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Hydrogenation by Hydrogen Bronzes

II. Hydrogenation of Ethylene by $H_xV_2O_5$

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Hydrogen vanadium oxide bronzes have been prepared by spillover of hydrogen from supported Pt particles. The crystallinity of the starting oxide disappears progressively during the insertion of hydrogen so that a bronze with an initial stoichiometry of about $H_{3.3}V_2O_5$ is quasi-amorphous. The recovery of the occluded hydrogen, using ethylene as a hydrogen-accepting molecule, depends upon the conditioning temperature, the reaction temperature, and principally on the amount of hydrogen initially inserted in the bronze. Molecular hydrogen and water are released upon outgassing. Upon back-titration with hydrogen, the initial stoichiometry of the bronze can be restored as long as the pretreatment or reaction temperature does not exceed 120°C. During the reaction with ethylene, CO_2 and H_2O are also formed. There is an inverse relationship between the ethane produced and the amount of oxygen extracted from the oxide lattice. Oxygen treatment results in the formation of crystalline V_2O_4. Back-titration with hydrogen cancels out this phase and the catalytic activity is only partly restored. Pt loadings up to 1% increase markedly the yields of ethane. Comparison is made between the present results and those obtained in a previous study on hydrogen molybdenum bronzes.

INTRODUCTION

The formation process and some of the physical properties of $H_xV_2O_5$ with $3.4 < x < 3.8$ have been recently reported (*1*). Crystalline powdered V_2O_5 is impregnated with 2% Pt (from H_2PtCl_6) and exposed to molecular hydrogen so that the vanadium hydrogen bronze is formed by the hydrogen spillover mechanism.

The rate of formation is slower by a factor of the order of 10 with respect to that reported under similar conditions for $H_{1.6}MoO_3$.

$H_xV_2O_5$ with $x > 3$ is X-ray and neutron diffraction quasi-amorphous so that it is impossible a priori to claim that the material characterized by $x \leq 3.8$ is a mixture of non-inserted and fully inserted oxide, as was the case for H_xMoO_3 (*2*).

The infrared spectrum of $H_{3.3}V_2O_5$ does not show an OH content exceeding that expected for a monolayer coverage of the surface area, namely ~10 m^2/g, but V–H stretching bands appear in the region 1100–1200 cm^{-1}. Both the NMR and the ir results stem from a direct link between V and H, the V–H bond length being about 2 Å, as discussed thoroughly by Tinet and Fripiat (*3*).

XPS studies of $H_{\sim 3}V_2O_5$ reveals a surface composition with about 52% V^{4+}, 36% V^{3+}, and 12% V^{5+} (*1*).

The physical characterization performed by Tinet and Fripiat (*3*) indicates that a transition of several properties occurs at about $x = 3.3$. Below this stoichiometry a strong EPR signal which can be assigned to V^{4+} is observed. Above $x = 3.3$, this signal disappears. This has been explained in terms of magnetic transitions, originating from the interactions between V^{4+} and V^{3+} paramagnetic species, between a frustrated superparamagnetic state ($x < 3.3$) and a

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non-frustrated superparamagnetic state ($x > 3.3$).

No information on the mobility is obtained from the NMR study because the spin-lattice relaxation mechanism is dominated completely by the paramagnetic centers and the lines are too broad. Quasi-elastic neutron scattering indicates that the proton diffusion coefficient is at least 2 orders of magnitude lower than that observed for $H_{1.6}MoO_3$, at room temperature (*4*).

Recently, Legay *et al.* (*5*) have shown, by electrochemical methods, the existence of five different domains in the range $0 < x < 3$. They are observed for the following values of $x: 0 < x < 0.5$ (domain I), $0.5 < x < 1.0$ (II), $1 < x < 1.5$ (III), $1.5 < x < 2.2$ (IV), and $2.2 < x < 3.0$ (V).

In domains I and II, only V^{4+} species are present; in domain III, V^{3+} species appear; V^{3+} and V^{4+} species are created in equal number in domain IV, while in domain V, these two species tend to form V^{3+}–V^{4+} pairs.

These results confirm partially those of Schöllhorn (*6*), who found two different kinds of vanadium bronze: β-$H_{0.5}V_2O_5$ and ε-$H_{0.8}V_2O_5$.

The interesting catalytic properties of the $H_{1.6}MoO_3$ hydrogen reservoir recently published (*7–10*) prompted us to carry out a comparable study with $H_xV_2O_5$. This paper is devoted to that purpose and, in addition, a comparison with the behavior of $H_{1.6}MoO_3$ will be attempted. For both materials, a simple reaction, namely the hydrogenation of ethylene into ethane, has been studied.

EXPERIMENTAL

The apparatus used in this study is the same as that described in a previous paper (*10*).

Materials. Analytical grade V_2O_5 was impregnated with $H_2PtCl_6 \cdot 6H_2O$ according to the procedure reported earlier (*10*). Unless indicated, the Pt loading was in all cases 2.4 wt%.

Preparation of the bronze. The impregnated oxide was heated under vacuum at 200°C for 2 h. This treatment results in the partial decomposition of H_2PtCl_6 into $PtCl_4$ and $PtCl_2$. The temperature was then lowered to 60–65°C and the powder was exposed to 200 Torr of H_2 in the presence of a liquid nitrogen getter. The consumption of H_2 was measured and assigned to the bronze formation, the amount corresponding to the reduction of $Pt^{4+} \rightarrow Pt^0$ being negligible with respect to the amount of H_2 inserted. The excess H_2 was removed by rapidly degassing the material at 60°C, using a primary vacuum pump.

Reaction conditions. The reaction was carried out by circulating C_2H_4 onto the catalyst for periods of time up to 24 h and pressures between 40 and 140 Torr of C_2H_4. As in the parallel study carried out with H_xMoO_3, about 0.8 g of catalyst was used.

Chromatographic analysis. The procedure is the same as that mentioned in Part I (*10*). C_2H_6, C_2H_4, and eventually H_2, H_2O, CO_2, and CH_4 were quantitatively determined with a 5880 H.P. chromatograph using a Porapak Q column and He as carrier gas.

