JOURNAL OF CATALYSIS 146, 586–590 (1994)

NOTE

Kinetic Oscillations during Acetylene Hydrogenation over Pt/Al_2O_3 and Pd/Al_2O_3 in the Presence of CO

Systems that exhibit kinetic self-oscillations are fascinating. It is not surprising that this subject has received much attention, and many papers dealing with theoretical and experimental work concerning self-oscillations have been published during the last decade. A complete survey of the subject is given, e.g., in (1–6).

The most extensively studied reaction is the oxidation of CO over Pt, Pd, and CuO, where self-oscillations have been found. Self-oscillations have also been found in the oxidation of H_2, NH_3, and different hydrocarbons. The decomposition of N_2O over CuO catalyst and the NO + CO reaction over Pt are further examples of catalytic systems where oscillations have been found. Examples of catalytic hydrogenation reactions that show self-oscillations are not very common. Self-oscillations have been reported for the hydrogenation of CO (7, 8), nitrobenzene (9), ethylene (10, 11), and acetylene (12). This field has, however, not been extensively studied.

Numerous mechanisms have been proposed in order to explain the oscillations in different systems. Examples of these are adsorption-induced surface reconstruction (1), mechanisms involving a subsurface reservoir of a reactant (13, 14), and periodic formation of an oxide or a carbon layer (15, 16). All these models have in common the fact that the reactivity of the catalyst is periodically changed.

The aim of this paper is to report a new catalytic system that exhibits kinetic oscillations, namely the hydrogenation of acetylene in the presence of CO over Pt/Al_2O_3 and Pd/Al_2O_3. Under present conditions, CO does not take part in any reaction. Despite this, CO probably plays a significant role for the oscillations. Earlier experiments have shown that strongly adsorbed CO can be displaced by acetylene (17, 18). A periodic change in the CO coverage on the surface is therefore not unlikely.

The selective hydrogenation of acetylene from an ethylene stream is an industrially important process. It is essential that the ethylene feed for production of polyethylene should be free from acetylene. In order to achieve a good selectivity, the presence of CO is necessary. In this light, the oscillations described below are very interesting even from an industrial point of view.

Two commercial catalysts, Pt/Al_2O_3 (Aldrich) and Pd/Al_2O_3 (Aldrich), were used in all the experiments. The active metals of the two catalysts are deposited at the exterior of the catalysts pellets. The characteristics of the catalysts are presented in Table 1. About 0.5 g of the catalyst (11 $\frac{1}{8}$ pellets) was packed together in a stainless-steel tube reactor (∅ = 3 mm, L = 10 cm). The reactor was placed in a precision oven (Perkin–Elmer) and the temperature was measured by a thermocouple at the end of the reactor.

The gases used, N_2, H_2, D_2, C_2H_2, and 0.56% CO in Ar, with a purity of >99.98%, were all delivered by AGA (Sweden). The flow rate through the reactor was measured and controlled by mass flow controllers. In the experiment with 2-ethyl-hexenal, N_2 was passed through a heated evaporator filled with the aldehyde. The aldehyde was 99.5% pure and it was delivered by Nest Oxo (Sweden). The HD formation was measured every second with a quadrupole mass spectrometer (Balzers QMG 311).

In earlier studies (17, 18) we found that acetylene rapidly displaced CO from a Pd catalyst. In a completely different study (19), concerning the hydrogenation of aldehydes over Pt/Al_2O_3, we also found that the catalyst was poisoned by CO produced by decarbonylation of the aldehyde in a side reaction. With these two findings in mind we tried to increase the hydrogenation rate of the aldehyde by having a small amount of acetylene present during the hydrogenation. The idea was that acetylene should continuously displace CO from the catalyst and thus prevent the deactivation during the hydrogenation of the aldehyde.

