JOURNAL OF CATALYSIS 73, 309–328 (1982)

Hydrogenation by Hydrogen Bronzes

I. Hydrogenation of Ethylene by H_xMoO_3

J. P. MARCQ,* X. WISPENNINCKX,* G. PONCELET,* D. KERAVIS,† AND J. J. FRIPIAT*,†

*Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium, and †Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite, 1B Rue de la Férollerie, 45045 Orléans, France

Received November 13, 1979; revised May 14, 1981

Hydrogenation of ethylene has been studied on hydrogen molybdenum oxide bronzes prepared by spillover of hydrogen from supported Pt particles. The temperature of the formation and of the outgassing of the bronze, as well as the Pt content, was found to influence the rate of the reaction of ethylene. Water molecules are formed at the expense of lattice oxygens and inserted H atoms when the bronze is outgassed at temperatures higher than 120°C. The removal of water is accompanied by structural modifications and the external layers of the oxide become partially amorphous. Freshly prepared bronzes are completely oxidized upon exposure to oxygen; after back-titration with hydrogen, the bronzes exhibit higher catalytic performances than before the oxygen treatment. The hydrogenation reaction is zero order with respect to ethylene pressure and small amounts of water present in the gas phase have no significant influence on the reaction. In the presence of gaseous H_2, the rate of hydrogenation increases with increasing hydrogen pressure, showing that gaseous H_2 is first consumed. From the experimental data, it is reasonable to consider the Pt particles as gates through which the H atoms leave the host lattice, according to a reverse spillover process, the rate-limiting step being the motion of hydrogen toward the platinum surface.

INTRODUCTION

Metal oxides in which H atoms are occluded have been called hydrogen bronzes by analogy with insertion compounds of alkali metals in the same type of host lattices. Typical hydrogen bronzes are those prepared from WO_3 or MoO_3. The preparation procedure may involve a wet chemical method, for instance, preparation of nascent hydrogen from Zn and HCl in an aqueous suspension of the desired oxide (*1*, *2*), but it has been shown also that hydrogen bronzes may be obtained using hydrogen spillover (*3–7*).

In that case, finely divided metal particles of Pt or Pd are dispersed on the oxide surface by impregnation: when brought into contact with molecular hydrogen, the hydrogen atoms produced on the metal diffuse inside the host oxide lattice with or without the help of a co-catalyst such as adsorbed water (*8*, *9*).

The physical and chemical properties of $H_{0.35}WO_3$ and of $H_{1.6}MoO_3$ obtained by these methods are already well documented (*10–24*). These bronzes may be considered to some extent as bimetallic catalysts. Indeed, these oxide lattices in which H is occluded have a metallic character because a fraction of the hydrogen electron is transferred into a conduction band as in an alkali-metal bronze (*18*). The Pt or Pd metal particles on the surface may be expected to interact with the modified oxide.

It is therefore interesting to investigate the catalytic properties of these "bimetallic" catalysts, keeping in mind that the bronze works as a hydrogen reservoir.

It is possible to use the hydrogen from this reservoir to carry out hydrogenation of alkenes, as proposed by Bond and coworkers (*25–27*). Practical applications in that direction have been suggested by Neikam (*28*) and by Tseung and Hobbs (*29*). In that case what is the role of Pt?

0021-9517/82/020309-20$02.00/0

Does hydrogen proceed by what could be called a "reverse spillover" process (*25*)? Is the alkene adsorbed on the Pt particle and does hydrogen contained in the oxide come back on the Pt surface where hydrogenation occurs? What is the degree of reversibility of the hydrogen storage? What would be the role of hydrogen in the gas phase in a mixture with the alkene?

At least at the level of the knowledge of fundamental catalytic processes, these questions are important and the present work attacks some of them.

NOMENCLATURE

The various symbols used in this paper are

nH_2	number of millimoles of H_2 occluded in the bronze
$X = H/Mo$	number of H atoms per Mo atom
$P^i_{C_2H_4}$	initial ethylene pressure (Torr)
nC_2H_6	number of millimoles of C_2H_6 produced by the reaction
V^i	initial reaction rate (mmole g^{-1} h^{-1})
ΔnH_2 (tit.)	number of millimoles of H_2 reintroduced after outgassing the bronze (back-titration)
ΔX (tit.)	variation of X corresponding to ΔnH_2 (tit.)
$\Delta n'H_2$	number of millimoles of H_2 reintroduced after 24 h of reaction with ethylene
$\Delta X'$	variation of X corresponding to $\Delta n'H_2$
ΔnH_2 (H_2O)	number of millimoles of H_2 removed as H_2O during the conditioning
ΔX (H_2O)	variation of X corresponding to ΔnH_2 (H_2O)
ΔnO_2	number of millimoles of O_2 consumed
ΔX (O_2)	variation of X corresponding to the O_2 consumption ($O_2 + 4H \rightarrow 2H_2O$)

EXPERIMENTAL

The all-glass apparatus consisted of a circulation pump moving the reactant, namely, C_2H_4 or a mixture of H_2 and C_2H_4, through a reactor which contained a thin bed of MoO_3 coated with Pt and which was maintained at constant temperature between 100 and 200°C.

To this circulation system were added a gas buret allowing measurement of the hydrogen consumption resulting from the formation of the bronze *in situ*, and a gas chromatograph with a catharometer detector. Continuous analysis of the gas mixture, namely, C_2H_4 and C_2H_6, was achieved by means of a six-way sampling valve. All stopcocks were greaseless in order to avoid as far as possible the contamination of the catalyst. The system could be evacuated at a pressure limit of about 10^{-5} Torr.

Materials. MoO_3 and $H_2PtCl_6 \cdot 6H_2O$ (analytical grade) were the starting materials. A 0.2 *M* hexachloroplatinic acid solution was added to an aqueous suspension of MoO_3 in order to obtain Pt/MoO_3 mixtures with Pt contents between 0.05 and 2%. Evaporation of the solvent was carried out at 60°C under continuous stirring. The powder was then dried at 120°C overnight in the oven. The BET specific surface area of this powder was of the order of 2 m^2/g. Dry H_2 and C_2H_4 were analytical products. They were used as such.

Preparation of the bronze. The impregnated oxide was heated under vacuum at 200°C for 2 h in order to achieve the decomposition of H_2PtCl_6 and to dry the sample. The temperature was then lowered to 60°C and the powder was exposed to H_2 in the presence of a liquid nitrogen getter in order to trap traces of water that could be produced. The consumption of H_2 was measured and assigned to the bronze formation. Indeed, the amount of H_2 chemisorbed on platinum is negligible and water was not detectable.

Following the above treatment, the bronze was again evacuated for 14 h at

120°C at a residual pressure of about 10^{-5} Torr and hydrogen was added back. This last step aimed to condition the bronze as closely as possible to the working temperatures which were between 120 and 160°C. This procedure is occasionally modified for reasons indicated in the text.

Reaction conditions. The reaction was carried out by circulating C_2H_4 onto the catalyst for periods of up to 24 h and at pressures between 30 and 140 Torr. With the reactor and circulation pump used in this work it was found that the amount of C_2H_6 formed at 160°C after 24 h is proportional to the weight of the catalyst from 0.6 up to 1.15 g; 1 g of bronze can hydrogenate 0.9×10^{-3} mole C_2H_4 at 160°C under a pressure of 33 Torr. Thus using about 0.8 g of catalyst prevents diffusion through the catalytic bed becoming rate determining.

Chromatographic analysis. The separation of H_2O, C_2H_4, and C_2H_6 was made on a Porapak R column, 2.5 m long and ⅛ in. in diameter. The carrier gas was helium. The oven temperature was programmed between 50 and 120°C, at a rate of 8°C/min. The catharometer temperature was 200°C.

Physical characterization. In order to obtain structural information after the outgassing and back-titration, X-ray diffraction analyses were carried out on small amounts of bronzes contained in glass capillaries which were sealed after submitting the sample to the same treatment as in the reactor. Mo*K*α radiation was used.

RESULTS AND DISCUSSION

The following experiments are designed to investigate the reaction

$$yC_2H_4 + H_xMoO_3 \xrightarrow[Pt]{} yC_2H_6 + H_{x-2y}MoO_3$$

It was first desirable to look at the variation of the hydrogen content with respect to the outgassing conditions, since the reaction was studied in the absence of gaseous hydrogen. Then the loss of activity of the catalyst had to be studied in order to find the meaningful working conditions of the catalyst. Subsequently the reaction order with respect to C_2H_4 and to the solid was established and the reaction activation energy was measured. An additional series of experiments with mixtures of C_2H_4 and H_2 was finally carried out.

In order to understand better the significance of the experimental results, it is of prime interest to point out the physical changes in the catalyst after its formation. When hydrogen invades the MoO_3 lattice, the oxide microcrystal has a strong tendency to cleave in planes parallel to its *c* crystal axis. This increases the surface area and decreases the contact between the oxide layers and the Pt particles. An illustration of these effects is shown on electron micrographs in Figs. 1a and b. The microprobe analysis performed on these samples gives the location of the Pt particles, as shown by the arrows in Figs. 2a and b. It was observed that some of the Pt particles aggregate in rather large clusters. If, as suggested by Sermon and Bond (*25*), a reverse spillover process is responsible for the migration of H towards the Pt surface where hydrogenation of ethylene takes place, the poor dispersion of the metal onto the bronze surface and the lack of good contacts between the bronze and the metal resulting from the cleavage of the oxide lattice suggest that only a small fraction of the Pt content is really active.

