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In Situ Infrared Spectroscopic and Catalytic Studies on the Oxidation of Ethane over Supported Palladium Catalysts

Noble metals are known to be very active catalysts in hydrocarbon reactions; they are therefore widely used in the refining, petrochemical, and fine chemical industries as well as in exhaust gas cleaning (*1*). Because of their industrial importance, the fundamentals of the catalytic transformation of hydrocarbons has often been investigated on such catalysts. However, little is known about the intermediates occurring in the interaction of saturated hydrocarbons with metal catalyst surfaces. Infrared spectroscopic (IRS) studies have shown that the adsorption of short-chain paraffins on solid surfaces is generally very weak. For example, such studies on the adsorption of C_2H_6 on supported metal catalysts have shown that only physically adsorbed or very weakly chemisorbed hydrocarbon surface species may exist under high-vacuum conditions and at low temperatures (*2–4*). Oxygenated surface intermediates were observed by Davydov *et al.* (*5*), who studied the interaction of C_2H_6 with Cr–Mo oxide catalysts; at room temperature no adsorption of C_2H_6 was observed, while at temperatures from 473 to 573 K absorption bands characteristic for surface carboxylate, adsorbed water, and adsorbed aldehyde appeared. Harrison and Maunders (*6*) reported similar results for the interaction of C_2H_6 with tin oxide surfaces in the temperature range 320 to 740 K; surface acetate was identified on SnO_2–SiO_2 and SnO_2–PdO and was decomposed to carbonate above 580 K.

To our knowledge, no *in situ* IRS studies that deal with the oxidation of C_2H_6 over supported noble metal catalysts have been reported yet. From catalytic studies it is known that oxidation of short-chain paraffins leads predominantly to total oxidation over such metals. In the present article we report results of *in situ* IRS measurements (323–523 K) and of catalytic experiments (473–873 K) on the oxidation of C_2H_6 over γ-Al_2O_3-supported and SiO_2-supported Pd catalysts which have been carried out at ambient pressure.

Supported Pd catalysts were prepared by the incipient wetness method; i.e., either γ-Al_2O_3 (Aluminiumoxid C, Degussa) or SiO_2 (Aerosil 200, Degussa) used as support materials were impregnated with an aqueous solution of $Pd(NO_3)_2 \cdot 2H_2O$ resulting in a Pd loading of 5 wt%; further details of the method of preparation will be published by Gerstenberger and Papp (*7*).

For the IRS studies the powdered samples were pressed into self-supporting discs (10 × 30 mm) with a density of 10–20 mg cm^{-2}. In addition to the γ-Al_2O_3-supported and SiO_2-supported Pd catalysts, pure γ-Al_2O_3 was also used as adsorbent. After H_2 treatment at 673 K for 2 h, the samples were exposed to 0.2–4 vol% C_2H_6 in synthetic air ($P_{C_2H_6}/P_{O_2} = 0.01$–$0.2$) at different temperatures (323–523 K). The overall flow rate was 100 ml min^{-1} at a total pressure of 0.1 MPa. The gases used in this study, N_2 (99.999%), H_2 (99.999%), synthetic air, and C_2H_6 (99.95%), were purified by molecular sieves or Oxisorb (Messer Griesheim) and controlled by mass-flow meters. Acetic acid (98–99%) and acetaldehyde (99%) used for identification of absorption bands were introduced into the IR cell by a continuous N_2 stream which was saturated with these compounds at room temperature. Spectra were based on 16 scans at a resolution of 2 cm^{-1} and were recorded in the range 4000 to 1200 cm^{-1} using a Perkin–Elmer 1710 spectrometer. The IR cell has been de-

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TABLE 1

Infrared Absorption Frequencies (cm^{-1}) of C_2H_6/O_2, CH_3COOH, and CH_3CHO on Pd(5 wt%)/A_2O_3 at 423 K

C_2H_6		CH_3COOH		CH_3CHO		
cm^{-1}	OD[a]	cm^{-1}	OD	cm^{-2}	OD	Type of vibration
3763	−0.05	3732	−0.16	3733	−0.16	$\nu_{O\text{-}H}$[c]
3733	−0.10	3702	−0.12	3697	−0.12	
3667	−0.04					
2941	0.05	3021	0.06	2977	0.08	$\nu_{C\text{-}H}$
2915	0.04	2941	0.07	2939	0.09	
2873	0.04					
2845	0.04					
2345	0.04					$\nu_{(CO_2)}$
		1655(sh)[b]	0.53	1620(sh)	0.42	$\delta_{O..H}$
1748	0.16			1720(sh)	0.11	$\nu_{C=O}$
1658	0.25			1650(sh)	0.37	
1577	0.54	1579	1.04	1579	0.72	ν_{as}(COO)
1468	0.56	1470	0.91	1470	0.68	ν_s(COO)
1398	0.32	1396	0.61	1395	0.46	$\delta_{as}(CH_3)$
1334	0.23	1331	0.40	1333	0.30	$\delta_s(CH_3)$
1273	0.10					$\nu_{C\text{-}O}$

[a] Optical density.

