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Partial oxidation of ethanol over Pd/CeO_2 and Pd/Y_2O_3 catalysts

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ABSTRACT

The effect of the support nature on the performance of Pd catalysts during partial oxidation of ethanol was studied. H_2, CO_2 and acetaldehyde formation was favored on Pd/CeO_2, whereas CO production was facilitated over Pd/Y_2O_3 catalyst. According to the reaction mechanism, determined by DRIFTS analyses, some reaction pathways are favored depending on the support nature, which can explain the differences observed on products distribution. On Pd/Y_2O_3 catalyst, the production of acetate species was promoted, which explain the higher CO formation, since acetate species can be decomposed to CH_4 and CO at high temperatures. On Pd/CeO_2 catalyst, the acetaldehyde preferentially desorbs and/or decomposes to H_2, CH_4 and CO. The CO formed is further oxidized to CO_2, which seems to be promoted on Pd/CeO_2 catalyst.

1. Introduction

Fuel cell based on hydrogen produced from renewable sources is an attractive alternative to fossil fuels since it can contribute to the reduction of global dependence on fossil fuels, greenhouse gas emissions and atmospheric pollution [1]. Ethanol has been considered a promising renewable fuel for H_2 production since it can be manufactured from biomass and does not contribute to CO_2 emissions. Hydrogen may be generated from ethanol by different technologies: steam reforming (SR); partial oxidation (POX) and autothermal reforming (ATR) [2]. SR provides a high hydrogen yield, which represents an important advantage in hydrogen-production applications. However, SR is a highly endothermic reaction and therefore, high operation temperatures are necessary [2]. An alternative approach is partial oxidation of ethanol, an exothermic reaction that exhibits fast start up and response times while potentially offering a more compact reactor design, desirable features for vehicle fuel cell applications [3]. ATR, also know as oxidative steam reforming, combines SR and POX in one reactor, thereby avoiding the need for an external heat supply [4]. Nevertheless, the major barriers to all of these technologies are the by-products formation and catalytic deactivation [5,6]. Recently, we reported that the support plays an important role on the product distribution obtained on POX over Al_2O_3, ZrO_2, CeO_2 and $CeZrO_2$ supported Pt catalysts [3]. Then, the aim of this work is to evaluate the effect of the nature of the support on the performance of Pd supported catalysts (Pd/CeO_2 and Pd/Y_2O_3) on partial oxidation of ethanol.

2. Experimental

Y_2O_3 and CeO_2 supports were prepared by calcination of yttrium nitrate and cerium (IV) ammonium nitrate, respectively, at 1073 K. Pd (1.0 wt%) was added to the supports by incipient wetness impregnation with an aqueous solution of $PdCl_2$. Then, samples were calcined at 673 K.

The chemical composition of the samples was determined by X-ray fluorescence in a RIGAKU (RIX3100) equipment. The BET surface areas of the catalysts were measured using a Micromeritics ASAP 2000 analyzer by nitrogen adsorption at liquid nitrogen temperature. The temperature programmed reduction (TPR) experiments were performed in a quartz micro reactor coupled to a thermal conductivity detector. The sample was heated to 1273 K under a H_2 + Ar mixture containing 1.53% of H_2. Transmission electron microscope (TEM) analyses were performed in a JEOL 2010 equipment operated in imaging mode. The particle size was measured using Axion Vision 4.0 software. Before the TEM analysis, the catalysts were reduced under H_2 at 923 K and passivated under 2% O_2/He mixture at 77 K for 1 h and at 298 K for 1 h.