The method used in this work to impregnate the oxide with platinum may not be the most suitable, given the small surface area of the starting oxide. This aspect of the problem is worth a new set of experiments where the quality of the Pt dispersion would be considered more carefully.

Degree of Reversibility of the Bronze Formation

A given sample of H_xMoO_3, 2% Pt was submitted to three cycles of outgassing followed by H_2 titrations. The outgassing time was 14 h for each cycle and the titrations were always carried out at 60°C. The out-

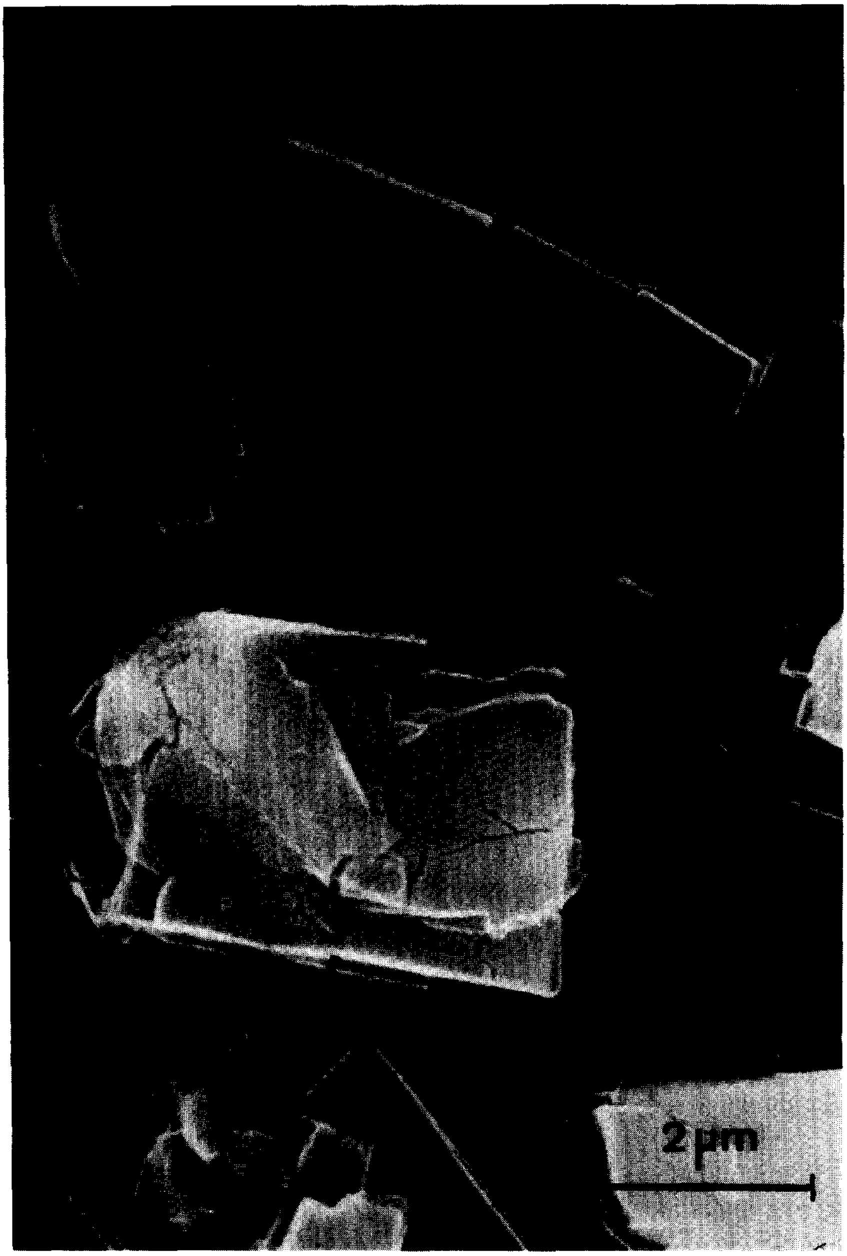

FIG. 1a. Scanning electron micrograph of a bronze particle showing the cleavage planes.

gassing temperatures were 60, 120, and 160°C.

As seen in Table 1, after an outgassing at 60°C, the hydrogen content is practically constant, whereas upon outgassing at 120 and 160°C, ΔX changes appreciably. The change of ΔX with the number of outgassing cycles clearly shows that the removal of H_2 is not completely reversible at temperatures higher than 120°C. If depletion in H_2 affects mainly the surface layers, the catalytic activity is expected to decrease

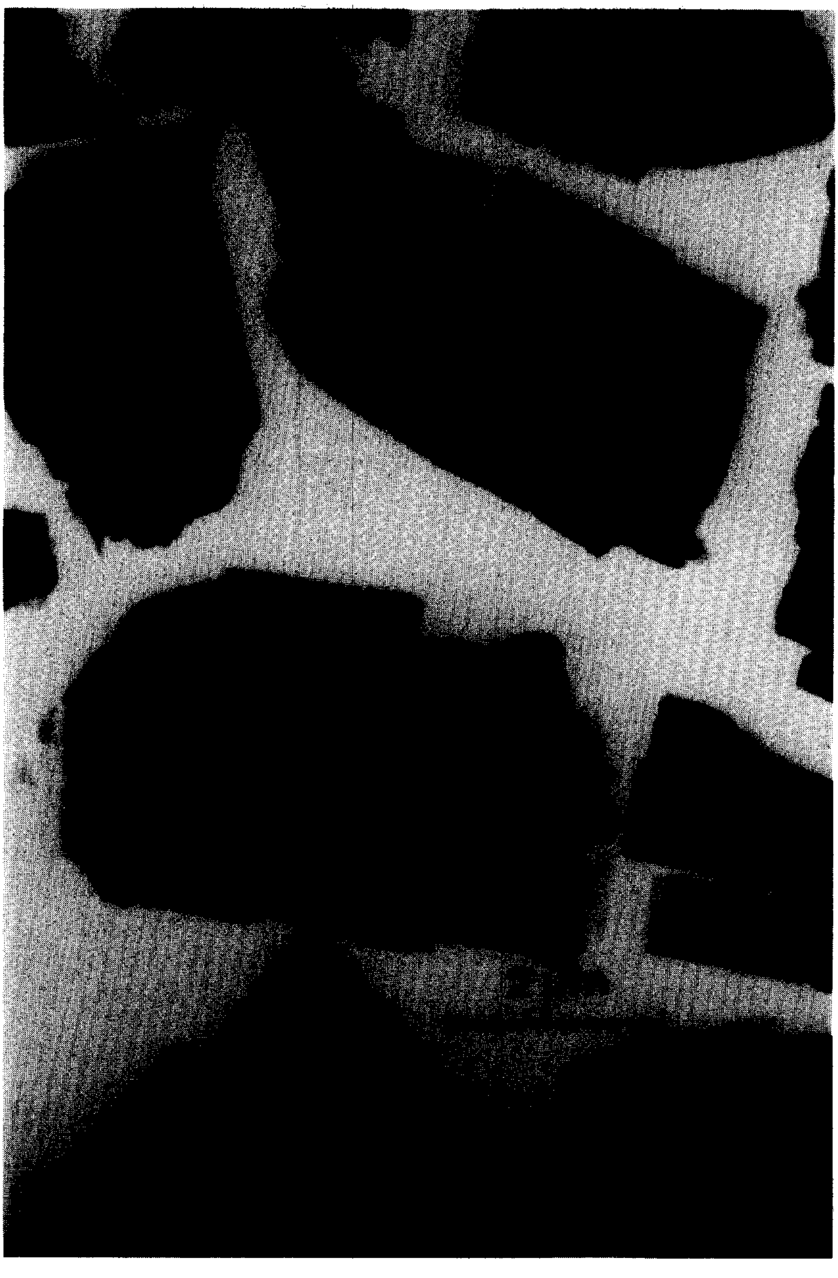

FIG. 1b. TE micrograph on the same sample as Fig. 1a, showing the microcracks.

with time, especially if the removal of H_2 from the surface layers provokes some irreversible structural rearrangements. This seems to be the situation occurring for the second cycle. Indeed, ΔX after the second outgassing cycle at 160°C is lower than that measured after the first cycle at 160°C (second series).

