

Catalytic Oxidation of 1-Butene and Butadiene Study of MoO₃-TiO₂ Catalysts

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Mo-Ti-O catalysts have been investigated in order to obtain active and selective catalysts for the oxidation of butenes to maleic anhydride. Three methods of catalyst preparation have been used, namely, impregnation, coprecipitation, and decomposition of tartrates. The results suggest that, with all catalysts, active and selective sites are formed at the interface of the two oxides by action of TiO₂ on molybdenum oxide. Catalysts obtained by the decomposition of tartrates are amorphous, more active and selective than the others. The highest activities and selectivities are obtained with Mo-Ti-O catalysts containing about 15 mole% MoO₃ (selectivity 53% at 60% conversion). It has been shown that bases such as water or halide ions can change the activity of impregnated catalysts by increasing the surface acidity. The relation between acidity and activity in olefin oxidation is thus confirmed.

INTRODUCTION

For many years, the catalytic oxidation of benzene has been the main source of maleic anhydride but the oxidation of butenes is also economically interesting and a certain number of catalysts are described in the patent literature (1).

The V-P-O catalysts were the first to be extensively investigated (2), but more recently the Mo-Ti-O mixed oxides have received some attention: Akimoto and Echigoya (3) report selectivities of 42% when butadiene is oxidized to maleic anhydride. According to Ai (4), selectivities of 70% are obtained when 1-butene is oxidized to butadiene over TiO₂, and in the oxidation of butadiene a selectivity of 50% with respect to maleic anhydride is reported over Mo-Ti-O catalyst. In both cases, the catalysts were prepared from titanium hydroxide and an aqueous solution of ammonium molybdate. Yields of 48%

for the oxidation of 1-butene were reported in a patent (5) with a catalyst prepared by evaporation of a suspension of anatase in an aqueous solution of ammonium molybdate, but the activity is low.

This work was carried out in order to compare the properties of catalysts of this series for the oxidation of 1-butene and butadiene to maleic anhydride. They were prepared following three different procedures: impregnation of anatase (I) according to (5), coprecipitation of hydroxides (C), and decomposition of tartaric acid complexes of titanium and molybdenum (A). In each series the selectivities, expressed as the yields in compounds forming maleic anhydride, were measured at different compositions of the catalyst.

Activities were also measured, but the A series appeared to be the most active, and only in this case was the influence of the composition on this parameter studied.

EXPERIMENTAL METHODS

Reagents. All gases were purchased from Air Liquide. The purity of 1-butene was over 99%, and the other hydrocarbons were isobutene and butadiene. For butadiene, the purity exceeded 99.5%, impurities being butenes and dimeric butadiene. The gases were dried before introduction into the reactor.

All materials used in the preparation of catalysts were Prolabo R.P. reagents, except anatase which was purchased from Fluka.

Catalysts. Impregnated catalysts (I series) were prepared by mixing anatase with an aqueous solution containing 0.04 mole liter⁻¹ molybdic acid and 0.5 mole liter⁻¹ oxalic acid. The slurry was evaporated to dryness and calcined at 500°C for 5 hr. The grain size was 0.06 to 0.16 mm, and the specific surface area 12 m² g⁻¹.

For coprecipitated catalysts (C series), titanium chloride (95.25 g) was dissolved in 150 cm³ of an aqueous hydrochloric solution (1:1) and added to a hydrochloric solution of molybdic acid. The addition of ammonia produced the coprecipitation of hydroxides at pH = 4. The precipitate was filtered, washed, dried and calcined for 5 hr at 500°C; finally, it was sieved to 0.06 to 0.16 mm size.

Amorphous catalysts (A series) were prepared starting from two aqueous solutions of tartaric acid complexes of molybdenum and titanium. Molybdic acid (43.6 g) and tartaric acid (131 g) were dissolved in 1 liter of water at 100°C, and the concentration of molybdenum was verified by spectrometry at 330 nm of hydrogen peroxide complexes. Titanium chloride, dissolved in hydrochloric acid as before, was precipitated using concentrated ammonia. The precipitate was washed with a 2% aqueous solution of ammonium nitrate and then dissolved in 2 liters of a solution containing 240 g of tartaric acid. Titanium was determined by gravimetry. Known amounts of each component were

then mixed and the solution was dehydrated under vacuum, first at room temperature and subsequently at 80°C. An amorphous precursor was obtained and calcined for 5 hr at 500°C. The powder was used as a catalyst when activities were measured; when high conversions were to be obtained the powder was pressed into pellets which were crushed and sieved (0.8–1 mm). In some cases, the catalyst was deposited on a nonactive α -alumina (Norton) or was diluted with anatase.

