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Catalysis Today 54 (1999) 81–92

CATALYSIS TODAY

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VOC removal: investigation of ethylacetate oxidation over supported Pt catalysts

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Abstract

The oxidation of ethylacetate present in trace amounts in air has been investigated over supported Pt catalysts. Steady-state kinetic experiments have shown that Pt dispersed on W^{6+}-doped $TiO_2$is the most active catalyst. Acetic acid and acetaldehyde are the main byproducts at low and intermediate conversions. Temperature-programmed desorption (TPD) and oxidation (TPO) of labelled ethylacetate, ($^{13}CH_3{}^{13}COOCH_2CH_3$), as well as differential scanning calorimetry (DSC) of ethylacetate, ammonia and carbon dioxide have been employed to obtain information on the surface processes taking place under heating in inert or oxidizing atmosphere and on the acidic/basic character of the surface of the supports. The high activity of the Pt/TiO_2 (W^{6+}) catalyst under steady-state conditions is attributed to the presence of a large number of acidic sites with appropriate strength on the TiO_2 (W^{6+}) surface, which lead to the formation of a large pool of reactive intermediates with high mobility. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Ethylacetate adsorption; VOC; Platinum catalysts; TPD; DSC

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1. Introduction

Catalytic oxidation of volatile organic compounds (VOC) present in low concentrations in industrial waste streams is an important technique for control of VOC emissions [1–4]. A review on the field of removal of non-chlorinated VOCs can be found in Ref. [1]. Pt and Pd are the most efficient among metal catalysts in the oxidation of a variety of VOCs [1,5,6]. Because of this, the majority of commercial VOC oxidation catalysts consist of either Pt or Pd or both supported on alumina carriers in pellet or ceramic monolith forms [1,5]. Development of improved catalysts for VOC removal is necessary for satisfaction of strict standards on VOC emissions from stationary sources. More active catalysts will also permit operation of the incinerator at lower temperatures and, thus, help in reducing fuel consumption and operating costs.

Recent work from this laboratory has shown that Pt and Pd are generally the most active metals in the oxidation of a variety of VOCs [6] and, moreover, the activity of Pt and Pd catalysts in the oxidation of specific VOCs, such as ethylacetate (EAc), can be significantly increased when these metals are supported on TiO_2 doped with W^{6+} cations [7,8]. The observed activity enhancement was attributed to the high activity of the TiO_2 (W^{6+}) support for decomposition of EAc. Steady-state kinetic measurements showed that EAc decomposes initially to ethanol, acetaldehyde, ethylene and acetic acid on the support and these organic

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PII: S0920-5861(99)00170-4

intermediates are subsequently oxidized on the metal surface.

In the present work, the interaction of EAc with γ-Al_2O_3, TiO_2 and TiO_2 (W^{6+}) carriers and the corresponding supported Pt catalysts has been investigated with temperature-programmed desorption (TPD) and oxidation (TPO) techniques and differential scanning calorimetry (DSC), employing ^{13}C-labelled ethylacetate, $^{13}CH_3{}^{13}COOCH_2CH_3$. The specific isotope of EAc contains ^{13}C in the acetate group and, thus, makes possible the identification of the different reaction pathways of the acetate and ethoxide fragments of the parent molecule. TPD and TPO are useful and widely used techniques, because they can provide information on the processes of adsorption and surface reaction of a variety of adsorbates. DSC has been used in order to measure the heat of adsorption of EAc on the supports and catalysts employed. In addition, DSC has been used to characterize the acidic/basic nature of the surface of the supports, using ammonia and carbon dioxide. Ammonia and carbon dioxide are typical probe molecules for the estimation of the number and strength of acidic and basic sites on a catalyst surface [10].

This study has been triggered by the aforementioned results regarding the behavior of Pt/TiO_2 (W^{6+}) catalysts in EAc oxidation and aims at obtaining fundamental information on surface processes. To our knowledge, this is the first study of the adsorption of EAc on oxidic carriers and supported Pt catalysts by TPD and TPO techniques. Sawyer and Abraham [9] have investigated the reaction of EAc oxidation over Al_2O_3 and Pt/Al_2O_3 catalysts. They found that partial oxidation products are produced over the alumina support, while Pt produces complete oxidation products. They proposed that the total product distribution can be obtained by assuming no interaction between alumina and platinum.

2. Experimental

The supports employed in the present study were SiO_2 (400 m^2/g, Alfa Products), γ-Al_2O_3 (90 m^2/g, Alfa Products), TiO_2 (80% anatase, 45 m^2/g, Degussa P25) and TiO_2 doped with varying amounts of W^{6+} in the range of 0.22–0.67 at.% W^{6+}. Doped TiO_2 supports were prepared at the laboratory with high temperature calcination of TiO_2–WO_3 mixtures. Calcination transforms TiO_2 to the rutile phase and the surface area drops to $\sim$10 m^2/g. A detailed description of the preparation method is given in Ref. [7]. Alumina, silica and titania carriers were calcined at 600°C for 5 h, prior testing or impregnation with Pt. Corresponding Pt catalysts contained 0.3 wt.% Pt and were prepared by impregnation of the supports with H_2PtCl_6 aqueous solutions. Chloride-free catalysts were prepared using $H_2Pt(OH)_6$ as precursor compound. Details of catalyst preparation can be found elsewhere [6,7]. EAc labelled with ^{13}C, $^{13}CH_3{}^{13}COOC_2H_5$, was obtained from Sigma–Aldrich and was of 99% isotopic purity. Anhydrous ethanol and acetic acid were used as received.

The dispersion of the Pt metal was determined by equilibrium hydrogen chemisorption at room temperature in a constant-volume high-vacuum apparatus (Micromeritics, Accusorb 2100E). Dispersion was expressed as the H/Pt ratio at monolayer coverage obtained by extrapolation of the linear portions of the adsorption isotherms to zero pressure. Details of the experimental procedure are given elsewhere [6].

