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Radioactive Tracer Techniques for Study of Reactions on Industrial Catalysts

II. Enhanced Desorption of CO from a Pd/Al_2O_3 Catalyst Due to the Influence of C_2H_2 and NO in the Gas Phase

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Preadsorbed ^{14}CO on Pd/Al_2O_3 corresponding to a complete coverage of CO was exchanged by C_2H_2 (1000 ppm in Ar) or NO (1000 ppm in Ar) at atmospheric pressure and at different temperatures (230–375 K). The rate of the displacement and the amount of displaced labelled CO were dependent on the temperature. The exchange process was followed with an *in situ* method for measuring radioactivity of soft β^- emitters. Different mechanisms of this displacement process are discussed. © 1993 Academic Press, Inc.

INTRODUCTION

It has long been an accepted fact that the rate of desorption is dependent only on the temperature and on the fractional coverage of the adsorbed species. The first exception to this general rule was reported by Tamm and Schmidt (*1*, *2*), who observed that the desorption rate of one isotope of hydrogen was enhanced by the presence of another isotope of hydrogen in the gas phase. The desorption was found to be much faster than the thermal desorption. A corresponding result was reported by Klier *et al.* (*3*) for the desorption of CO. The influence of gas-phase CO on the CO desorption soon became the object of a great number of studies during the 1970s and 1980s (see Ref. (*4*) for references). No generally accepted explanation of this phenomenon has hitherto been given. One main question is whether this enhanced desorption can be explained by a mechanism resulting in a direct pressure dependence. Many authors, who have performed the experiments at conditions where the coverage of CO is not complete, state that the enhanced desorption may be explained by an increased coverage of CO at the somewhat increased CO pressure obtained as a result of the CO flux coming into the vacuum chamber. This explanation is based on the fact that the desorption energy of CO is decreased by higher CO coverage.

The desorption of one kind of substance can also be enhanced by another substance in the gas phase. As found by Tamaru *et al.* (*5*), the desorption of H_2 was much more rapid in the presence of CO in the gas phase than the common thermal desorption. Most interestingly, observation is that the contrary effect has also been reported (*6–11*), i.e., the enhanced desorption of CO due to the presence of H_2 in the gas phase. These effects were both observed at high vacuum conditions.

At reaction conditions more related to an industrial process, Cider and Schöön (*12–14*), and Cider *et al.* (*15*) found that C_2H_2 in the gas phase strongly enhanced the desorption of CO from a Pd/Al_2O_3 catalyst. Thus a short pulse of C_2H_2 displaced CO from the catalyst and thereby temporarily restored the activity for the hydrogenation of C_2H_4 in the presence of CO in the gas

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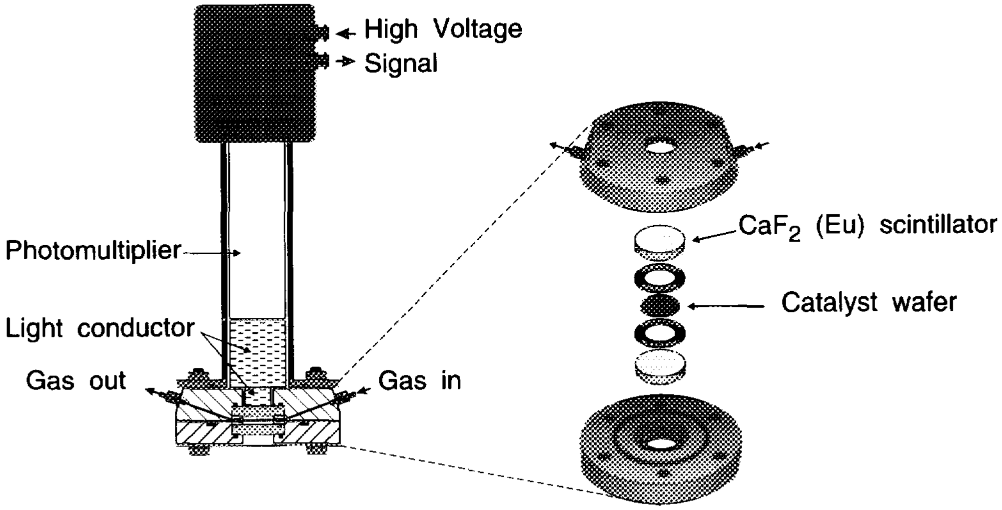