In order to examine the structural modifications accompanying the removal of hydrogen, experiments were carried out in which the influence of the parameters in-

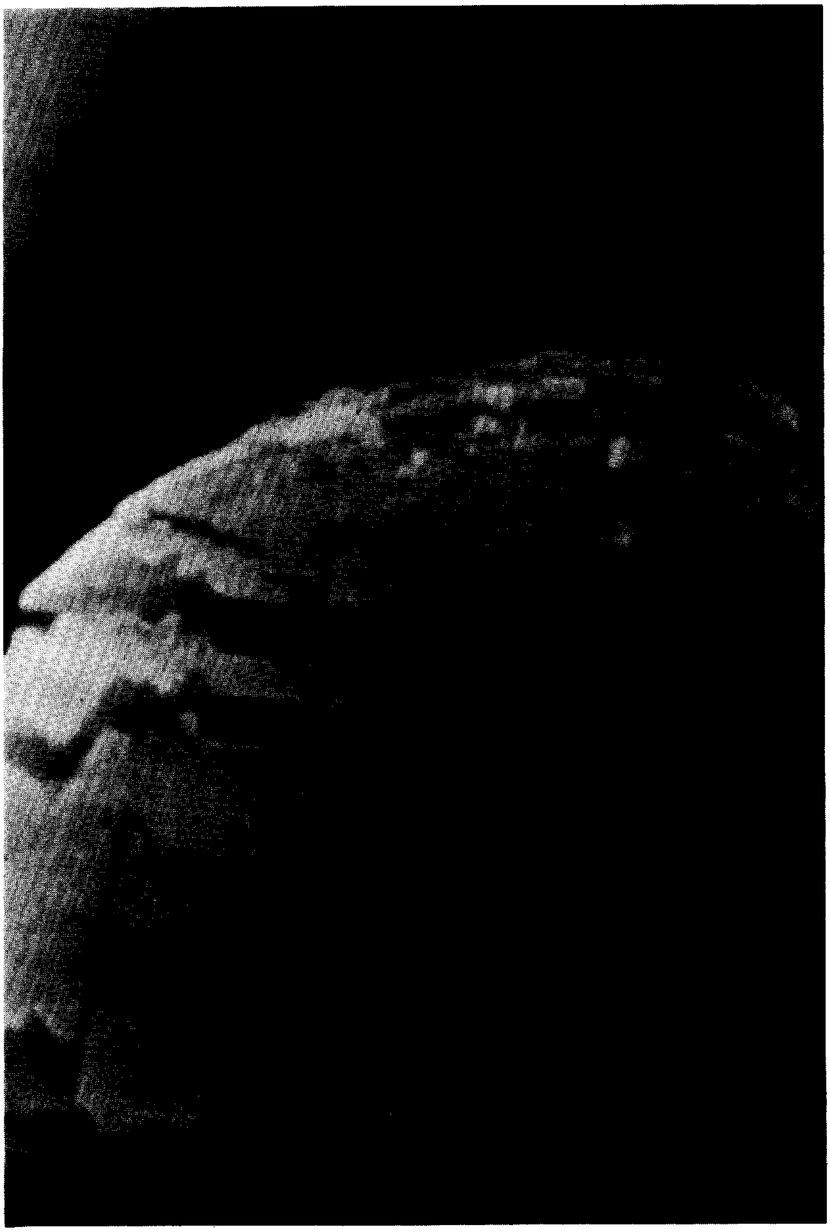

FIG. 2a. Scanning electron micrograph showing the Pt particles on a crystallite of MoO_3.

volved in the conditioning of the bronze on the formation of water was investigated. Indeed, if water is produced during the outgassing, oxygen atoms must necessarily be removed from the oxide lattice, and consequently lower oxides should be formed. For that purpose, three bronzes prepared at 60°C were treated in the following ways:

(i) the first one was outgassed under dynamic vacuum at 160°C for 14 h;

(ii) the second bronze was outgassed at 60°C, and thereafter the reactor was isolated from the pumping system and the temperature was raised and maintained at 160°C for 14 h;

(iii) the third bronze was treated as in (ii),

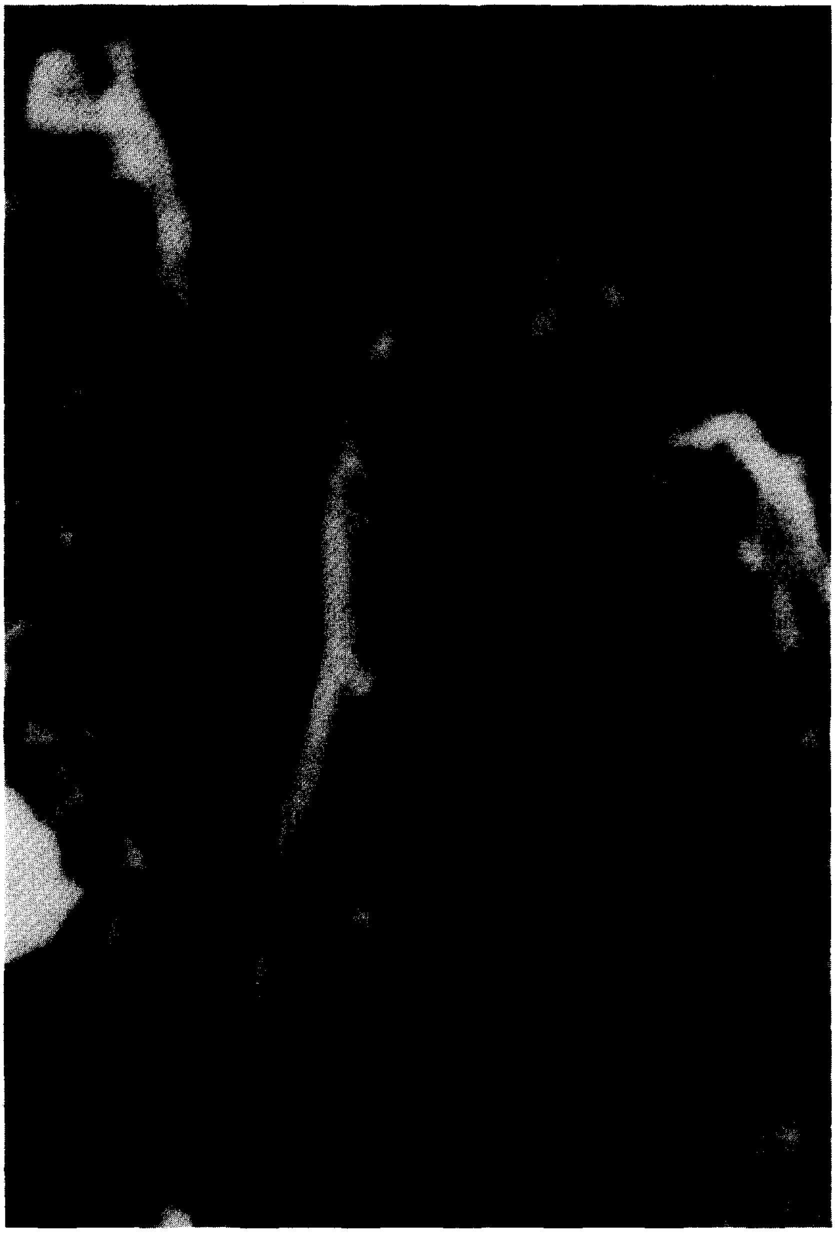

FIG. 2b. Scanning electron micrograph showing Pt particles on a crystallite of MoO_3.

but the water formed during the conditioning was continuously removed from the gas phase, using a liquid nitrogen getter.

The treatment used in runs (ii) and (iii) will be referred to hereafter as "static outgassing" in order to distinguish it from the "dynamic outgassing" used in run (i).

At the end of the conditioning period, the three bronzes were back-titrated with hydrogen, after determining the amount of water formed by gas chromatography in runs (ii) and (iii).

The results are shown in Table 2. More water is found in run (iii) where the water was continuously removed from the system

TABLE 1

Degree of Reversibility of the Bronze Formation for Samples of MoO_3 Contianing 2% Pt by Weight

	First series	Second series
Sample weight (g)	0.8	0.8
nH_2 (mmole)	3.7	3.95
X_{initial}	1.4	1.5
First cycle		
Temperature (°C)	60	160
ΔnH_2 (tit.) (mmole)	0.11	0.55
ΔX (tit.)	0.04	0.21
Second cycle		
Temperature (°C)	120	160
ΔnH_2 (tit.) (mmole)	0.54	0.18
ΔX (tit.)	0.21	0.07
Third cycle		
Temperature (°C)	160	
ΔnH_2 (tit.) (mmole)	0.33	
ΔX (tit.)	0.13	

by using a cold trap. Whereas the amount of hydrogen back-titrated is nearly identical to that removed as water in run (ii), the discrepancy between ΔnH_2 (H_2O) and ΔnH_2 is rather appreciable in run (iii). The highest value of H_2 consumed in the back-titration is observed for run (i), e.g., when the bronze is conditioned under dynamic vacuum.

A second set of experiments was carried out in order to investigate the influence of time and temperature of the conditioning (static vacuum, with and without cold trap) on the amount of water produced from the bronze. A bronze with $X_{\text{initial}} = 1.55$ (prepared at 60°C following the standard procedure described earlier) was heated at 160°C under static vacuum (without cold trap) and the water formed was determined as a function of time. Three other bronzes were treated under similar conditions for different times but in the presence of a cold trap. The results are compared in Fig. 3. It is clear that removing the water during the treatment strongly affects the shape of ΔX (H_2O) as a function of time and also the total amount of water released from the bronze. In the absence of a liquid N_2 trap (i.e., of a concentration gradient in the gas phase), the water formed at the surface of the bronze could work as a barrier for the desorption into the gas phase. When using a cold trap there is nearly four times as much

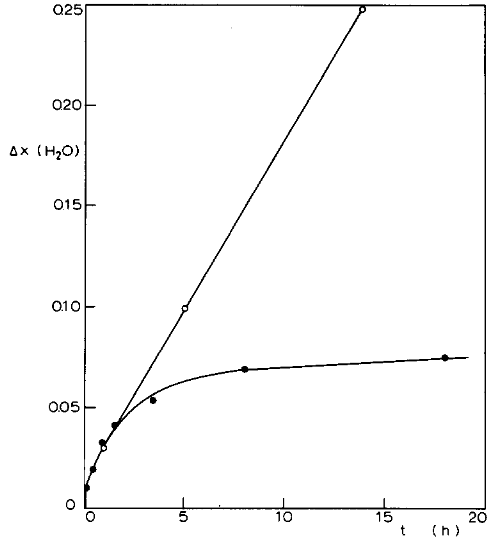

FIG. 3. Evolution of ΔX (H_2O) as a function of the outgassing time (h) at 160°C: ○, outgassing under "static" vacuum in the presence of a liquid N_2 getter; ●, same but without a cold trap.

