Combustion of Butyl Carbitol using Supported Palladium Catalysts

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Abstract Palladium catalysts supported on CeO_2, $Ce_{0.75}Zr_{0.25}O_2$, ZrO_2, TiO_2, Nb_2O_5, Al_2O_3 were studied on the total oxidation of butyl carbitol. Several techniques were used to characterize the samples such as diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR), cyclohexane dehydrogenation and CO temperature programmed desorption (TPD). DRS and TPR results revealed the presence of bulk PdO and PdO with strong interaction with the support. The catalytic tests showed the following order for decreasing activity:
$Pd/Ce_{0.75}Zr_{0.25}O_2 > Pd/CeO_2 > Pd/TiO_2 > Pd/Nb_2O_5 > Pd/Al_2O_3 > Pd/ZrO_2$. However, when the *turnover frequency* (TOF) was calculated, all the samples had similar values.

Keywords Butyl carbitol - Volatile organic compounds - Palladium - Combustion

1 Introduction

During the 20th century, the growing human population associated to the correspondent increase in the industrial activities has caused severe pollution problems throughout the world. Even nowadays, large quantities of pollutants are still released to the atmosphere or to water streams untreated. Fortunately, several countries are now regulating the emission of pollutants from both stationary (industries) and mobile (cars, trucks, etc.) sources [1, 2]. Among all kinds of atmospheric pollutants special attention must be given to carbon monoxide, nitrogen oxides, sulfur compounds and the volatile organic compounds (VOCs). These substances are critical not just due to their toxic characteristics but also because of the large quantities that are produced and released to the atmosphere by industrial and agricultural activities [3, 4].

Volatile organic compounds are known as one of the biggest classes of atmospheric pollutants. They are used in a variety of processes and their replacement is very difficult in the majority of these activities [5–8]. One of these applications is the use of a variety of oxygenated compounds as paint solvents in order to achieve the desired viscosity. Among these solvents, one must notice: a compound called butyl carbitol (diethylene glycol mono butyl ether) because it is widely used as solvent for automotive paints [9]. When this solvent evaporates inside the paint booths, it generates a gas stream that has a small concentration of this solvent in air. However, it has been demonstrated that this

solvent can cause severe respiratory problems to humans and animals, even at very low concentrations [10].

In order to comply with the environmental regulations already in place, both in Europe and in North American countries, it is necessary to eliminate this solvent from the air stream. Since the pollutant is present in very low concentrations, one of the best treatment options is the thermal or catalytic incineration [11–15]. The majority of the industrial processes still use thermal incineration, despite its high energy costs due to operation at high temperatures, and the formation of dangerous byproducts such as nitrogen oxides. The use of catalysts to burn VOCs has become increasingly advantageous since it is able to reduce the necessary temperature to transform the pollutants into carbon dioxide and water [2]. On the other hand, in order to use a catalyst efficiently, a previous study about its activity, selectivity and stability is mandatory. Very often, the lack of this kind of information restrains the use of catalysts by industries [11, 16].

Usually the catalysts that are used to eliminate VOCs are noble metal based due to their high activity and stability. Among all the noble metals, palladium has been widely studied for the incineration of pollutants not just because its high activity for oxidation reactions but also due to its lower cost when compared to other noble metals [5, 11, 17–19]. We could not find any studies in the literature about the catalytic elimination of butyl carbitol. Therefore, we decided to investigate the performance of supported palladium catalysts on the total oxidation of butyl carbitol.

2 Experimental
2.1 Catalyst Preparation and Characterization

CeO_2 and ZrO_2 supports were obtained from the calcination of $(NH_4)_2Ce(NO_3)_6$ (Aldrich) and $Zr(OH)_4$ (MEL), at 773 K during 1 h with a heating rate of 5 K/min. Ceria–zirconia mixed oxide (Ce/Zr ratio = 3) was prepared by co-precipitation of $(NH_4)_2Ce(NO_3)_6$ (Aldrich), $ZrO(NO_3)_2$ (Aldrich), in the presence of excess NH_4OH (Merck). The precipitate was washed with de-ionized water and calcined in air at 773 K, for 1 h. Al_2O_3 (Degussa) and TiO_2 (Degussa) were calcined under air flow at 773 K during 1 h with a heating rate of 5 K/min and Nb_2O_5 was obtained from the calcination of niobic acid (CBMM) in air, at 773 K for 1 h.

