



Conversion of *cis*-2-butene-1,4-diol to hydrofurans on Pd/SiO₂ and Pt/SiO₂ catalysts under mild conditions: A FT-IR study

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ARTICLE INFO

Article history:

Received 24 March 2010

Accepted 18 May 2010

Available online 4 June 2010

Keywords:

FT-IR spectroscopy

Supported palladium and platinum catalysts

Surface characterization

Cyclization and isomerization reaction

ABSTRACT

The gas-phase interaction of *cis*-2-butene-1,4-diol (C-2-OL) with silica supported Pd and Pt nanoparticles has been studied using infrared spectroscopy at room temperature. Samples were prepared according to standard recipes and characterized through TEM and the IR spectroscopy of adsorbed carbon monoxide at room temperature. Whereas the reaction with hydrogen of C-2-OL in ethanol solutions yields hydrogenated products through a complex network, and no reaction takes place in the absence of hydrogen, in the present case C-2-OL is converted first to 2,5-dihydrofuran (2,5-DHF) and water. This step occurs on the silica support at room temperature, probably through the intermediacy of the surface species $-\text{Si}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$. The presence of Pd nanoparticles allows, at ca. 100 °C, the subsequent isomerization of 2,5-DHF to 2,3-dihydrofuran (2,3-DHF). The same reaction requires a higher temperature (ca. 150 °C) with the Pt catalyst. At higher temperatures, the expected dehydrogenation of both 2,5- and 2,3-DHFs to furan takes place. On the support alone at 350 °C 2,5-DHF is converted to furan, and 2,3-DHF to carbonyl-containing species (as suggested in the literature), through thermal reactions.

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1. Introduction

With the purpose of tailoring a catalyst effective in the production of 2-hydroxytetrahydrofuran, some of the authors have studied in the past the behaviour of palladium and platinum nanoparticles on different supports (SiO₂, Al₂O₃, TiO₂, ZrO₂, MgO and ZnO) in the liquid-phase hydrogenation of *cis*-2-butene-1,4-diol (hereafter C-2-OL), as it concerns the effect on the catalytic activity and products distribution [1–3] of parameters such as the acid–base properties of the support, the metal particle size and the partial hydrogen pressure. In ethanol solutions, a complex reaction network is observed for C-2-OL (Scheme 1) [1–3], involving *cis/trans* isomerization, hydrogenation, and ring closure. In particular, 2-hydroxytetrahydrofuran is formed by internal cyclization of α -hydroxybutyraldehyde (formed by double bond isomerization of the starting material), whereas hydrogenolysis of the C–OH bond leads to *cis*-crotyl alcohol and, finally, to butyraldehyde and *n*-butanol.

On the other hand, the infrared studies of alkenes adsorbed on metals have attracted since the 80s much interest because they afford information on the structures of adsorbed species under various conditions [4,5]. In particular, Sheppard and

co-workers have studied in detail the infrared spectra deriving from hydrocarbons such as ethene, propene, but-1-ene and *cis/trans*-but-2-ene chemisorbed on oxide supported metals [6–8].

With the aim of investigating by means of infrared spectroscopy the mechanism in Scheme 1, a systematic study was undertaken of the gas-phase interaction of C-2-OL with the Pd/SiO₂ and Pt/SiO₂ catalysts. An entirely different reactivity was observed, involving the formation of both 2,5- and 2,3-dihydrofuran (DHF), which is the subject of the present paper. Hence, we report here a spectroscopic study focusing our attention on the overall reactivity and on the nature of the species adsorbed on the catalyst surface. It has to be noted that, at variance with catalytic studies, the measurements reported in the present paper have been run in a closed system. This means, *inter alia*, that instead of carrying out a complete reaction, the various steps in the observed mechanism have been studied individually.

Data are reported basically for the Pd system, those with Pt being used mainly as a reference.

