

NOTES

Methanation of Carbon Dioxide over Preoxidized Rhodium

There is now growing evidence that oxidation-reduction treatments of metal surfaces can greatly enhance their catalytic activity with regard to various hydrogenation reactions (1-13).

The simplest way of explaining this effect was to invoke the ability of O_2 to burn off impurities such as carbonaceous residues appearing under reaction conditions or, most frequently, C or S diffusing to the surface from the bulk. However, as such an assumption could not account for all the experimental observations, it was suggested that oxygen could play an important catalytic function aside from its role in the removal of surface contaminants (2). In the particular case of CO and CO_2 methanation over Ni and Co (2, 5), Fe (3), or Rh (1, 7), the preferred explanation has been that the catalytic activity depends directly on the oxygen concentration in the near-surface region as a promoting factor. However, more recently, experiments have been performed on powders of rhodium oxides (15) with the opposite conclusion that placing Rh atoms in an oxide environment leads to a diminution of their hydrogenation ability. Such opposite statements cannot be reconciled unless one assumes that there exists some optimum oxygen content in the near-surface region. Another tentative explanation is that some roughening of the surface might occur and thereby increase the surface area (1, 13) or introduce new crystal faces of higher reactivity (1).

In the case of C_2H_4 hydrogenation (8-11), we have shown that the preceding assumptions were not able to account for the whole catalyst behavior. We have been led to assume that the H_2-O_2 reaction (or the extraction by H_2 of the oxygen preincor-

porated into the bulk) is able to distort the surface lattice and to create new centers especially active toward the hydrogenation reaction. Very high enhancement factors can be expected from such an assumption. Furthermore, as a result of the increased mobility due to the oxidation-reduction events, a gross surface rearrangement could also be expected and was easily demonstrated (10, 14).

We are now turning our attention to the methanation of CO_2 over rhodium. This reaction has been chosen rather than the methanation of CO as it had been reported to occur at a higher rate (1, 16, 17), a circumstance particularly suited to the small area of our sample, which is a rhodium ribbon. The most recent studies either dealt with supported Rh and did not report upon the effect of oxidizing pretreatments (17) or confirmed such an effect in the case of CO methanation only (12).

The rhodium ribbon (Heraeus, 99.99% purity, 3/100 mm thick, 1 mm wide, and 2 cm long) was similar to those used previously (10, 11) and it was cleaned following the same procedure. The same equipment was used and the catalytic activity was measured under normal pressure with a mixture (95% H_2 + 5% CO_2). Before being added to purified H_2 , CO_2 was passed over CuO at 200°C (oxidation of CO) and a de-oxo catalyst. After mixing the gases passed through a trap filled with glass beads at dry ice temperature. In a number of experiments the catalyst was maintained under a flow of carefully purified H_2 and its activity was monitored by mere replacement of H_2 by the equally flowing reactant mixture for 30 sec only. This procedure allowed the surface to be contacted with pure H_2 for

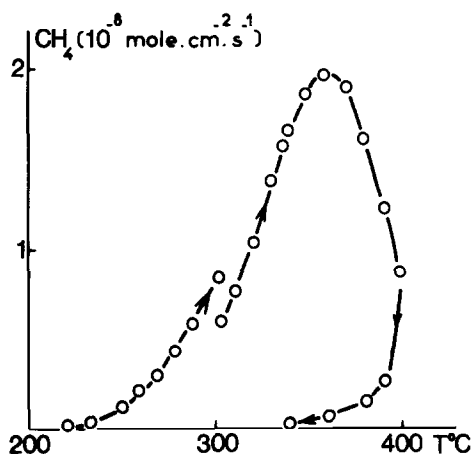


FIG. 1. Variation of the methanation rate as a function of temperature. Preoxidation with He + 15 ppm O₂ for 1 hr at 450°C. Cooling to 200°C in He + O₂. Permanent feed with H₂ + 5% CO₂ while the temperature was linearly increased (6°C/min). At 304°C, the temperature was maintained constant for 3 min.

most of the time and consequently to be protected against carbonaceous contamination to the most feasible extent.

