JOURNAL OF CATALYSIS 22, 324–332 (1971)

The Nature of the Active Component in a Fe_2O_3–MoO_3 Catalyst

II. Study of the Variations Occurring During High Temperature Treatment*

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Received September 21, 1970

In this paper the variation of both chemical and catalytic activity of Fe_2O_3–MoO_3 catalyst occurring as a result of high-temperature treatment is investigated.

Three variations with temperature are observed. The first occurs at about 350°C and is characterized by the start of bulk diffusion, increase of the electrical conductance, and formation of high amounts of CO in methanol oxidation. The second occurs at about 450–500°C and is characterized by the complete oxidation of Fe^{2+} to Fe^{3+} and by the decrease of the isomerization power of 1-butene of the catalyst. The third variation occurs at about 600°C and is characterized by a final decrease of surface area, by a strong decrease of catalytic activity and a variation of the IR spectra in the region of Mo═O stretching frequency.

INTRODUCTION

In a previous paper (*1*) we advanced the hypothesis that oxidative dehydrogenation of methanol to formaldehyde and to CO is typical of catalysts based on oxides and mixed oxides with a metal-oxygen bond having a double-bond character. This type of bond is characteristic of MoO_3 and of Mo-mixed oxides. This is the case, for instance, with the Fe_2O_3–MoO_3 industrial catalyst for the selective oxidation of methanol to formaldehyde. In a previous note (*2*) we reported that in Fe_2O_3–MoO_3 catalyst the role of Fe is to act so as to transfer O_2 and H_2O between surface and gas phase.

In order to reveal the role of the two metals in determining the special selectivity and activity of Fe_2O_3–MoO_3 for the oxidation of methanol to formaldehyde, we have investigated the modifications occurring at the catalyst surface as a result of activation at high temperature. Some authors (*3*, *4*) have proposed that this activation affects both selectivity and activity.

The present study was carried out both by spectroscopic analysis and by catalytic activity measurements at 250–500°C in the oxidation of CH_3OH and at lower temperatures (80–150°C) in other reactions. At these low temperatures further transformations of the catalyst are unlikely to occur.

EXPERIMENTAL

Materials. An industrial-type Fe_2O_3–MoO_3 catalyst was used. This catalyst was prepared by co-precipitation of $FeCl_3$ and ammonium molybdate at pH 2 and was subsequently dried in air at 420°C for 4 hr. The composition of the catalyst was (by wt %): Fe_2O_3 as $Fe_2(MoO_4)_3$ 17.5, MoO_3 as $Fe_2(MoO_4)_3$ 47.3, and MoO_3 excess 35.2. This catalyst was activated in air at 450, 500, 550, 600, and 700°C for 1 hr.

X-Ray powder data. X-Ray diffraction spectra were recorded with a Geiger

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* This work was sponsored by the Italian National Council for Research (C.N.R.).

counter Philips spectrogoniometer with Cu K_α radiation.

Infrared spectra. IR spectra (with KBr disc technique) and ATR spectra (with an ATR unit model ATR 1 of Connecticut Instrument Co.) were recorded for the catalyst activated at high temperature on a Grating Infrared Spectrophotometer-Perkin Elmer model 457.

Electronic spectra. Diffuse reflectance spectra of finely ground samples were recorded in the range 7–40 k*K* (7000–40 000 cm^{-1}) by the use of a Unicam SP 700 spectrophotometer with a SP 735 diffuse reflectance attachment against a blank of MgO.

Thermal balance. Reduction experiments were carried out on a thermal balance Adamel TH 59-2 in a flow of N_2–NH_3 at 20% of NH_3, with constant increase of temperature of 150°C/hr.

Surface area measurements. Surface area measurements were carried out with N_2 using a C. Erba Sorptomatic apparatus.

Electrical conductivity. Electrical conductivity measurements were carried out at high frequency (1 megacycle) with a Tesla dissipation factometer on powdered catalyst. The cell for electrical conductivity measurements was made of Pyrex glass with two gold electrodes immersed in the powdered catalyst.