Specific surface areas were determined using a Carlo-Erba Sorptomatic instrument and were reported with activity measurements. Samples were analyzed by X-ray diffraction using Ni-filtered CuK α radiation and a CGR Theta 60 diffractometer. From the diagrams, no new phases were identified: Samples of the I series contained the anatase form of titania and molybdena; for the C series, small amounts of titanium oxide in rutile form were obtained in addition and the catalysts of the A series were practically amorphous, only a few slight lines being observable on the X-ray diffraction diagrams.

Adzhamov *et al.* (6) have studied coprecipitated Mo-Ti-O catalysts and concluded the existence of two phases, namely, TiO₂ and a solid solution of Ti in MoO₃, having the structure of MoO₃.

Halide ion treatment. Some catalysts of the I and A series (5 g) were treated with 50 g of aqueous solutions of ammonium chloride or fluoride (12.5 wt%) or water (blank sample). All the samples were filtered and heated at 500°C in a stream of nitrogen for 24 hr before being calcined for 5 hr in air.

Apparatus and product analysis. The continuous flow reactor was made of a Pyrex tube of 1.2-cm i.d. with a sintered glass plate supporting the catalyst. The catalyst bed height was up to 15 cm and included a preheater section containing Pyrex balls (3 mm). The reactor was immersed in a salt bath.

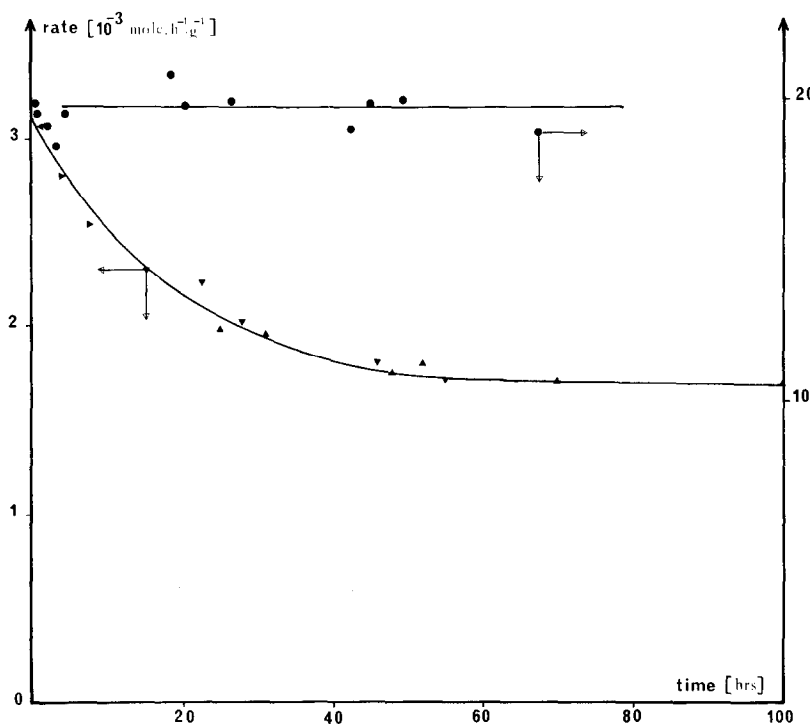


FIG. 1. Variation of the rate vs time in the oxidation of butadiene ▲ Catalyst: I series 5.8 at % Mo (0.5–0.63 mm), $T = 342^\circ\text{C}$, $P_{\text{H}} = 1.5 \times 10^{-3}$ atm. ● Catalyst: A series 15.6 at % Mo (0.5–0.63 mm), $T = 349^\circ\text{C}$, $P_{\text{H}} = 1.7 \times 10^{-3}$ atm.