RESULTS AND DISCUSSION

The experimental results will be described in the following sequence. After looking at the change of the crystallinity of V_2O_5 during the formation of the bronze, the effect of outgassing the bronze in the temperature range between 60 and 160°C will be discussed from the point of view of hydrogen removal as water as well as molecular H_2. Water evolution is especially important to measure in the present case, since there are no simple physical techniques which demonstrate the formation of lower oxides, the freshly prepared bronze being quasi-amorphous. The influence of the reaction temperature and of the hydrogen content on the catalytic activity of $H_xV_2O_5$ will then be described.

Finally, we shall consider the effect of an oxygen treatment on the performance of

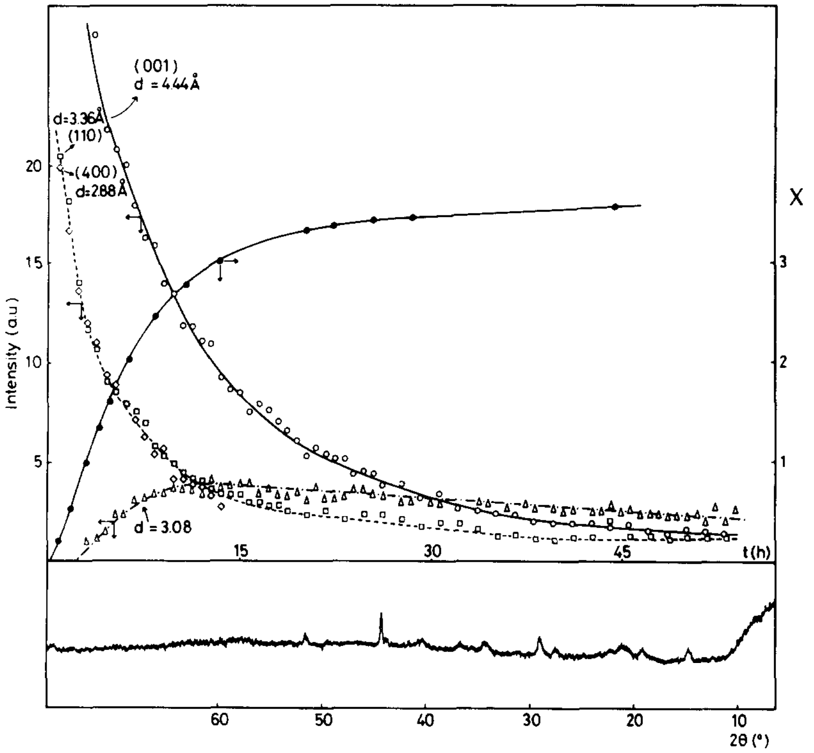

FIG. 1. Upper part: Change of the X-ray peak intensity (in arbitrary units) of the 001, 110, and 400 diffraction lines of V_2O_5 (open symbols) and of X (full symbols) during the formation of $H_xV_2O_5$. Lower part: X-ray diffractogram of $H_{3.8}V_2O_5$.

$H_xV_2O_5$, the reaction order with respect to ethylene pressure and the influence of the Pt content on the reaction rate.

Change of the Crystallinity during the Bronze Formation

The loss of crystallinity occurring during the formation of the bronze has been followed by X-ray diffraction, using a camera wherein the sample could be outgassed and heated. A sample of Pt/V_2O_5 previously heated under vacuum at 200°C was slightly compressed in the sample holder of the camera. After outgassing at room temperature, the oxide was heated at 60°C in the presence of pure hydrogen (200 Torr). The diffractograms were recorded between 18 and 38°2θ (Cu$K\alpha$ radiation) at time intervals of 45 min for over 50 h at a rate of 1/2°2θ/min.

Figure 1 shows the change of the intensity of the 001, 110, and 400 diffraction lines of V_2O_5 as a function of time. This figure also illustrates the kinetics of insertion of hydrogen into the oxide lattice. Obviously, there is an inverse relationship between the loss of the X-ray peak intensities and the hydrogen uptake. At the end of the formation, the solid is quasi-amorphous. Note that there is a new diffraction line (d = 3.08 Å) developing at the early stage of the formation of the bronze and which has almost the same intensity for $X > 2.5$. The lower part of Fig. 1 shows the diffractogram of a typical fresh bronze.

Effect of the Outgassing Conditions

The outgassing was carried out for 24 h either under "static" vacuum (no pumping) with a cold trap or under "dynamic" vacuum, the residual pressure being of the order of 10^{-5} Torr.

As shown in Table 1, at 120°C a small fraction of the inserted hydrogen is re-

TABLE 1

Influence of the Outgassing Temperature on the Formation of Water under Static Vacuum in the Presence of a Liquid-N_2 Getter (V_{12} – V_{15}) and under Dynamic Vacuum (V_2)

	Run		
	V_{12}	V_{15}	V_2
Sample weight (g)	0.8495	0.8458	0.8107
nH_2 (mmol)	7.65	8.20	7.26
X_{initial}	3.63	3.71	3.44
Outgassing temperature (°C)	120	160	60
$\Delta X(H_2O)$	0.03	0.45	NM[a]
$\Delta X(H_2)$	0.12	0.07	NM
ΔX tot.	0.15	0.52	NM
ΔnH_2 (tit.)(mmol)	0.30	0.53	0.84
ΔX (tit.)	0.14	0.24	0.40

[a] Not measurable.

moved as molecular hydrogen $\Delta X(H_2)$ under static vacuum. For the bronze outgassed at 60°C under dynamic conditions this fraction is appreciably higher, as inferred from the value of ΔX(tit.). It appears that pumping may decrease X down to about 3.

In Table 2 the percentages of the hydrogen recovered as $H_2 + H_2O$ after outgassing freshly prepared bronzes at 120 or 160°C, the fractions of this hydrogen which are reinserted upon back-titration and the fractions of H_2 that are irreversibly lost at the outgassing step are compared with the corresponding values obtained for $H_{1.6}MoO_3$ treated under similar conditions.

