

Effect of the metal nature on the reaction mechanism of the partial oxidation of ethanol over CeO₂-supported Pt and Rh catalysts

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Abstract

In this work, the effect of the metal nature on the reaction mechanism of the partial oxidation of ethanol on Pt/CeO₂ and Rh/CeO₂ catalysts was studied by using diffuse reflectance infrared spectroscopy (DRIFTS) analyses. The results showed that the nature of the metal affected the reaction mechanism. On Pt/CeO₂ catalyst, adsorption of ethanol gives rise to ethoxy species, which can be decomposed, producing CH₄, H₂ and CO, and dehydrogenated, forming acetaldehyde. The acetaldehyde species are dehydrogenated to acetyl species or may desorb. The acetyl species can be oxidized to acetate species or can be decomposed, forming CH₄, H₂ and CO. Furthermore, the acetate species previously formed can be decomposed to CH₄, CO and/or oxidized to CO₂ via carbonate species. On the other hand, for Rh-based catalyst, the ethoxy species can be also dehydrogenated to a cyclic compound (oxametallacycle). This intermediate is dissociated to CO, CH_x and C_x, which are oxidized to CO₂. Furthermore, it was observed that the oxidation of acetyl species to acetate species and the formation of CO₂ are favored depending on the presence of the O₂ in the feed on Pt/CeO₂ and Rh/CeO₂ catalysts, respectively.

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1. Introduction

Nowadays fossil carbon fuels are the main energy carrier used. However, burning of hydrocarbon fuels increases the emissions of greenhouse gases, such as CO₂, which has produced a sharp climate change. Furthermore, the use of fossil fuels contributes to the air pollution due to the CO and NO_x emissions. Then, clean forms of energy are needed to support global economic growth while reducing impacts on air quality and the potential effects of greenhouse emissions. Hydrogen is one promising alternative to fossil fuels that could contribute to the reduction of the global greenhouse gas emissions and the atmospheric pollution [1]. Recently, ethanol has been claimed as the best source of H₂ production for fuel cells since it can be manufactured from biomass and does not contribute to CO₂ emissions. Moreover, in countries like Brazil and USA, the

ethanol production and distribution infrastructure is already established.

Several technologies can be used to produce hydrogen from fuels such steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) [2]. Steam reforming of ethanol has been proposed for the production of hydrogen to fuel cells [3–14]. However, the routes for production of hydrogen from ethanol involve a complex reaction system [15–17]. Besides ethanol steam reforming, several reaction pathways take place depending on the catalysts and reaction conditions such as ethanol decomposition to methane, CO and H₂; ethanol dehydrogenation to acetaldehyde; water gas shift reaction; ethanol dehydration to ethylene; acetone and acetic acid formation from ethanol. Some of these reactions lead to the formation of by-products, which can affect the efficiency of fuel cells, and to the catalyst deactivation. For example, one of the sources of coke formation is the polymerization of ethylene produced or the decomposition of methane formed. Then, the previous knowledge of the reaction mechanism is fundamental for the design of optimized catalyst for a specific reaction.

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In the literature, there are several works about the reaction mechanism of ethanol over transition metal surface [18] and metal supported catalysts [19]. According to these studies, the intermediates species formed on the surface are strongly affected by the nature of the metal and the support.

In the case of the metal, some authors reported that the reaction pathway is similar on Pt, Pd and Ni, but it is different on Rh [18]. Although the adsorption of ethanol gives rise to ethoxy species over Pt, Pd, Ni and Rh, the dehydrogenation of these species produces acetaldehyde on Pt, Pd and Ni and a stable oxametallacycle intermediate over Rh. This compound decomposes to CH_4 and CO at high temperatures. Sheng et al. [20] observed the formation of the five-membered-ring oxametallacycle intermediate upon ethanol adsorption over Rh/CeO₂ and Rh–Pt/CeO₂ catalysts, using temperature-programmed desorption (TPD) and Fourier transform infrared spectroscopy (FTIR). They reported that the ethoxy species lose one hydrogen from the terminal (methyl) group and are thus adsorbed in a cyclic configuration onto the surface (oxametallacycle intermediate).

Most of the ethanol reaction mechanisms proposed in the literature was determined by studies of IR spectroscopy or TPD of ethanol adsorption followed by heating at different temperatures under vacuum. However, the presence of oxygen can affect significantly the nature of intermediates formed on the surface of CeO₂-supported metal catalysts. This can be attributed to the high oxygen storage capacity of cerium oxide. This capacity is associated to the ability of cerium to act as an oxygen buffer by storing/releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple [21]. The reduction degree of CeO₂ is a function of the metal and the reaction conditions.