No measurable increase in the hydrogenation rate was observed over the Pt/Al_2O_3 catalyst by the addition of acetylene. A H_2/D_2 mixture was used and the resultant HD formation was employed as a measure of the free surface for hydrogen adsorption. Surprisingly, however, the HD formation started to oscillate when acetylene was added. Figure 1 shows how the HD formation first decreased when the aldehyde was added to a feed of H_2, D_2, and N_2 but then started to oscillate when acetylene was also added. The decrease in the HD formation when the

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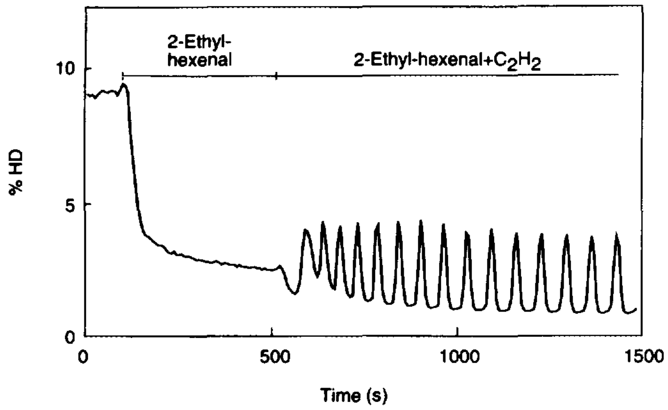

FIG. 1. HD formation over 0.5 g 0.5% Pt/Al_2O_3 in a tube reactor at 83□C. 10% H_2, 10% D_2, 0.36% 2-ethyl-hexenal, 1.5% C_2H_2, inert gas N_2, flow rate 1.7 ml/s.

aldehyde was added is attributed to CO formed from the decarbonylation of the aldehyde.

The aldehyde in the oscillations was suspected to produce CO. Therefore, it seemed probable that the hydrogenation of acetylene in the presence of CO would also oscillate even in the absence of the aldehyde. Indeed, this system did reveal oscillations in the HD formation. Figure 2 shows these oscillations during the hydrogenation of acetylene over a Pt/Al_2O_3 catalyst for different concentrations of CO at 363 K. At low concentrations of CO, the HD formation was high without any oscillations. Increasing the CO concentration resulted in oscillations, and at even higher CO concentrations the HD formation was almost completely inhibited.

TABLE 1

Catalyst Characterization

Catalyst	Wt% metal	BET surface area (m^2/g)	Dispersion[a] (H/*M*)
Pt/Al_2O_3 Aldrich 20.601-6	0.55	109.6	0.47
Pd/Al_2O_3 Aldrich 20.574-5	0.5	82.1	0.64

[a] From hydrogen adsorption assuming a 1 : 1 H : *M* ratio.

Figure 3 shows the oscillations over Pt/Al_2O_3 for different acetylene concentrations at 363 K and 146 ppm CO. At low and high concentrations of acetylene, the HD formation was low without any oscillations, and between these concentrations the HD formation oscillated. It is known that the hydrogen adsorption can be hindered by acetylene even in the absence of CO. Therefore, it is not surprising that the HD formation was very low at high concentrations of acetylene. Nor is it strange that the HD formation is inhibited at high concentration of CO, since CO hinders the adsorption of hydrogen and the adsorption energy of CO is very high.

The period time of the oscillations increased at lower temperature, and oscillations were found only in the temperature interval of 343 to 383 K under the present conditions (14–364 ppm CO, 0.8–2.5% acetylene).