All the catalysts were obtained by the incipient wetness impregnation of an aqueous solution of $Pd(NO_3)_2$ (Merck). After the impregnation, the samples were dried at 373 K during 24 h and calcined under an air flow of 50 mL/min at 773 K during 1 h, with a heating rate of 5 K/min. The palladium content of all samples was 1 wt%. The real palladium content was determined by atomic absorption and it was within 10% of the nominal loadings for all the samples.

BET surface area experiments were conducted using a Quantasorb Jr for all the calcined catalysts. The samples (300 mg) were dried at 393 K overnight and the N_2 adsorption was performed at 77 K with N_2 partial pressures between 0.05 and 0.3 atm. For each measurement, at least 5 points were taken..The catalysts presented the following values of BET surface areas: $Pd/CeO_2 = 24$ m^2/g; $Pd/Ce_{0.75}Zr_{0.25}O_2 = 105$ m^2/g; $Pd/ZrO_2 = 70$ m^2/g; $Pd/TiO_2 = 49$ m^2/g; $Pd/Nb_2O_5 = 65$ m^2/g and $Pd/Al_2O_3 = 80$ m^2/g.

X-ray diffraction analyses were done using a RIGAKU diffractometer with a CuKα radiation. The XRD data were collected for all supports between $2\theta = 20–65^o$ at 0.04 degrees/step with integration times of 1 s/step.

DRS analyses were carried out between 200 and 900 nm, using a Cary 500 spectrometer equipped with an accessory for DRS (Harrick). The supports were used as references during the analysis of the oxidized form of the catalysts.

Temperature Programmed Reduction (TPR) experiments were performed using a quadrupole mass spectrometer (Balzers, model PRISMA-QMS 200). Prior to reduction, the catalysts (200 mg) were dried under He flow at 50 mL/min at 423 K during 30 min with a heating rate 10 K/min. The samples were reduced under a 2% H_2/Ar mixture with a heating rate of 10 K/min up to 773 K. We monitored the masses correspondent to H_2, H_2O, CO, CO_2 and NO_x, although the last three were not detected.

The dehydrogenation of cyclohexane, which is a structure insensitive reaction, was used to evaluate the dispersion of Pd samples [20]. The reaction was performed at 10^5 Pa in a flow micro-reactor. The sample (10 mg) was previously dried in situ under N_2 flow (30 mL/min) at 393 K during 30 min. Then, the sample was cooled to room temperature and heated in pure hydrogen flow to 773 K at a heating rate of 10 K/min. This temperature was held for 1 h. The sample was then cooled in hydrogen flow to 543 K. The reaction mixture was obtained by bubbling hydrogen through a saturator containing cyclohexane (99.9%) at 285 K (H_2/C_6H_{12} = 13.2). The space velocity was (WHSV) 170 h^{-1} and the reaction temperatures varied form 520 to 570 K. At these conditions, no mass transfer or equilibrium limitations were observed. The conversions were kept bellow 10% in order to guarantee differential conditions. The composition of effluent gas phase was measured by online gas chromatograph equipped with a thermal conductivity detector and Carbowax 20-M in a Chromosorb W column.

2.2 Catalytic Tests

The catalyst pretreatment consisted on drying the sample (30 mg) for 30 min under He flow of 30 mL/min at 423 K (heating rate of 10 K/min). Then, the sample was reduced for 1 h under pure H_2 flow 30 mL/min at 773 K with the same heating rate. The catalytic test was done using a reaction mixture of 1,000 ppm of butyl carbitol in air. This mixture was obtained by passing air through a saturator containing this solvent kept at 339 K. After the reduction, the temperature was lowered to 573 K in helium flow and then the reaction mixture was fed to the reactor. In order to obtain a light-off curve, the reaction temperature was raised until 100% conversion was obtained. The reactor effluent was analyzed using a GC equipped with a thermal conductivity detector and a 3 m Porapak R column. No partial oxidation products were detected.

