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New supported Pd catalysts for the direct transformation of ethanol to ethyl acetate under medium pressure conditions

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Abstract

The direct transformation of ethanol to ethyl acetate was studied over supported palladium catalysts with low palladium content (1%, w/w Pd) at 1 MPa pressure. SiO_2, Al_2O_3, ZnO, SnO_2 and WO_3-ZrO_2 (29%, w/w WO_3) were used as supports. The catalytic behaviour of samples was related to the characteristics of the support and the presence of mono- or bimetallic entities. The best catalytic results were obtained with ZnO- and SnO_2-supported catalysts, which can easily lead to alloyed palladium phases.

Keywords: Ethyl acetate synthesis; Supported palladium; Ethanol dehydrogenation

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1. Introduction

There is a growing interest in developing ecofriendly chemicals and processes in the context of a new green chemistry concept. In this area, ethyl acetate is replacing the use of aromatic compounds used as solvents of paints and adhesives. However, the classical processes of obtaining ethyl acetate

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$$

$$C_2H_4 + CH_3COOH \rightarrow CH_3COOCH_2CH_3$$

$$2CH_3CHO \rightarrow CH_3COOCH_2CH_3$$

require acetic acid or acetaldehyde as feedstock and both reactants are difficult to handle due to corrosion or toxicity problems.

An alternative route to conventional processes is the production of ethyl acetate by dehydrogenative dimerization of ethanol

$$2CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2$$

This alternative route shows the advantage of using only ethanol as feedstock and the production of H_2, which can be used for several purposes. Moreover, if bio-derived ethanol is used, then the production of ethyl acetate will be based on biomass and the process will not depend on fossil fuels as do the above-mentioned conventional processes.

There is a commercial process (Davy process technology) which is based on the dehydrogenative dimerization of ethanol to synthesize ethyl acetate [1–3]. However, the ethyl acetate stream, which is produced over a copper-based catalyst, is impure and passes through consecutive units of selective hydrogenation and distillation to remove by-products [4].

Although several papers dealing with the use of copper-based catalysts for the above-mentioned reaction have been reported [5–8], other active phases have not been extensively studied. Taking into account that the selectivity is a major problem for the production of ethyl acetate from ethanol, further studies addressed to a better knowledge of new catalysts and their catalytic behaviour are desired. One of the few studies which have been reported using other catalytic phases is that of Iwasa et al. with Pd-based catalysts (10–30%, w/w Pd loading) under atmospheric pressure conditions [9]. The authors have proposed a relation between the

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yielding of acetaldehyde and ethyl acetate and the presence of Pd–Zn, Pd–Ga or Pd–In alloys. However, no surface characterization of the catalysts was reported and the behaviour of catalysts was referred to Pd-alloys determined by means of X-ray diffraction (XRD) analysis [9].

The aim of this work is to evaluate the catalytic behaviour of supported palladium catalysts with low palladium content (ca. 1%, w/w Pd loading) on the ethanol transformations at 1 MPa of pressure. ZnO, SnO_2, SiO_2, Al_2O_3 and a WO_3-ZrO_2 mixed oxide were used as supports. The catalytic evaluation of supports and supported palladium catalysts and the surface characterization by X-ray photoelectron spectroscopy and FTIR of CO adsorption as probe molecule, allowed us to discuss the catalytic behaviour of samples in terms of the support used in the preparation and the presence of bimetallic palladium entities.