Measurements of catalytic activity. 1. Oxidation of methanol with air was carried out in a differential recirculating reactor at temperature ranging from 250 to 500°C. The reactor scheme is reported elsewhere (*5*). 2. Oxidation of 1-butene with air was carried out both at 150°C in a batch-stirred tank reactor (the reactor scheme is reported elsewhere (*6*)) and in a pulse reactor linked to a gas chromatograph. 3. Epoxidation of cyclohexene was carried out in a glass tube, sealed under vacuum, after introduction of cyclohexene, tert-butylhydroperoxide, tert-butyl alcohol and catalyst. The glass tube was thermostatted at 80°C in an oil bath.

Chemical analysis. This was carried out with a Hewlett-Packard gas chromatograph (model 5750). The following columns were used:

1. A 12-ft dimethylsulfolane column to separate air, 1-butene, *cis*-2-butene, and *trans*-2-butene.
2. A 6-ft. di-isodecylphthalate column to separate *tert*-butyl alcohol, cyclohexene, *tert*-butyl hydroperoxide and cyclohexene-oxide.
3. A 4-ft. Ethofat 60/25 (polyoxyethylene soya amine) column to separate formaldehyde, methanol and water. The analysis of formaldehyde was also carried out by iodometric titration.
4. The analysis of CO and CO_2 was carried out, respectively, in a column of Molecular Sieve 5A and silica gel.

Results

Electronic Spectra

The diffuse reflectance spectra of the Fe_2O_3–MoO_3 catalyst activated at high temperature are reported in Figs. 1 and 2. A broad band between 38 and 29 k*K* is

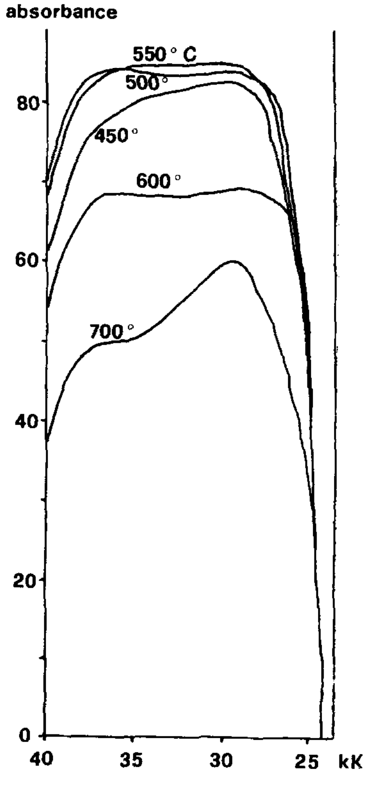


FIG. 1. Electronic spectra of the catalyst at different activation temperatures in air (uv region).

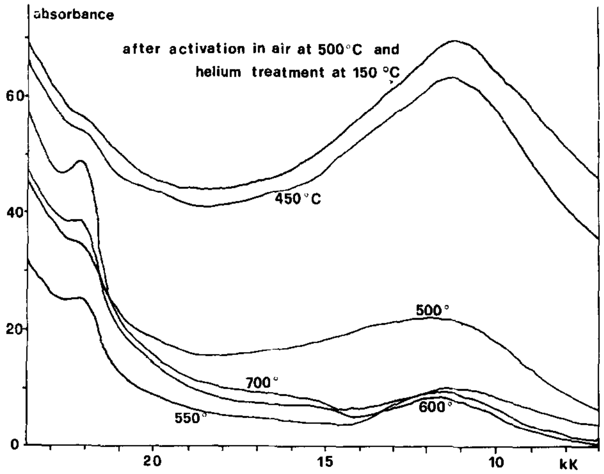


FIG. 2. Electronic spectra of the catalyst at different activation temperatures in air (visible region).

present in the uv part of the spectrum (Fig. 1). The spectra are typical of molybdenum compounds having tetrahedral and octahedral coordination (e.g., Mo in $Na_2Mo_2O_7$) (*7*). After activation at 600°C the absorbance of the surface in the uv region decreased strongly.

