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RESEARCH NOTE

Surface Formates as Side Products in the Selective CO Oxidation on Pt/γ-Al_2O_3

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Selective CO oxidation over Pt/γ-Al_2O_3 can be used for the purification of CO-contaminated H_2-rich gas produced by steam reforming of organic fuels (1, 2). Here we report *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements which reveal that, in addition to adsorbed CO, surface formate species are formed during CO oxidation in *simulated reformer gas* (1% CO, 75% H_2, and ~25% N_2). It is demonstrated that this process requires the presence of hydroxyl groups and that the formation rate is strongly enhanced by either H_2O in the gas phase or, most efficiently, by H_2O produced on the catalyst due to the $H_2 + O_2$ side reaction.

The 0.5% Pt/γ-Al_2O_3-catalyst (Degussa, Type F 213 XR/D) had a dispersion of ~0.4 (3). The *in-situ* IR reaction cell (Harrick, Inc.) allowed continuous gas flow through the catalyst bed during spectra acquisition. Gas flow rates through the catalyst (0.1 g) in the reaction studies were typically 120 Nml/min. Spectra were obtained on a Mattson Infinity AR 60 spectrometer (MCT narrow band detector) at a resolution of 4 cm^{-1} and an acquisition time of 2.5 min (0.85 min in TPD measurements). All spectra were evaluated in Kubelka–Munk units which are linearly related to the absorber concentration in DRIFTS (4). Except where noted otherwise, catalysts were conditioned at 400°C, first in a mixture of 10% O_2 in N_2 (20 min), followed by reduction in H_2 (20 min), and finally cooled down to the reaction temperature in pure N_2. Prior to exposing the catalyst to the reaction mixture, background spectra were acquired at the corresponding temperatures.

The time evolution of DRIFTS spectra upon exposing freshly conditioned Pt/γ-Al_2O_3 to simulated reformer gas and 1% O_2 at 180°C is shown in Fig. 1. Besides gas phase absorption, linearly bonded (2073 and 2048 cm^{-1} (5)) and multiply bonded (1791 cm^{-1} (6)) CO, and adsorbed H_2O (1636 cm^{-1} (7)), the most striking features are the large band at 1590 cm^{-1} and the doublet at 1375/1393 cm^{-1}, both of which are related to adsorbed formate species (additional peaks at ~2900 and ~3000 cm^{-1}) (8, 9). The small peak at 1324 cm^{-1} also seems to be related to the formate species, because its intensity behavior is identical to that of the formate bands. The appearance of surface formates is well known for the hydrogenation reaction of CO or CO_2 on metal–oxide supported Pt-group catalysts (8, 10–12), and they are often considered intermediates in the methanation reaction (13–15). Bicarbonate species (HCO_3^-), which we observed during CO oxidation in H_2-free gas mixtures (bands at 1658, 1435, 1304, and 1229 cm^{-1} (8)), do not form in simulated reformer gas. The absence of bicarbonate species in H_2-rich gas is probably due to their complete reduction to surface formates which was proposed earlier (10, 16).

The integrated intensity of linearly bonded CO quickly approaches its saturation value (~7% increase between 2 and 90 min; see inset) under reaction conditions. It corresponds to within 10% to the CO equilibrium coverage reached in a gas mixture of 1% CO in pure N_2 and therefore implies that the selective CO oxidation occurs on a CO dominated surface, i.e., in the so-called "low rate branch" (3, 17). In contrast to the rapid equilibration of the CO coverage, the formate bands (1590 and 1393/1375 cm^{-1}) grow continuously and only reach saturation after ~6 h. The fact that the CO coverage is not affected by the accumulation of formates suggests that the latter are located on the oxide support (11). This is also supported by the invariance of the vibrational frequencies of the formate species with different platinum metals if the support (Al_2O_3) remains the same (8, 10–12).

Following the mechanism for CO hydrogenation proposed by Bell (14), surface formates are produced at the metal/support interface by the coordination of the oxygen-end of adsorbed CO (the carbon-end being bonded to the metal) with the cation of the support material (Lewis acid/base reaction) and its subsequent reaction with neighboring hydroxyl groups on the oxide support. An analogous mechanism was suggested for the interaction of CO with OH-groups on K-promoted Al_2O_3 (9). Consistent with