2. Experimental

2.1. Preparation of catalysts

SiO_2, γ-Al_2O_3, ZnO, SnO_2 and WO_3-ZrO_2 supported palladium catalysts were prepared by incipient-wetness or wet impregnation methods. Commercial SiO_2 (hydrophobic silica HDK-20, BET 170 $m^2 g^{-1}$, from Wacker) and γ-Al_2O_3 (T-126, BET 180 $m^2 g^{-1}$ from Girdler) were used. The other oxides used as supports were synthesized in our laboratory as follows: for the preparation of ZnO aqueous solutions of $Zn(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_2CO_3$ were mixed at room temperature. After filtering and washing, solid was dried at 373 K and then it was treated under Ar at 573 K. SnO_2 was prepared by treating under vigorous stirring an ethanolic solution of anhydrous $SnCl_4$ with an aqueous solution of NH_3, then solvent was evaporated at 303 K and the solid was washed until the removing of chloride ions was achieved. Finally, it was dried and calcined under air at 373 and 573 K, respectively. WO_3-ZrO_2 was prepared by a sol–gel method, an ammonia solution of H_2WO_4 diluted with *n*-propanol was mixed with a solution containing the Zr(IV) precursor (Zr(IV) *n*-propoxide). The suspension was aged at 343 K for 6 h, then the solid was filtered and subsequently dried at 373 K for 16 h and calcined at 873 K for 4 h.

$Pd(CH_3COO)_2$ in acetone solution was used as precursor when catalysts were prepared by incipient wetness impregnation. These catalysts were labelled Pd/SiO_2, Pd/Al_2O_3, Pd/ZnO, Pd/SnO_2 and Pd/WO_3-ZrO_2, depending on the support used in the preparation.

Over SnO_2, a catalyst by wet impregnation was prepared from a solution of $[Pd(NH_3)_4]^{2+}$, this catalyst was named $Pd(NH_3)/SnO_2$. All catalysts were dried at 373 K and then calcined at 573 K. The reduction was carried out at 523 K with a 1:1 H_2:Ar mixture.

The metallic content of catalysts was determined by inductively coupled plasma techniques.

2.2. Catalytic activity

Catalytic tests were performed in a fixed-bed continuous-flow reactor equipped with a thermocouple allowing temperature measurement inside the catalytic bed. Reaction was carried out at 1 MPa of pressure and 523 K using ethanol (HPLC purity grade) as reactant.

The catalyst (0.3 g, 0.3–0.6 mm sieved) was diluted with inactive SiC, giving a catalyst bed volume of 1.5 ml and introduced between wool plugs in a tubular reactor (i.d. 1.1 cm, height 34 cm) made of stainless steel. Ethanol was supplied by a Gilson 307 piston pump, vaporized at 523 K and diluted with He (purity 99.9990%) before entering the reaction chamber (EtOH:He = 1:4.7 molar basis). LHSV was 0.2 h^{-1}.

Supported palladium catalysts were re-reduced in situ at 10^5 Pa of pressure with H_2 and 523 K, then pressure was increased to 1 MPa and catalysts were exposed to the gas mixture. Products were analyzed on-line using a suitable micro gas chromatograph (Varian 4900) equipped with four independent channels with Ar or He as carriers and four micro-TCD detectors.

2.3. Characterization of catalysts

BET surface areas were determined by N_2 adsorption at 77 K using a Micromeritics ASAP9000 apparatus.

X-ray diffraction profiles were collected in the 2θ angle between 15° and 70°, at a step width of 0.02° and by counting 10 s at each step with a Siemens D-500 instrument equipped with a Cu target and a graphite monochromator.

X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer equipped with a Mg Kα ($h\nu$ = 1253.6 eV, 1 eV = 1.6302×10^{-19} J) X-ray exciting source, a hemispherical electron analyser and a pre-treatment chamber. The residual pressure in the ion-pumped analysis chamber was maintained below 4.2×10^{-9} mbar (1 mbar = 101.33 Pa) during data acquisition. The binding energies (BE) were referred to the C 1s peak at 284.9 eV, which gave BE values with an accuracy of ±0.1 eV. Peak intensity was calculated as the integral of each peak after smoothing and subtraction of a Shirley [10] background and fitting of the experimental curve to Gaussian/Lorentzian lines.

Infrared spectra (FTIR) were obtained at room temperature on a Nicolet 520 Fourier transform instrument at 2 cm^{-1} of resolution by collecting 128 scans. For these experiments special greaseless vacuum cells with CaF_2 windows which allowed thermal treatments were used.