Yee et al. [22] observed the appearance of the band corresponding to acetate species on the IR spectrum of unreduced CeO₂ after ethanol adsorption at room temperature. On the other hand, no evidence of acetate formation was shown on the reduced CeO₂ sample. According to the authors, the reduced CeO₂ surface does not have enough oxygen atoms for acetate formation. Sheng et al. [20] studied the reaction of ethanol over Rh–Pt/CeO₂ catalyst by IR spectroscopy. On the unreduced sample, acetaldehyde formation occurred after ethanol adsorption at room temperature and heating to 373 and 423 K whereas acetaldehyde was not detected on the reduced catalyst under the same conditions. Mattos and Noronha [23] reported that the acetaldehyde desorption was observed in the temperature-programmed surface reaction (TPSR) experiments of ethanol with oxygen, while no acetaldehyde was detected in the TPD of ethanol analysis. They proposed that in the absence of oxygen in the feed, a fraction of the ethoxy species can be dehydrogenated, which readily reacts with oxygen from the support, producing acetate species. The extension of the oxidation reaction depends on the amount of oxygen from the support. Under an oxygen atmosphere, the dehydrogenated species formed may desorb as acetaldehyde while the Ce⁴⁺–O site is recovered.

Taking into account the results described above, the IR experiments carried out under reaction conditions (in presence of O₂) could provide a better correlation between the reaction

intermediates and the products distribution obtained on partial oxidation of ethanol.

Then, the aim of this work is to study the effect of the metal nature on the reaction mechanism of partial oxidation of ethanol over CeO₂-supported Rh and Pt catalysts. The reaction mechanism was determined through diffuse reflectance infrared spectroscopy (DRIFTS) analyses carried out under reaction conditions.

2. Experimental

2.1. Catalyst preparation

CeO₂ support was prepared by calcination of cerium(IV) ammonium nitrate (Aldrich) at 1073 K for 1 h in a muffle. Platinum (1.0 wt%) and rhodium (1.0 wt%) were added to CeO₂ by incipient wetness impregnation with an aqueous solution containing H₂PtCl₆·6H₂O and RhCl₃·H₂O, respectively. After impregnation, the samples were dried at 393 K and calcined under air (50 cm³/min) at 673 K, for 2 h. Then, two catalysts were obtained: Pt/CeO₂ and Rh/CeO₂.

2.2. X-ray fluorescence (XRF)

The chemical composition of the samples was determined by X-ray fluorescence on a RIGAKU (RIX3100) equipment.

2.3. BET surface area

The BET surface areas of the catalysts were measured using a Micromeritics ASAP 2000 analyzer by nitrogen adsorption at liquid nitrogen temperature.

2.4. Diffuse reflectance infrared spectroscopy (DRIFTS)

Diffuse reflectance infrared spectroscopy analyses were performed using a Fourier transform infrared spectrometer (Nicolet, Magna 560) coupled to a high temperature cell (SpectraTech). Four samples were analyzed: (i) reduced CeO₂ support; (ii) unreduced Pt/CeO₂ catalyst; (iii) reduced Pt/CeO₂ catalyst and (iv) reduced Rh/CeO₂ catalysts. The reduced samples were pretreated under flowing H₂ (30 cm³/min) at 773 K for 1 h. After reduction, the samples were cooled down to room temperature under He. The reference spectra were collected at room temperature for all samples. The reactants were fed to the cell by bubbling air through a saturator containing ethanol at 319 K, in order to obtain the desired ethanol/O₂ ratio (2:1). Then, the spectra were collected at different temperatures. In the case of reduced Pt/CeO₂ catalyst, DRIFTS analyses were also carried out at different temperatures, using a mixture of acetaldehyde and N₂.

2.5. Reaction conditions

Ethanol partial oxidation was performed in a fixed-bed reactor at atmospheric pressure. Prior to reaction, the catalysts were reduced at 773 K, for 1 h, and then purged under N₂ at the

same temperature for 30 min. The reaction was carried out at different temperatures and $W/Q = 0.16 \text{ g s/cm}^3$ (W = weight of catalyst and Q = volumetric flow rate). Furthermore, it was performed during 50 min time on stream at each temperature studied. 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 air ($30 \text{ cm}^3/\text{min}$) and N_2 ($30 \text{ cm}^3/\text{min}$) through two saturators containing ethanol at 319 K, in order to obtain the desired ethanol/ O_2 ratio (2:1). The exit gases were analyzed using a chromatograph (Micro GC Agilent 3000 A) containing two channels equipped with thermal conductivity detectors and two columns: a molecular sieve and a Poraplot U.