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3 Results and Discussion
3.1 Characterization
Figure 1 presents the XRD profiles of the supports ZrO_2, $Ce_{0.75}Zr_{0.25}O_2$ and CeO_2. Profile A is correspondent to ZrO_2 and shows that there are two zirconia crystalline phases: tetragonal (JCPDS—14-534) e monoclinic (JCPDS—13-307). On the other hand, profile C shows that ceria exhibits the lines characteristics of the cubic phase (JCPDS—4-0593) [21–24]. For ceria-zirconia sample (profile B), it can be observed

that the peaks are similar to the ones obtained for ceria. However, there is a displacement of the peaks to higher 2θ positions. Comparing the higher intensity peaks, for CeO_2 the positions are $2\theta = 28.6^o$ and 33.2^o and for $Ce_{0.75}Zr_{0.25}O_2$ these peaks appear at $2\theta = 29.0^o$ and 33.5^o. Accordingly to the literature, this shift in the position of the peaks is probably due to the decrease on the ceria´s lattice parameter caused by the addition of zirconium in the lattice [22]. The lack of peaks characteristic of zirconia phases in the $Ce_{0.75}Zr_{0.25}O_2$ profile is an indication that the cubic phase of ceria was maintained after the addition of zirconium and that probably a ceria-zirconia solid solution was obtained. This result is consistent with several studies in the literature [22–24]. For the other supports, the XRD showed the presence of γ-Al_2O_3, a mixture of anatase (80%) and rutile (20%) phases for TiO_2 , and a mixture of T and TT phases for Nb_2O_5.
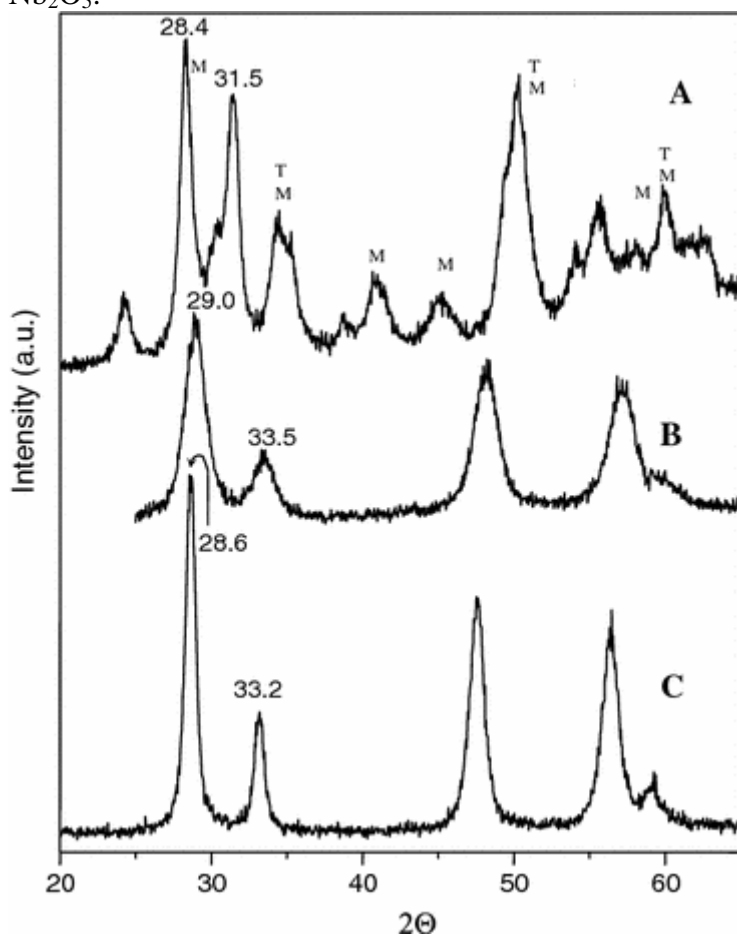

Fig. 1 X-Ray diffraction profiles for A-Pd/CeO_2, B-Pd/$Ce_{0.75}Zr_{0.25}O_2$, C-Pd/ZrO_2 samples, T – zirconia tetragonal phase, M- ziconia monoclinical phase

