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Catalytic Activation of Cobalt Induced by Oxidizing Treatments in the Methanation of Carbon Dioxide

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A ribbon of Co catalyzing CO_2 hydrogenation at atmospheric pressure and temperatures ranging from 200 to 500°C has been taken as an example for studying the activating effect of pre-oxidation upon the activity of metals in hydrogenation reactions. The chemical state of the Co surface could be determined at any time by direct and quick transfer of the sample from the reactor into the ultrahigh vacuum chamber of an electron spectrometer. After cleaning and prolonged exposure to H_2 (15 h, 1 bar, 500°C) the sample displayed no visible activity up to 500°C despite the absence of any visible contaminant on its surface. Activities ranging over several orders of magnitude could be induced in the metal by adequate pre-oxidations according to their severity. A large part of this activation was transient and its progressive decay required periods of time which were longer the more severe the pre-oxidation and the lower the temperature of reaction. The activity at any time after treatment was shown to depend not only on the oxidation but also on the subsequent reduction, since an increase of the rate of reduction resulted in a corresponding though transient increase of the activity. Reduction of most of the surface region was shown to occur very quickly, whereas deeper layers continued to reduce during the progressive decay of the activity. No visible contamination occurred during deactivation. The activation is interpreted in terms of the creation of surface defects by the alternate oxidations and reductions whereas the deactivation is considered to originate in the thermal restructuring of the surface. © 1987 Academic Press, Inc.

1. INTRODUCTION

The strong influence of oxidizing treatments upon the catalytic activity of metals in hydrogenation reactions is still a point at issue. Although it was formerly supposed that the most likely effect of successive oxidations and reductions of a metallic sample was one of cleaning (*1, 2*), it has become increasingly evident that the enhancement of catalytic activity often observed after such treatments could not originate in the surface decontamination only. Based upon the results of surface spectroscopic examinations the explanation most often referred to rests upon the assumption that the oxygen remaining in the near-surface region displays some kind of promoting action (*3–7*). Another interpretation taking into account surface modifications induced by successive oxidations and reductions has been put forward (*8–17*).

Most of our own previous contributions to this subject (*12, 13, 16, 17*) were based upon the kinetic analysis of a number of transients which the catalyst displays after oxidizing treatments and which remained commonly unexplored.

Although generally much less studied than its neighbors in the periodic table, Co is one of the metals upon which high effects have been reported (*3*). This fact, added to the interest of this metal in Fischer–Tropsch synthesis, prompted us to take it as the subject of the present study. Our aim has been to examine the effects of pre-oxidations, to scrutinize the influence of every possible factor of the catalyst treatment, and to carry out experiments able to allow one to discriminate between concurrent in-

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terpretations. To this end we have proceeded to the kinetic analysis of the catalytic behavior of the metal in the CO_2 hydrogenation and to the parallel analysis of the surface by Auger, X-ray, or UV photoelectron spectroscopies (AES, XPS, or UPS). Surface examinations were carried out just after (or before) treatment or kinetic measurement. This could be achieved by means of an electron spectrometer with a direct introduction capability and quick transfer of the sample from a small space where it could operate as a catalyst under ordinary pressure into the analysis chamber where ultrahigh vacuum conditions were maintained.

2. EXPERIMENTAL

The experimental setup just referred to, although particularly well suited to the aim of this work, suffers from drawbacks as regards precise kinetic determinations. In effect the metal sample had to be resistively heated, which entailed an unavoidable thermal profile. Furthermore the space offered to the flow of gases did not display simple geometry, which resulted in a questionable type of reactor. It was therefore advisable to carry out similar experiments in a more conventional unit (reactor *A*) operating under well-defined conditions and using an equivalent catalyst submitted to treatments identical to those applied to the sample fixed in the reactor chamber (reactor *B*) attached to the spectrometer. In this way we could make sure that no spurious effect vitiated the catalytic observations and measurements made with reactor *B*.

2.1. *Catalyst*

The catalyst used in reactor *A* was made of five ribbons 10 mm long, 1 mm wide, and 50 μm thick (1-cm^2 geometric area) cut from a Co foil (Goodfellow Metals, 99.99+ LT).

In reactor *B* a sample of identical origin was used but consisted of a single ribbon 50 mm long and 1 mm wide. Due to the dimensions of the parts welded at each corner of the U-shaped sample the ribbon was heated along a length of approximately 40 mm (Fig. 3).

2.2. *Kinetic Measurements in Reactor A*

The experiments were performed in a flow-type apparatus operated at atmospheric pressure (Fig. 1). Reactor *A* consisted of a quartz U-tube (i.d., 0.4 cm; length, 20 cm; volume of the reactor occupied by the sample, 0.1 cm^3) situated along the axis of an electric furnace. A 4-port switching valve allowed the tube to be fed with the flow of reactant mixture (or any other gas) or to be closed. The temperature was measured by an iron–constantan thermocouple attached to the tube and was electronically controlled (kept constant or linearly ramped).

The main gases used in this work were He, H_2, and CO_2. He was passed first through a bed of CuO dispersed on alumina (250°C; oxidation of CO and H_2), then through a powder of an unsaturated Mn oxide (Engelhard) as an "oxytrap" (20°C). A trap filled with glass beads and cooled by liquid air removed most of the condensable gases. The purification was completed by a column of molecular sieve at liquid air temperature. H_2 was purified from O_2 by a Pt–Ni/molecular sieve catalyst (250°C), followed by two traps at liquid-air temperature as for He. CO_2 was purified from CO traces over CuO dispersed on alumina (250°C) and from O_2 on an "oxytrap" (20°C). Its condensable impurities were eliminated, after mixing with H_2, in a trap cooled at dry ice temperature. Flow rate controllers allowed gas mixtures of appropriate composition to be easily prepared.

The extent of reaction was known from a chromatographic analysis (FID for CH_4 or TCD for CO and CO_2). The O_2 content of He–O_2 mixtures used in pre-oxidations was given by an O_2-meter (Engelhard Mark II electrochemical meter). The H_2O production rate could be measured by an electrochemical meter (Beckman). The latter

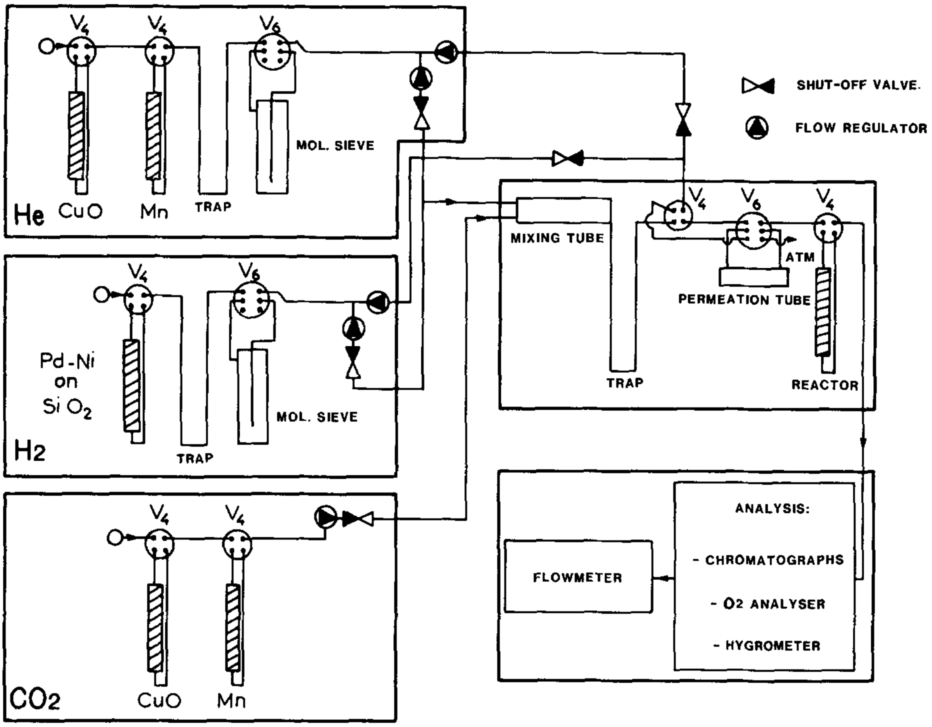

FIG. 1. Apparatus for kinetic measurements (reactor *A*).

could measure H_2O contents in the range 1–1000 ppm.

2.3. *Kinetic Measurements in Reactor B*

Reactor *B* is designed as a part of the introduction device of a Leybold–Heraeus electron spectrometer. A transfer rod supporting the sample to be analyzed (the Co ribbon in the present case) can bring it from the atmospheric loading position (A) into an intermediate position situated in the cylindrical space of the reactor (B) (see Fig. 2) or into the center of the ultrahigh-vacuum chamber where its surface is analyzed (C). The volume of the reactor is about 10 cm^3. It can be continuously flushed with the reactant mixture or any other gas at atmospheric pressure. It can also be evacuated and maintained under vacuum.