3. Results and discussion

3.1. Catalysts characterization

Pt/CeO₂ and Rh/CeO₂ catalysts contained 0.89 and 1.12 wt% of platinum and rhodium, respectively. These values are closed to the nominal values (1.0 wt%). The surface areas of the Pt/CeO₂ and Rh/CeO₂ catalysts were similar and very low (11 and $12 \text{ m}^2/\text{g}_{\text{catalyst}}$, respectively).

3.1.1. Diffuse reflectance infrared spectroscopy (DRIFTS)

Fig. 1 shows the IR spectra of adsorbed ethanol on the reduced CeO₂ support at different temperatures. At room temperature, the bands at 1057, 1095, 1118, 1380 and 1450 cm^{-1} can be attributed to ethoxy species [18,20,22–26]. The band at 1265 cm^{-1} has been reported to ethanol molecularly adsorbed on the Lewis acid sites of the oxide [26].

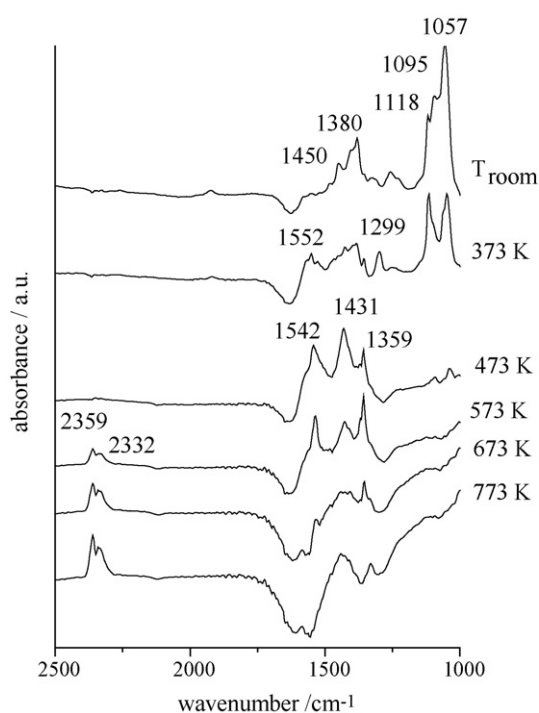


Fig. 1. Infrared spectra of the surface species formed by ethanol adsorption on reduced CeO₂ support at different temperatures (ethanol/ O_2 molar ratio = 2).

When the sample was heated at 373 K, the intensity of the bands corresponding to ethoxy species was reduced. However, the bands characteristics of acetate species (1299 , 1383 and 1552 cm^{-1}) were now present. These bands were formed by the oxidation of ethoxy species [22,23,27]. At 473 K, the bands associated to ethoxy species completely disappeared. The increase of temperature led to a decrease of the intensity of the bands related to acetate species. Moreover, at temperatures higher than 473 K, it was detected the presence of the bands around 2300 – 2400 cm^{-1} , which were associated to the CO_2 formation. The presence of CO_2 could be attributed to the decomposition of carbonate species. These species were produced by the oxidation of acetate species [22,23,27]. At 773 K, the bands corresponding to acetate species were no longer detected. These results are similar to those reported by Yee et al. [22] who studied the ethanol adsorption on unreduced and reduced CeO₂. In spite of the same reduction temperature (765 K), the bands characteristic of acetate species appeared at higher temperatures (523 K) than on our work (373 K). Furthermore, the bands attributed to ethoxy species only completely disappeared at 623 K while they were no longer detected at 473 K in our work. These differences are probably related to the conditions that the experiments were carried out. We performed our IR experiments under reaction conditions (ethanol/ O_2 mixture) while the majority of the studies in the literature were done after ethanol adsorption followed by heating at different temperatures under vacuum. Our results demonstrated that the intermediates on the surface may change significantly in the presence of the reaction mixture. Actually, ceria is a material with a high oxygen exchange capacity which depends on the reaction atmosphere. Under oxidizing conditions, the vacancies of the support created during reduction are replenished by oxygen from the feed. In this case, ceria could have sufficient oxygen atoms for acetate formation. Therefore, a better correlation between the reaction intermediates determined by IR experiments and the catalytic tests will be achieved if IR experiments are carried out under reaction conditions.