TPD and TPO experiments were conducted in a home-built flow system connected to a quadrupole mass spectrometer (Sensorlab 200D). The TPD cell was a quartz tube of 6 mm OD, enlarged to 10 mm at the middle, where the catalyst bed was contained. A 0.5 mm type K thermocouple inserted in a 3 mm quartz thermowell was placed in the center of the catalyst bed for measurement and control of temperature. 0.1–0.2 g of catalyst or blank support with particle size of 63–125 μm were used. Prior to each TPD and TPO run, the catalyst sample was treated under 3% O_2/He at 773 K for 0.5 h followed by H_2 reduction at 573 K for 1 h and subsequent cooling to room temperature under He. This procedure was found to give reproducible results. EAc was introduced into the system by injecting liquid EAc (1–5 μl) into the He flow upstream of the catalyst bed. The EAc uptake measured in DSC experiments served as a guide to determine the required size of EAc injection in TPD and TPO experiments. The effect of the amount of injected EAc on the surface coverage obtained was examined by varying the injected amount in the range of 1–10 μl. It was found that the quantity of adsorbed EAc did not depend on the injected amount, when

Table 1
Catalytic activity of Pt catalysts for EAc combustion under differential conditions at 180°C

Catalyst	H/Pt	TOF (s^{-1})	Catalyst	H/Pt	TOF (s^{-1})
Pt/γ-Al_2O_3	1.0	6×10^{-6}	Pt/TiO_2 (0.22 at.% W^{6+})	0.8	1.5×10^{-3}
Pt/SiO_2	0.9	1.4×10^{-4}	Pt/TiO_2 (0.45 at.% W^{6+})	0.7	2.4×10^{-3}
Pt/TiO_2 (80% anatase)	1.0	2.2×10^{-4}	Pt/TiO_2 (0.67 at.% W^{6+})	1.0	1.3×10^{-3}
Pt/TiO_2 (rutile)	0.8	1.5×10^{-4}			

this was at least 1 μl in the case of TiO_2 and TiO_2 (W^{6+}) and 2 μl in the case of Al_2O_3. This implies that TPD and TPO experiments have been carried out at a near saturation coverage of EAc on all catalysts. After evaporation and adsorption of the compound on the catalyst, temperature programming was commenced with a heating rate of 20 K/min. Helium was used as the carrier gas for TPD and a 3% O_2/He mixture for TPO, with a flow rate of 45 cm^3/min in both cases. Preliminary TPD and TPO experiments were conducted on all catalysts, in order to identify the compounds appearing in the gas phase during TPD or TPO. This was accomplished by scanning continuously mass numbers (*m*/*e*) from 1 to 100 during the TPD/TPO run. The following products were identified during TPD experiments: $^{13}CH_3{}^{13}COOC_2H_5$, ethanol, acetaldehyde, ethylene, CH_4, $^{13}CH_4$, CO, ^{13}CO, CO_2, $^{13}CO_2$ and H_2. In TPO experiments, the products were: $^{13}CH_3{}^{13}COOC_2H_5$, ethanol, acetaldehyde, ethylene, CO_2 and $^{13}CO_2$. Response factors for CO, CO_2, CH_4, C_2H_4 and EAc were determined using calibrated mixtures of these compounds in helium, while the response factors of isotopes (^{13}CO, $^{13}CO_2$, $^{13}CH_4$ and $^{13}CH_3{}^{13}COOC_2H_5$) were taken equal to those of the corresponding normal compounds. Response factors for ethanol and acetaldehyde were calculated using data of Ref. [12]. Cracking patterns were determined individually for all aforementioned compounds. The following mass numbers were used for measurement of the various products: H_2 (2), CH_4 (15), $^{13}CH_4$ (16), C_2H_4 (27), CO (28), ^{13}CO (29), CH_3CHO (29), C_2H_5OH (31), O_2 (32), CH_3COOH (43), CO_2(44), $^{13}CO_2$ (45) and $^{13}CH_3{}^{13}COOC_2H_5$ (45). Multiple linear regression was employed to calculate the gas phase concentration of desorbing species. TPD of ethanol and acetic acid adsorbed on blank supports was also studied for comparison purposes. The procedure of these experiments was identical to that employed in the case of EAc.

Measurements of heat of adsorption were performed in a DSC apparatus (Setaram DSC 111). The outlet of the DSC cell was connected on-line to a mass spectrometer for continuous monitoring of the gas phase composition. The pretreatment procedure was identical to the one employed during TPD experiments. Adsorption was carried out at 40°C using a mixture of 380 ppm EAc in He. Mixtures of 0.5% NH_3 or CO_2 in He were used for the measurement of the heat of adsorption of ammonia and carbon dioxide. A flow rate of 45 cm^3/min of the corresponding gas mixtures was used in all experiments. The amounts of EAc, NH_3 and CO_2, which adsorbed on the catalyst during a DSC experiment, were determined by measurement of the area between the blank response curve of the corresponding mass spectrometer signal (using quartz pieces in place of the catalyst sample) and the actual response curve in each case.

3. Results

3.1. Steady-state rate measurements

Steady-state rate measurements of EAc combustion over various carriers and corresponding Pt catalysts have been reported previously [7] and they are also reported in Table 1. Catalytic activity, in the form of TOF as it appears in Table 1, refers to combustion of EAc to CO_2 under differential conditions, and not partial oxidation or decomposition to other products. It can be observed that Pt/SiO_2 and Pt/TiO_2 catalysts have comparable activity. The crystallographic form of TiO_2 (rutile or anatase) is not an influencing factor, as Pt/TiO_2 (80% anatase) and Pt/TiO_2 (rutile) catalysts also show comparable activity. The much lower activity of Pt/γ-Al_2O_3 was found to be due to residual chloride inhibition [6]. The activity of Pt catalysts prepared from chloride-free and chloride-containing precursors was found to be comparable, when Pt is supported on TiO_2 or TiO_2 (W^{6+}) supports. On the other hand, Pt/Al_2O_3 catalysts prepared from chloride-free precursors are more active than the corresponding Pt/Al_2O_3 catalysts prepared from H_2PtCl_6. Doping of the TiO_2 support with W^{6+} cations leads to an increase of activity by an order of magnitude and the Pt/TiO_2 (0.45 at.% W^{6+}) catalyst exhibits the highest activity among all Pt catalysts. During preparation of TiO_2 (W^{6+}) supports, TiO_2 transforms to the rutile phase. The fact that the Pt/TiO_2 (rutile) catalyst has slightly lower activity than Pt/TiO_2 (80% anatase) (Table 1) implies that the enhanced activity of Pt/TiO_2 (W^{6+}) catalysts is due to the effect of W^{6+} cations. The optimal TiO_2 (0.45 at.% W^{6+}) support and the corresponding Pt catalyst have been used in TPD, TPO and DSC experiments, which are described in the following sections.

