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Formation of CHO during interaction of CO and H_2 on alumina-supported Pd catalysts

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The reaction of CO and H_2 on alumina-supported Pd catalysts (2, 5 and 10 wt% Pd) has been studied by a transient pulse technique in vacuum (Temporal-Analysis-of-Products (TAP) reactor). CHO species were formed on a hydrogen-treated catalyst surface at temperatures between 423 and 530 K by the interaction of hydrogen solved in the palladium metal and CO (adsorbed at 300 K after reduction). The CHO species were released into the gas phase when hydrogen was pulsed over the catalysts. CHO is assumed to be an intermediate in the hydrogenation of CO to CH_4 starting at 560 K. No methanol was observed under the experimental conditions applied.

Keywords: hydrogenation of carbon monoxide; reaction mechanism; application of transient techniques; Pd/γ-Al_2O_3 catalyst

1. Introduction

Various reactions are catalyzed by supported palladium, such as CO oxidation [1–3], CO methanation [4,5], methanol synthesis [6–8], synthesis of higher alcohols [9] and partial oxidation of ethane to oxygenates [10]. Recently, much attention has been paid to the nature of surface species formed by the interaction of CO and H_2 with supported Pd catalysts [7,11–17]. Palazov et al. [11] observed different CH_xO species when passing mixtures of CO and H_2 over a Pd/Al_2O_3 catalyst applying in situ IR spectroscopy; methoxy surface species were identified for a H_2/CO ratio of 350, while a formate structure which probably originated from CHO species bonded to an Al–O group of the carrier was observed for a H_2/CO ratio of 3. The authors postulated that oxygenated species formed on the Pd and migrated onto the carrier by spillover, where they were stabilized. The carrier material appeared to be important, because on silica-supported Pd no formation of formate species was observed. It was further assumed that the methoxy species are intermediates in methanol formation and that the formate species were precursors leading to methane. Hindermann et al. [7], however, determined the surface con-

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centration of formyl species (CHO) on Pd–MgO–SiO_2 via chemical trapping and found a direct correlation between its concentration and the catalytic activity for methanol formation. Falconer and co-workers investigated the spillover process of partially hydrogenated CH_xO species on Pd/Al_2O_3 by TPD, TPR and isotopic labelling experiments [14,15]. They postulated that CH_xO is formed on Pd by the interaction of H_2 with preadsorbed CO which then spills over to the alumina support where it is really hydrogenated to CH_4. The above results underline the importance of CH_xO species in the reaction pathways of CO methanation and of methanol formation on supported Pd.

In the present study the formation of CH_xO intermediates in the interaction of CO and H_2 on alumina supported Pd was further elucidated by applying a transient vacuum pulse technique.

2. Experimental

2.1. CATALYSTS

γ-Al_2O_3 supported Pd catalysts of different Pd loadings (2, 5 and 10 wt%, designated as A2, A5 and A10) were prepared by incipient wetness method from γ-Al_2O_3 (Aluminiumoxid C, Degussa) and aqueous solutions of $Pd(NO_3)_2 \cdot 2H_2O$ (Fluka). The catalysts were characterized by BET-surface measurements and CO adsorption after reduction (cf. table 1).

The fresh catalyst was heated in vacuum to 773 K in order to remove any loosely bonded species from the surface. After reduction in hydrogen flow (10 ml min^{-1}) at ambient pressure for 1 h at 473 K the catalyst was cooled to 300 K in vacuum. TPD of H_2 (25 K min^{-1}) from these catalysts revealed desorption peaks at temperatures between 765 and 880 K, which increase in intensity with increasing Pd content of the catalysts. In the literature peaks at these temperatures are ascribed to the desorption of hydrogen dissolved in the palladium crystallites [19,20].

2.2. GASES

The following purity grades were applied: CO/He (1 : 10), CO (>99.996%), He (>99.999%) and H_2 (>99.999%). All gases were purchased from Messer-Griesheim.