It may be concluded that, as for the molybdenum bronze, the initial stoichiometry of the vanadium bronze can be almost completely restored when the outgassing temperature does not exceed 120°C.

An outgassing at 160°C has a more pronounced effect on the reversibility of H_xMoO_3 than is the case for $H_xV_2O_5$.

Catalytic Activity

The effect of the reaction temperature on the catalytic activity of bronzes (2.44% Pt) with initial stoichiometry $X_{\text{in}} = 3.62 \pm 0.06$ is illustrated in Fig. 2, where the values of ln V have been plotted against ΔX calculated from the yield in ethane. The experimental data are given in Table 3.

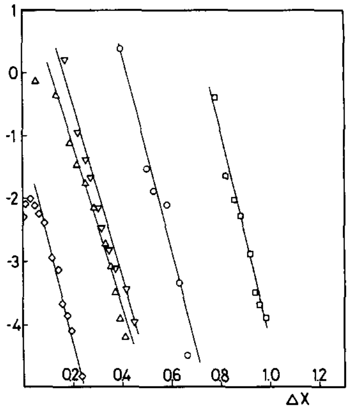

FIG. 2. Effect of the temperature on the reaction of C_2H_4 with $H_xV_2O_5$ ($X = 3.62$, $P^{i}_{C_2H_4} = 46 \pm 5$ Torr). Relationship between ln V and ΔX at: 60°C ◇ ; 80°C △; 100°C ▽; 120°C ○; and 160°C □.

Obviously, the slope of these relationships is not affected by the reaction temperature.

The rate equation may be written as

$$V = \frac{d(nC_2H_6)}{dt} = \frac{d(\Delta X)}{dt} = k \exp^{-B\Delta X} \qquad (1)$$

where $\Delta X = X_{\text{in}} - X_t$ and $B = 16$. In this

TABLE 2

Percentage of the Hydrogen Recovered as H_2 and H_2O (a), Fraction Reinserted by Back-titration with H_2 (b), and Percentages of Hydrogen Irreversibly Lost (c) after Outgassing $H_xV_2O_5$ and H_xMoO_3 in Static Vacuum at 120 and 160°C

	Outgassing temperature (°C)			
	$H_xV_2O_5$		H_xMoO_3	
	120	160	120	160
(a) $\frac{\Delta X \text{ tot.}}{X \text{ in.}} \cdot 100$	4.2	14	3.3	16
(b) $\frac{\Delta X \text{ (tit.)}}{\Delta X \text{ tot.}} \cdot 100$	95	46	80	35
(c) $\frac{\Delta X \text{ tot} - \Delta X \text{ (tit.)}}{X \text{ in.}} \cdot 100$	0.2	7.5	0.7	11

TABLE 3

Influence of the Reaction Temperature on the Hydrogenation of Ethylene

		Run				
		V_{11}	V_{10}	V_7	V_{14}	V_{13}
Bronze formation	Sample weight (g)	0.7358	0.7764	0.7854	0.7939	0.8504
	nH_2 (mmol)	7.06	7.34	7.45	7.36	8.06
	X initial	3.68	3.63	3.64	3.56	3.62
Reaction with C_2H_4	Temperature (°C)	60	80	100	120	160
	$P^i_{C_2H_4}$ (Torr)	41.84	44.58	42.66	49.90	51.76
	V^i (mmol/g h)	0.12	0.89	2.41	5.31	10.40
	nC_2H_6 (fin.) (mmol/g)	0.67	1.31	1.33	1.85	2.75
	nH_2O (fin.) (mmol/g)	0	0	0	0	0.26
	nCH_4 (fin.) (mmol/g)	0	0	0	0.004	0.024
	nCO_2 (fin.) (mmol/g)	0	0	0	0.03	0.12
	ΔX recovered	0.26	0.50	0.51	0.71	1.17
Back-titration at 60°C	$\Delta n'H_2$ (tit.) (mmol/g)	—	—	—	1.76	2.25
	$\Delta X'$ (tit.)	—	—	—	0.68	0.86
	$\Delta n'H_2$ (untit.) (mmol/g)	—	—	—	0.98	0.81

expression, k, the initial rate, is influenced by the temperature according to

$$k = k_0 \exp \frac{-E_A}{RT} \tag{2}$$

The experimental value of E_A is 36.9 kcal/mol.

Integrating (1) $\displaystyle\int_0^{(\Delta X)_t} \frac{d(\Delta X)}{\exp^{-B\Delta X}} = \int_0^t k\,dt$

yields

$$\frac{1}{B}\,[\exp\{B(\Delta X)_t\} - 1] = kt \tag{3}$$

or

$$(\Delta X)_t = \frac{1}{B}\ln[B\,kt + 1] \tag{4}$$

In (4), $(\Delta X)_t = 0.384\ (nH_2)_t = 0.384\ (nC_2H_6)_t$, i.e., the number of mmoles of hydrogen given back at time t, or the number of millimoles of ethane formed at time t. Hence,

$$(nC_2H_6)_t = \frac{2.606}{B}\ln[B\,kt + 1] \tag{5}$$

Introducing (2) into (5) gives

$$(nC_2H_6)_t = \frac{2.606}{B}\ln[Bt\,k_0\exp^{-E_A/RT} + 1] \tag{6}$$

By replacing in (6) B, k_0, and E_A by their experimental values, a good agreement between the observed and calculated values of nC_2H_6 is obtained.