Diffuse reflectance infrared spectroscopy analyses (DRIFTS) were carried out using a Fourier transform infrared spectrometer (Magna 560 Nicolet) coupled to a SpectraTech high temperature cell. Samples were first reduced at 773 K under H_2. The catalysts were purged in He at 773 K, prior to cooling in He to 313 K. The DRIFTS spectra were recorded at different temperatures by using

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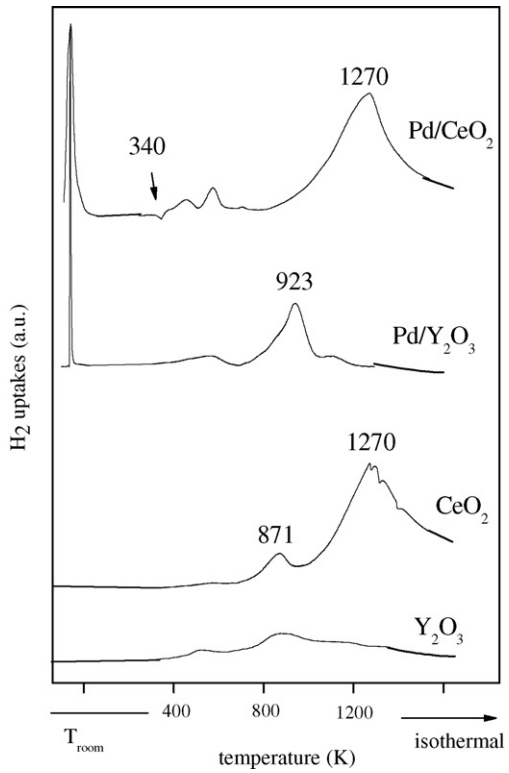

Fig. 1. TPR profiles of the supports (CeO_2 and Y_2O_3) and the catalysts (Pd/CeO_2 and Pd/Y_2O_3).

an ethanol + oxygen mixture, containing a O_2/ethanol molar ratio of 0.5.

POX reactions were performed in a fixed-bed reactor at atmospheric pressure. Prior to reaction, the catalysts were reduced at 923 K under pure H_2, for 1 h, and then purged under N_2 at the same temperature for 30 min. The reaction was carried out at different temperatures and $W/Q = 0.16$ g s/cm^3 (W is the weight of catalyst and Q is the volumetric flow rate). All catalysts were diluted in SiC (SiC/catalyst ratio mass = 3) to avoid hot spots and temperature gradients. The reactants were fed to the reactor by bubbling O_2 and He through one saturator containing ethanol at the temperature required to obtain the desired O_2/ethanol molar ratio (1:2). The exit gases were analyzed using a gas chromatograph (VARIAN, CP 3800) equipped with two columns (molecular sieve and parabond Q/CP 7424—select permanent gases/CO_2) coupled in parallel and a thermal conductivity and a flame ionization detectors connected in series.

3. Results and discussion

Pd/CeO_2 and Pd/Y_2O_3 catalysts contained 0.97 and 0.93% of Pd, respectively. The BET surface areas were very low for both catalysts (Pd/CeO_2: 9.8 m^2/g and Pd/Y_2O_3: 16.1 m^2/g).

The TPR profiles obtained for the supports and the catalysts are displayed in Fig. 1. The TPR profile of CeO_2 exhibited two peaks at 871 and 1270 K. The first peak is related to superficial CeO_2 reduction and the second is ascribed to bulk CeO_2 reduction [7]. No significant consumption of H_2 was detected on Y_2O_3 support. In the case of the catalysts, TPR profile of the Pd/CeO_2 exhibited a large peak related to H_2 consumption at room temperature, which corresponds to the reduction of PdO. It was also detected a small desorption of H_2 at 340 K that correspond to the decomposition of PdH phase formed at low reduction temperature [8] or hydrogen weakly adsorbed on Pd [9]. In addition, a H_2 consumption was observed between 360 and 640 K and a peak of high intensity was detected at 1270 K. The consumption between 360 and 640 K can be attributed to the reduction of superficial CeO_2 promoted by Pd due to the hydrogen spillover from metal particles onto the support [10]. The peak at 1270 K is assigned to reduction of bulk CeO_2. The TPR profile of Pd/Y_2O_3 showed H_2 consumption at room temperature and a peak at high temperature (923 K). The peak at room temperature was assigned to the reduction of PdO, whereas the one at 923 K, may be tentatively ascribed to the reduction of a compound containing Pd and Y_2O_3 such as Pd_2O_4Y [11]. Some authors have reported the formation of $RhYO_3$ and $PtYO_3$ compounds by TPR experiments [12,13]. The Pd/CeO_2 catalyst exhibited complete reduction of palladium oxide. In the case of Pd/