When the sample was subjected to pure H₂ for a few hours at 400°C, no methanation activity could be observed up to 450°C (rate < 10⁻¹¹ CH₄ s⁻¹) regardless of whether the catalyst was fed in a continuous or a discontinuous mode.

On the contrary, oxidizing pretreatments resulted in a methanation activity which was easily observable. Typically the metal was exposed to a flow of O₂ doped He (He + 15 ppm O₂) for 1 hr at 450°C before being cooled to 200°C under He-O₂. The methanation activity was monitored while a linear program of heating was applied. The result is displayed in Fig. 1. The activity appeared near 220°C and passed through a maximum near 350°C. At 300°C, the temperature was kept constant for 3 min in order to see whether the rate remained constant. The contrary was observed, so the temperature was again increased. Once it reached 400°C, the temperature was decreased linearly to 200°C. The activity fell off rapidly. A new program of heating displayed no

more than residual activities. A third program resulted in a negligible activity.

Figure 2 shows the influence of the length of the oxidation pretreatments. It can be noticed that the four curves coincide at low temperatures whereas higher maxima activities are obtained and occur at higher temperatures for increasing times of preoxidation. In each case only a transient activity was induced.

When the probing procedure was replaced by the permanent feed of the catalyst with the reactant mixture, an appreciable decrease of rate soon occurred, most probably as a result of a partial contamination of the surface by carbonaceous material. The efficiency of the probing procedure was further attested by the fact that the variation of the catalytic activity did not depend on the probing frequency inasmuch as the time lag between two successive probings was higher than a few minutes (usually 3). More frequent probings did not allow enough time for H₂ to clear the surface.

Finally, another way of revealing the potential activity conferred to the catalyst by the pretreatment was applied. After the

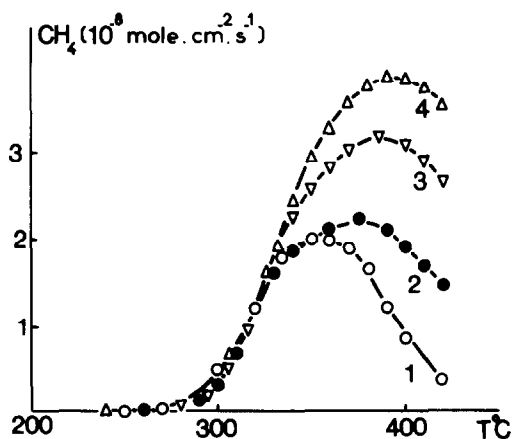


FIG. 2. Influence of the time of preoxidation upon the variation of the resulting methanation activity as a function of temperature. Preoxidation with He + 15 ppm O₂ at 450°C for 1 hr (curve 1, ○), 3 hr (curve 2, ●), 15 hr (curve 3, ▽), and 46 hr (curve 4, △). Permanent feed with H₂ + 5% CO₂. Rate of heating: 6°C/min.

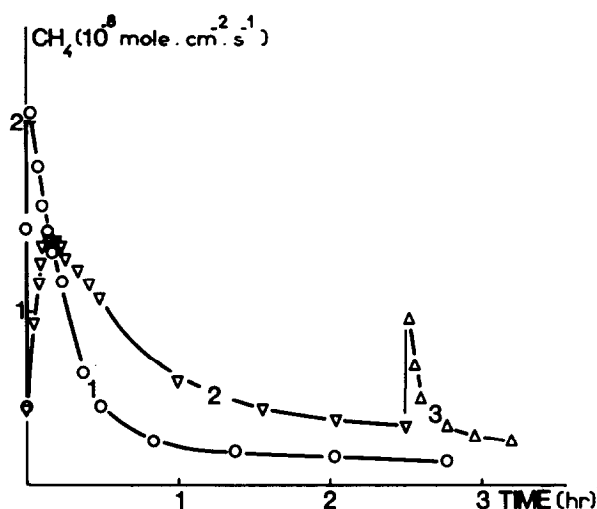


FIG. 3. Variation of the methanation rate as a function of time on stream at 325°C. Preoxidation with He + 15 ppm O₂ for 1 hr at 450°C. Cooling to 325°C in He + O₂. Discontinuous probing of activity with H₂ + 5% CO₂, the catalyst being permanently fed either with pure H₂ (curve 1, ○) or pure He (curve 2, ▽). Curve 3 (△) was obtained following curve 2, when substituting H₂ for He.