Also, a Pd/Al_2O_3 catalyst exhibited oscillations in the

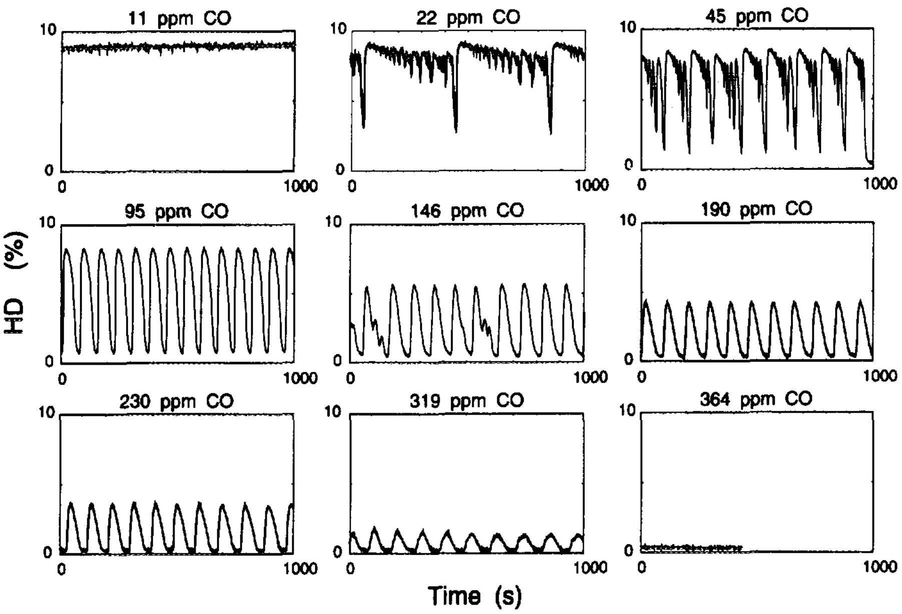

FIG. 2. Oscillations in the HD formation during hydrogenation of acetylene over 0.5 g 0.5% Pt/Al_2O_3 at different CO concentrations. $H_2 : D_2 : N_2$ = 10 : 10 : 80, 1.2% C_2H_2, T = 363 K, overall flow rate 2 ml/s.

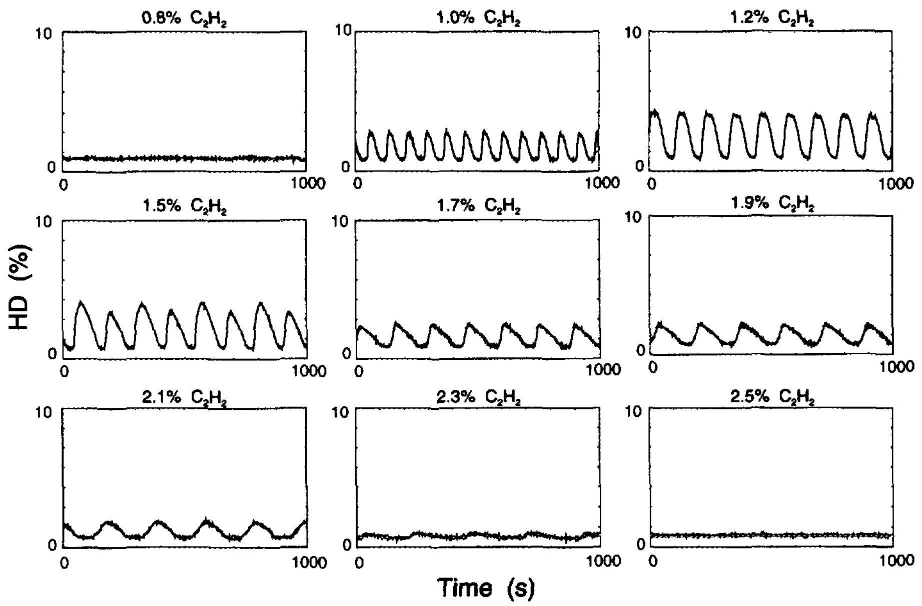

FIG. 3. Oscillations in the HD formation during hydrogenation of acetylene in the presence of 146 ppm CO over 0.5 g 0.5% Pt/Al_2O_3 at different C_2H_2 concentrations. $H_2:D_2:N_2 = 10:10:80$, $T = 363$ K, overall flow rate 2 ml/s.

hydrogenation of acetylene in the presence of CO. The temperature interval where the oscillations occurred was, however, lower compared with that for the Pt/Al_2O_3 catalyst. In Fig. 4 the oscillations are shown for different CO concentrations at 323 K.

Recently, Bos and Westerterp (12) reported oscillations in the temperature during the hydrogenation of acetylene without any addition of CO over a single pellet of a Pd/Al_2O_3 catalyst. However, they did not report the purity of the gases used. Based on our observations, the presence of CO is believed to be necessary to achieve oscillations. Even a very low concentration of CO may affect the oscillations over a single pellet of Pd/Al_2O_3 at low temperatures. Detection of CO at such low levels is not always possible.