It was interesting to see whether a similar relationship would be obtained when starting with incompletely inserted bronzes. Bronzes with $X_{in} = 1.06$, 2.07, 3.01, 3.39, and 3.64 were thus reacted with ethylene at 100°C, $P^i_{C_2H_4}$ being of the order of 42 ± 2 Torr. The change of ln V as a function of ΔX for the different bronzes is shown in Fig. 3. Linear relationships are obtained with slopes (B) that depend upon X_{in}, up to $X_{in} = 3.4$ (see Fig. 4a), according to the equation

$$B = e^{6.88}\,X_{in}^{-3.66} \tag{7}$$

Extrapolating ln V to $\Delta X = 0$ yields the logarithm of the initial rate, ln k. Figure 4b shows that for X_{in} ranging between 1 and 3.4, a linear relationship is obtained between ln k and X_{in}. Its equation is given by

$$\ln k = 2.49X_{in} - 6.01 \tag{8}$$

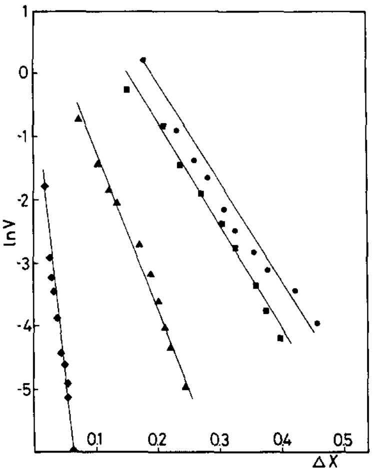

FIG. 3. Hydrogenation of ethylene at 100°C ($P^{i}_{C_2H_4}$ = 42 ± 2 Torr) by $H_xV_2O_5$ with different values of X_{in}: change of ln V vs ΔX: X_{in} = 2.07 ◆; 3.01 ▲; 3.39 ■; 3.64 ●.

By replacing in Eq. (1) (in its logarithmic form) ln k and B by their experimental values, it follows that

$$\ln V = 2.49X_{in} - 6.01 - [X_{in}^{-3.66}e^{6.88}]\,\Delta X \quad (9)$$

For $X_{in} \geq 3.4$, i.e., for bronzes that are fully inserted, ln k and ln B tend toward a constant value. For $X_{in} < 1$, the rate is not measurable, while between 1 and 3.4, it increases continuously with X_{in}. In the light of the findings of Legay *et al.*, the chemical activity of the vanadium oxide bronze requires the presence of V^{3+} species, since it is only for the domains where such species have been evidenced that the hydrogenation of ethylene takes place.

The effect of temperature on the reaction rate may be written, in a general way, as

$$V = k_0^* \exp^{-\Delta F^*/RT} = k^* \exp^{-\Delta H^*/RT} \exp^{\Delta S^*/R} \quad (10)$$

The empirical law obtained by introducing (2) into (1) is given by

$$V = k_0 \exp^{-E_A/RT} \exp^{-B\Delta X} \quad (11)$$

In (11), B is constant and independent of temperature when $X_{in} \geq 3.4$. Below this value, B depends upon X_{in} at a given temperature. If one assumes that $E_A \simeq \Delta H^*$, (10) and (11) give

$$k_0^* \exp^{\Delta S^*/R} = k_0 \exp^{-B\Delta X} \quad (12)$$

where k_0 is a function of X_{in}, or

$$\ln \frac{k_0^*}{k_0} = -B\Delta X + \frac{\Delta S^*}{R} = -B(X_{in})[X_{in} - X_t] + \frac{\Delta S^*}{R}$$

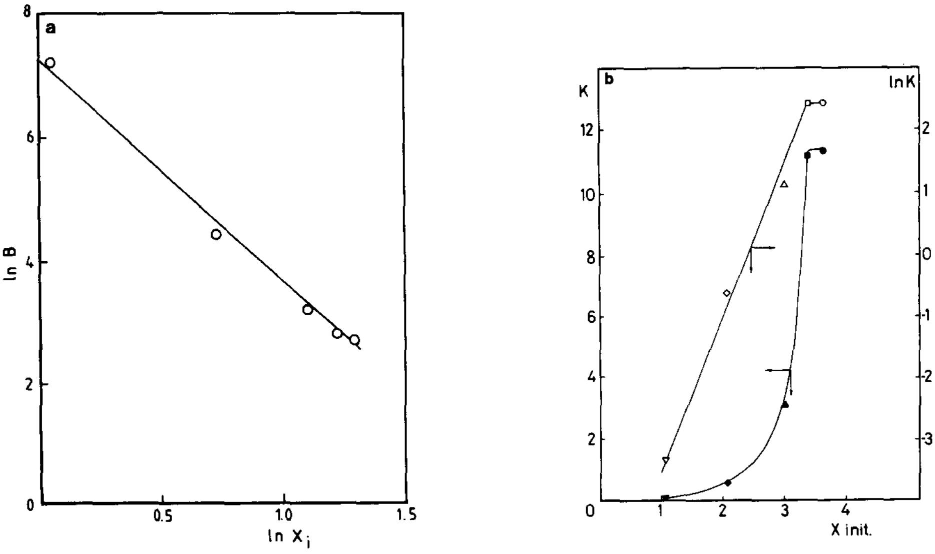

FIG. 4. (a) Relationship between ln B and ln X_{in}. (b) Relationship between ln k (k = initial rate of reaction) and X_{in} (initial insertion rate).

TABLE 4

Influence of the Outgassing Temperature on the Hydrogenation of Ethylene at 160°C (See also Table 1)

	Run	
	V_{12}	V_{15}
Outgassing temperature (°C)	120	160
$P^{i}_{C_2H_4}$ (Torr)	51.26	40.00
V^{i} (mmol/g h)	6.73	6.48
nC_2H_6 (fin.) (mmol/g)	3.14	1.85
nH_2O (fin.) (mmol/g)	0.30	0.00
nCH_4 (fin.) (mmol/g)	0.03	0.02
nCO_2 (fin.) (mmol/g)	0.35	0.05

or

$$\Delta S^* = R \ln \frac{k_0^*}{k_0} + RB\Delta X = R \ln \frac{k_0^*}{k_0} + RB(X_{\text{in}})[X_{\text{in}} - X_t]$$

and

$$\frac{d\Delta S^*}{d\Delta X} = RB$$

Thus, the variation of entropy per mole of H_2 given back by the bronze would be constant for a given X_{in}.

