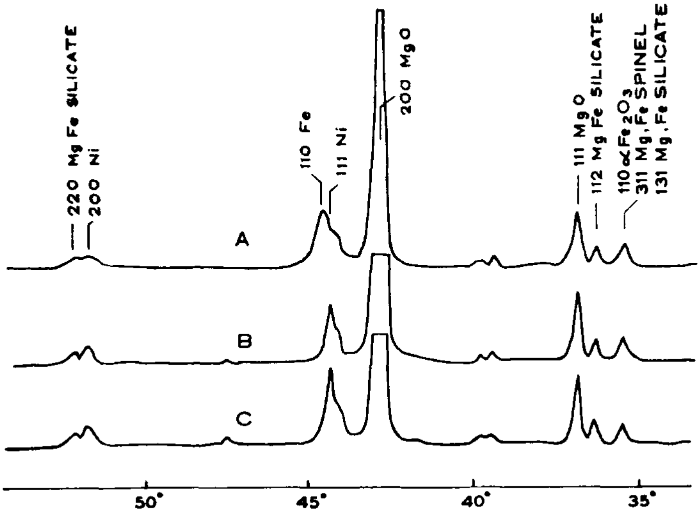

FIG 4. X-Ray diffractograms of an MSC$_7$ reduced catalyst: A, fresh specimen; B, after 1000 hr industrial processing; C, after 5000 hr industrial processing.

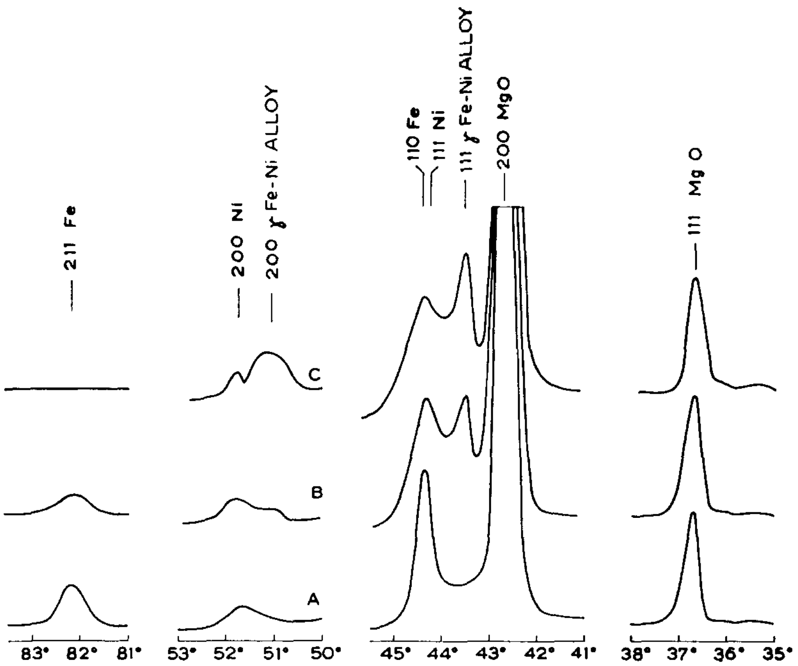

FIG. 5. X-Ray diffractograms of an imperfectly prepared MSC_7 catalyst, submitted alternately to oxidations and reductions, 3 hr each, at 950°C: A, after the firstreduction; B, after the second reduction; C, after the fourth reduction.

