JOURNAL OF CATALYSIS 31, 408–418 (1973)

Disproportionation of *cis*-2-Pentene Over Mo/Al_2O_3 and $Co–Mo/Al_2O_3$. Kinetic Study and Nature of Active Site

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Received December 22, 1972

The determination of the active site for the olefin disproportionation catalyst Mo/Al_2O_3 is the object of the present ESR, uv and kinetic investigation. Comparison of the rate of disproportionation with that of reduction $Mo^{6+} \rightarrow Mo^{5+}$ shows that Mo^{6+} is the active site, the aging of the catalyst being the result of the reduction of Mo^{6+} to Mo^{5+} by the reactant. The variation of catalytic activity with Mo content shows a maximum at 7% Mo, which is also the case for the number of oxidizing sites Mo^{6+}. The highest activity is obtained for a pretreatment temperature of 580°C under O_2, which is also in favor of Mo^{6+} as the active species. Ultraviolet spectroscopy shows that two types of symmetry occur in the case of Mo/Al_2O_3 catalyst: tetrahedral and octahedral. However, by comparing the ESR and uv spectrum of Mo^{5+}, it seems that only Mo^{6+} in octahedral coordination is the active species. A model of the active Mo^{6+} site with a symmetry C_{4v} is proposed. New considerations must be advanced for the mechanism of disproportionation taking into account the C_{4v} symmetry and the high oxidation state of the active site. Kinetic studies have also shown a high selectivity in favor of the *cis* isomer of butene at low temperature.

INTRODUCTION

Disproportionation of olefins was indicated for the first time in 1964 by Banks and Bailey (*1*, *2*). In general this reaction is athermal and equilibrated. Although it was discovered in a heterogeneous system, it may be also carried out in the homogeneous phase. The most efficient catalysts for olefin disproportionation contain molybdenum, tungsten or rhenium (*3*) ions deposited on various supports (alumina, silica, silica–alumina) (*2*) or surrounded by various ligands (in homogeneous catalysis) (*4*, *5*). It is relevant that, depending on the nature of the carrier (*2*) or of the ligand (*4*, *5*), very drastic changes of catalytic activity are observed. In fact several parameters must be determining, such as the electronic configuration of the metal, its oxidation number, and its symmetry. If the transition metal is really playing the role suggested by Mango (*6*), that is to allow a thermally forbidden concerted mechanism (*7*) by interaction of the olefin orbitals with metal orbitals of appropriate symmetry, then the symmetry of the cation must be a key function of the catalyst.

Little work has been reported in the literature concerning the oxidation state of molybdenum in a Mo/Al_2O_3 catalyst active for disproportionation. Most of the patents (*2*) and some publications (*2*, *8*) claim that a catalyst activation under air or oxygen at high temperature is necessary to obtain a good activity. However, Furukawa (*9*) mentioned that hydrogen treatment at 300°C of a Mo/Al_2O_3 catalyst enhances catalytic activity. In the same way, traces of oxygen (*2*, *10*) are reported to reduce this activity. Furukawa (*9*) concluded from their X-ray and kinetic data that the highest efficiency of the catalyst was obtained when the valency of molybdenum was between 4 and 6. There are many literature data (*11–14*) concerning the symmetry of Mo in various molybdenum containing solids, but so far there is no correlation between this symmetry and the catalytic activity for disproportionation.

The present work deals with the determination of the oxidation number and the symmetry of the active species of various Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts. Some kinetic data are also reported.

EXPERIMENTAL METHODS

1. Catalysts

$MoO_3–Al_2O_3$ (M) of various molybdenum contents were prepared by impregnation of a γ-alumina with a solution of ammonium paramolybdate containing the required amount of Mo. The solids were dried at 110°C and then heated in a stream of air at 500°C. Samples contained between 2 and 7% (wt) Mo. Data for the catalysts have been given in previous publications (*15*, *16*). X-ray analysis, except for MoO_3/Al_2O_3 containing more than 12% Mo, gave no line attributable to MoO_3 (*16*). $Co–Al_2O_3$ catalyst (M–C) contained 2.3% cobalt, 2% silicon, and 9.1% molybdenum deposited on alumina.

2. ESR Technique

X-Band ESR spectra were registered with a Varian V.4502 spectrometer. A dual sample cavity with diphenylpicrylhydrazyl (DPPH; $g = 2.0036$) as external reference was used for signal intensity and g factor measurements.

The techniques of adsorption of perylene (Pe) on the catalyst after various treatments have already been described (*15*). The ESR spectrum of Pe^+ was taken at room temperature.