The DRIFTS spectra of ethanol adsorption on reduced Pt/CeO₂ catalyst obtained at different temperatures are presented in Fig. 2. At room temperature, besides the bands associated to ethoxy species (1045 , 1084 , 1404 and 1450 cm^{-1}) and to ethanol molecularly adsorbed (1265 cm^{-1}), it was detected the presence of the bands at 1651 and 2044 cm^{-1} . The band at around 1651 cm^{-1} was attributed to the $\nu(\text{CO})$ vibrational mode of acetyl species [27,28], which are intermediates that take part of the reaction mechanism of the oxygenated compounds decomposition on the metal surface [18]. These oxygenated compounds are produced by dehydrogenation of ethoxy species. The band at 2044 cm^{-1} has been attributed to linearly adsorbed CO on metal particles [23,29–31]. This result suggests that the ethanol was decomposed to CH_4 , H_2 and CO even at room temperature [23]. When the sample was heated to 373 K, the intensity of the bands related to ethoxy and acetyl species decreased and the band corresponding to acetate species (1550 cm^{-1}) was detected. Yee et al. [24] studied the ethanol adsorption on reduced Pt/CeO₂ catalyst and they did not

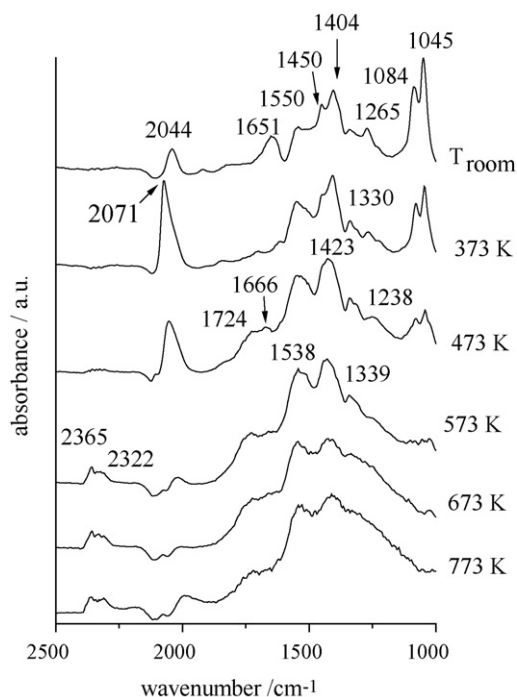


Fig. 2. Infrared spectra of the surface species formed by ethanol adsorption on reduced Pt/CeO₂ catalyst at different temperatures (ethanol/O₂ molar ratio = 2).

observe the formation of the acetate species. The presence of these species in our work could be attributed to the O₂ contained in the feed, which replenishes the vacancies of the CeO₂ support, promoting the oxidation of ethoxy species to acetate species. Moreover, the intensity of the bands associated to adsorbed CO on Pt strongly increased at 373 K and this band was shifted to higher frequency (2071 cm⁻¹). On the other hand, at temperatures higher than 373 K, the amount of adsorbed CO on metal particle decreased.

The spectrum of reduced Pt/CeO₂ catalyst also presented a band around 1724 cm⁻¹, which was poorly defined due to the strong intensity of the band related to acetate species. In the literature, the bands around 1700–1745 cm⁻¹ have been attributed to $\nu(\text{CO})$ mode of adsorbed acetaldehyde [27,28,32]. In order to identify the band at 1724 cm⁻¹, acetaldehyde adsorption on reduced Pt/CeO₂ catalyst was studied with DRIFTS, using a mixture of acetaldehyde and N₂ (Fig. 3). At room temperature, it was observed the presence of the bands at 1720 and 1760 cm⁻¹. The band at 1669 cm⁻¹ is probably associated to acetyl species and the bands at 1545, 1413 and 1353 cm⁻¹ are assigned to acetate species. The presence of the acetate species indicates that a fraction of acetaldehyde species was oxidized at room temperature. These results agree with those reported by Idriss et al. [27] who studied the acetaldehyde adsorption on Pd/CeO₂, Co/CeO₂ and Pd-Co/CeO₂ catalysts, using IR analyses. However, there are no evidences of ethoxy species in our work.

At 323 K, the intensity of the band at 1760 cm⁻¹ decreased while the intensity of the band at 1720 cm⁻¹ remained unchanged. Furthermore, the appearance of a new band at 1708 cm⁻¹ is noticed (Fig. 4). Above 373 K, the bands at 1720

