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RESEARCH NOTE

On The Reaction between Carbon Dioxide, Ethylene, and Water over Supported Platinum–Tin Catalysts. A Combined Drift–Mass Spectrometry Study

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The reaction between CO_2 and C_2H_4 in the presence of H_2 over Pt and PtSn-based (SiO_2, Al_2O_3, MgO) supported catalysts has been studied at 34 bar of total pressure and 423 K by *in situ* diffuse reflectance infrared Fourier transform spectroscopy and on-line mass spectrometry experiments. Over silica-supported PtSn alloy, the reaction yields 2-hydroxypropanoic acid through a C2-carbonylic species and CO_2 nondissociatively coordinated. C_2H_4 chemisorption on PtSn/SiO_2 produces a C2-carbonylic species which interacts with the hydroxyl groups of SiO_2, and this C2-carbonylic species evolves to acetaldehyde at 423 K. 2-Hydroxypropanoic acid is also produced over PtSn/SiO_2 from acetaldehyde, CO_2, and H_2, but not from ethanol and CO_2. © 2001 Academic Press

Key Words: **CO_2 reactions; lactic acid; silica support; PtSn bimetallics.**

INTRODUCTION

Catalytic activation of CO_2 and its reaction with unsaturated hydrocarbons is an attractive way to obtain useful organic compounds with new C–C bonds. Several reports describe the coupling between CO_2 and alkenes to give carboxylic acids, esters, and lactones (1, 2). However, there are few reports on heterogeneous catalysis (3, 4). We have shown that silica-supported PtSn alloy catalyzes selectively the reaction between CO_2, C_2H_4, and H_2O, which produces 2-hydroxypropanoic acid (lactic acid), and that there is a support effect on the catalytic properties of PtSn systems in the above reaction (5). The particles of the well-defined silica-supported PtSn alloy coordinate the CO_2 molecule at subatmospheric pressure and a dilution effect of Pt sites by Sn atoms is evidenced by infrared spectroscopy in CO chemisorption experiments (6). To better understand the catalytic reaction, we studied the evolution of chemisorbed species under reaction conditions by *in situ* diffuse reflectance infrared Fourier transform spectroscopy and on-line mass spectrometry (DRIFT-MS) experiments. We present evidence for the participation of adsorbed acetaldehyde in the synthesis of lactic acid.

METHODS

The samples were prepared by impregnation in a vacuum-gas line as described elsewhere (4, 5). The supports were Degussa Aerosil-type silica ($200\,m^2\,g^{-1}$), Girdler γ-Al_2O_3 ($188\ m^2\,g^{-1}$), and MgO ($110\ m^2\,g^{-1}$), which were partially dehydrated under high vacuum at 473 K for 16 h. Platinum–tin catalysts with a nominal atomic ratio of Pt/Sn = 1 were prepared from *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$, and samples containing only platinum from *cis*-$[PtCl_2(PPh_3)_2]$. Samples were reduced in a glass reactor under hydrogen ($40\,ml\ min^{-1}$) at 673 K for 16 h. The bimetallic and monometallic catalysts obtained are referred to as PtSn/*s* and Pt/*s*, respectively, where *s* indicates the support. Platinum loading was kept at ca. 3% w/w. Characterization of monometallic platinum samples by transmission electron microscopy (TEM) showed homogeneously distributed platinum particles, with a mean particle size of 1.5–1.8 nm (7). On the other hand, the characterization of bimetallic platinum–tin catalysts had been accomplished by X-ray diffraction (XRD), TEM, energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and in some cases electron nanodiffraction techniques (ED) (5, 7). Infrared spectroscopy was performed with a Nicolet Magna-IR 750 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector using a catalytic DRIFT chamber (Spectra Tech Inc., Model 0030-102). The recorded interferograms consisted of 200 averaged scans using 2 cm^{-1} resolution. The outlet of the DRIFT chamber was connected through a capillary tube held at 423 K to a Balzers instrument equipped with

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a QMS 200 quadrupole mass spectrometer and a Pfeiffer turbomolecular drag pump. In such a configuration, products that evolved in the gas phase from the DRIFT chamber could be analyzed on-line by mass spectrometry (MS). Prior to the various experiments, samples were pretreated *In situ* under an $H_2:He = 1:1$ mixture at 673 K and atmospheric pressure and cooled to 298 K, where the first interferogram was recorded and used as a background reference of all subsequent interferograms recorded for that particular catalyst. Precise gas flow rates were maintained using mass flow controllers (Brooks, Model 5850TR). Sensitivity factors of selected mass values for all used and expected products were calibrated using appropriate standards.