Kinetics of reduction of the catalyst by H_2 or *cis*-pentene-2 were followed by intensity measurement of the Mo^{5+} signal. The procedure was the following: after treatment of the catalyst under O_2 at the required temperature, the catalyst was cooled to the reduction temperature and then evacuated. It was then contacted with the reducing agent and after a given time the reaction was stopped by immersion of the sample in liquid N_2, and the ESR spectrum was taken at −195°C.

3. Ultraviolet Spectroscopy

The diffuse reflectance spectra of finely ground samples were recorded in the spectral range 200 nm–2.5 μm with an Optica Milano CF4 NI instrument. The catalyst was compressed under 100 kg/m^2 pressure and we used the pure carrier as a standard. The cell allowed various heat treatments under controlled atmosphere or under vacuum. The spectra were recorded after cooling the sample to room temperature.

4. Kinetic Studies

Apparatus. Kinetic studies were carried out in a dynamic microreactor at low conversion; the reactor temperature, regulated at ±0.2°C, was measured by means of a thermocouple inserted in a thin tube located very close to the catalytic bed. All the apparatus was free of any grease. The gases introduced in the apparatus were dried on molecular sieves which were regenerated every day. The *cis*-2-pentene pressures were maintained at constant values by means of a bubbler system, which included an evaporator and a condenser at constant temperature. At the outlet of the reactor were set two glass loops in order to store the emerging mixture.

Analysis. The analysis of the products was carried out on an ionization flame chromatograph with a 9 m column of Fractonitrite II 25% on Embacel (30–60 mesh) at 40°C.

Procedure. 200 mg of catalyst were calcinated at a given temperature (usually 580°C) for 16 hr under pure oxygen flow. Then the reactor was swept for 1 hr by nitrogen, isolated and the temperature was lowered to the reaction temperature. Reactant was introduced under hydrogen flow.

The reaction rate was formulated as the

number of olefinic molecules produced per second and per gram of catalyst according to the formula where τ is the conversion, D

$$r = \tau \frac{D}{22.400} \times \frac{273}{298} \times \frac{P}{760} \times \frac{1}{m} \quad (\text{mole s}^{-1}\ \text{g}^{-1}),$$

the total flow rate (ml s^{-1}), P the reactant pressure (Torr) and m the catalyst weight (g).

5. *Reactants*

The compounds used had the following purities: *cis*-2-pentene (95% purity pract grade Fluka); *trans*-2-pentene (99% purity purum grade Fluka); hydrogen (ultra high purity, purified through a palladium thimble).

RESULTS

1. *Product Distribution*

As shown in Fig. 1, the product of double bond migration are detected in significant amount only for temperatures higher than 120°C. If one keeps in mind that *cis–trans* isomerization and double bond migration usually occur at the same temperature on acidic aluminas, the formation of *trans*-pentene-2 at 20°C might well be the result of a metathesis mechanism rather than isomerization on acidic sites. In fact no pentene-1, no butene-1 (or their disproportionation products) are observed at 20°C when *trans*-pentene-2 is produced in significant amount.

2. *Aging of the Catalyst*

The variations of the rate with time are shown in Fig. 2. The rate of butene production increases for the first few minutes and then quickly decreases. Simultaneously the *cis*-2-pentene pressure slightly decreases then increases. The maximum and minimum appear almost at the same time t_{eg}. When working at low temperature ($T < 90°\text{C}$) we have observed that for time t_{eg} the rate of hexenes formation was lower than that of butenes and the maximum is displaced about 30 sec above t_{eg}; beyond this maximum equal amount of butenes and hexenes are detected. A similar observation was made by Davie, Whan and Kemball (*17*) for propylene disproportionation, namely a higher amount of ethylene in comparison with butenes. In order to explain the increase of the rate of disproportionation several assumptions can be made:

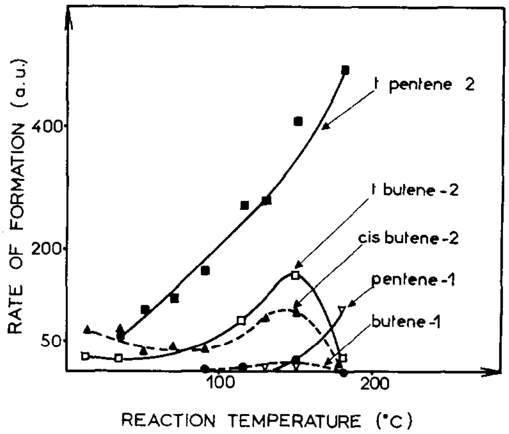


FIG. 1. Distribution of the reaction products as a function of temperature. For clarity hexenes have been omitted.