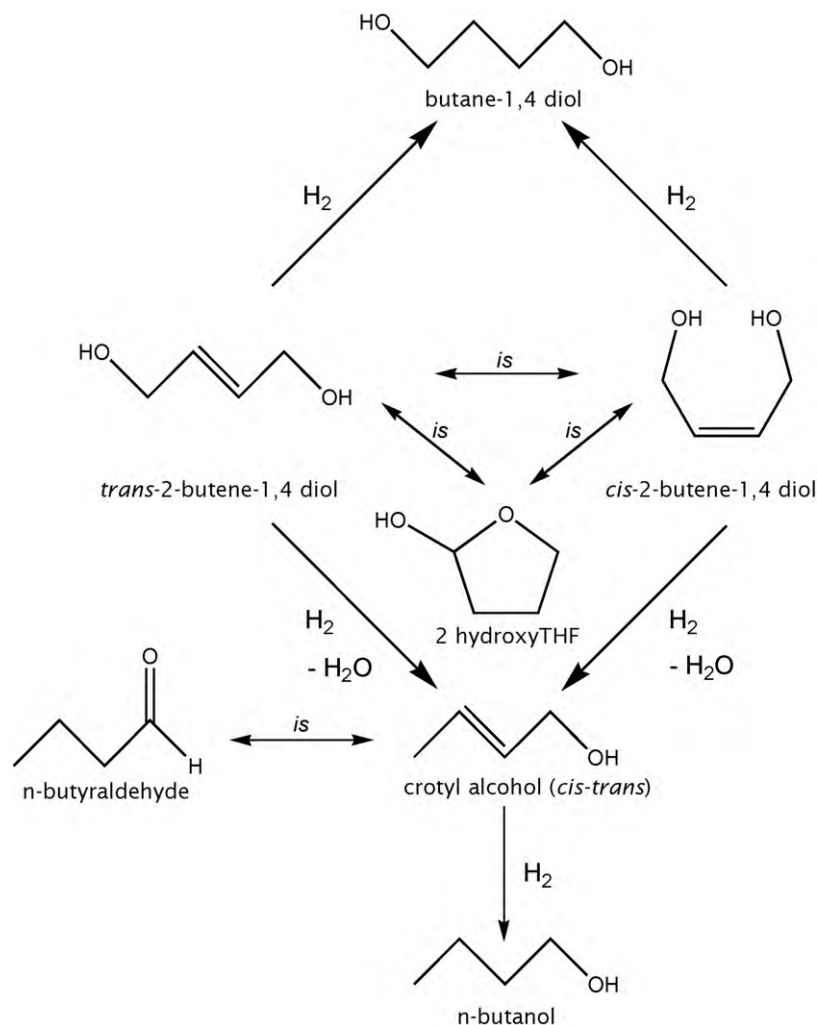
2. Experimental

2.1. Materials

C-2-OL (impurity of *trans* isomer 5%), 2,5-DHF, 2,3-DHF, furan and SiO₂ (BET specific surface area = 500 m²/g) were commercial

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Scheme 1. Overall reaction mechanism concerning the hydrogenation of C-2-OL over Pd and Pt silica catalysts in ethanol solution.

products from Sigma–Aldrich, which were used without further purification.

The preparation of the impregnated 0.5% Pd/SiO₂ and 2.5% Pt/SiO₂ catalysts has been described in detail elsewhere [1–3].

2.2. Measurements

TEM analysis was performed with a Philips instrument Model CM12 operating at 120 kV and directly interfaced with a computer for real-time image processing.

For FT-IR measurements, powder samples were pressed into thin self-supporting wafers. Spectra were collected at a resolution of 2 cm⁻¹ on a Bruker FT-IR Equinox 55 spectrophotometer equipped with MCT detector.

Pre-treatments were carried out using a standard vacuum frame in an IR cell equipped with a KBr window. In order to be as close as possible to the experimental conditions used in the catalytic liquid-phase experiments, in the activation step the catalysts were treated at 200 °C for 2 h under flowing hydrogen and finally cooled to room temperature under inert gas. When appropriate, the activation temperature was raised to 300 °C.

Adsorption of vapours was carried out by connecting the IR cell to a vacuum frame (residual pressure <10⁻³ mbar). C-2-OL and all other molecules were adsorbed at room temperature.

FT-IR spectra are reported as difference spectra from the spectrum of disc before adsorption and, where necessary, from the spectrum of any vapour phase present.

3. Results and discussion

3.1. TEM characterization of the catalysts

Fig. 1 illustrates the TEM characterization of the samples Pd/SiO₂ and Pt/SiO₂ catalysts reduced in H₂ at 200 °C.

Two representative pictures of the samples are reported, together with the corresponding particle size distribution. Palladium particles have a nearly spherical shape with a diameter of about 4.5 nm, whereas platinum particles are bigger (about 40 nm in diameter) and their distribution is less homogeneous. From the data in Fig. 1, it can be deduced that the specific surface exposed by the metal particles is about 1.1 and 0.07 m²/g, respectively.

$$SSA_s = \frac{n_s \pi d^2}{n_s \rho_{Pd/Pt} (\pi/6) d^3} = \frac{6}{\rho_{Pd/Pt} d} \quad (1)$$

The geometrical specific surface areas were calculated according to Eq. (1): where ρ is the particles density of Pd and Pt nanoparticle and d is particle average dimension as determined by TEM micrographs.