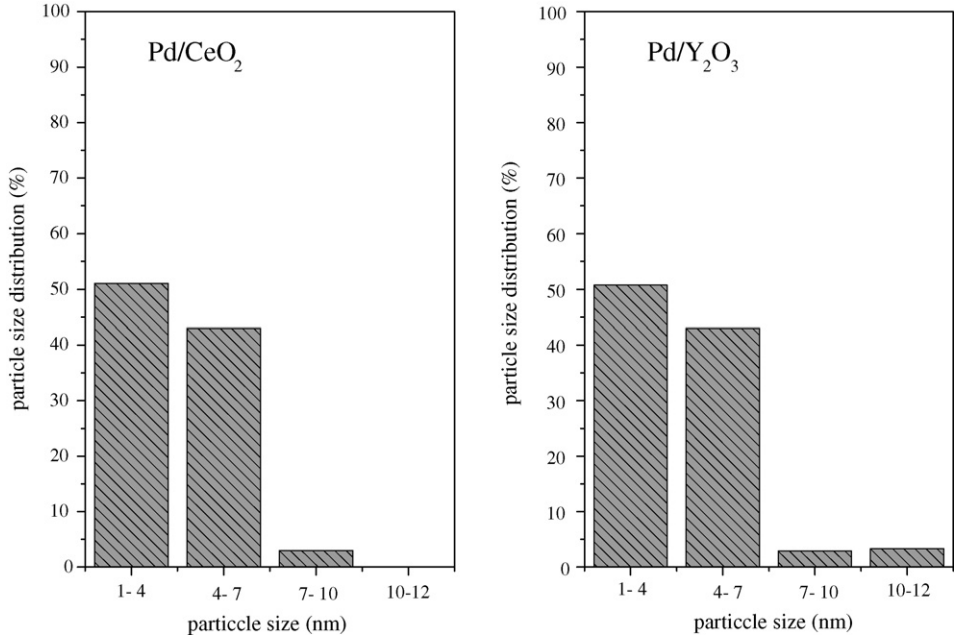

Fig. 2. Particle size distribution obtained by TEM analyses for Pd/CeO_2 and Pd/Y_2O_3.

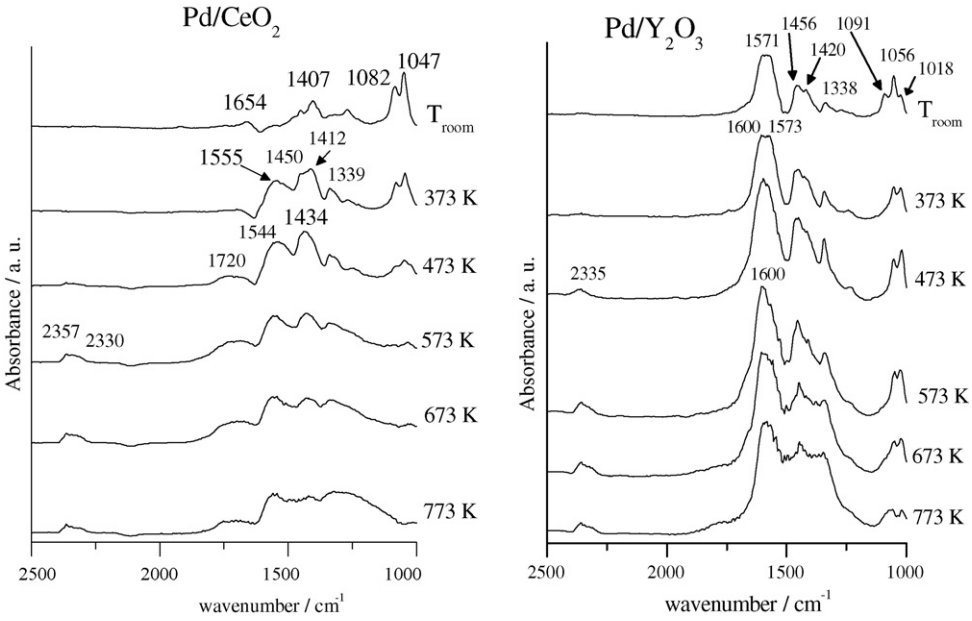

Fig. 3. DRIFTS spectra at different temperatures and under ethanol + oxygen obtained on Pd/CeO_2 and Pd/Y_2O_3 catalysts.