1. A fast reduction of the catalyst by the reactant could promote the activity of the catalyst. In fact further experiments rule out this hypothesis.
2. *cis*-2-Pentene adsorbs on the catalyst and reaches its equilibrium of adsorption at time t_{eg}. Moreover the equilibrium between adsorbed and gaseous butenes and hexenes is not achieved instantaneously. As a matter of fact, the product distribution in favor of butenes during the first minutes at low temperature indicates that a noticeable amount of hexenes is first adsorbed on the catalyst before equilibrium of desorption is reached.

The decrease of the rate is exponential and different parameters playing a role on the decay have been shown to be operative. These are:

a. Reaction temperature: the higher the temperature, the faster the deactivation. At 130°C the rate is reduced to one-tenth of its initial value in 25 min; at 70°C the rate halves in 25 min whereas at 35°C it

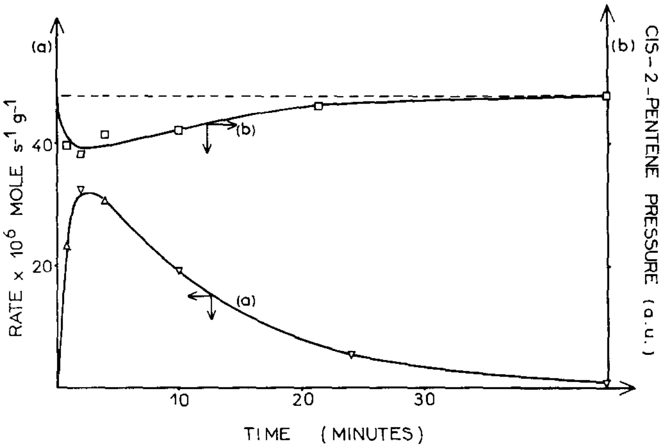


FIG. 2. Rate variation as a function of time: (a) butenes formation rate; (b) *cis*-2-pentene pressure.

is constant for 3 hr. This result agrees with the observation made in the propylene disproportionation on the same type of catalyst (*18*).

b. *cis*-2-Pentene pressure: as shown in Fig. 3, the higher the reactant pressure, the faster the deactivation.

c. Changing the carrier gas, H_2 or N_2, does not interfere.

All these results allow us to reject a poisoning by an impurity of the carrier gas or a reduction of the catalyst by the carrier gas. Only a secondary reaction of *cis*-2-pentene having an activation energy higher than that of the disproportionation is able to explain pressure and temperature dependency of the deactivation process. This secondary reaction might be of two types:

i. Polymerization of the olefin on the acidic sites of the carrier, followed by a blockage of the other sites.

ii. Reduction by *cis*-2-pentene of the catalyst which would thus be active only when oxidized. This reaction process is expected to strongly depend on pressure and temperature.

Though it is difficult to come to a decision only from kinetic results, the second assumption is more likely to occur considering the temperature influence. In fact we shall show below that the reduction of Mo^{6+} to Mo^{5+} is at the origin of the behavior.

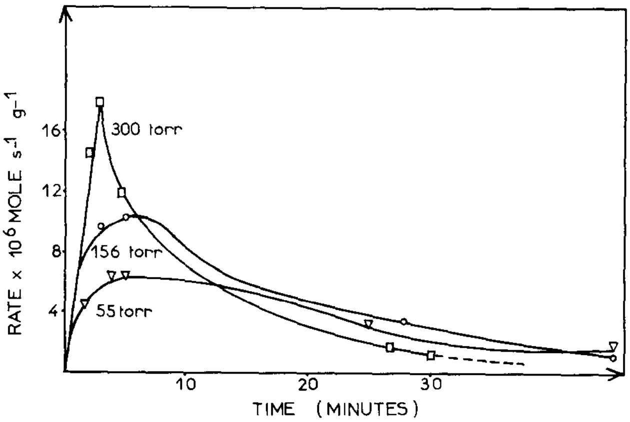


FIG. 3. Rate variation as a function of time for different pressures of reactant (T = 90°C).

3. Kinetics of the Reaction

When no steady state activity is observed, treatment of kinetics is difficult and one of the major problems is the choice of a relevant rate. We have assumed that the maximum of the rate r_M was the best characteristic of the rate and we have investigated the influence of temperature and pressure on r_M.