The Co ribbon used as a catalyst was spotwelded on the electrical feedthrough of the sample supporting rod (Fig. 3). It was heated by Joule effect and its temperature was measured by a chromel–alumel thermocouple which was spotwelded to the middle of the back side of the sample. Care had to be taken of the composition and flow rate of the gaseous environment as the power to be supplied strongly depended on them and this correction was done automatically by integrating the sample into the low resistance branch of a self-balancing Wheatstone bridge. Due to the low value of the resistance R_s of the cold sample, the second resistance of this branch was chosen to be close to $10R_s$. The reference branch of the bridge contained a constant resistance ($\simeq 10^4\ R_s$) and an adjustable one, next to the sample, and that allowed one to choose the resistance of the ribbon and hence its temperature. An operational amplifier connected across the midpoints of the bridge automatically kept the bridge in balance by adjusting the power supply in such a way that the voltage drop across the sample was equal to that across the adjust-

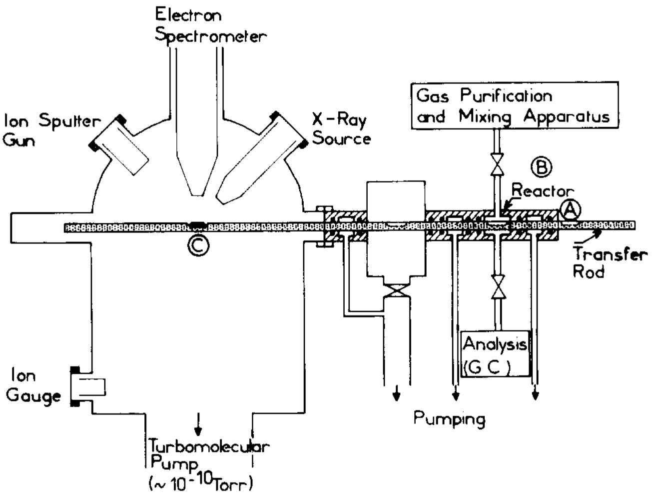

FIG. 2. Schematic of ultrahigh vacuum apparatus with attached sample transfer system and reactor for catalytic rate measurements (reactor *B*). The sample can be moved by pushing the stainless-steel rod from the atmospheric loading position (position *A*) into the reactor for kinetic measurements (position *B*) and to the center of the ultrahigh vacuum chamber for the surface analysis (position *C*).

able resistance. A thermal profile along the axis of the ribbon could not be avoided and was determined in calibration experiments by the use of several thermocouples. A linear ramp of temperature could not be applied to the catalyst when situated in reactor *B*, contrary to what could be achieved with reactor *A*. However, this could be approximated by proper increase of the power supplied, resulting in a temperature jump of 50°C every 20 min, for example (time needed for measuring the catalytic activity and proceeding to the surface analysis). This will be called a pseudolinear ramp of temperature in the following.

Purification of the gases, preparation of their appropriate mixtures, and gas analysis were exactly the same as with reactor *A*.

2.4. Surface Analysis

The sample was quickly cooled from the reaction (or pre-oxidation) temperature to room temperature before being transferred into the ultrahigh-vacuum chamber for the analysis. Surface analysis was usually performed at room temperature. For some special experiments, the sample was heated in the analysis chamber and analysis performed either at the experiment temperature or at room temperature.

Electron emission of the Co surface could be induced by X-rays (AlK_α or

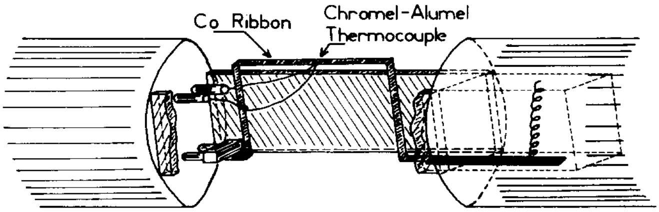

FIG. 3. Details of the sample mounting.

MgK_{α}), electrons, or UV photons (He I or II). The sample could also be submitted to bombardment by Ar^+ ions. AES was usually performed to follow the surface composition during its cleaning, after its pre-oxidation, and during the course of reaction. UPS He_{II} spectra appeared as one of the best ways of controlling the purity of the sample. Both UPS and XPS spectra of Co were used to characterize the chemical nature of the oxide overlayer obtained after pre-oxidations.

The electrons emitted were analyzed through a hemispherical electron analyzer operating either at constant $\Delta E/E$ (XPS, AES) or ΔE (UPS). The residual pressure in the analysis chamber was in the range 10^{-10} Torr. Gases desorbed from the sample could be analyzed by a quadrupole mass spectrometer (Riber QMM 17).

2.5. *Sample Cleaning*

Several authors have proposed cleaning procedures applicable to Co surfaces. Ionic bombardment (*18–22*) was frequently used in association with previous exposures to O_2 at elevated temperatures and subsequent heating of the sample. Initial exposures to H_2 at high temperatures, followed by alternate exposures to H_2 and O_2 (*3*), as well as combined procedures using both ionic bombardment and chemical cleaning (*23*) were also used. As cleaning by ionic bombardment necessarily displays a localized character, a cleaning procedure based solely on chemical action was necessary. Furthermore, only chemical procedures are applied in most current catalytic experiments.

Before being installed in the reactors (*A* or *B*) both samples were washed with various common solvents. Figure 4a shows the initial surface composition as revealed by AES. S (152 eV), Cl (181 eV), C (272 eV), and O (510 eV) appear as the only contaminants, whereas the three Co (LMM) peaks (656, 716, 775 eV) are already present. In some cases Ca (291 eV) could also appear.

Exposure of the metal to a flow of H_2 (1 bar) at 600°C for 24 h resulted in the disappearance of Cl, Ca, and C, the decrease of the O peak and the increase of S and Co peaks.

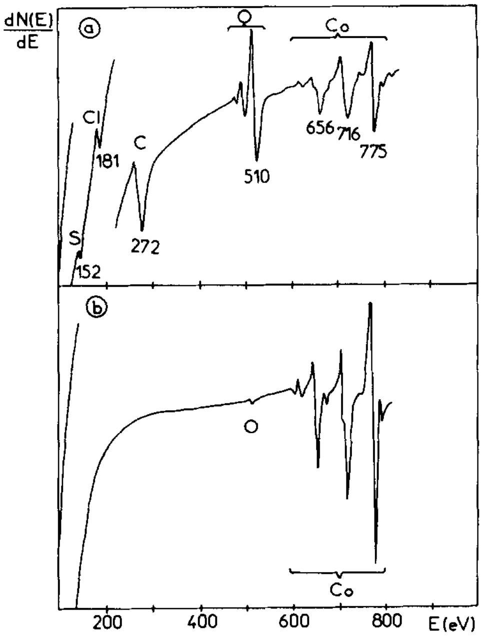

FIG. 4. Auger electron spectra of the Co sample after (a) washing with common solvents (water, alcohol, acetone), and (b) chemical cleaning and transfer under H_2 (see text).

A succession of oxidizing and reducing exposures was then applied. Oxidations were carried out by feeding the sample with a flow of (He + 20 ppm O_2) at ordinary pressure, 550°C, for 2 or 3 h. Reductions were effected with a flow of H_2 at 600°C for 10 or 15 h. Each cycle was followed by AES. The S peak decreased as the cycles increased in number. After 10 such cycles, the S peak disappeared (Fig. 4b) and no reappearance of S occurred even after maintaining the sample under H_2 at 600°C for 15 h. In no circumstances could the $O_{(510\,eV)}/Co(L_3M_{4,5}M_{4,5})_{(775\,eV)}$ ratio be made lower than 0.05 ± 0.01, which is the value observed in Fig. 4b and which corresponds to what has been considered as a "clean" Co surface in this work. We shall show in the next section that this O peak is indicative of some irreducible O content, not only on the surface but also in the bulk of the metal, and which does not exceed 1 at.% of each layer.

2.6. *Characterization of the Residual Oxygen of the "Clean" Surface*

To obtain deeper information about the coverage corresponding to the residual oxygen of the "clean" Co, the latter has been characterized by its He_{II} spectrum (Fig. 5, curve a).

For the sake of comparison, another cobalt ribbon has been directly installed in the analysis chamber, cleaned by successive ionic bombardment using Ar^+ ions (P_{Ar} = 10^{-7} Torr, 10 mA cm^{-2}, 15 min) and annealings. The He_{II} spectrum of this second sample was exactly superimposed on the corresponding one of our usual and "clean" sample (Fig. 5, curve a) but no oxygen could be detected by AES ($O_{510}/Co_{775} < 0.01$). After having been cleaned, this second sample was exposed to 1 Langmuir O_2 at room temperature, which corresponds to one-third of a monolayer of oxygen atoms (*24, 25*). The subsequent O_{510}/Co_{775} Auger signal ratio had the same value as in the case of our usual "clean" sample ($\simeq$5%) and the corresponding He_{II} spectrum is reported on curve b of Fig. 5. This spectrum presents a structure at about 5 eV below the Fermi level, which is assigned to O_{2p} orbitals. Clearly no such structure exists in spectrum 5a and it may be concluded that if oxygen of the "clean" catalyst were only located on the first layer, as was the case for the second sample after it had been exposed to 1 Langmuir O_2, the oxygen coverage of the "clean" surface could not exceed 1/10 of the coverage corresponding to curve 5b and which is equal to 1/3 of a monolayer. This would not be consistent with AES results.

It follows that oxygen is located on and below the surface. In a model where the oxygen atoms would be uniformly located within the whole analyzed depth, and taking into account the ratio O_{510}/Co_{775} ($\simeq$3.4) obtained when analyzing superficial CoO (Figs. 8b and 9b), the residual signal of oxygen would correspond to about 1 at.% for each atomic layer.