FIG. 1. The reactor for *in situ* radioactive tracer experiments.

phase. The competition between C_2H_2, C_2H_4, H_2, and CO for the active sites was mainly studied indirectly by these authors on the basis of the outlet gas composition. With the new radioactive tracer technique described in the first paper in this series (*4*), we demonstrated the possibility to monitor directly, in a simple way, the adsorbed amount of a soft β^- emitting compound in a very thin disc of a commercial catalyst. This technique was used to follow the very fast desorption of preadsorbed labelled CO in the presence of unlabelled CO in the gas phase. In the present study, the enhanced desorption of CO influenced by C_2H_2 or NO in the gas phase is studied in greater detail with this technique.

EXPERIMENTAL

Figure 1 shows the continuous flow reactor, which has been described in detail elsewhere (*4*, *16*). The emitted β^- particles from the radioactive labelled CO are absorbed in a europium-doped CaF_2 crystal, which emits light upon the absorption. The intensity of the light, which is proportional to the amount of labelled CO on the catalyst and in the gas phase, is measured by a photomultiplier (Thorn Emi 9900).

The reactor cell was heated by cartridge heaters and the experiments below 25°C were performed with the reactor immersed in a refrigerant.

A 5 wt% Pd/Al_2O_3 catalyst (Aldrich, catalogue no. 20,571-0) with a particle size of less than 44 μm was used in all experiments. About 0.15 g of the catalyst powder was pressed under 7 tons of pressure into a disc and placed in the reactor. This preparation of the disc followed the common procedure used in FTIR studies. Before the experiments the catalyst disc was treated with H_2 at 100°C for 1 hr. The percentage exposed of Pd (Pd dispersion) in the catalyst was determined to be 13% by CO adsorption, assuming the stoichiometry CO/Pd = 1. This determination was performed with the catalyst disc mounted in the reactor after treatment with H_2. The characteristics of the catalyst disc are given in Table 1. The gases used, Ar, H_2, C_2H_2, NO, and CO, 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 labeling procedure, 5 mCi ^{14}CO (53 mCi/mmol) Amersham (England), delivered in a glass ampoule, was transferred to a 1-

TABLE 1

Catalyst Disc Properties

Pd content	5 wt%
Pd dispersion	0.13
BET area	118 m^2 g^{-1}
Average pore radius	75 Å
Catalyst disc porosity, ε	0.59
Catalyst disc density, ρ	1506 kg m^{-3}
Disc thickness	0.23 mm
Disc diameter	18 mm
Mass transfer coefficient for CO, k_c (25°C)	6.3×10^{-3} m s^{-1}
Effective diffusivity for CO in the disc, D_{eff} (25°C)	1.2×10^{-6} m^2 s^{-1}
Absorption coefficient for β^- particles in the catalyst, μ	12,389 m^{-1}

liter evacuated gas flask. This was then filled to 3.5 MPa with 5700 ppm unlabelled CO in Ar. The total CO concentration in the labelled gas was 5775 ppm.

RESULTS AND DISCUSSION

1. *Displacement of Adsorbed CO by C_2H_2 or NO*

It was previously shown (*4, 16*) that preadsorbed labelled CO, on the same kind of catalyst as used in the present work, was rapidly displaced by unlabelled CO in the gas phase at 50 Pa $\leq P_{CO} \leq$ 200 Pa. This displacement was very fast even at −43°C with a rate proportional to the CO pressure. In the absence of CO in the gas phase, the desorption was negligible.