Product distribution when the reaction is carried out over the TiO_2 and TiO_2 (W^{6+}) supports and the Pt/TiO_2 (W^{6+}) catalyst is shown in Fig. 1. When the reaction is carried out over blank supports, EAc is initially decomposed to acetic acid, ethanol, acetaldehyde and ethylene, which are subsequently oxidized to CO_2 at higher temperatures (Fig. 1(a) and (b)). Acetic acid is resistant to oxidation over blank supports, and, as a result, the main products of the reaction at temperatures around 300–350°C are CO_2 and acetic acid. Doping of TiO_2 with W^{6+} cations has a significant effect on the catalytic behavior of TiO_2. TiO_2 (W^{6+}) is more active than TiO_2 in EAc decomposition, as is indicated by a significant shift of the corresponding curves towards lower temperatures (Fig. 1(b)). Complete conversion of EAc on TiO_2 (W^{6+}) takes place at ~250°C, compared to ~330°C in the case of TiO_2. Ethylene formation is also higher on TiO_2 (W^{6+}), while, in both cases, the amount of acetic acid produced indicates that part of it is formed by ethanol and acetaldehyde oxidation. According to reaction stoichiometry, the maximum concentration of acetic acid should be 250 ppm (equal to the EAc concentration on the feed). As the measured concentration of acetic acid is ~300 ppm, the remaining 50 ppm are produced by oxidation of ethanol and acetaldehyde (a total mass balance also confirms that).

In the case of Pt catalysts (Fig. 1(c)), formation of organic intermediates is greatly reduced and complete conversion of EAc to CO_2 is obtained at ~240°C over the Pt/TiO_2 (W^{6+}) catalyst, compared to ~280°C in the case of Pt/TiO_2 (not shown). Another noteworthy difference is that at intermediate conversions Pt/TiO_2 is very selective towards CO_2 production (only traces of organic byproducts are formed), while Pt/TiO_2 (W^{6+}) produces moderate amounts of acetic acid and acetaldehyde (the latter mainly at low conversions). The lower selectivity of the Pt/TiO_2 (W^{6+}) catalyst has no practical significance, as this catalyst is able to achieve complete conversion of EAc to CO_2 and H_2O at temperatures lower than those required in the case of Pt/TiO_2 or any other Pt catalyst examined in the course of this study.

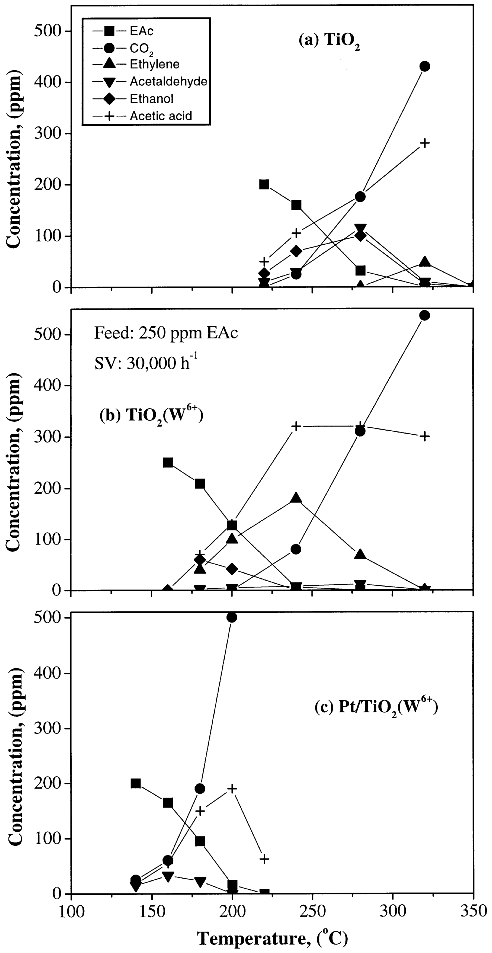

Fig. 1. Product distribution during EAc oxidation under steady-state conditions as a function of reaction temperature. (a) TiO_2, (b) TiO_2 (W^{6+}), (c) Pt/TiO_2 (W^{6+}).

Table 2
Adsorption of EAc, ammonia and carbon dioxide on blank supports and Pt catalysts

Catalyst	Ethylacetate		Ammonia		Carbon dioxide	
	Amount (molecules/nm^2)	ΔH (kJ/mol)	Amount (molecules/nm^2)	ΔH (kJ/mol)	Amount (molecules/nm^2)	ΔH (kJ/mol)
γ-Al_2O_3	0.8	100	1.5	109	0.13	92
TiO_2	0.5	38	1.9	46	0.09	121
TiO_2 (W^{6+})[a]	2.3	54	6.4	63	0.18	84
Pt/ γ-Al_2O_3	0.9	192	nm[b]		nm	
Pt/TiO_2	0.2	134	nm		nm	
Pt/TiO_2 (W^{6+})[a]	2.5	96	nm		nm	

[a] W^{6+} content is 0.45 at.%.

[b] Not measured.

3.2. Heat of adsorption of EAc on blank supports and Pt catalysts

The heat of adsorption of EAc on blank supports and the corresponding Pt catalysts was measured by DSC at 40°C. A mixture of 380 ppm EAc in He was used to dose the samples in a continuous flow mode. The heat of adsorption of ammonia and carbon dioxide was also measured, for comparison purposes, employing 0.5% NH_3 or CO_2 in He mixtures. In all cases, an integral heat of adsorption was determined, i.e. pertaining to surface coverages between zero and unity. The heat of adsorption and the amounts of EAc, ammonia and carbon dioxide adsorbed are presented in Table 2.

The heats of adsorption of EAc and ammonia follow a similar trend among the supports studied. For both molecules, the largest heat of adsorption is found in the case of γ-Al_2O_3 and the lowest in the case of TiO_2. This implies that, overall, the alumina carrier has acidic sites of higher strength than titania. The heat of adsorption of ammonia is, in all cases, larger by 8–9 kJ/mol than that of EAc. On the other hand, the heat of adsorption of carbon dioxide varies in a narrower range and the largest heat of adsorption is observed in the case of TiO_2.

It can also be observed that the amounts adsorbed on γ-Al_2O_3 and $TiO_2$are comparable, while TiO_2 (W^{6+}) has higher adsorptive capacity per unit surface area. This is especially true for EAc and ammonia, where the adsorbed amounts on TiO_2 (W^{6+}) are 3–4 times higher compared to the other supports. This implies that the number of acidic sites is larger on the TiO_2 (W^{6+}) support. It should also be noted that the coverage of carbon dioxide is one order of magnitude lower compared to that of ammonia and EAc.