[b] sh, shoulder.

[c] Bands at ca. 3500 cm^{-1} ($\nu_{O..H}$) are not listed.

scribed in detail elsewhere (*8*). The spectra are presented as absorbance after subtracting the background absorption of the catalyst sample.

Catalytic oxidation of C_2H_6 over the Pd/Al_2O_3 catalyst (162.5 mg; d = 0.3 cm, l = 0.5 cm) was performed in a fixed-bed reactor made of quartz (d = 0.8 cm, l = 35 cm) between 473 and 873 K at a total pressure of 0.1 MPa. C_2H_6 conversion and product distribution were determined at different flow rates (30–110 ml min^{-1}) and ratios of $p_{C_2H_6}/p_{O_2}$ (0.2–0.9); He was used as diluent (20–95 ml min^{-1}). Prior to the catalytic runs, the sample was reduced by H_2 (20 ml min^{-1}) at 700 K for 16 h. Gaseous products were analyzed with an on-line gas chromatograph (FID and TCD; columns packed with molecular sieve 5A and Porapak Q) for separation of O_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, and C_3H_6. Condensable substances at 195 K that might have been formed in addition to water were analyzed by off-line gas chromatography (FID and Porapak T column).

During the oxidation of C_2H_6, strongly adsorbed surface species were observed by IRS studies on Pd/Al_2O_3 at temperatures between 323 and 523 K; no adsorption, however, occurred on Pd/SiO_2 or pure Al_2O_3 under the same experimental conditions. Therefore, in the following, only results obtained on Pd/Al_2O_3 for oxidation of C_2H_6 are reported. Typical spectra of adsorbed surface species detected on Pd/Al_2O_3 after the catalyst was exposed for 16 h to C_2H_6 (2 vol%) in air are shown in Fig. 1. A maximum in the adsorbed amount characterized by the intensity of absorption bands was reached at 423 K and at $P_{C_2H_6}/P_{O_2}$ = 0.1. Above 423 K, a decrease in the adsorbed amount was observed; at temperatures higher than 523 K, no absorption bands were detectable. Increasing the ratio of $P_{C_2H_6}/P_{O_2}$ from 0.01 to 0.2 at a constant temperature led first to an increase in the adsorbed amount, while constant values in band intensities were reached at $P_{C_2H_6}/P_{O_2}$ = 0.1, i.e., at $P_{C_2H_6}/P_{O_2} > 0.1$, no further increase in the adsorbed amount occurred. The wave numbers and respective assignments of absorption bands are summarized in Table 1 and are described below.

Bands at 1577 and 1468 cm^{-1} represent stretching vibrations of carboxylates, while bands at 1398 and 1334 cm^{-1} are due to deformation vibrations of methyl groups; both groups of bands are ascribed to surface acetate species. Bands observed at 1748 and 1658 cm^{-1} indicate that C_2H_6 is also oxidized to carbonyl containing surface compounds, most probably to a surface aldehyde species. The band at 1273 cm^{-1} characteristic for $\nu_{C\text{-}O}$ vibration may be ascribed to the same species. In the range of CH-stretching vibrations, only very weak absorption bands appeared between 2940 and 2845 cm^{-1}. Additionally, a very weak band characteristic for molecularly adsorbed CO_2 is visible at 2345 cm^{-1}. The assignments of

