

Ethanol reforming processes over ZnO-supported palladium catalysts: Effect of alloy formation

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Abstract

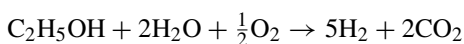
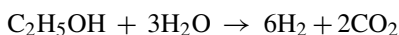
ZnO- and SiO₂-supported palladium catalysts were evaluated in the ethanol steam-reforming and oxidative ethanol steam-reforming reactions in the temperature range 548–723 K. The catalysts were characterized before and after reaction by X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy and infrared spectroscopy using CO as a probe molecule. On silica-supported Pd catalyst, ethanol decomposes into H₂, CO and CH₄ in both steam-reforming and oxidative steam-reforming reactions. In contrast, ZnO-supported catalysts containing the PdZn phase exhibit a better catalytic performance for hydrogen production through dehydrogenation of ethanol into acetaldehyde and ulterior reforming.

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1. Introduction

The use of non-fossil derived fuels, which are renewable and environment-friendly, for the supply of hydrogen is currently an emergent research area. In this context, ethanol is a very promising alternative as hydrogen carrier and supplier. Ethanol is an easy-to-handle liquid combustible and has low toxicity, and it can be readily produced from biomass sources [1]. Hydrogen can be obtained from ethanol through the catalytic steam-reforming (SR) and oxidative steam-reforming (OSR) reactions:



For both of these reactions, the nominal ratios of mol of hydrogen produced by mol of ethanol in the reactant mixture are high.

In addition, several advantages make these reactions interesting from the point of view of application. One major advantage is

the fact that they are based on well-known technologies. Moreover, oxidative steam reforming offers a proper energy balance for autothermal operation. Thus, ethanol reformers have a strong potential for providing hydrogen for fuel cells in stationary and portable power applications [2,3]. Today, however, a needed line of research lies in the development of catalysts for these reactions, which operate with high levels of activity, selectivity and stability. Supported noble metal catalysts constitute suitable systems for these purposes, in particular under oxidative conditions. Among these systems, palladium-based catalysts: Pd/MgO [4], Pd/Al₂O₃ [5–8] and Pd/CeO₂-ZrO₂ [5], have been used with varying degrees of success in these reactions. Depending on the catalyst and the reaction conditions, products besides hydrogen are usually CO, CO₂, CH₄, C₂H₄ and CH₃CHO. This indicates that the reforming process is complex and that different reaction pathways may be operative, such as dehydration or dehydrogenation of ethanol, decomposition of ethanol and acetaldehyde into CO and CH₄, the occurrence at different extension of the water gas shift reaction (WGSR), and the reforming of ethylene and methane. It is now well established that the support plays an active role in the transformation of ethanol, as a function of its acid/basic and redox properties [8–11]. In this context, ZnO has been demonstrating a very useful support for cobalt-based

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systems, and these have shown an interesting catalytic performance for hydrogen production from ethanol steam reforming [10,12]. On the other hand, when ZnO-supported palladium catalysts are considered, the presence of bimetallic phases, which are formed under reducing conditions, has been shown to determine the behaviour of palladium-based catalysts in different reactions [13–15]. Here, we present the study of ZnO-supported palladium catalysts in the ethanol SR and OSR reactions. Catalytic performances are then discussed in the light of their structural and surface characteristics.

2. Experimental

Pd/ZnO catalysts with a Pd content of 2.8 wt.% were prepared by the incipient wetness impregnation method from nitrate precursor over high-surface area ZnO support (ca. 100 m² g⁻¹). Samples were calcined at 673 K and reduced separately at 498 and 723 K under hydrogen, giving catalysts Pd/ZnO498 and Pd/ZnO723, respectively. For comparative purposes, a Pd/SiO₂ catalyst with a similar Pd content was prepared using a commercial SiO₂ support (Degussa-Hüls, 200 m² g⁻¹). In this case, the sample was calcined at 673 K and reduced at 523 K.