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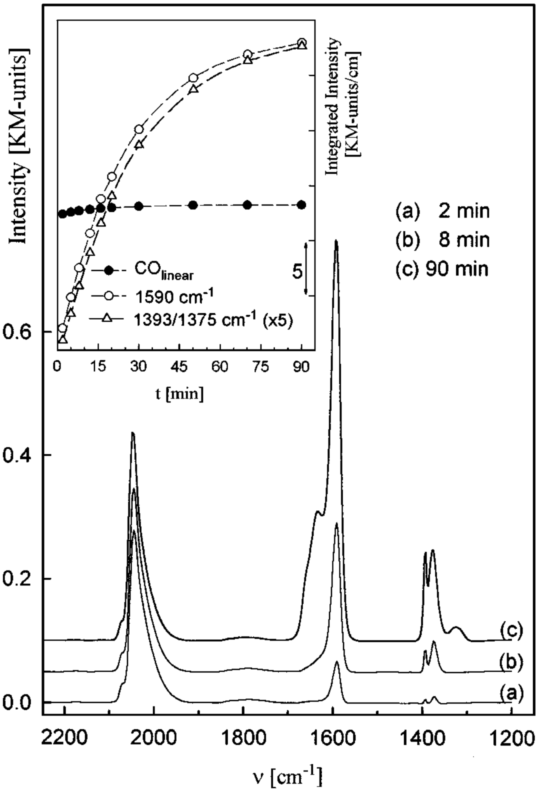

FIG. 1. Time evolution of DRIFTS spectra during selective CO oxidation on 0.5% Pt/γ-Al_2O_3 (180°C; 1% CO, 1% O_2, 75% H_2, the rest N_2).

this hypothesis, formate species were detected neither for the pure support material under any of the conditions used in our experiments nor during reaction on carbon supported Pt (20% Pt/C, E-TEK). On the basis of the above mechanism, the growth rate of surface formates should be directly related to the concentration of surface hydroxyl groups. Therefore, on catalysts conditioned at high temperature, above the dehydroxylation temperature of γ-Al_2O_3 (~400°C; e.g., (18)), formate formation should be suppressed as long as there is no water vapor in the reaction gas. This issue is addressed in the following experiment with various gas mixtures. To exclude mass transport effects, it was conducted at the rather low temperature of 135°C.

If a mixture of 1% CO in H_2 is passed over 0.5% Pt/γ-Al_2O_3 conditioned at 400°C, formate bands barely reach the detection limit even after 1 h on-stream. Passing the same gas mixture over 0.5% Pt/γ-Al_2O_3 which was conditioned at 310°C (see Fig. 2a) so that the support is not completely dehydrated, the resulting formate bands are still rather small, but their growth rate (deduced from the increase in the intensity of the band at 1590 cm^{-1}) is larger by at least one order of magnitude more than on the catalyst conditioned at 400°C. If 0.6% H_2O is added to a mixture of 1% CO in N_2, thereby promoting the hydroxylation of the support, the growth rate increases by a factor of ~300 (Fig. 2b) with respect to the first case (i.e., 1% CO in H_2, catalyst conditioned at 400°C). This behavior parallels the reported conversion of adsorbed CO to surface formates on Ru/γ-Al_2O_3 in the presence of water vapor (15). Nevertheless, even after prolonged reaction in the CO/H_2O/N_2-mixture the formate intensities are small if compared to the reaction in simulated reformer gas. To rule out the high H_2 concentration in the latter experiments as origin of the observed formate formation, the N_2 background was substituted with H_2 (i.e., 1% CO, 0.6% H_2O, the rest H_2; Fig. 2c). Quite clearly, H_2 does not affect the growth rate of formate species, so that the determining factor seems to be the water-induced hydroxylation of γ-Al_2O_3. Finally, simulated reformer gas with 1% O_2 was passed through the catalyst bed (Fig. 2d), producing an additional fivefold increase in the formate growth rate if compared to the water-containing gas mixtures. This may be rationalized by a more effective hydration of the Pt/support interface by water formed directly at the Pt particles. In that case, the effect of O_2 on formate growth is indirect via H_2O formation. In conclusion it seems that both a hydroxylated support and CO adsorbed on Pt are essential for an appreciable formation of surface formates. The fact that their growth rate is between two and three orders of magnitude lower in the absence of water now clearly explains why the intensities observed in our study were at least one order of magnitude higher than what is reported in the literature in the context of CO hydrogenation (8, 11, 13, 15).