For activity measurements, only the catalysts (A) were studied: They were used in the form of a fine powder (100–500 mg) diluted with 9 parts of nonactive α -alumina (0.5 mm); the gas flow rates were over the range 100 to 200 liter h^{-1} . Under these conditions, total conversion did not exceed 10% and the rate was shown to be independent of the flow rate. The hydrocarbons, 1-butene and butadiene, were oxidized in air at low partial pressures (10^{-3} – 10^{-2} atm), and the products were mainly butadiene or furan.

For selectivity measurements, high conversion levels were obtained by varying the mass of the catalyst (0.8–2 g) which in this case was pelleted: Conversions up to 80% were obtained without any significant increase in the temperature of the catalyst bed; the main products were maleic anhydride and carbon oxides.

Analyses were performed on line by gas chromatography with a flame ionization detector, using a 3-m-long column of Chromosorb P impregnated with 15% of cross-linked diethylene glycol adipate (LAC 446) (7). The separation of products was obtained from ambient temperature to 150°C at a rate of 4°C min^{-1} .

Permanent gases: CO, CO_2 , butenes, and butadiene were separated on hexamethyl phosphoramide and 13X molecular sieve columns, using a Fisher gas partitioner at room temperature.

The other products of butene oxidation were acetaldehyde, furan, acrolein, methacrolein, methylvinyl ketone, crotonaldehyde, acetic acid, propionic acid, acrylic acid, methacrylic acid, and maleic anhydride, in order of elution; traces of some other compounds were also present.

The conversions of the hydrocarbons were determined by analysis at the inlet and the outlet of the reactor; the production of carbon oxides was estimated from chromatograms after calibration. The other oxidation products were estimated from chromatographic peak areas.

Acidity measurements. The method used was that described by Ai and Ikawa (8). The adsorption of pyridine at 130°C was carried out chromatographically by injecting measured amounts, and this compound was then determined by means of a katharometer double-detector; only the irreversible part of the adsorption was taken into account.

RESULTS AND DISCUSSION

A. Activities

(1) *Catalyst deactivation.* As shown in Fig. 1, a rapid drop in the reaction rate of both oxidations (1-butene and butadiene) was observed in the first 24 hr for the new catalysts of the I series, after which the catalysts remained practically stable for a few days. The catalysts of the other series did not exhibit such variations and the rate remained constant.

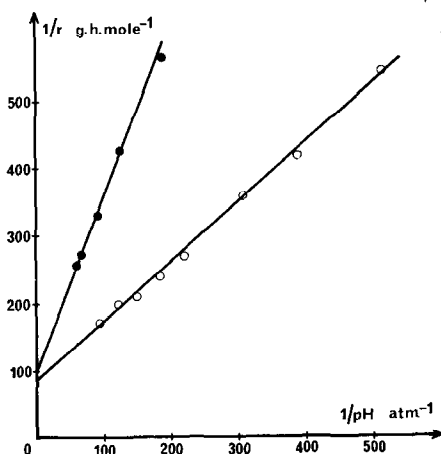


FIG. 2. Variation of the inverse of reaction rate with the inverse of the partial pressure of hydrocarbon. $T = 395^{\circ}\text{C}$; $P_{\text{O}_2} = 0.21$ atm. Catalyst: I series 5.8 at% Mo. ●, 1-butene; ○, butadiene.

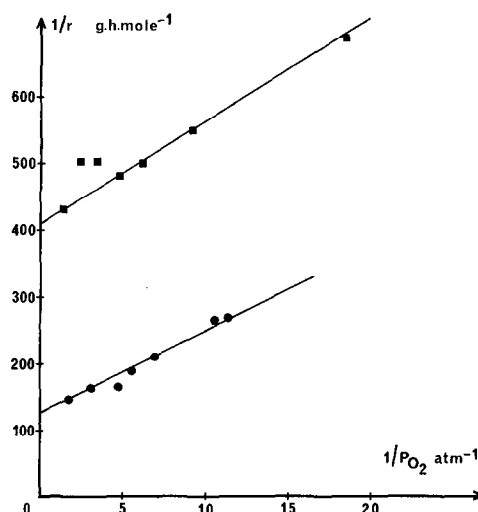
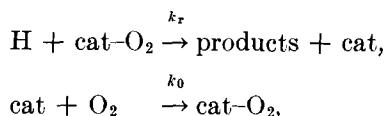


FIG. 3. Variation of the inverse of reaction rate with the inverse of the partial pressure of oxygen. $T = 395^{\circ}\text{C}$. Catalyst: I series 5.8 at% Mo. ■, 1-butene (11×10^{-3} atm); ●, butadiene (5×10^{-3} atm).