Catalytic tests were carried out at atmospheric pressure in the temperature range 548–723 K with a C₂H₅OH:H₂O = 1:13 mixture (bioethanol-like, molar basis) or a C₂H₅OH:H₂O:O₂ = 1:13:0.5 mixture. In both cases, the reactant mixture was diluted in Ar (Ar/(C₂H₅OH + H₂O) = 4), maintaining a gaseous ethanol flow of 0.5 mL min⁻¹. Complete product analysis was accomplished by on-line gas chromatography as described in detail elsewhere [10].

For the high-resolution transmission electron microscopy (HRTEM) analysis, the instrument used was a Philips CM-30 equipped with a LaB₆ source and operated at 300 kV, with 0.19 nm point resolution.

X-ray diffraction (XRD) profiles were collected 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 X-ray exciting source, a hemispherical electron analyzer and a pre-treatment chamber. The binding energies (BE) were referred to the C 1s peak at 284.9 eV or the Zn 2p_{3/2} at 1022 eV, which gave BE values with an accuracy of ±0.1 eV.

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 using special greaseless vacuum cells.

3. Results and discussion

The catalytic results are compiled in Table 1 (SR) and Table 2 (OSR). Over Pd/SiO₂, similar amounts of H₂, CO and CH₄ are produced under SR conditions and, besides these three products, only minor amounts of CO₂ and acetaldehyde are obtained under oxidative steam-reforming conditions. This selectivity pattern indicates that the main reaction that occurs over silica-supported Pd under SR and OSR conditions is ethanol (or acetaldehyde) decomposition (C₂H₅OH → H₂ + CO + CH₄), which is catalyzed by palladium particles. At the highest reaction temperature used, a slight diminution of methane is noted, which is related to the concurrence of the CH₄ reforming process. This has also been observed over a Pd/Al₂O₃ catalyst. At temperatures higher than 733 K it has been reported that CH₄ can be effectively reformed as a function of the water/ethanol ratio [8].

The selectivity pattern of ZnO-supported catalysts differs from that of Pd/SiO₂, since mainly H₂ and CO₂ as well as CH₄, acetaldehyde and dimethylketone are obtained, thus indicating

Table 1
Catalytic performance of supported Pd catalysts in the ethanol steam reforming reaction

Catalyst	T (K)	Conv. (%)	mol C ₂ H ₅ OH/mol Pd h	Selectivity (%) ^a						
				H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	CH ₃ CHO	(CH ₃) ₂ CO
Pd/ZnO498	548	98.7	47.0	57.0	0.7	1.2	9.5	–	31.7	–
	573	100	n.a.	60.9	0.9	2.5	9.6	–	25.9	0.1
	623	100	n.a.	67.3	0.2	10.3	9.6	–	9.1	3.6
	673	92.4	44.0	69.1	–	10.5	1.3	0.7	12.4	6.0
	723	100	n.a.	73.1	–	15.0	0.6	1.5	0.2	9.5
Pd/ZnO723	548	65.8	31.3	51.7	–	–	4.6	–	43.7	–
	573	79.3	37.7	52.3	–	0.3	4.5	–	42.9	–
	623	89.5	42.6	56.8	–	2.6	5.4	–	34.3	0.8
	673	72.9	34.7	67.8	–	7.6	2.3	0.6	17.7	3.9
	723	99.3	47.3	71.2	–	13.8	0.5	1.0	3.7	9.7
Pd/SiO ₂	548	50.1	23.9	36.6	28.9	–	34.4	–	–	–
	573	74.5	35.5	36.5	30.5	–	33.1	–	–	–
	623	99.4	47.3	34.7	32.7	–	32.6	–	–	–
	673	91.2	43.4	38.3	31.4	0.1	30.2	–	–	–
	723	95.7	45.6	39.2	33.0	0.9	27.0	–	–	–

C₂H₅OH:H₂O:O₂ = 1:13:0 (molar ratio); GHSV = 5200 h⁻¹, 0.1 g of catalyst, test run total time of 6 h.

^a Molar percentage of products (water excluded).