RESULTS AND DISCUSSION

Adsorption of Ethylene

After pretreatment under an $He:H_2$ mixture, samples were flushed with pure He and then exposed to an $He:C_2H_4$ (1 : 1) mixture at 298 K up to 34 bar total pressure. Samples were then exposed to He to remove the contribution of ethylene from the gas phase to the spectra. In the $PtSn/SiO_2$ sample, the adsorption of ethylene resulted in the appearance of bands at 1701 and 1716 cm^{-1}, which could be ascribed to species containing a carbonyl group, and bands in the ν(C–H) stretching region at 3017, 2970, and 2934 cm^{-1}. Simultaneously, a significant decrease of the peak due to terminal hydroxyl groups on silica at 3747 cm^{-1} took place and a broad band centered at 3410 cm^{-1} appeared. When the surface species resulting from the adsorption of ethylene on $PtSn/SiO_2$ were treated under He at increasing temperature, acetaldehyde was desorbed at 423 K as determined by MS. It is important to note that the optimum working temperature of $PtSn/SiO_2$ catalyst in the reaction between CO_2, C_2H_4, and H_2O to yield lactic acid is 423 K (5). When acetaldehyde appeared, the bands at 3410, 3017, 2970, 2934, 1716, and 1701 cm^{-1} vanished and the partial recovery of the silanol band of silica at 3747 cm^{-1} was observed by infrared spectroscopy.

The behavior of all the other samples differed from that of $PtSn/SiO_2$. After ethylene adsorption no bands in the ν(CO) stretching region evolved from the other samples except for PtSn/MgO, where a broad and very weak band centered at 1710 cm^{-1} was encountered. Also, no changes in the ν(OH) spectra took place after the adsorption of ethylene. When samples after ethylene adsorption were treated under helium at increasing temperatures, residual ethylene was analyzed in all cases and traces of acetaldehyde were evolved at 573 K only from the PtSn/MgO sample.

In a separate experiment acetaldehyde was adsorbed over the $PtSn/SiO_2$ catalyst. When the catalyst was exposed to 10 bar of a mixture of acetaldehyde (0.05%) and helium, the formation of an asymmetric band centered at 1725 cm^{-1} together with absorptions at 3008, 2968, and 2924 cm^{-1} appeared in the spectrum. Besides the displacement to lower wavenumbers of the acetaldehyde ν(CO) band with respect to gaseous acetaldehyde, the intensity of the ν(OH) band corresponding to terminal OH groups of the silica decreased. Simultaneously, a broad band arose at ca. 3400 cm^{-1}. The simultaneous perturbation of both OH and CO stretching bands indicates interaction between them; a similar situation is observed when acetaldehyde is adsorbed on silica (8). After acetaldehyde adsorption, the catalyst was flushed with He at increasing temperatures to 423 K; during this desorption no bands due to coordinated CO were detected. This behavior contrasts with that of a Pt/SiO_2 catalyst, where the partial decomposition of adsorbed acetaldehyde to CO and ethanol at room temperature has been reported (9).

Adsorption of Carbon Dioxide

Samples were exposed to an $He:CO_2$ (1 : 1) mixture at 34 bar and 298 K and flushed with helium in a way similar to that described for the ethylene adsorption experiments above. Only the interaction of carbon dioxide with the $PtSn/SiO_2$ catalyst resulted in the formation of a stable CO_2 surface species, characterized by an infrared band at 2339 cm^{-1}. We had reported similar results on CO_2 coordination in experiments carried out at subatmospheric pressure (6). For comparison, carbon dioxide adsorbed dissociatively onto the Pt/SiO_2 sample and a broad band corresponding to linear-bonded CO appeared at 2062 cm^{-1}.

Reaction between Adsorbed Ethylene, Carbon Dioxide, and Hydrogen

The reaction between carbon dioxide and ethylene over the $PtSn/SiO_2$ catalyst in the presence of either water or hydrogen produces lactic acid. However, lactic acid is not obtained over platinum monometallic catalysts or magnesia or alumina PtSn-supported catalysts (4, 5, 10).

When the reaction is carried out over $PtSn/SiO_2$ with hydrogen the reverse water–gas shift reaction results in the formation of water, necessary for the overall reaction :

$$CO_2 + C_2H_4 + H_2O \rightarrow CH_3CH(OH)COOH.$$

At 35 bar and 423 K no lateral reactions involving CO such as hydrogenation or hydroformylation have been observed to occur. In our DRIFT–mass spectrometry study we used hydrogen in order to attain a better control of the amount of water introduced in the reactant mixture. At 34 bar, we raised the temperature from 298 to 423 K under a $CO_2:C_2H_4 = 1:1$ mixture. At room temperature there were no significant differences between the initial spectra obtained in the experiments with a mixture of $CO_2 + C_2H_4$ (see Fig. 1) or in the studies performed with CO_2 or C_2H_4 separately, which have been discussed above.