The DRS spectra of different Pd samples are shown in Fig. 2. It can be observed that all catalysts presented a band around 470 nm. Pd/TiO_2 and Pd/Nb_2O_5 also exhibits a band around 420 nm, while Pd/ZrO_2 and Pd/Al_2O_3 showed another one at 380 nm. In addition, Pd/ZrO_2 had an extra band at 247 nm.
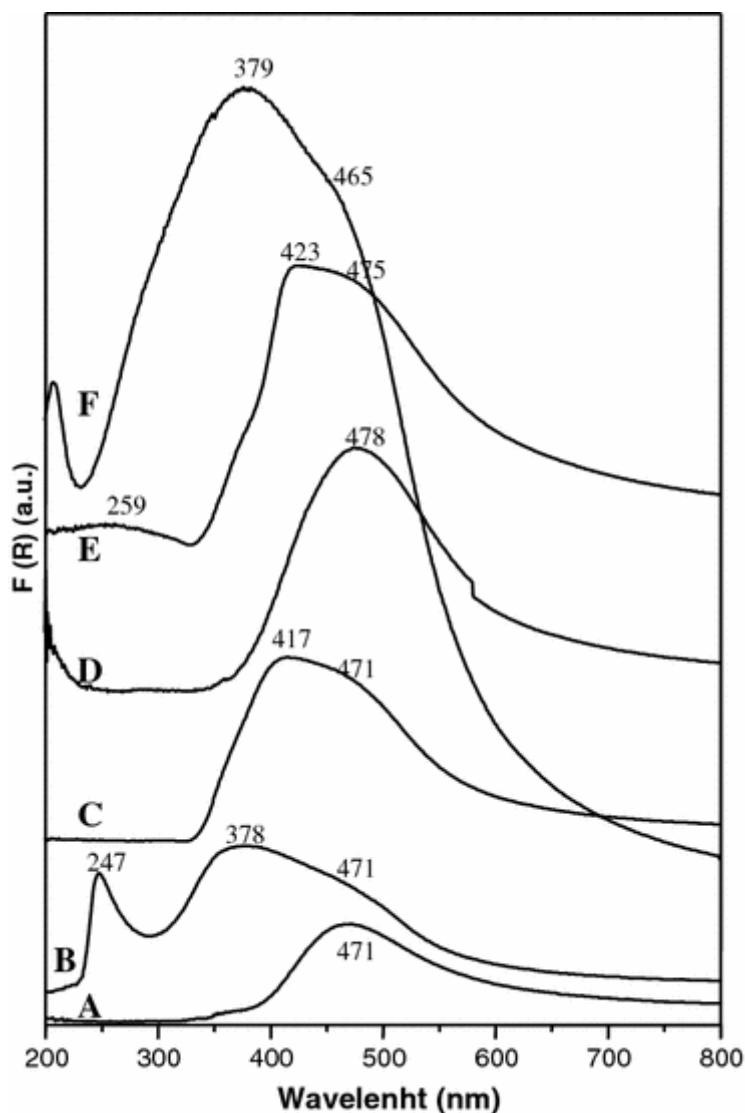
Fig. 2 DRS spectra for Pd supported catalysts. A-Pd/CeO$_2$, B-Pd/ZrO$_2$, C-Pd/Nb$_2$O$_5$, D-Pd/Ce$_{0.75}$Zr$_{0.25}$O$_2$, E-Pd/TiO$_2$, F-Pd/Al$_2$O$_3$

According to the literature, the bands around 400 and 470 nm can be attributed to the palladium oxide d–d transition. Rakai et al. [25] studied unsupported and alumina supported palladium catalysts using DRS. For the unsupported samples, they verified the presence of a large band between 380 and 500 nm. For Pd/Al$_2$O$_3$, the authors observed a band around 450 nm, when they used palladium chloride as a precursor, and another band at 460 nm when the precursor was palladium acetyl acetonate. These bands were attributed to the d–d transition of Pd^{+2}. Lomot et al. [26] also verified the presence of these d–d transition bands in Pd/SiO$_2$ calcined at different temperatures. Noronha et al. [27] used UV–visible diffuse reflectance spectroscopy to study Pd/Al$_2$O$_3$ and Pd/Nb$_2$O$_5$ catalysts. The DRS spectrum of the Pd/Al$_2$O$_3$ sample exhibited 3 bands at 287, 325, and 458 nm, which were attributed to metal-ligand charge transfer, Pd(H$_2$O)$_4^{2+}$ complex and d–d transition, respectively. The Pd/Nb$_2$O$_5$ sample spectrum showed only one band around 407 nm. According to the authors, the band at 287 nm was due to the presence of PdO$_x$Cl$_y$ species on the Pd/Al$_2$O$_3$ sample whereas the Pd/Nb$_2$O$_5$ sample showed only PdO particles corresponding to the band at 407 nm. The bands around 380 nm that were present in the spectra obtained for Pd/Al$_2$O$_3$ and Pd/ZrO$_2$ samples can be attributed to the presence of water in the coordination sphere of

palladium $[Pd(H_2O)^{2+}_4]$ [25]. The appearance of isolated bands around 247 nm as the ones verified for Pd/ZrO$_2$ may be due to the charge transfer from the oxygen of the support to the d orbitals of palladium [28].