Table 2
Catalytic performance of supported Pd catalysts in the oxidative ethanol steam reforming reaction

Catalyst	T (K)	Conv. (%)	mol C ₂ H ₅ OH/mol Pd h	Selectivity (%) ^a						
				H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	CH ₃ CHO	(CH ₃) ₂ CO
Pd/ZnO498	548	95.1	45.3	40.9	2.1	8.6	14.8	–	33.6	–
	573	100	n.a.	45.8	1.2	9.9	13.0	–	30.2	–
	623	100	n.a.	48.1	2.5	16.6	17.3	–	13.1	2.3
	673	89.8	42.8	56.0	0.3	18.0	5.7	1.3	12.0	6.6
	723	100	n.a.	60.9	0.1	22.0	3.1	1.1	1.1	11.5
Pd/ZnO723	548	93.9	44.7	31.5	6.1	8.4	18.3	–	35.8	–
	573	100	n.a.	37.6	4.9	6.6	17.2	–	33.6	–
	623	100	n.a.	45.1	6.1	11.4	17.4	–	18.8	1.1
	673	83.7	39.8	47.7	1.2	12.2	8.0	0.9	25.7	4.3
	723	100	n.a.	61.4	0.1	21.1	3.7	1.2	0.5	11.9
Pd/SiO ₂	548	34.5	16.4	35.0	25.0	5.6	34.3	–	–	–
	573	31.1	14.8	28.8	28.6	2.9	39.7	–	–	–
	623	27.6	13.1	26.6	31.2	0.7	41.5	–	–	–
	673	24.9	11.9	26.5	27.8	0.3	37.7	–	7.7	–
	723	48.7	23.2	34.7	30.6	0.3	33.0	–	1.4	–

C₂H₅OH:H₂O:O₂ = 1:13:0.5 (molar ratio); GHSV = 5200 h⁻¹, 0.1 g of catalyst, test run total time of 6 h.

^a Molar percentage of products (water excluded).

that the steam-reforming mechanism is operative. Acetaldehyde is produced by ethanol dehydrogenation, and it has been shown to be the first step in the ethanol steam-reforming reaction over ZnO-supported cobalt catalysts [16,17]. On the other hand, the production of dimethylketone has been related to the presence of basic surface sites on ZnO [9]. Under OSR there is an increase of selectivity to CO and CH₄, probably due to an increase of ethanol decomposition in the presence of oxygen with respect to SR conditions.

The yields of H₂ (mL min⁻¹) as a function of reaction temperature are shown in Fig. 1a (SR) and Fig. 1b (OSR) for all catalysts studied. For a proper discussion of results, data for ZnO and SiO₂ supports are also included. An increase of temperature produced an increase on the H₂ yield for all palladium catalysts except when Pd/SiO₂ was tested under OSR. It has already been reported for Rh/Al₂O₃ systems that the presence of oxygen could be responsible for the formation of larger metal particles and consequently of the decrease of activity [18]. On the other hand, additional experiments at 548 K under SR conditions, in which mainly acetaldehyde and H₂ are produced, evidenced that the stability of Pd/ZnO723 was higher than that of Pd/ZnO498 (after 25 h Pd/ZnO723 and Pd/ZnO498 deactivated 5 and 20%, respectively).

As stated above, one goal of our research was to study the importance of bimetallic phases which may arise from the interaction of palladium with reducible supports in the catalytic performance for the ethanol SR and OSR reactions. Thus, different reduction temperatures were used during the preparation procedure of ZnO-supported Pd catalysts. As was shown in Table 1, under SR conditions and at low reaction temperature, the sample reduced at lower temperature, Pd/ZnO498, was more active in converting ethanol than that reduced at higher temperature, Pd/ZnO723. In contrast, significantly lesser amounts of undesired products such as CH₄ and CO are obtained over Pd/ZnO