When compared with experiments carried out under similar conditions (160°C, 2.44 wt% Pt, $P^{i}_{C_2H_4} = 42$ Torr) on $H_{1.6}MoO_3$, the initial rate of the reaction is much higher for $H_{3.6}V_2O_5$: the ratio is 20 in favor of the vanadium bronze and nC_2H_6 produced after 20 h is about 3 times as high.

Moreover, when the values of ln V are plotted against ΔX for H_xMoO_3, the slope of the linear relationships is affected by the reaction temperature, which suggests that the motion of the H atoms from the bulk toward the Pt particles, upon which the reaction is supposed to occur, is rate limiting.

The amount of hydrogen recovered as water, $\Delta X(H_2O)$, corresponds to 0.10 when using the vanadium bronze (see Table 3) whereas water was practically not detectable for the molybdenum bronzes (*10*). In addition, after 20 h of reaction at 160°C, CO_2 is produced with the vanadium bronze, the ratio CO_2/C_2H_6 being 0.045. CO_2 was not detected with the molybdenum bronze. These observations indicate that at 160°C the oxidizing power of $H_xV_2O_5$ is higher than that of H_xMoO_3, as might be expected from the behavior of the two oxides (*11*).

The amounts of ethane produced at the end of the reaction at 120 and 160°C (see Table 3) correspond to hydrogen recoveries of 20 and 32.3%, respectively, of the total hydrogen inserted in the fresh bronze. Upon back-titration with hydrogen, 96 and 73% of the hydrogen recovered are reintroduced into the oxide lattice. This again shows that the bronze is almost totally reversible for temperatures below 120°C.

The effect of the pretreatment temperature on the catalytic activity has been measured on the bronzes outgassed at 120 and 160°C in the presence of a getter and back-titrated after pretreatment (see Table 1). The reaction temperature was 160°C. As shown in Table 4, less ethane is produced from the sample pretreated at 160°C, but in this case no water is formed during the reaction.

These results and those of Table 1 show that a fraction of the total oxygen content of the bronze can be extracted from the lattice either as H_2O and/or CO_2. When this fraction is removed during the pretreatment (namely at 160°C), the back-titration does not restore the hydrogen content to its value in the freshly prepared bronze. As a result, the activity of the bronze is depressed and only minor amounts of water and CO_2 are further formed during the reaction with ethylene. On the contrary, when the pretreatment is carried out under conditions such that the formation of water is negligible (i.e., 120°C), the hydrogenation activity at 160°C is higher and so are the amounts of H_2O and CO_2 among the reaction products.

In another set of experiments, successive hydrogenation reactions have been carried out at 160°C on the same bronze ($X_{\text{in}} = 3.62$ in the freshly prepared bronze). At the end

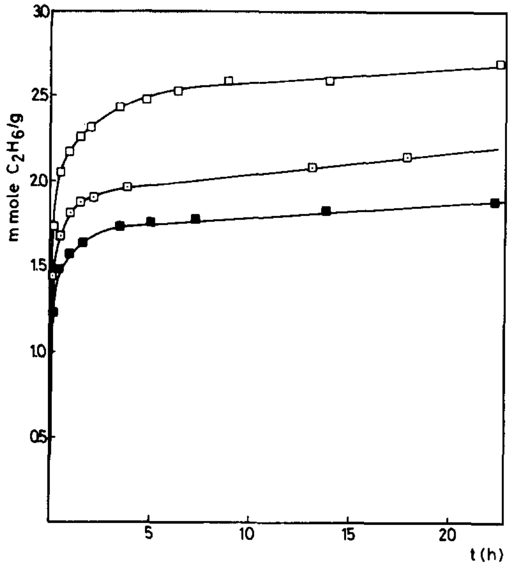

FIG. 5. Repeated hydrogenation reactions at 160°C on the same bronze (X_{in} = 3.62) with back-titration between two runs: □, ⊡, and ■: first, second, and third runs, respectively.

of each run, the reaction apparatus was evacuated and the bronze was back-titrated with H_2 at 60°C.

As shown in Fig. 5, the kinetic functions are similar, but there is a progressive loss of activity between two successive runs. A similar trend is observed for the amounts of CO_2 and H_2O produced (see Table 5).

The loss of structural oxygen atoms may explain, as was proposed for the molybdenum bronzes, why the amounts of H_2 reinserted during back-titration diminish from one run to the next (see Table 5). As a result, there is an increasing discrepancy between the hydrogen content of the initial bronze and the real H content in the back-titrated bronze at the beginning of the second and third runs. As shown in Fig. 6, this difference is proportional to the amount of oxygen atoms lost as H_2O and CO_2. A similar relationship was also observed for H_xMoO_3. Since the conversion of ethylene into ethane is strongly dependent upon X, less and less ethane is formed as the number of runs increases.

In this case also, there is a linear relationship between the slope (B) and X_{in} at the beginning of each run, and the following empirical equation applies

$$B = e^{11} X_{in}^{-6.4}$$

TABLE 5

Successive Catalytic Runs Performed at 160°C

	First run	Second run	Third run
V^i (mmol/g h)	10.40	8.66	7.40
nC_2H_6 (after 4 h) (mmol/g)	2.47	1.96	1.74
nC_2H_6 (fin.) (mmol/g)	2.75	2.28	1.89
nH_2O (fin.) (mmol/g)	0.26	0.12	0.08
nCH_4 (fin.) (mmol/g)	0.02	0.01	0.01
nCO_2 (fin.) (mmol/g)	0.12	0.08	0.05
nO (fin.)[a] (mmol/g)	0.51	0.28	0.18
$\Delta n'H_2$ (tit.) (mmol/g)	2.25	2.05	1.88
$\Delta X'$ (tit.)	0.86	0.78	0.72
$\Delta n'H_2$ (untit.)[b] (mmol/g)	0.66	0.28	0.05

Note. Sample weight: 0.8504 g; X_{in} = 3.62 ($nH_{2\,in}$ = 9.434 mmol H_2/g); $P^i_{C_2H_4}$ = 52.3 ± 0.5 Torr.