Table 1
Physical properties of the applied alumina supported Pd catalysts [18]

Catalyst		S_{BET} (m^2 g^{-1})	CO adsorption [a] (μmol g^{-1})	Dispersion [a] (%)
A2	Pd(2 wt%)/Al_2O_3	80.1	10.1	5.9
A5	Pd(5 wt%)/Al_2O_3	74.6	31.9	7.5
A10	Pd(10 wt%)/Al_2O_3	68.0	80.0	7.4

[a] Determined by GC pulse method assuming an adsorption stoichiometry of Pd/CO = 1.

2.3. METHOD

The details of the vacuum transient pulse method applying the Temporal-Analysis-of-Products (TAP) reactor is described elsewhere [21]. Hence, only conditions specific to the present work are described in the following.

The reactor applied was made of Inconel with an inner diameter of 5.4 mm and a length of 42 mm. The catalyst (50 mg) was located between two layers of quartz; the total bed length amounted to approximately 28 mm. The reactor was placed in a vacuum chamber at a pressure of approximately 10^{-4} mbar. In the temperature range studied the temperature gradient over the whole reactor length amounted to less than 30 K, while the catalyst zone could be considered as isothermal.

The size of the gas pulses passed through the catalyst bed was approximately 10^{15} molecules per pulse. Under these conditions the gas transport through the reactor is dominated by Knudsen diffusion, where collisions in the gas phase are negligible. Therefore, active short-lived intermediates that desorb from the catalyst surface could be detected.

A quadrupole mass spectrometer (UTI 100 C) was used for monitoring the intensity of a given AMU as function of time. On the basis of the measured fragmentation patterns molar masses were chosen to identify the different compounds H_2 (AMU = 2), He (4), CH_4 (15,16), CO,CO_2 (28), CHO (29), CH_2O (30), CH_3OH (31), CO_2 (44), and HCOOH (46).

3. Results and discussion

In the following results are reported concerning the surface interaction of CO and hydrogen. For the different experiments performed a description of the catalyst pretreatment is given first.

The freshly reduced catalysts were treated with CO pulses at 330 K in order to precover the surface with chemisorbed CO. To achieve complete CO coverage of the different catalysts the quantity of pulsed CO amounted to five times the corresponding chemisorption capability, which was determined in separate experiments (cf. table 1).

After this pretreatment the catalyst was heated up in vacuum to reaction temperature, which varied from 300 to 725 K, and H_2 was pulsed over the catalyst. In the temperature range between 423 and 530 K a signal at AMU 29 was detected at the reactor outlet in the response to the H_2 pulse (cf. fig. 1). This signal was attributed to CHO species desorbing from the catalyst surface. Other substances that exhibit mass fragments at AMU 29, e.g., formaldehyde, methanol or formic acid, could be excluded because their characteristic AMUs 46, 31 and 30 were not observed. Together with AMU 29 a response at AMU 28 was observed that was ascribed to the fragmentation of CHO and desorbing CO. It should be mentioned that the signal at AMU 29 could also not be explained by the natural occurrence of

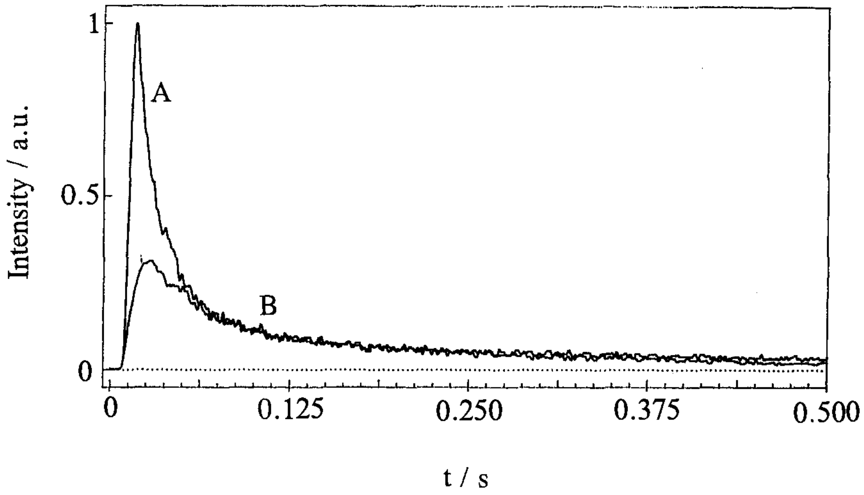

Fig. 1. Comparison of the maximum amount of CHO (AMU 29) formed in the response to a H_2 pulse over alumina-supported Pd catalyst with Pd-loadings of 10 wt% (curve A) and 5 wt% (curve B) after identical pretreatment (reaction temperature = 523 K).

