



# Effect of support on acetic acid decomposition over palladium catalysts



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## ABSTRACT

Acetic acid decomposition for hydrogen production was investigated on Pd/SiO<sub>2</sub>, Pd/Nb<sub>2</sub>O<sub>5</sub>, Pd/La<sub>2</sub>O<sub>3</sub> and Pd/Fe<sub>2</sub>O<sub>3</sub> catalysts. The conversion of acetic acid started at 673 K and the products of the reaction were H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>O. Pd/Fe<sub>2</sub>O<sub>3</sub> was the most active catalyst for conversion of acetic acid and showed high hydrogen selectivity and good catalytic stability, followed by Pd/Nb<sub>2</sub>O<sub>5</sub> and Pd/La<sub>2</sub>O<sub>3</sub>, whereas in the case of Pd/SiO<sub>2</sub>, there was not any H<sub>2</sub> formation. The Pd/Fe<sub>2</sub>O<sub>3</sub> catalysts presented reduced Pd–Fe and Pd<sup>0</sup>/Fe<sub>2</sub>O<sub>x</sub> sites, producing complete conversion of acetic acid and a higher level of hydrogen selectivity (73%). Additionally, acetic acid adsorption on Pd/Fe<sub>2</sub>O<sub>3</sub>, Pd/Nb<sub>2</sub>O<sub>5</sub> and Pd/La<sub>2</sub>O<sub>3</sub> catalysts yielded the formation of acetate surface species. However, in the case of Pd/SiO<sub>2</sub>, there was molecular adsorption of acetic acid. During the reaction, there was formation of an ordered and disordered carbon mixture on Pd/La<sub>2</sub>O<sub>3</sub>, Pd/Nb<sub>2</sub>O<sub>5</sub> and Pd/SiO<sub>2</sub> catalysts, while carbon of a more ordered nature was produced on Pd/Fe<sub>2</sub>O<sub>3</sub>.

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## 1. Introduction

The growth of population and expansion of industry all over the world have caused an increase in the global demand of energy. Nowadays, energy is produced mainly from fossil fuels that are not renewable and that emit large amounts of CO<sub>2</sub>, contributing to the greenhouse effect. Therefore, alternative energy sources are needed to decrease pollutant emissions and nature degradation. Lignocellulosic biomass has been proposed as an alternative feedstock to provide a CO<sub>2</sub>-neutral energy supply [1]. Pyrolysis is an example of a thermochemical biomass conversion process that consists of the thermal decomposition of organic material without oxygen. In this process, a mixture of gases is obtained, constituted mainly by CO, CO<sub>2</sub>, low hydrocarbons, vegetal carbon and bio-oil. The flash pyrolysis of lignocellulosic biomass provides a yield of around 70 wt.% of liquid (bio-oil), using simple technologies with small capital assets [2]. The bio-oil can be obtained in delocalized rural areas and subsequently stored and transported to a refinery (biorefinery) for large-scale valorization. Crude bio-oil is a polar and hydrophilic brown liquid with a water content of around 30 wt.% (that obtained from herbaceous biomass may exceed

50 wt.%) and an oxygen content of 45–50 wt.%, as a result of water content and its oxygenated composition, with compounds (acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans and others) derived from the fragmentation of biomass cellulose, hemicellulose and lignin [2–4]. Its heating value (15–18 MJ/kg), although limited by the water content, is interesting for its use as fuel [5]. However, the transformation of oxygenated compounds in the bio-oil by catalytic processes into hydrocarbons or H<sub>2</sub> is of greater interest. Therefore, due to its complexity, model oxygenate components or individual components present in bio-oil are usually selected to establish structure–activity correlations in the hydrogen formation process. In addition, the mechanism of conversion of oxygenates has not been sufficiently elucidated to date, which has hampered the development of efficient and stable catalysts. Thus, we investigated the decomposition of acetic acid to hydrogen production over supported palladium catalysts. Acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) is one of the major components of bio-oil (up to 19%) [6], depending on the nature of biomass and on the pyrolysis conditions and can be considered a model compound of bio-oil. Hydrogen is an important raw material and has significant potential to be the new clean energy vector of the world.