(2) *Activities.* A kinetic model was established in differential conditions for the oxidation of the two hydrocarbons on impregnated catalysts after stabilization. The results show a linear dependence of inverse rate with inverse partial pressures of oxygen and hydrocarbon (Figs. 2 and 3).

According to these results, the simplest model was the Mars-Van Krevelen mechanism (9) with kinetic orders equal to unity.



where H signifies the hydrocarbon, cat the reduced form of the active site, and cat-O₂ the oxidized form.

On the basis of these assumptions, the initial rate of hydrocarbon consumption was expressed by

$$r = \frac{k_0 P_{\text{O}_2} k_r P_{\text{H}}}{k_0 P_{\text{O}_2} + k_r P_{\text{H}}} S,$$

where S is the number of active sites per gram of catalyst.

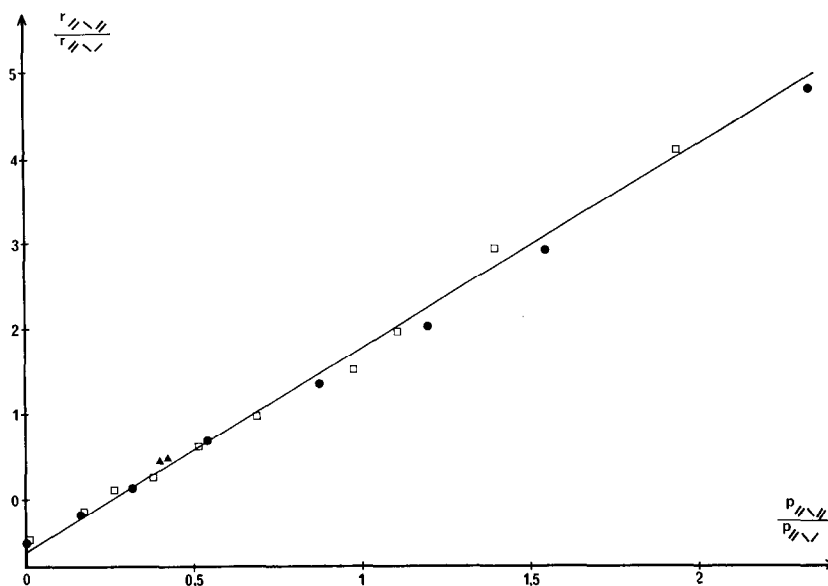


FIG. 4. Ratio of reaction rates as a function of the ratio of partial pressures in the competitive oxidation of 1-butene and butadiene for different partial pressures of oxygen. Catalyst: I series 5.8 at% Mo, $T = 395^{\circ}\text{C}$. \square , $P_{\text{O}_2} = 0.4$ atm; \bullet , $P_{\text{O}_2} = 0.21$ atm; \blacktriangle , $P_{\text{O}_2} = 0.14\text{--}0.06$ atm.

This equation was verified for the oxidation of each hydrocarbon and in competitive reactions (Fig. 4).

The kinetic parameters were obtained from these plots and were used for the Arrhenius plots (Fig. 5).

As this model matches the experimental results, it followed that the catalytic activity could be expressed, using this kinetic equation, by the rate constant of the surface reaction, $k_r S$. For the catalysts of the other series, the linear dependence of the inverse rate with partial pressure of hydrocarbon was also verified, and the same kinetic parameter was used as the expression of catalytic activity.

B. Selectivities

The selectivities of Mo-Ti-O catalysts were investigated by varying two parameters, namely, composition and method of preparation.