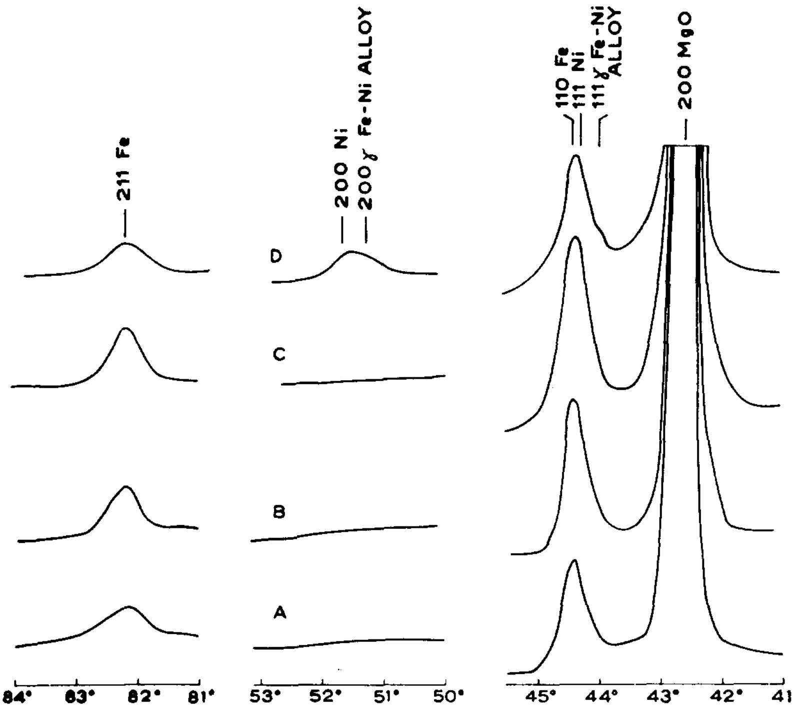

FIG. 6. X-Ray diffractograms of an imperfectly prepared MSC_7 catalyst: A, after a 15 min reduction at 950°C; B, after a 45 min reduction at 950°C; C, after a 75 min reduction at 950°C; D, after a 135 min reduction at 950° C.

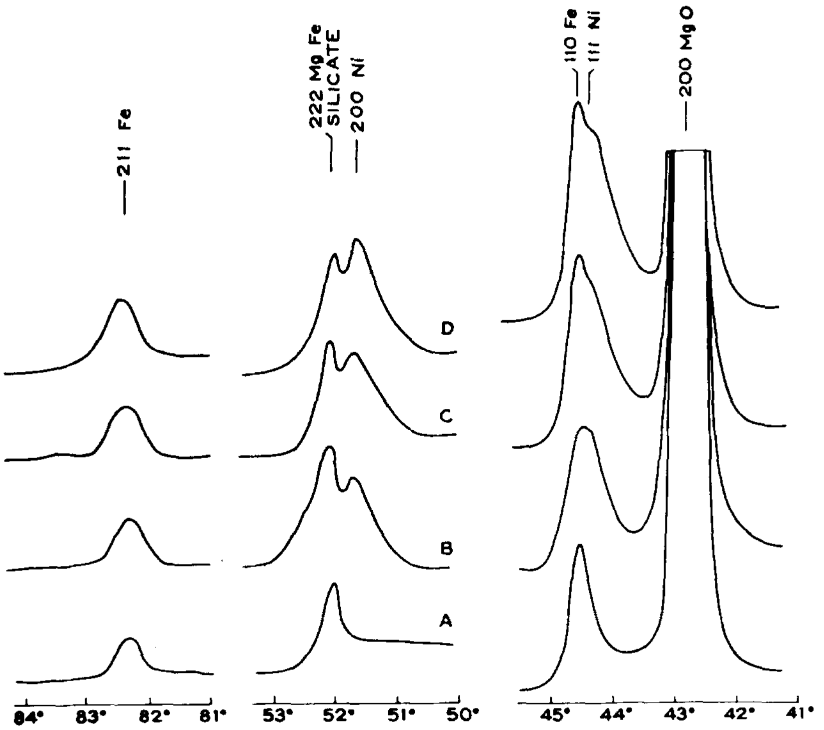

FIG. 7. X-Ray diffractograms of a standard MSC$_7$ catalyst: A, after a 15 min reduction at 950°C; B, after a 45 min reduction at 950°C; C, after a 75 min reduction at 950°C; D, after a 135 min reduction at 950°C.

imens in the reduced state) at values of 2θ inferior to those stated in the literature. The constant repetition of this phenomenon, which could in no case be attributed to experimental uncertainty, provided the elements for pinpointing the causes of the bad quality of the material considered.