TABLE 2

Influence of the Outgassing Conditions on the Amount of Water Formed after 14 h at 160°C from 2% Pt/H_xMoO_3

Conditioning	X_{initial}	ΔnH_2 (H_2O) (mmole)	ΔX (H_2O)	ΔnH_2 (tit.) (mmole)	ΔX (tit.)
(i) Dynamic vacuum	1.44	—	—	0.35	0.13
(ii) Static vacuum	1.63	0.23	0.07	0.20	0.07
(iii) Static vacuum + liq N_2 trap	1.55	0.74	0.26	0.25	0.08

TABLE 3

Influence of the Outgassing Time on the Formation of Water under Static Vacuum in the Presence of a Liquid N_2 Getter

Sample weight (g)	nH_2 (mmole)	X_{initial}	T (°C)	t (h)	ΔnH_2 (H_2O) (mmole)	ΔX (H_2O)	ΔnH_2 (tit.) (mmole)	ΔX (tit.)
0.8110	4.25	1.60	160	1	0.08	0.03	0.11	0.04
0.8293	4.56	1.67	160	5	0.27	0.10	0.18	0.07
0.8485	4.56	1.63	160	14	0.74	0.26	0.25	0.09

water released after 14 h as compared to the amount obtained in the absence of a cold trap.

The bronzes outgassed in the presence of a liquid N_2 trap were back-titrated with hydrogen. As shown by the values given in Table 3, after 1 h of outgassing the number of millimoles of H_2 reinserted in the bronze, ΔnH_2 (tit.), corresponds approximately to the amount of H_2 removed as water, ΔnH_2 (H_2O). This result suggests that a thin surface layer of suboxides does not prevent the formation of a bronze which of course may have a different stoichiometry from that of the bulk. For increasing outgassing times, there is an increasing discrepancy between these two values. After 14 h, only one-third of the total H_2 lost as H_2O could be added back to the host lattice, suggesting an irreversible damage of the surface.

Considering now the effect of the outgassing temperature, freshly prepared bronzes were conditioned at different temperatures and back-titrated with hydrogen after 14 h of heating. The experimental data are given in Table 4. There is a linear relationship between the amount of water released and the conditioning temperature. The activation energy obtained from the Arrhenius plot is 14.5 kcal/mole H_2O.

Figure 4 shows the relationship between the amount of H_2 back-titrated, ΔX (tit.), and the yield of water, ΔX (H_2O), formed after 14 h of treatment. As long as ΔX (H_2O) is lower than 0.1, the initial stoichiometry of the bronze is apparently restored. Beyond this value, the elimination of H_2 as water becomes irreversible: it may be concluded that the bronze is no longer restored in its initial state.

In order to confirm this point, X-ray diffractograms were recorded on samples taken at different steps of the conditioning in sealed tubes at room temperature. The

TABLE 4

Influence of the Outgassing Temperature on the Formation of Water under Static Vacuum in the Presence of a Liquid N_2 Getter

Sample weight (g)	nH_2 (mmole)	X_{initial}	T (°C)	ΔnH_2 (H_2O) (mmole)	ΔX (H_2O)	ΔnH_2 (tit.)	ΔX (tit.)
0.8874	4.40	1.50	120	0.14	0.05	0.12	0.04
0.9026	4.86	1.63	120	0.14	0.05	0.18	0.06
0.8134	4.34	1.62	140	0.27	0.10	—	—
0.8440	4.17	1.50	140	0.25	0.09	0.34	0.12
0.8304	4.40	1.61	150	0.45	0.16	0.36	0.13
0.8485	4.56	1.63	160	0.74	0.26	0.25	0.09
0.7942	3.85	1.47	160	0.64	0.24	0.29	0.11
0.8647	4.40	1.55	180	0.87	0.30	0.28	0.10

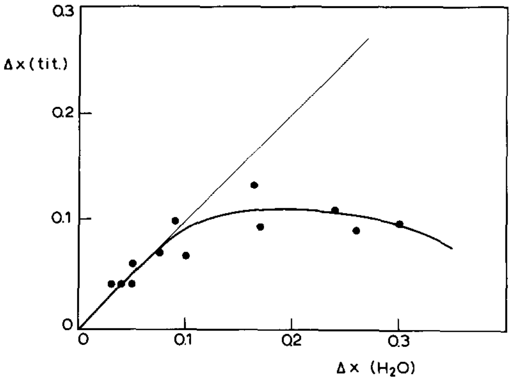

FIG. 4. Relationship between ΔX (tit.) and ΔX (H_2O).

spectra shown in Fig. 5 correspond to the initial bronze (A), the compound outgassed at 160°C for 14 h (B), and back-titrated with H_2 (C), respectively. The outgassed bronze differs from the initial one by the presence of several diffraction lines at 2.9, 5.9, 6.25, 7.8, and 8.55°θ; the intensity of the main peaks is also weaker. The additional peaks have almost completely disappeared in the X-ray diffractogram of the back-titrated sample, but the intensity of the main peaks of the bronze is not restored to the initial value.

It may be concluded that outgassing the bronze brings about two important modifications: (i) production of a transient phase, which is almost completely removed after back-titration and (ii) the initial bronze structure is restored partially upon back-titration. The fact that the background between $\theta = 3°$ and $\theta = 6°$ has significantly increased suggests that the material has become partially amorphous. These structural data confirm the experimental observations discussed earlier. The additional weak peaks observed in spectrum B have not been identified on the basis of the X-ray data available in the literature, but undoubtedly they are characteristic of a mixture of suboxides. The diffraction peaks of the initial bronze coincide relatively well with those given by Birtill and Dickens (*16*) for $H_{1.68}MoO_3$.

Catalyst Activity

It can be anticipated from the results described in the previous section that the

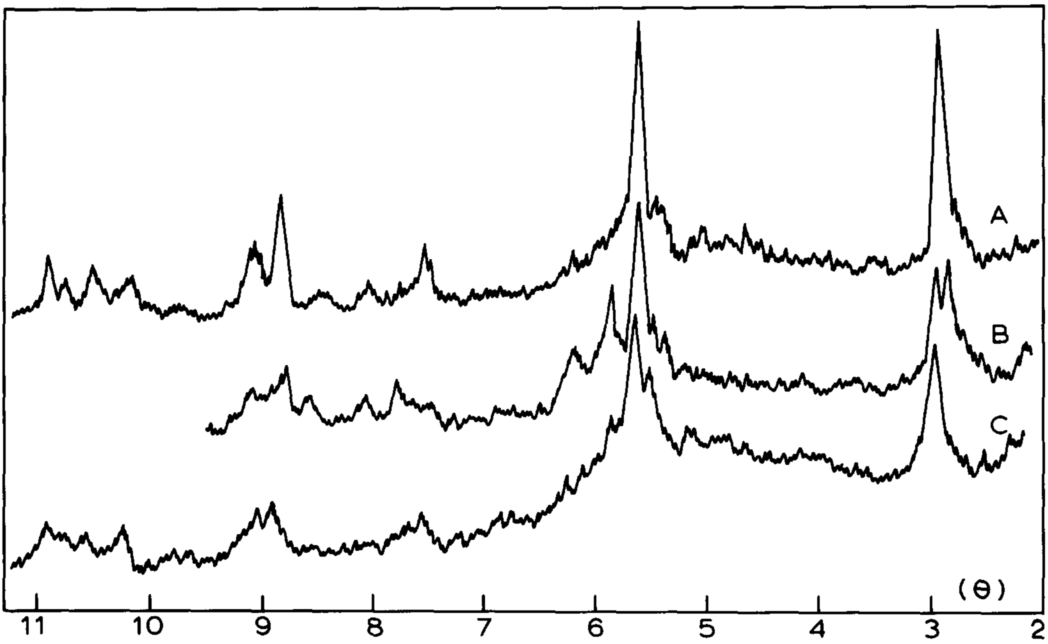

FIG. 5. X-Ray diffractograms recorded after the bronze formation (A), after outgassing the bronze at 160°C for 14 h (B), and after back-titration of the outgassed bronze (C).

