



Short Communication

Ceria-based palladium zinc catalysts as promising materials for water gas shift reaction

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ABSTRACT

The production of hydrogen for fuel cell applications requires several fuel processing steps, including CO removal by means of the water gas shift (WGS) and CO preferential oxidation reactions. In this work we investigate the behavior of palladium–zinc supported on CeO₂, Ce_{0.5}Zr_{0.5}O₂ and ZrO₂ as a promising alternative to low temperature WGS catalysts for fuel processing. WGS activity is optimized when the PdZn alloy is formed. Ceria-containing materials show little deactivation during startup–shutdown cycles in reformat gas and for palladium–zinc supported on pure ceria the activity can be fully recovered by an in situ reduction treatment.

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1. Introduction

Hydrogen is the most efficient, cleanest energy source with zero emission of air pollutants. In the last few years the so-called “hydrogen economy” has received increasing attention, in particular in the field of fuel cell technology. Water–gas shift reaction (WGS), together with CO preferential oxidation, is a key step in fuel processing for fuel cell power systems in order to minimize CO levels in the reformat gas that can poison proton exchange membrane (PEM) fuel cell anodes.

Industrial WGS catalysts (e.g. Cu, Zn, Al) do not have sufficient mechanical stability during startup–shutdown cycles and will rapidly deactivate when exposed to air or liquid water. Pt-based catalysts have low activity at temperatures below 523 K [1–4], and as well as commercial catalysts are subjected to deactivation during startup–shutdown cycles [2]. For these reasons the development of stable, highly active and cost effective materials is still under investigation. Recently palladium-based catalysts have been studied for WGS [5] and the formation of alloys between Pd and other metals has been considered as a valid approach for preparing durable and active materials [6–9]. In particular the alloying of Pd with ZnO is a requirement for producing active WGS catalysts as already established for methanol steam reforming [10]. PdZn has an electronic structure similar to that of copper [11,12], which is the state-of-the-art catalyst for the low temperature industrial WGS. Two groups first studied the behavior of alumina-supported PdZn for water gas shift [13,14], and the results obtained indicate that these materials are active and stable. In a recent paper Wei et al. consider the PdZn alloy as the active site for the WGS reaction

and suggest that on these sites WGS is likely to proceed through a carboxyl mechanism in the absence of a large number of hydroxyl groups on catalyst surface [15].

In this work we investigate the behavior of PdZn supported on CeO₂ and Ce_{0.5}Zr_{0.5}O₂ recognized as suitable supports for the WGS reaction due to their unique redox properties [1]. PdZn supported over ZrO₂ is also considered for comparison. Catalytic activity is studied under a typical reformat mixture and stability is evaluated with time-on-stream and after startup–shutdown cycles.

2. Experimental

Palladium–zinc based catalysts were prepared by wet impregnation of Pd(NO₃)₂ and Zn(NO₃)₂ solutions on CeO₂, ZrO₂ and Ce_{0.5}Zr_{0.5}O₂ (see Supplementary material). After impregnation the catalysts were dried at 348 K for 16 h and calcined in air at 773 K for 3 h. The composition of the samples is reported in Table 1. The materials were characterized by ICP (Inductively Coupled Plasma) elemental analysis, BET surface area measurements (Table 1), X-ray diffraction (XRD) analysis and Temperature Programmed Reduction experiments (Supplementary material).

Catalytic tests were carried out in a typical reformat mixture (38% H₂, 6.5% CO, 9.5% CO₂, 27% H₂O, and 19% N₂) with a GHSV of 10,000 h⁻¹. Catalytic activity was recorded for fresh and in situ reduced samples (indicated as PdZnCe/r, PdZnCZ50/r and PdZnZr/r).

3. Results and discussion

Fig. 1 presents the powder XRD spectra of fresh, reduced and spent samples. On fresh samples only the peaks of ZnO and the characteristic features of the support are present. Neither Pd nor PdO can be detected.

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Table 1
Composition, BET surface area and PdZn particle size for all samples.

| Sample | Composition (wt.% from ICP) | Surface area (m ² /g) | PdZn particle size (nm) | |
|----------|------------------------------------------------------------------------|----------------------------------|-------------------------|---------|
| | | | Spent | Reduced |
| PdZnCe | 6.7%Pd 11.9%Zn 81.4%CeO ₂ | 41.7 | 12 | 17 |
| PdZnCZ50 | 7.4%Pd 12.2%Zn 80.4%Ce _{0.5} Zr _{0.5} O ₂ | 63.7 | 16 | 24 |
| PdZnZr | 6.9%Pd 12.3%Zn 80.8%ZrO ₂ | 46.5 | 14 | 18 |

XRD profiles of in situ reduced catalysts show clearly the formation of the PdZn alloy that is believed to be the active phase for the WGSR. Along with PdZn alloy, also peaks belonging to ZnO are detected while again no traces of Pd or PdO are observed. XRD spectra of spent catalysts (i.e. after a WGS test run) are very similar to those of reduced samples, indicating that alloying of Pd with Zn occurs also during reaction. PdZn particle sizes calculated by Scherrer's formula range between 12 and 16 nm for the spent catalysts and between 17 and 24 nm for the reduced ones (Table 1). The difference can be ascribed to the longer period at 773 K during reduction treatment (2 h) with respect to a WGS run where the samples remain only few minutes at 773 K, and likely also to the different reaction atmospheres.