Specimens taken from the same plant, at consecutive time intervals, and reduced with hydrogen at 950°C for 3 hr, evidenced a progressive decrease in the nickel and iron peak height, while the appearance of a new series of peaks was remarked, with indexes similar to those of nickel and with a similar relative intensity, but with 2θ values corresponding to a cubic cell with $a = 3.57$ Å. Peaks that could be referred to iron oxidized compounds were not observed.

With the same materials, oxidized with oxygen at 950°C for 3 hr, no further peaks were remarked that could be referred to reduced metals, while the spinel reflections appeared, but with a very weak intensity.

Cyclic oxido-reduction was applied to fresh material at different temperatures, over a period of 3 hr for each operation; the patterns of this process were effectively defined at a temperature of 950°C (Fig. 5); after the first reduction the spinel peaks disappear, while the free metal (Fe and Ni) peaks clearly appear in positions that can be theoretically foreseen. During the following reduction a peak appears, at $2\theta = 43.4°$, quite distinct from the iron and nickel peaks, while at $2\theta = 44.5°$ there still appear the reflections 111 of Ni and 110 of Fe which practically overlap; similarly each nickel peak appears together with a weaker peak, at lower 2θ.

During the third, and even more during the fourth reduction, as usual preceded by an oxidation at the said temperature for 3 hr, the peak at $2\theta = 43.4°$ becomes stronger than the peak at $2\theta = 44.5°$, so does the analogous one. The iron peaks, on the contrary, disappear gradually.

The change occurring has been followed by examining reduction, at limited time intervals (always performed with hydrogen, at 950°C); after 15 min (Fig. 6) there appear only the series of iron reflections, while the peaks in the position foreseen for nickel do not appear; after 45 min and 75 min the situation has not changed qualitatively; the iron peaks have become stronger, while the nickel peaks are still absent. After 135 min the iron peaks appear decidedly weakened, while at about the values corresponding to the nickel peaks the phenomena already pointed out show their first appearance.

In a good MSC_7 specimen after 45 min, beside the series of iron reflections, there appears the series of nickel reflections in theoretically foreseen positions; as the reduction proceeds both series increase in intensity, but do not vary their position (Fig. 7).

Comparison of a standard MSC_7 catalyst with an imperfectly prepared one having the same iron content shows that the diffractograms for freshly oxidized material differ only by stronger spinel peaks from the standard catalyst (Fig. 8).

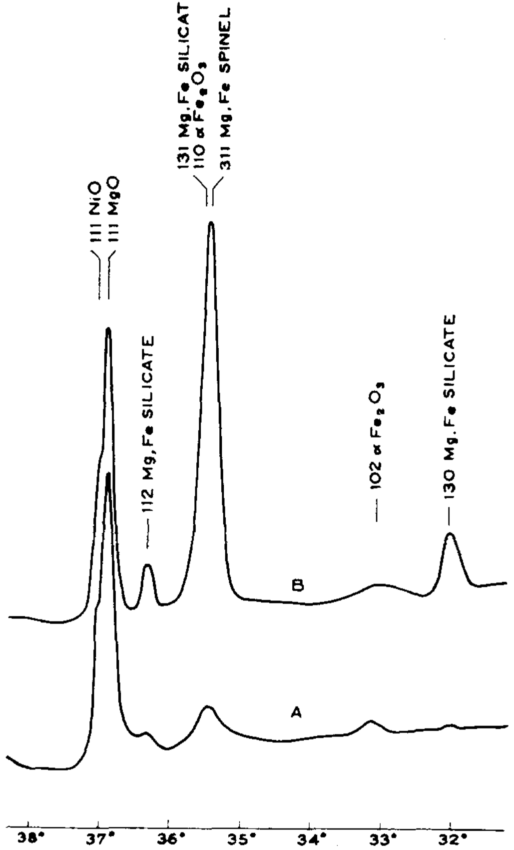

FIG. 8. X-Ray diffractograms of, A, an imperfectly prepared MSC_7 catalyst in the oxidized state; B, a standard MSC_7 catalyst in the oxidized state.

