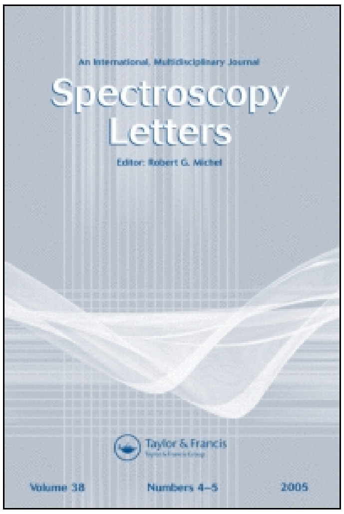

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Abdalla, Atef M. , Hefni, M. A. and El-Awad, A. M.(1993) 'Electron Paramagnetic Resonance and Mössbauer Studies of Fe^3 Ions in the Fe_2O_3 = MoO_3 System', Spectroscopy Letters, 26: 9, 1695 — 1708
To link to this Article: DOI: 10.1080/00387019308010768
URL: http://dx.doi.org/10.1080/00387019308010768

SPECTROSCOPY LETTERS, 26(9), 1695-1708 (1993)

ELECTRON PARAMAGNETIC RESONANCE AND MÖSSBAUER STUDIES OF Fe^{3+} IONS IN THE Fe_2O_3 - MoO_3 SYSTEM

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The electron paramagnetic resonance (EPR) and Mössbauer spectra of iron-molybdenum mixed oxides system have been investigated. Both EPR and Mössbauer measurements revealed the formation of ferric molybdate, $Fe_2(MoO_4)_3$ and the existence of two different Fe^{3+} species. The EPR spectra of $Fe_2(MoO_4)_3$, show two resonance lines of Fe^{3+} ions indicating that a strong exchange interaction is dominates in pure iron molybdate. Mösbauer measurements revealed that the isomer shift (I.S) increases with increasing the iron content. A maximum of quadrupole splitting (Q.S) is observed at the stoichiometric concentration corresponding to the formation of $Fe_2(MoO_4)_3$. The effect of a catalytaic dehydration process on the redox behaviour of Fe^{3+} located in iron molybdate frame work is investigated. Results indicate that the catalytaic dehydration of 2-proppanol over this catalyst reduces Fe^{3+} ions to Fe^{2+} leading to the formation of the inactive phase $FeMoO_4$. the essential role of oxygen, in the alcohol gas feed, in regeneration the activity of the catalysts was demonstrated.

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INTRODUCTION

Iron-molybdenum mixed oxides are well known as effective catalysts for many industrial processes[1]. The role of oxides composition and the nature of the active sites as well as the reaction mechanism involved in such processes have been investigated by many authors[2-4].

Iron, as a transition element, plays an important role in these catalyst systems. It occurs in the oxidation state Fe^{3+} and Fe^{2+}. Although it is very easy to identify Fe^{2+} (d^6, D^5) with the optical and Mössbauer spectroscopies, there are few methods with high sensitivity for Fe^{3+}. The EPR spectroscopy coupled with the large spin intensities expected for ferromagnetic metals would appear to make this technique attractive and the most used to elucidate the structural analysis of Fe^{3+} [5-8]. The method takes the advantage of the electron and its magnetic moment to reveal infromation on the density distribution of the unpaired electrons (Spin).

The Mössbauer technique has the advantae of being sensitive to small concentrations of ^{57}Fe and provides direct information on the states of all of the iron atoms in catalytic materials. In previous work the results of a study on Fe^{3+}-molybdate-based catalysts with an without Mo and Bi oxides have been reported[9,10].

In the present work a further examination is given using the EPR and Mössbauer measurements in order to obtain more detailed information about the structure of iron ions in the iron-molybdenum mixed oxides system.

EXPERIMENTAL

All the reagents used in the present investigation are of analytical grade (BDH Chemicals). A series of iron-molybdenum oxides was prepared by the impregnation method. The appropriate amounts of $Fe(NO_3)_3.9H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ were mixed in different values of X where $X = Fe^{3+}/(Fe^{3+} + Mo^{6+})$, X% = 1,5,10,20,30,40 and 50 mol. % Fe^{3+}. Distilled water was added to form a pasts, which was then dried over a water-bath with occasional mixing. The mixed samles were further dried at 110°C. The parent mixtures were calcined in air at 500°C for 4H.

