Short communication

Acetylene semi-hydrogenation over Pd-Zn/CeO$_2$: Relevance of CO adsorption and methanation as descriptors of selectivity

Frederic Meunier[a,*], Marion Maffre[a], Yves Schuurman[a], Sara Colussi[b], Alessandro Trovarelli[b]

[a] Univ Lyon, Université Claude Bernard Lyon1, CNRS, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, IRCELYON, 2, Av. Albert Einstein, F-69626 Villeurbanne, France
[b] Univ Udine, Dipartimento Politecnico, I-33100 Udine, Italy

A B S T R A C T

The most selective Pd-Zn surfaces for the selective hydrogenation of acetylene to ethylene were recently proposed to be intermetallic in nature, exhibiting only Pd-Zn-Pd units and no Pd-Pd pairs, the later forming bridged CO upon exposure to CO. Ceria-supported Pd-Zn formulations apparently free of Pd-Pd ensembles were prepared and yet led to poor selectivity to ethylene. CO methanation was actually shown to be a better selectivity descriptor in the present case. Only the samples most selective for acetylene semi-hydrogenation, which were obtained by reduction at temperatures equal or higher than 550 °C, led to negligible CO methanation rates.

1. Introduction

The acetylene contained in the ethylene stream produced by naphtha cracking must be removed not to poison downstream polymerization catalysts. Palladium is active for the hydrogenation of acetylene, but poorly selective as mostly ethane is obtained instead of the desired ethylene. Silver is used as a modifier in industrial catalysts to improve the selectivity to ethylene [1,2,3]. Yet, Pd-Ag formulations lead to heavy product formation (green oil) that can lead to long-term deactivation and selectivity to ethylene drops markedly at high acetylene conversion. Many other promoters for Pd used for selective hydrogenation reactions have been investigated, such as Zn [4], Sn [5], Au [6], Ni [7], Ga [8], In [9], Cu [10] and Pb [11].

ZnO-supported Pd-Zn phases were reported [4] to exhibit high selectivity to ethylene even at high acetylene conversion at temperatures below 373 K. The most selective Pd-Zn surfaces were proposed to be intermetallic that exhibited mostly Pd-Zn-Pd units and not Pd-Pd pairs [4]. Bulk CeO$_2$ is also active and selective for the semi-hydrogenation of acetylene to ethylene, yet at temperature somewhat higher (> 420 K) [12]. To our knowledge, Pd-Zn/CeO$_2$ has not yet been investigated for this reaction. The activity of Zn-modified Pd supported over CeO$_2$ is presented here, with a particular interest at determining whether the preparation of catalysts free of Pd-Pd pairs (i.e. showing no bridged (Pd)$_2$-CO by FT-IR during CO adsorption) was a sufficient condition to obtain high selectivity to ethylene.

2. Experimental section

2.1. Catalyst synthesis and characterization

Palladium-zinc based catalysts were prepared by wet impregnation of Pd(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ solutions on CeO$_2$ obtained by precipitation. The nominal Pd and Zn loadings were 7.5 wt.% and 12 wt.%, respectively. After impregnation, the catalysts were dried at 348 K for 16 h and calcined in air at 773 K for 3 h. The CeO$_2$ support was synthesized by precipitation of nitrate precursor at pH = 9.5 in the presence of H$_2$O$_2$ using ammonia as precipitating agent. The support was then dried and calcined at 773 K for 4 h.

X-ray diffraction analysis of the calcined samples only revealed peaks belonging to cubic CeO$_2$ and ZnO, while no evidence of metallic Pd or PdZn could be found (not shown). The Pd-Zn/CeO$_2$ reduced at 773 K exhibited additional PdZn peaks associated with crystalline domains of ca. 10 nm calculated by Scherrer equation [13].