Y_2O_3 catalyst, considering that the H_2 consumption at room temperature and at 923 K corresponds to the reduction of PdO and Pd_2O_4Y phase, respectively, the degree of reduction calculated was 103%. This result confirms that a fraction of palladium (around 55%) was incorporated into a Pd_2O_4Y phase. The presence of Pd_2O_4Y compound reveals the existence of a strong interaction between Pd and Y_2O_3 support, which shifts the reduction of palladium to higher temperature.

Fig. 2 shows the particle size distribution obtained by TEM analyses for Pd/CeO_2 and Pd/Y_2O_3 catalysts. Most of the particles exhibited a particle size between 1 and 4 nm on CeO_2 based catalyst. In the case of Pd/Y_2O_3 catalyst, the majority of the particles were in the range between 1 and 7 nm, which reveals that Pd/Y_2O_3 catalyst shows larger particle size distribution.

The DRIFTS spectrum obtained on Pd/CeO_2 catalyst at room temperature (Fig. 3) exhibited bands at 1047, 1082, 1407 and 1654 cm^{-1}. The bands at 1047, 1082 and 1407 cm^{-1} are related to the ν(CO) vibrational mode of ethoxy species, which were formed by dissociative adsorption of ethanol [14,15]. The band at 1654 cm^{-1} is related to the ν(CO) vibrational mode of acetyl species. The ethoxy species can be dehydrogenated to acetaldehyde, which may be further dehydrogenated to acetyl species [16]. At 373 K, it is detected the appearance of bands at 1021, 1339, 1450 and 1555 cm^{-1}, which are due to the $\rho(CH_3)$, $\delta_s(CH_3)$, $\delta_a(CH_3)$ and $\nu_a(OCO)$ vibrational modes of acetate species, respectively. In addition, the intensity of the bands assigned to ethoxy and acetyl species strongly decreased. In the case of the acetate species formation, two routes should be considered [6]: (i) the reaction between acetyl species and the oxygen from the support and/or (ii) acetaldehyde reaction with surface OH groups. Taking into account the TPR profile of Pd/CeO_2 catalyst, the CeO_2 surface is likely completely reduced after H_2 treatment at 773 K. However, oxygen of the feed can partially replenish the vacancies of the support and then, the presence of oxygen available for reaction may not be rule out. Therefore, both routes from ethoxy to acetate species involving oxygen from the support and Type II bridging OH groups should be considered. When the temperature was heated to 473 K, no significant changes were observed in the intensity of the bands related to acetate species and the bands corresponding to ethoxy species decreased. In addition, the band attributed to acetaldehyde (1720 cm^{-1}) was detected. Increasing temperature decreased the intensity of the bands assigned to acetate species. Above 473 K, the bands assigned to ethoxy species disappeared and the bands characteristic of gas phase CO_2 (2357 and 2330 cm^{-1}) were present.

In addition to the ethoxy species (1056 and 1091 cm^{-1}), the spectrum of ethanol adsorption over Pd/Y_2O_3 at room temperature shows the appearance of the bands due to the acetate species (1018, 1056, 1338, 1420, 1456 and 1571 cm^{-1}) and the hydrogen carbonate species (1600 cm^{-1}) (Fig. 3). The carbonate species were formed by oxidation of acetate species [14]. Since Y_2O_3 is not a reducible oxide, the transformation of ethoxy to acetate species by surface O does not occur. Therefore, the acetate species should be produced through the route involving the OH groups on Pd/Y_2O_3