Electron paramagnetic resonance (EPR) spectra were recorded ot room temperature on an E-109 Varian Spectrometer Operataing in the X-band (9.5 GHz), with 100 KHz magnetic field modulation.

The Mössbauer spectra were taken in transmission geometry by Austin Science Associates. Using source of Co^{57} in a palladium matrix as a γ-rays of 14.4 Kev energy. The spectrometer consists mainly of Austin 6800 compouter wiich serves as a maltichannel Scaler, the memory is arranged as two separate sets of 1022 channel memories. the Mössbauer spectrum is accumulated in one set and the laser velocity data is simultaneously accumulated in the other set. The spectrometer operated in constant acceleration drive with flyback mode and the velocity calibration in the spectrometer was achieved by Helium-Neon Laser interferometry. The detector used is krypton dioxide proportional counter linked to a signal amplifier and a data acquistion system that segregates signals according to their energy orthe relative velocity of the source. The spectrum of an iron foil (National Bureau of Standard thickness of 0.005") was used to determine the velocity increment per channel and the isomer shifts of ^{57}Fe in the sample.

The catalytic decomposition of 2-propanol was taken as a test reaction to follow the activity of the different calalysts, using a conventional flow reactor[11] and two different alcohol feeds, one consists of alcohol in air and the other is alcohol in pure nitrogen. the exit feed was analyzed using a Perkin Elmer gas chromatograph (Sigma 3B).

RESULTS AND DISCUSSION

EPR Spectra:

Seven samples having different basic compositions (Table 1) have been investigated. The obtained spectra are shown in (Figs. 1 and 2). The detected EPR spectra of Fe ions in the samples are attributed to Fe^{3+} alone, because Fe^{2+} ions in the samples, although paramagnetic, did not exhibit EPR spectra at rom temperature and sometimes not even at the liquid helium temperature[12]. EPR spectra of low concentration of Fe_2O_3 (sample 1 and 2) are show in (Fig. 1). The EPR signature of a paramagnetic molybdenum ion is an intense central line accompanied by six weak hyperfine lines with g-value = 1.973 as shown in (Fig. 1-A). Hefni et al.[11,13] proves that the signature is attributed to Mo^{5+}

Table 1. Mössbauer parameters for iron-molybdenum mixed oxides system.

Sample number	X^* mol. % Fe^{3+}	Species	(I.S) mm/sec.	(Q.S) mm/sec.
1	1	-	-	-
2	5	-	-	-
3	10	Fe^{3+}	0.411	0.179
4	20	Fe^{3+}	0.412	0.187
5	30	Fe^{3+}	0.414	0.191
6	40	Fe^{3+}	0.416	0.197
7	50	Fe^{3+}	0.422	0.194

$$^*\ X\ \% = \frac{Fe^{3+}}{Fe^{3+} + Mo^{6+}} \times 100$$

which may be originally presents in the parent mataerial or formed during the callcination process. The signature is superimposed on a very broad line (ΔH = 470 G) and g_{eff} - value = 2.00. The latter is attributed to a condensed iron phase and can be assigned to $Fe_2(MoO_4)_3$[8]. Addition of Fe_2O_3 to the mixture (sample 2) is accompanied by partially disappearance of the Mo^{5+} signal (g - value = 1.973), as shown in (Fig. 1-B). Increasing the concentration of Fe_2O_3 (sample 3) leads to a complete disappearance of the signal at g-value = 1.973. The only detectable signal is the broad one with line-width (ΔH = 470 G) at g_{eff} - value = 2.00 (Fig. 2-C) can be attributed to Fe^{3+} in the sample. The impotant result here appears to be the complete oxidation of Mo^{5+} in the sample upon adding Fe_2O_3. On the other hand, when Fe_2O_3 concentration reachs 20 mol. % Fe^{3+} (sample 4), another two signals appear around the preceeding one (Fig. 2-D). The g-values