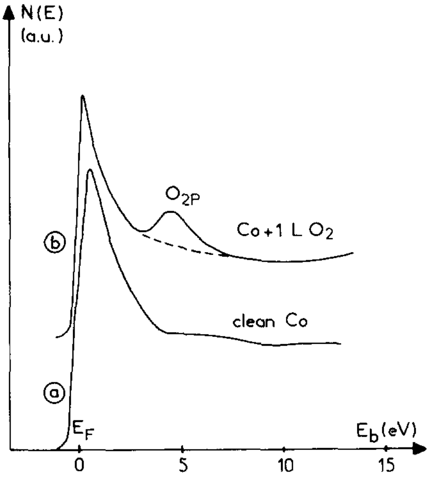

FIG. 5. Comparison of ultraviolet photoelectron spectra of two cobalt samples: (a) usual sample after chemical cleaning in the preparation chamber and transfer under H_2; or second sample directly setup in the analysis chamber, cleaned by ionic bombardment and annealed; (b) the second preceding sample after cleaning and subsequent exposure to 1 Langmuir O_2.

3. RESULTS

3.1. *Preliminary Observations*

Once cleaned the Co sample was fed with the standard reactant mixture (H_2 + 11% CO_2) at the usual flow rate (133 cm^3 min^{-1}) corresponding to a contact time of less than 0.1 s in reactor *A*. No reaction product could be observed up to 500°C, which means that the rates of CO and CH_4 production were lower than the detection limits. Taking into account the sample area the latter were 10^{-10} mol cm^{-2} s^{-1} and 3.10^{-9} mol cm^{-2} s^{-1} for CH_4 and CO, respectively. The equivalent turnover frequencies are 6×10^{-2} s^{-1} and 2 s^{-1} approximately, using the conventional and approximate assumption of 10^{15} sites/cm^2. The lack of sensitivity for CO detection compared to that for CH_4 was of little importance as activations and deactivations are best viewed through

CH_4 which is the final product of reaction rather than through CO, as will be discussed later.

This state of Co, deprived of any visible activity despite the cleanliness of the surface, will be considered as *the reference state of the catalyst.* As will be reported, the metal could be activated by oxidizing treatments. Heating at 500°C under H_2 for 5–6 h was initially enough to re-obtain the reference state. However, as more and more treatments were applied, complete overnight heatings (15 h) were not sufficient to re-obtain the reference state and we were led to use deactivated catalysts with low levels of activity corresponding to two or three times the limiting value mentioned above. This catalysts behavior will be discussed further.

The permanent presence of a low O_2 content (20 ppm) in the reactant mixture or stepwise introductions of O_2 doses (0.1 cm^3, 1 bar) into the reactant mixture resulted in no activation of the cleaned and deactivated metal. We shall see later on (Section 3.2.1, Fig. 7) that once activated the catalyst behaved similarly.

The same observations were effected in reactor *B* with parallel checking of the surface cleanliness.

3.2. *Effects of Pre-oxidations*

3.2.1. Experiments in reactor A. The strength of the effects that pre-oxidation can entail is illustrated by Figs. 6 and 7. In both reactors, after a prolonged exposure to H_2 at 550°C resulting in a clean though deactivated catalyst, an oxidation was applied under a flow of He + 20 ppm O_2 at 500°C for 1 h.

In the first experiment (Fig. 6) the sample was then cooled quickly to 200°C under He–O_2 and submitted to the reducing reactant mixture as a temperature ramp (4°C min^{-1}) was applied. Strong activities such as that seen in Fig. 6 could thus be ascribed to the metal owing to pre-oxidation. Several reaction products were observed, among which CH_4 and H_2O were expected.

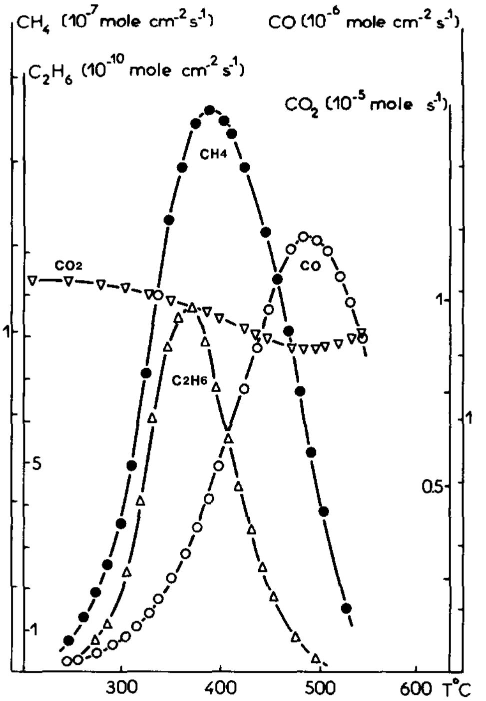

FIG. 6. Variations of the rates of production of CH_4, CO, and C_2H_6 and of the molar flow rate of CO_2 at the reactor outlet as a function of linearly increasing temperatures. Reactor *A*: rate of heating, 4 K min^{-1}; reactant mixture, H_2 + 11% CO_2; flow rate, 133 cm^3 min^{-1}; catalyst pretreatment, (He + 20 ppm O_2) at 500°C for 1 h.

It could easily be shown that H_2O mainly originated in CO_2 hydrogenation rather than in the reduction of the oxide layer (as much less H_2O was formed when CO_2 was removed from the reducing mixture). CO was the main reaction product in this experiment; it was roughly 6 times as abundant as CH_4 and resulted from the reverse water gas shift reaction. A small production of C_2H_6 was also observed. Very small though detectable amounts of C_2H_4 and C_3H_8 could be equally identified. All of the reaction products displayed maxima in the variations of their rate as a function of the temperature and the CO maximum always occurred at a temperature much higher than that of CH_4. No such maximum was displayed when a decreasing temperature ramp was applied just at the end of the heating program and the curves (not reported to avoid overloading the figure) only indicated a monotonic decrease of activity. (The corresponding rates were about 30 times lower for CH_4 and 2 to 3 times lower for CO.)

Figure 7 shows the extent of activation as observed under isothermal conditions at 375°C, a temperature close to that of the CH_4 maximum in the previous experiment. For this second experiment, once the preoxidation was achieved, the sample was cooled quickly to 375°C and then fed with the same reactant mixture as previously. The rate of CO production was initially increased by a factor of at least 2.5×10^2 (8×10^{-7} instead of 3×10^{-9} mol cm^{-2} s^{-1}) and that of CH_4 by a factor of 6×10^3 (6×10^{-7} instead of 1×10^{-10} mol cm^{-2} s^{-1}). Fast initial deactivation was observed as a function of time after treatment as only about 1/10 of the initial activity remained for CH_4 and C_2H_6 after 45 min. The deactivation was markedly less fast for CO as the rate of formation of the latter product was divided by only 2 within the same time. Due to the strength of the activation, the rate of CH_4 production remained two orders of magnitude higher than in the reference state even after this initial loss of activity, and several days would have been needed at 375°C to deactivate the metal completely. Furthermore no modification of the time variation of the rates resulted from the presence of a continuous low O_2 content in the reactant mixture, as shown from Fig. 7. Nor was any modification of the time variation of the rates observed when the catalyst was permanently fed with pure H_2 or pure He, the rate measurements being then done by periodically substituting the reactant mixture for H_2 or He during 30 s.

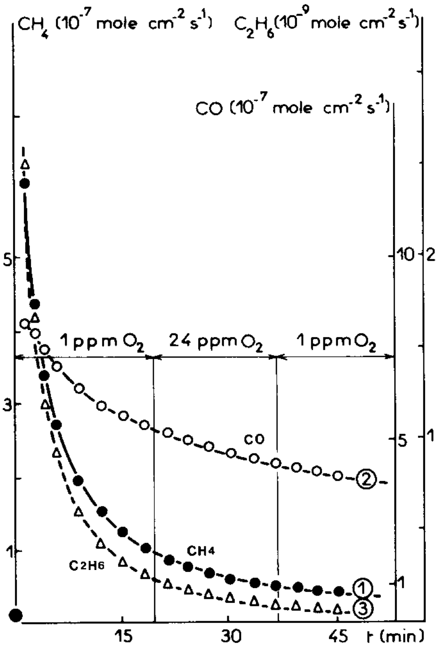

FIG. 7. Variations of the rates of production of CO, CH_4, and C_2H_6 as a function of time on stream. Reactor *A*: reactant mixture, H_2 + 11% CO_2, 375°C; flow rate, 133 cm^3 min^{-1}; catalyst pretreatment, (He + 20 ppm O_2) at 500°C for 1 h. The solid circle on the CH_4 axis corresponds to the residual production of CH_4 before pretreatment.