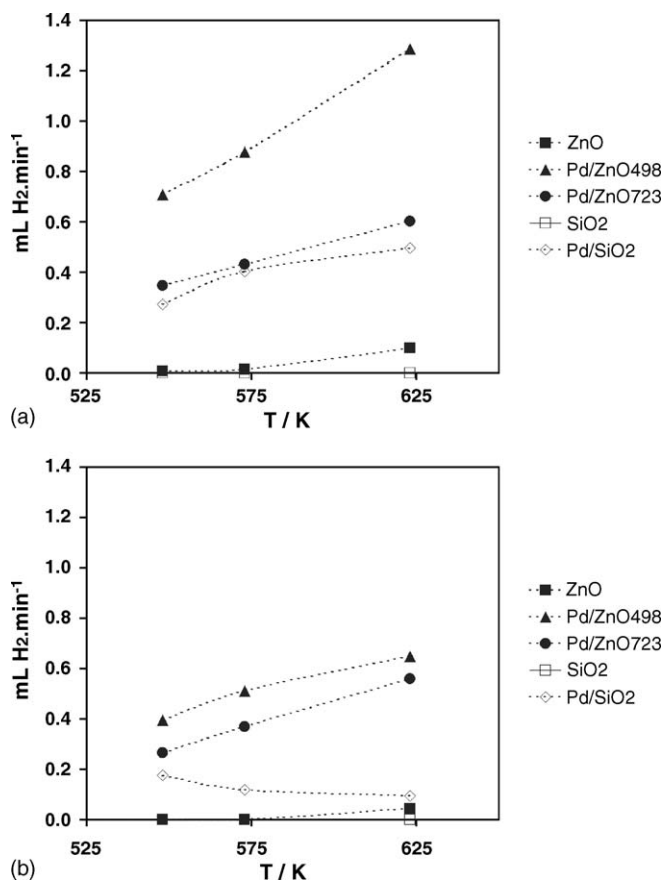


Fig. 1. Hydrogen production (a) in the steam reforming and (b) oxidative steam reforming of ethanol over several samples in the temperature range 548–623 K and GHSV = 5200 h⁻¹.

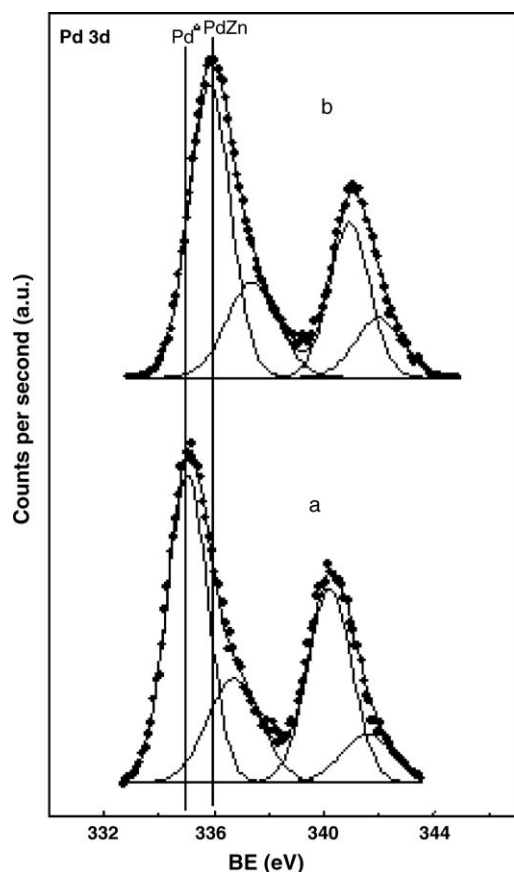


Fig. 2. X-ray photoelectron spectra in the Pd 3d region for fresh catalysts (a) Pd/ZnO498 and (b) Pd/ZnO723.

reduced at 723 K, although the catalytic performance of all catalysts at the highest reaction temperature, 723 K, is fairly similar. In order to understand these catalytic trends, Pd/ZnO498 and Pd/ZnO723 catalysts were characterized both before and after catalytic tests.