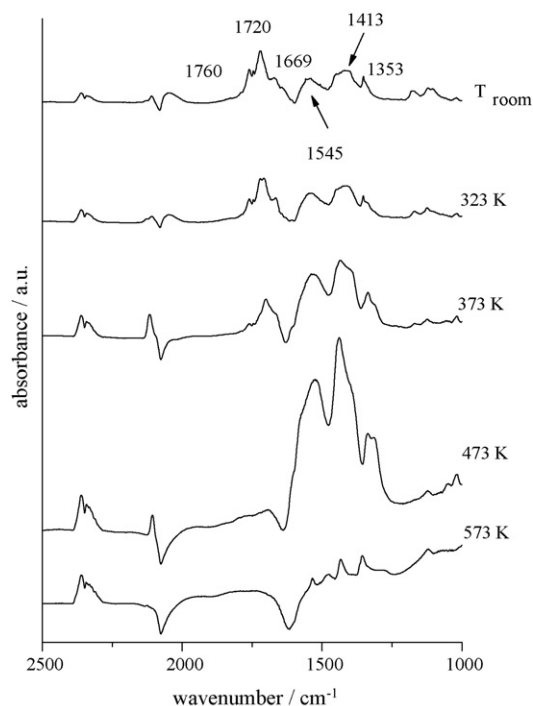


Fig. 3. Infrared spectra of the surface species formed on reduced Pt/CeO₂ catalyst at different temperatures, using a mixture of acetaldehyde and N₂.

and 1760 cm⁻¹ almost completely disappeared and most of the acetaldehyde was oxidized to acetate (Fig. 3). It is important to stress that acetaldehyde was present even at higher temperatures in DRIFTS spectra when the mixture of acetaldehyde and

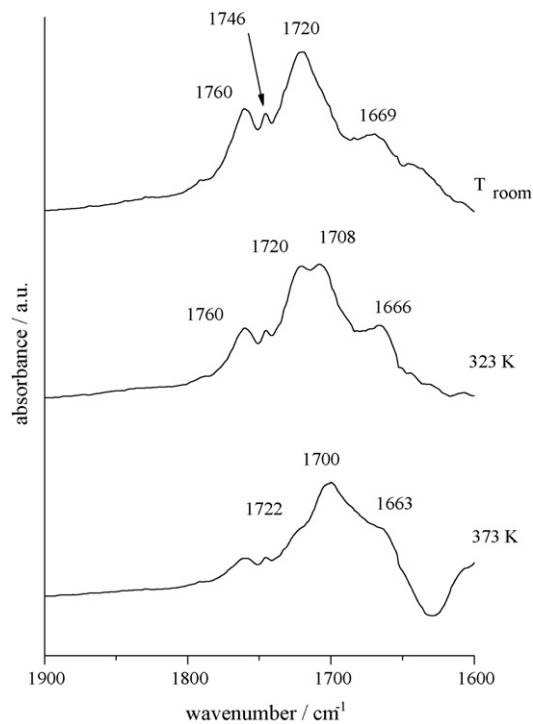


Fig. 4. Infrared spectra of the surface species formed on reduced Pt/CeO₂ catalyst at different temperatures in the region between 1900 and 1600 cm⁻¹, using a mixture of acetaldehyde and N₂.

N_2 was used. It can be attributed to the lower desorption rate of acetaldehyde species or to the lower activity of the catalyst for the acetaldehyde oxidation.

In order to better understand the role of the support on the reaction mechanism, the DRIFTS analyses were also performed for unreduced Pt/CeO₂ catalyst (not shown). At room temperature, besides the ethoxy species, the acetate species were also detected. This result can be attributed to the redox properties of CeO₂. These properties are associated to the ability of cerium to act as an oxygen buffer by storing/releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple [21]. Since reduced Pt/CeO₂ catalyst has a larger amount of oxygen vacancies than unreduced Pt/CeO₂ catalyst, the oxidation of the ethoxy species to acetate species is not favored on the reduced sample.

The DRIFTS spectra obtained at different temperatures for reduced Rh/CeO₂ catalyst are presented in Fig. 5. The spectrum obtained at room temperature for this catalyst is very similar to the one of the reduced Pt/CeO₂ catalyst. The bands corresponding to ethoxy species (1045, 1082, 1403 and 1452 cm⁻¹), acetyl species (1638 cm⁻¹) and adsorbed CO on Rh particles (2027 cm⁻¹) were detected. The increase of the temperature also led to the disappearance of the bands characteristic of the ethoxy and acetyl species and to the formation of the acetate species (1336 and 1550 cm⁻¹). These bands almost completely disappeared at 773 K on Pt/CeO₂ while they are still present on Rh/CeO₂ catalyst. The decrease of the intensity of the bands related to acetate species is followed by the appearance of the bands corresponding to CO₂ formation. When our results are compared with those reported in the literature for Rh/CeO₂ catalyst [20], it was observed that