Selectivity was determined by taking into account the sum of the yields of butadiene, furan, maleic anhydride, and croton-

aldehyde, this last compound being, in fact, present in small quantities. Methacrolein was not taken into account, because it is nevertheless important to mention that appreciable amounts of this compound can be obtained (up to 10% of the 1-butene converted) but only if the total conversion is low, and if the amount of MoO₃ in the mixed oxide is important. Up to now this production of methacrolein could not be related to any properties of the catalysts.

In the oxidation of butadiene, the amounts of furan were low ($\leq 2\%$); therefore the total selectivity with respect to furan, maleic anhydride, and crotonaldehyde remained practically constant even within a large range of conversion. The selectivities of the catalysts could thus be determined even at low conversion of the hydrocarbon and were representative of the final selectivities with respect to maleic anhydride.

However, in the case of 1-butene, a large amount of butadiene (60%) was formed at

low conversion and the successive oxidation of this intermediate caused a slight decrease in selectivity as the conversion increased. However, when the catalysts were pelleted, and at high conversions of the hydrocarbon ($\approx 80\%$), the total amount of butadiene and furan did not exceed 2%, so that the selectivities were determined under these conditions (Table 1).

I Series. A small number of samples was tested, but from these experiments it appeared that, in this series and for the oxidation of 1-butene, the selectivity with respect to C_4 compounds (methacrolein excepted) was enhanced when the amount of molybdenum oxide was very low, whereas it is independent of composition over a wide range when butadiene is oxidized. Since pure titanium oxide is unselective, the best catalyst for the oxidation of 1-butene appears to have a low proportion of MoO_3 in TiO_2 . This result agrees very well those reported in the patent literature (5) and suggests the existence of an optimal combination of the two oxides for this reaction. Thus, in order to determine its composition new catalysts were prepared by other methods. In addition it was hoped

TABLE 1
Selectivities of the Mo-Ti-O
Catalysts at 50-60% Conversion

Mo (at%)	Selectivity (in %) in oxidation of	
	1-Butene	Butadiene
I Series		
0	≈ 0	25
5.8	43	48
15.6	30	54
35.7	38	48
62.5	30	55
83.3	35	48
C Series		
0	0	29
10	35	34
25	33	47
50	27	43
75	29	49
90	30	49
A Series		
5.8	21.4	16.6
10.9	36.8	—
11.1	38.5	—
15.6	38.3	39.7
35.7	34.2	51.1
62.5	28.1	60
70.0	—	55

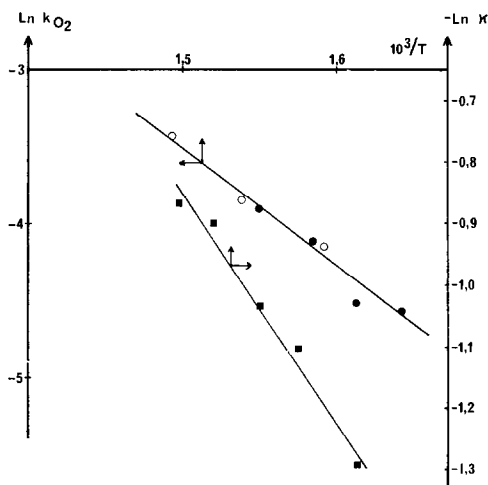


FIG. 5. Arrhenius plots for $\kappa = (k_r)_{\text{1-butene}} / (k_r)_{\text{butadiene}}$ (■) and k_{O_2} (○, 1-butene; ●, butadiene). Catalyst: I series 5.8 at% Mo.

that an increase in activity would be obtained.

C Series. Coprecipitated oxides gave the same variations of selectivity with composition but the values obtained were generally lower than before; in addition the homogeneity and the reproducibility of the samples appeared to be very poor.

Thus, a method of preparation of the oxides in a very highly dispersed state was researched in order that there should be regular positioning of the oxides in the mixed phase.