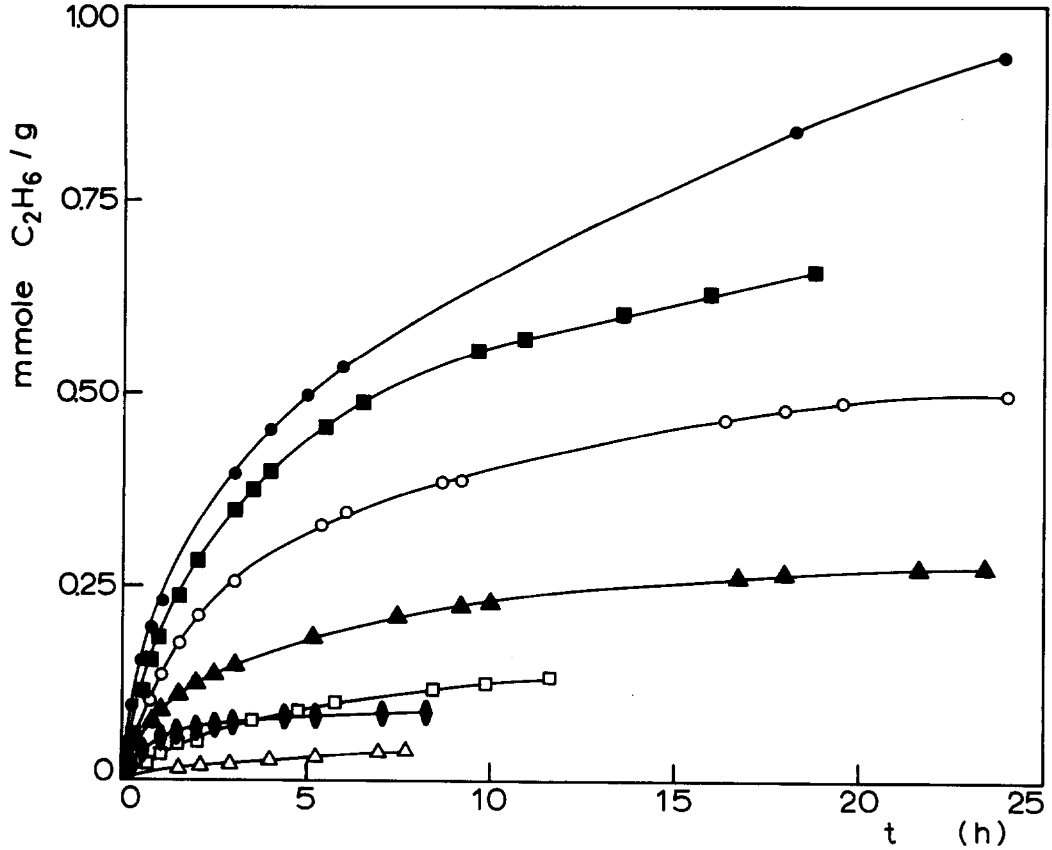

FIG. 6. Hydrogenation of ethylene at 160°C on bronzes outgassed at different temperatures (dynamic vaccum). Solid symbols: outgassing with back-titration with H_2; open symbols: outgassing without back-titration. ●, ○: outgassing at 120°C; ■, □: at 140°C; ▲, △: at 160°C; ◆: at 180°C.

structural modifications provoked by the pretreatment conditions may affect the catalytic properties. Accordingly, experiments were carried out in which the bronzes were exposed to ethylene in the following ways: three samples of 0.8 g of MoO_3, 2% Pt were treated with H_2 at 60, 120, and 160°C: X was 1.44 ± 0.02 for all three samples. They were then outgassed (dynamic vacuum) for 14 h at 120°C and back-titrated with H_2. ΔX was 0.2 with respect to the bronze made initially at 60°C. For the bronzes formed at 120 and 160°C, ΔX was 0.13 ± 0.01. Here again, despite a similar initial stoichiometry, the H_2 depletion produced by outgassing the three samples at the same temperature is sensitive to the temperature at which they were obtained.

After back-titration, the bronzes were reacted at 160°C with C_2H_4 (P^i = 35 Torr, i.e., 2.45 mmole). At the end of the reaction, 0.75, 0.37, and 0.34 mmole C_2H_4 were hydrogenated for the bronzes formed at 60, 120, and 160°C, respectively.

In a second set of experiments, four bronzes prepared at 60°C were outgassed at 120, 140, 160, and 180°C for 14 h (dynamic outgassing). The initial stoichiometry was 1.42 ± 0.04, and in each case, C_2H_4 hydrogenation was carried out on catalysts which were or were not back-titrated. The experimental curves are shown in Fig. 6, and the kinetic parameters are given in Table 5. As expected, back-titration and outgassing temperature affect the initial rate and the yield of C_2H_6.

TABLE 5

Influence of the Depletion of the Outside Layers of H_xMoO_3 on the Catalytic Properties

Outgassing temperature (°C)	nH_2 (tit.) (mmole)	ΔX (tit.)	V^i (mmole/g h)	nC_2H_6 (after 24 h) (mmole)	$\Delta n'H_2$ (mmole)	$\Delta X'$
		(a) Back-titration after outgassing				
120	0.54	0.20	0.46	0.76	0.68	0.26
140	0.59	0.23	0.28	0.52	0.60	0.23
160	0.35	0.13	0.13	0.22	0.64[a]	0.24
180	0.36	0.14	0.10	0.07	0.18	0.07
		(b) No titration after outgassing				
120			0.20	0.40	1.00	0.38
140			0.03	0.10	0.74	0.28
160			0.02	0.03	0.83	0.32

Note. Sample weight, 0.8 g. $X_{\text{initial}} = 1.42 \pm 0.04$.

[a] Amount of H_2 reinserted after 17 h, instead of 3 h for all the other cases.

The bronzes which were submitted to various conditionings under static vacuum at several temperatures (cf. the preceding section) were back-titrated and reacted with ethylene at 160°C. The experimental data are given in Table 6, while Fig. 7 shows the extent of the ethane production versus time. Here again it is clear that the catalyst activity is strongly influenced by the temperature and how the bronze was outgassed. Indeed, for an identical conditioning temperature, the yields of C_2H_6 obtained for the bronzes pretreated under static conditions are higher than those obtained with the bronzes outgassed under dynamic vacuum (compare the curves in Fig. 7 with those in Fig. 6, with back-titration).

These results confirm that the structural modifications due to the loss of lattice oxygens as H_2O during the outgassing step have a pronounced influence on the catalytic activity, and that the more severe the outgassing conditions, i.e., the structural damage, the lower is the bronze performance.

In order to illustrate this point, the amounts of C_2H_6 produced after 24 h of reaction were plotted in Fig. 8 against ΔX (H_2O) detected after outgassing. A linear relationship is obtained.

It is most important to point out that

TABLE 6

Influence of the Conditioning Temperature on the Reaction with Ethylene at 160°C

Outgassing temperature (°C)	$P^i_{C_2H_4}$ (Torr)	V^i (mmole/g h)	nC_2H_6 (after 4 h) (mmole/g)	nC_2H_6 (after 20 h) (mmole)	nH_2O (final) (mmole)	$\Delta n'H_2$ (tit.) (mmole)	$\Delta X'$ (tit.)
120	38.08	0.68	0.77	1.01	0.05	1.29	0.44
140	43.26	0.64	0.60	0.83	0.06	0.50	0.18
150	41.40	1.49	0.58	0.79	—	—	—
160	42.34	0.14	0.39	0.57	0.00	0.33	0.12
160	39.44	0.24	0.36	0.51	0.02	0.34	0.13
180	41.60	0.40	0.31	0.40	0.02	0.10	0.04