3. Results and discussion

Supports prepared in this work were characterized by X-ray diffraction and BET surface areas. X-ray diffraction patterns corresponded to expected ZnO and SnO_2 phases.

Table 1
Prepared catalysts and their palladium content

Catalyst	Pd%, w/w
Pd/ZnO	0.85
Pd/SiO_2	1.11
Pd/Al_2O_3	0.98
Pd(NH_3)/SnO_2	0.82
Pd/SnO_2	0.91
Pd/WO_3-ZrO_2	0.93

For WO_3-ZrO_2 (29%, w/w WO_3), the pattern indicated the presence of tetragonal ZrO_2, this phase was stabilized by the incorporation of tungsten. The materials showed surface area values of 70 $m^2\,g^{-1}$ for ZnO, 135 $m^2\,g^{-1}$ for SnO_2 and 96 $m^2\,g^{-1}$ for WO_3-ZrO_2. Table 1 shows catalysts prepared and their metallic content.

Surface characterization of catalysts was carried out by XPS. Depending on the support, binding energy values for Zn $2p_{3/2}$ at 1022.1 eV, Si $2p_{3/2}$ at 103.4 eV, Sn $3d_{5/2}$ at 487.0 eV and Al $2p_{3/2}$ at 74.5 eV were obtained. For the Pd/WO_3-ZrO_2, it was not possible to obtain information about the Pd 3d core level due to its superposition with the intense signal of Zr 3p peaks of the ZrO_2 support. Figs. 1 and 2 show the spectra of the Pd 3d level for the remainder of the catalysts and Table 2 summarizes the Pd $3d_{5/2}$ BE values. Single peaks for Pd/ZnO and Pd/SiO_2 can be observed (Fig. 1). However, the position of the peaks indicates differences in the corresponding binding energy values (see Table 2). For Pd/SiO_2 sample, a value of 335.3 eV indicates the presence of Pd° [11–13]. The increase on the BE observed for the Pd $3d_{5/2}$ peak and also the largest full width at half maximum (FWHM) for this peak (3.3 eV) in the Pd/ZnO sample point out to the formation of Pd–Zn alloys [14–16]. All the other catalysts showed more complex Pd $3d_{5/2}$ level spectra (Fig. 2) and their deconvolution showed two components, whose location appears in Table 2. The component at higher BE can be assigned to oxidized Pd; that at lower BE is due to reduced palladium. Values corresponding to SnO_2-supported catalysts were ca. 1 eV higher than that assigned to Pd° particles supported on SiO_2 or alumina, that points to the presence of Pd–Sn entities or strong Pd/SnO_2 interactions [17].

Table 2
Binding energy values (eV) of Pd $3d_{5/2}$ core level and XPS atomic ratios of catalysts

Catalyst	Pd $3d_{5/2}$[a]	Pd/M[b]
Pd/ZnO	335.6	0.030
Pd/SiO_2	335.3	0.003
Pd/Al_2O_3	335.2 (45) 336.8 (55)	0.006
Pd(NH_3)/SnO_2	336.2 (66) 337.2 (32)	0.006
Pd/SnO_2	336.3 (63) 337.3 (37)	0.009

[a] Values in parentheses are peak area percentage.

[b] M = Zn, Sn, Si, Al.

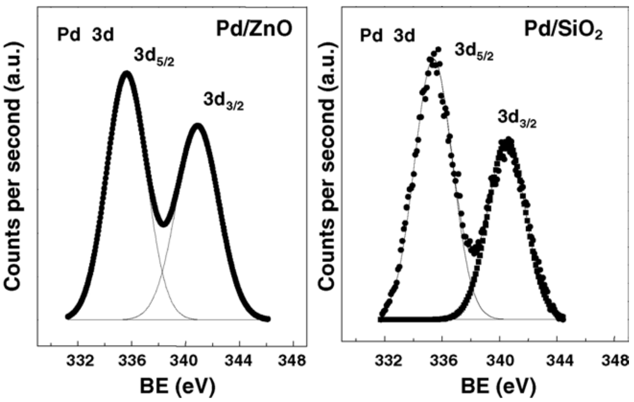

Fig. 1. XP core level spectra of Pd/ZnO and Pd/SiO_2.