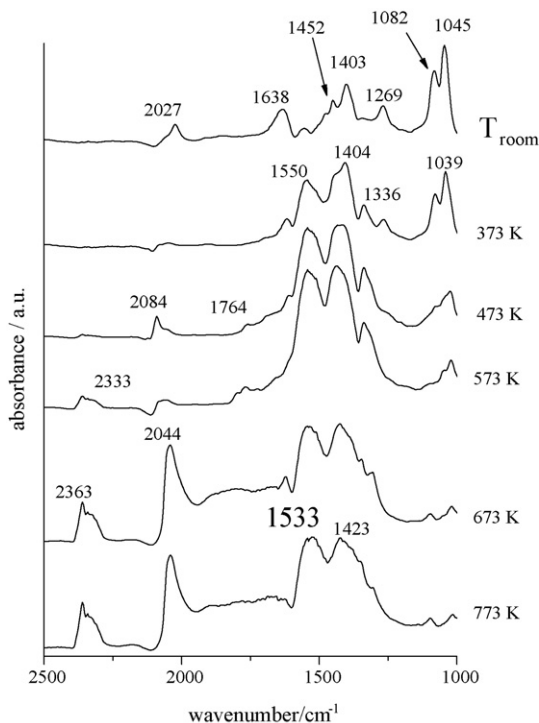


Fig. 5. Infrared spectra of the surface species formed by ethanol adsorption on reduced Rh/CeO₂ catalyst at different temperatures (ethanol/O₂ molar ratio = 2).

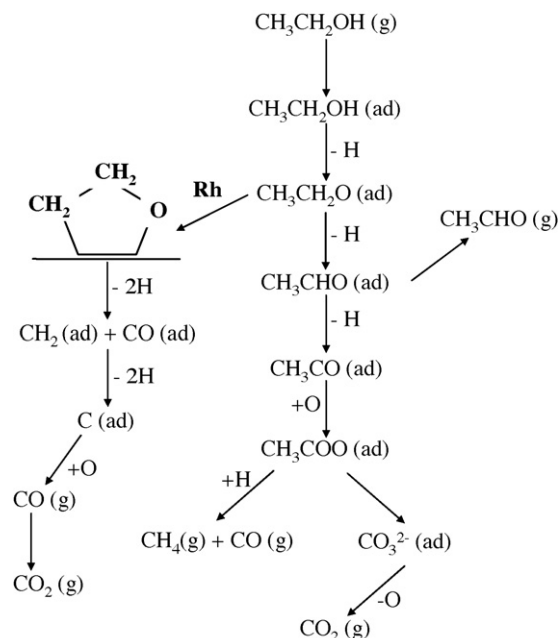


Fig. 6. Scheme of reaction mechanism proposed for the partial oxidation of ethanol on Pt, Pd and Rh surface.

the presence of O₂ in the feed on our work led to a higher CO₂ formation.

Concerning the band due to CO adsorption on metal surface, two different trends were observed, depending on the nature of the metal. On Pt/CeO₂ catalyst, the intensity of the band assigned to adsorbed CO achieved a maximum at around 373 K and almost completely disappeared at high temperature (773 K). On the other hand, the intensity of this band increased continuously as a function of temperature and is higher at 773 K on Rh/CeO₂ catalysts.

According to the literature [23], the production of CO at low temperatures could be assigned to the decomposition of dehydrogenated species. But ethoxy species were no longer detected at high temperatures, indicating that CO formation stem from another pathway on Rh/CeO₂ catalyst. Several authors [18,20] suggested that the reaction pathway of ethanol is similar on Pt and Pd, but it is quite distinct on Rh (Fig. 6). For Pt and Pd, adsorption of ethanol gives rise to ethoxy species, which are dehydrogenated, producing acetaldehyde. The acetaldehyde species are dehydrogenated to acetyl species or may desorb. The acetyl species can be oxidized to acetate species or can be decomposed, forming CH₄, H₂ and CO. Furthermore, the acetate species previously formed can be decomposed to CH₄, CO and/or oxidized to CO₂ via carbonate species. For Rh-based catalysts, the ethoxy species lose one H atom from the terminal methyl group and then is adsorbed in a cyclic configuration (oxametallacycle intermediate) [18]. This intermediate is more stable on Rh than $\eta^2(C,O)$ and $\eta^1(O)$ configurations of acetaldehyde and is decomposed at high temperatures, producing CO, CH_x and C_x, which are oxidized to CO₂. In this work, the bands corresponding to oxametallacycle intermediate that occur below 1000 cm⁻¹ could not be detected due to the poor resolution of the DRIFTS spectrum in this