3.2.2. Experiments in reactor B. In this case also there was no activity observable with the clean and reduced Co.

The results of a detailed study of the oxidation of polycrystalline cobalt have been published elsewhere (*24, 25*). Different oxidizing conditions were applied and they varied over a large range of temperature (20–500°C) and pressure (10^{-6} to 760 Torr O_2). For oxidations conducted under a flow of He + 20 ppm O_2 at atmospheric pressure, the amount of O_2 reacted could be measured using an O_2 electrochemical meter, XPS and UPS spectra allowed us to discriminate the nature of the oxide overlayer between the two oxides (CoO and Co_3O_4) which are known to be produced under dry oxidation of Co. In the following, only the data concerning the catalytic experiments will be summarized (Table 1). Oxidations effected under O_2 at atmospheric pressure always gave rise to a surface overlayer of Co_3O_4 at $T \geq 250$°C. Oxidations conducted under He + 20 ppm O_2 (1.5×10^{-2} Torr) for 1 h resulted in the formation of an oxide layer which could be identified with Co_3O_4 for temperatures ranging from 250 to 450°C and with CoO at

TABLE 1

Nature of the Co Oxide Formed near the Surface after 1 h Exposures to O_2 at Different Pressures and Temperatures[a]

P_{O_2} (Torr) / T (°C)	10^{-6}	1.5×10^{-2}	760
20	CoO CH_4: 2 CO: 1.4	CoO CH_4: 2.6 CO: 2	CoO CH_4: 3 CO: 2.5
250	CoO CH_4: 2.5 CO: 1.7	Co_3O_4 CH_4: 182 CO: 29	Co_3O_4 CH_4: 203 CO: 32
400	CoO CH_4: 3.5 CO: 2.2	Co_3O_4 CH_4: 3690 CO: 101	Co_3O_4 CH_4: 4010 CO: 103
500	CoO CH_4: 6.7 CO: 6	CoO CH_4: 9520 CO: 187	Co_3O_4 CH_4: 9940 CO: 205

[a] Quantitative data represent the total amounts of CH_4 (10^{-7} mol cm^{-2}) and CO (10^{-5} mol cm^{-2}) produced within 1 h at 250°C after each oxidation when the catalyst (reactor *B*) was fed with (H_2 + 11% CO_2) flowing at 133 cm^3 min^{-1}.

lower as well as higher temperatures (see Table 1). CoO is known to be stable up to 1000°C, whereas Co_3O_4 can easily turn into CoO (*26–28*). We observed in fact that the Co_3O_4 layer once formed could desorb O_2 when heated at 400°C under vacuum, thus decomposing into CoO.

After oxidation and subsequent analysis of the surface in the analysis chamber the sample was replaced inside the reactor for reduction by either pure H_2 or the reactant mixture or still else by H_2 with periodic probing of the catalytic activity. This probing procedure was expected to protect the surface cleanliness at the most feasible extent. At regularly spaced intervals the sample could be brought again into the analysis chamber for determining its surface composition.

In a first experiment the ribbon was maintained at a constant temperature (250°C). Figure 8a reports the results of the periodic measurement of the rates of production of CH_4 and CO as a function of the length of reduction. Reduction was carried out under a flow of pure H_2 (1 bar) and the rate measurements were performed by substituting the reactant mixture for H_2 during 1 min. Figure 8b reports the results of the parallel analysis by AES and clearly shows that a very fast surface reduction occurred. After a few minutes of reduction, no oxide of cobalt could be detected by XPS (sampling depth ≃30 Å) and the O/Co ratio determined by AES quickly decreased from 3.4 to 0.05 (±0.01). No significant amount of C could be observed on the surface. No significant variation of the curves occurred either when continuous exposure of the metal to the reactant mixture took place instead of the probing procedure. This was in agreement with the absence of formation of a significant amount of C on the surface (Fig. 8b). Beyond the first 6 min, submitting the catalyst to He (1 bar) or to ultrahigh vacuum instead of H_2 (1 bar) induced no modification of the variations of either the rates or the surface composition vs time.

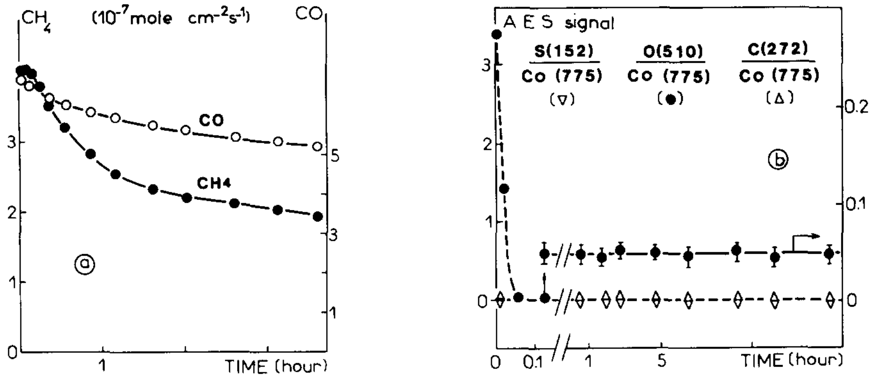

FIG. 8. (a) Variations of the rates of production of CO and CH_4 as a function of time of reduction at 250°C under H_2 (1 bar). Reactor *B*: pre-oxidation by (He + 20 ppm O_2) for 1 h at 500°C; rate probings (see text) by (H_2 + 11% CO_2) flowing at 133 $cm^3\ min^{-1}$. (b) AES analysis of the pre-oxidized Co sample during reduction, corresponding to Fig. 8a. Signals reported here correspond to the ratios of the peak-to-peak heights of S, O, and C to the peak-to-peak height of Co.

The strong activation of the metal as a result of pre-oxidations and its transient character were therefore confirmed.

In another experiment, a pseudolinear ramp of increasing temperatures (see Experimental, Section 2.3) was applied to the catalyst fed with either the reactant mixture or H_2, the rate measurements being then performed according to the probing procedure previously described. After each catalytic measurement the catalyst was taken away from the reactor for examination in the analysis chamber. As was the case for the isothermal experiments, the results did not significantly differ whether the reducing gas was the reactant mixture or H_2. Figure 9a is qualitatively very similar to Fig. 6 for the corresponding experiment conducted in reactor *A*. As seen from Fig. 9b, the surface cleanliness was preserved as in the case of the isothermal experiment (Fig. 8b). The O/Co ratio determined by AES quickly decreased as soon as the temperature was equal to 150°C to become equal to 0.05 (±0.01) at 200°C. At this temperature, no oxide of cobalt could be detected by XPS.

During the analysis the composition of the surface may be affected by some desorption phenomena or by some "surface segregation–bulk solution effect." However, it is worth noting that the curves "activity vs time" or "activity vs temperature" were the same whether the measurements were interrupted by the analysis procedure or not. Furthermore, proceeding to the surface analysis did not induce any extratransient.

3.3. *The Factors of the Oxidizing Pretreatment*

Three factors can be expected to determine the effect of pre-oxidation, namely, the O_2 content of the oxidizing gas, the temperature, and the length of oxidation. A systematic study of each of them should give evidence for the way into which they affect the catalyst behavior. To avoid repetition we shall report only temperature-programmed experiments carried out with reactor *A* and isothermal ones carried out with reactor *B*, even though both kinds of experiment were carried out with both reactors, since they led to consistent results. The experiments were conducted in the same way as described in Sections 3.2.1 and 3.2.2, respectively. When reactor *B* was used, periodic interruptions of reaction allowed us to examine the chemical state of the metal surface in the analysis chamber. Prior to every pre-oxidation, the catalyst

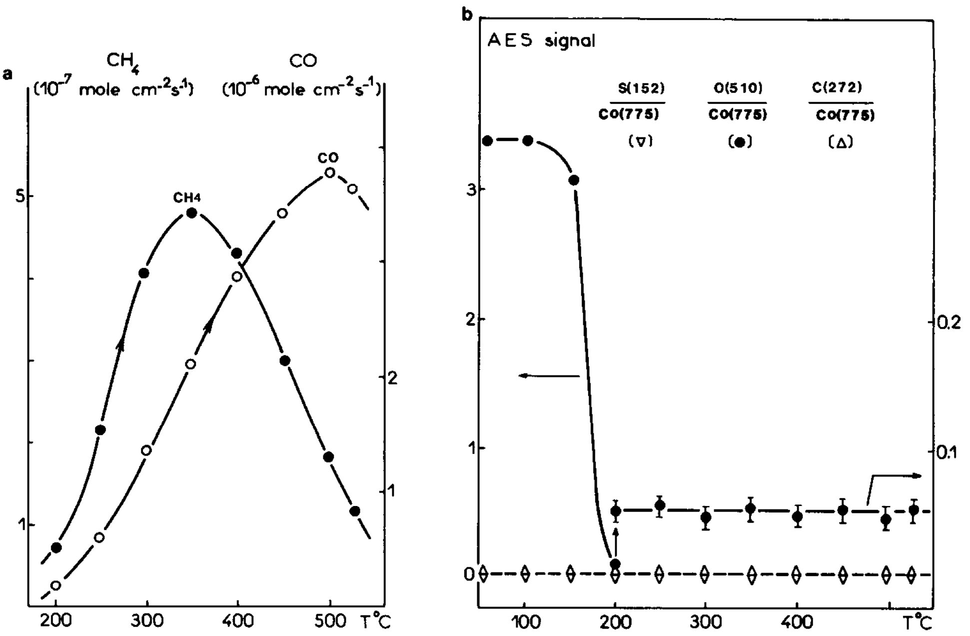

FIG. 9. (a) Variations of the rates of production of CH_4 and CO as a function of the reaction temperature. Reactor *B*: catalyst pretreatment, oxidation with (He + 20 ppm O_2) for 1 h at 500°C; sample permanently fed by H_2 or (H_2 + 11% CO_2) (see text); pseudolinear ramp of heating (see text), $\simeq$2.5 K min^{-1}. (b) Variation of the surface composition of the pre-oxidized Co sample during reduction, corresponding to Fig. 9a. Signals reported here correspond to the ratios of the peak-to-peak heights of S, O, and C to the peak-to-peak height of Co.

was heated at 500°C under H_2 for about 15 h so as to erase most of the preceding activation and approximately reattain the reference activity level.