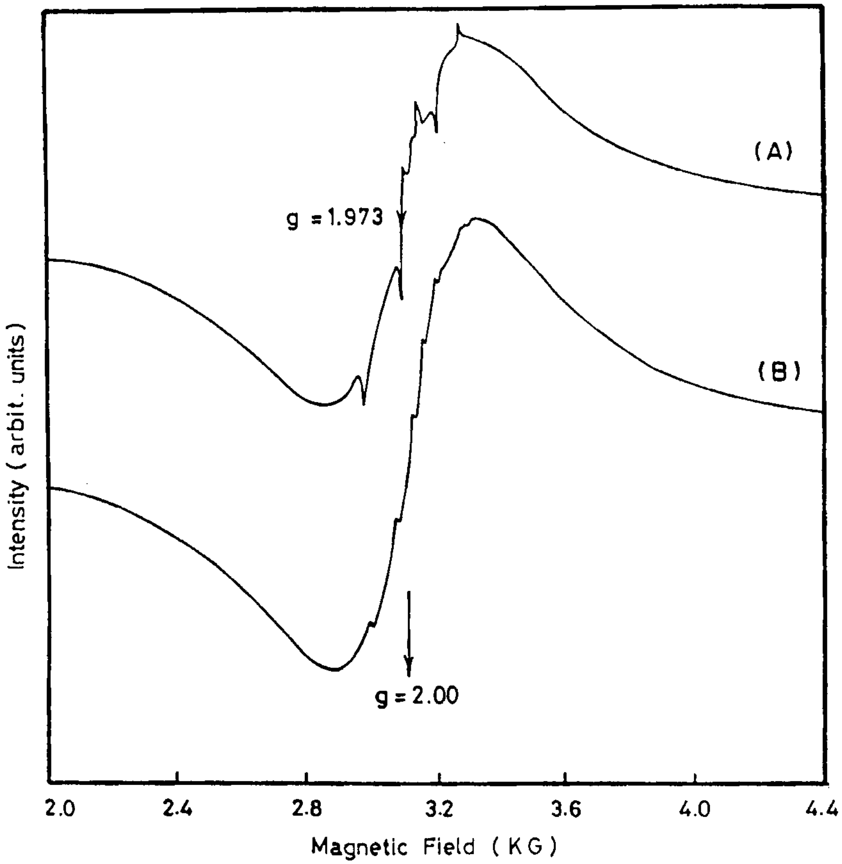


Fig. 1: EPR spectra of sample 1 and sample 2 at room temperature

A) sample 1   B) sample 2.

of the low and high field signals are 2.175 and 1.828 respectively. The line width (ΔH) of each signal equal to 290 G. By continous increasing of Fe_2O_3 (sample 5), the signal corresponding to the g-value = 2.00, totally disappeares and the separation between the two new signals increases (Fig. 2-E). At 40 mol. % Fe^{3+} (sample 6), the maximum separation between the two signals is found (Fig. 2-F). The g-values corresponding to the low and high field signals are equal to 2.571 and 1.75, respectively.