There is quite a good agreement between the adsorbed amounts measured in this work and those reported in the literature for γ-Al_2O_3 and TiO_2. In the case of ammonia, the data of Auroux and Gervasini [10] are $1 \times 10^{18}\,m^{-2}$ for γ-Al_2O_3 and $2 \times 10^{18}\,m^{-2}$ for TiO_2, compared to the values of 1.5×10^{18} and $1.9 \times 10^{18}\,m^{-2}$ measured in this work. In the case of carbon dioxide, the same authors have reported values of 2×10^{17} and $1.8 \times 10^{17}\,m^{-2}$ for γ-Al_2O_3 and TiO_2 compared to the values of 1.3×10^{17} and 0.9×10^{17}, respectively, measured in this work. Regarding the values of the heat of adsorption, comparison is not straightforward, as the heats of adsorption determined in this work correspond to integral values. An estimate of the integral heat of adsorption of NH_3 on Al_2O_3 and TiO_2 pertaining to the results of Auroux and Gervasini has been made using the data in Fig. 4 of Ref. [10]. The calculated values are ~95 kJ/mol for γ-Al_2O_3 and ~105 kJ/mol for TiO_2. The former value is in good agreement with the value of 109 kJ/mol measured in the present work (Table 2). The latter value is significantly larger than the value of 46 kJ/mol measured in this work for TiO_2. The TiO_2 sample used in Ref. [10] contained considerable amounts of SO_4 (1%) and P_2O_5 (0.4%) impurities. There is a possibility that the larger value measured in this sample is due to the effect of these acidic impurities.

Addition of Pt on the blank supports leads to a significant increase of the heat of adsorption of EAc, obviously due to the higher heat of adsorption of EAc on Pt compared to the supports. There is no

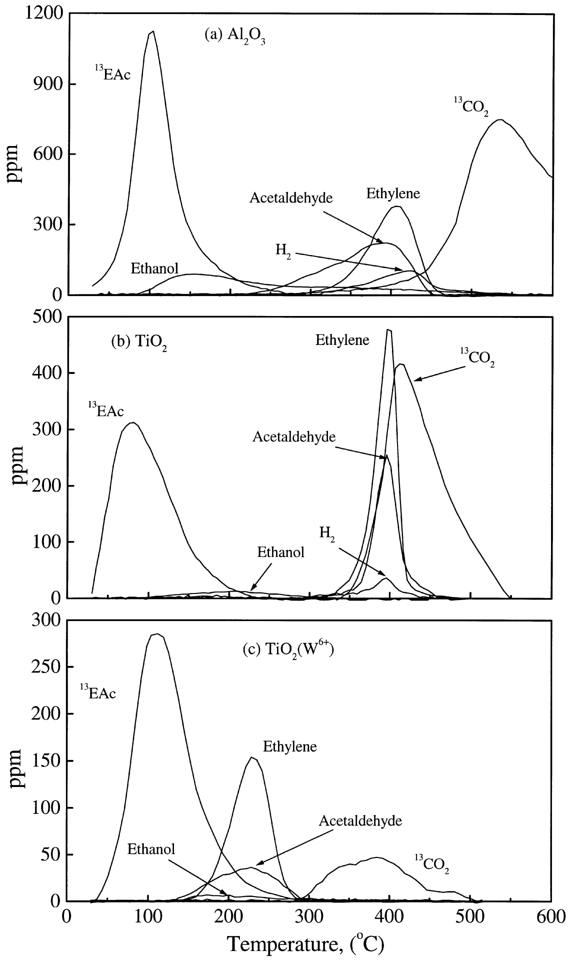

Fig. 2. TPD profiles following adsorption of $^{13}CH_3{}^{13}COOC_2H_5$ on (a) γ-Al_2O_3, (b) TiO_2, (c) TiO_2 (W^{6+}) (*note the different scales of y-axis*).

straightforward way, however, to estimate the heat of adsorption of EAc on the Pt surface because of the interference of the support.

3.3. TPD of EAc following adsorption on blank supports and Pt catalysts

3.3.1. Blank supports

TPD profiles following adsorption of $^{13}CH_3$ $^{13}COOC_2H_5$ on γ-Al_2O_3, TiO_2 and TiO_2 (W^{6+}) with the procedure, which was described in Section 2, are presented in Fig. 2(a)–(c), respectively. The selected isotope of EAc makes possible the identification of the different surface reaction pathways of the acetate and ethoxide parts of the EAc molecule. Non-dissociated EAc desorbs only at low temperatures with a peak at around 100°C. Larger amounts of EAc desorb from alumina, because of its higher surface area compared to the other two supports. The initial surface transformation of EAc appears to be surface reaction with hydroxyl groups towards adsorbed ethoxide and acetate species. This can be readily deduced from the TPD profile on γ-Al_2O_3 (Fig. 1(a)), in which ethanol appears in the gas phase at 100°C.

TPD profiles for all three supports correspond to the superposition of TPD profiles of adsorbed ethanol and acetic acid, as it has been found by additional TPD experiments of ethanol and acetic acid, which were carried out for comparison purposes. During TPD of ethanol adsorbed on γ-Al_2O_3, it was found that ethanol starts to desorb at the same temperature region (∼100°C) as during TPD of EAc, which implies that, during TPD of EAc, ethanol appearance in the gas phase is rather desorption than reaction limited. The ethoxide part of the EAc molecule, which is composed of ^{12}C, undergoes the typical reactions of adsorbed ethanol, producing mainly ethylene and smaller amounts of acetaldehyde [11,12]. The acetate part of EAc, which is ^{13}C-labelled, is quite stable and mainly $^{13}CO_2$ (and traces of $^{13}CH_4$) appear at high temperatures. Titration of residual carbon with oxygen at the end of the TPD experiment led to formation of mainly $^{13}CO_2$ and very small amounts of $^{12}CO_2$. It may be assumed that the carbon atom (^{13}C) of the methyl group of acetate species remains on the surface, as it has been also suggested by other investigators [11]. The relative amount of residual carbon was slightly higher on TiO_2 and TiO_2 (W^{6+}) compared to Al_2O_3. Although it appears that residual carbon should be larger on TiO_2 (W^{6+}) (due to the low amount of desorbed $^{13}CO_2$), there is an uncertainty because of the very low concentration of all desorbing species (maximum concentration of $^{13}CO_2$ is ∼50 ppm, Fig. 2(c)). It is evident in Fig. 2 that the support influences considerably the reactivity of adsorbed EAc. The TiO_2 (W^{6+}) support is significantly more active in the transformation of surface species originating from adsorbed EAc. Formation of ethylene and acetaldehyde takes place at 230°C compared to ∼400°C in the case of γ-Al_2O_3 and TiO_2 supports. The TiO_2 (W^{6+}) support is also more selective for ethylene formation, in other words, it favors dehydration vs. dehydrogenation of adsorbed ethoxide species. In addition, formation of $^{13}CO_2$ takes place at lower temperatures on doped TiO_2 (W^{6+}) compared to the other supports.