3.3.1. Influence of the O_2 content of the oxidizing He–O_2 Mixture. No significant change resulted from the variation of the O_2 content from 20 to 2×10^4 ppm in pre-oxidations conducted for 1 h at 500°C. This was expected as a consequence of the smallness of the O_2 fraction reacted in the flow of oxidizing gas, which was easily checked in both reactors. However, it was possible to expose the sample studied in reactor *B* to a pressure of 10^{-6} Torr of pure O_2 for the same period of time (1 h) and at temperatures ranging from 20 to 500°C. No activation resulted from any of these latter treatments.

3.3.2. Influence of the pre-oxidation temperature. A series of oxidizing treatments by He + 20 ppm O_2 for 1 h was applied to the Co sample at temperatures increasing regularly from 250 to 550°C. Figure 10a, b, c, d shows the results of temperature-programmed experiments (reactor *A*) and Fig. 11a, b those obtained at a constant temperature of reduction (reactor *B*).

A definite activation was ascribed to Co inasmuch as the pre-oxidation was effected at $T \geq 250$°C and its extent was an increasing function of the pre-oxidation temperature for $250 \leq T \leq 500$°C. Beyond 500°C, the activation did not increase any more but the time required to make a given part of it disappear became longer. Figure 10 clearly indicates also that the temperatures of the maximum rates shifted toward higher values as the severity of pre-oxidation increased.

In every case and independently of the activation induced by the treatment, the

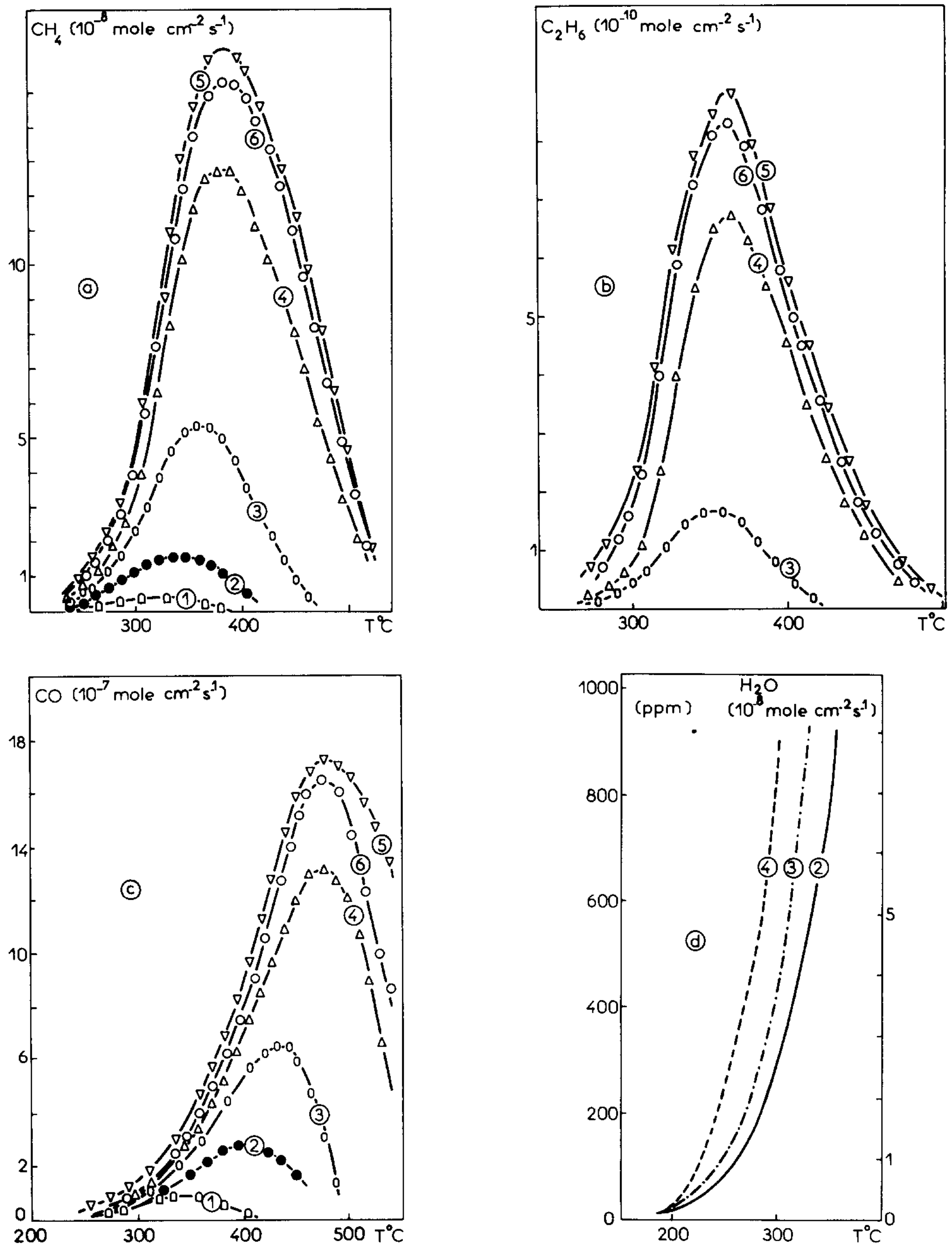

FIG. 10. Influence of the pre-oxidation temperature upon the resulting catalyst activation and the variations of the catalytic activity as a function of the reactor temperature. Reactor *A*: catalyst pretreatment, (He + 20 ppm O_2) for 1 h at 300°C (1), 350°C (2), 400°C (3), 450°C (4), 500°C (5), and 550°C (6); reactant mixture, (H_2 + 11% CO_2), flowing at 133 cm^3 min^{-1}; rate of heating, 4 K min^{-1}.

O/Co ratio determined by AES displayed the same behavior as depicted in Figs. 8b and 9b.

3.3.3. Influence of the length of exposure to O_2. In a new series of experiments the catalyst was oxidized in reactor *A* by the same mixture He + 20 ppm O_2 at 500°C but for increasing periods in successive trials. As shown in Fig. 12 relating to temperature-programmed experiments (reactor *A*,

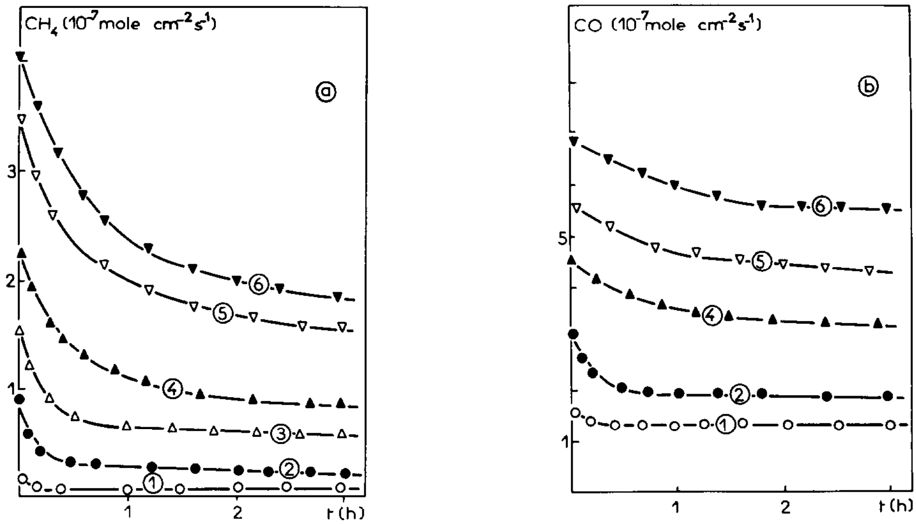

FIG. 11. Influence of the pre-oxidation temperature upon the resulting catalyst activation and the variation of the catalytic activity as a function of time on stream after treatment. Reactor *B*: catalyst pretreatment, (He + 20 ppm O_2) for 1 h at 250°C (1), 300°C (2), 350°C (3), 400°C (4), 450°C (5), and 500°C (6); reduction under a permanent flow (133 cm^3 min^{-1}) of (H_2 + 11% CO_2) at 250°C.

increasing activations resulted from longer oxidizing exposures. Too strong oxidations had to be avoided in order not to obtain catalyst states which would have required exceedingly long periods of heating under H_2 before they disappeared. Similar results were obtained in reactor *B*.

3.4. Influence of the Pressure and Flow Rate of H_2 Used as the Reducing Agent of Pre-Oxidized Cobalt upon the Resulting Catalytic Activity

Usually the reactant mixture allowed the catalyst activity to be determined during the simultaneous reduction of the pre-oxidized metal. In an attempt to disconnect the reduction process from rate measurements the following procedure was adopted. After a given initial oxidation (1 h, 500°C, He + 20 ppm O_2) the catalyst was fed with either pure H_2 or H_2 + He mixtures and the activity level reached after a given period of reduction was measured by short substitutions (30 and 60 s for reactors *A* and *B*, respectively) of the usual reactant mixture for H_2 or H_2 + He. In this way the pressure of the reducing agent could be varied and the effects of such variations could be unambiguously determined under *constant conditions of rate measurements*. The effect of the variations of the H_2 flow rate could also be shown in a similar way.