The effect of the formation of PdZn alloy is evident when comparing the catalytic activity of fresh and reduced catalysts (Fig. 2). CO conversion at 523 K increases for all samples, with PdZnCe showing the highest improvement and PdZnZr giving generally poor results. This might be related to a stabilization of the active phase (an increase of PdZn particle size of 5 nm against 8 nm of PdZnCZ50) coupled with the redox properties of ceria. In particular, the formation of oxygen vacancies on reduced ceria surface that can react with water favoring the formation of surface OH groups as reported by Shido and Iwasawa [16] might be involved in the higher improvement observed on PdZnCe with respect to the other two samples. Fig. 3a reports CO conversion curves for all fresh samples, with PdZnCZ50 showing the highest conversion at low temperature. For PdZnCe the curve has been corrected in order to take into account the CO conversion due to the formation of methane, that has been detected

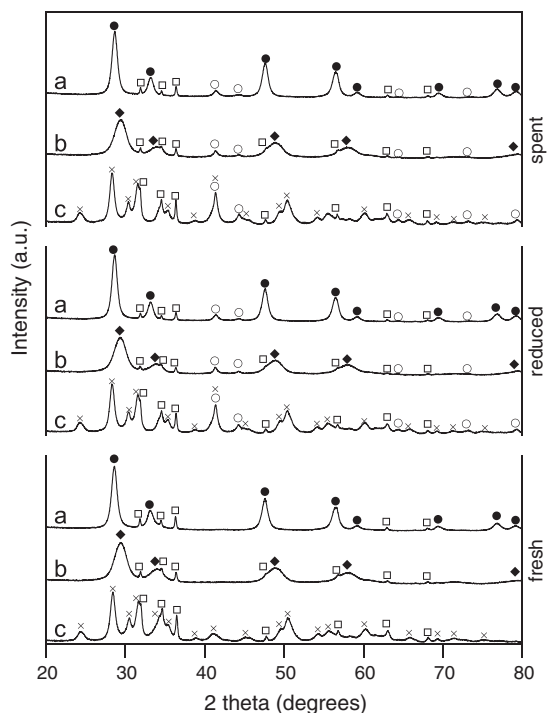


Fig. 1. X-ray diffraction profiles for the samples considered in this work (a: PdZnCe, b: PdZnCZ50, c: PdZnZr) ● = CeO₂ (cubic); × = ZrO₂; ◆ = CeZr (tetragonal); □ = ZnO; ○ = PdZn.

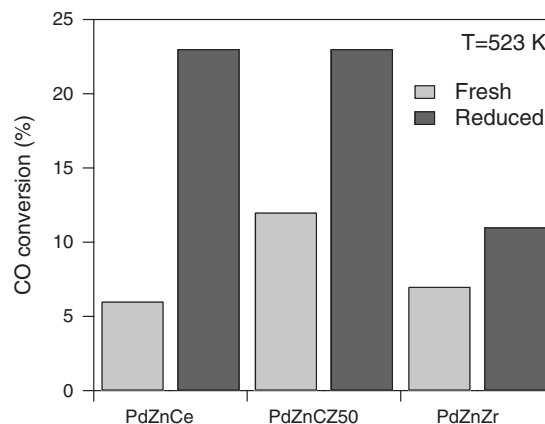


Fig. 2. Comparison of CO conversion for fresh and reduced samples at T = 523 K.

in the products in the 623–773 K temperature range. In Fig. 3b CO conversion curves for the reduced samples are shown. In this case no methane is detected on PdZnCe/r and its catalytic behavior is almost identical to that of PdZnCZ50/r.

Since these two reduced catalysts showed the best performances, further investigations were carried out in order to check their stability. Time-on-stream activity tests carried out in the reformate mixture at 523 K for 24 h did not reveal any significant deactivation for either PdZnCe/r or PdZnCZ50/r (Fig. S2). The same samples were tested during

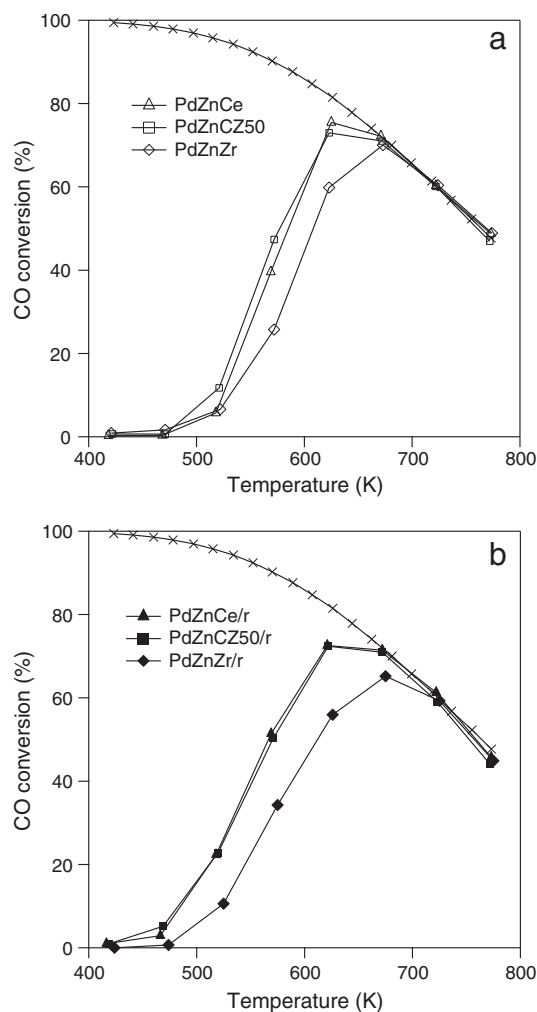


Fig. 3. CO conversion curves (WGSR) for a) fresh catalysts and b) reduced catalysts.

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