Figures 3 and 4 present the reduction profiles of all the catalysts. It can be noticed that all samples had H$_2$ consumption at room temperature. Several studies in the literature attributed this peak to the reduction of palladium oxide (PdO) and to the adsorption and absorption of hydrogen on the metallic palladium [29–32]. These results are consistent with the DRS data of these catalysts which presented bands around 400 and 470 nm attributed to d–d transitions, revealing the presence of large particles of PdO.
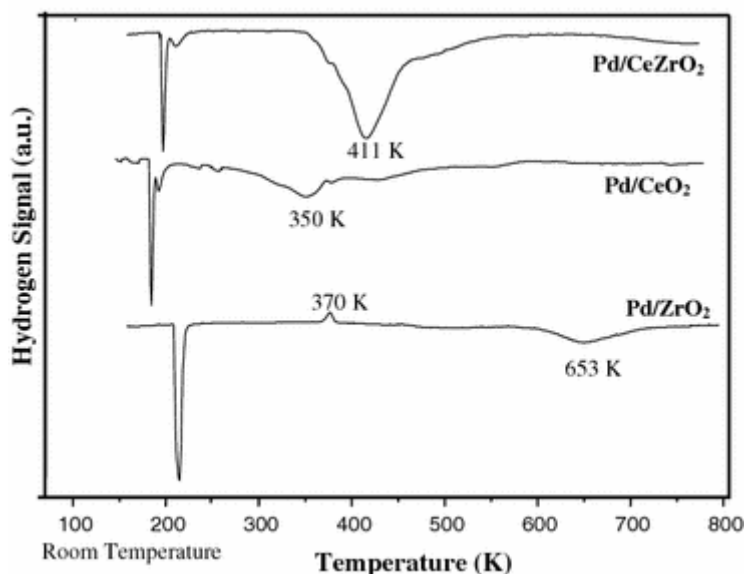

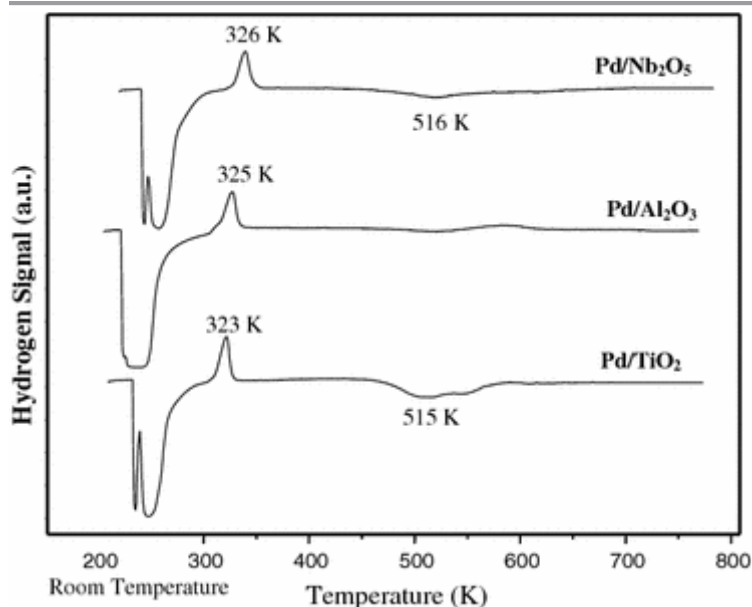Fig. 3 Temperature programmed reduction profiles for Pd/CeO$_2$, Pd/ZrO$_2$, and Pd/Ce$_{0.75}$Zr$_{0.25}$O$_2$ catalysts

Fig. 4 Temperature programmed reduction profiles for Pd/TiO$_2$, Pd/Al$_2$O$_3$ and Pd/Nb$_2$O$_5$ catalysts