3.3.2. Pt catalysts

TPD profiles following adsorption of $^{13}CH_3$ $^{13}COOC_2H_5$ on Pt/γ-Al_2O_3, Pt/TiO_2 and Pt/TiO_2 (W^{6+}) catalysts are presented in Fig. 3(a)–(c), respectively. In this case, desorption profiles are very complicated because of decomposition reactions occurring on the Pt surface. It can be observed that Pt promotes decomposition of adsorbed EAc towards CO, CO_2, CH_4 and H_2. EAc desorbs unreacted at low temperatures (∼100°C), as in the case of blank supports. A fraction of EAc, however, dissociates towards adsorbed ethoxide and acetate species. The reactivity of these two species is different and is influenced by the support employed to disperse Pt. This is more clearly seen in the case of the Pt/γ-Al_2O_3 catalyst, where gaseous compounds (CO, CH_4, CH_3CHO, C_2H_5OH and H_2) originating from ethoxide species are observed in the temperature range of 150–300°C, while gaseous compounds ($^{13}CO_2$, ^{13}CO, $^{13}CH_4$ and H_2) originating from acetate species are observed in the temperature range of 300–500°C. In the case of the Pt/TiO_2 (W^{6+}) catalyst, the difference in the reactivity of ethoxide and acetate species is smaller, as acetate species decompose at a significantly lower temperature range (200–350°C) compared to Pt/Al_2O_3. The TPD profile of the Pt/TiO_2 catalyst is the most complicated. Decomposition of ethoxide takes place in a form of multiple peaks of CO, CH_4 and H_2, while CO_2 is also produced (CO_2 was not observed in the case of Pt/γ-Al_2O_3 and Pt/TiO_2 (W^{6+}) catalysts). Part of ethoxide species react in the same temperature range as that of acetate species. The peaks of CH_4, CO and H_2 are similar in shape and position indicating that appearance of these molecules in the gas phase is reaction and not desorption limited. This can be explained taking into account that the binding strength of CO, CH_4 and H_2 on Pt is different. Therefore, the only way that these molecules can appear simultaneously in the gas phase is when they are produced from a common intermediate (ethoxide or acetate species) at a temperature higher than their desorption temperature. Regarding the origin of the multiple peaks, it might be proposed that they correspond to different ethoxide species, although no such evidence was obtained from the TPD profiles of the blank TiO_2 support. The amount of residual carbon, which consisted essentially of ^{13}C, is significantly reduced in all cases and noteworthy differences do not exist among the catalysts studied.

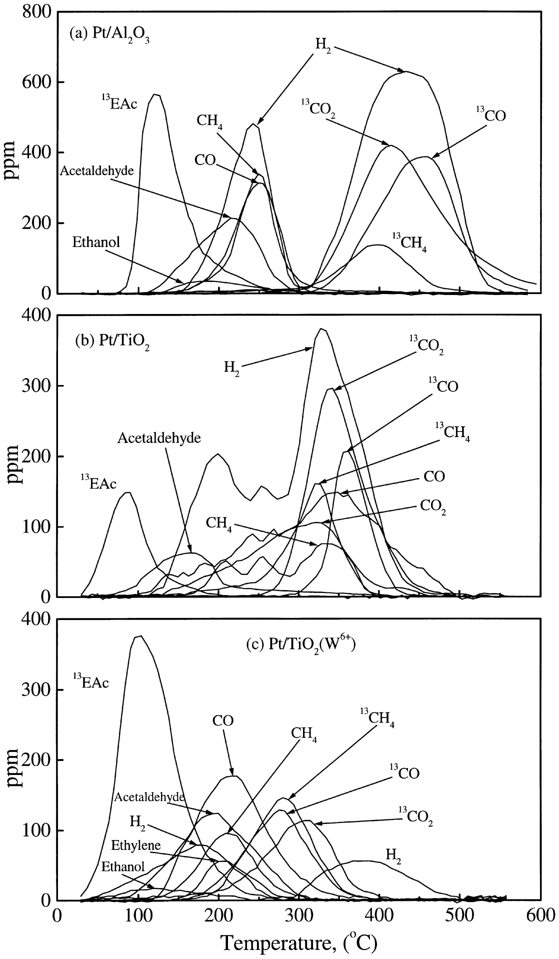

Fig. 3. TPD profiles following adsorption of $^{13}CH_3{}^{13}COOC_2H_5$ on (a) Pt/γ-Al_2O_3, (b) Pt/TiO_2, (c) Pt/TiO_2 (W^{6+}) (*note the different scales of y-axis*).

Table 3
Amounts of compounds detected during TPO of $H_3OOC_2H_5$ (μmol/g)

Catalyst	EAc	C_2H_5OH	CH_3CHO	C_2H_4	CO_2	CO_2	O_2	O_2 consumed	
					1st peak	2nd peak		1st peak	2nd peak
γ-Al_2O_3	50	9	34	–	42	50	170	88	211
TiO_2	6	2	13	–	35		62	115	
TiO_2 (W^{6+})	19	0.7	6	1	11	–	22	17	19
Pt/γ-Al_2O_3	71	7	22	–	17	83	150	56	245
Pt/TiO_2	2	–	–	–	30		31	73	
Pt/TiO_2 (W^{6+})	12	0.4	2.3	–	4	9	15	32	

3.4. TPO of EAc following adsorption on blank supports and Pt catalysts

3.4.1. Blank supports

TPO profiles following adsorption of $^{13}CH_3$ $^{13}COOC_2H_5$ on γ-Al_2O_3, TiO_2 and TiO_2 (W^{6+}) are presented in Fig. 4(a)–(c), respectively. It can be seen that, in all cases, EAc desorbs unreacted at low temperatures, as during TPD experiments. The following observations can be made:

(i) *Comparison of reactivity of ethoxide and acetate species towards oxidation*. Under TPO conditions, ethoxide species formed by EAc are oxidized towards CO_2 and acetaldehyde (in the case of γ-Al_2O_3 and TiO_2 (W^{6+}) small amounts of ethanol (γ-Al_2O_3) and ethylene (TiO_2 (W^{6+})) are also formed). Acetate species, on the other hand, are oxidized exclusively towards $^{13}CO_2$. Formation of $^{13}CO_2$ takes place at higher temperatures compared to formation of $^{12}CO_2$ and acetaldehyde, indicating that the reactivity of acetate species is considerably lower than that of ethoxide species. The largest reactivity difference is observed in the case of γ-Al_2O_3, where two $^{12}CO_2$ peaks are also observed. The second high temperature peak has the same shape and position as the $^{13}CO_2$ peak and it appears that it is due to oxidation of acetate species, which have been formed by partial oxidation of ethoxide ones. This seems to be also true in the case of the TiO_2 support, where the CO_2 profile consists of two overlapping peaks, and the second CO_2 peak is at the same temperature range as the $^{13}CO_2$ peak.

The amounts of compounds detected, as well as of oxygen consumed, during TPO of EAc are presented in Table 3. The profile of oxygen concentration during TPO followed closely the profile of carbon dioxide,

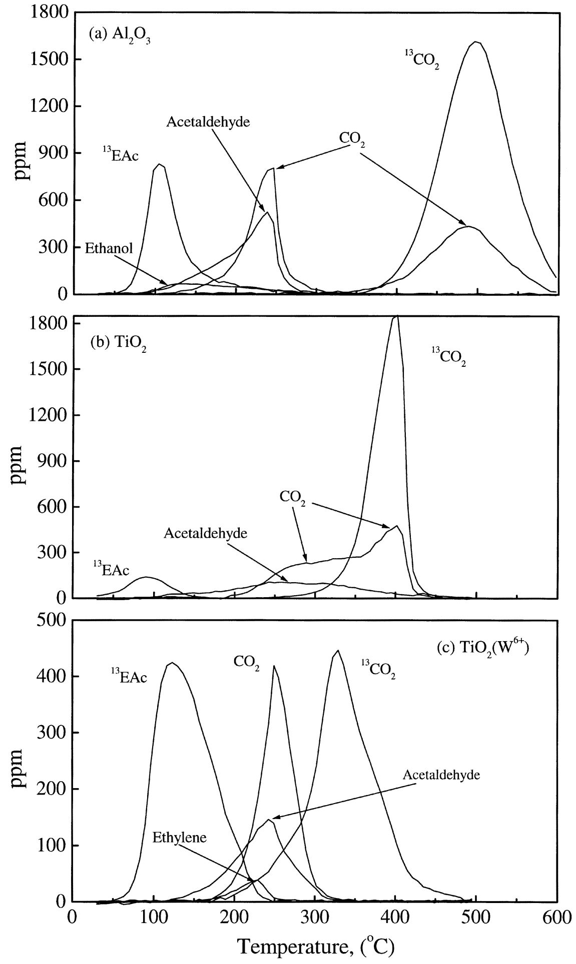

Fig. 4. TPO profiles following adsorption of $^{13}CH_3OOC_2H_5$ on (a) γ-Al_2O_3, (b) TiO_2, (c) TiO_2 (W^{6+}) (*note the different scales of y-axis*).

Table 4
Comparison of adsorbed amounts of EAc during TPO and DSC experiments (molecules/nm^2)

Catalyst	Desorbed ethylacetate (1)	Reacted ethylacetate (2)	Total (1) + (2)	Amount adsorbed during DSC
γ-Al_2O_3	0.33	0.60	0.93	0.80
TiO_2	0.08	0.44	0.52	0.49
TiO_2 (W^{6+})	1.15	0.78	1.93	2.29
Pt/γ-Al_2O_3	0.47	0.53	1.00	0.89
Pt/TiO_2	0.03	0.20	0.23	0.20
Pt/TiO_2 (W^{6+})	0.73	0.54	1.27	2.42

showing negative oxygen peaks whenever a carbon dioxide peak appeared during TPO. The amount of oxygen consumed during the second high temperature peak of CO_2 was almost equal (generally within ±15%) to the amount of CO_2 produced, which is in very good agreement with the stoichiometry of oxidation of acetate species (stoichiometric O_2/CO_2 ratio is 1 : 1). Oxygen consumption in the low temperature region is in good agreement with the stoichiometry of oxidation of ethoxide species to CO_2 (stoichiometric O_2/CO_2 ratio is 3 : 2) and acetate species plus the stoichiometry of acetaldehyde formation (stoichiometric CH_3CHO/O_2 ratio is 2 : 1).

Although the oxidation pathway of acetate species formed from EAc is straightforward (only $^{13}CO_2$ is formed), the oxidation pathway of ethoxide species is more complicated. A small fraction is not oxidized at all and desorbs as ethanol, another fraction oxidizes partially and appears as acetaldehyde, while the remaining is oxidized to CO_2, either directly (low temperature CO_2 peak) or via intermediate formation of acetate (high temperature CO_2 peak). In the case of γ-Al_2O_3, where all four pathways can be easily observed, the contribution of each path is 10%, 38%, 24% and 28%, respectively.

(ii) *Comparison of behavior of supports*. The type of the support material influences considerably the oxidation reactivity of adsorbed ethoxide and acetate species originating from the EAc molecule. The largest effect is found in the oxidation of acetate species, whereas such species formed on γ-Al_2O_3 exhibit the smallest reactivity (the peak of $^{13}CO_2$ is at 500°C), while acetate species on TiO_2 (W^{6+}) are the most easily oxidized (the peak of $^{13}CO_2$ is at 330°C). The effect of the support on the reactivity of ethoxide species is not so pronounced and it mainly refers to whether or not the support promotes partial oxidation of ethoxide to acetate species or not. It appears that γ-Al_2O_3 and TiO_2 tend to oxidize part of ethoxide to acetate, while TiO_2 (W^{6+}) does not.