1% ^{13}C in carbon monoxide because the observed intensity ratio 29/28 was 10–100 times higher. Additionally, the intensity of the response AMU 29 decreased to zero after a limited number of H_2 pulses, while no comparable change of the CO intensity was observed.

3.1. INFLUENCE OF TEMPERATURE

Formation of CHO started at 423 K and passed through a maximum with increasing temperature between 473 and 500 K. At these temperatures the formation of CHO was observed for some hundred H_2 pulses, before the intensity decreased to zero. At temperatures higher than 530 K only small amounts of CHO were detected, possibly due to its desorption or subsequent reaction. The temperature range in which CHO species were detected in the present work is close to that for the formation of surface formate structures on Pd/Al_2O_3 as observed in IR spectroscopic investigations by Palazov [11]. They reported on IR bands responsible for formate that showed maximum intensity at 423 K and decreased until 498 K.

When pulsing H_2 at temperatures $\geqslant 560$ K CH_4 was detected instead of CHO. The intensity of the CH_4 response remained stable for more than 1000 pulses of H_2. From the temperature dependence an activation energy of 71 ± 6 kJ/mol for the formation rate of CH_4 was determined when using catalyst A10. This activation energy is by 25–45 KJ/mol smaller than that observed over Pd/TiO_2 and Pd/SiO_2 amounting to about 95 and 115 kJ/mol, respectively [19].

No methanol or formic acid was detected in any of these experiments.

3.2. EFFECT OF Pd LOADING

The amount of CHO observed as response to the H_2 pulse increased with increasing amount of Pd surface (cf. fig. 1). This indicates that CHO is formed on Pd and not on the carrier. The increase might be explained by a larger number of palladium active sites on the surface and/or by the increased amount of dissolved hydrogen in the palladium bulk as will be discussed below.

3.3. MECHANISM OF CHO FORMATION

After the formation of CHO decreased to zero, the catalyst was cooled down to 300 K and additional CO was pulsed over the catalyst. Then the catalyst was heated to reaction temperature again. However, no CHO was observed in the response of the hydrogen pulses. This indicates that the decrease of the CHO signal cannot be attributed to the decrease in the CO surface coverage. Additionally, this experiment indicates that hydrogen in the formyl species does not originate from the gas phase hydrogen that is pulsed over the catalyst. Moreover, CHO formation predominantly occurs with participation of hydrogen dissolved in the palladium bulk. The role of the H_2 pulsed is therefore mainly to displace the surface-bonded CHO from its adsorption sites.

This assumption was further tested by pulsing D_2 instead of H_2 over the reduced and CO-precovered catalyst. Fig. 2 shows the responses of CHO (AMU 29) and