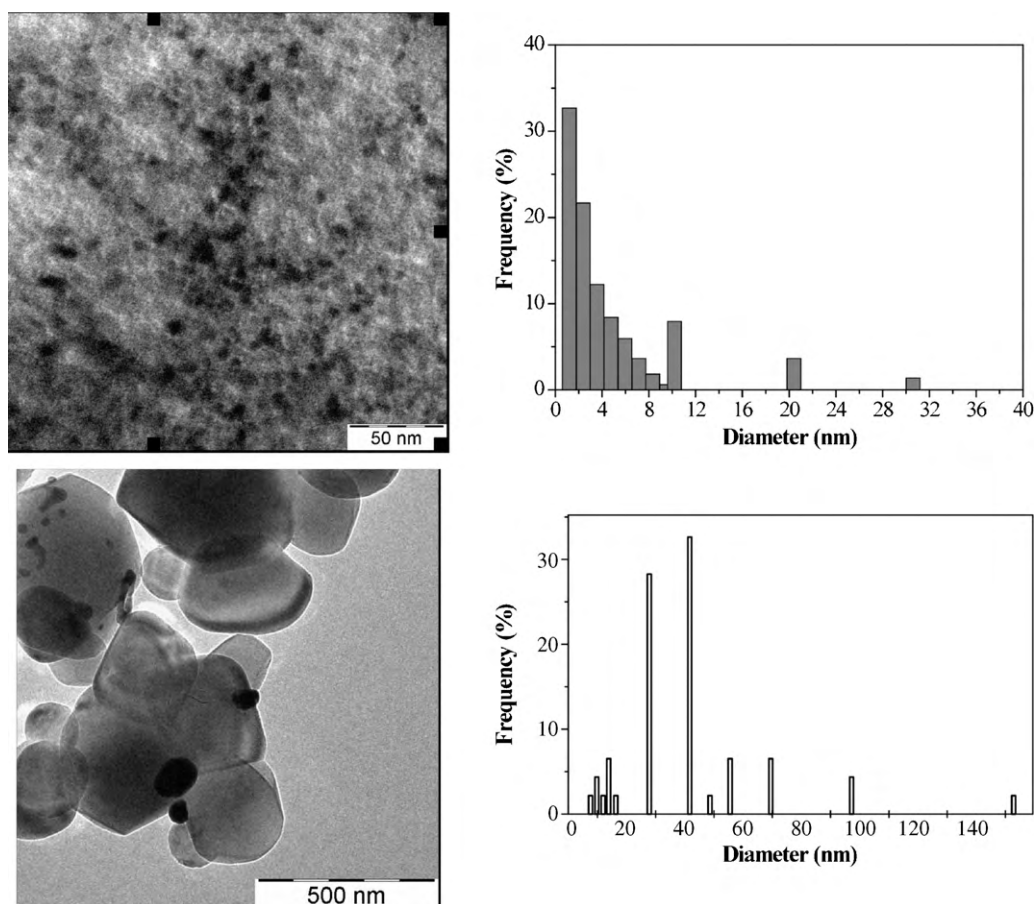


Fig. 1. TEM images and particle size distributions of Pd/SiO₂ (above) and Pt/SiO₂ catalysts (below).

3.2. FT-IR characterization of the naked sample and CO adsorption

Fig. 2 reports the FT-IR spectrum of the Pd/SiO₂ catalyst outgassed at 200 °C in the 3800–1400 cm⁻¹ range. Two absorptions are seen in the OH stretching region: a sharp band at 3745 cm⁻¹ and a broad ill-defined envelope at ca. 3500 cm⁻¹. These bands are due respectively to the νOH vibration of free silanol groups (3745 cm⁻¹)

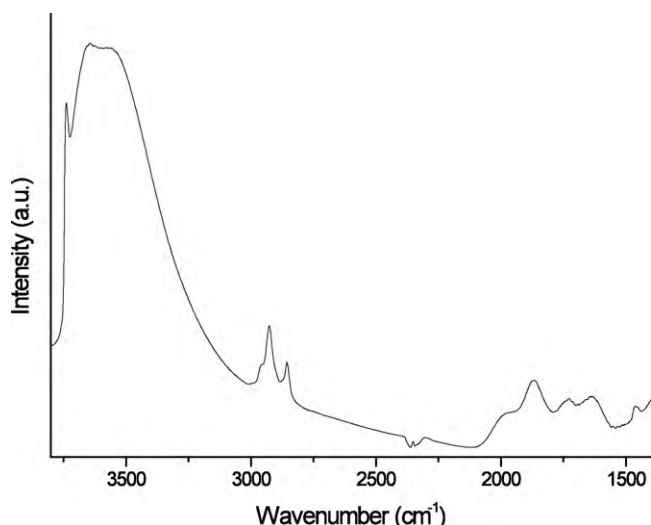


Fig. 2. IR spectrum of the Pd/SiO₂ catalyst outgassed at 200 °C.

and to the same vibrational mode of silanols interacting each other via H-bonding [9,10]. The other bands can be attributed to carbonaceous and water impurities probably not totally removed by outgassing at 200 °C.

The spectra of the sample does not appreciably differ from that of a pure silica support treated in the same way, in agreement with the low metal load.

Carbon monoxide was used at room temperature as a probe molecule for metal sites. Fig. 3 reports the FT-IR spectra of CO chemisorbed at room temperature on the Pd/SiO₂ catalyst in the range 2200–1800 cm⁻¹. Spectra similar to those in Fig. 3 have been reported in the literature [11–16]: an overall agreement is observed.

As to the assignment, three types of CO species chemisorbed on palladium are possible:

- linearly adsorbed on-top sites (~2130–2000 cm⁻¹).
- bridge-bonded on (1 0 0) and (1 0 1) faces (~2000–1870 cm⁻¹)
- multibonded on (1 0 0) and (1 0 1) faces (~1880–1800 cm⁻¹).

Basically, the observed bands – not seen on pure silica treated in the same conditions (Fig. S1 Supplementary Material) – are attributed to the CO (~2080 cm⁻¹) linearly adsorbed on coordinatively-unsaturated Pd sites such as those at corners and edges of crystallites; and to the 2-fold bridged Pd-carbonyls (~1930 cm⁻¹) on planar surfaces, such as the (1 0 1) and (1 0 0) faces. The absence of 3-fold bridged species is ascribed to the fact that at the CO pressures adopted coverage is high enough to force the 3-fold bridged to convert into 2-fold geometry.

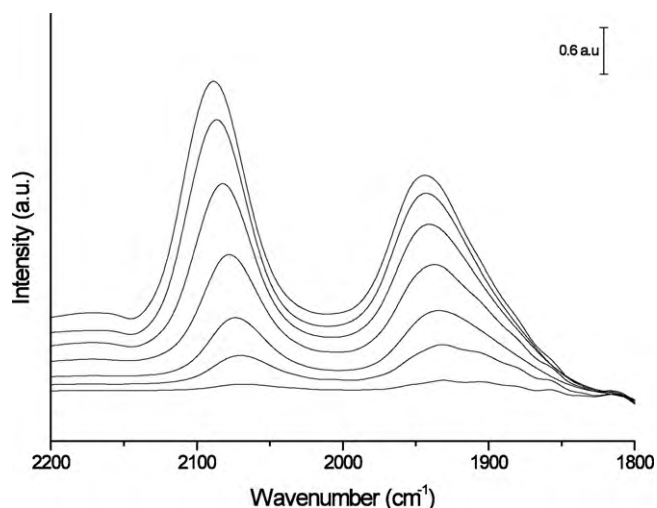


Fig. 3. FT-IR spectra of CO adsorbed at increasing equilibrium pressure (0.01–1 mbar) at room temperature on the Pd/SiO₂ catalyst.