Several authors have investigated hydrogen production from steam reforming of acetic acid. Transition metals (Ni, Co, Cu), noble metals (Pt, Rh, Ru, Pd, Rh), and different supports (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) have been studied [6–8]. For example, steam reforming of acetic acid was studied over a Pt/ZrO<sub>2</sub> catalyst. This

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catalyst was very active, completely converted acetic acid and showed a hydrogen yield of 60%, but was deactivated by formation of oligomers derivated from acetic acid on  $ZrO_2$ , which blocked the active sites. A bifunctional mechanism was proposed on Pt/ $ZrO_2$ , where both Pt and  $ZrO_2$  participated in the reaction: the acetic acid activation occurs on surface Pt, followed by bond breaking of acetic acid to form  $H_2$ , CO,  $CH_4$  and  $CO_2$ , whereas the water activation occurs on the support, creating surface hydroxyl groups that react to gasify the residue on Pt to produce  $H_2$  and  $CO_2$ . This mechanism was established through in situ IR analysis. Also, the reaction occurred at the Pt periphery in close proximity of  $ZrO_2$  [8,9].

Other catalysts, such as Ni and Rh, supported on a  $CeO_2$ - $ZrO_2$ -mixed oxide, were also examined in the steam reforming of acetic acid to produce hydrogen. The main reactions were steam reforming, water gas shift, and decarboxylation on the support alone. In parallel, dehydrogenation led to the formation of carbon deposits on the surface of the mixed oxide. The addition of the metals allowed the reforming reactions to proceed at high rates, producing hydrogen yields and decreasing the deposited coke on the catalysts, either by inhibiting its formation or by facilitating the oxidation reactions. The synergy of the support and metal is a key factor for the low coke deposition, which is even lower for the Rh catalyst. The nature of the carbonaceous deposits was analyzed: on the Ni/ $CeO_2$ - $ZrO_2$  catalyst, there was the formation of graphitic or filamentous coke, and on Rh/ $CeO_2$ - $ZrO_2$ , carbonaceous species of amorphous type was observed [10]. The main disadvantage of the steam reforming process is the high formation of carbonaceous deposits on the catalyst surfaces, causing a loss of activity, which limits their large scale application, especially in conventional fixed bed reactors [11].

The catalytic decomposition of acetic acid is a reaction that can yield hydrogen during bio-oil catalytic conversion, but it has received less attention. Nevertheless, its investigation may lead to a better understanding of activity–structure correlations that could help to optimize bio-oil conversion. The decomposition of acetic acid to form hydrogen may be represented by the global reaction as shown in Eq. (1):



Alcala et al. [12] carried out preliminary studies on acetic acid conversion on Pt (111) and  $Pt_3Sn$  (111) surfaces using DFT calculations. Two possible initial dissociation steps for acetic acid ( $CH_3COOH$ ) were proposed: dehydrogenation to acetate species ( $CH_3COO$ ) and dihydroxylation to acyl species ( $CH_3CO$ ). The calculations also showed that the transition-state energy for cleavage of the  $CH_3CO$ –OH bond in acetic acid increased by only 12 kJ/mol on  $Pt_3Sn$  (111) compared to Pt (111). These findings were used to explain why, at temperatures from 500 K to 600 K, Pt–Sn/ $SiO_2$  was selective for conversion of acetic acid to form acetaldehyde and ethanol, whereas Pt catalysts completely decomposed acetic acid to CO and  $CH_4$ . Li et al. [13] focused the DFT calculations to Co surfaces, and showed the adsorption on stepped surfaces was favored compared to flat surfaces. The most kinetically favorable decomposition pathway was  $CH_3COOH/CH_3CO/CH_2CO/CH_2/CH$  and the rate-determining step was  $CH_3CO$  dehydrogenation, with a reaction barrier of 0.52 eV. Acetate plays an important role as an intermediate in many catalytic reactions exploited in industrial processes and often carboxylic acids are used as a primary source. As observed for a range of low carboxylic acids on transition and noble metals [14,15], acetic acid decomposes to form acetate, liberating hydrogen and forming  $CO_2(g)$ ,  $H_2(g)$  and C. Bowker and Madix [16] studied the adsorption and oxidation of acetic acid on Cu (110) at 140 K under ultra-high vacuum (UHV); acetic acid was partially decomposed via C–C bond scission, while a large fraction of acetic acid was desorbed molecularly or was converted into acetaldehyde or ketene without C–C bond scission. The acet-