As the temperature is increased, new peaks of hydrogen consumption can be observed. For Pd/ZrO$_2$ (Fig. 3), there is a negative peak around 350 K. This same peak is observed for Pd/Nb$_2$O$_5$, Pd/Al$_2$O$_3$ and Pd/TiO$_2$ samples (Fig. 4). Usually this feature is attributed

to the desorption of the weakly adsorbed hydrogen on the metal surface and to the decomposition of the palladium hydride formed at room temperature [30, 33]. The hydrogen consumption at higher temperatures can be attributed to the reduction of small particles of PdO and to the reduction of the support [34]. For instance, it can be seen in Fig. 4, there was a small consumption of hydrogen for Pd/Nb_2O_5, around 516 K and for Pd/TiO_2, around 515 K. These consumptions at higher temperatures have been usually attributed to the partial reduction of Nb_2O_5 and TiO_2 [27, 30]. On the other hand, for $Pd/Ce_{0.75}Zr_{0.25}O_2$ and Pd/CeO_2 these peaks were observed in Figure 3 at 411 and 350 K, respectively. As the total hydrogen consumption (Table 1) for these samples is above the theoretical value necessary to reduce all the palladium oxide (94 μmol of H_2/g_{cat}), it is correct to affirm that there is a partial reduction of the support (Ce^{+4} to Ce^{+3}) for these catalysts. Although zirconia is difficult to reduce, the presence of zirconium in the ceria lattice favors the reduction of Ce^{+4} to Ce^{+3}. According to the literature, the presence of this atom generates defects, increasing the oxygen mobility in the ceria lattice [20, 21]. This can explain the high hydrogen consumption observed for $Pd/Ce_{0.75}Zr_{0.25}O_2$. This result agrees with the ones observed by Luo and Zheng [34] for $Pd/Ce_{0.50}Zr_{0.50}O_2$ and by Hori et al. [24] for platinum supported on CeO_2, ZrO_2 and $Ce_{0.75}Zr_{0.25}O_2$. For Pd/ZrO_2 sample, the hydrogen consumption was lower than the theoretical value for the reduction of palladium. Since zirconia is very difficult to reduce, the small peak observed at 640 K may be attributed to the reduction of small particles of PdO that had higher interaction with the support.

Table 1 H_2 consumption during temperature programmed reduction experiments

Catalyst	μ moles of H_2 g catalyst	
	Room temperature	Total
Pd/CeO_2	10	126
$Pd/Ce_{0.75}Zr_{0.25}O_2$	18	383
Pd/ZrO_2	11	65
Pd/Al_2O_3	110	110
Pd/Nb_2O_5	80	110
Pd/TiO_2	71	108

The values of reaction rate and metal dispersion are presented in Table 2. The results show that all the catalysts have low dispersions, between 9 and 14%. These metal dispersion values are in agreement with TPR and DRS experiments, which revealed the presence of large PdO particles [32, 35].

Table 2 Cyclohexane reaction rates and Pd dispersions

Sample	Reaction rate (mol/g.*h)	Dispersion(%)
Pd/CeO_2	0.0113	9
$Pd/Ce_{0.75}Zr_{0.25}O_2$	0.0199	11
Pd/ZrO_2	0.0309	14
Pd/Al_2O_3	0.0190	11
Pd/Nb_2O_5	0.0198	11
Pd/TiO_2	0.0317	14

3.2 Catalytic Tests

The light off curves for the reaction of total oxidation of butyl carbitol are shown in Fig. 5. $Pd/Ce_{0.75}Zr_{0.25}O_2$ catalyst reached a conversion of butyl carbitol of 95% at 488 K.