Fig. 2 depicts X-ray photoelectron spectra corresponding to the Pd 3d level of fresh catalysts. PdZnO498 sample showed a broad Pd 3d_{5/2} peak which can be deconvoluted in two components. The major component located at 335.0 eV corresponds to metallic palladium. The less intense signal at 336.7 eV may correspond to oxidized palladium or, alternatively, to very small metallic Pd particles strongly interacting with the ZnO support. In contrast, the Pd 3d_{5/2} level spectrum of the catalyst reduced at high temperature, Pd/ZnO723, shows two components at 335.8 and 337.4 eV. A large positive shift in the Pd 3d_{5/2} XPS peak has previously been taken as a clear evidence of the formation of PdZn alloys in Pd/ZnO catalysts [15,19,20]. This is in accordance with FTIR spectra recorded by using CO as a probe molecule. The spectrum recorded for Pd/SiO₂ shows a band located at ca. 2070 cm⁻¹ and a main absorption at 1950–1975 cm⁻¹ which are assigned to linearly coordinated and bridging coordinated CO, respectively [21]. A similar spectrum is obtained for Pd/ZnO498, which shows a weak and broad band at 2040–2070 cm⁻¹ and a main absorption centred at 1910 cm⁻¹. In contrast, no $\nu(\text{CO})$ bands after CO adsorption are encountered on Pd/ZnO723, and this may be due to a high dilution

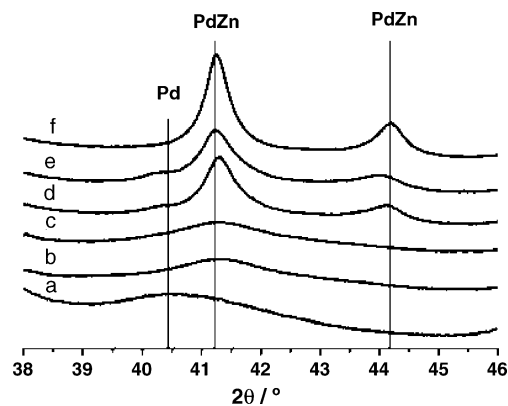


Fig. 3. X-ray diffraction profiles of Pd/ZnO498 and Pd/ZnO723 catalysts: (a) fresh Pd/ZnO498; (b) Pd/ZnO498 after ethanol steam reforming at 548 K; (c) Pd/ZnO498 after ethanol steam reforming at 598 K; (d) Pd/ZnO498 after ethanol steam reforming at 723 K; (e) Pd/ZnO498 after oxidative ethanol steam reforming at 723 K; (f) fresh Pd/ZnO723.

effect of Zn in the bimetallic particles. Additional valuable information was obtained by means of XRD (Fig. 3) and HRTEM (Fig. 4) studies performed over the fresh catalysts as well as for Pd/ZnO498 after SR reaction at different temperatures. Catalyst Pd/ZnO498 as prepared contains well-dispersed Pd metal particles of 4–5 nm in diameter, as deduced from XRD (Fig. 3a), and lattice spacing analysis from HRTEM images (Fig. 4a and b). Individual Pd particles of ca. 6–8 nm have also been identified in the SiO₂-supported catalyst. After SR over the Pd/ZnO498 catalyst at the lowest temperature tested, 548 K, the X-ray diffraction peak at 40.4°, corresponding to Pd(1 1 1) disappears, and a new, broad peak is visible at 41.2° (Fig. 3b). This peak likely corresponds to diffraction of PdZn(1 1 1). The same is observed after SR at 598 K (Fig. 3c). After reaction at 723 K (Fig. 3d), this peak at 41.2° becomes well-defined, and a new diffraction peak at 44.2° corresponding to PdZn(2 0 0) appears. The lattice fringe analysis of this sample by HRTEM (Fig. 4c and d) confirms the presence of individual PdZn crystalline particles in the size range of 1.5–5 nm. After OSR new peaks corresponding to PdZn(1 1 1) and PdZn(2 0 0) appeared (see Fig. 3e). Thus, it appears that metallic Pd particles of catalyst Pd/ZnO498 transform into PdZn alloy particles under steam-reforming or oxidative steam-reforming conditions.