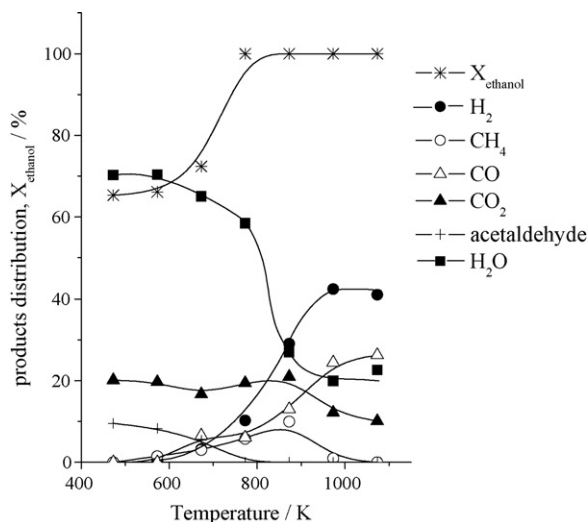


Fig. 7. Products distribution and ethanol conversion (X_{ethanol}) obtained at different temperatures for reduced Pt/CeO₂ catalyst on partial oxidation of ethanol. Reaction conditions: $W/Q = 0.16$ g s/cm³; ethanol/O₂ molar ratio = 2.

region. Moreover, the bands associated to the five-membered ring oxametallacycle species above 1000 cm⁻¹ are similar to the bands related to ethoxy species and could not be distinguished. The higher stability of this oxametallacycle intermediate could explain the large CO formation at high temperature (773 K) on Rh/CeO₂ catalyst. A comparison between our DRIFTS experiments and the results reported in the literature [20,24] showed that some reaction pathways are favored depending on the presence of the O₂. In our work, the O₂ present in the feed enhanced the oxidation of acetyl species to acetate species and the formation of CO₂ on Pt/CeO₂ and Rh/CeO₂ catalysts, respectively.

3.2. Partial oxidation of ethanol

Figs. 7 and 8 show ethanol conversion (X_{ethanol}) and products distribution obtained on partial oxidation of ethanol over Pt/CeO₂ and Rh/CeO₂ catalysts, respectively, at different temperatures.

The results showed that the complete ethanol conversion was achieved at lower temperature (673 K) over Rh/CeO₂ catalyst, indicating that this material is more active than Pt/CeO₂ catalyst.

Concerning H₂ production, significant amounts of H₂ were only observed at temperatures above 673 K for both catalysts. Furthermore, the increase of the reaction temperature favored the H₂ production, which reached a maximum at 973 K (for Pt/CeO₂ catalyst) and 873 K (for Rh/CeO₂ catalyst). The H₂ formation was followed by CO production over Pt-based catalyst. Nevertheless, this effect was not observed on Rh/CeO₂ catalyst, which exhibited significant production of CO from 473 K and remained approximately constant in all range of temperatures studied. This result can be explained by the mechanism proposed for Pt/CeO₂ and Rh/CeO₂ catalysts through DRIFTS analyses. On Pt-based catalysts, CO and H₂ were formed by decomposition of dehydrogenated species. On

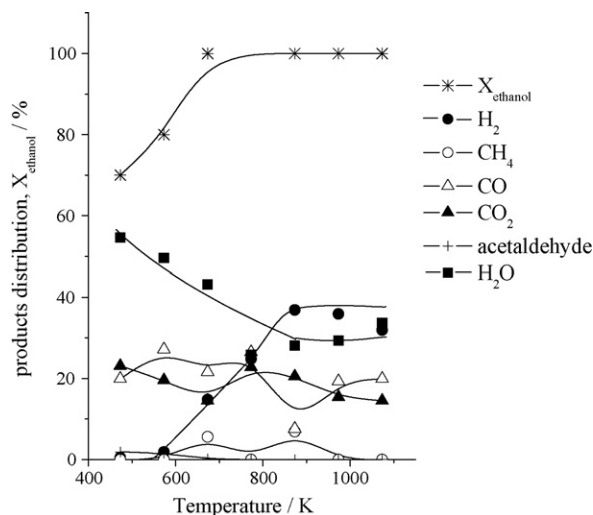


Fig. 8. Products distribution and ethanol conversion (X_{ethanol}) obtained at different temperatures for reduced Rh/CeO₂ catalyst on partial oxidation of ethanol. Reaction conditions: $W/Q = 0.16$ g s/cm³; ethanol/O₂ molar ratio = 2.

the other hand, for Rh-based catalyst, the CO production at low temperatures could also be attributed to the decomposition of oxametallacycle intermediate, as previously described (Fig. 6).

The CO₂ production followed the same trend on Pt/CeO₂ and Rh/CeO₂ catalysts, remaining practically unchanged until 873 K. At temperatures above 873 K, the CO₂ formation decreased. It was also observed that increasing reaction temperature decreased H₂O production for both catalysts.