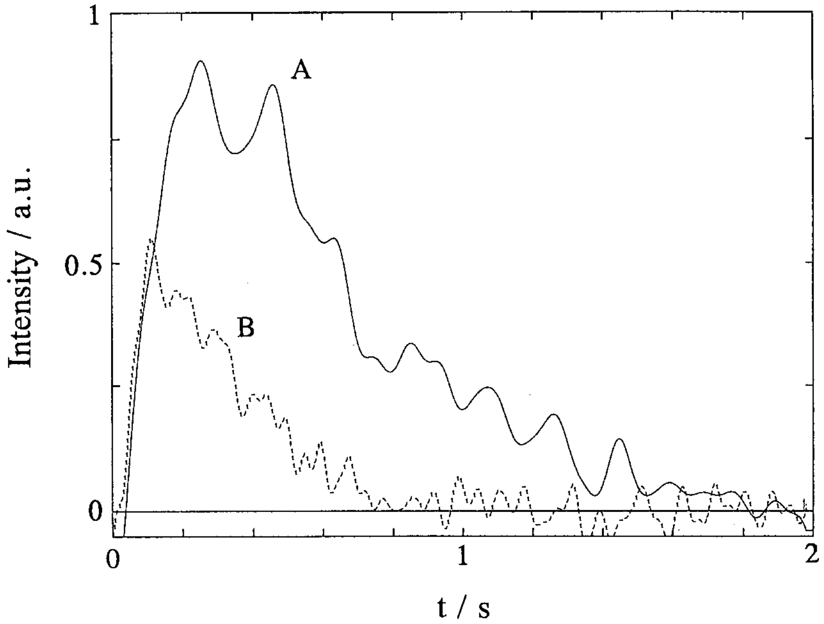

Fig. 2. Responses of CHO (AMU 29, curve A) and CDO (AMU 30, curve B) formation to a D_2 pulse at 473 K over Pd(10 wt%)/Al_2O_3.

CDO (AMU 30). It is obvious that CHO is the main product also when D_2 was pulsed; this supports the mechanism proposed above. However, to a much smaller extent also CDO was detected. This can be explained as follows: it was observed in separate experiments that at this temperature the interaction of D_2 leads to the predominant formation of HD and H_2 due to dissociative adsorption and incorporation. It can be assumed that the first incorporation of D leads to an enrichment of D especially in the subsurface, where it is available for the reaction with surface CO resulting in the formation of CDO. However, because the amount of D_2 pulsed was very small compared to dissolved H (which remained in the Pd crystallites after the reduction) the main product is CHO. However, it cannot be totally ruled out that the CDO observed is formed by the interaction of the pulsed gaseous D_2 with adsorbed CO.

The importance of dissolved hydrogen for the CHO formation was further investigated by the following experiment: a freshly reduced catalyst was preheated first to 1000 K to remove most dissolved hydrogen from the palladium bulk, after this it was cooled to 300 K and covered with CO like before. When pulsing H_2 at higher temperatures much less CHO formation was observed in the responses to the hydrogen pulses compared to similar experiments without prior removement of the dissolved hydrogen (cf. fig. 3). Furthermore, the amount of CHO decreased to nearly zero after 50 H_2 pulses while in the same experiment with hydrogen present in the palladium bulk no decrease was observed after 50 pulses.

The detected amount of CHO depended on the time interval between two conse-

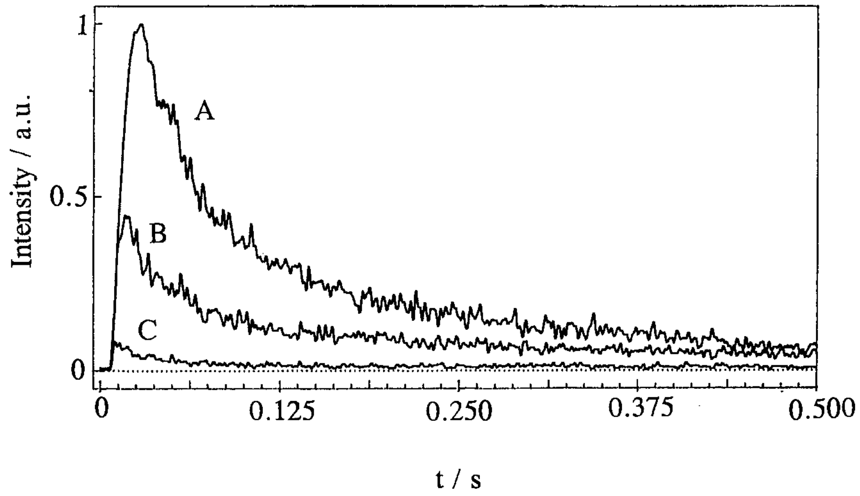

Fig. 3. CHO formation over 5 wt% Pd/Al_2O_3 at 530 K in the response of H_2 pulses in the absence and presence of H_2 dissolved in the palladium: (A) after normal reduction/CO coverage pretreatment, (B) after reduction, subsequent heating to 1000 K (removal of hydrogen solved in Pd) and CO coverage, (C) same as B after 50 pulses of H_2. (No decrease of the formed amount of CHO was observed under the experimental conditions of A.)