The curves of Fig. 4 show the pressure dependency on r_M at various temperatures. Classical curves are obtained with a first order law for temperatures higher than 100°C and variable order less than unity at lower temperatures. It must be pointed out that in no case can a second order law be found with those experiments.

The effect of temperature on disproportionation conversion over Co–Mo/Al_2O_3 catalyst has already been studied by various authors (*1, 2, 9, 19, 20*). In all cases a maximum is observed between 140 and 200°C, depending on the starting olefin. With *cis*-2-pentene we also observed a maximum at around 150°C (Fig. 1). At this temperature, the rate of isomerization of *cis*-2-pentene to *trans*-2-pentene is much higher than that of disproportionation. Besides, we have observed that the disproportionation rate for *trans*-2-pentene is 10 times lower than that of the *cis* isomer. Therefore a simple explanation for the rate maximum would be the competitive isomerization of *cis*-2-pentene. However, this phenomenon is certainly not the only one which occurs at high temperature: an irreversible poisoning of the sites considered by Moffat and Clark (*19*) might be also at the origin of the temperature maximum. In fact we shall see below that *cis*-2-pentene reduced the active Mo^{6+} site to inactive Mo^{5+}; this explains first the aging of the catalyst and might also explain, to a certain extent, the rate temperature maximum.

4. Distribution of the Isomers

The stereochemistry studies of disproportionation have not led yet to definitive conclusions. Starting from 2-pentene, Banks and Bailey (*1, 2*) observe roughly the thermodynamic equilibrium ratio *trans/cis* of 2-butenes. But when starting from α-olefins (butene-1 or pentene-1) a high degree of stereoselectivity is observed in favor of the *cis* isomer. Furukawa (*9*), with propylene, obtained the equilibrium ratio *trans/cis* of butenes. Hughes (*21*), working in homogeneous phase with 2-pentene found in contrast with Co–Mo/Al_2O_3 a high selectivity for the *cis* isomers. Most of the results by Davie, Whan and Kemball (*17*) on propylene disproportionation (in a static system) show equilibrium *trans/cis* values. However, they mention that during the very early stages of the reaction the initial *trans*:*cis* ratio differed from the equilibrium ratio attaining values of 1:2.

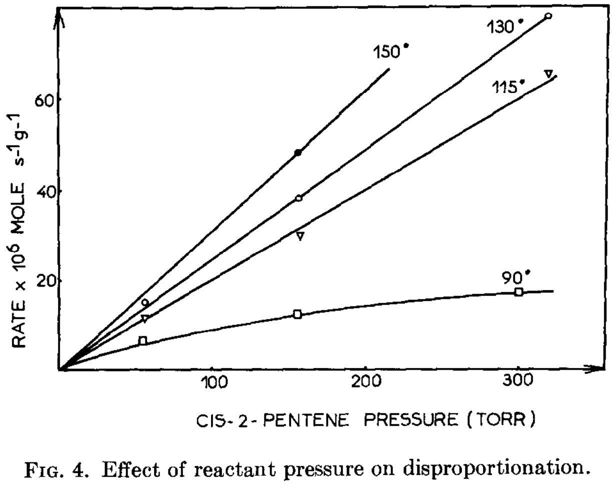


FIG. 4. Effect of reactant pressure on disproportionation.

In another study (*22*) they show that a disproportionation catalyst is also a *cis–trans* isomerization catalyst, so that *cis–trans* isomerization is shown to occur by a bimolecular reaction of the disproportionation type.

In Fig. 5 are plotted the experimental *trans/cis* ratios of butenes versus the reaction temperature; for comparison we have shown the equilibrium ratios. These results indicate a very high selectivity in favor of the *cis* isomer especially at low temperature.

5. Interaction Between cis-Pentene-2 and the Catalyst at various Temperatures

a. ESR. The adsorption of *cis*-pentene-2 on the M–C catalyst at room temperature resulted in the appearance of an anisotropic paramagnetic signal which has already been observed by various authors (*15*, *23–26*). Such a signal, which is usually obtained after a high temperature evacuation of Mo/Al_2O_3 catalyst (*15*) or reduction under hydrogen, has been attributed by Dufaux, Che and Naccache (*25*) to the paramagnetic species Mo^{5+}. The following values of g were observed:

$$g_\parallel = 1.912,$$
$$g_\perp = 1.952.$$

They are very close to those obtained with catalysts M.