ZnO- and SnO_2-supported catalysts were characterized by FTIR using CO as probe molecule (see Fig. 3). CO adsorbed over Pd/ZnO raised bands centered at 2037, 1986 and 1889 cm^{-1} (Fig. 3, spectrum a). The position of the band due to linearly coordinated CO (2037 cm^{-1}) and its relative intensity to the intensity of the bands assigned to bridged CO, accords with the presence of nonadjacent Pd atoms interacting with Zn [18]. For the Pd/SnO_2 catalyst a small band located at 2039 cm^{-1} is also visible (Fig. 3, spectrum b). However, in this case the relative intensity of the linear band with respect to the bridged ones is lower; and the presence of small Pd particles [19], which strongly interact with the support, should not be discarded.

From the integrated peak areas of XP spectra and atomic sensitivity factors [20], the atomic ratios Pd/M (M = Si, Al, Zn, Sn) were calculated (see Table 2). Pd/ZnO shows the highest value, which seems to point out that the Pd_xZn_y particles of this catalyst are smaller than the palladium entities on the other catalysts.

The catalytic behavior of samples is shown in Table 3 and Fig. 4 shows the ethanol conversion profiles for monometallic-supported catalysts. Pd/SiO_2, Pd/WO_3-ZrO_2 and Pd/Al_2O_3 showed a poor catalytic performance in the desired reaction. Over these catalysts, high yield to methane and carbon monoxide was obtained. Their catalytic behaviour could be related to the presence of palladium particles which favoured the ethanol decomposition reaction [9]

$$CH_3CH_2OH \rightarrow CH_4 + CO + H_2$$

Moreover, supports with acid properties such as γ-Al_2O_3 and WO_3-ZrO_2 produced high selectivity to dehydration products ethylene and di-ethylether

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O$$

$$2CH_3CH_2OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

The best catalytic performances were obtained over SnO_2- and ZnO-supported catalysts. High selectivity to ethyl acetate and to the dehydrogenated intermediate product, acetaldehyde, were obtained. Moreover, SnO_2- and ZnO-

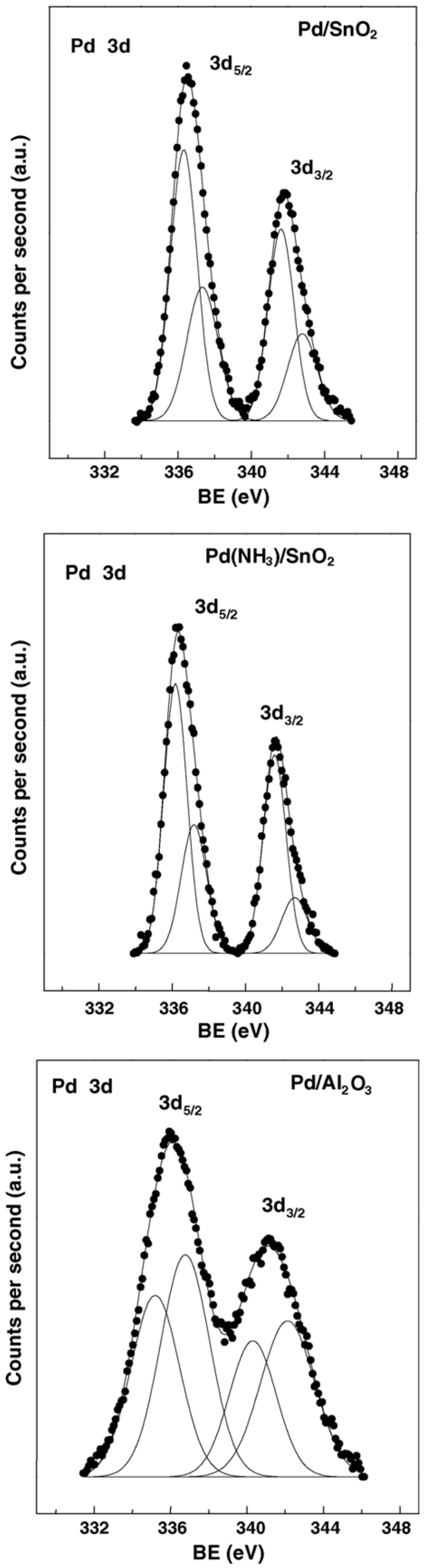

Fig. 2. XP core level spectra of Pd/SnO_2, Pd(NH_3)/SnO_2 and Pd/Al_2O_3.