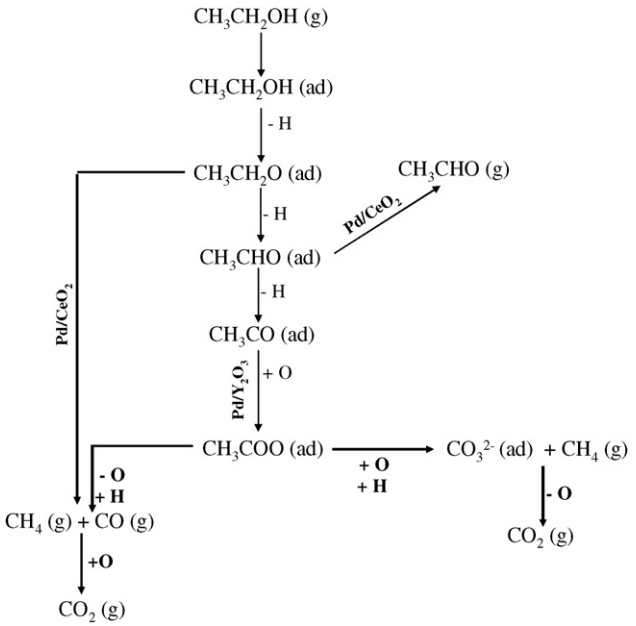

Fig. 4. Reaction pathway proposed for partial oxidation of ethanol over Pd/CeO_2 and Pd/Y_2O_3 catalysts.

catalyst. Increasing temperature to 473 K, the intensities of the bands corresponding to acetate species increased while the bands ascribed to ethoxy species decreased. However, at this temperature, the IR spectrum of Pd/Y_2O_3 catalyst already presented the gas phase CO_2 bands (2300–2400 cm^{-1}), which were only detected at 573 K on Pd/CeO_2 catalyst. At 573 K, the bands related to CO_2 formation increased, whereas the bands corresponding to acetate species decreased. At 773 K, the intensity of the bands assigned to acetate species strongly decreased while the bands due to carbonate species are now present.

The DRIFTS results suggest that the reaction mechanism of partial oxidation of ethanol is the same for Pd/CeO_2 and Pd/Y_2O_3 catalysts. The reaction mechanism proposed for partial oxidation of ethanol over Pd/CeO_2 and Pd/Y_2O_3 catalysts is shown in Fig. 4. However, some reaction pathways are favored depending on the nature of the support. At low temperatures, the DRIFTS analyses showed that the ratio between the intensities of the bands assigned to acetate species and ethoxy species (acetate/ethoxy ratio) was higher on Pd/Y_2O_3 catalyst. In addition, Pd/CeO_2 catalyst exhibited the band corresponding to acetaldehyde even at high temperatures. These results suggest that the transformation of ethoxy species to acetate species is favored on Pd/Y_2O_3 catalyst, which could be attributed to the absence of oxygen vacancies on Y_2O_3 support.

The ethanol conversion and products distribution obtained on partial oxidation of ethanol over Pd/CeO_2 and Pd/Y_2O_3 catalyst are depicted in Fig. 5. Pd/CeO_2 exhibited higher activity than Pd/Y_2O_3 at temperatures lower than 673 K. The complete ethanol conversion was achieved at 873 K for Pd/Y_2O_3 and 973 K for Pd/CeO_2 while oxygen was no longer detected above 673 K. TPR analyses showed that the interaction between Pd and Y_2O_3 support is very strong, that led to a low reduction degree of Pd. Therefore, the low activity of Pd/Y_2O_3 catalyst seems to be due to the low reducibility of Pd, which leads to a lower fraction of active sites. Regardless of the catalysts used, H_2, CO, CO_2, CH_4, acetaldehyde and water were always formed. Increasing temperature increased the selectivity to