In the visible region, a strong absorption between 20 and 10 k*K* appeared for the sample activated at 450°C. After thermal treatment at $T > 500°C$, this absorption almost completely disappeared and simultaneously a band between 22 and 23 k*K* appeared.

Allen and Hush (*8–9*) report that electronic transitions between Fe^{II} and Fe^{III} simultaneously present in a compound give an absorption band between 18 and 14 k*K*. We also attribute the absorption in the 20–10 k*K* region observed in the spectra of the sample activated at 450°C to electronic interaction between Fe^{II} and Fe^{III}.

In Fig. 2, spectra of the catalyst activated at 500°C in air and then kept under helium at 150°C are also reported. It is possible to see the presence of an absorption band in the 10 k*K* region due to the formation of Fe^{II} by reduction of the catalyst.

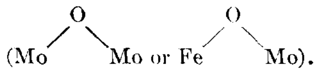
X-Ray Pattern

No variation in the X-ray pattern of the catalyst was observed as a result of activation of the catalyst between 450 and 600°C. The X-ray pattern presented the characteristic diffractions of ferric molybdate and of MoO_3.

IR Spectra

In Fig. 3, ir and ATR spectra of the high-temperature activated sample are reported. For the sample activated in air at 500°C, it is possible to see in the ATR spectrum a band at 980 cm^{-1} corresponding to MoO_3 and another one at 960 cm^{-1} corresponding to ferric molybdate. For the sample activated at 550°C, these two bands are clearly present also in the transmission spectrum. A shift to low frequency of the stronger band between 850 and 870 cm^{-1} of the transmission spectra was observed in the ATR spectra of the sample activated at $T \leqslant 600°C$.

The surface of a solid largely contributes to its ATR spectrum. The difference we observed between ATR and ir spectra means that the structure of the surface differs from that of the bulk in the catalysts activated up to 600°C. The band at ~ 860 cm^{-1}, which is shifted in the ATR spectra to 800 cm^{-1}, must probably be attributed to the bridge oxygen



$$(\mathrm{Mo}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{Mo\ or\ Fe}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{Mo}).$$

Therefore, these bonds are either labilized

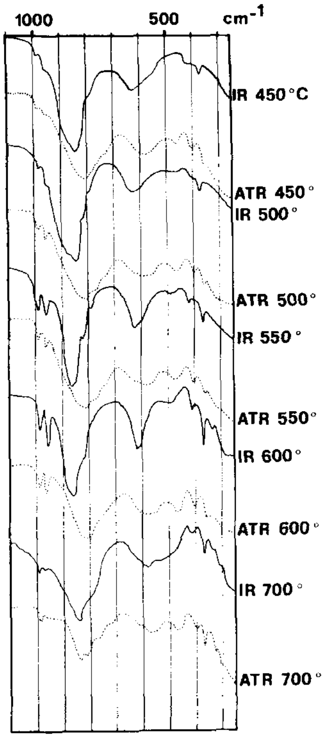


FIG. 3. IR and ATR spectra of the catalyst at different activation temperatures in air.

at the surface or the surface composition is different from that of the bulk.

Oxidation of 1-Butene and of Propylene

1. Oxidation runs in a batch stirred tank reactor. Oxidation experiments on 1-butene (concn 5% in air) were carried out at 150°C with 1 g of the different samples of catalyst activated in air at high temperature. In these tests we observed isomerization of 1-butene. In Fig. 4, the overall conversion of 1-butene and the conversion to 2-butenes are reported vs the reaction time. Analyses of oxidized products were not carried out. The catalyst activated at 450°C has the highest isomerization power. The amount of oxidized products was highest for the catalyst activated at 500°C. We may observe that the surface area (Fig. 5) of these catalysts is lower than the one corresponding to the catalysts activated at lower temperature. The *cis*:*trans* ratio of 2-butene was 1 with catalysts activated at 450°C, and 1.5 in those activated at 500 and 550°C.