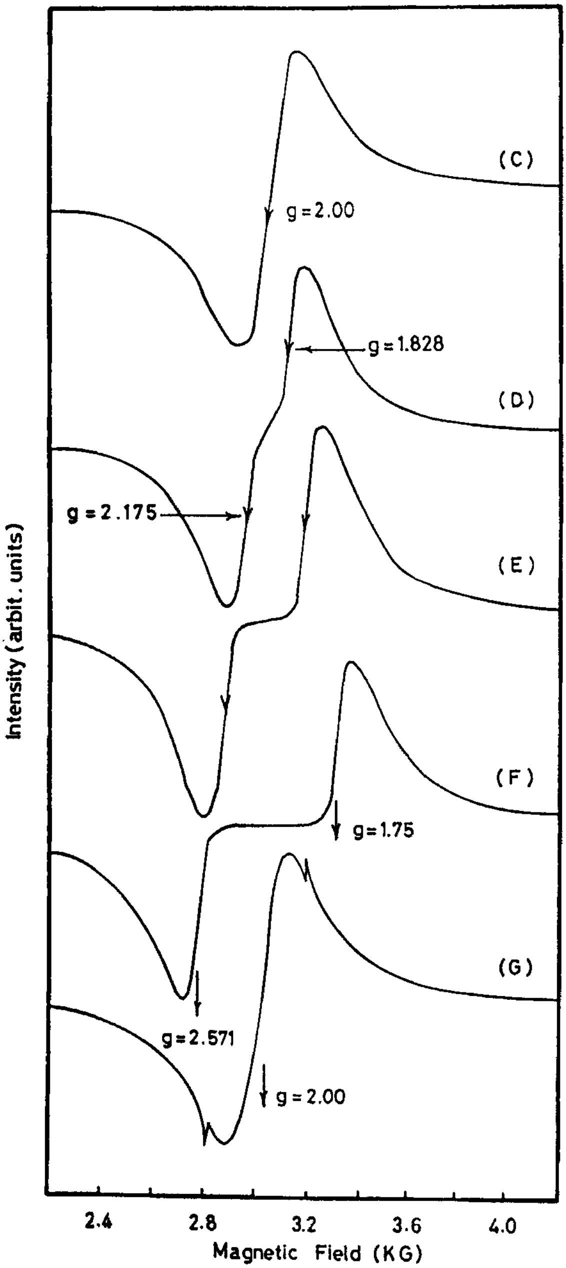


Fig. 2: EPR spectra of samples 3,4,5,6 and 7 at room temperature

C) sample 3 D) sample 4 E) sample 5

F) sample 6 G) sample 7

Their linewidth (ΔH) is the same and equals to 192 G. At Fe_2O_3 greater than 40 mol. % Fe^{3+} in the mixture, a very broad and strong signal appears between the precceding two signals and can be assigned to the presence of excess Fe_2O_3 in the sample (Fig. 2-G).

Mössbauer Spectra:

The spectra taken at room temperature for five samples (3,4,5,6 and 7) are shown in (Fig. 3). In this measurements Lorentzians were used for the resonant absorption curves, assuming a thin absorber. A programme for least square analysis curve fit was used. The off-resonance background, the width, the intensity and the central line position of each Lorentzian were left as variable and the interactions for fitting were kept to continue until the minimum difference between the theoritical and experimental data is achieved and remains constant.

The spectra of the samples are identical. The presence of broad Mössbauer lines suggest a distribution of iron sites with slightly different quadrupole interactions. The lines are characterized by values of isomer shifts (I.S) = 0.411 - 0.422 mm/sec. and quadrupole splitting (Q.S) ranging from 0.179 mm/sec. for sample 3 to 0.194 mm/sec. for sample 7. These parameters are very similar to those reported previously[14,15]. When the (I.S) values of $Fe_2(MoO_4)_3$ are compared to those of $Fe_2(SO_4)_3$[16-18] and $Na_3Fe_2(PO_4)_3$[19] which have related structures, a significant increase is observed is the sence $(I.S)_{molybd.} < (I.S)_{phosph.} < (I.S)_{sulf.}$ (for example, at room temperature, $(I.S)_{phosph.} = 0.45$ mm/sec. and $(I.S)_{sulf.} = 0.49$ mm/sec. This trend likely corresponds to an increase of the ionic character of the Fe-O bond as a consequence of increasing covalency of the antagonistic bond X-O from molybdate to sulfate.

The compositional dependence of the (I.S) obtaied from the position of the doublet is shown in (Fig. 4). It is seen that the (I.S) tends to increase with increasing the content of iron in the samples. This means that the covalency of the Fe^{3+} - O bond decreases as the content of iorn increases[20]. The relation between the Fe^{3+} concentration and (Q.S) is also observed (Fig.4). It is interesting that a maximum (Q.S) is observed for sample 6 whch contains 40 mo. % Fe^{3+} (stoichiometry amounts formation). The maximum of (Q.S) may thus be attributed to a higher degree of