[a] nO (fin.) = nH_2O (fin.) + $2nCO_2$ (fin.).

[b] $\Delta n'H_2$ (untit.) = nC_2H_6 (fin.) + nH_2O (fin.) + $2nCH_4$ (fin.) $-\Delta n'H_2$ (tit.) $- nCO_2$.

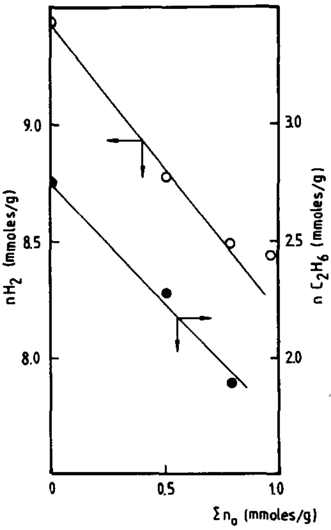

FIG. 6. Relationship between the hydrogen content (nH_2) at beginning of each run (○) or between the amount of ethane produced, nC_2H_6 (●) and the quantity of lattice oxygens removed as H_2O and CO_2, ΣnO.

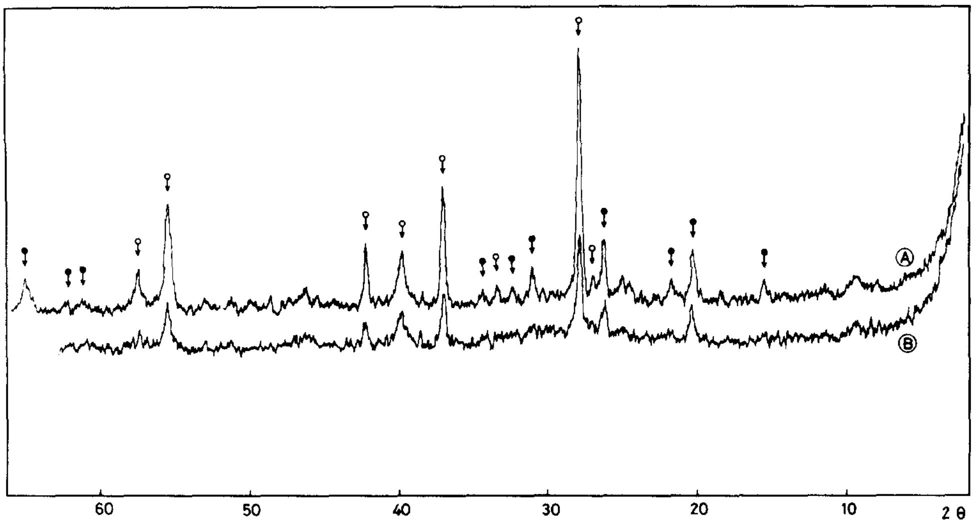

FIG. 7. X-Ray diffractograms after oxygen treatment at 120 (A) and 160°C (B). Open symbols refer to the diffraction lines of V_2O_4; full symbols: V_2O_5.

As for Eq. (7), the slope (*B*) increases as X_{in} decreases but the exponents are greater at 160°C than at 100°C.

For the molybdenum bronze, the loss of activity between two successive runs was more pronounced. Indeed, with respect to the amount of C_2H_6 formed after 20 h of reaction at the first run, the yields of C_2H_6 at the end of the second and third runs represented 64 and 40%, respectively. For $H_xV_2O_5$, the corresponding values are 81% for the second run and 70% for the third run.

Oxygen Treatment

As reported by Tinet *et al.* (*1*), after exposing $H_{3.8}V_2O_5$ to gaseous oxygen at 65°C, in the presence of a 3A molecular sieve getter, 90% of the initial hydrogen content is reinserted upon back-titration. Thus the oxidation–reduction process is apparently reversible, as was observed for $H_{1.6}MoO_3$. For the molybdenum bronze, the oxygen treatment at 160°C followed by back-titration at 60°C was found to restore the activity for the conversion of ethylene (*10*). It was therefore interesting to submit the vanadium bronze to a similar treatment.

Two freshly prepared bronzes (containing 2.4% Pt) were exposed to 230 Torr of O_2 (purity 99.999%) at 120 and at 160°C for 20 h. The introduction of O_2 was accompanied by a highly exothermic effect. The water was continuously withdrawn using a frozen *n*-heptane getter. The O_2 consumption and water formation were determined by measuring the O_2 pressure drop and by gas chromatography, respectively. Most of the pressure drop occurs during the first hour. The X-ray diffractogram indicates the formation of V_2O_4 and of some V_2O_5, but these crystalline compounds represent only a fraction of the sample (see Fig. 7).

Afterwards the samples were exposed to dry H_2 at 60°C. The hydrogen pressure drops still faster (namely within about 5 min). The hydrogen reintercalation is extremely exothermic and water is again formed. This reaction component trapped in a liquid-N_2 getter was again analyzed by gas chromatography. The experimental data, given in Table 6, show that at both temperatures, the oxygen consumption exceeds by a large margin the water formed.

A similar observation has been reported for the molybdenum bronze (*10*). Noteworthy are the unusually high amounts of water

TABLE 6

Effect of Oxygen Treatment at 120 and 160°C on the Catalytic Performances of $H_xV_2O_5$

Successive steps of the experiments	Sample weight (g)	Run	
		V_{33} 0.8262	V_{39} 0.8515
1. Bronze formation at 60°C	nH_2 (mmol)	7.72	8.46
	X_{in}	3.59	3.81
2. Oxygen treatment	Temperature (°C)	120	160
	Time (h)	20	20
	$P^i_{O_2}$ (Torr)	233.40	219.80
	ΔnO_2 (mmol)	2.97	3.11
	ΔXO_2	2.76	2.80
	nH_2O (mmol)	2.39	2.20
	ΔX (H_2O)	1.11	0.99
3. Back-titration at 60°C	ΔnH_2 consumed (mmol)	5.80	5.69
	nH_2O (mmol)	1.34	0.61
	ΔnH_2 (tit.)	4.46	5.07
	ΔX (tit.)	2.07	2.29
4. Reaction with C_2H_4 at 120°C	$P^i_{C_2H_4}$ (Torr)	59.26	47.42
	V^i (mmol/g h)	4.89	4.74
	nC_2H_6 (after 4 h) (mmol/g)	1.35	1.25
	nC_2H_6 (fin.) (mmol)	1.26	1.24

formed during the back-titration. The hydrogen reinserted in the solid, ΔX(tit.), is lower than the amount recovered during the oxygen treatment, ΔX O_2, even at 120°C. As seen earlier, at this temperature the stoichiometry of the bronze outgassed could be restored to its initial value. The X-ray diffractogram of the back-titrated sample no longer shows the V_2O_4 phase.