A Series. Courty and Delmon (10) have synthesized mixed oxides of known composition by forming citric acid complexes of cations, but the method has not been

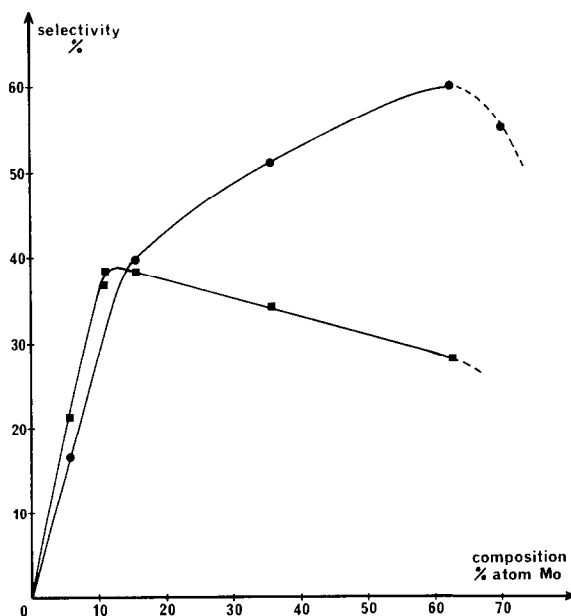


FIG. 6. Selectivities in C₄ products (methacrolein excepted) vs composition for catalysts of the A series at 60% conversion. ■, 1-butene; ●, butadiene.

applied to Mo⁶⁺-Ti⁴⁺. Tartaric acid has been found adequate for the complexation of these cations, so it was used for the preparation of mixed titanium-molybdenum oxides.

The variation of selectivity with catalyst composition was very regular in this series and thus proved the high degree of homogeneity of the catalyst samples. In the case

of 1-butene, the optimal selectivity was obtained for a composition of about 12 at% Mo (Fig. 6); for the same composition, a change was also observed in the variation of the selectivity for the oxidation of butadiene, which became optimal at 65 mole% MoO₃.

In this series, the observed phenomena seem to be more representative of the

TABLE 2
Activities of the A Series Catalysts at 400°C^a

Mo (at%)	Specific surface area (m ² g ⁻¹)	<i>k_rS</i> butene		<i>k_rS</i> butadiene		$\frac{(k_r S)_{\text{butadiene}}}{(k_r S)_{\text{butene}}} = \kappa$	
		mole h ⁻¹ g ⁻¹ atm ⁻¹	mole h ⁻¹ m ⁻² atm ⁻¹	mole h ⁻¹ g ⁻¹ atm ⁻¹	mole h ⁻¹ m ⁻² atm ⁻¹		
5.8	62	11	0.18	3	0.05	0.27	
11.1	98	23	0.23	12.8	0.13	0.56	
15.6	74	37	0.5	45	0.61	1.22	
35.7	67	9	0.13	14	0.21	1.55	
62.5	36	9	0.24	12	0.32	1.33	
70.0	10	—	—	0.4	0.04	—	
80.3	—	Inactive				—	—

^a ≤ 10% Conversion.

properties of the $\text{MoO}_3\text{-TiO}_2$ system than with the other catalysts. The relation between activity and composition was thus particularly investigated for these catalysts.

From the results reported in Table 2, an increase in the activity for both reactions was observed for a composition of 15.6 at% Mo and could not be explained by variations in specific surface areas, as proved by the comparison of intrinsic activities (Table 2).

Meanwhile, the activity of this catalyst was of a different order of magnitude from that of other samples and, in this case, mass transfer could have a strong influence on the selectivity, measured with pelleted catalysts. Therefore, in order to eliminate internal diffusion, the more active catalysts were deposited on an inactive α -alumina; under these conditions, the conversion did not exceed 60% and the amount of butadiene was increased. The results obtained with deposited catalysts are reported in Table 3: selectivity up to 53% was obtained, and the activity, in terms of the total weight of catalyst, remained of the same magnitude as in the impregnated catalysts, with the active component ten times less abundant.

TABLE 3
Selectivities of Supported and Diluted Catalysts
of the A Series

Mo (at%)	Selectivity (in %) in Oxidation of	
	1-Butene ^a	Butadiene
Deposited on $\alpha\text{-Al}_2\text{O}_3$ (10% wt)		
10.9	40.5 (28)	—
11.1	52	—
15.6	52.7 (40)	59.8
Diluted in anatase (10% wt)		
15.6	30	—

^a At 60% conversion, with maleic anhydride production in parentheses.