ate did not decompose until 590 K. The oxidation reaction products indicated the formation of another intermediate, acetic anhydride, which decomposed to yield mainly  $CO_2$ ,  $CH_4$ ,  $H_2C_2O$  (ketene), and carbon fragments. Reactions involving the C–C bond scission on metallic surfaces are generally complex and lead to a multitude of different products. Different sets of products have been reported, depending on the type of surface. Neitzel et al. [17] investigated the role of coadsorbed atomic oxygen during the decomposition of acetic acid on Pt (111) and  $p(2 \times 2)$ -O/Pt(111). Acetate and molecularly adsorbed acetic acid were formed on both samples during the adsorption of acetic acid at 150 K. On  $p(2 \times 2)$ -O/Pt (111), the acetyl was identified as the principal species. Above 222 K, decomposition of acetate on Pt (111) yielded acetic acid, hydrogen, methane, and CO. On  $p(2 \times 2)$ -O/Pt(111), the reaction of acetyl with atomic oxygen and surface hydroxyl groups produced methanol and acetic anhydride at 300 and 450 K, and methane and  $CO_2$  at 390 K. Bowker et al. [18] studied the acetic acid adsorption and decomposition on Pd (110) using temperature-programmed desorption (TPD). They found that the adsorption of acetic acid was efficient and hydrogen and acetate formation occurred at room temperature. The acetate decomposed between 320 K and 440 K to form  $CO_2$  and hydrogen and left carbon adsorbed on the surface. At higher temperatures, the acetate was unstable (>450 K), but the adsorption of acetic acid continued at a steady-state rate and was not poisoned by the buildup of carbon on the crystal. This was due to the fact that most of the carbon deposited was lost from the surface to the bulk in a facile manner above about 450 K, therefore leaving a reactive surface that was apparently continuously available for acetic acid decomposition. In other studies,  $H_2$  was observed on Rh (110) [19], while a combination of CO,  $CO_2$ ,  $H_2$ , and  $H_2O$  was reported on Rh (111) [20] and Ni [21,22].

The conversion of acetic acid into acetone was studied on  $Al_2O_3$ ,  $TiO_2$  and  $CeO_2$ . The results indicated that on  $Al_2O_3$ , the acetic acid was irreversibly, non-dissociatively adsorbed in the form of hydrogen-bonded molecules, and dissociatively in the form of bidentate bound acetate species. On  $TiO_2$ , the gas phase remained unchanged on heating up to 573 K, but at 673 K, the acetic acid was transformed into acetone,  $CO_2$ ,  $H_2O$ , isobutene and methane. A similar behavior was observed on  $CeO_2$ . The structural and chemical stability of the surface and bulk of  $TiO_2$  and  $CeO_2$  were related to the catalytic nature of the acetic acid conversion. The catalytic sites were suggested to be reducible Lewis acid–base pair sites ( $Ti^{4+}$  or  $Ce^{4+}$ ) [23].

Despite the above-mentioned information, there have not been systematic studies about the effect of the support on acetic acid decomposition over supported metal catalysts. It is well known that, depending of the nature of support, different types of metal–support interactions (morphological and electronics) may occur and sometimes these interactions can have a significant effect in determining catalytic activity and selectivity. Therefore, the present work examined the use of  $Fe_2O_3$ -,  $Nb_2O_5$ -,  $La_2O_3$ - and  $SiO_2$ -supported palladium catalysts in hydrogen production from acetic acid decomposition. Generally, the decomposition of oxygenated compounds is produced through carbon–carbon, carbon–hydrogen and hydrogen–oxygen bond breaking. Group VIII metals, such as palladium, are frequently used because they exhibit high activity and selectivity to break C–C bonds [24]. On the other hand, oxides, such as  $Fe_2O_3$  [25],  $Nb_2O_5$  [26,27] and  $La_2O_3$  [28,29], are reducible and may decorate the metal particles, while  $SiO_2$  is considered inert [30,31].

## 2. Experimental

### 2.1. Catalyst preparation

The Pd/ $Fe_2O_3$ , Pd/ $Nb_2O_5$ , Pd/ $La_2O_3$  and Pd/ $SiO_2$  catalysts were prepared by incipient wetness impregnation of the supports with

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