The present study concerned the displacement of preadsorbed labelled CO on Pd/Al_2O_3 by C_2H_2 or NO. All the experiments were performed at atmospheric pressure, and in the preadsorption procedure the catalyst was treated with labelled CO (1000 ppm CO in Ar) at the same temperature as the experiment in question. Figure 2 shows the displacement of CO by C_2H_2 (1000 ppm in Ar) as a function of temperature at atmospheric pressure. The displacement was very rapid just after a step to C_2H_2, but decreased as the coverage of CO became lower. Moreover, the total displaced amount of CO was found to be very dependent on the temperature. In contrast to the incomplete displacement of CO by C_2H_2, preadsorbed labelled CO is completely displaced by unlabelled CO. The displacement by 663 ppm CO in Ar at atmospheric pressure and 25°C is shown as a dotted line in Fig. 2.

Preadsorbed labelled CO was also rapidly displaced by NO (1000 ppm in Ar) as shown in Fig. 3. The rate and the total amount of CO displaced by NO were again temperature-dependent.

It is important to stress that the desorption of CO in the presence of C_2H_2 or NO in the gas phase cannot be explained by any reactions between CO and these compounds. The outlet gas was carefully examined for every conceivable product due to possible reactions with these compounds.

The enhanced desorption of CO in the presence of C_2H_2 or NO in the gas phase is not easy to account for. It is natural to examine the different explanations proposed for the corresponding exchange of adsorbed CO by CO in the gas phase.

2. *Displacement via Intermediates or Transition-State Complexes*

As mentioned in the introduction, the rapid displacement at vacuum conditions of preadsorbed CO by CO in the gas phase was assumed to be explained by an increased coverage of CO, due to increased pressure of CO when a flux of CO is introduced into the vacuum chamber. But the fact that the catalyst surface is almost completely covered with CO before the desorption starts in the present study contradicts an explanation based on an increased coverage. The thermal desorption is negligible even at this high coverage in the temperature interval studied from −43 up to 100°C. It should be emphasized in this connection that Yamada *et al.* (*17*) reported that the desorption rate, in fact, is directly proportional to the CO pressure. Thus alternative explanations are worth seeking.

To explain the direct dependence of the

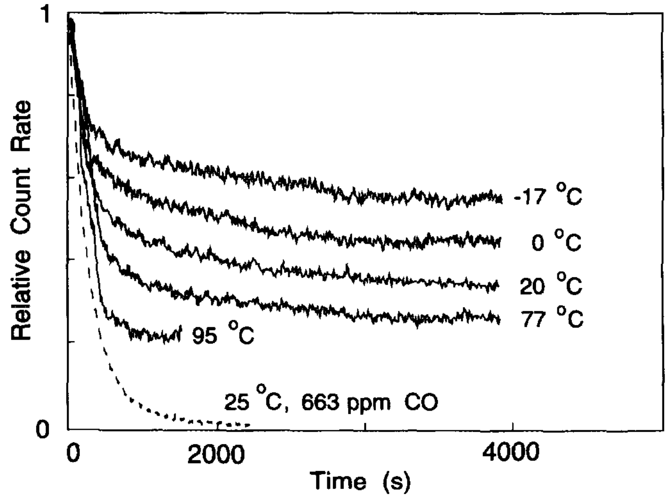

FIG. 2. The displacement of adsorbed labelled CO from Pd/Al_2O_3 by C_2H_2 (1000 ppm in Ar) as a function of temperature at atmospheric pressure. The relative count rate was defined as the ratio between the count rate at the time *t* and the count rate at the start of the isotopic exchange.

desorption rate on the pressure of CO, C_2H_2, and NO, some kind of interaction between the gas molecule and the adsorbate molecule has to be considered. A mechanism involving some intermediate or transitional state might be imagined. Accordingly, Yates *et al.* (*18*) discussed the formation of the intermediate $Rh(CO)_3$ as a possible explanation for the displacement of adsorbed CO on isolated rhodium atoms by CO in the gas phase. In applying this mechanism to the displacement of adsorbed CO by C_2H_2 or NO, it is important to refer to Dictor (*19*), who did not find any experimental evidence for the presence of the Rh(NO)(CO) complex on the Rh surface in displacement of CO by NO at 250°C. This result indicates that the enhanced desorption of CO by the influence of C_2H_2 or NO does not proceed via the formation of such intermediates. Moreover, no evidence for a direct exchange mechanism via a transitional state similar to the SN2 mechanism has yet been put forward. It should be mentioned that ordinary displacement processes between species in gas phase and loosely bonded adsorbed species have been described in terms of an SN2 mechanism (*20*). A first-order dependence on the desorption rate would be expected with an SN2 mechanism.