From this investigation into the influence of composition and of the method of preparation on the activity and selectivity of Mo-Ti-O catalysts, it appears that the amorphous mode of preparation gives more homogeneous catalysts. These are more active and selective than those resulting from other preparations commonly used. The best catalyst for activity and for selectivity is an amorphous one containing 15% atom Mo whose selectivity attains 53% at 60% conversion, and this is as selective and more active than the patented one.

Furthermore the optimal composition differs for the various series, and these results lead to the conclusion that the support effect is not a global one of the bulk of TiO_2 on MoO_3 but is the result of the proximity of Mo and Ti ions in the catalyst. Such an effect of the catalyst support is well known and has already been demonstrated for the catalytic oxidation of *o*-xylene over $\text{V}_2\text{O}_5\text{-TiO}_2$ or for the hydrodesulfuration on Co-Mo catalysts (11).

In the case of impregnated catalysts (I series), and with 1-butene, the selectivity rises when the amount of MoO_3 deposited on the anatase surface decreases to 5.8%. Under these conditions, the proportion of molybdenum ions interacting with the support is more important, and, in this case, the active molybdenum ions seem to be located in the first layers of MoO_3 .

The results obtained with amorphous catalysts (A series) confirm this hypothesis. In this case, the two phases (MoO_3 and TiO_2) are evenly dispersed and the distribution between Mo and Ti ions is much more regular. Consequently, the activity and the selectivity vary in a regular manner over the whole range of compositions studied. For a given reaction, one can obtain a composition such that the distribution of Mo-Ti ions enhances the number of active sites and thus, the selectivity. For example, a 12 to 15% MoO_3 catalyst is active and selective for the oxidation of

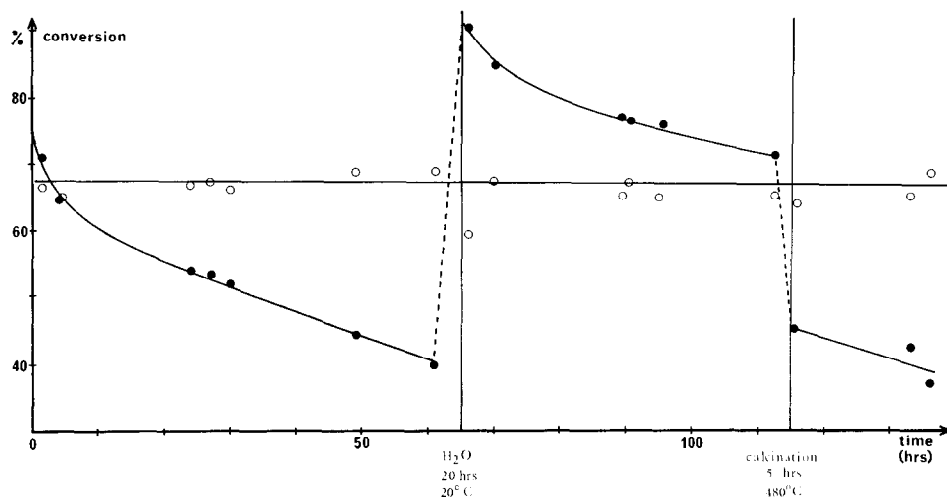


FIG. 7. Variation of the conversion (●) and selectivity (○) with time after various treatments in the oxidation of butadiene. Catalyst: I series 5.8 at% Mo, $T = 394^{\circ}\text{C}$, $P_{\text{H}} = 1.5 \times 10^{-3}$ atm, $P_{\text{O}_2} = 0.21$ atm, $W/F \approx 450$ g-h mole⁻¹.

1-butene and a 60 to 65% MoO₃ is the best for the selective oxidation of butadiene. An excess of each oxide causes a decrease in the activity and in the selectivity.

Thus, the optimal composition depends very greatly on the nature of the hydrocarbon being oxidized.

C. Deactivation and reactivation of impregnated catalysts

As already mentioned, the catalysts of the I series were rapidly deactivated; this fact is unusual for oxidation catalysts and was not observed for the other series. It was carefully investigated in order to determine the factors determining catalytic activity in these systems.

Chemical titrations on deactivated catalysts have shown that practically all the molybdenum ions were in the +6 form, and various oxidative treatments of the catalysts were without effect on the activity; the deactivation could not therefore be attributed to an irreversible reduction of active sites.