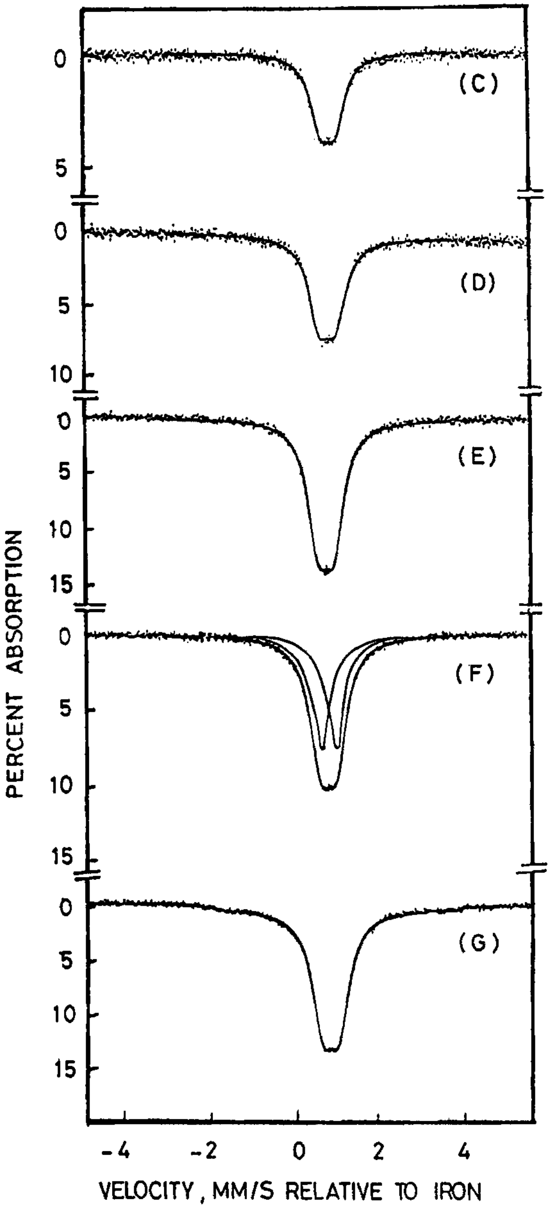


Fig. 3: Room temperature Mössbauer spectra for samples 3,4,5,6 and 7

C) sample 3 D) sample 4 E) sample 5

F) sample 6 G) sample 7.

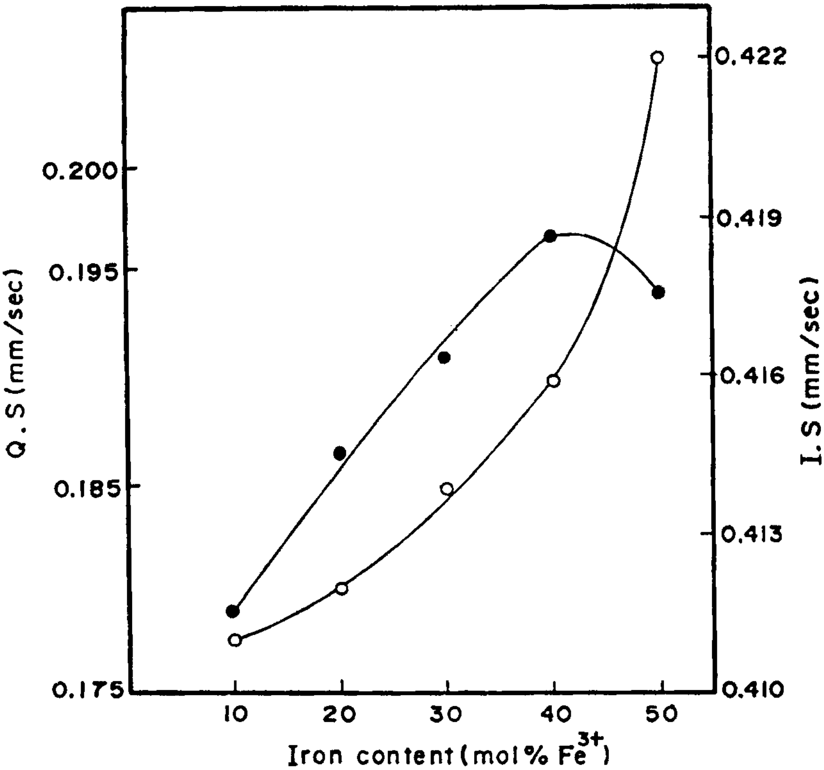
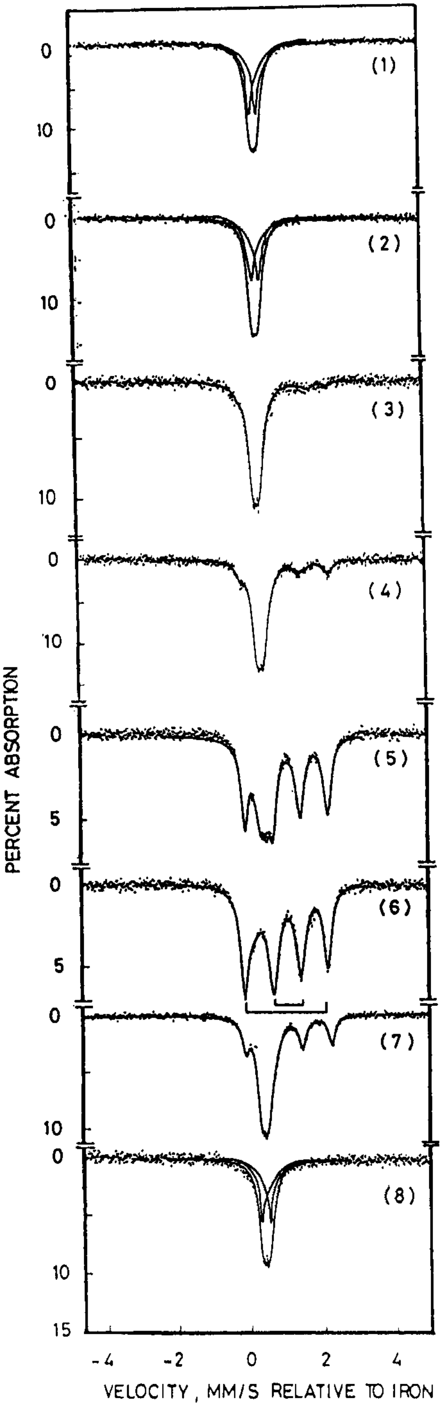