This is more than 80 K of temperature reduction when comparing with the less active catalyst, Pd/ZrO_2, which had a conversion of 95% only at 574 K. The temperatures necessary to reach 50% of conversion (light-off temperatures) are shown in Table 3 and the order of increasing light-off temperatures is:
$Pd/Ce_{0.75}Zr_{0.25}O_2 > Pd/CeO_2 \approx Pd/TiO_2 > Pd/Nb_2O_5 \approx Pd/Al_2O_3 \approx Pd/ZrO_2$. The stability of all the samples was tested by repeating a high temperature point and a low temperature point after the light off experiment. All the samples were approximately stable. Table 3 also presents the results of turnover frequencies (TOF) calculated at 448 K, using conversions between 12 and 15%. All the samples had very similar TOF values, around $4.5 \times 10^{-3} \, s^{-1}$.
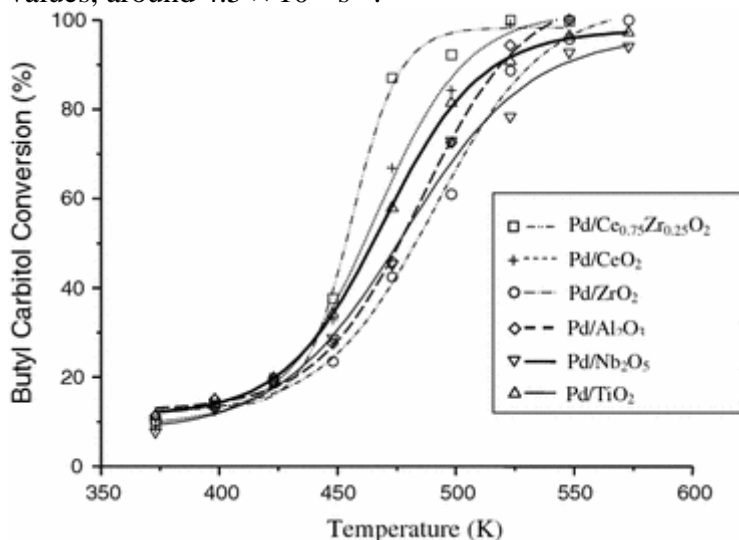

Fig. 5 Butyl carbitol conversion as a function of temperature for Pd supported catalysts after reduction at 573 K for 1 hour

Table 3 Light-off temperatures and turnover frequencies (TOF) obtained during the total oxidation of butyl carbitol using supported palladium catalysts

Catalyst	Light-off Temperature (K)	TOF (s^{-1})
$Pd/Ce_{0.75}Zr_{0.25}O_2$	453	$4.6 \ 10^{-3}$
Pd/CeO_2	462	$5.7 \ 10^{-3}$
Pd/TiO_2	466	$3.9 \ 10^{-3}$
Pd/Al_2O_3	478	$4.9 \ 10^{-3}$
Pd/Nb_2O_5	476	$4.2 \ 10^{-3}$
Pd/ZrO_2	483	$3.5 \ 10^{-3}$

In the literature, the effect of the particle size on the catalytic hydrocarbon oxidation is controversial. A strong dependence between the activity and the particle size has been reported [36]. This effect has been extensively discussed on the total oxidation of methane. These studies are scarcer for other hydrocarbons such as benzene and for oxygenated compounds like butanol, ethyl acetate [3]. However we were unable to find a study about particle size dependence on butyl carbitol oxidation.

Chin and Resasco [22] reported a strong dependence of the TOF for methane oxidation with Pd particle size, taking into account literature data. They observed that the activity increased as dispersion decreased. Also Papefthimiou et al. [36] studied the effect of

metal dispersion on the intrinsic activity of the oxidation of different volatile organic compounds (benzene, butanol, ethyl acetate) on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts. Benzene and ethyl acetate oxidation over Pt/Al_2O_3 catalyst revealed to be structure sensitive reactions. The TOF of ethyl acetate oxidation enhanced 25 times as Pt particle increased from 1 to 30 nm. On the other hand, the TOF of butanol oxidation was independent of Pt particle size. In the case of Pd catalyst, the TOF of all three compounds was practically independent of dispersion.

Accordingly to the literature [36], the particle size effect on the total oxidation of hydrocarbons is directly correlated to the PdO species that are present on the catalyst surface and with the strength of the Pd–O bond. In general, there are two types of palladium oxide: bulk PdO and PdO with a strong interaction with the support. The first kind is present in samples with low metal dispersions, while the second one is characteristic of catalysts with higher dispersions, which would provide a stronger interaction with the support. These two different PdO species present distinct oxygen adsorption and desorption properties [37]. Accordingly to Fugimoto et al. [33], small PdO_x particles have higher interaction with the support and would have a stronger Pd–O bond than larger particles. This Pd–O bond would cause a decrease in the stability and density of oxygen vacancies that are necessary during the oxidation reaction. Therefore, the catalysts with lower dispersion would present a higher turnover frequency.