As shown in Table 6, in spite of their high hydrogen content, the reduced samples have a lower hydrogenating activity for conversion of ethylene into ethane (compare the values of nC_2H_6 (fin) of run V_{33} with the corresponding value for V_{14} in Table 3). Their behavior is thus markedly different from the molybdenum bronzes treated in a similar way.

Reaction Order with respect to Ethylene

Two bronzes (X_{in} = 3.66 ± 0.03) prepared at 60°C were reacted with 49 and 130 Torr C_2H_4 at 120°C. As for the molybdenum bronzes, a zero-order with respect to ethylene was found.

Influence of the Pt Content

V_2O_5 was impregnated with different amounts of H_2PtCl_6 in order to load the oxide with 0.03, 0.12, 0.61, 1, and 2.4% Pt. The bronzes were formed as usual at 60°C. The insertion rate of hydrogen for the sample containing 0.03% Pt was very slow, so that after 6 weeks, X_{in} was only 2.05. For all the other bronzes, X_{in} was 3.7 ± 0.04. They were reacted with C_2H_4 ($P^i_{C_2H_4}$ = 46 Torr) at 120°C.

As shown in Fig. 8, the yield of C_2H_6 obtained at the end of the reaction increases markedly up to 1% Pt. Higher Pt loadings do not increase any more the ethane production. A similar effect was also observed for the molybdenum bronzes, but the production of ethane was lower. It should be noted that the value of B in Eq. (1) is independent of the Pt content, while k varies with the metal loading.

The reality of the so-called reverse spillover appears thus at first sight questionable. However, the BET surface area of V_2O_5 is about 3 times larger than that of MoO_3. This seems to favor a better dispersion of the Pt particles, as observed on the scanning electron micrograph in Fig. 9, which shows a more homogeneous distribution of the Pt particles (about 100–200 Å in diameter). No segregated large Pt particles

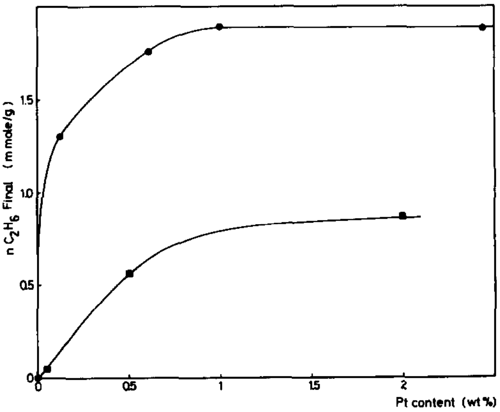

FIG. 8. Influence of the Pt loading on the yields of ethane produced after 20 h of reaction at 120°C ($P^i_{C_2H_4}$ = 46 Torr). ●: $H_xV_2O_5$; ■: H_xMoO_3.