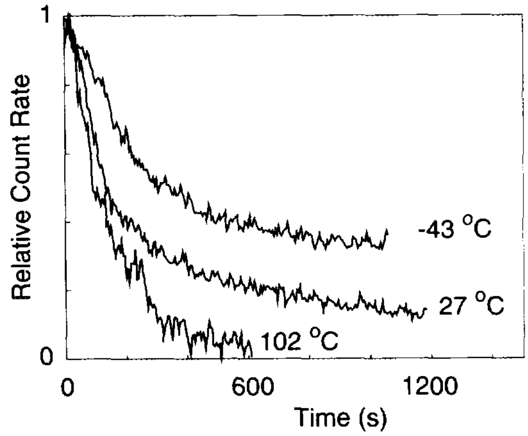

FIG. 3. The displacement of adsorbed labelled CO from Pd/Al_2O_3 by NO (1000 ppm in Ar) as a function of temperature at atmospheric pressure.

3. *Displacement via Redistribution of Adsorbed CO to CO Islands*

Even if the fractional coverage of CO is high at the present experimental conditions, we cannot exclude the possibility that there is a small fraction of vacant sites or a small fraction of very loosely adsorbed CO. This loosely bonded CO was found to desorb when flushing the catalyst disc with Ar at room temperature. Hence it is possible that C_2H_2 or NO can reach vacant sites without the formation of any intermediate complex or transition state. In regard to the enhanced desorption of CO in the presence of gas-phase CO, it must be noted that Yates and Goodman (*21*) found that preadsorbed $C^{18}O$, on strongly bonded states at vacuum conditions, was spread out over all the desorption states by further adsorption of $C^{16}O$, indicating a high mobility of CO on the surface. The enhanced desorption of the preadsorbed $C^{18}O$ was ascribed to an increased total coverage of CO at the somewhat higher pressure of CO due to the incoming CO flux. Thus, the initially strongly bonded $C^{18}O$ was desorbed from states of low desorption energy. These were populated by the further adsorption of $C^{16}O$.

A similar account of the displacement process has recently been supported by Parker *et al.*(*11*) in order to explain the very surprising enhanced desorption of adsorbed CO on Pt(111) caused by H_2 at low pressure. It is significant that all the adsorbed CO was desorbed in the presence of the gas-phase H_2. This effect was found at 45–75°C and 0.2 Torr H_2 pressure. These authors assumed that the large decrease in the desorption energy was caused by repulsive interaction in compressed CO islands formed on the surface as a result of the coadsorption with H_2.

It is not, however, likely that this kind of compressed CO islands is formed in the coadsorption of CO and C_2H_2, since the displacement of CO by C_2H_2 does not proceed to completion like the displacement by H_2. A reasonable explanation could be that some part of the C_2H_2 is rapidly dehydrogenated on the surface, giving rise to products which hinder the formation of CO islands with low desorption energy. This hypothesis is provisional since we know very little about the coadsorption of CO and C_2H_2 and how the desorption energy for CO depends on the coverage of CO in the presence of C_2H_2 on the surface.

4. The Incomplete Displacement of Adsorbed CO by C_2H_2

If we disregard the model of CO islands, it is logical to expect that the remaining adsorbed CO after initial displacement by C_2H_2 is more strongly adsorbed due to weaker repulsive interaction between adsorbed CO molecules. This weaker interaction is explained by the dilution of the adsorbed CO layer with C_2H_2, which contrary to CO lacks a dipole moment. A continuous increase of the desorption energy is therefore expected as a result of increased displacement of CO by C_2H_2. Since theoretical calculations have shown that the adsorption energy for C_2H_2 is lower than for CO, it follows that the activation energy for the displacement of CO by C_2H_2 will always be greater than the difference between the adsorption energies for CO and C_2H_2. According to the discussion above, this difference will increase with the displacement of CO. Consequently, the activation energy for the displacement should also increase with displacement, explaining the observed temperature dependence.