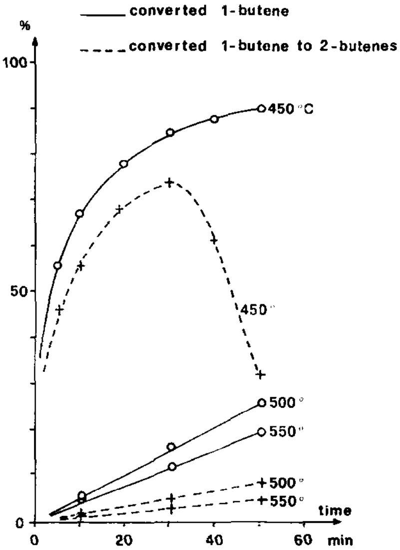


FIG. 4. Oxidation runs of 1-butene with stirred tank reactor carried out at 150°C with catalysts activated in air at the indicated temperatures.

Oxidation of propylene was also carried out on the catalysts activated at 450 and 500°C. Acetone was formed as the oxygenated product. The catalyst activated at 600°C showed no activity either in oxidation or isomerization of 1-butene.

2. Oxidation runs with a pulse reactor. Oxidation of 1-butene was carried out at 150°C in a pulse reactor by using 1 g of catalyst and 5% of butene in air. The

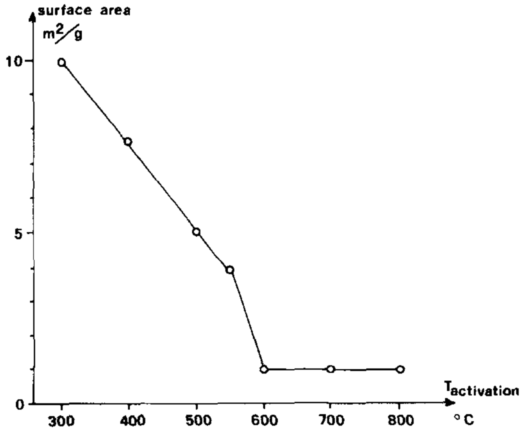


FIG. 5. Surface area of the catalyst at different activation temperatures.

TABLE 1
OXIDATION OF 1-BUTENE IN A PULSE REACTOR[a]

Activation temperature (°C)	Global conversion % 1-butene	Conversion 1-butene to 2-butene (%)
450	40	36
	18[b]	8[b]
500	49	40
	15[b]	4[b]
550	35	28
	13[b]	3[b]
600	0	0
	0	0

[a] $T = 150°C$; 5% 1-butene in air; in helium flow; catalyst 1 g; 1-cm^3 syringe sample.

[b] Values obtained after introduction of formaldehyde.

samples activated at 450, 500, and 550°C had a strong isomerization and oxidation power. The *cis*:*trans*-2-butene ratio in the products was 1. The catalyst activated at 600°C showed no activity (Table 1).

Pulses of CH_2O were also injected in the pulse reactor before introduction of 1-butene. Both the isomerization and the oxidation power showed a sharp decrease.

Epoxidation of Cyclohexene

Epoxidation of Cyclohexene was carried out in the liquid phase with tert-butyl hydroperoxide, using tert-butyl alcohol as solvent. Volume percentages were: 15% tert-butyl hydroperoxide; 15% tert-butyl alcohol; and 70% cyclohexene.

One-tenth gram of the Fe_2O_3–MoO_3 catalyst was used for each run. The cyclohexene oxide obtained after 1 hr of reaction at 80°C is reported in Fig. 6. The same figure also reports the value obtained for 0.032 g of MoO_3. Figure 6 shows that the activity of the catalyst for the reaction of epoxidation does not change if it is activated at a temperature lower than 550°C. The reaction of epoxidation very probably occurs in a homogeneous liquid phase, and therefore, it is influenced by the catalyst solubility. After activation at 600°C, the catalyst activity approaches that of MoO_3, as may be seen in Fig. 6.