The slowly decaying growth rate of formate species (inset in Fig. 1) suggests either a saturation of the surface with formate species or the existence of a formation/decomposition equilibrium. These two possibilities shall be examined in more detail by evaluating the temperature dependence of the formate concentration on Pt/γ-Al_2O_3 in simulated reformer gas with 1% O_2. This TPR-experiment was started at 70°C, and then the temperature was raised by 25°C every

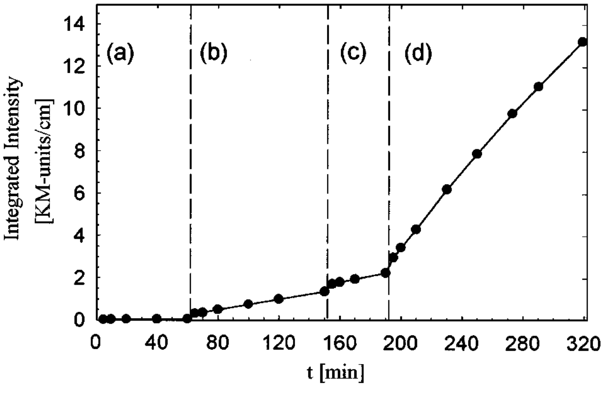

FIG. 2. Formate production (integrated area of 1590 cm^{-1} peak) on 0.5% Pt/γ-Al_2O_3 (cond. at 310°C) in different feed gas streams at 135°C: (a) 1% CO, rest H_2; (b) 1% CO, 0.6% H_2O, the rest N_2; (c) 1% CO, 0.6% H_2O, the rest H_2; (d) 1% CO, 1% O_2, 75% H_2, the rest N_2.

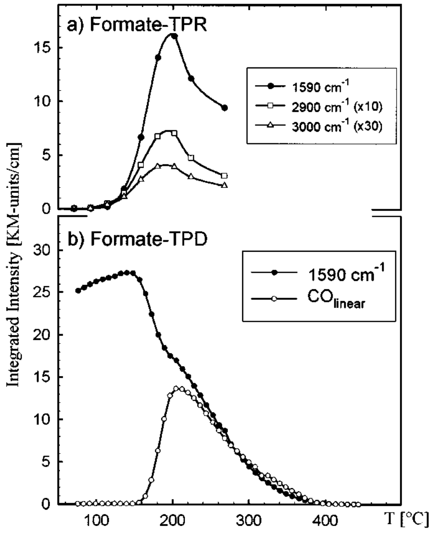

FIG. 3. (a) IR-intensity of formate bands vs T during the selective CO-oxidation (1% CO, 1% O_2, 75% H_2, the rest N_2); (b) IR-intensities of the formate band at 1590 cm^{-1} and of the CO_{linear} band during a TPD experiment (3°C/min in pure N_2) with formate-enriched catalyst.

15 min. In addition to the 1590 cm^{-1} band, we also evaluated the integrated intensities of the other formate bands at 3000 and 2900 cm^{-1}. The intensity behaviour of these bands (see Fig. 3a) reveals a substantial buildup of formates above 120°C, the same temperature at which the onset of CO oxidation (and, therefore, also of H_2O formation) occurs (3). The intensity of the formate bands reaches a maximum at a temperature of ~200°C, above of which decomposition becomes dominant.

A more precise determination of the onset of surface formate decomposition may be deduced from a TPD experiment: (i) surface formates were accumulated by exposing the Pt catalyst to simulated reformer gas with 1% O_2 for 3 h at 160°C; (ii) CO adsorbed on the Pt particles was removed by oxidation at 80°C in 10% O_2 in N_2; (iii) O_2 was removed by purging with N_2 followed by a linear temperature ramp (3°C/min). Initially, a large concentration of formates (indicated by the intensity at 1590 cm^{-1}) is present on the catalyst surface (Fig. 3b) and no significant change in the coverage of preadsorbed formate species is observed up to ~150°C. The small increase in intensity between 80 and 150°C may be due to a reduced coupling of formate species at higher temperatures, similar to the behavior of CO on platinum (19, 20). Above ~150°C, the intensity at 1590 cm^{-1} decreases rapidly with temperature, accompanied by the simultaneous appearance and growth of the band of linearly adsorbed CO at the same wavenumber range which was observed in Fig. 1. This essentially represents the reversal reaction of the proposed formate formation reaction. A similar behavior was reported by Benítez *et al.* (10) on Rh/Al_2O_3. In terms of the decomposition/formation mechanism, surface migration of formate species must be possible and was proposed to occur via molecular formic acid (21), but it was not observed in our DRIFTS spectra. The concentration of adsorbed CO reaches a maximum at ~210°C, above of which its intensity decreases continuously, probably due to increasing CO desorption from Pt. The surface signals of CO and formate species disappear simultaneously at ~400°C, far above the commonly observed high-temperature peaks in CO TPD on alumina supported Pt (210 to 240°C (3, 20)). This formation of CO from formate species might explain the observed additional high-temperature features (>250°C) in CO-TPD studies (see Ref. in (3)). Owing to the large cross-section of CO_{ad} in comparison to gas phase CO_2, the extent of the other decomposition pathway into CO_2 and H_2, which was proposed previously (10) cannot be determined by DRIFTS. In fact, additional IMR-MS (ion molecule reaction mass spectrometry) measurements showed that CO is not the major decomposition product (to be published elsewhere).

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