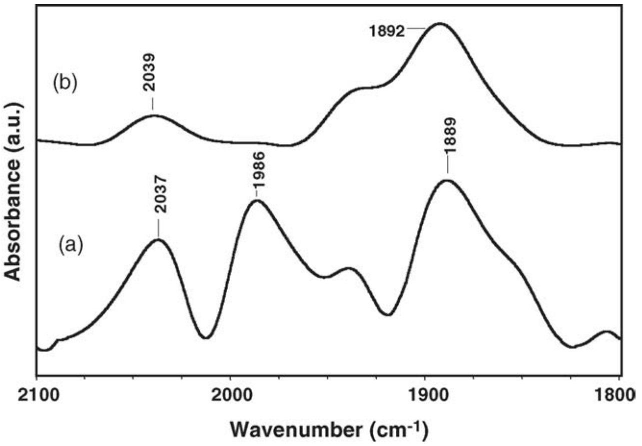

Fig. 3. FTIR spectra in the ν(CO) region of (a) Pd/ZnO and (b) Pd/SnO_2. Spectra were taken at room temperature after admission of 300 mbar of CO and subsequent vacuum treatment (10^{-1} mbar).

supported catalysts did not show deactivation during the catalytic test (see Fig. 4). For comparative purposes Table 3 also includes the data corresponding to the behaviour of SnO_2 and ZnO supports. Both supports were much less active than the corresponding Pd-supported catalyst. However, their selectivity to acetaldehyde and ethyl acetate was also high and only diethyl ether was obtained as by-product under the experimental conditions used. This indicates that both oxides are appropriate to be used as supports in the preparation of supported catalysts for the title reaction. It has been proposed that acetaldehyde suffers a nucleophilic addition of ethanol (or ethoxide) and transformed to ethyl acetate [8]. This nucleophilic addition could be favoured over ZnO- or SnO_2-supported catalysts.

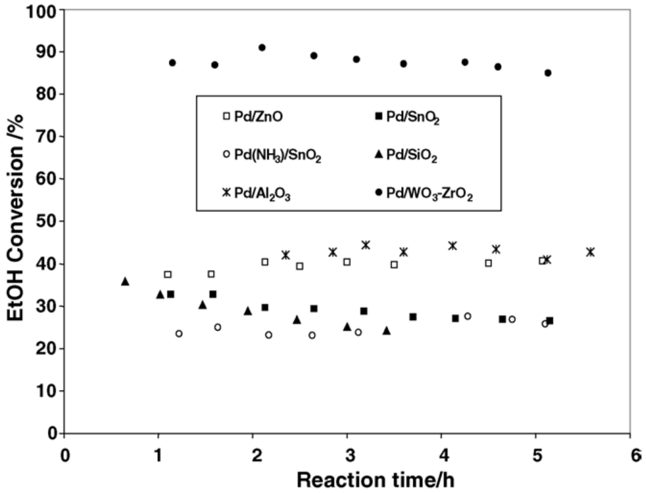

Fig. 4. Ethanol conversion profiles vs. time for monometallic-supported catalysts. Reaction conditions: P_T = 1 MPa; T = 523 K; EtOH:He = 1:4.7 (molar basis) and LHSV = 0.2 h^{-1}.