Many explanations can be advanced to justify the formation of the Mo^{5+} species upon contacting the catalyst with *cis*-pentene-2, such as:

a. Formation of a charge transfer complex between hexavalent molybdenum and pentene which has a relatively low ionization potential (9.11 eV):

$$Mo^{6+} + C_5H_{10} \rightarrow Mo^{5+} \ldots C_5H_{10}^+.$$

However, such a complex, if present, should be characterized by the paramagnetic species $C_5H_{10}^+$ that we were not able to detect. When polynuclear compounds are adsorbed on Mo/Al_2O_3, such positive radical ions were detected (*15*, *23*).

b. Reduction of $Mo^{6+}O^{2-}$ by the reactant with formation of an allyl complex (*26*):

$$Mo^{6+}O^{2-} + C_5H_{10} \rightarrow Mo^{5+}C_5H_9 + OH^-.$$

The presence of such a complex could explain why no $C_5H_{10}^+$ signal was detected.

As shown in Fig. 6, the intensity of the Mo^{5+} signal is increasing with the contact time for a given temperature. For a given contact time, the amount of Mo^{5+} is increasing with the temperature. Upon differentiation of the curves of Fig. 6, we were able to deduce the rate of reduction $Mo^{6+} \rightarrow Mo^{5+}$. This rate of reduction R_R has been compared in Fig. 7 with the rate of disproportionation R_D performed in very similar conditions of temperature and pressure; since the evolution of R_R with time is very similar to the evolution of R_D, it can be concluded that both reactions occur

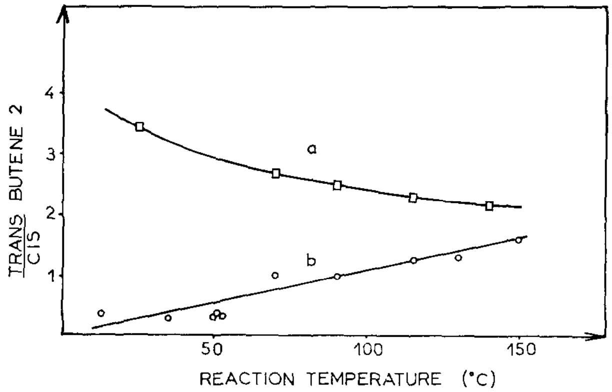


FIG. 5. Effect of reaction temperature on *trans*-2-butene/*cis*-2-butene ratio: (a) thermodynamic equilibrium; (b) experimental values.

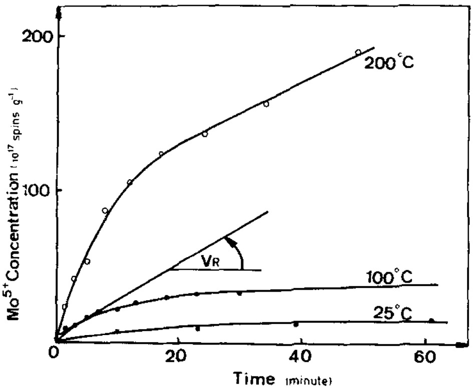


FIG. 6. Variation of (Mo^{5+}) with time at different temperatures.

on the same site which is therefore Mo^{6+}. In the kinetic study of the disproportionation we showed that the fouling of the catalyst was due to a reaction between the reactant and the solid, without further evidence concerning the nature of this reaction. It seems, therefore, that the reduction Mo^{6+} to Mo^{5+} is in fact responsible for the loss of activity. At 100°C, R_R being equal to ca 10^{-3} R_D, we can deduce that the Mo^{6+} site performs 10^3 disproportionations before being reduced to Mo^{5+}.

b. Ultraviolet spectroscopy: Symmetry of molybdenum in catalysts. The electronic spectra of solids MC or M after treatment by O_2 at 580°C show an intense absorption with maxima around 250–260 and 300–320 nm attributed to the charge transfer $O^{2-} \rightarrow Mo^{6+}$ $(4\,d^0)$. From the literature data (*11–14*, *27*) and from our own experiments with various molybdenum compounds prepared in the same way (Mo/MgO, Mo/SiO_2, Mo/γAl_2O_3, Mo–Co/γAl_2O_3, the Mo percentage varying from 2.2 to 12.1), it should be possible to correlate the variations of intensities and the shifts of the observed transitions with the possible structure of surface species. Mo^{6+} in tetrahedral coordination absorbs at shorter wavelengths than Mo^{6+} in octahedral coordination and, on alumina, both symmetries are observed. It seems that at low molybdenum content (2.2, 5.5%) the amount of the tetrahedral form is higher than at high molybdenum content. Moreover, in the MC catalyst, this amount of tetrahedral form will be higher than in the M catalyst of same molybdenum percentage.