rhodium sample had been submitted to the most frequent pretreatment (He-15 ppm O₂, 450°C, 1 hr) its temperature was maintained constant at some given value between 260 and 400°C. The catalyst was then fed with pure H₂ and the usual probing of activity showed that the rate started to increase for a few minutes before displaying a decrease which was faster the higher the temperature. After some time (from 20 min to 1 hr) the decrease of rate as a function of time was much slower (about 15%/hr). Curve 1 of Fig. 3 illustrates this behavior at 325°C. After deactivation the catalyst was resubmitted to the same reactivating pretreatment and was thereafter maintained at 325°C. It was then flushed with pure He instead of pure H₂ whereas its activity was probed in the same discontinuous manner. Contacting the preoxidized catalyst with short flushes of reactant mixture caused the reduction of a part of the surface as well as permitting the measurement of the resulting activity. This procedure gave rise to the transient behavior depicted by curve 2 of Fig. 3. After having been subjected to these conditions for a little more than 2 hr, the catalyst was suddenly fed with pure H₂

while its activity continued to be monitored in the same way. A fast reactivation resulted and was followed by deactivation (curve 3).

The experiments reported here confirm that preoxidation of Rh causes a dramatic enhancement of its activity in the methanation of CO₂. The extent of the enhancement cannot be appreciated accurately as no CH₄ formation could be detected when no preoxidation was applied. Therefore we can state that preoxidation allows the rate to be increased by a factor of 100 (and more probably a factor of 1000) at the lowest estimate. So strong an activation cannot result from a mere roughening effect. Moreover, the ribbon remained smooth after the experiments.

We have shown previously (10) that a prolonged exposure of Rh to pure H₂ at 300 or 400°C maintained its surface clean as no contaminant could be detected by means of Auger electron spectroscopy. Moreover, our probing procedure most often used protected the surface against carbon contamination. The reactivation by oxidizing pretreatment cannot therefore be viewed as consisting only of a cleaning effect. The in-

roduction of oxygen on the surface and in the near-surface region is an essential step in the drastic strengthening of activity. Conversely, the deactivation observed upon prolonged exposures to H_2 must be ascribed to the depletion of the preincorporated oxygen. Increasing the time of preoxidation at a given temperature causes a thickening of the oxide film and therefore a delayed depletion under H_2 reduction. This behavior is clearly illustrated by the curves of Fig. 2.

When the variation of the catalytic activity conferred on the metal was studied as a function of time on stream at a constant temperature an initial increase of activity was always observed for a few minutes. This fact had not been reported by other authors probably by reason of the inadequacy of their experimental set-up to monitor rapid variations of rate. This behavior might suggest at first that there exists some optimum oxygen content of the surface (or the near-surface region). However, the results reported in Fig. 3 are at variance with that point of view. Thus when the catalyst was fed with pure He and submitted to reduction but for the probing periods (curve 2), one could expect a slower attainment of the optimum oxygen content, but the corresponding activity should have been the same as in curve 1. Moreover, when H_2 was substituted for He a faster decrease of activity should have occurred as a result of the increased rate of reduction. However, exactly the reverse was observed.

The complete catalyst behavior can be rationalized on the basis of our preceding views. If the reduction process itself is taken as responsible for the activation by reason of its *transient* distorting effect upon the surface, the initial increase of activity under reduction conditions is understood as an increase of the surface content of active centers. Dwyer and Somorjai (3) have suggested a related idea in the case of Fe. The passage through the maximum activity corresponds to the rate of production of active

sites being equal to that of their spontaneous decay. We can therefore easily understand the rate increase resulting from the replacement of He by H_2 as due to the acceleration of the rate of reduction.

Work is now in progress to describe the very strong preoxidation effect more fully and to deepen the discrimination between an interpretation based upon the beneficial effect which might result from the mere presence of oxygen and an activation due to the reduction process itself. The latter can be understood as resulting from the poor structural order which may reasonably be assigned to the nascent metal surface as a transient property.

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