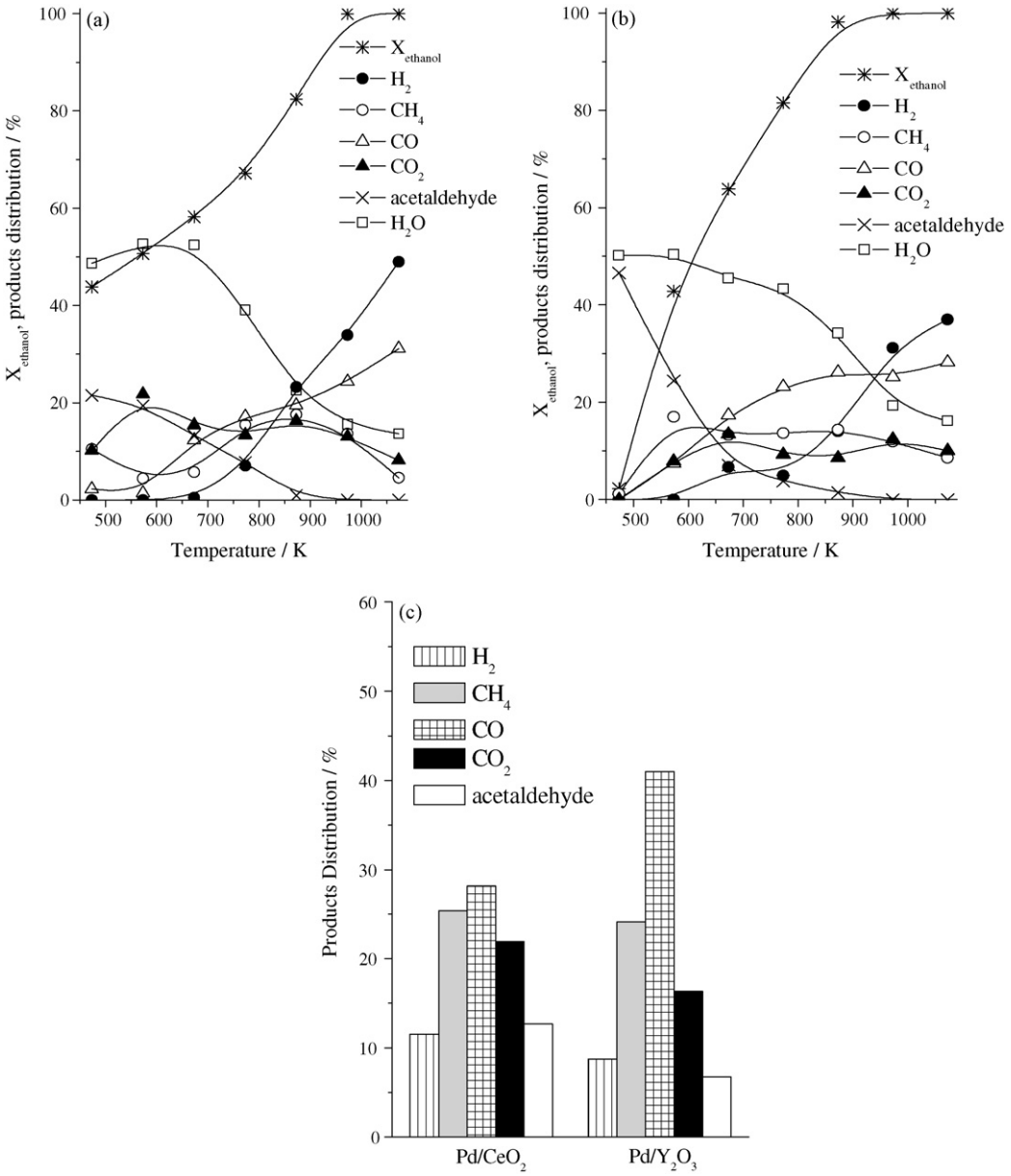

Fig. 5. Ethanol conversion obtained on POX of ethanol for Pd/CeO_2 (a) and Pd/Y_2O_3 (b) and products distribution obtained at the same conversion (~65%; 673 K) in dry basis (c).