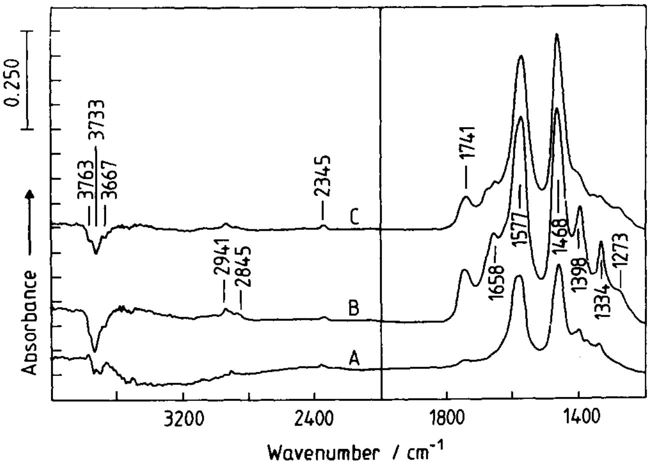

FIG. 1. Infrared spectra after exposing Pd(5 wt%)/Al_2O_3 catalyst for 16 h to 2 vol% C_2H_6 in air ($P_{C_2H_6}/P_{O_2} = 0.1$) at different temperatures: (A) 373 K, (B) 423 K, and (C) 473 K.

absorption bands are also based on IRS adsorption studies of CH_3COOH and CH_3CHO which were carried out on the same catalyst sample resulting in the formation of similar adsorbed surface species as observed in the oxidation of C_2H_6 (see Table 1).

From the IRS results it was possible to elucidate the participation of surface OH groups on the Pd/Al_2O_3 catalyst during the oxidation of C_2H_6. In the range of OH stretching vibrations, negative bands were observed at 3763, 3733, and 3667 cm^{-1}, indicating a decrease of isolated OH groups on Pd/Al_2O_3 while oxygenated surface species are formed. In addition a broad negative band due either to a decrease of nonisolated OH groups or possibly to adsorbed water on the catalyst surface was detected at ca. 3500 cm^{-1} at lower temperatures (see Fig. 1A). From this, it may be assumed that surface OH groups are participating in the formation of acetate and aldehyde surface species on Pd/Al_2O_3.

Further conclusions from IRS results were possible by following the desorption of the adsorbed surface species with increasing temperature in air, which led to a decrease in all band intensities while CO_2 appeared in the gas phase. As shown in Fig. 1, exposing the catalyst to the C_2H_6–air mixture at temperatures higher than 423 K led to a decrease in the adsorbed amount; mainly carboxylate absorption bands remained while bands of methyl groups became much weaker. From the above observations it is suggested that oxidative degradation of the observed acetate and aldehyde species on the catalyst surface leads to a desorption of CO_2.

Catalytic oxidation of ethane on a Pd/Al_2O_3 catalyst was carried out to elucidate whether the observed acetate and aldehyde surface species represent intermediates for total oxidation of C_2H_6 to CO_x or whether it might be possible to detect oxygenated products, e.g., CH_3OOH or CH_3CHO. When applying the same temperatures as for the IRS studies, no C_2H_6 conversion was observed, while at 600 K a sharp increase in conversion was obtained; above 650 K conversion amounted to 100%. No products other than CO, CO_2, and H_2O, besides some CH_4 (selectivity < 5%), could be detected. From these results it may be derived that the acetate and aldehyde surface species on Pd/Al_2O_3, as observed by *in situ* IRS, are intermediates in total oxidation of C_2H_6 to CO_x.

To sum up, acetate and aldehyde surface species detected on a Pd/Al_2O_3 catalyst during *in situ* IRS studies of the oxidation of C_2H_6 are intermediates in the deep oxidation of C_2H_6 to CO_x, which was confirmed by catalytic studies showing CO_x and H_2O as the oxidation products. Under the same experimental conditions as for Pd/Al_2O_3, no adsorption occurred on Pd/SiO_2 or the pure γ-Al_2O_3. From this result one may assume that both Pd and the Al_2O_3 support are required for the formation of the oxygenated surface species. The influence of the Al_2O_3 support may be due to a stronger surface acidity compared to SiO_2. Acid–base pairs on γ-Al_2O_3 and η-Al_2O_3 are considered as active sites for heterolytic dissociation of hydrocarbons (*9*). By pyridine adsorption on the support material used in this study it was indeed possible to observe that no acidic sites exist on SiO_2 while γ-Al_2O_3 exhibited strong Lewis-type acidity (*10*).

IRS studies that were also performed in the absence of oxygen by introducing C_2H_6/N_2 into the IR cell did not show any adsorbed surface species. In addition microcalorimetric studies with C_2H_6 did not show any heats of adsorption at room temperature suggesting that no interaction between C_2H_6 and the catalyst surface takes place under these conditions and that O_2 is required for the formation of the oxygenated surface species.

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