Moreover, no change was observed in the surface when examined through a scanning electron microscope.

It was noted that the initial rate was attained again when the catalyst was treated with air saturated with water vapor at room temperature, but the calcination of the sample at 500°C for 5 hr led to an important decrease in the reaction rate. Multiple deactivation-reativation cycles were carried out (Fig. 7) and the connection between conversion and hydration of the catalyst was demonstrated. The various treatments with water vapor or involving calcination did not cause any change in either the variation of activity with time or the selectivity. Only the initial conversion was affected. It is therefore concluded that the deactivation of these catalysts proceeds by a slow dehydration of the surface in the course of the reaction at 400°C.

D. Acidity measurements—activation

The role of the adsorbed water may be a double one:

(a) hydration of molybdenum oxide generating polymolybdic acids with formation of Brønsted-type acid sites;

(b) ligand effect of coordinated water, enhancing Lewis-type acidity.

TABLE 4
Influence of Various Treatments on Activity and Acidity of Impregnated
Catalyst (I Series 5.8% Mo)

	$k_r S$ butadiene, $T = 450^\circ\text{C}$, (mole $\text{h}^{-1}\text{g}^{-1}\text{atm}^{-1}$)	$\mu\text{mole pyridine}$ adsorbed/g catalyst	Electronegativity donor atom
Water calcined (500°C, 5 hr)	0.52	4.6	
NH_4Cl calcined (500°C, 5 hr)	1.0	6.1	3.0
Water no calcination	not measured	8.6	3.5
NH_4F calcined (500°C, 5 hr)	2.43	9.2	4.0

In both cases, the catalyst acidity is increased. Thus, using the method described by Ai and Ikawa (8), the irreversible part of the adsorption of pyridine was used to measure the acidity of the hydrated catalysts (5.8%, I series) which was then compared with that of the calcined sample and the results, in Table 4, show the great increase in acidity after hydration of the catalyst; the activity could not be compared under the same conditions because of the rapid deactivation.

In the last few years, Ai has demonstrated that catalyst activity for the oxidation of butenes and butadiene is related to the surface acidity for a number of mixed oxide catalysts (4, 8, 12). In this work, the variations of acidity were generally obtained by changing the composition of mixed oxides, the main problem arising from this procedure being that, not only the acidity changes, but also the phase nature and the specific surface area. Moreover, titanium oxide is acidic but inactive for oxidation; thus, the variation of composition could introduce acid sites other than the active ones.

In order to eliminate these uncertainties, the acidity of the same sample (I series; 5.8% atom Mo) was modified by treatment

with ammonium halides, as described in the experimental part. The activity for butadiene oxidation ($k_r S$) and the irreversible adsorption of pyridine were measured on these samples, and the results are reported in Table 4.

The influence of halide ions on acidity and activity for isomerization on silica has been demonstrated (13); electronegative elements are able to attract the electrons of the metal-halide bond, and thus enhance the strength of acid sites. The same effect was observed with $\text{MoO}_3\text{-TiO}_2$ catalysts, as seen in Table 4. The fluorinated catalyst was five times more active than the normal one, but the relative amounts of products and the selectivity remained unchanged.

With amorphous catalysts, where MoO_3 was intimately mixed with TiO_2 , the effect of water and halide ions on activity was not significant. A greater proportion of the molybdenum ions was probably stabilized in this structure in an active form and thus was not affected by the action of the donor elements.

It is concluded that an Mo-Ti-O catalyst can be used in the selective oxidation of butenes. The method of preparation of the catalyst is an important factor and with a better dispersion of the mixed oxides,

the number of active sites is increased because of the greater interaction of TiO₂ and MoO₃. Therefore, the intrinsic activity and the selectivity are much greater than with other preparations.

It has been demonstrated, in agreement with Ai's conclusions, that activity and acidity are closely related for the oxidation of olefins. The treatment with bases, such as halide ions or water, increases the activity of MoO₃ on anatase without perturbing its selective properties.

Nevertheless, the variation of activity and selectivity with catalyst composition is also dependent on the structure of the hydrocarbon undergoing oxidation.

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