H_2 and CO. At 1073 K, Pd/CeO_2 catalyst exhibited the highest hydrogen selectivity. The CO_2 production remained practically constant for both catalysts between 573 and 973 K. On the other hand, selectivity to CH_4 showed a maximum value at 873 K on Pd/CeO_2 catalyst, whereas the CH_4 production increased from 473 to 573 K, and, only slightly decreased above 1000 K over Pd/Y_2O_3 catalyst. In addition, increasing temperature decreased the acetaldehyde and water formation. Acetaldehyde was no longer detected at 973 K. According to DRIFTS experiments (temperatures below 773 K), the decrease of acetaldehyde production and the increase of CH_4, H_2 and CO formation observed on both catalysts could be assigned to the decomposition of the dehydrogenated species and acetate species. Above 773 K, the decrease of CH_4 formation and the increase of H_2 and CO selectivity is likely due to the occurrence of the reaction between the produced methane and the gas phase oxygen or the steam reforming and dry reforming of methane, forming H_2 and CO. Recently, we have studied the partial oxidation of methane over ceria and yttria supported Pt catalysts [13]. TPSR experiments revealed that methane and oxygen consumption began at lower temperature on Pt/CeO_2 catalyst indicating that ceria supported catalyst is much more active than Pt/Y_2O_3. This result may explain the strong decrease of methane concentration at above 1000 K while a large amount of methane is still present on yttria-supported catalyst.

The equilibrium composition was calculated using the non-stoichiometric method through the direct minimization of the Gibbs free energy for a given set of compounds that are detected during the reaction. Comparing the product distributions obtained (Fig. 5) with the thermodynamic equilibrium composition (not shown), it is clear that the product composition is far from thermodynamic equilibrium in the whole range of temperature.

Fig. 5 also displays the product distribution results at the same level of conversion (~64%, dry basis, 673 K) for both catalysts tested. Pd/CeO_2 catalyst exhibited the highest selectivity to H_2, CO_2 and acetaldehyde. On the other hand, the CO formation was favored on Pd/Y_2O_3 catalyst.

These results suggest an important influence of the nature of the support on the resulting product distribution and are consistent with the respective DRIFTS experiments. The DRIFTS analyses showed that the formation of carbonate species is favored on Pd/Y_2O_3 catalyst. According to the literature [14], the acetaldehyde and acetate species can be decomposed to CH_4 and CO, which could explain the highest formation of CO detected on partial oxidation of ethanol over Pd/Y_2O_3 catalyst. In the case of Pd/CeO_2 catalyst, since the formation of acetate species was not favored, the acetaldehyde formed by the dehydrogenation of ethoxy species can desorb and/or decompose to H_2, CH_4 and CO. The CO formed can be further oxidized to CO_2. In fact, Pd based catalysts are generally used on CO combustion reaction. This reaction seems to be promoted on Pd/CeO_2 catalyst. These results could explain the highest formation of H_2, acetaldehyde and CO_2 on partial oxidation of ethanol over Pd/CeO_2 catalyst.

4. Conclusions

The nature of the support significantly affected the product distribution obtained on POX of ethanol over supported Pd catalysts. At low reaction temperature (<773 K), Pd/CeO_2 catalyst exhibited the highest selectivity to H_2, CO_2 and acetaldehyde, whereas the CO formation was favored on Pd/Y_2O_3 catalyst. These results are explained by a reaction mechanism determined by DRIFTS analysis. The adsorption of ethanol gives rise to ethoxy species on both catalysts. These species can be decomposed, producing CH_4, H_2 and CO or dehydrogenated, forming acetaldehyde. The acetaldehyde species are dehydrogenated to acetyl species or may desorb. The dehydrogenated species may also be oxidized to acetate species or can be decomposed, forming CH_4, H_2 and CO. Furthermore, the acetate species previously formed can be decomposed to CH_4, CO and/or oxidized to CO_2 via carbonate species. On Pd/Y_2O_3 catalyst, the transformation of ethoxy species to acetate was favored, which, could explain the higher CO formation and the lower acetaldehyde production over Y_2O_3 based catalyst. On Pd/CeO_2 catalyst, acetaldehyde formed may desorb and/or decompose to H_2, CH_4 and CO. The CO formed was further oxidized to CO_2, which seems to be promoted on Pd/CeO_2 catalyst. These results could explain the highest formation of H_2, acetaldehyde and CO_2 on partial oxidation of ethanol over Pd/CeO_2 catalyst. At high reaction temperature, Pd/CeO_2 catalyst exhibited higher selectivity to H_2 and lower formation of CH_4 than Pd/Y_2O_3 catalyst.

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