The shift in the peak position with coverage is due to the electronic repulsion between adsorbed species (induced heterogeneity) [17].

3.3. C-2-OL interaction with the Pd/SiO₂ catalyst at room temperature

The upper section of Fig. 4 illustrates the changes in the FT-IR spectra of the Pd/SiO₂ sample due to the contact with increasing

equilibrium pressure (0.5×10^{-2} to 10 mbar) of C-2-OL at room temperature. For clarity, the figure is divided into two regions (A and B).

Perturbation of the ν OH band of surface silanols occurs during adsorption (section A), because of H-bonding interactions. Indeed, the band envelope due to free O–H stretches is observed to decrease (negative band), whereas a band grows at lower frequencies, more intense and broader. In the negative band of Fig. 4 two components at 3745 and 3715 cm⁻¹ may be identified, due respectively to the stretching mode of free silanols and to the vibration of the H-acceptor hydroxyl in a SiOH pair freely interacting (the corresponding absorption of the H-acceptor silanol is at ca. 3500 cm⁻¹).

Also in the growing positive band envelope two components are seen, at ca. 3320 and 3200 cm⁻¹, together with an isobestic point at 3690 cm⁻¹. The presence of two components in the envelope of H-bonded silanols is not due to the presence of the 3745 and 3715 cm⁻¹ bands, which are associated with silanol species of marginally different acidic strengths. They could either be representative of a dual mode of interaction of the C-2-OL molecule (e.g., through the double bond or the basic hydroxyl oxygen) or be related to the presence of two adsorbed molecules, arising from the fact that C-2-OL has reacted on the surface.

This latter hypothesis is confirmed by the results reported in section B of Fig. 4. None of the IR modes of C-2-OL is present (Table 1); instead, IR bands observed are compatible with the presence of 2,5-DHF and water.

For comparison, both water and 2,5-DHF were separately adsorbed at room temperature on the Pd catalyst. The lower section of Fig. 4 reports the corresponding difference spectra. Spectra are dominated by the bands characteristics of water molecularly

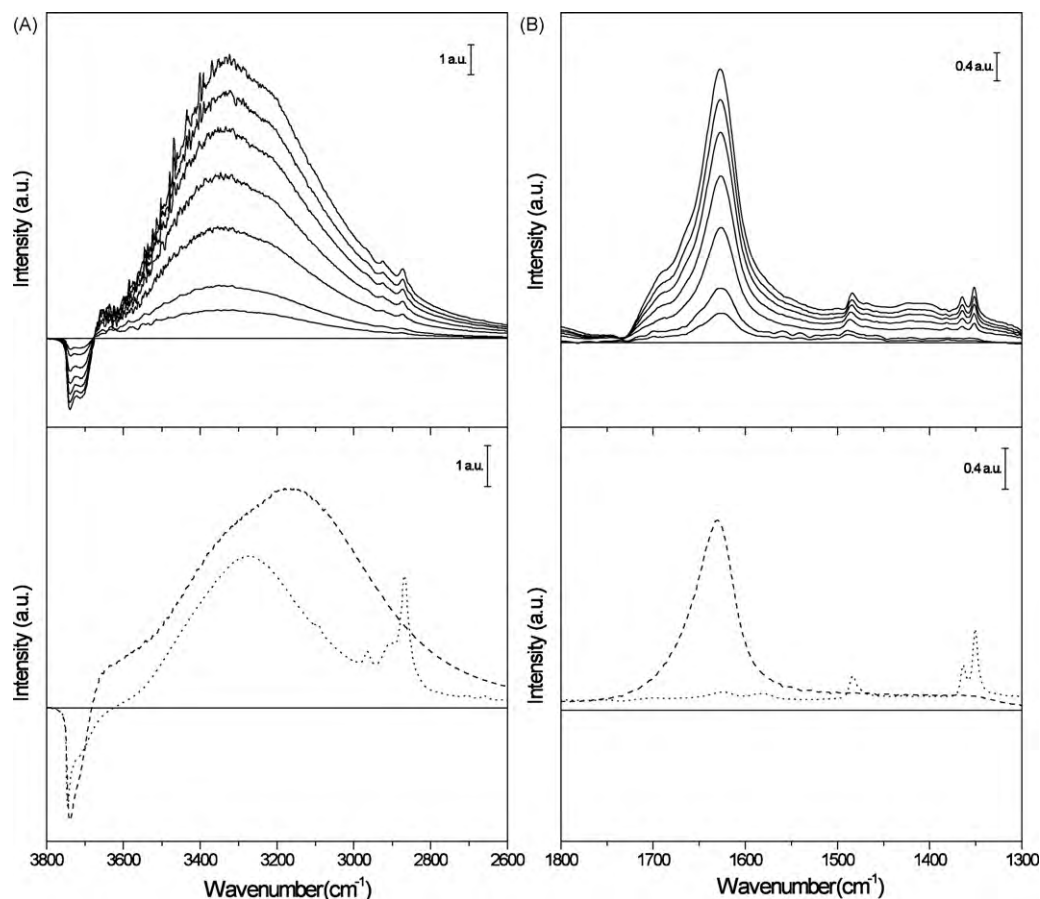


Fig. 4. Upper part: FT-IR difference spectra of C-2-OL adsorbed at room temperature on the Pd/SiO₂ catalyst in the range 3800–2600 cm⁻¹ (section A) and 1800–1300 cm⁻¹ (section B). Lower part: FT-IR difference spectra related to the adsorption on Pd/SiO₂ catalyst of H₂O (dashed line) and 2,5-DHF (dotted line) at the equilibrium pressure of 8.3 and 9.1 mbar, respectively. (Section A) 3800–2600 cm⁻¹ range; (section B) 1800–1300 cm⁻¹ range.