Table 3 shows the physical-chemical characteristics and the percent pore diameter distribution of a specimen of an anomalous MSC_7 catalyst, fresh and after 1 month of service in an industrial plant.

TABLE 3

PHYSICAL-CHEMICAL CHARACTERISTICS AND PERCENT PORE DIAMETER DISTRIBUTION OF A SPECIMEN OF AN ANOMALOUS MSC_7 CATALYST, FRESH AND AFTER 1 MONTH'S SERVICE IN AN INDUSTRIAL PLANT

Characteristics	Fresh	After a month's working
Apparent density (g/ml)	2.78	2.86
Real density (g/ml)	3.69	3.66
Surface area (m^2/g)	8.50	5.10
Total pore volume (ml/g)	0.089	0.076
Average pore diameter (Å)	420	600
Pore volume (by porosimeter) (ml/g)	0.079	0.063
Pore distribution (%)		
75 000 ÷ 15 000 Å	4.7	8.4
15 000 ÷ 5 000 Å	8.4	22.2
5 000 ÷ 1 000 Å	28.7	54.4
1 000 ÷ 100 Å	55.0	13.0

Surface area and porosity measurements taken on specimens submitted to oxido-reduction confirm the appearance of a remarkable alteration: the surface area is reduced from 8.5 m^2/g (fresh material) to 3.9 m^2/g after the last process and the total pore volume goes from 0.089 ml/g to 0.052 ml/g. The curves of the pore integral distribution show (Fig. 9) a gradual shift towards pores of increasing diameter (disappearance of some pores with a radius from 100 to 1000 Å and appearance of bigger pores).

DISCUSSION

In good MSC_7 specimens taken in the oxidized state, iron oxide reacts with magnesium oxide to give a spinel, as a consequence of the diffusion of the trivalent metal in the MgO lattice (occurring during

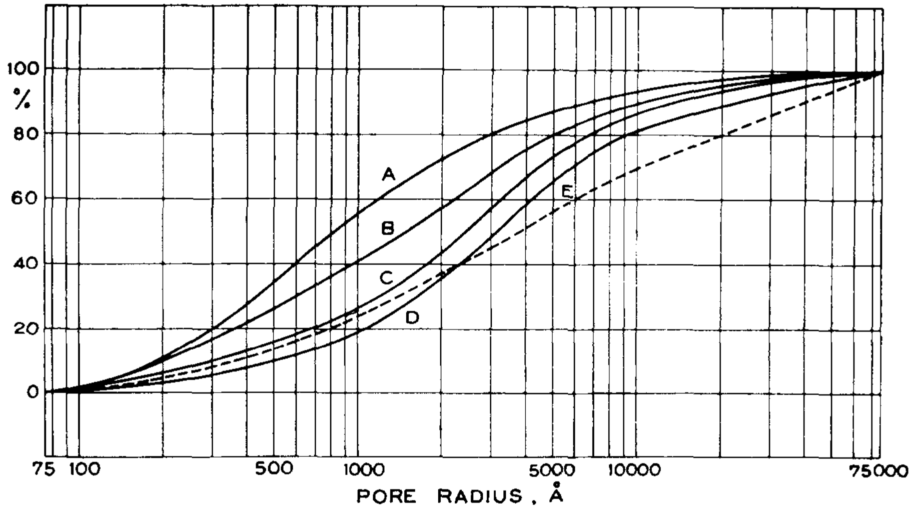

FIG. 9. Pore-size distribution of an imperfectly prepared MSC_7 specimen submitted to oxido-reduction at 950°C: A, after the first reduction; B, after the second reduction; C, after the third reduction; D, after the fourth reduction; E, standard MSC_7.

the support sintering process); in anomalous specimens, the spinel peaks are not very strong, so that in some cases they cannot be identified (in these specimens iron may be present either in a wüstitic form, which has developed during the firing, or as α-Fe_2O_3 that is almost amorphous).