After sublimation of MoO_3, observed by us after activation of the catalyst at 700°C when the catalyst essentially consists of pure ferric molybdate, the activity is almost nil.

Oxidation of Methanol

Oxidation of methanol (5% in air) was carried out in a differential recirculating reactor at temperatures between 250 and 500°C. The rate of formation of CH_2O, CO, and CO_2 at different temperatures is reported in Fig. 7. In the same figure, the weight loss of catalyst in a flow of N_2–NH_3 and the conductance are also reported.

DISCUSSION

The temperature dependence of various properties of the catalyst are reported in Fig. 8. The temperature concerned is the activation temperature in air of the catalyst or for the tests concerning oxidation

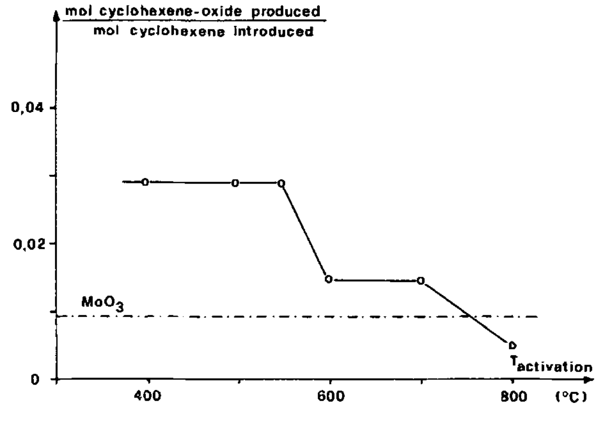


FIG. 6. Epoxidation of cyclohexene.

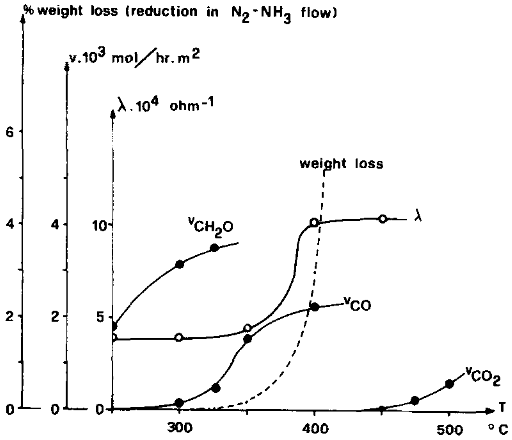


FIG. 7. Methanol oxidation. Electrical conductivity (λ). Reduction of the catalyst in N_2-NH_3 flow.

of methanol it is the reaction temperature. According to the results reported above, it is possible to observe three ranges of temperature in which some strong change in the properties of the catalyst occurred.

First Variation

A first variation in the properties of the catalyst occurred at about 300–350°C. This variation is evidenced by the sharp increase of electrical conductance (Fig. 7) and by the start of bulk reduction of the catalyst in N_2–NH_3 flow. In this range of temperature, it was possible to observe the production of higher amounts of CO in the oxidation of methanol.

The bulk reduction and the change in conductance of the catalyst must be connected with the same type of phenomenon since they present a sharp variation at about the same temperature. Since the product of first reduction of the catalyst is Fe^{II}–molybdate, as reported by us in a previous paper (*2*), we can attribute the sharp increase in conductance and in bulk reduction to the higher rate of electronic transfer between surface Fe^{II} and bulk Fe^{III}. Also the formation of CO in the oxidation of CH_3OH could be connected with the high rate of electronic transfer between Fe^{II} and Fe^{III}.

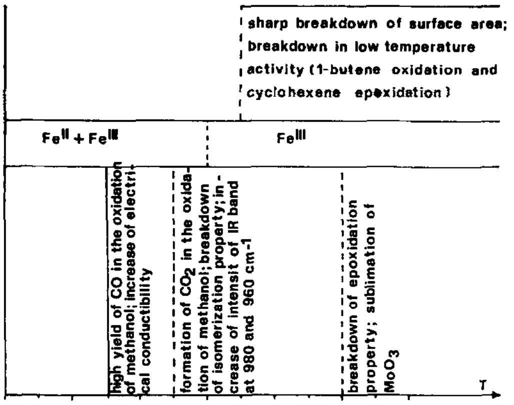


FIG. 8. Overall behavior of the catalyst at different temperatures.