Besides the particle size effect, the catalytic activity of hydrocarbon oxidation can also be influenced by the nature of the support [22]. Yazawa et al. [38] studied the effect of the nature of support on the propane combustion over Pd supported on Al_2O_3, SiO_2, ZrO_2, SiO_2–Al_2O_3, MgO and SO_4^{2-}–ZrO_2. After reaction at 773 K, XRD and XPS analyses revealed that the presence of metallic palladium and palladium oxide was a function of the oxygen/propane ratio. XPS spectra of Pd/ZrO_2, Pd/Al_2O_3, Pd/SiO_2–Al_2O_3 exhibited the peak of $Pd3d_{5/2}$ at 335.0–335.1 eV, which is assigned to metallic palladium and at 336.5–336.6 eV corresponding to PdO. Furthermore, the catalytic activity was significantly affected by the oxidation state of palladium. The highest activity was observed on the catalysts containing partially oxidized palladium. According to the authors, the nature of the support affects the resistance of palladium oxidation and consequently the catalytic activity. Acidic supports prevent the palladium oxidation.

Noronha et al. [27] also observed a support effect on the propane oxidation over Pd/Al_2O_3, Pd/Nb_2O_5 and $Pd/Nb_2O_5/Al_2O_3$ catalysts. The niobia addition promoted the propane oxidation at lower temperatures than Pd/Al_2O_3 catalyst. In fact, infrared spectroscopy of adsorbed CO on Pd/Al_2O_3 and $Pd/Nb_2O_5/Al_2O_3$ catalysts after propane oxidation showed that the amount of Pd^o and Pd^{2+} species was function of Nb_2O_5 loading. These results suggested that the partially reduced niobia species prevented the palladium oxidation.

The support may also take part in the mechanism of oxidation reactions [22]. In this study, de Leitenburg et al. investigated the oxidation of isobutane using ceria and ceria-zirconia oxides. Although the presence of zirconia did not affect the conversion, the selectivity to isobutene was significantly higher for ceria-zirconia sample. This effect was attributed to higher oxygen mobility in the ceria-zirconia lattice caused by the presence of zirconia.

In our work, all catalysts exhibited the same Pd dispersion. Therefore, the particle size effect could be rule out and the results could be evaluated as a function of the nature of support. However, the TOF were the same, regardless the support. A difference was observed on the light off temperatures of the catalysts, which was around 30 K between the most ($Pd/Ce_{0.75}Zr_{0.25}O_2$) and less (Pd/ZrO_2) active catalysts. It is worth noting that the activity order was the same of the hydrogen consumption on the TPR experiment. This correlation between activity and support reduction degree suggests that the support may play a role on the reaction mechanism. In fact, it is well established that $Ce_{0.75}Zr_{0.25}O_2$ and CeO_2 have a high oxygen exchange capacity, which is associated to the ability of cerium to act as an oxygen buffer by storing/releasing O_2 due to the Ce^{4+}/Ce^{3+} redox couple [21]. The incorporation of ZrO_2 into CeO_2 lattice promotes the CeO_2 redox properties. The presence of ZrO_2 strongly increases the oxygen vacancies of the support, increasing its reducibility. This result is in agreement with our TPR measurements. One possible explanation is that these oxides could be participating in the reaction as oxygen donors and promoting the oxidation through the Max-van-Krevelen mechanism.

In order to try to identify changes in the palladium phases present during the total oxidation of butyl carbitol, the following experiment was carried out: we decided to measure the palladium dispersion of a catalyst before and after the reaction. To simplify the experimental work, the dispersion was estimated using CO chemisorption and the sample selected was Pd/ZrO_2, since it presented higher metal dispersion than the others and it does not have the problem of adsorption of CO on the support. The sample was reduced in pure H_2 with the same procedure used during catalytic tests and submitted to the reaction mixture with reaction temperatures varying from 373 and 573 K. After the reaction, the sample was cooled to room temperature in air flow and then purged with He. Only then, the second CO adsorption was performed. Considering a stoichiometry of CO/Pd = 1, the results show an initial dispersion value of 20% and after the reaction it dropped to 3%. This result is a good indication that although metallic palladium is present, the predominant palladium phase during the reaction is PdO. Probably, the interchangeability between Pd^0/PdO is crucial for the catalytic activity during the total oxidation of butyl carbitol.

4 Conclusions

This study showed that supported palladium catalysts are active for the total oxidation of butyl carbitol and the active phase is probably Pd^0/PdO. All the samples presented similar and very low palladium dispersions, so we could not verify particle size effects on the catalytic activity. DRS and TPR experiments confirmed the presence of large PdO particles on the catalysts surface. $Pd/Ce_{0.75}Zr_{0.25}O_2$ and Pd/CeO_2 were the most active samples probably due to the participation of ceria in the reaction through a Max-van-Krevelen type of mechanism.

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