3.4.1. Influence of the H_2 pressure. Figure 13 shows the results concerning the influence of H_2 pressure at 220°C for experiments conducted in reactor *B*. Curves 1 (CH_4) and 1′ (CO) refer to a reduction which occurred throughout under He + 15% H_2, whereas curves 3 and 3′ refer to a reduction effected with pure H_2. A faster reduction was then shown to result initially in a rate enhancement. This effect is well evidenced in curves 2 and 2′ which relate to reduction under diluted H_2 during period *A*. When the H_2 + He mixture was quickly replaced by pure H_2 (period *B*), a clear increase of reaction rate was produced and was followed, soon after, by the usual and progressive deactivation.

3.4.2. Influence of the H_2 flow rate. The same kind of experiment was carried out in relation to a possible effect of the flow rate which was suspected to play a role as the water produced is able to act as an inhibitor

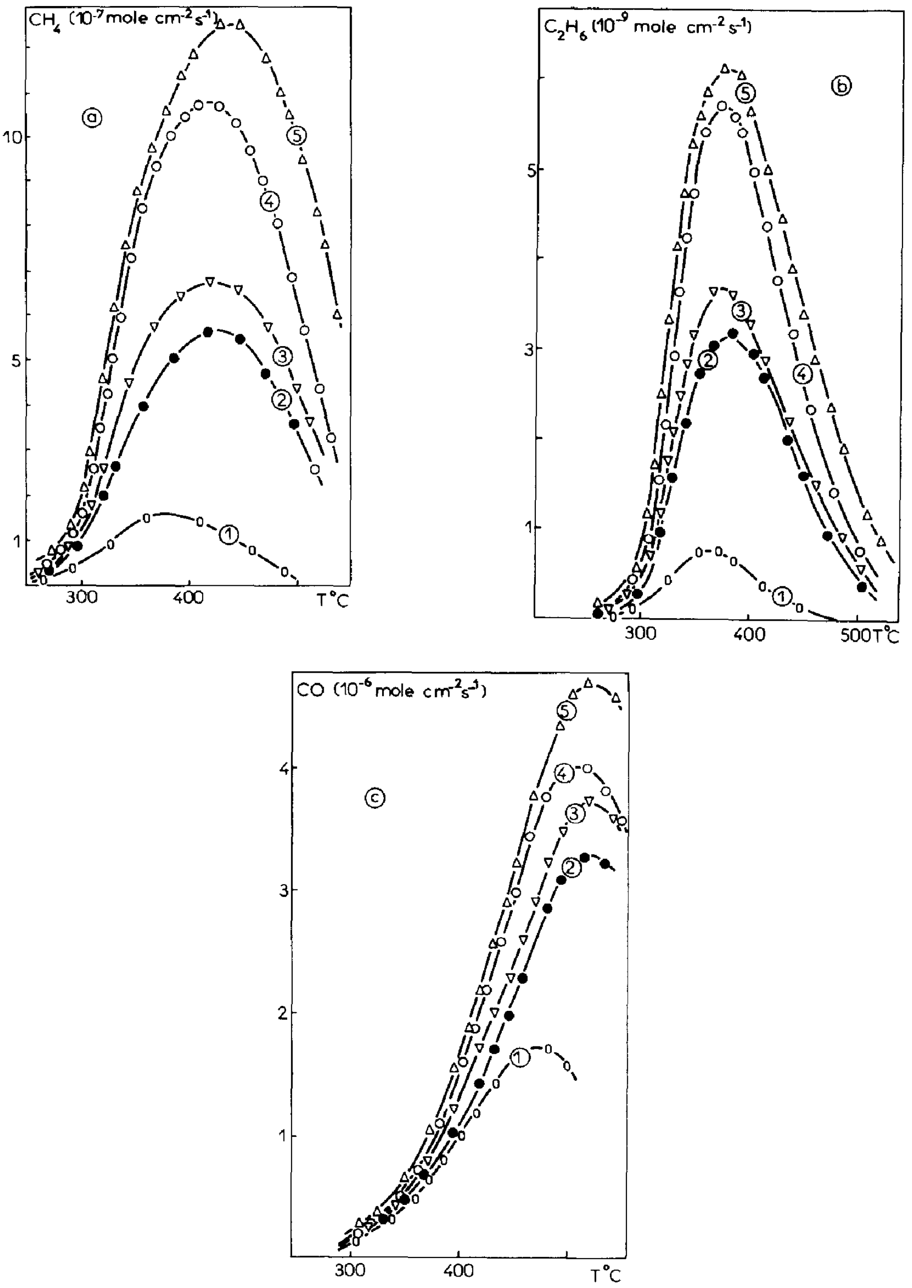

FIG. 12. Influence of the length of pre-oxidation upon the resulting catalyst activation and the variation of the catalytic activity as a function of the reaction temperature. Reactor *A*: catalyst pretreatment, (He + 20 ppm O_2) at 500°C for 1 h (1), 3 h (2), 5 h (3), 11 h (4), and 21 h (5); reactant mixture, H_2 + 11% CO_2, flowing at 133 cm^3 min^{-1}; rate of heating, 4 K min^{-1}.

of the reduction. Any increase of the H_2 flow rate must then result in a greater dilution of the water produced and accordingly in a decrease of the inhibition effect. Figure 14 reports the results of a reduction which was done in reactor *A* with an increasing ramp of temperature after the oxidizing treatment and a permanent feed by H_2 at a

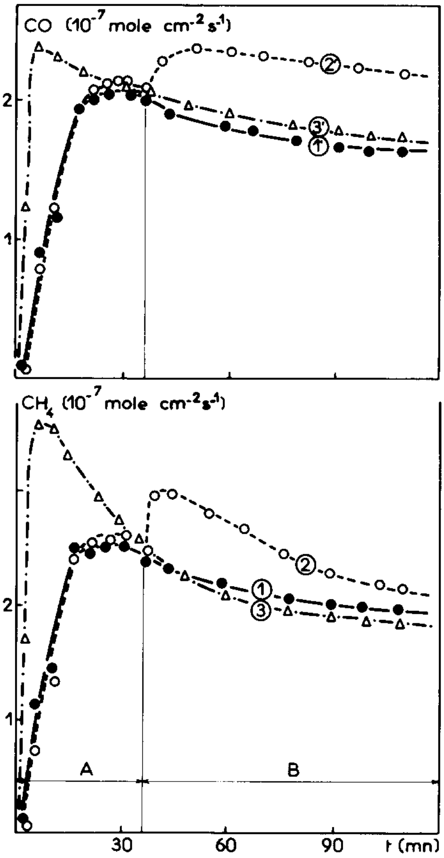

FIG. 13. Influence of the pressure of H_2 used as a reducing agent upon the catalytic activity of the pre-oxidized sample. Reactor *B*: probings of the catalytic activity with the mixture (H_2 + 11% CO_2) flowing at 133 cm min^{-1}; temperature, 220°C; flow of reducing gas, 133 cm^3 min^{-1}. Curves 1 and 1′, continuous reduction with (He + 15% H_2); curves 2 and 2′, continuous reduction with (He + 15% H_2) during period *A* and with H_2 during period *B*; curves 3 and 3′, continuous reduction with H_2. Catalyst pretreatment, oxidation with O_2 (1 bar) at 550°C for 1.5 h.

flow rate of 25 cm^3 min^{-1} (periods *A*, *C*, and *E*) or 133 cm^3 min^{-1} (periods *B* and *D*). The reactant mixture was used only for the probings of activity. The activity increases and decreases due to the corresponding variations of the flow rate are in agreement with the observations of the preceding experiment inasmuch as every speeding up or slowing down of the reduction process entails a corresponding increase or decrease of the activation.

In a further experiment water was added to the H_2 used as the reducing agent and observations consistent with the preceding ones could be done.

3.5. *Relation between the Catalytic Activation and the Amount of Oxygen Reacted during the Pre-oxidation*

As already reported, sufficiently severe pre-oxidations result in almost equal initial levels of activity but can be distinguished by the period of time which is then required for deactivating the metal and which is the longer the stronger the initial activation. To make this relation more quantitative it is convenient to characterize the activating power of a given pretreatment by the total amount of CO_2 that the catalyst is then able to turn over into CO and CH_4 within a given period of time under some reference reaction conditions. Figure 15 refers to the same series of experiments as Fig. 11 and shows the variations of the total amount of products (CH_4, CO, or CO + CH_4) formed at 250°C during the period of 3 h immediately following oxidations of increasing strength as a function of the amounts of O_2 which had been reacted during pretreat-

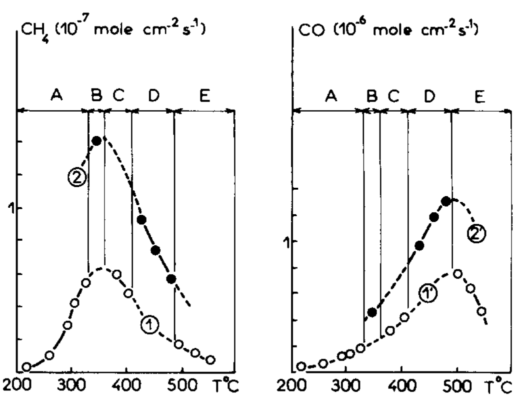

FIG. 14. Influence of the flow rate of H_2 used as a reducing agent upon the catalytic activity of the pre-oxidized sample. Reactor *A*: probings of the catalyst activity with the mixture (H_2 + 11% CO_2) flowing at 133 cm^3 min^{-1}; flow rate of H_2, 25 cm^3 min^{-1} during periods *A*, *C*, and *E*; 133 cm^3 min^{-1} during periods *B* and *D*; catalyst pretreatment, oxidation with (He + 24 ppm O_2) (1 bar) at 515°C for 1 h.