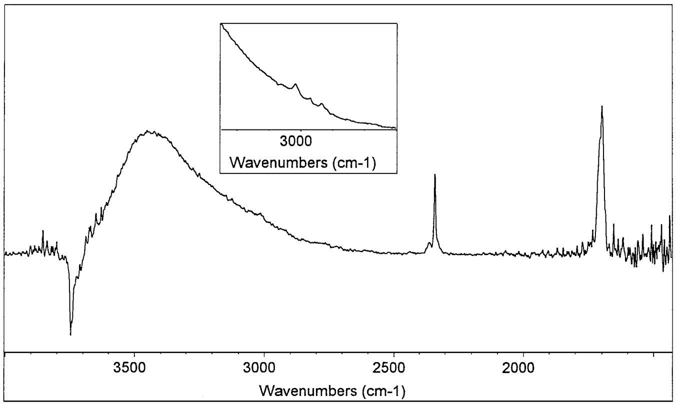

FIG. 1. Infrared spectra resulting from the adsorption of ethylene and CO_2 over $PtSn/SiO_2$ at 298 K and 34 bar after flushing with He.

At 423 K, hydrogen was introduced to a final molar ratio of $CO_2:C_2H_4:H_2 = 9:9:2$. Products that evolved from the reaction between CO_2, C_2H_4, and H_2 were analyzed by on-line mass spectrometry. Besides reactants, methane, ethane, butene, water, acetaldehyde, ethanol, acrylic acid (ac. 2-propenoic), and lactic acid were also monitored. In all the DRIFT–MS experiments, water was produced through the reverse gas shift reaction when hydrogen was incorporated into the reactant mixture. When the reaction was carried out over the monometallic platinum samples, besides the reverse water–gas shift reaction, only the hydrogenation of ethylene took place under these conditions (34 bar and 423 K). The same applied to a lesser extent for the alumina-supported PtSn bimetallic sample. When the reaction was performed over PtSn/MgO, ethane was also the main product, but minor amounts of acetaldehyde were also detected. Substitution of the reactant mixture by helium under reaction conditions for different catalysts gave, in all samples except for $PtSn/SiO_2$, bands at 2988, 2974, 2954, 2933, 2894, 2881, 2776, and 2753 cm^{-1} in the ν(C–H) stretching region, which could be attributed to the presence of ethane besides residual ethylene (11), also in accordance with mass spectrometry data. In contrast, the reaction between CO_2, C_2H_4, and H_2 carried out at 423 K over the $PtSn/SiO_2$ catalyst produced lactic acid and, at the initial steps of the reaction, ethanol, which progressively vanished as the reaction proceeded. No ethane or acetaldehyde was detected at any step of the reaction. Figure 2a shows the evolution of products for the $PtSn/SiO_2$ catalyst as determined by mass spectrometry. The introduction of hydrogen resulted in the simultaneous formation of water, ethanol, and lactic acid. As the reaction proceeded, the production of ethanol ceased and lactic acid was selectively formed.

At this point two different reaction schemes can be proposed for the production of lactic acid: (i) the carbonylic surface species produced after ethylene adsorption is hydrogenated to ethanol, and then adsorbed ethanol reacts with coordinated CO_2 to yield lactic acid; or (ii) the carbonylic surface species produced after ethylene adsorption reacts with coordinated CO_2 in the presence of water to produce lactic acid. In order to determine whether either of these reaction schemes occurs over $PtSn/SiO_2$, two experiments were carried out. In one the reaction between adsorbed ethanol and CO_2 was tested, and in the other the reaction between adsorbed acetaldehyde, CO_2, and hydrogen was carried out.

Reaction between Adsorbed Ethanol and Carbon Dioxide

Ethanol diluted in helium (~7%) was first adsorbed at 1 atm onto the $PtSn/SiO_2$ catalyst and then He and carbon dioxide were successively incorporated in the reactant mixture and used to increase the total pressure up to 15 and 34 bar, respectively. After that, catalyst was treated with a $CO_2:He$ (1:1) flowing mixture at room temperature. DRIFT spectra showed bands at 2984, 2940, 2907, and 2882 cm^{-1} corresponding to ethoxy species (12). The temperature was then raised to 423 K. The monitoring of products by on-line mass spectrometry showed only the desorption of ethanol. In this case, no lactic acid was produced.