In a reduced state, the standard product shows the nickel and iron peaks in their foreseen positions, with weak variations of intensity and position (in the long run over a period of time). In anomalous products, on the contrary, it can be noticed that there is a gradual decrease of these peaks and the appearance of others, with different positions (face-centered cubic lattice, $a =$

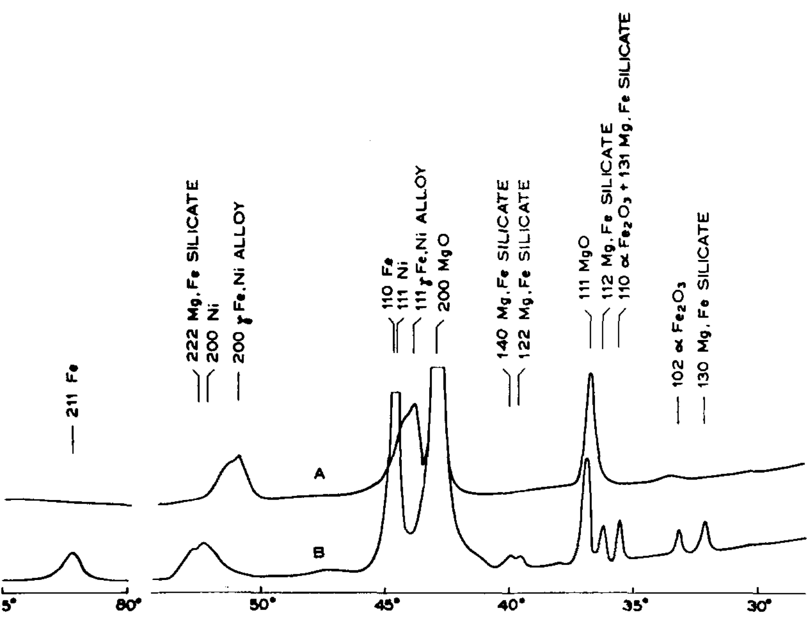

FIG. 10. X-Ray diffractograms of two MSC_7 catalyst specimens: A, standard catalyst after 1 year's service; B, imperfect catalyst after 2 months' service.

3.57 Å); these peaks may be ascribed to an Fe-Ni alloy, which can be formed by interaction of the two free metals on the support crystallite surface.

The lattice parameters found correspond to the data in the literature (*6*) for the limit value of this alloy (γ-phase); the percent composition of the alloy that is formed at the beginning is not easy to assess, as it depends on a great number of parameters (percent free iron, crystallite sizes, porosity, heating temperature, etc.). Since experimentally it has been noticed that, during the reduction of imperfectly prepared MSC_7 specimens, the iron peaks appear first, it is likely that the alloy is formed at once, by solution of the nickel into the iron with a body-centered cubic structure (α-phase) and that, as the reduction proceeds, the alloy becomes richer in nickel, taking a face-centered cubic shape.

Figure 10 shows the X-ray patterns of an MSC_7 standard specimen after 1 year's industrial service and of an imperfectly prepared MSC_7 specimen, after 2 months' service.

Alloying is subordinate to the presence of the two reduced metals on the support crystallite surface: during the production stages of the cyclic processes, remarkable reduction phenomena can be noticed and these may accelerate the process.

With a standard product, however, only nickel is present on the support surface, as iron is mostly found to be dispersed in MgO, owing to the original spinel formation; besides, the support lattice, statistically well arranged, hinders the iron rising to the crystallite surface.

Instead, if the support has not been properly prepared due to the use, e.g., of too course MgO and Fe_2O_3 powders, of Fe_2O_3 that is not very reactive because of unsuitable crystalline characteristics, or of nonhomogeneous mixture of the powders, or due to insufficient firing of the small cylinders (owing to time and temperature), etc., iron may be found little spinelized, yet able to take a structure—in the plant working conditions—in the form of magnesium-wüstite (bivalent iron). This solid solution is marked by high concentration of cationic vacancies which help iron to rise from the lattice inside to the surface, where it can alloy with nickel.

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