For the high-temperature reduced catalyst, Pd/ZnO723, PdZn alloy particles are initially present, as deduced from HRTEM and XRD measurements on fresh sample (Fig. 3e). This sample does not appear to suffer structural changes under reaction. These results are in full accordance with XPS data for fresh samples. The higher catalytic activity of catalyst Pd/ZnO498 with respect to Pd/ZnO723 at low temperature (Tables 1 and 2) is clearly related to the presence of small Pd particles in the former. On the other hand, the better selectivity towards the ethanol-reforming products and the low ethanol decomposition shown by Pd/ZnO723 under these conditions is attributed to the existence of PdZn alloy. In this respect, we have recently shown how the formation of alloyed phases from palladium-supported catalysts are very effective for the dehydrogenation of ethanol to acetaldehyde [22], which can easily evolve to the desired

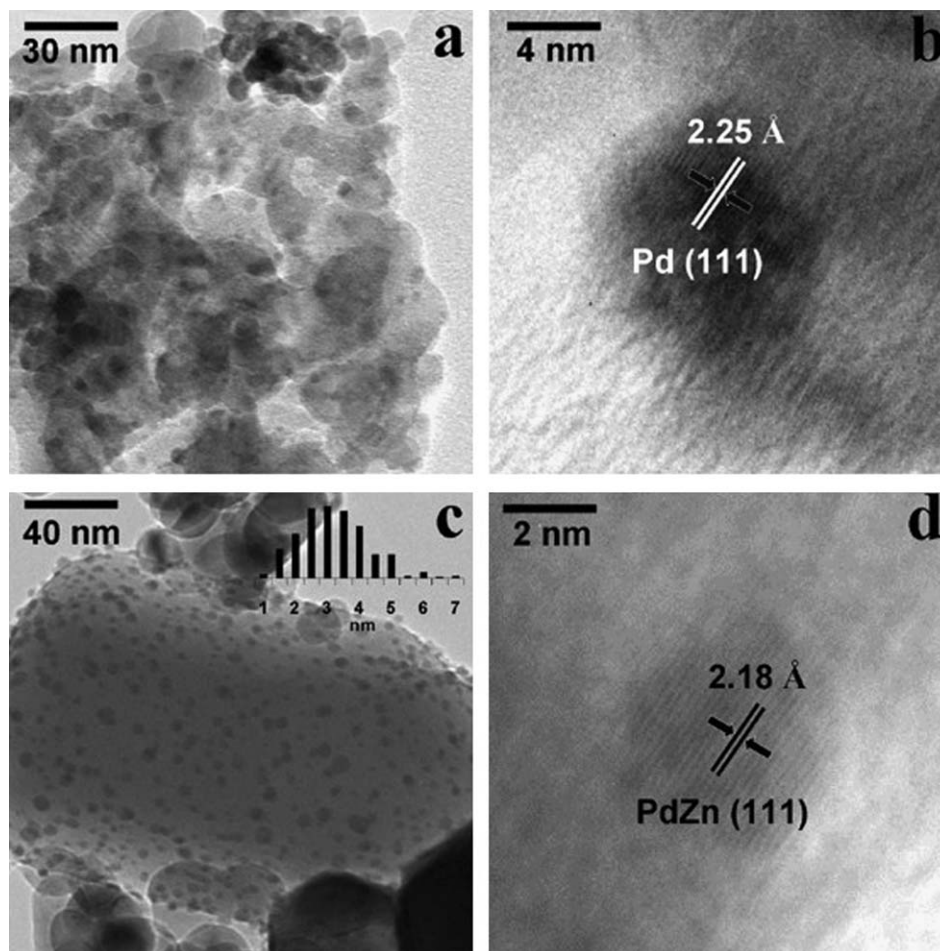


Fig. 4. Bright-field and high-resolution images from transmission electron microscopy of catalyst Pd/ZnO498, (a and b) before and (c and d) after, ethanol steam reforming at 723 K (GHSV = 5200 h⁻¹).

products under SR and OSR conditions over palladium-based catalysts.

4. Conclusions

ZnO-supported metallic palladium really forms a PdZn alloy in ethanol steam-reforming or oxidative steam-reforming environments. The catalytic performance in the above-mentioned reactions is conditioned as a result of the high ability of PdZn alloys to dehydrogenate ethanol to the intermediate acetaldehyde. Moreover, the catalytic behaviour of Pd/ZnO catalysts is improved with respect to that of their silica-supported counterpart which produces mainly ethanol decomposition and lower amounts of H₂.

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