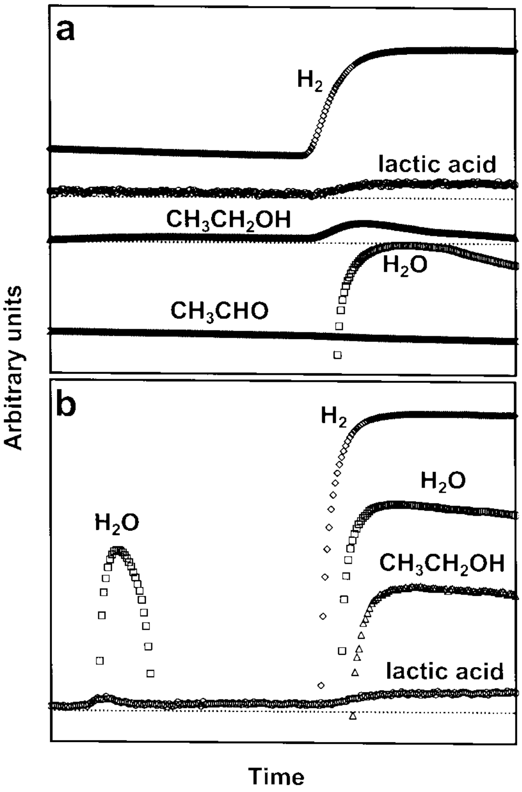

FIG. 2. Evolution of products, as determined by mass spectrometry (raw data), resulting from the incorporation of hydrogen to (a) $CO_2 + C_2H_4$ and (b) $CO_2 + CH_3CHO$ over $PtSn/SiO_2$ at 34 bar and 423 K.

Reaction between Adsorbed Acetaldehyde, Carbon Dioxide, and Hydrogen

Acetaldehyde diluted in helium (0.05%) was first adsorbed onto the PtSn/SiO_2 catalyst at 10 bar, and then He and carbon dioxide were incorporated successively in the reactant mixture and used to increase the total pressure up to 17 and 34 bar, respectively. After that, catalyst was treated with an He : CO_2 (1 : 1) flowing mixture at room temperature. Absorptions at 3010, 2968, 2923, and 1725 cm^{-1} corresponding to adsorbed acetaldehyde were observed. The temperature was then raised to 423 K and hydrogen was introduced in the flowing mixture, $CO_2 : He : H_2 = 9 : 9 : 2$. Products evolved during all of these steps were monitored by mass spectrometry. From Fig. 2b it is deduced that the formation of lactic acid took place when adsorbed acetaldehyde, carbon dioxide, and water reacted at 423 K over the PtSn alloy supported on silica. In fact, when the temperature was first raised to 423 K in the absence of hydrogen the desorption of water was observed along with the synthesis of lactic acid. Later, at 423 K, the incorporation of hydrogen resulted in the formation of water via the reverse gas shift reaction and both ethanol and lactic acid evolved. Therefore, adsorbed acetaldehyde, carbon dioxide, and water yield lactic acid over this catalyst. In addition, adsorbed acetaldehyde is also hydrogenated to ethanol when hydrogen is introduced into the reactant mixture, and again bands corresponding to an ethoxy species are obtained.

Results of characterization obtained by XRD, TEM, EDX, and ED indicate that bimetallic catalysts contained well-defined PtSn 1 : 1 hcp alloy particles with platelet shape and mean particle size depending on the support (PtSn/SiO_2, 26 nm; PtSn/Al_2O_3, 17 nm; PtSn/MgO, 13 nm) (5, 7). However, XPS analysis of catalysts indicates some differences in their surface composition (5, 7). Phosphorus and chlorine species remained on the surface of the PtSn/Al_2O_3 catalyst after the reduction step, which may have a negative influence on its catalytic behavior. On the other hand, in all cases alloyed Sn was determined by XPS. However, oxidized Sn was also present, and the surface composition determined by XPS depended on the support. Specifically, for PtSn/SiO_2 only 22% of total Sn was oxidized, whereas for PtSn/MgO the Sn(oxidized)/Sn(total) ratio was 75%. The Pt/Sn(alloyed) ratio determined by XPS was also very different for silica- and magnesia-supported catalysts. For PtSn/SiO_2 it was 0.74, but for PtSn/MgO the Pt/Sn(alloyed) ratio was 2.96. This value is far from that corresponding to the PtSn alloy. It is likely that the surface characteristics of PtSn particles on the different supports affect the adsorption properties of catalysts and consequently their catalytic behavior.

CONCLUSIONS

A relationship between the production of lactic acid from ethylene, carbon dioxide, and water over the PtSn/SiO_2 catalyst and its adsorption properties has been established. PtSn/SiO_2 coordinated the CO_2 molecule and gave, after the ethylene adsorption, a carbonylic surface species which interacted with the hydroxyl groups of the support and evolved to acetaldehyde at 423 K. Lactic acid was obtained from the reaction between adsorbed acetaldehyde, carbon dioxide, and hydrogen over this catalyst, and ethanol was produced simultaneously. But when adsorbed ethanol reacted with CO_2 over PtSn/SiO_2 catalyst the production of lactic acid was not observed.

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