The amounts of EAc, which have desorbed and reacted during TPO, are compared to the amounts adsorbed during the DSC experiments in Table 4. It has to be noted that adsorption in DSC experiments was performed employing a gas flow of 380 ppm non-labelled EAc in helium until saturation was obtained, while adsorption in TPO experiments was performed by injecting a small (1–5 μl) amount of liquid, ^{13}C-labelled EAc upstream of the catalyst bed. It can be observed that the amounts of adsorbed EAc obtained with these totally different methods are similar (a discrepancy is found only in the case of Pt/TiO_2 (W^{6+}) for unknown reasons). As stated in Section 2, the amount of adsorbed EAc did not increase when larger quantities of EAc (∼10 μl) were injected for adsorption in the catalyst bed. Based on the above, it can be proposed that the results of Table 4 correspond to near monolayer coverages of EAc.

3.4.2. Pt catalysts

TPO profiles following adsorption of $^{13}CH_3{}^{13}COOC_2H_5$ on Pt/γ-Al_2O_3, Pt/TiO_2 and Pt/TiO_2 (W^{6+}) catalysts are presented in Fig. 5(a–c), respectively. The following observations can be made:

(i) *Comparison of catalysts with the corresponding blank supports*. Comparison of the TPO profiles of the catalysts and the corresponding blank supports (Fig. 5(a) and Fig. 4(a), etc.) shows that addition of Pt has the following effects:

- Peaks of oxidation products are shifted to lower temperatures, as shown in Table 5. For example, the $^{13}CO_2$ peaks shift to a lower temperature by 80°C.
- The product distribution and the relative magnitude of the dual CO_2 peaks changes. In the case of Pt/γ-Al_2O_3, for example, the ratio of the amount of

CO_2 produced in the high temperature peak to that in the low temperature peak is 5 : 1, compared to a value of 1.2 : 1 in the case of blank γ-Al_2O_3. This implies that a higher amount of ethoxide species are initially oxidized to acetate species in the presence of Pt. In the case of Pt/TiO_2, it appears that the total quantity of ethoxide species is initially oxidized to acetate species, as the CO_2 and $^{13}CO_2$ peaks are identical and no other products are formed. In the case of Pt/TiO_2 (W^{6+}), approximately half of the ethoxide species are oxidized to acetate species. In addition, lower amounts of acetaldehyde and ethanol are formed on Pt catalysts (on Pt/TiO_2 these disappear altogether), because they are further oxidized to CO_2. These observations imply that the role of Pt is to enhance the rate of oxidation of organic intermediates to CO_2, either directly or via formation of adsorbed acetate species.

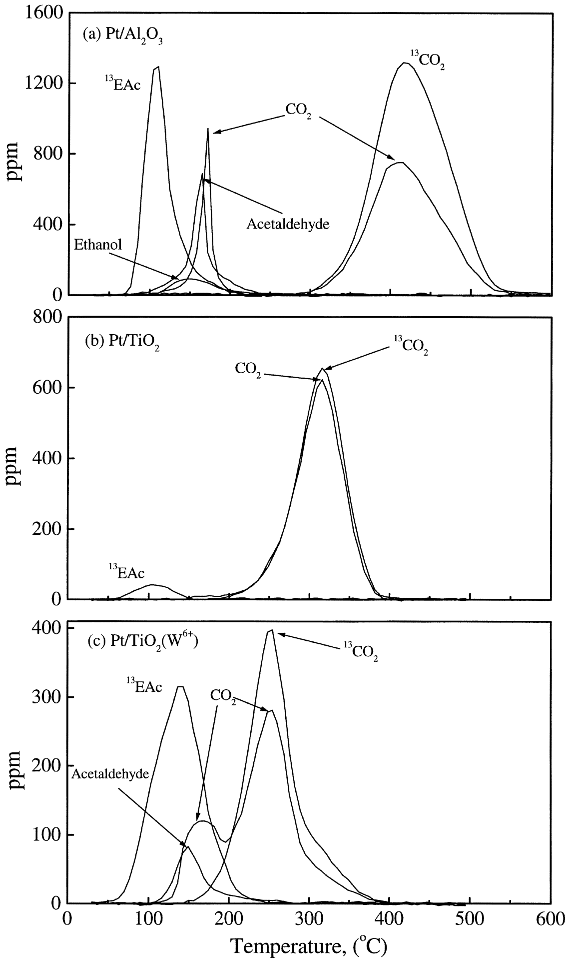

Fig. 5. TPO profiles following adsorption of $H_3OOC_2H_5$ on (a) Pt/γ-Al_2O_3, (b) Pt/TiO_2, (c) Pt/TiO_2(W^{6+}) (*note the different scales of y-axis*).

Table 5
Comparison of peak temperatures during TPO of EAc (°C)

Catalyst	CH_3CHO	CO_2	CO_2	O_2
		1st peak	2nd peak	
γ-Al_2O_3	240	240	490	500
Pt/γ-Al_2O_3	170	180	420	420
TiO_2	220–300	270–300	400	400
Pt/TiO_2	–	320		320
TiO_2 (W^{6+})	240	240		330
Pt/TiO_2 (W^{6+})	150	170	250	250

(ii) *Comparison of Pt catalysts*. The Pt catalysts, which were investigated, differ significantly in reactivity under CPO conditions, with Pt/TiO_2 (W^{6+}) being the most active and Pt/γ-Al_2O_3 the least active. Pt/TiO_2 has intermediate activity, but, on the other hand, appears to be the most selective with minimal formation of organic intermediates. This is not due to modification of Pt catalytic properties induced by the support, but is rather related to the adsorption strength of ethoxide and acetate species on the support surface. This is further analyzed in Section 4.

4. Discussion

The results of the present study have shown that γ-Al_2O_3, TiO_2 and TiO_2 (W^{6+}) carriers adsorb EAc and are active in the transformation of this molecule towards other organic intermediates. This is in accordance to results of other investigators [9]. Addition of a small amount of Pt on the support modifies substantially the transformation pathway. It is understandable that the majority of adsorbed EAc is located on the support surface, as is shown in Table 2, Figs. 2 and 4 and as is also expected by the low loading of Pt in the catalysts (0.3 wt.%). The heat of adsorption of EAc, however, is 1.9–3.5 times larger on Pt containing catalysts compared to the corresponding blank supports, indicating that Pt adsorbs EAc very strongly. The heat of adsorption of EAc follows the sequence: γ-$Al_2O_3 > TiO_2$ (W^{6+}) $> TiO_2$. The same sequence was also observed in the case of ammonia adsorption. The surface concentration of EAc, on the other hand, was found to be 2–4 times lower than that of ammonia. As EAc is a bulkier molecule compared to NH_3, adsorption of two EAc molecules on neighboring sites of the support will not be favored due to steric factors. Therefore, it is expected that the saturation coverage of EAc will be smaller than that of NH_3. It can be proposed that EAc adsorbs on the same type of support surface sites as ammonia does. These sites will be acidic in nature and adsorption will take place through the oxygen atom of the carbonyl group of the EAc molecule, either on a Brønsted or a Lewis acid site. The TiO_2 (W^{6+}) support which has the largest number density of acidic sites also adsorbs the largest amount of EAc on a per unit surface area basis.