In a previous work (*1*) we put forward the hypothesis that the activity of molybdates for the oxidation of methanol is tied to the presence of a terminal Mo–oxygen bond (Mo–oxygen with double-bond character). We attribute to this bond the typical dehydrogenation activity of molybdates for methanol oxidation. Therefore, the product of initial reduction of the catalyst must be Mo^{V} and Mo^{IV}. However, since the product of overall catalyst reduction is Fe^{II}–molybdate, there must occur an electronic interaction between the reduced form of molybdenum and Fe^{III} which gives formation of Fe^{II}. If the formation of CO is essentially due to successive oxidations of CH_2O (*10*), the faster the reoxidation of the reduced form of Mo by Fe^{III} the more probable is the successive dehydrogenation of CH_2O to CO.

Two mechanisms of reoxidation of surface Fe^{II} can occur:

1. $Fe^{II} \xrightarrow{O_2} Fe^{III}$,
2. $Fe_{surf}^{II} + Fe_{bulk}^{III} \rightarrow Fe_{surf}^{III} + Fe_{burk}^{II}$.

If both these mechanisms operate, the reoxidation of the reduced initial form of Mo is very probably quickened; therefore, we should expect the formation of a higher amount of CO in successive oxidations of formaldehyde. These hypotheses agree with our experimental results. Therefore, the high yield of CO observed above 300°C was attributed by us to the start of electronic interaction between surface and bulk of the catalyst. This effect, which we can call the electronic factor in the oxidation catalysis by Fe–molybdate, determines the low selectivity observed in the oxidation of methanol at high temperature. In the oxidation at low temperature the formation of CO can also occur by other mechanisms (*11*).

Second Variation

This second transformation was observed during treatment of the catalyst in air at 500°C and consists in an almost total reoxidation of Fe^{II} with elimination of water; reoxidation of Fe^{II} was revealed by the disappearance of the absorption band in the region 20–10 k*K* in the diffuse reflectance spectrum of the catalyst (Fig. 2). Water formation was observed by collecting it at solid CO_2 temperature in a side arm when heating the catalyst in a glass tube.

In a previous paper (*2*) we reported that at $T < 450°C$ the reoxidation rate of the reduced catalyst is low and that in reduction runs carried out at 350 and 500°C at the same reduction level, in the formation of Fe^{II}–MoO_4 and MoO_2, the weight loss of the catalyst was lower at 350°C than at 500°C. This may be explained by the water retention from the reduced catalyst. Hence either water or two hydroxyl groups are in some way bound to Fe^{II}.

Two mechanisms of oxidation of the reduced catalyst may occur, both at the surface and in the bulk:

1. $4Fe^{II} + 4OH^- + O_2 \rightarrow 4Fe^{III} + 2H_2O + 4O^{2-}$,
2. $4Fe^{II} + O_2 \rightarrow 4Fe^{III} + 2O^{2-}$.

The first mechanism occurs without weight gain of catalyst. We assume that the first mechanism occurs mainly at $T < 450°C$ and the second at $T > 450°C$. The first mechanism can explain the slow rate of reoxidation of the reduced catalyst at $T < 450°C$ (*2*), the presence of Fe^{II} in the catalyst in air at $T < 450°C$ and the retention of water by the reduced catalyst. At $T > 450°C$, owing to the dehydration of the catalyst, the second mechanism of oxidation could be operating and this explains the almost total reoxidation of Fe^{II} in air treatment at 500°C.

The decrease of the isomerization power of the catalyst after oxidation in air at about 500°C led us to conclude that isomerization activity is tied to Fe^{II} or to the hydroxyl bond to Fe^{II} at the catalyst surface.