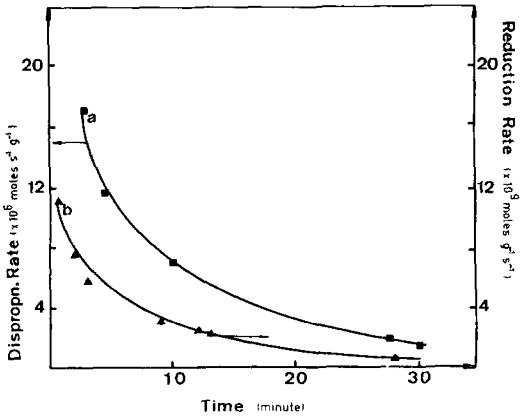


FIG. 7. Simultaneous variation of disproportionation (a) and $Mo^{6+} \rightarrow Mo^{5+}$ reduction (b) rates with time.

With the MC solid, three other bands at around 540 (shoulder), 580–600, 640 nm are due to tetrahedral Co^{2+} ions (*11–13*).

Upon contacting catalyst MC with *cis*-pentene-2 at 120°C, the color of the solid turned from blue to grey and the electronic spectrum of the solid presented an intense absorption at around 450 nm, absorption which increased in intensity with the contact time. A similar behavior was obtained by treatment of catalyst MC under hydrogen for temperatures of 200–350°C. It was also observed upon evacuation of the catalyst at 580°C during 15 hr. Whatever the way it was obtained, such absorption was completely removed by treatment under O_2 at 580°C. Let us mention that the same results were obtained with the catalyst M. Therefore it seems logical to ascribe this band (which appears and disappears in conditions similar to those of the ESR signal) to the Mo^{5+} species $(4d^1)$, this band corresponding to a *d–d* transition and not to a charge transfer (*28*, *29*).

6. Influence of the Conditions of Pretreatment of the Catalyst

According to the results of the preceding paragraph, Mo^{6+} seems to be the active species for disproportionation. This is rather surprising if we consider the promoting effect of hydrogen at 300°C mentioned by Furukawa (*9*). It was therefore necessary to study carefully the role played by hydrogen on the catalytic activity. The catalyst MC was treated under O_2 at 580°C and then cooled to the temperature required for the hydrogen treatment. After a purge with nitrogen, hydrogen was allowed to pass over the catalyst for various times and then the catalytic activity was determined. Similar experiments were performed in another apparatus in order to determine by ESR the amount of Mo^{5+} sites. The reduction of Mo^{6+} to Mo^{5+} [and probably to Mo^{4+} when reduction was performed at 400°C (*21, 24*)] is followed by a drastic decay of the catalytic activity. If the reduction was performed at 300°C during 2 min, the drop of activity was also very marked, which is in disagreement with the work of Furukawa (*9*). Hydrogen treatment at 115°C did not appear to modify the catalytic activity significantly.

The conditions of pretreatment and of regeneration of the catalyst after a severe loss of activity were also studied by treatments (or pretreatments) of the solids with various gases. With a fresh catalyst the catalytic activity was the highest when the gas of pretreatment was O_2 instead of N_2 or H_2. In the case of an aged catalyst the regeneration could be total, when it was performed at 580°C under O_2 whereas no significant regeneration was obtained under nitrogen. It seems therefore that an oxidation of molybdenum to its highest oxidation state is necessary for good catalytic activity.

7. *Dependence of the Number of Oxidizing Sites on the Catalytic Activity*

Since it was strongly suggested from the results described in the preceding paragraphs that the activity was due to the oxidizing sites of the solid, we tried to correlate the variations of catalytic activity with the variation of the number of oxidizing sites. This number can be evaluated by adsorption of polynuclear compounds having low ionization potentials; when adsorbed on oxidizing sites these compounds give radical ions easily detected by ESR.

In the case of MoO_3–Al_2O_3 catalysts, it has been advanced that the electron transfer from perylene (Pe) (*15*) (ionization potential = 6.83 eV) or thianthrene (*23*), to the solid is due to the presence of Mo^{6+}. Indeed, alumina alone gives no paramagnetic signal with perylene in the absence of O_2, whereas a spectrum with nine hyperfine lines is obtained with MoO_3–Al_2O_3 (*15*). Simultaneously the Mo^{5+} signal is detected so that the global equation:

$$Pe + Mo^{6+} \rightarrow Pe^{+} \ldots Mo^{5+}$$

can be advanced, although it does not reflect exactly the role played by aluminum ions (*15, 17*).