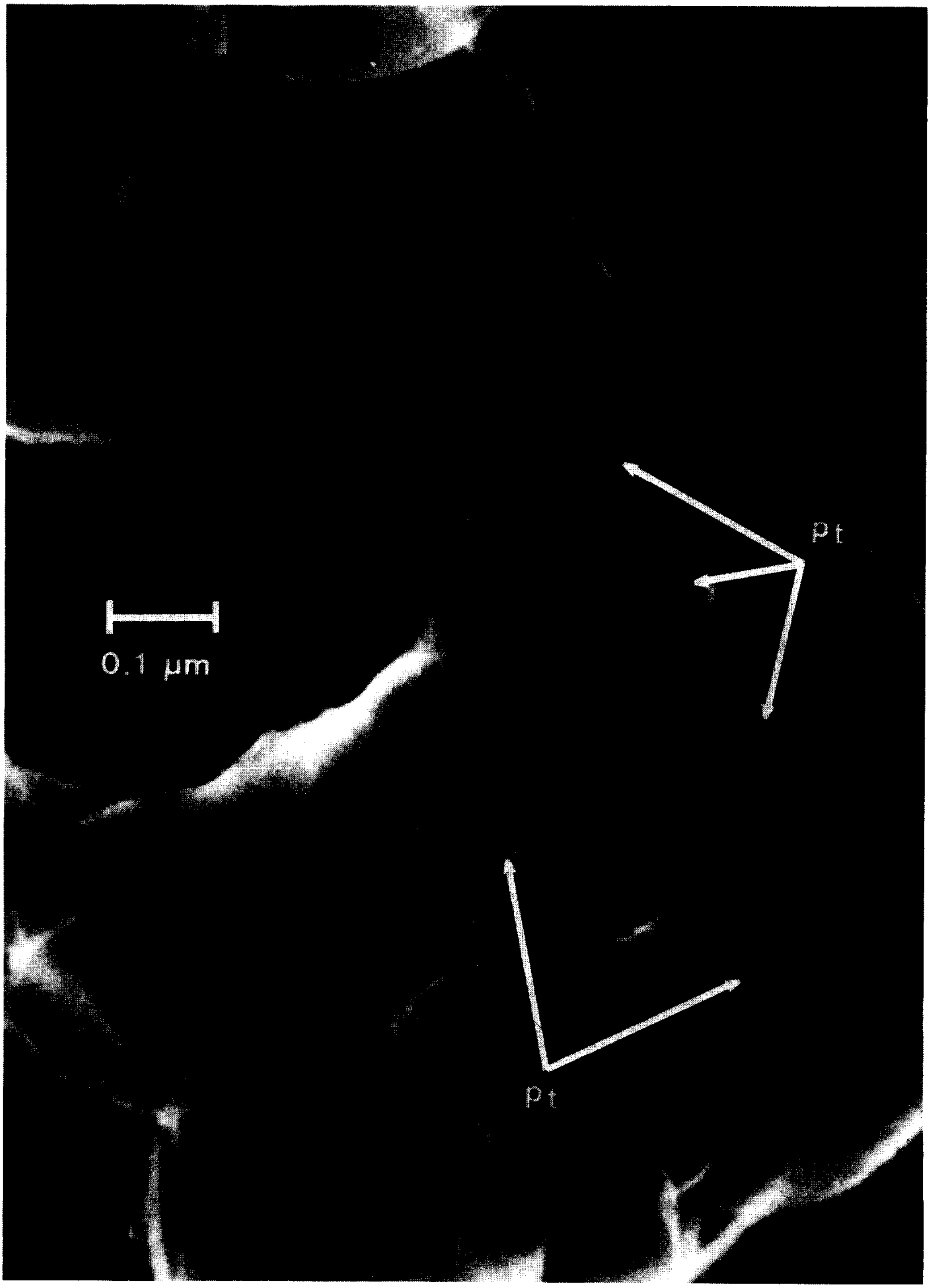

FIG. 9. Scanning electron micrograph of $Pt/H_xV_2O_5$. Arrows indicate Pt particles.

could be observed, as was the case for the molybdenum bronzes, where the distribution was much more heterogeneous.

CONCLUSIONS

The results show that the hydrogen vanadium bronzes behave to a certain extent like the hydrogen molybdenum bronzes, but in other respects the two bronzes are quite different. The main conclusions can be summarized as follows:

1. The general shape of the insertion kinetics of hydrogen into the vanadium oxide lattice is similar to that observed for the molybdenum bronze, but the H/M ratio is slightly higher in the former (1.9) than in the latter (1.6) which is also more readily formed.

2. The formation of the hydrogen vanadium bronze is accompanied by a loss of crystallinity while the crystallinity of the molybdenum bronze was relatively better preserved. The more pronounced amorphous character of $H_xV_2O_5$ may reflect its greater heterogeneity.

3. As was the case for H_xMoO_3, back-titration with hydrogen of $H_xV_2O_5$ that has been conditioned under vacuum restores the stoichiometry nearly to its value in the freshly prepared bronze, as long as temperatures not higher than 120°C have been used. However, the reversibility is better achieved in the case of the vanadium bronze. For both bronzes, the outgassing temperature clearly affects the hydrogen recovery in the reaction with ethylene.

4. The initial rate of hydrogenation of ethylene is much higher for $H_xV_2O_5$ than for H_xMoO_3. The amounts of ethane obtained at the end of the reaction are three times higher for $H_xV_2O_5$ than for H_xMoO_3. Note that a similar factor exists between the surface areas of the starting oxides (1.7 m^2/g for MoO_3 and 5 m^2/g for V_2O_5).

5. Even as bronzes, the vanadium pentoxide compound remains more oxidizing than molybdenum trioxide. Water is more easily formed from $H_xV_2O_5$ than from H_xMoO_3 during the outgassing. During the reaction with ethylene, neither CO_2 nor water were formed with H_xMoO_3, even at 160°C (10).

6. The temperature effect on the yield of ethane produced at the end of the reaction is similar for the two bronzes, but the thresholds are different. At 120°C, substantial amounts of ethane are obtained from $H_{3.8}V_2O_5$ while almost no hydrogenation occurred at this temperature with $H_{1.6}MoO_3$.

7. For $H_xV_2O_5$ where $X_{in} > 3.4$, the hydrogenation rate of ethylene is not affected by temperature: only the initial rates are. For H_xMoO_3, the hydrogenation rate is dependent upon temperature. For vanadium bronzes where $1 < X_{in} < 3.4$, there is an exponential relationship between the rate of hydrogenation and X_{in}.

8. Repeated runs performed on the same sample of $H_xV_2O_5$ result in a loss of activity, even if back titration is carried out between two consecutive experiments. A similar observation was reported for H_xMoO_3.

9. Oxygen treatment followed by back-titration lowers the catalytic activity of $H_xV_2O_5$. It restored it in the case of H_xMoO_3.

10. Similar effects of the Pt loading on the ethane production are observed for the two bronzes.

11. For both bronzes, the hydrogenation of ethylene is zero-order with respect to ethylene pressure.

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APPENDIX: NOMENCLATURE

nH_2	number of millimoles of H_2 occluded in the bronze
$X = H/2V$	number of H atoms per 2V atoms

ΔX	variation of X corresponding to the hydrogen given back to ethylene
$P^{i}_{C_2H_4}$	initial pressure of ethylene (Torr)
nC_2H_6	number of millimoles of C_2H_6 produced by the reaction
V^{i}	initial reaction rate (mmol g^{-1} h^{-1})
$\Delta X(H_2)$	variation of X corresponding to the hydrogen removed during the outgassing
$\Delta nH_2(H_2O)$	number of millimoles of H_2 removed as H_2O during the conditioning
$\Delta X(H_2O)$	variation of X corresponding to $\Delta nH_2(H_2O)$ or to nH_2O
ΔnO_2	number of millimoles of O_2 consumed
$\Delta X(O_2)$	variation of X corresponding to O_2 consumption ($O_2 + 4H \rightarrow 2H_2O$)
ΔnH_2(tit.)	number of millimoles of H_2 reintroduced by back-titration, after outgassing the bronze or after O_2 treatment
ΔX(tit.)	variation of X corresponding to ΔnH_2(tit.)
$\Delta n'H_2$	number of millimoles of H_2 reintroduced after reaction with ethylene
$\Delta X'$	variation of X corresponding to $\Delta n'H_2$.

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