The most extensively investigated system that shows

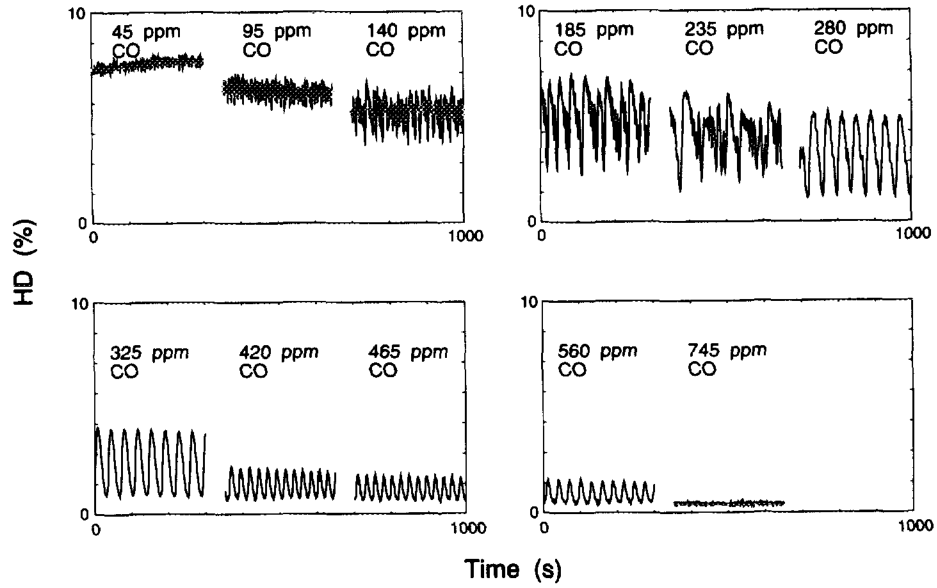

FIG. 4. Oscillations in the HD formation during hydrogenation of acetylene over 0.5 g 0.5% Pd/Al_2O_3 at different CO concentrations. $H_2:D_2:N_2 = 10:10:80$, 1.2% C_2H_2, $T = 323$ K, overall flow rate 2 ml/s.

oscillatory behavior is the oxidation of CO over different platinum single crystals at vacuum conditions. These systems are, in contrast to real catalysts at high pressures, very well defined, and isothermal conditions can easily be achieved. On supported catalysts the temperature on the small crystallites may differ from that of the support material and isothermal conditions therefore cannot be guaranteed. This is a problem since the oscillations may be associated with non-isothermal conditions. In the present study, the temperature was measured in the outflow of the reactor and no temperature changes were seen within ±0.1 K during the oscillations. However, this does not guarantee strictly isothermal conditions on the metal crystallites of the catalyst.

In a review by Ertl (1), the author discussed different mechanisms for the oscillations in the CO oxidation at high vacuum conditions. He concluded that the oscillations over certain platinum crystals can be explained in terms of CO-induced surface reconstruction, and that the sticking coefficient of oxygen is markedly increased over the reconstructed surface. Over platinum crystals such as Pt(111) and Pt(210), which do not reconstruct upon the adsorption of CO, no oscillations occur according to Ertl (1).

A surface which does not reconstruct upon the adsorption of CO but still shows oscillatory behavior is Pd(110). Bassett and Imbihl (13) have explained this by a model involving subsurface oxygen. This oxygen is believed to be situated just beneath the surface and will act as an oxygen reservoir. The sticking coefficient of oxygen is assumed to decrease as the reservoir fills. Both the subsurface oxygen and the surface reconstruction model have in common the fact that the sticking coefficient of oxygen changes with the coverage.

The present system differs from the oxidation of CO in that there is no reactive removal of CO. However, in other studies it has been found that CO is displaced by acetylene (17, 18). A model involving CO-induced surface reconstruction would perhaps be possible. Also, a model similar to that of Bassett and Imbihl might be possible. Instead of subsurface oxygen, a model with subsurface hydrogen would be imaginable. There is some evidence that hydrogen is adsorbed in state just beneath the surface on palladium and platinum (20). Perhaps the sticking coefficient of hydrogen is decreased by the presence of hydrogen in the subsurface state, analogous to the case with oxygen.

Other models that have been proposed are the "oxygen" and the "carbon" models (15, 16). In these models the surface is assumed to be covered periodically with an oxide and a carbon layer, respectively. However, under the present conditions, formation of these layers seems rather unlikely.

In order to reveal the mechanism for the oscillations during the hydrogenation of acetylene in the presence of CO, experiments under more well-defined conditions are necessary. Here the purpose has been to point out the phenomenon.

Kinetic self-oscillations in the HD formation were found during the hydrogenation of the α,β-unsaturated aldehyde, 2-ethyl-hexenal, over a Pt/Al_2O_3 catalyst in the presence of acetylene. The role of the aldehyde in the oscillations was believed to be the production of CO in a side reaction (R–CHO → R–H + CO). This was confirmed by the fact that the hydrogenation of acetylene exhibited self-oscillations even in the absence of the aldehyde when small amounts of CO were added to the feed.