The influence of the temperature of pretreatment under O_2 on the catalytic activity and on the number of Pe^+ radical ions are represented in Fig. 8. Both curves present the same characteristics with a maximum at around 550°C. This confirms the very close relationship between catalytic activity and the number of oxidizing sites.

Alumina with various molybdenum contents gave the results of Fig. 9. Catalytic activity as well as the number of Pe^+ radical ions increases with molybdenum content up to a value of 7% Mo. The maximum observed afterwards for the Pe^+ number has been explained by Dufaux, Bandiera and Naccache (*15*) in the follow-

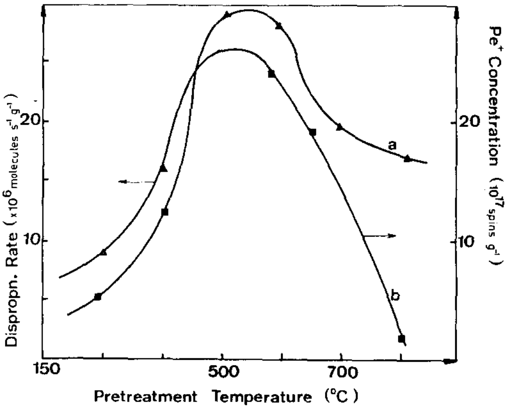


FIG. 8. Influence of pretreatment temperature on Pe^+ concentration (b) and on disproportionation rate (a).

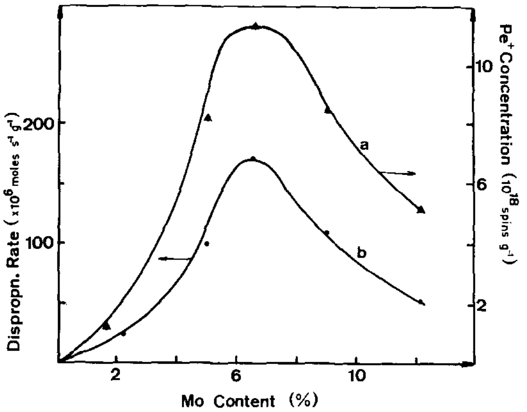


FIG. 9. Influence of Mo content on Pe^+ concentration (a) and on disproportionation rate (b).

ing way: for low molybdenum content, molybdenum is present as Mo^{6+} in the alumina lattice (probably in octahedral cavities), whereas at higher content, MoO_3 is deposited above the surface. It can be detected by X-rays for molybdenum contents higher than 10%.

DISCUSSION

The purpose of our work was to try to elucidate the nature of the active site for olefin disproportionation catalyst Mo/Al_2O_3 or $Mo–Co/Al_2O_3$.

First at all we must say that we did not find any significant difference of behavior between Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts so that we do not think that cobalt plays an important role in this kind of catalysis. It is mainly the molybdenum which is involved in the catalytic process and we will discuss now its oxidation state and symmetry.

1. Oxidation State of Molybdenum

The site responsible for the catalytic activity seems to be Mo^{6+} for the following reasons:

a. The reduction to Mo^{5+} (and perhaps Mo^{4+} which could not be detected by ESR) by either the reactant or H_2 is followed by a drop of catalytic activity.

b. The catalytic activity follows the same trend as the concentration of Pe^+ when the temperature of pretreatment or molybdenum content varies.

c. Oxygen treatment at high temperature is the only treatment which is able to regenerate the catalyst quantitatively.

2. Symmetry of Molybdenum

Ultraviolet measurements have shown that molybdenum was probably present in our catalysts in two coordination numbers without deciding if both or only one correspond to the active Mo^{6+}. However, by comparing uv and ESR data it is possible to determine the symmetry of the Mo^{5+} ion and, by extrapolation, of the active Mo^{6+}, since Mo^{5+} results from the reduction of this active Mo^{6+} species. If we assume that Mo^{5+} is situated in a given symmetry it is possible to correlate the values of g ($g_\parallel$ and $g_\perp$) with the difference of energy between the various d orbitals of the $4d^1$ ion (Mo^{5+}). Let us suppose that the Mo^{5+} ions are located in sites of C_{4v} symmetry.