Regarding oxygenated products and hydrocarbons, Pt/CeO₂ catalysts presented small amounts of acetaldehyde and methane. Acetaldehyde was only detected at temperatures between 473 and 673 K over this catalyst. Moreover, when the temperature was increased, the acetaldehyde formation decreased. This effect was also observed by Sheng et al. [20], who studied the partial oxidation of ethanol over Rh–Pt/CeO₂ catalysts. They also reported that the production of acetaldehyde was higher at 473 K. In our work, the methane formation started at 573 K, reaching a maximum at 973 K on Pt/CeO₂ catalyst. At temperatures above 973 K, methane was no longer detected. For Rh/CeO₂ catalyst, only traces amount of acetaldehyde was observed at 473 K. Furthermore, the methane formation was detected between 573 and 973 K on Rh-based catalyst, but its production was lower than that observed on Pt/CeO₂ catalyst. Acetone and ethylene were not detected on Pt/CeO₂ and Rh/CeO₂ catalysts at the temperature range studied.

The products distribution in dry basis obtained at 773 K (ethanol conversion = 100%) for Pt/CeO₂ and Rh/CeO₂ catalysts are presented in Fig. 9. The results showed that the nature of the metal affected the products distribution. Pt/CeO₂ and Rh/CeO₂ catalysts exhibited the formation of H₂, CO₂, CO and CH₄. A comparison between the results obtained for Pt/CeO₂ and Rh/CeO₂ catalysts revealed that the latter presented the higher CO formation. This result is in agreement with our DRIFTS experiments, which also presented a higher production of CO at 773 K on Rh/CeO₂ catalyst. On the other hand, Pt/CeO₂ catalyst exhibited the higher CH₄ formation. Moreover, it

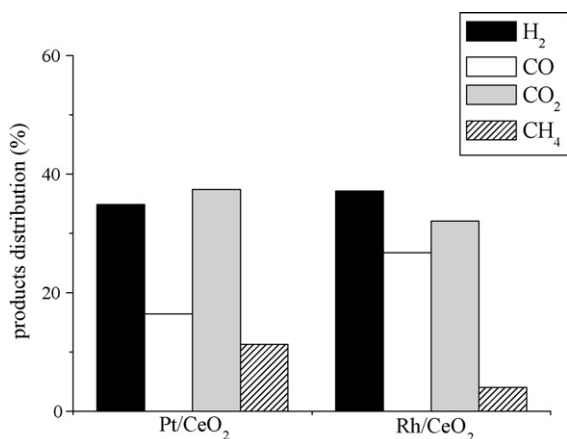


Fig. 9. Products distribution obtained at 773 K (ethanol conversion = 100%) for reduced Pt/CeO₂ catalyst and Rh/CeO₂ catalyst. Reaction conditions: $W/Q = 0.16 \text{ g/cm}^3$; ethanol/O₂ molar ratio = 2.

was not observed significant changes in the selectivity to H₂ and CO₂. The higher CO production and the lower methane formation on Rh/CeO₂ catalyst agree with the reaction mechanism previously proposed.

4. Conclusions

The results showed that the nature of the metal affected the products distribution obtained on the partial oxidation of ethanol. Pt/CeO₂ catalyst presented the lower formation of CO and the higher selectivity to methane. Moreover, the CO formation was followed by the H₂ production on this catalyst. This effect was not observed on Rh/CeO₂ catalyst. In order to explain the products distribution observed, different reaction mechanisms were proposed for Pt/CeO₂ and Rh/CeO₂ catalysts taking into account the DRIFTS experiments. For Pt/CeO₂ catalyst, ethanol adsorption on the support gives rise to ethoxy species. These species are dehydrogenated, producing acetaldehyde, which are further dehydrogenated to acetyl species or may desorb. The acetyl species can be oxidized to acetate species or can be decomposed, forming CH₄, H₂ and CO. Furthermore, the acetate species previously formed can be decomposed to CH₄, CO and/or oxidized to CO₂ via carbonate species. On Rh/CeO₂ catalyst, the ethoxy species are dehydrogenated by H elimination from terminal methyl group generating a cyclic intermediate with five atoms (oxametallacycle compound). This compound is more stable on Rh than acetaldehyde forms (η_1 , η_2) and is decomposed at high temperatures, producing CO, CH_x and C_x, which are oxidized to CO₂. The O₂ present in the feed favored the oxidation of acetyl

species to acetate species and the formation of CO₂ on Pt/CeO₂ and Rh/CeO₂ catalysts, respectively.

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