Table 1
Observed vibrational frequencies (cm^{-1}) of 2,5-DHF, 2,3-DHF and furan adsorbed on Pd/SiO₂ catalysts.

Compound	Mode	Frequency
2,5-DHF	C–H str.	2972
	C–H ₂ str.	2910
	C–H ₂ str.	2865
	Asym. CH ₂ sciss.	1484
	Sym. CH ₂ wag	1365
	Asym. $\Delta\text{CC-H}$ bend	1351
2,3-DHF	C–H str.	3113
	C–H str.	2972
	C–H str.	2931
	C–H str.	2903
	C–H ₂ str.	2872
	C–H ₂ str.	2868
	C=C str.	1624
	α,β -CH ₂ sciss.	1480
	α,β -CH ₂ sciss.	1455
	$\Delta\text{CC-H}$	1375
	Furan	C–H str.
C–H str.		3131
C=C str.		1600
C=C str.		1489
C=C str.		1380

adsorbed on silica (3800–2600 cm^{-1} range and the conspicuous band at 1630 cm^{-1} , due to the bending mode). Spectral contributions coming from the chemisorbed 2,5-DHF are relatively weaker.

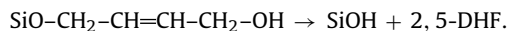
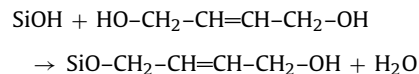
The spectra are completely consistent with that arising from the adsorption of C-2-OL, so suggesting that the vapour-phase interaction of this molecule with the Pd/SiO₂ catalysts give rise to the formation of H₂O and 2,5-DHF species.

In a parallel experiment, C-2-OL has been adsorbed on the silica support alone, and the same spectra as with the Pd catalyst have been recorded. This is clear evidence that the reaction is a dehydration of C-2-OL without any intervention of the metallic centres, catalysed by the acidic surface of silica. It is therefore reasonable to assume that 2,5-DHF is the observed product, because no double bond migration has probably occurred. The bands observed at 1484, 1365 and 1351 cm^{-1} are therefore attributed, respectively, to the CH₂ scissor, symmetric CH₂ wag and asymmetric $\Delta\text{CC-H}$ bend mode of the 2,5-dihydrofuran ring (Table 1) [18,19].

The cyclodehydration mechanism of C-2-OL to 2,5-DHF is expected on thermodynamic grounds, because the related ΔG^0 is slightly negative. Its mechanism, in the presence of either acidic or basic sites, was recently studied using the AM1 semiempirical method [20]. Such calculations show that conversion takes place without any activation barrier.

In the present case the reaction probably occurs via a chemisorbed species. As alcohols react on silica with formation of

esters of silicic acid [21], the following scheme can be envisaged:



A probable mechanism of the cyclodehydration reaction of C-2-OL to 2,5-DHF on silica surface is shown in Scheme 2. This also constitutes the first stage (a) in the reaction route described in Scheme 3.

The reactivity of C-2-OL in ethanol solution and in the gas-phase thus appears radically different. This can be accounted for considering that in the former case, the diol alcoholic moieties are stabilized by solvation interactions, so hindering the possible cyclization of the molecule. In the absence of the solvent, the 1,4-OH groups are free to form the more stable five member cyclic compound. Moreover, as said above, alcohols react on silica with the formation of Si–O–R groups: it is therefore probable that the acidic silanols of silica when in contact with an ethanolic solution are not available for catalysing acidic reactions.

Another possible explanation is that the ethanol, reacting with the silica through the hydrogen bonding interactions between the surface silanol groups and the ethanol hydroxyl groups, deactivates the SiO–H surface not permitting the cyclodehydration mechanism.

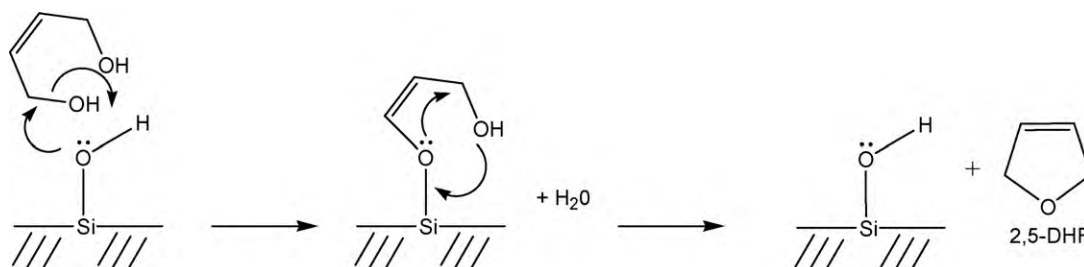
3.4. Further reactions at higher temperatures

Thermal treatments of the system as coming from the reaction of C-2-OL, i.e. in the presence of a mixture water/2,5-DHF, brings about the reaction of water with the metal nanoparticles, i.e. deactivation of the catalyst.