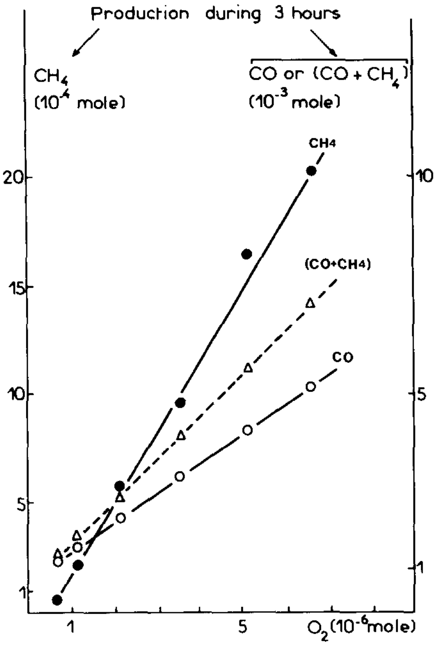

FIG. 15. Variations of the total amounts of CH_4, CO, and (CH_4 + CO) produced within 3 h at 250°C with a permanent feed of the pre-oxidized catalyst as a function of the amount of O_2 reacted with Co during 1-h pre-oxidations with (He + 20 ppm O_2) at different temperatures. The amounts of carbonaceous products are calculated from Fig. 11.

ments. A linear relationship between the co-ordinates is evident.

As an example, the points on the right-hand side of Fig. 15 refer to the strongest oxidation performed during this series of experiments: He–20 ppm O_2, 1 h, 500°C. The amount of O_2 absorbed was equal to 6.5 × 10^{-6} mole which was enough to complete 4000 layers of an oxide supposed to be CoO (≃3% of the sample thickness).

Table 1 gives some additional information by indicating the nature of the oxide overlayer resulting from oxidations conducted for 1 h in a large range of temperature (20–500°C) and pressure (10^{-6} to 760 Torr O_2) and also the corresponding amounts of CH_4 and CO produced within 1 h at 250°C with the usual reactant mixture. No activation resulted from exposures to 10^{-6} Torr O_2 which always led to surface CoO whatever the temperature of the pretreatment. A surface layer of CoO was also formed after a pre-oxidation conducted at 500°C under an oxygen pressure of 1.5 × 10^{-2} Torr, but in that case a large activation was obtained. Nearly the same activation was obtained after the exposure of the catalyst to O_2 at 500°C and 760 Torr, whereas the surface oxide in this case was Co_3O_4. Clearly no relation appears to hold between catalyst activation and the nature of the oxide.

3.6. Catalytic Activation Resulting from Successive Oxidation and Reduction Cycles

In a new kind of experiment, performed in reactor *B*, we tried to make O_2 react with the sample in a sequential way. After having deactivated the metal under H_2 at 500°C and checked the cleanliness of its surface, the treatment consisted in successive exposures to He + 2% O_2 at 300°C during 6 min and to the reactant mixture at the same temperature during 1 min. A flow of pure He during 2 min was used to clear the reactor from H_2 before feeding it with the oxidizing gas so that the total length of each cycle was 9 min. After each sequence of 4 or 5 cycles the sample surface was analyzed and the catalytic activity was measured at the end of each feed with the reactant mixture (Fig. 16).

In order to compare the results of this mode of activation with that caused by a continuous oxidizing treatment, the ribbon was deactivated and then submitted to a flow of He + 2% O_2 at the same temperature (300°C) and for the same total time (1 h). The initial activity level reached was close to that obtained after the sequential treatment (20% less CO_2 reacted per second). In fact it must be observed that each cycle of the sequential treatment comprised deactivating periods (feed with the reactant mixture and He) and if account was taken of that, the sequential treatment had to be considered as twice as efficient as the continuous one.

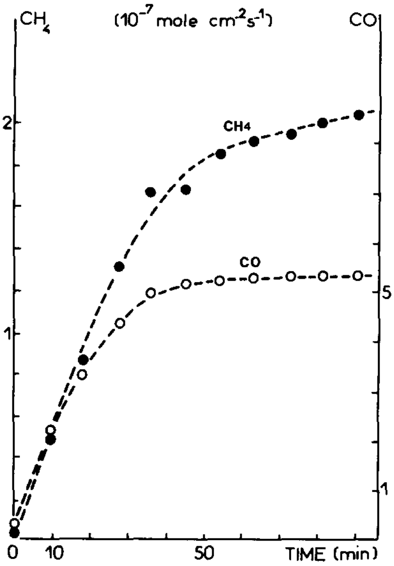

FIG. 16. Progressive activation of Co as a result of successive oxidations and reductions. Catalyst pretreatment: deactivation under H_2 at 500°C for 15 h; cooling to 300°C under H_2; submission to cycles of 9 min each and composed of successive feeds with He (2 min), (He + 2% O_2) (6 min), (H_2 + 11% CO_2) (1 min). Temperature: 300°C.

4. DISCUSSION

In usual catalytic experiments, cleaning of the metal is obtained by chemical means and by successive subjections of the metal to H_2 and O_2 at temperatures not higher than 500°C. In the present work this procedure has been shown to be able to clean the surface of the sample. A depth of metal sufficient for present purposes must also have been cleaned as no surface contamination occurred during prolonged heating of the ribbon under H_2 at 600°C (15 h, atmospheric pressure).

4.1. Kinetic Features of the System under Study as Related to the Mechanism of the CO_2 Reduction

The cleaned metal surface has been shown to display no visible activity in CO_2 hydrogenation, which means that the turnover frequencies were lower than 2 s^{-1} and 6×10^{-2} s^{-1} for CO and CH_4, respectively. Pre-oxidation of the metal can entail catalytic activation which is the greater the more severe the oxidation. The oxidation used in this work (500°C, 1 h, He + 20 ppm O_2) increases the rate of reaction over 2 or 3 orders of magnitude concerning the CO or the CH_4 production, at the lowest estimate. An accurate estimation of the strongest possible rate enhancement could not be easily obtained for two reasons. First, the catalyst area was too small for allowing rate measurements to be performed in its reference state (see Section 3.1). Secondly, most of pre-oxidations led to very high activities, so that the reactor could not operate in a differential mode, which led to an underestimation of the catalytic activity induced by the pretreatment. Higher reaction rates could have been observed if higher space velocities had been used. The dependence of the rates of production of CO and CH_4 on the space velocity and therefore on the contact time of the reactant mixture in the reactor is furthermore illustrated when the results of a same pretreatment are compared in reactors *A* and *B*. Despite the fact that not all the ribbon length was heated at the maximum temperature the rates observed with reactor B were always significantly higher than with reactor *A*. This was due to the choice of the same flow rate of gases in both experimental setups, whereas the volume of reactor *B* (10 cm^3) was much higher than the useful one of reactor *A* (0.1 cm^3). This was all the more important as the design of reactor *B* made it closer to the well-stirred type of reactor instead of the plug-flow type for reactor *A*.

Cobalt was already reported to be a metal highly sensitive to oxidizing treatments. Its pre-oxidation has been shown to increase the rate of CH_4 production in CO methanation by over 2 orders of magnitude (*3*). In the case of CO_2 methanation, but on a Rh ribbon, Sexton and Somorjai (*4*) ascribed activating power to oxidizing treatments but the effects that they reported were much lower. The difference may obviously stem from the different nature of both metals. However, we also reported high effects in the case of the same reaction catalyzed by Rh (*16, 17*) and we are prone to think that the method of rate measurements greatly affects the right estimation of the activation effect. The reactor used in Ref. (*4*) was of the batch type with recirculating gases and the reaction rate was measured through accumulation of CH_4 vs time. This method prevents transient regimes of activity from being clearly evidenced and leads to an underestimation of the extent of activation. Batch reactors also prevent the catalyst from being submitted to various sudden changes of working conditions such as modification of H_2 pressure or flow rate. Among other advantages the response of the catalyst to such actions shows that its reduction is still under progress, which would be obscured if the reduction was monitored by spectroscopic means only.

As large as they may be the activations of the catalyst by oxidizing pretreatments display a transient character. This is shown unambiguously by the rate decrease as a function of time after treatment whether the catalyst remains under the reactant mixture, under pure H_2 or even vacuum or He once its surface has been reduced (cf. Section 3.2.2). AES examination of the surface showed moreover that no or little carbonaceous residue was formed under $H_2 + CO_2$ so that the deactivation observed was intrinsically that of the metal. The transient character of the activation is also exemplified by the occurrence of a maximum versus temperature in the temperature-programmed experiments following a pretreatment. In this case in effect the rate increase due to heating interferes with the speedup of deactivation process for rising temperatures so that the maximum does not express some kinetic property of the reaction but the neutralization of the usual rate increase due to heating by the loss of activity. Such a compensation cannot occur on cooling which only resulted in the expected decrease of rate.