Fig. 4: Variation of the Fe^{3+} isomer shift (I.S) and quadrupole splitting (Q.S) with iron content mole. % Fe^{3+}
O—O: (I.S) ●—●: (Q.S)

asymmetric distribution of the iron electron density in $Fe_2(MoO_4)_3$. It is assume that the value of the (I.S) and the (Q.S) are related to the predominant contribution of the Fe^{3+} ions, as observed for the doublet through out the Fe^{3+} concentration in the samples. It is noted from (Fig. 4) that the symmetry of the Fe^{3+} ions decreases from sample 3 (10 mol. % Fe^{3+}) to sample 6 (40 mol. % Fe^{3+}), with the appearance of different sites of Fe^{3+}.

Previous studies of the room temperature single crystal X-ray structure of $Fe_2(MoO_4)_3$ show that, it consist of (FeO_6) octahedra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VELOCITY, MM/S RELATIVE TO IRON

sharing corners with (MoO_4) tetrahedra. All the octahedra are isolated from each other and so are the tetrahedra. Each oxygen is linked only to one iron and to one molybdenum[15,21]. Thus, the structdure of ferric molybdate exhibits features analogous to those of ferric sulfate[22,23] or sodium iron phosphate[24] as far as the three-dimensional network of (FeO_6) octahedra and of (XO_4) tetrahedra is concerned.

The decrease of (Q.S) and the increase of (I.S) by increasing the concentraiton of Fe^{3+} in the sample 7 with more than 40 mol. % Fe^{3+} may be attributed to a disturbance of $Fe_2(MoO_4)_3$. This is due to the excess of Fe^{3+} present in the form of Fe_2O_3[5].

The EPR spectra could be interpreted on the basis of the Mössbauer results in the following manner: the appearance of two signals at g-value = 2.571 and g-value = 1.75 for sample 6 (40 mol. % Fe^{3+}), agrees with the idea that there are two possible sites for Fe^{3+} in $Fe_2(MoO_4)_3$ (Fig. 2-F). These sites are responsible for the intense doublet in the Mössbauer spectra (Fig. 3-F).

Fig. 5: Room temperature Mössbauer spectra for sample 6 after its using as a catalyst in different experimental conditions:

1) Oxygen-containing alcohol feed at t_c*= 200°C.
2) Oxygen-containing alcohol feed at t_c = 400°C.
3) Oxygen free alcohol feed (using the nitrogen gas as a carrier gas) at t_c = 200°C.
4) Oxygen free alcohol feed (using the nitrogen gas as a carrier gas) at t_c = 300°C.
5) Oxygen free alcohol feed (using the nitrogen gas as a carrier gas) at t_c = 350°C.
6) Oxygen free alcohol feed (using the nitrogen gas as a carrier gas) at t_c = 400°C.
7) Reaxidation of the sample at t_c = 400°C.
8) Reaxidation of the sample at t_c = 500°C.