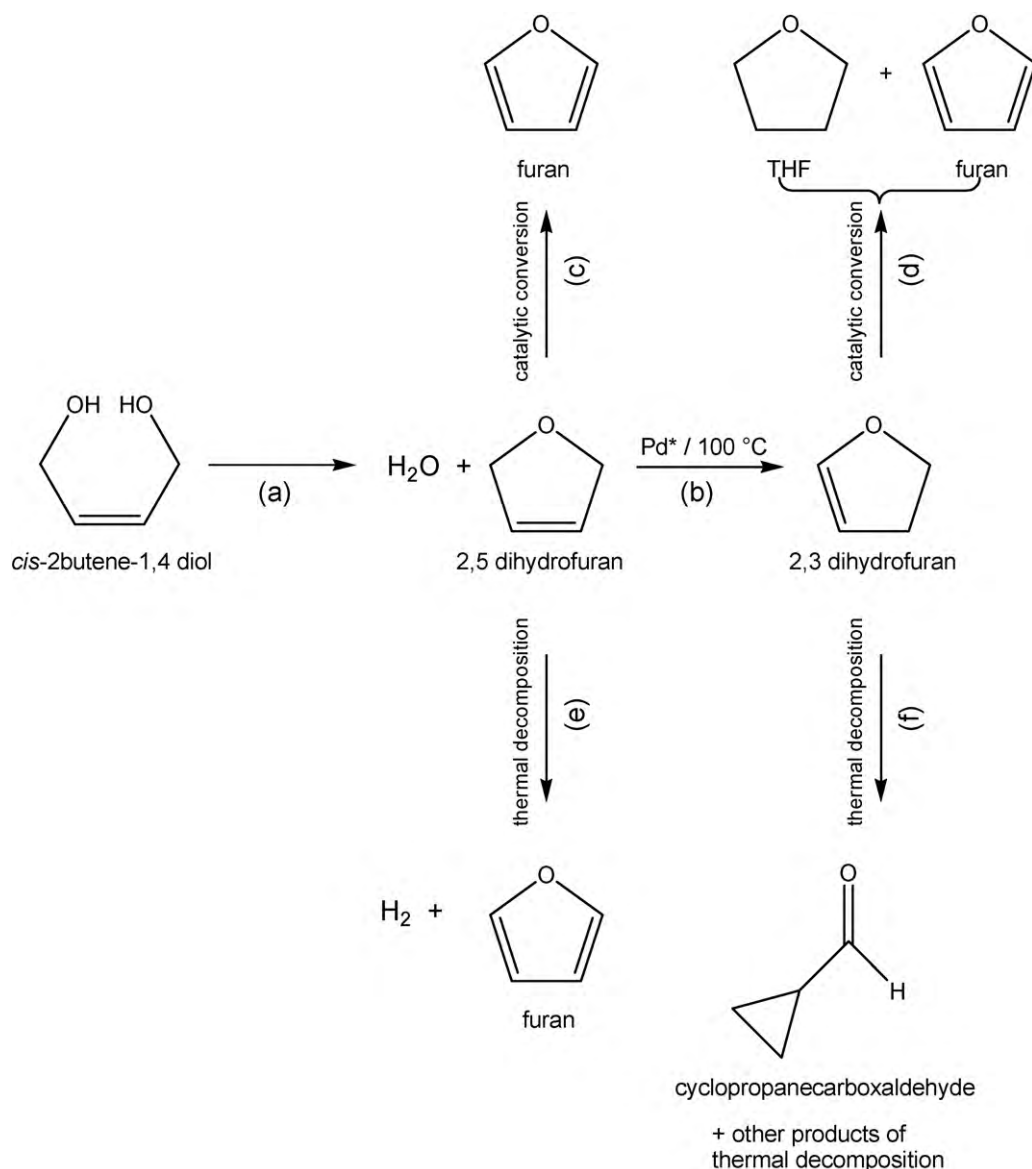
For this reason, the further possible reactions have been followed on fresh specimens of the Pd and Pt catalysts after the adsorption of the sole 2,5-DHF. Heating at 100 °C on Pd/SiO₂ catalyst brings about the changes in the IR spectra of adsorbed species described in Fig. 5 (section A). These indicate the conversion of 2,5-DHF (dotted curve) into 2,3-DHF (solid curve). Indeed, the C=C stretching band at 1624 cm^{-1} , nearly inactive in the symmetric 2,5 molecule, has a substantial intensity in the 2,3 isomer because of the asymmetry brought about by the nearby O atom. Simultaneously, other bands typical of 2,3-DHF appear (Table 1). This reaction does not take place on the support alone, as it is related to the presence of metal sites (Scheme 3b).

Such a reaction is expected on thermodynamic grounds, because 2,3-DHF is stabler, at room temperature, than 2,5-DHF by 7.47 kJ/mol [22]. A probable mechanism consists in the abstraction of one of the four H atom in position 1 or 4 (very reactive because in alpha position to an oxygen atom), with formation of an allylic intermediate.

Note the absence, in Fig. 5 (section A), of any band related to either furan or THF. This fact is worth of note, because at variance with literature reports. The isomerization of 2,5-DHF to 2,3-DHF



Scheme 2. Proposed cyclodehydration reaction of C-2-OL to 2,5-DHF on silica surface.



Scheme 3. Reaction network for the gas-phase interaction of C-2-OL on Pd/SiO₂: (a) cyclodehydration of to 2,5-DHF and H₂O on SiO₂; (b) selective isomerization of 2,5-DHF to 2,3-DHF; (c) catalytic conversion of 2,5-DHF to furan and H₂; (d) catalytic conversion of 2,3-DHF to furan and THF (e) thermal decomposition of 2,5-DHF to furan and H₂; (f) thermal decomposition of 2,3-DHF to cyclopropanecarboxaldehyde.

over 1% Pd/SiO₂ was recently reported by Monnier et al. [23]: the selectivity to 2,3-DHF was approximately 70%, and equimolar amounts of furan and tetrahydrofuran were also formed; the complete isomerization of 2,5- to 2,3-DHF required addition of CO to the reaction feedstream.