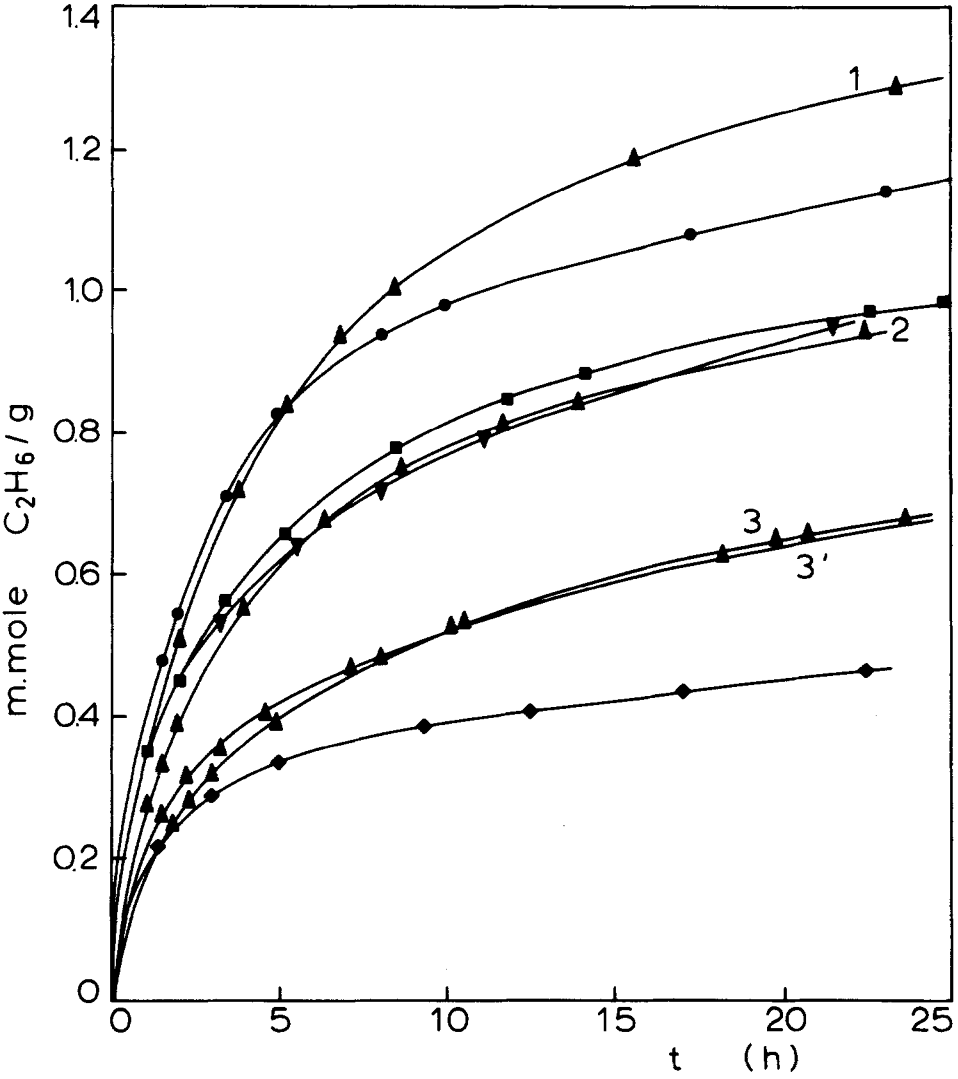

FIG. 7. Hydrogenation of ethylene at 160°C on bronzes outgassed at different temperatures (static vacuum with liquid N_2 getter): ●, ■, ▼, ◆: outgassed for 14 h at 120, 140, 150, and 180°C, respectively; ▲1, ▲2, ▲3, and ▲3′: outgassed at 160°C for 1, 5, and 14 h, respectively.

during the hydrogenation of ethylene, the quantity of water formed is almost undetectable. Traces of water were found after 24 h of reaction only, i.e., when the C_2H_6 formation tends toward a plateau.

Benson *et al.* (*8*) have shown that a small amount of water has a promoting effect on the hydrogen spillover. In order to see whether a similar effect is also observed on the reverse spillover, two runs were carried out, one in which water (1 Torr) was reacted together with ethylene (40 Torr), and the second one without water. The bronze ($X_{\text{initial}} = 1.6 \pm 0.02$) was prepared at 60°C and outgassed at 120°C for 14 h. No significant difference in the initial rate could be observed. After 24 h of reaction, 1.2 (with H_2O) and 1.1 (C_2H_4 alone) mmole C_2H_6 were formed.

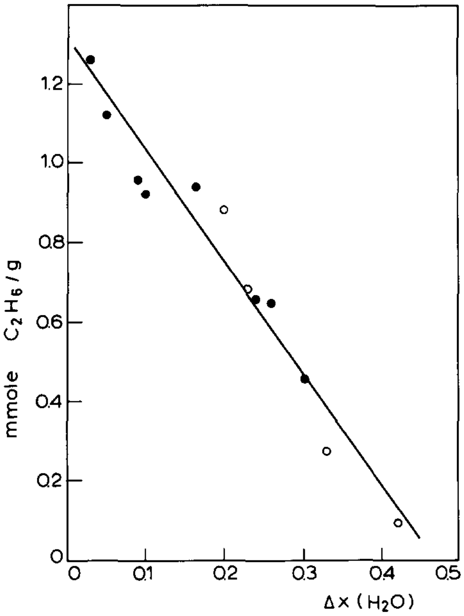

FIG. 8. Relationship between the number of millimoles of C_2H_6 obtained after 24 h at 160°C and ΔX (H_2O). Solid symbols: experimental values from Tables 4 and 6; open symbols: values extrapolated from Fig. 4 and Table 5.

Effect Oxygen Treatment on the Catalytic Performance

Comparing several hydrogen acceptor molecules, Sermon and Bond (*27*) observed that the most efficient one was O_2, initiating the reverse spillover in 1% Pt/H_xWO_3 at the lowest temperature (17°C). On the other hand, Tinet and Fripiat (*19*) reported that the O_2 consumption during the titration of 0.5% Pt/$H_{1.6}MoO_3$ at 60°C corresponds exactly to the stoichiometry $4H + 2O \rightarrow 2H_2O$.

It has been shown in this study that outgassing the bronze at temperatures higher than 120°C results in the formation of water molecules, the oxygen atoms being necessarily taken away from the host lattice. It was therefore interesting to establish the effect of an oxygen treatment on the catalytic performances of these compounds. Hence, three bronzes (2% Pt) were contacted with oxygen, each one at a different stage during a run. The results given hereafter are not completed yet but do show this effect. In the first experiment, the bronze was outgassed at 160°C (14 h) and treated at the same temperature with O_2. The second bronze was brought into contact with O_2 directly after its formation, i.e., without outgassing it. The third one, after being outgassed, back-titrated with hydrogen, and submitted to a catalytic run with ethylene, was contacted with oxygen at 160°C. The experimental data are shown in Table 7. As in the previous experiments, H_2 consumption was determined volumetrically, while all the other analyses were performed by gas chromatography.

In the absence of an outgassing (run 2), it is seen that the O_2 consumption corresponds to a ΔX (O_2) equal to X_{initial}. Assuming that one molecule of O_2 reacts with four H atoms, all the hydrogen inserted in the bronze lattice is recovered, which is consistent with the results of Tinet and Fripiat (*19*). After back-titration with hydrogen, ΔX (tit.) is nearly equal to X_{initial}, which suggests that the bronze is almost completely restored to its initial state. For the bronze which has been outgassed at 160°C (run 1), less oxygen is consumed. This is expected since, as reported earlier, a fraction of the hydrogen content is removed as water during the outgassing. Summation of the ΔX (H_2O) and ΔX (O_2) values gives 1.56 g which is close to X_{initial}. In run 3, the bronze was submitted to a catalytic reaction before the oxygen treatment: still less oxygen is consumed despite the fact that the amount of hydrogen reinserted during the back-titration performed after the first catalytic run is nearly equal to the quantity of ethane formed.

The decreasing degree of oxidation reflects that each additional step to which the bronze is submitted is marked by a diminution of the quantity of hydrogen recovered when oxygen is used as an acceptor, although the number of hydrogen atoms involved in the reverse spillover and the rate of oxidation are much higher than when ethylene is the acceptor.

TABLE 7

Effect of an Oxygen Treatment on the Catalytic Performances

	Run:	1	2	3
	Weight (g):	0.8234	0.8816	0.8144
Bronze formation at 60°C	nH_2 (mmoles)	4.37	4.74	4.01
	X_{initial}	1.61	1.63	1.50
Static outgassing at 160°C with liquid N_2 getter	ΔnH_2 (H_2O)	0.43	—	0.45
	ΔX (H_2O)	0.16	—	0.17
Back-titration with H_2 at 60°C	ΔnH_2 (tit.)	—	—	0.25
	ΔX (tit.)	—	—	0.09
Reaction with C_2H_4 at 160°C	$P^1_{C_2H_4}$ (Torr)	—	—	45.52
	V^1 (mmole/g h)	—	—	0.95
	nC_2H_6 (after 4 h) (mmole/g)	—	—	0.42
	nC_2H_6 (after 20 h) (mmole)	—	—	0.57
	nH_2O (after 20 h) (mmole)	—	—	0.00
Back-titration at 60°C	$\Delta n'H_2$ (tit.)	—	—	0.52
	$\Delta X'$	—	—	0.19
Oxygen treatment at 160°C	$P^i_{O_2}$ (Torr)	379.02	193.16	100.88
	ΔnO_2 consumed	1.93	2.37	1.27
	ΔX (O_2) consumed	1.40	1.61	0.95
	ΔnH_2O	0.98	0.82	0.69
	ΔX (H_2O)	0.36	0.28	0.26
Back-titration at 60°C	ΔnH_2 (tit.)	3.38	4.45	3.15
	ΔX (tit.)	1.24	1.53	1.17
Reaction with C_2H_4 at 160°C	$P^1_{C_2H_4}$ (Torr)	45.44	46.62	44.74
	V^1 (mmole/g h)	0.64	0.61	0.86
	nC_2H_6 (after 4 h) (mmole/g)	0.72	0.82	0.63
	nC_2H_6 (after 20 h) (mmole)	0.77	1.00	0.65
	nH_2O (after 20 h) (mmole)	0.02	0.02	0.02
Back-titration with H_2 at 60°C	ΔnH_2 (tit.)	—	1.16	0.38
	$\Delta X'$	—	0.40	0.14

The amounts of water found in the gas phase at the end of the oxygen treatment are unexpectedly low. A possible explanation is that using a frozen heptane getter the retrodiffusion of gaseous water is more difficult in the presence of a gas atmosphere than under vacuum, so that more water remains adsorbed on the bronze surface, perhaps in the microcracks or between the cleavage planes. This point needs clarification.

After pumping out the excess of oxygen, the bronzes were back-titrated and contacted with ethylene. The amounts of ethane formed versus time are compared in Fig. 9. These curves clearly show that treating the bronze with oxygen has a pronounced influence on the hydrogenation of ethylene (compare the three upper curves to the lower one). As pointed out earlier, almost no water is formed during the reaction of the bronze with ethylene. It should also be noted that submitting the bronze first to an oxygen treatment and thereafter to a hydrogen titration between two catalytic runs not only regenerates the catalytic performance of the bronze, but improves it.