1-Butene oxidation runs carried out in a pulse reactor, where the catalyst was reduced in a helium flow, did not show any difference in the isomerization power among the catalysts activated at 450, 500, and 550°C. This agrees with the fact that spectra after treatment of the catalyst in helium for 1 hr are similar, whether the temperature of activation is 450, 500, or 550°C.

No difference in epoxidation rate was observed in catalysts activated at 450, 500, and 550°C.

The formation of CO_2 in the oxidation of methanol is typical of a reaction catalyzed by Fe_2O_3. Formation of Fe_2O_3 can occur through the second mechanism: If this mechanism is operating, the reduced form of catalyst has not the same structure as that of the oxidized form. Since there is a continuous variation of structure during the local redox mechanism occurring at the catalyst surface, these variations of structure can decompose the molybdate to the single oxides.

When the first mechanism is operating, the reduced form, owing to water retention, can have the same structure as that of the oxidized form; this can stabilize the surface structure of the catalyst in the continuous redox mechanism.

Third Variation

This variation occurs at about 600°C, and it is characterized by a sharp and definitive decrease in the surface area of the catalyst (Fig. 5) and in a breakdown of the activity of the catalyst in a reaction carried out at low temperature. In fact, the activity of the catalyst after activation at this temperature for the oxidation of 1-butene at 150°C was practically nil both in the stirred tank and in pulse reactor, and the activity in epoxidation of cyclohexene at 80°C was strongly reduced.

Since no change was observed in the

X-ray pattern and very little variation was observed in the ir transmission spectra, the breakdown of the catalytic activity for the catalyst activated at 600°C can be reasonably linked with sintering phenomena occurring at this temperature.

In our opinion, this strong influence of the surface area on the activity of the catalysts (more than the one we can expect from a proportional relationship) means that the activity is tied to a particular defective structure of the catalyst, which is destroyed during sintering phenomena.

The decrease of absorbance observed in the diffuse reflectance spectra in the uv region of the catalyst after activation at 600°C (in the uv region Mo–oxygen compounds present absorption band) can allow us to assume that this defective structure destroyed at 600°C is associated with a particular coordination of Mo.

In addition, both ir and ATR spectra show that, during the activation of the catalyst from 450 to 600°C, the band at 980 cm^{-1} of Mo=O of MoO_3 and the band at 960 cm^{-1} of molybdate, appear more intense and sharper. This could mean that at $T < 600°C$, MoO_3 and Fe–molybdate can be combined in a compound that can have a defective structure destroyed by sintering.

The results obtained in the epoxidation of cyclohexene also showed that a transformation occurs at the catalyst surface during activation at $T = 600°C$, and that at $T < 600°C$ the surface chemistry of the catalyst could not be like that of MoO_3 and ferric molybdate.

It is known that molybdates of alkali metals, where the coordination of Mo is tetrahedral, can form with an excess of MoO_3 dimolybdate and trimolybdate, where Mo can have different types of coordination (*12*, *13*).

The uv spectra of the catalysts are similar to that of Na–dimolybdate. In this compound, Mo presents corner shared octahedra also bound together by tetrahedra.

Two terminal oxygens are present in the octahedra of Mo. A structure like that of Na–dimolybdate can occur in the Fe–molybdate by substitution of the octahedral coordinated Fe by Mo coming from the excess of MoO_3 present in the catalyst (*14*).

The fact that an octahedral coordination of Mo is necessary to have active catalysts is also supported by the high activity and selectivity shown by Co–molybdate and Ni–molybdate in the oxidation of methanol to formaldehyde (*15*). It is known that in these compounds Mo shows octahedral coordination (*16*).

The higher activity presented by a defective Fe–molybdate that presents also octahedral coordination of Mo can be related to the hypothesis of the existence of two terminal oxygens in the octahedral coordination sphere of Mo.

The presence of two types of this bond allows the reacting molecules to be bonded simultaneously in two points. For instance for methanol absorption:

The activation of the hydrogen of the hydroxyl group and the formation of CH_3O^- like species can labilize the methylenic hydrogen.

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