The authors explain this phenomenon assuming that the formation of furan and THF occurs on the basal (1 1 1) and/or (1 0 0) planes of the Pd crystallites and that the adsorption of CO reduces the size of surface Pd ensembles present on these facets, so that disproportionation of 2,5-DHF to furan and THF is suppressed.

In our case, in order to understand the complete isomerization of 2,5-DHF to 2,3-DHF (without formation of furan and THF) it is useful to remember the FT-IR characterization of the catalyst in Section 3.2: the adsorption of CO on Pd/SiO₂ catalyst causes the growing of two bands at 2080 and 1930 cm⁻¹ related, respectively, to coordinatively-unsaturated Pd sites (corners and edges of crystallites) and (1 0 1) and (1 0 0) planar surfaces of Pd nanoparticles.

Hence, the population of coordinatively-unsaturated Pd sites is significant (note the intensity of the related FT-IR band centred at ca. 2080 cm⁻¹), thus favouring the selective isomerization of 2,5-DHF to 2,3-DHF at corner and edges of crystallites.

Fig. 5 (section B) reports the results of the isomerization reaction of 2,5-DHF promoted by 2.5% Pt/SiO₂ catalyst: together with the bands related to 2,3-DHF (i.e. the intense of C=C stretching mode at 1624 cm⁻¹), other bands are seen due to species arising from the catalytic conversion of 2,5-DHF to THF and furan. It is probable that, in this case, the larger amount of platinum (2.5%) and the larger size of particles (40 nm), exposing flat surfaces, favours the disproportionation reaction of 2,5-DHF to furan and THF.

It is worth of note that for Pt/SiO₂ catalyst it was necessary to rise the temperature up to 150 °C, this result being in agreement with the overall higher activity of supported Pd systems in olefin isomerization with respect to analogous Pt samples [24–26].

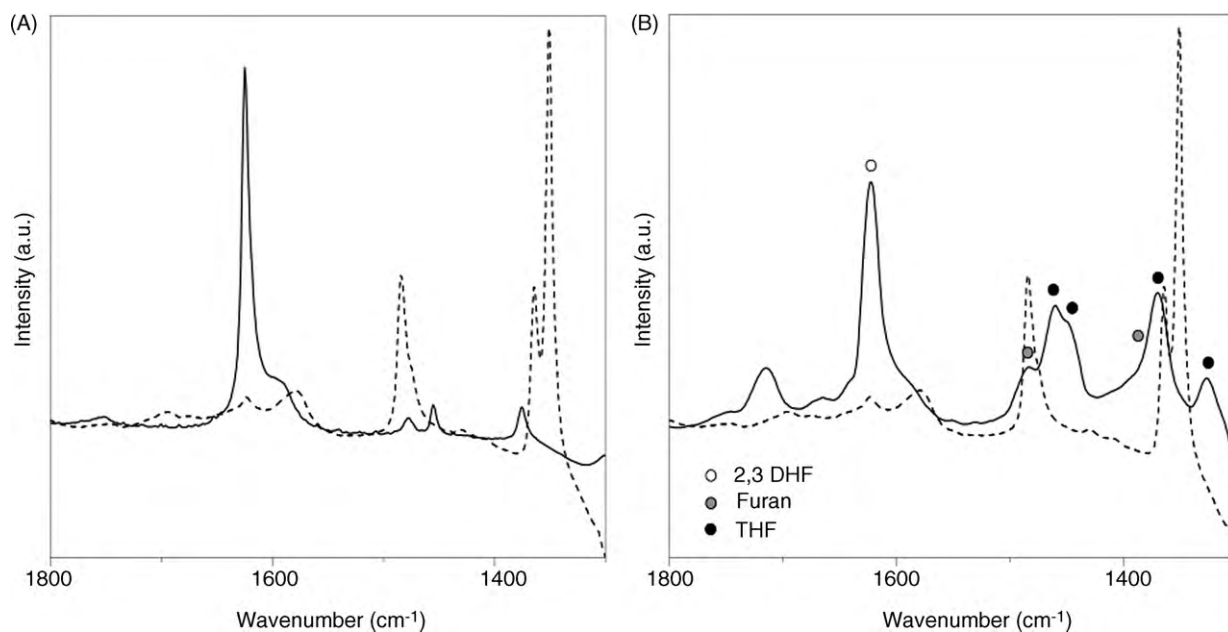


Fig. 5. (Section A) FT-IR spectra of 2,5-DHF adsorbed on Pd/SiO₂ catalyst before (dotted line) and after (full line) heating at 100 °C. (section B) FT-IR spectra of 2,5-DHF adsorbed on Pt/SiO₂ catalyst before (dotted line) and after (full line) heating at 150 °C.

As a final step, the reaction has been studied of both 2,5- and 2,3-DHF upon heating at ca. 250 °C (steps c and d of Scheme 3). This causes, in agreement with the literature [27], in both cases the expected dehydrogenation of DHFs to furan, which was accompanied in the case of 2,3-DHF with a partial disproportionation to both furan and THF.

If the catalysts were deactivated by the presence of water, thermal decomposition of the two DHFs is observed. In the literature the product of thermal transformation of 2,3-DHF is identified as cyclopropanecarboxaldehyde [28], a molecule with the same gross composition C₄H₆O. In the case of 2,5-DHF the product of thermal reaction is furan [29,30] (steps e and f of Scheme 3).

3.5. Adsorption modes of products and reactants

Molecules observed at the surface of catalysts in the present work are basically 2,3-DHF, 2,5-DHF and furan. The question arises what is the modality of interaction of all these species with the surface, both as it concerns the silica part and the metallic portion. Let us consider 2,3-DHF which has a fairly intense C=C stretching mode, so that the involvement of this functionality in the adsorption can be monitored: the other molecules probably show a similar behaviour.