5. Displacement of Remaining Adsorbed CO after Initial Displacement by C_2H_2

Irrespective of the explanation for the limited ability of C_2H_2 to displace adsorbed CO, one immediate question is whether the remaining adsorbed labelled CO after the initial C_2H_2 treatment can be displaced by unlabelled CO in the gas phase. It should be noted that adsorbed C_2H_2 cannot be displaced by CO in the gas phase at these conditions (*12*). Figure 4 indicates that about 50% of the preadsorbed CO was replaced by 500 ppm C_2H_2 in Ar at 25°C and atmospheric pressure. A further treatment with 1000 ppm CO in Ar displaced another 30% of the preadsorbed labelled CO.

Since C_2H_2 is not displaced by CO, the enhanced displacement of labelled CO by

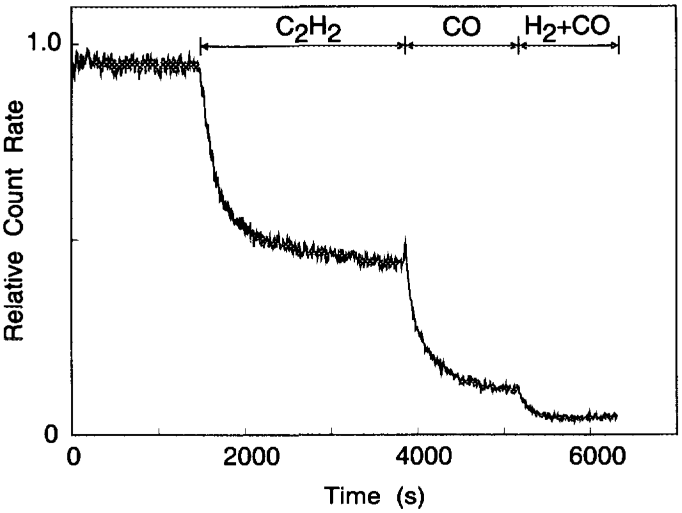

FIG. 4. The displacement of adsorbed labelled CO from Pd/Al_2O_3 by 500 ppm C_2H_2, followed by 1000 ppm CO and by a mixture of 10% H_2 and 1000 ppm CO at atmospheric pressure (Ar) and 25°C.

unlabelled CO in this second step of the experiment given in Fig. 4 probably cannot be explained by an increased coverage of CO due to the influence of gas-phase CO. This may support the idea of a simultaneous adsorption-desorption process with a direct energy transfer similar to the SN2 mechanism. According to this model, the activation energy for the displacement of CO by CO will be lower than for that of CO by C_2H_2 due to the lower adsorption energy of C_2H_2 compared to CO. Furthermore, the displacement rate would be pressure-dependent even at one and the same coverage according to this SN2 model.

In the final step of the experiment given in Fig. 4, the inflow to the reactor cell was changed to H_2 (10%) and CO (1000 ppm) in Ar at atmospheric pressure and 25°C. The remaining 20% of the preadsorbed labelled CO was almost completely desorbed by this treatment. It should be mentioned that treatment with only H_2 did not displace the preadsorbed labelled CO at these conditions. However, the treatment with H_2 results in a hydrogenation of the adsorbed C_2H_2 leaving vacant sites for CO adsorption. Adsorption of unlabelled CO on these sites makes the displacement of the remaining adsorbed labelled CO possible.

CONCLUSION

The unexpectedly fast displacement of preadsorbed CO on a Pd/Al_2O_3 catalyst disc by C_2H_2 or NO (1000 ppm in Ar) at atmospheric pressure and room temperature is likely to proceed through some direct exchange mechanism similar to the SN2 mechanism. In an alternative explanation of this exchange, it is important to note that a small fraction of vacant sites may exist despite the complete coverage of CO. The population of these vacant sites with C_2H_2 or NO may facilitate the exchange with the gas phase. In this exchange the adsorbed C_2H_2 or NO may force some adsorbed CO to move to adsorption states with lower desorption energy, which may act as an intermediate stage for the subsequent exchange process.

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