This is in contrast with the results ob-

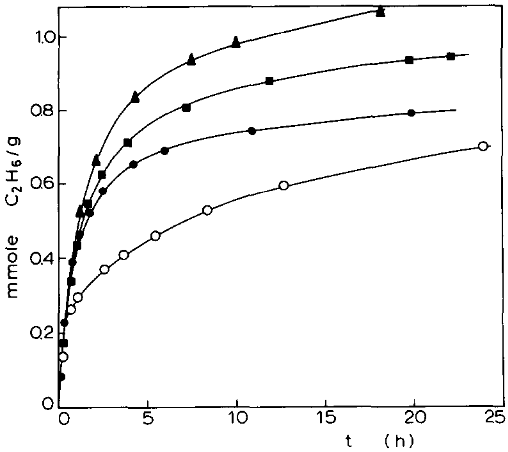

FIG. 9. Influence of an oxygen treatment on the hydrogenation of ethylene at 160°C: ○, ●: before and after O_2 treatment (run 3, Table 7); ■: bronze outgassed and treated with O_2 (run 1, Table 7); ▲: bronze directly treated with O_2, without outgassing (run 2, Table 7).

TABLE 8

Successive Hydrogenations of Ethylene on the Same Sample of 0.5% Pt/$H_{1.52}MoO_3$ (Sample Weight: 0.7955 g) at 160°C

Run	$P^{i}_{C_2H_4}$ (Torr)	V^{i} (mmole/g h)	nC_2H_6 (after 20 h) (mmole)	$\Delta n'H_2$ (tit.) (mmole)
1	34.7	0.34	0.84	1.00
2	35.0	0.19	0.54	0.65
3	35.0	0.14	0.34	0.60

tained when several catalytic runs are performed on the same bronze, the bronze being back-titrated with hydrogen between two runs. As seen in Table 8, an important loss of activity is observed, although the amounts of hydrogen reinserted exceed the number of millimoles of ethane formed.

Finally, comparing the catalytic data of run 2 (Table 7) with those obtained on a bronze outgassed at 160°C (Table 6), i.e., on bronzes which differ from each other by an oxygen treatment, it is seen that a higher initial rate, i.e., higher rate of reverse spillover, is achieved in the former run.

It may thus be concluded that treating the bronze with oxygen improves markedly the catalytic performance and the rate of the reverse spillover. Moreover, O_2 is a more efficient hydrogen acceptor than ethylene, which confirms the results of Sermon and Bond (*25*) on a tungsten bronze.

Influence of the Platinum Content on the Rate Process

In these experiments 0.8 g of MoO_3 with three different Pt contents, namely, 0.05, 0.5, and 2%, were treated at 60°C with hydrogen in order to obtain the bronze. Figure 10 shows the kinetics of the bronze formation, the initial pressure of H_2 being 200 Torr in each case. With 0.05% Pt the equilibrium composition was not yet reached after 5 h. Since, according to Tinet and

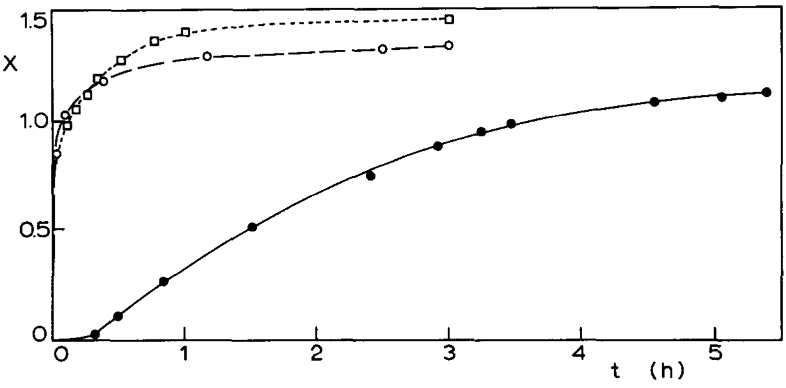

FIG. 10. Influence of the Pt content on the kinetics of the bronze formation in the presence of 200 Torr of H_2: ●: 0.05% Pt; ○: 0.5% Pt; □: 2% Pt.

Fripiat (*19*), there is no intermediate composition between $X = 0$ and $X = 1.5$ in H_xMoO_3 bronzes formed by spillover, it must be concluded that at low Pt content a fraction of MoO_3 has not reacted after that time.

A bronze with 0.05% Pt was impregnated a second time with a solution of H_2PtCl_6. The salt was decomposed at 200°C under vacuum and thereafter the sample with a total Pt content of 0.13% was treated at 60°C with H_2 in order to form the bronze. The idea of the double impregnation was to make use of the development of microcracks in the bronze particles which appear during the first hydrogen treatment, i.e., of the enhancement of the specific surface area, to introduce Pt particles in these microcracks.

The four bronzes were then outgassed at 120°C for 14 h and H_2 was added back: ΔX's were as follows: $\Delta X = 0$ for the sample with 0.05% Pt, $\Delta X = 0.12$ for that containing 0.5% Pt, and $\Delta X = 0.2$ for 2% Pt. For the doubly impregnated bronze, ΔX was 0.08. At this stage about 35 Torr C_2H_4 was introduced and the reaction was carried out at 160°C. The yields of C_2H_6 versus time are shown in Fig. 11. The initial rates are 0.016, 0.14, 0.273, and 0.461 × 10^{-3} mole/g h for the bronzes with 0.05, 0.13, 0.5, and 2% Pt, respectively. They are thus in the ratio 1 : 3.1 : 5 : 9.4, whereas the Pt contents are in the ratio 1 : 2.6 : 10 : 40.

If the average radius of the Pt particles is proportional to the cube root of the Pt weight, assuming the number of particles to be constant, the surface areas of these particles should follow the ratio 1 : 1.88 : 4.6 : 11.7.

Thus, except for the doubly impregnated bronze, the initial rates and the average Pt surface areas are more or less in the same ratio. The conversion rate of C_2H_4 into C_2H_6 as well as the rate of the bronze formation and the amount of H_2 added back after outgassing at 120°C are strongly dependent upon the Pt content. For the bronze obtained by double impregnation, the catalytic activity is 1.7 times higher than that for the oxide which had been submitted to a single impregnation treatment, which might indicate that Pt particles are indeed located in the microcracks.

In conclusion, the Pt particles seem to be the gate by which hydrogen may leave the host oxide lattice under vacuum as well as in the hydrogenation reaction. This path-

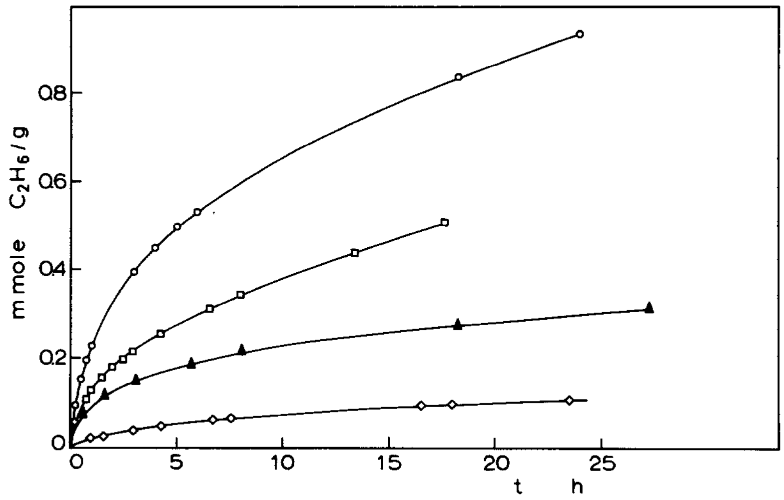

FIG. 11. Influence of the Pt content on the hydrogenation of ethylene at 160°C: ○: 2% Pt; □: 0.5%; ▲: 0.13% Pt; ◇: 0.05% Pt.

way is the opposite to the spillover process and has been called by Sermon and Bond (*25*) the "reverse spillover" phenomenon.

The Reaction Order with Respect to Ethylene and the Activation Energy

A bronze containing 0.5% Pt was reacted at 160°C with 35, 68, and 134 Torr C_2H_4. The initial rates of the reaction were 0.27, 0.32, and 0.30 × 10^{-3} mole/g h, respectively.

At 120°C the corresponding initial rates were 0.044, 0.04, and 0.08 × 10^{-3} mole/g h, whereas at 140°C in the presence of 31, 68, and 137 Torr C_2H_4, 0.08, 0.12, and 0.11 × 10^{-3} mole/g h were measured. It may thus be concluded that the reaction is zero order with respect to C_2H_4.

Plotting the initial rates with respect to the inverse of temperature yields an activation energy of 16.4 kcal $mole^{-1}$ (see Fig. 12), which is of the order of magnitude found by Cirillo and Fripiat (*15*) for the proton correlation time within the oxide lattice measured by NMR.

The Reaction Order with Respect to Hydrogen

This reaction order is difficult to measure since only a fraction of the hydrogen occluded in the solid is used in the hydrogenation reaction. Moreover, there is a progressive change in the availability of H_2 as the outgassing and/or the reaction temperature increase. This has already been illustrated. Under these conditions, it is impossible to measure the reaction order with respect to H_2.