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* t_c = Catalytic reaction temperature.

However, in literature[20], the Mössbauer spectra at room temperature of pure $Fe_2(MoO_4)_3$ and $Fe_2(MoO_4)_3 \cdot MoO_3$ catalysts display a single line with (I.S) = 0.57 mm/sec., which is in the typical range for high spin ferric ions. The data are interpreted in terms of isolated Fe^{3+} at low concentrations of iron and superexchange coupled oxygen bridged Fe^{3+} pairs in distorted octahedral sites at higher concentrations. In the presence of excess Mo^{6+} with respected to Fe^{3+}, the ions has only one site (samples 1-3) which indicates that the Mo^{6+} removes the Fe^{3+} ions from the other possible sites. This is the reason of the appearance of only one signal in the EPR resonance spectra for low iron concentrations at g-value = 2.00. The broad superparamanetic pattern (Fig. 2-G) with g-value = 1.989 for sample 7 (50 mol. % Fe^{3+}) is due to the presence of excess Fe_2O_3 in ferric molybdate. The spectrum shows less exchange interaction as well as a decrease in the magnetic response of $Fe_2(MoO_4)_3$.

The redox properties of Fe^{3+} in $Fe_2(MoO_4)_3$ catalyst:

The accompanied changes of the oxidation state of Fe^{3+} on $Fe_2(MoO_4)_3$ catalyst was followed using the Mössbauer spectroscopic measurements. Results as obtained for the pre-used sample 6 seem to be greatly influenced by the catalytaic reaction conditions. In an oxygen-containing alcohol feed the Mössbauer spectra for catalyst used at different catalytaic reaction temperatures, namely at 200 and 400°C, appear nearly identical to the spectra of the original one (Fig. 5-1,2). Hence there is no change in the values of the (I.S) and the (Q.S) (I.S - 0.416 mm/sec., Q.S = 0.197 mm/sec.). On the other hand, the Mössbauer spectra for pretreated catalyst in an oxygen-free alcohol feed (i.e., when we used the nitrogen gas as a carrier gas) the reduction of Fe^{3+} to Fe^{2+} can be easily distinguised (Fig. 5-3 to 6). The spectra obtained (Fig. 5-3,4) can be interpreted as a superposition of some quadrupole doublets on the predominant one. The (I.S) and the (Q.S) of the predominant doublet have the some values as the one measured before the reaction (I.S. = 0.416 mm/sec., Q.S. = 0.197 mm/sec.). The doublet is therefore due to Fe^{3+} ions of the unreduced catalyst, while the observed doublet which appear after the reaction is due to iron ions of that part of the catalyst which has participated in the reaction. The concentration of Fe^{2+}

becomes much greater with raising the catalytaic reaction temperature up to 400°C where $Fe_2(MoO_4)_3$ is completly reduced to $FeMoO_4$.

As a result the intensity of the predominant doublet decreases and consequently the observed quadrupolar doublets become more evident (Fig. 5-5,6). We can conclud that when the catalytic reaction temperature is low, only a part of the catalyst has participated in athe reaction (Fig. 5-3,4). On the other hand all the catalyst has taken part, at high catalytic reaction temperature (Fig. 5-6). It is clear that, the whole catalyst can partaicipate in the reaction which implies the reduction of Fe^{3+}ions to Fe^{2+} located in two different sublattaices. In scoup of previous studies[20], the four measured lines in the spectra (Fig. 5-6) can be interpreted in two different ways: (i) as a superposition of two quadrupole doublets due to Fe^{3+} ions and Fe^{2+} ions or (ii) as due only to Fe^{2+} ions located in two different lattice sites. In either cases, the presonce of Fe^{2+} ions indicates the formation of a $FeMoO_4$ compound in the reduced catalyst.

Reoxidation process:

The reoxidation process was observed, when exposing the reduced catalyst to a flow of pure air. The observed quadrupolar doublets gradually decreased and consequently, the predominant doublet due to Fe^{3+} appeared. The reoxidizability of Fe^{2+} ions increases with increasing the reaction temperature (Fig. 5-7,8), at 500°C complete reoxidation of Fe^{2+} to Fe^{3+} takes place. This proved the essential role of oxygen to keep the catalyst in an active form.

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Date Received: June 7, 1993
Date Accepted: July 9, 1993