Self-oscillations in the HD formation during the hydrogenation of acetylene were also found over a Pd/Al_2O_3 catalyst. The temperature regime where the oscillations occurred over the Pd/Al_2O_3 catalyst was, however, lower than that of the Pt/Al_2O_3 catalyst.

The presence of CO was thought to be essential for the oscillations. This was because no oscillations were found during the hydrogenation of acetylene in the absence of CO, and because acetylene is able to displace CO from the catalyst surface. The coverage of CO and acetylene on the catalyst surface is also believed to oscillate. In order to reveal the mechanism for these oscillations, however, experiments under more specific conditions are necessary.

ACKNOWLEDGMENT

The financial support of the Swedish Research Council for Engineering Sciences (TFR) is gratefully acknowledged.

REFERENCES

1. Ertl, G., *Adv. Catal.* **37,** 213 (1990).
2. Razón, L. F., and Schmitz, R. A., *Chem. Eng. Sci.* **42**(5), 1005 (1987).
3. Mukesh, D., Goodman, M., Kenney, C. N., and Morton, W., *in* "Catalysis," Vol. 6. Alden Press, Oxford, 1983.
4. Gurel, O., and Gurel, D., *in* "Topics in Current Chemistry" (F. L. Boschke, Ed.), Vol. 17. Springer-Verlag, Berlin, 1983.
5. Sheintuch, M., and Schmitz, R. A., *Catal. Rev.—Sci. Eng.* **15**(1), 107 (1977).
6. Slin'ko, M. G., and Slin'ko, M. M., *Catal. Rev.—Sci. Eng.* **17**(1), 119 (1978).
7. Pyatnitskii, Ju. I., Filonenko, G. V., Stasevith, V. P., Shaprinskaya, T. M., and Gritsenko, V. I., *in* "Unsteady State Processes in Catalysis, Proceedings on the International Conference (Y. S. Matros, Ed.), p. 401. VSP, Novosibirsk, USSR, 1990.
8. Pyatnitskii, Ju. I., and Filonenko, G. V., *React. Kinet. Catal. Lett.* **44**(2), 499, (1991).
9. Petrov, L., Vladov, Ch., Eliyas, A., Kirkov, N., Tenchev, K., Bonev, Ch., Filkova, D., and Prahov, L., *J. Mol. Catal.* **54,** 237 (1989).
10. Nijama, H., and Suzuki, Y., *Chem. Eng. Commun.* **14,** 145 (1982).
11. Lielmezs, J., and Aleman, H., *Thermochim. Acta* **161,** 267 (1990).
12. Bos, A. N. R., and Westerterp, K. R., *in* "Unsteady State Pro-

cesses in Catalysis, Proceedings on the International Conference" (Y. S. Matros, Ed.), p. 503. VSP, Novosibirsk, USSR, 1990.
13. Bassett, M. R., and Imbihl, R., *J. Chem. Phys.* **93**(1), 811 (1990).
14. Ladas, S., Imbihl, R., and Ertl, G., *Surf. Sci.* **219,** 88 (1989).
15. Yeates, R. C., Turner, J. E., Gellman, A. J., and Somorjai, G. A., *Surf. Sci.* **149,** 175 (1985).
16. Collins, N. A., Sundaresan, S., and Chabal, Y. J., *Surf. Sci.* **180,** 136 (1987).
17. Cider, L., Schröder, U., Schöön, N.-H., and Albinsson, B., *J. Mol. Catal.* **67,** 323 (1991).
18. Schröder, U., Cider, L., and Schöön, N.-H. *in* "Preprint and Abstract Book, 10th International Congress on Catalysis, Budapest, 1992," p. 91. Inst. Isotopes Hung. Acad. Sci., Budapest, 1992.
19. Schröder, U., and Andersson, B., *J. Catal.* **132,** 402 (1991).
20. Christmann, K. R., *in* "Hydrogen Effects in Catalysis: Fundamentals and Practical Application" (Z. Paál and P. G. Menon, Eds.), Vol. 31, p. 44. Dekker, New York, 1988.

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Received February 23, 1993; revised September 8, 1993