An attempt to correlate the measured heats of adsorption with the TPD profiles, however, is not straightforward. First of all, despite the large difference in heats of adsorption, non-dissociated EAc desorbs from all supports at around 100°C. Secondly, there is not a certain trend in peak temperatures of organic intermediates during TPD, which would correlate with the measured heats of adsorption. This can be explained by taking into account the fact that the appearance of organic products is influenced by both the kinetics of the corresponding surface reactions and the adsorption strength of the starting molecule.

A relevant question refers to the temperature at which EAc decomposes to adsorbed ethoxide and acetate species. The appearance of ethanol in the TPD profiles at around 100°C in the case of γ-Al_2O_3 and at around 130°C in the case of TiO_2 and TiO_2 (W^{6+}), indicates that decomposition has already started at these temperatures. It was found by separate TPD experiments of ethanol, that ethanol starts to desorb at around 50–70°C in the case of TiO_2 and TiO_2 (W^{6+}). Therefore, appearance of ethanol during TPD of EAc is reaction limited in these two catalysts. In the case of γ-Al_2O_3, ethanol desorption during TPD of ethanol starts at ∼100°C, i.e., at the same temperature as during TPD of EAc. Therefore, the temperature, at which EAc decomposes to ethoxide species, cannot be known (it can only be said that it is <100°C), because appearance of ethanol in the gas phase appears to be desorption limited.

By performing separate TPD studies of ethanol and acetic acid, it was found that the TPD profiles following EAc adsorption are essentially a superposition of the TPD profiles of ethanol and acetic acid. Thus, the molecule of EAc provides a means of coadsorbing equimolar amounts of ethoxide and acetate species. The use of partially ^{13}C-labelled ethylacetate in this work, has, of course, removed the ambiguity in the assignment of the origin of desorbing molecules, especially during TPO, where CO_2 is produced both by ethoxide and acetate species.

The behavior of Pt-containing catalysts under TPD and TPO conditions can be explained by assuming that surface-diffusion of organic intermediates from the support to Pt crystallites is the key process. During TPD, ethoxide and acetate species diffuse to the Pt surface, where cleavage of the C–C bonds takes place and C_1 molecules are desorbed in the gas phase. Because acetate is more strongly adsorbed than ethoxide, it becomes sufficiently mobile only at higher temperatures and formation of ^{13}C-labelled decomposition products is delayed. This is nicely shown in the TPD profile of the Pt/γ-Al_2O_3 catalyst (Fig. 3(a)). During TPO, diffusing species are oxidized on Pt. Ethoxide species can be oxidized to acetaldehyde, CO_2 or acetate species. Acetate species are oxidized to CO_2. Surface diffusion has been also proposed by Cordi and Falconer [11] to explain results obtained during TPD and TPO of methanol, ethanol, acetaldehyde and acetic acid on Al_2O_3 and Pd/Al_2O_3 catalysts. An alternative explanation of the observed behavior could be the diffusion of atomic oxygen from the surface of Pt to the organic intermediates adsorbed on the support surface and their subsequent oxidation. This explanation, however, is not probable for the following reasons:

1. Oxygen is quite strongly adsorbed on Pt (its heat of adsorption is ∼250–290 kJ/mol [13]) and, therefore, atomic oxygen is not expected to have sufficient mobility in the temperature region where oxidation of organic intermediates takes place (100–400°C).
2. TPD experiments provide solid evidence that ethoxide and acetate species diffuse to the surface of Pt, where they decompose forming C_1 compounds and H_2.

Regarding the origin of the higher activity of the doped Pt/TiO_2 (W^{6+}) catalyst, it can be said that it is mainly due to the higher surface concentration and mobility of ethoxide and acetate species on the TiO_2 (W^{6+}) surface compared to Al_2O_3 or TiO_2. The cause for this feature of the TiO_2 (W^{6+}) surface is not clear. An indication, which has been found in this work, is that TiO_2 (W^{6+}) has a larger number density of acidic sites than Al_2O_3 or TiO_2 and these sites serve as adsorption centers for the EAc molecule. Based on the measurements of heat of adsorption, these sites appear to be of intermediate strength overall compared to those on Al_2O_3 or TiO_2. It can be then assumed that these sites are of the right strength to favor adsorption and decomposition of EAc to acetate and ethoxide species, which are not too strongly bound on the support surface and can become sufficiently mobile at low temperatures to reach the Pt surface. Kinetic studies of EAc oxidation reported previously, [7], have shown that the apparent reaction orders with respect to EAc and oxygen, as well as the activation energy of the reaction, are the same for Pt supported on Al_2O_3, TiO_2 and TiO_2 (W^{6+}) carriers. This implies that the higher activity of the Pt/TiO_2 (W^{6+}) catalyst is not due to a different reaction mechanism or a modification of the catalytic properties of platinum. This is in accordance to the findings of this work, which show that the high activity is a result of the larger rate of diffusion of organic intermediates from the support to the Pt surface. This, in turn, appears to be a result of the presence of a larger number of acidic sites with appropriate strength on the TiO_2 (W^{6+}) surface.

5. Conclusions

The following conclusions can be drawn from the results of the present study.

- EAc adsorbs on the blank supports (Al_2O_3, TiO_2, TiO_2 (W^{6+})) and forms ethoxide and acetate species. Surface processes taking place during TPD and TPO correspond to reactive transformations of these species.
- In the case of Pt catalysts, ethoxide and acetate species formed on the support by decomposition of adsorbed EAc reach the Pt surface by surface diffusion, where they decompose to C_1 molecules (CO, CH_4, CO_2) in the absence of oxygen or are oxidized mainly to CO_2 in the presence of oxygen.
- The high activity of the Pt/TiO_2 (W^{6+}) catalyst under steady-state conditions may be attributed to the higher rate of diffusion of organic intermediates from the doped support to the Pt surface. This appears to be a result of the presence of a larger number of acidic sites with appropriate strength on the TiO_2 (W^{6+}) surface, which lead to the formation of a large pool of reactive intermediates with high mobility.

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