If the ground state is b_{2g} (with a d_{z^2} ground state $g_\parallel = 2$), we can correlate the g values with the transitions $b_{2g} \xrightarrow{\delta} e_g$ and $b_{2g} \rightarrow b_{1g}$:

$$g_\parallel = g_e - \frac{8\lambda}{\Delta}, \qquad (1)$$

$$g_\perp = g_e - \frac{2\lambda}{\delta}, \qquad (2)$$

where λ is the spin–orbit coupling constant of molybdenum ($\lambda = 270\ \mathrm{cm}^{-1}$ (*28*)) and g_e is the g factor of the free electron ($g_e = 2.0023$). The values of $g_\parallel$ and $g_\perp$ were calculated from the spectrum of the Mo^{5+} ion ($g_\parallel = 1.912$ and $g_\perp = 1.952$). The values that we deduce from Eqs. (1) and (2) for δ and Δ are:

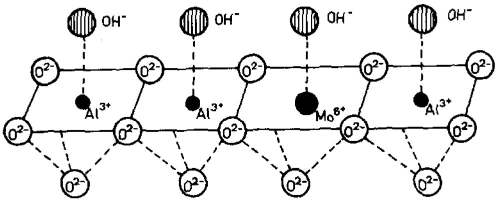
$$\delta = 10.800\ \mathrm{cm}^{-1}\ (925\ \mathrm{nm}),$$

$$\Delta = 24.000\ \mathrm{cm}^{-1}\ (420\ \mathrm{nm}).$$

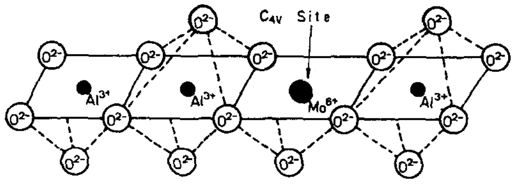
The value of 420 nm is in fairly good agreement with the maximum observed at 450 nm, and the C_{4v} symmetry that we assumed for this calculation seems to be confirmed. As an additional confirmation we must say that many compounds of Mo^{5+} ($4d^1$) of C_{4v} symmetry present, in this wavelength region, a *d–d* transition which has been ascribed to the transition $b_2 \rightarrow b_1$ (σ) (*28, 29*). Moreover, Kazanskii (*27*) has found a C_{4v} symmetry corresponding to a square pyramidal structure for Mo^{5+} deposited on γ-alumina.

3. Nature of the Active Site

Although two types of symmetry are observed for molybdenum deposited on γ-alumina, the active species for disproportionation seems to be the Mo^{6+} ion situated in an octahedral cavity of symmetry C_{4v}. This active Mo^{6+} is probably located inside the lattice of the alumina since at high Mo content, when the formation of MoO_3 is very likely to occur (MoO_3 is detected by X-rays for Mo content higher than 10%), the catalytic activity is greatly lowered. Such a site would be produced after dehydration of the alumina carrier at high temperature. If we assume that the (100) face of the alumina is the most exposed one (*30, 31*), the surface of the solid may be represented in the following way:



Mo^{6+} is covered with OH groups when the alumina is evacuated at low temperature. Upon dehydration at high temperature (600°C) the solid takes a new surface composition due to the condensation of adjacent OH groups with formation of gaseous water:



4. Mechanism of the Disproportionation

At this stage it is necessary to discuss our results concerning the nature of the active site in relation to our kinetic data and the various mechanisms proposed in the literature (*2*). First of all the active site that we propose is limited to the very particular case of molybdenum oxide on alumina. So far we have no proof to conclude that a high oxidation state of the transition metal is a necessary condition for activity in all the disproportionation catalysts.

However, the fact that Mo^{6+} is the active site in our catalyst raises a new problem concerning the electronic path of the reaction. Indeed the very high selectivity that we observe in favor of the *cis* isomer would suggest a kind of concerted mechanism. But according to Mango (*6*) at least one *d* electron of the metal is to be present to allow this transformation. Since Mo^{6+} had no *d* electron a new theoretical approach for the intermediate must be considered. The only hypothesis that we can make is the following: since the two molecules of *cis*-pentene-2 are not adsorbed at the same time on Mo^{6+}, we must have a relatively stable complex between the "first" molecule of *cis*-pentene-2 and Mo^{6+}. Due to the fact that no [*cis*-pentene-2]$^+$ signal is detected by ESR this could be a π complex obtained by overlapping of the π orbitals of the olefin with an empty *d* orbital of Mo^{6+}, without transfer of one single electron to the molybdenum. Since no back-bonding is possible the complex thus obtained is not very stable and might react easily with another molecule of *cis*-pentene-2, gaseous or physisorbed depending on the reaction temperature, according to a mechanism which remains to be determined more theoretically, taking into account the symmetry of Mo^{6+}.

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