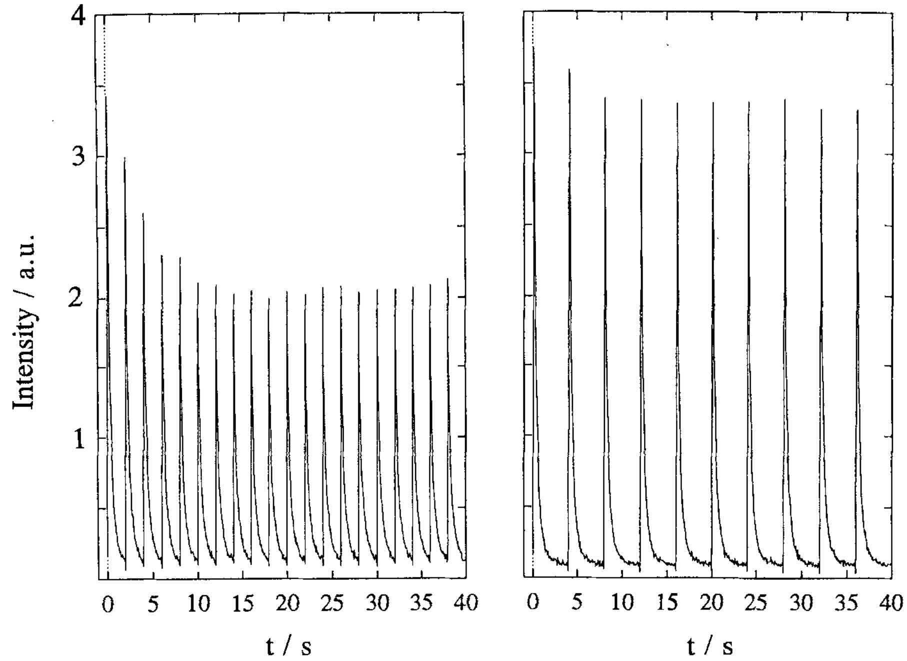

Fig. 4. Influence of the time interval between consecutive H_2 pulses on the CHO formation over Pd/Al_2O_3 at 443 K: (A) time interval = 2 s, (B) time interval = 4 s.

cutive H_2 pulses over the catalyst (cf. fig. 4); with increasing time difference the CHO formation increased. From this it can be concluded that the rate-limiting step of the process is the formation of CHO on the surface and not its desorption. This might be explained by the necessary diffusion of hydrogen from the Pd bulk to the active sites to replenish the reservoir of surface CHO precursor. Leary et al. [13] observed such diffusion of H_2 from subsurface sites to the surface of Pd/SiO_2 caused by the depletion of the surface during a TPD experiment; the activation energy of this process was calculated to 63 kJ/mol [13].

However, no effect of the length of the time intervals between consecutive H_2 pulses on methane formation at only slightly higher temperatures of >560 K was observed. Thus, it must be assumed that the pulsed hydrogen is directly involved in the methane formation from adsorbed CO.

4. Conclusions

Gaseous CHO species were detected during the interaction of adsorbed CO with H_2 on an alumina-supported Pd at temperatures between 423 and 530 K. The results obtained with differently pretreated catalysts show that the rate limiting step in the formation of the CHO species is the interaction of adsorbed CO with hydrogen dissolved in the palladium bulk, most probably from subsurface sites.

Methane was observed as the only stable product at temperatures higher than 560 K which indicates that CHO is the probable precursor in the formation of methane. However, it cannot be excluded that under different operating conditions, especially much higher pressures, the reactions on the surface as well as the role of CH_xO surface intermediates in the complex reaction network over Pd/Al_2O_3 are different.

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