2.2. Catalytic tests

Acetylene hydrogenation was carried out in a tubular stainless steel reactor (length 300 mm, 4 mm ID, 6 mm OD) using a feed composed of 1.2% C$_2$H$_2$ + 4.3% H$_2$ + 32% C$_2$H$_4$ in He. The total gas flow rate was 16.2 mL min^{-1}. Catalyst masses precisely weighted comprised between 3 and 10 mg were diluted at least 10-fold in silicon carbide particles (size between 100 and 200 μm). Such low masses and dilution in SiC were used to limit the occurrence of hot spots due to the high

* Corresponding author.
  E-mail address: fcm@ircelyon.univ-lyon1.fr (F. Meunier).

exothermicity of acetylene hydrogenation. Catalyst and SiC were held between plugs of quartz wool. Prior to testing, the samples were reduced in situ for 30 min under a flow of 40 mL min^{-1} of 50% H_2/He at 673 K (unless otherwise stated) using a heating rate of 10 °C min^{-1}. The temperature was then decreased to 390 K, at which point the reaction mixture was introduced. The sample activity was determined down to 330 K by varying temperature stepwise.

Reactant and product analysis was carried out using an IR gas-cell (Specac ®, 10 cm path length) fitted in a Bruker Tensor 27. Acetylene, ethylene and ethane concentrations were quantified using calibration curves obtained using standard mixtures. No internal standard was used to correct for changes in the total number of moles and therefore mass balance was assumed on the measured products, as no other products were detected in the gas cell. Yet, any heavy product (e.g. green oil) that would condense before the gas cell would not have been accounted for. No evidence of heavy product was found after the sample bed after reaction, so any side products can be considered as being at the trace levels. The conversion of acetylene was calculated according to the formula:

$$\text{Acetylene conversion} = \frac{x(C_2H_2)^\circ - x(C_2H_2)}{x(C_2H_2)^\circ}$$

where $x(C_2H_2)$ and $x(C_2H_2)^\circ$ are the acetylene and initial acetylene mole fractions, respectively. The selectivity to ethylene was calculated according to the formula:

$$\text{Selectivity to Ethylene} = \frac{x(C_2H_4) - x(C_2H_4)^\circ}{x(C_2H_2)^\circ - x(C_2H_2)}$$

where $x(C_2H_4)$ and $x(C_2H_4)^\circ$ are the ethylene and initial ethylene mole fractions, respectively. The selectivity to ethylene could possibly be negative, if more ethylene was hydrogenated to ethane than ethylene was produced from acetylene.

A diffuse reflectance FT-IR (DRIFTS) cell was also used as reactor to investigate CO hydrogenation to methane and determine the mode and heat of adsorption of CO in *operando* conditions. The DRIFTS cell reactor was modified and temperature of the surface determined through a calibration as described elsewhere [14,15]. The methanation feed consisted of a mixture of 2.5% CO + 50% H_2 in He. Precise amounts of Pd/CeO$_2$ and Pd-Zn/CeO$_2$ (between 2 and 5 mg) were placed on top of a SiC bed. Heats of adsorption of CO were calculated according to the method developed by Bianchi and co-workers [16], which can be extended to reactive mixture such as CO + H_2, as long as CO conversion remains low [17].

3. Results

3.1. Catalytic activity for acetylene semi-hydrogenation

The Pd/CeO$_2$ and Pd-Zn/CeO$_2$ (whichever reduction temperature was used) were active below 400 K, with similar temperatures for 50% acetylene conversion comprised between 350 and 370 K (data not shown), in accordance to the data reported by Zhou et al. [4]. The selectivity to ethylene varied greatly depending on the presence of Zn and the reduction temperature. The Zn-free sample exhibited negative values of selectivity to ethylene, meaning that the converted acetylene and some of the fed ethylene were hydrogenated to ethane (Fig. 1).