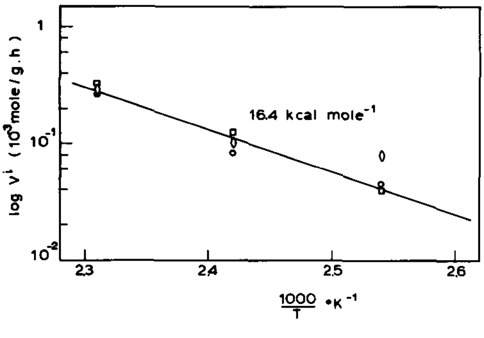

FIG. 12. Arrhenius-type plot for ethylene hydrogenation. $P^i_{C_2H_4}$: 35 Torr (○); 68 Torr (□); and 137 Torr (◇).

TABLE 9

Hydrogenation of C_2H_4 in Presence in H_2 with 0.8 g of 2% Pt H_xMoO_3

$P^i_{C_2H_4}$ (Torr)	$P^i_{H_2}$ (Torr)	V^i (mmole/g h)	nC_2H_6 (after 20 h) (mmole)	$\Delta n'H_2$ (mmole)	$\Delta X'$
32.6	0	0.52	0.81	0.67	0.25
36.9	7.3	0.91	1.52	0.64	0.24
43.3	22.8	3.75	2.16	0.34	0.13
36.5	39.4	8.00	2.62	0.10	0.04

Note. Reaction temperature: 160°C.

Hydrogenation of C_2H_4 Carried out in the Presence of Gaseous H_2

In this series of experiments, the ethylene hydrogenation was performed in the presence of the bronze containing 2% Pt and with a mixture of C_2H_4 and H_2. The reaction temperature was 160°C and the bronze was prepared as usual. Table 9 shows the experimental conditions. As shown in Fig. 13, the completion of the

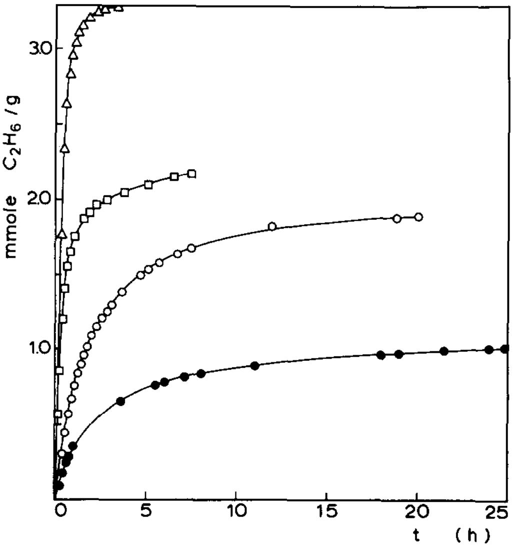

FIG. 13. Hydrogenation of ethylene at 160°C in the presence of H_2. Effect of the hydrogen pressure: ●: no hydrogen; ○; $P^i_{H_2}$ = 7.5 Torr; □: $P^i_{H_2}$ = 22.8 Torr; △: $P^i_{H_2}$ = 39.4 Torr.

reaction occurs more rapidly at increasing pressure of H_2. Plotting the logarithm of the initial rate with respect to the log of $P_{H_2}{}^{i}$ yields a straight line with a slope of about 1.3. $\Delta n'H_2$ and $\Delta X'$ decrease also with the H_2 pressure.

This shows either that gaseous H_2 is consumed first or that the bronze is continuously regenerated. Pt supported on the bronze is a good hydrogenation catalyst which favors the reaction at the expense of H_2 in the gas phase.

CONCLUSIONS

The main conclusions are as follows:

1. Outgassing hydrogen molybdenum oxide bronzes at temperatures higher than 120°C is accompanied by the formation of water molecules, in amounts that depend on the time and temperature of outgassing. Upon removal of water, and hence of oxygen atoms from the host lattice, irreversible structural modifications occur: suboxides are formed and the external surface layers become partially amorphous. Back-titration with hydrogen does not restore the bronze to its initial state.

2. The rate of ethylene hydrogenation which can be related to the rate of the hydrogen reverse spillover, is lower than the rate of spillover. The total number of H atoms which are recovered during the reaction is strongly dependent upon the conditions of the bronze formation and of its outgassing. The linear relationship between the amount of water removed during the conditioning of the bronze and the yield of C_2H_6 suggests that the motion of the H atoms from the bulk toward the Pt particles is inhibited by the perturbations resulting from the conditioning. The more severe the perturbation, the lower is the hydrogen recovery.

3. Despite the fact that the amounts of water formed during the reaction with ethylene are negligible compared to those removed when outgassing the bronze, the experimental results seem to indicate that structural modifications also occur during the catalytic run, but they are probably less important. This may account for the progressive decrease of the reaction rate, and for the loss of activity between successive reactions, although the number of H atoms reinserted between two runs slightly exceeds the number of millimoles of ethane formed after the first run. This effect, which exists in addition to the one due to the conditioning, also contributes to the modification of the diffusion of the H atoms outward. Trace amounts of water, which promote the rate of hydrogen spillover, do not influence the reverse process.

4. Oxygen is a more efficient hydrogen acceptor as compared to ethylene. The oxygen consumption of an undamaged bronze (i.e., a bronze which has not been outgassed) corresponds to the stoichiometry $4H + O_2$, which confirms the results obtained by other authors. In addition, an oxygen treatment has a pronounced influence on the catalytic performances, i.e., on the total number of H atoms retrieved. It also regenerates the activity of the bronze. This might suggest that the suboxides formed during the conditioning are reoxidized.

5. Increasing Pt contents enhance the rate of the bronze formation, and the rate and the conversion of ethylene, i.e., the number of H atoms given back. The Pt particles play a double role: they are the gates by which the H atoms may leave the host lattice and they are the catalytic sites. The microcracks and the cleavage of the particles occurring during the formation of the bronze, as observed by scanning electron microscopy, by decreasing the number of contacts between the Pt clusters and the bronze particles constitute a supplementary factor which probably affects the hydrogen reverse spillover process.

ACKNOWLEDGMENTS

The authors acknowledge the SPPS (Service de Programmation de la Politique Scientifique) for financial support. J. P. Marcq is indebted to IRSIA for a doctoral grant.

REFERENCES

1. Glemser, O., and Lutz, G., *Z Anorg. Allg. Chem.* **264,** 17 (1951).
2. Birtill, J. J., and Dickens, P. G., *J. Solid State Chem.* **29,** 367 (1979).
3. Khoobiar, S., *J. Phys. Chem.* **68,** 411 (1964).
4. Kohn, H. W., and Boudart, M., *J. Catal.* **32,** 304 (1964).
5. Bond, G. C., and Tripathi, J. B. P., *J. Less Common Met.* **36,** 31 (1974).
6. Sermon, P. A., and Bond, G. C., *Trans. Faraday Soc.* **72,** 770 (1976).
7. Bond, G. C., and Tripathi, J. B. P., *Trans. Faraday Soc.* **72,** 933 (1976).
8. Benson, J. E., Kohn, H. W., and Boudart, M., *J. Catal.* **5,** 307 (1966).
9. Levy, R. B., and Boudart, M., *J. Catal.* **32,** 304 (1974).
10. Vannice, M. A., Boudart, M., and Fripiat, J. J., *J. Catal.* **17,** 359 (1970).
11. Dickens, P. G., Moore, J. H., and Neild, N. J., *J. Solid State Chem.* **7,** 241 (1973).
12. Wiseman, P. J., and Dickens, P. G., *J. Solid State Chem.* **6,** 374 (1973).
13. Dickens, P. G., Murphy, D. J., and Halstead, T. K., *J. Solid State Chem.* **6,** 370 (1973).
14. Wright, C. J., *J. Solid State Chem.* **20,** 89 (1977).
15. Cirillo, A., and Fripiat, J. J., *J. Phys. (Paris)* **39,** 247 (1978).
16. Birtill, J. J., and Dickens, P. G., *Mater. Res. Bull.* **13,** 311 (1978).
17. Dickens, P. G., Birtill, J. J., and Wright, C. J., *J. Solid State Chem.* **28,** 185 (1979).
18. Tinet, D., Canesson, P., Estrade, H., and Fripiat, J. J., *J. Phys. Chem. Solids* **41,** 583 (1979).
19. Tinet, D., and Fripiat, J. J., *J. Chim. Phys.* **76,** 867 (1979).
20. Schöllhorn, R., *Angew. Chem. Int. Ed. Engl.* **19,** 983 (1980).
21. Taylor, R. E., Silva-Crawford, M. M., and Gerstein, B. C., *J. Catal.* **62,** 401 (1980).
22. Taylor, R. E., Ryan, L. M., Tindall, P., and Gerstein, B. C., *J. Chem. Phys.* **73,** 5500 (1980).
23. Slade, R. C. T., Halstead, T. K., and Dickens, P. G., *J. Solid State Chem.* **34,** 183 (1980).
24. Cirillo, A. C., Ryan, L., Gerstein, B. C., and Fripiat, J. J., *J. Chem. Phys.* **73,** 3060 (1980).
25. Sermon, P. A., and Bond, G. C., *Catal. Rev. Sci. Eng.* **8,** 211 (1973).
26. Bond, G. C., Sermon, P. A., and Tripathi, J. B. P., *Ind. Chim. Belge* **38,** 506 (1973).
27. Sermon, P. A., and Bond, G. C., *Trans. Faraday Soc.* **76,** 889 (1980).
28. Neikam, W. C., U.S. Patent 3.883.607 (1975).
29. Tseung, A. C. C., and Hobbs, B. S., Brit. Patent 1.309.636 (1973).