Table 3
Catalytic behaviour of supported Pd catalysts and several oxides used as supports

Catalyst	Selectivity[a] (%)							EtOH conversion (%)	Activity (mol EtOH mol^{-1} Pd h^{-1})	Activity (mol EtOH g_{cat}^{-1} $h^{-1} \times 10^3$)
	C1	CO_2	C_2H_4	AcOEt	MEK	DEE	AcH			
Pd/ZnO	0.0	2.4	3.2	40.9	3.7	1.3	48.5	40.4	65.2	5.2
Pd/SnO_2	0.0	0.0	1.9	27.2	7.4	1.1	62.4	29.7	60.1	5.1
$Pd(NH_3)/SnO_2$	9.6	0.0	1.7	22.7	1.7	0.8	63.5	23.3	51.8	4.0
Pd/SiO_2	86.2	0.0	1.7	0.1	0.0	1.2	10.8	28.9	49.2	5.0
Pd/Al_2O_3	58.0	0.7	2.3	2.3	1.3	29.4	6.0	40.7	76.0	7.0
Pd/WO_3-ZrO_2	41.0	0.4	49.2	3.7	0.0	4.5	1.2	96.3	189.2	17.0
Pd/WO_3-ZrO_2[b]	31.5	0.1	8.6	1.5	0.3	51.4	6.6	46.1	269.1	23.0
ZnO	0.0	0.0	0.0	27.2	0.0	13.0	59.8	5.6	–	0.7
SnO_2	0.0	0.0	0.0	29.8	0.0	4.0	66.3	10.8	–	1.1
$PdZn/SiO_2$	0.8	0.0	0.0	1.1	0.7	1.8	95.6	23.1	69.5	16.3
Pd_3Sn_2/SiO_2	26.1	0.0	0.0	0.0	0.0	2.0	71.9	4.5	5.0	1.1

C1, CH_4 + CO; AcOEt, ethyl acetate; MEK, methyl ethyl ketone; DEE, diethyl ether; AcH, acetaldehyde.

[a] Molar percentage of carbon-containing products. Reaction conditions: $P_T = 1$ MPa; $T = 523$ K; EtOH:He = 1:4.7 (molar basis); LHSV = 0.2 h^{-1}, data after 2 h under reaction.

[b] Total pressure = 1 MPa; $T = 523$ K; EtOH:He = 1:0.63 (molar basis); LHSV = 0.6 h^{-1}, run with 100 mg of catalyst.

As stated above, the characterization of Pd/SnO_2 or Pd/ZnO indicated the presence of Pd/M (M = Zn, Sn) interactions. In order to elucidate if these interactions are the responsible for the catalytic behaviour of these samples: two catalysts containing the PdZn and Pd_3Sn_2 alloys supported on silica [17,18] ($PdZn/SiO_2$ and Pd_3Sn_2/SiO_2, respectively) were tested under the same experimental conditions. $PdZn/SiO_2$ and Pd_3Sn_2/SiO_2 catalysts showed the highest selectivity to acetaldehyde (see Table 3), thus indicating that the first step of the reaction, the dehydrogenation of ethanol to acetaldehyde could be favoured by the presence of alloyed palladium with Sn or Zn.

On the other hand, SnO_2-supported catalysts showed differences in the catalytic behaviour depending on the preparation method (Table 3). The catalyst prepared by wet impregnation from the ammine precursor ($Pd(NH_3)/SnO_2$) exhibited higher selectivity to C1 products and lower selectivity to methyl ethyl ketone than Pd/SnO_2. XPS characterization of both catalysts only showed differences in the Pd dispersion, which was higher for Pd/SnO_2. Further studies are needed to clarify these aspects.

4. Conclusions

ZnO and SnO_2 are appropriate supports for preparing Pd-supported catalysts with low palladium content active in the dehydrogenative dimerization of ethanol. These reducible supports favour the formation of alloyed phases, which are very effective for the dehydrogenation of ethanol to acetaldehyde. Then, in a second step, ethyl acetate is produced.

Under 1 MPa and at 523 K, Pd/ZnO catalyst (1%, w/w Pd) produces under ca. 40% ethanol conversion, an ca. 40% ethyl acetate/48% acetaldehyde mixture.

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