A large difference exists between the temperatures of the maxima corresponding to CH_4 and CO as the rate of production of the latter product goes on increasing up to a temperature 100°C higher than that for CH_4 (see Fig. 6). This is to be paralleled with the slower deactivation with respect to CO during isothermal experiments (see Fig. 7). On a qualitative basis it can easily be understood why the catalyst deactivation is slower when viewed through CO rather than through CH_4. In effect the formation of CO chemisorbed on the catalyst surface can reasonably be imagined as the first step in the process of CO_2 reduction. The rate at which further reduction of CO_{ads} proceeds is an increasing function of the activity of the surface so that an increase of the amount of CO remaining adsorbed on the surface is expected as the result of the decay of activity and gives rise to an increased rate of CO desorption. This is well illustrated by the curves of Fig. 11 which show that at some given temperature every progress in the catalyst activation due to a strengthening of the oxidation makes the ratio CO/CH_4 decrease (by a factor of 4 from curves 1 to 6, at 250°C).

4.2. Origin of the Activating Effect

The question of the origin of the catalytic activation induced by oxidizing pretreatments can now be discussed in the light of the results obtained in this work.

As it looks hardly possible to explain the successive activations and deactivations by corresponding cleanings and contaminations of the surface, arguments must be put forward to explain why a clean metal surface may exhibit such a high sensitivity to oxidizing and reducing treatments. The assumption most often proposed consists in ascribing a definite promoting effect to the oxygen present on or near the surface region due to some beneficial effect on the electronic environment of the Co atoms (*3–7*). The progressive deactivation of the catalyst would then originate in the slow withdrawal of oxygen so that more severe oxidations would naturally result in more persistent activating effects due to larger amounts of bulk oxygen back-diffusing to the surface. A reasonable additional assumption should be made concerning the necessary existence of some optimum oxygen content of the surface region since a completely covered surface would be inhibited. This would explain why the activity increased as a function of time before displaying a maximum at the beginning of an isothermal reduction (Figs. 8a and 13). In such an assumption, the same activity level would be attained at the optimum oxygen coverage. Such is not the case as the induced activity reaches a level which is the higher the more severe the pre-oxidation (Figs. 10 and 12). We have previously discussed this point of view and have concluded that it fails in interpreting the results in every detail (*12, 16, 17*).

The electron spectroscopy results supply new arguments against the previous hypothesis. The O/Co ratio determined by AES reached its lowest value soon after the beginning of reduction independently of the strength of the oxidation. Very different levels of activity could thus be ascribed to the metal by more or less severe oxidations with no apparent relation to the oxygen content of the surface which remained very small (1 at.%; cf. Section 2.6). Similarly, maintaining the catalyst under vacuum at the temperature of the experiment resulted in a deactivation despite the constancy of the O/Co ratio. In connection with that, the experiment illustrated by Fig. 16 shows how a surface cyclically reverting to the same composition could be progressively activated as a result of repeated oxidations and reductions. Close activity levels were attained corresponding to the same total exposure to oxygen although in both final situations the metal happened to be in two completely different states.

Another conclusion which may be drawn from the experiments is that activation does not depend on the nature of the surface oxygen species (cf. Table 1 and Section 3.5). Clearly no relation appears to hold between catalyst activation and the chemical nature of the surface oxide involved (either CoO or Co_3O_4). This is consistent with the swiftness of the reduction of the oxide layer, as seen by AES (cf. Section 3.2.2. and Figs. 8b and 9b).

The length and the temperature of the pre-oxidation have a significant effect on the activation (cf. Section 3.3 and Figs. 10–12). What appears as a matter of fact as a meaningful factor of activation is the *total amount of* O_2 *reacted during the pre-oxidation* (cf. Section 3.5 and Fig. 15). However, the experiments depicted in Fig. 16 and previously referred to show that the amount of oxygen still present in the metal at the time of the activity measurements exerts little influence on the latter. The instantaneous activity level appears essentially determined, apart from the usual conditions of reaction, by the previous history of the catalyst, i.e., the successive incorporations of O_2 into the bulk, followed by the removal of O_2 from the surface during reduction and the subsequent back-diffusion of O_2 from deeper layers to the surface. The instantaneous activity level depends then on the amount of oxide reduced before and the factors of activation are not only those of pre-oxidation but also those of reduction.

The results of other experiments bring additional support to this view. We can indeed see in Figs. 13 and 14 what happens when the pressure or the flow rate of H_2 are suddenly increased at any time after treatment. It is worth recalling here that such modifications only concerned the time intervals during which the catalyst was maintained under a flow of pure H_2 or He + H_2 and that the rate measurements were effected after return to the usual reaction conditions. The variations of activity which were observed were therefore due to the modifications of the reducing conditions. If the loss of activity beyond the maximum were due to the decrease of the oxygen content of the surface, the increase of H_2 pressure or flow rate would have brought about a faster deactivation due to the speeding-up of the reduction. However, just the reverse was immediately observed before another maximum was passed and deactivation ran its course again but a little faster for a while. The immediate increase of activity so evidenced appears as the result of the speeding up of the reduction, which makes appear clearly the rate of reduction as a meaningful factor of activation. However, a faster reduction implies a faster depletion of the oxygen lying in the surface layers, so that soon afterwards the deactivation sets in again and at a transiently faster rate. This behavior, most unexpected on the basis of usual views, is also a strong indication *that the reduction itself constitutes a key factor of the catalyst activation.* Obviously no reduction of the catalyst could occur if no previous oxidation had taken place so that sequential oxidations and reductions are the true agent of activation and they are all the more efficient as the reduction goes the faster. Such kinetic experiments clearly support the opinion that *the activation following pre-oxidations is of a dynamic nature.*

We previously arrived at the same conclusion in the case of solid (*16, 17*) or powdered (*17*) rhodium catalyzing the same reaction. We explained the activation induced by pre-oxidations by assuming that when oxygen is extracted from the surface and subsurface region by H_2, the structural state of the top layers is altered and defects are created. Several kinds of metal surfaces are known to undergo reconstruction when adsorbing O_2 (*29–33*). Fast reduction of such oxidized surfaces should lead to transient disorder. Active though unstable configurations might appear under these conditions. In the present work, pretreatment of the catalyst was not a mere chemisorption but consisted in an oxidation involving up to several thousands of oxide layers. In such a case, oxygen has to back-diffuse from the bulk to the surface before being extracted by H_2 and the sequence of these processes has the best chances of greatly disturbing the surface. Some of the defects thus created may be expected to fit kinetic requirements in a better manner than others and may so constitute active catalytic centers with limited lifetimes. The surface content in defects is able to remain higher than at thermal equilibrium during prolonged periods of time if there exists a continuous process of production of such defects offsetting their spontaneous decay, even if it does so incompletely. This process may be identified with the reduction of the pre-oxidized metal. It is clear that the higher the rate of reduction the higher the activation, on account of a greater concentration of surface defects.

From such a dynamic point of view, the spontaneous reorganization of defects is expected to bring about a retexturing of the surface. The latter ends by becoming visible after subjection of the sample to numerous treatments. It has been known for a long time that certain metallic catalysts experience gross surface rearrangements when involved in oxidation reactions (*12, 34–44*). Some among the authors of this present work have contributed to the development of this aspect of catalysis (*12, 41–43*) and especially in the case of Co (*42, 43*). These rearrangements are visible on a macroscopic scale but must obviously start at the atomic level (*45*) and different atomic configurations may be easily imagined on a surface undergoing such a "churning" action (*46*).

However, these macroscopic modifications themselves might be proposed as an alternative explanation for the activating effect due to oxidzing treatments.

First, an area increase may stem from facetting and disruption of the surface. This was recently considered as the origin of the activation of Fe in the CO/H_2 reaction (*14, 15*) following deep oxidation of the metal. However, a macroscopic sintering process is little expected at moderate temperatures (250°C, e.g.) and its extent could hardly concern orders of magnitude. Hence it would be very surprising if the quick initial decrease of activity following a reactivation could be due to sintering. If atom displacements are taken as being responsible for the variations of the catalytic activity, both events need to occur in the same scale of time and therefore movements in the range of atomic distances have to be considered. On another side the ribbon area should have been increased over three orders of magnitude for explaining the extent of the activating effects. Some crumbling of the sample would have resulted; nothing like that happened and the sample kept its entirety.

A second possible effect of surface rearrangement and faceting is the development of crystalline faces of higher catalytic activity as well as that of numerous facet edges. In this respect an extensive development of edges appeared on the ribbon surface retextured by numerous treatments. If these edges are hypothesized to display high catalytic activity, a mode of activation can thus be accounted for. The latter factor added to some possible though limited area increase is able to explain why the sample ended up by acquiring some permanent and slowly increasing level of activity since the reaction rate obtained after a 15 h exposure to H_2 at 500°C became less and less small as the number of treatments increased. The area of the sample under study was too small for allowing us to study this residual activity. Some observations in this direction have already been made by using a much greater area of Co (×30) (*47*) but this work is still in progress.

Nevertheless, neither a limited area increase nor the appearance of new crystalline faces or facet edges can explain the transient behavior of the catalyst after preoxidation treatments. The catalyst behavior discussed in this work appears therefore to be hardly explicable on the assumption of a rigid catalyst surface made of motionless atoms.

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