The Pd-Zn/CeO$_2$ sample reduced at 673 K and 773 K exhibited positive selectivity to ethylene values, decreasing from about 90% at low conversions down to 60% at 98% acetylene conversion (Fig. 1). Reduction of the Pd-Zn/CeO$_2$ at 823 K and 923 K resulted in markedly improved selectivity to ethylene of 95 and 98% at 98% acetylene conversion, respectively.
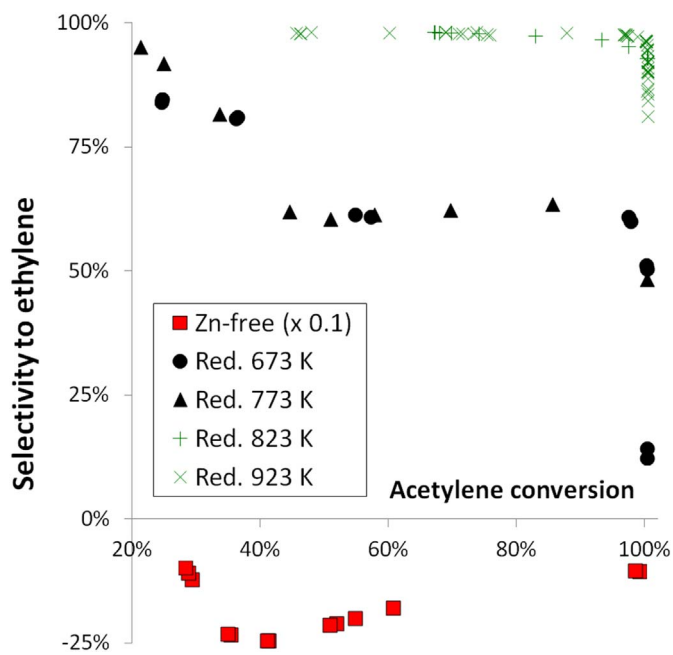

Fig. 1. Selectivity to ethylene versus acetylene conversion measured on Pd/CeO$_2$ and Pd-Zn/CeO$_2$. Feed: 1.2% C$_2$H$_2$ + 4.3% H$_2$ + 32% C$_2$H$_4$ in He. Temperature ranged from 330 K up to 380 K. The selectivity values for the Zn-free sample were divided by a factor 10.
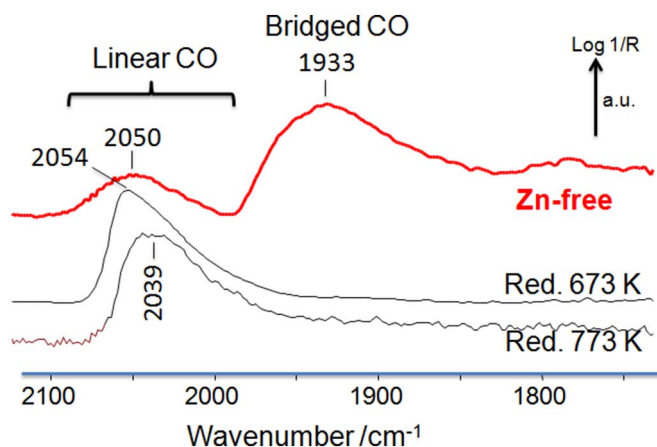

Fig. 2. *Operando* DRIFTS spectra recorded at 330 K over the Pd/CeO$_2$ and Pd-Zn/CeO$_2$ reduced at 673 K and 773 K. Feed: 2.5% CO + 50% H$_2$ in He.

3.2. Operando CO adsorption and methanation

The *operando* DRIFTS spectra obtained under a CO and H$_2$ feed over the Zn-free sample and the Pd-Zn samples reduced at 673 K and 773 are shown in Fig. 2. Unfortunately, the Pd-Zn samples reduced at 823 K and 923 K became too dark after reduction to be analyzed by DRIFTS. The Pd/CeO$_2$ exhibited both linearly adsorbed CO (band at 2050 cm^{-1}) and bridged CO (band at 1933 cm^{-1}) [18,19]. Interestingly, the Zn-promoted samples reduced at 673 K and 773 K exhibited only linear CO, indicating that the concentration of Pd-Pd pairs, necessary to form bridged CO, was negligible. The linear CO band exhibited maxima at different wavenumbers (i.e. 2054 and 2039 cm^{-1}) and the band were quite broad and asymmetric, suggesting that more than one type of adsorption site was present.

The *operando* DRIFTS spectra were recorded between 623 and 330 K with a view at obtaining CO enthalpies of adsorption at low and high coverages [19,20]. Typical spectral evolution is shown for the Pd-Zn sample reduced at 673 K (Fig. 3), stressing again the absence of bridged