Fig. 6 shows the IR spectra concerning the adsorption of this molecule on the Pd catalyst at room temperature and at increasing

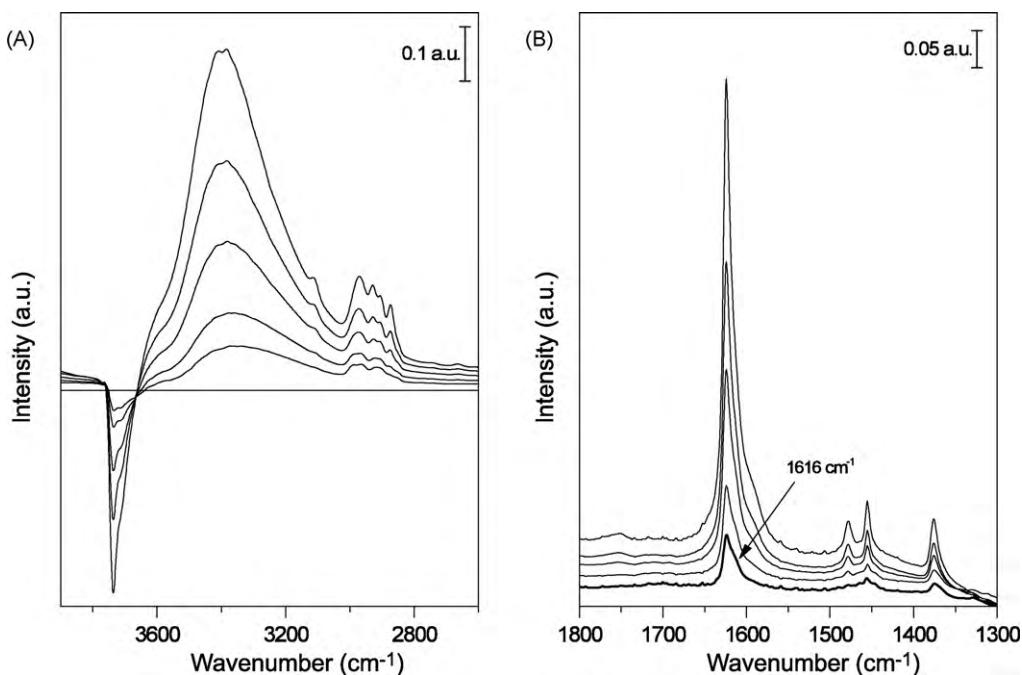


Fig. 6. FT-IR difference spectra related to the adsorption of 2,3-DHF, at increasing equilibrium pressure, in the range of 3800–2600 (section A) and 1800–1300 cm⁻¹ (section B).

equilibrium pressures. Section A reports the O–H stretching region, and section B that of C=C stretching. In the former region, the two bands at 3735 and 3715 cm^{-1} (due to the isolated silanol and the terminal species in a pair, respectively) decrease and a broad band at ca. 3390 cm^{-1} increases, due these silanols species H-bonded to 2,3-DHF molecules. The extent of the shift (ca. 350 cm^{-1}) is strongly indicative of a coordination through the O atom. Indeed, this is the order of magnitude of the shift imparted to the SiO–H stretching mode by O-containing molecules like ethers [31].

As the double bond in 2,3-DHF is not directly engaged in the interaction, its frequency coincides with the gas-phase molecule, and is observed at 1624 cm^{-1} (Fig. 6, section B). Also physisorbed molecules contribute to this adsorption. A shoulder of the main band is observed at 1616 cm^{-1} . Both the main component and the shoulder are also observed in the interaction of 2,3-DHF with the support alone. Comparison with the literature [32] shows that interaction of silanol species SiO–H with the olefinic double bond is weak and shifts the C=C stretching mode by only 8–10 cm^{-1} . The interpretation of the 1616 cm^{-1} band is therefore the double interaction of a 2,3-DHF molecule via both the oxygen atom and the double bond, favoured by the relatively high silanol population.

The question arises of the modality of adsorption on the metallic particles. A molecule with a C–C double bond may interact with a metal surface in various ways, by forming π -type adducts or doubly σ -coordinated species, to leave aside more complex ethylenic species formed at higher temperatures [6–8]. In these two cases, a substantial decrease in the C–C bond order takes place, so that the related C–C vibration markedly decreases. In the present case, however, no bands related to metallic centres are present in the spectra of 2,3-DHF adsorbed on the catalyst. This fact may be due to the limited surface exhibited by the metallic phase, as indicated by the TEM characterization of the catalysts.

Another possible reason, though, is the orientation of the double bond with respect to the surface. As shown by Sheppard and De La Cruz, because, at the surface of a metal, the bulk electrons respond to the oscillating dipoles of a molecule with a mirror image dipole, the selection rule is different from those at the surface of insulators, and in particular parallel vibrations become inactive [4].

The absence of C=C stretching bands in the spectra seem to be an indication of the fact that all molecules studied in the present work lie flat on it, so that the metal-surface selection rule becomes operative

4. Conclusion

The comparison between the reactivity of the catalyst with that of the support alone has enabled a fairly complete characterization of the vapour-phase interaction of C-2-OL with silica supported Pd and Pt nanoparticles. The reaction network reported in Scheme 3 envisages a few steps, all of which fairly expected, the ensemble of which, however, constitutes an original picture. The reason why the chemistry of C-2-OL in ethanol solutions is drastically different has

been highlighted. Curiously, the IR technique affords information on the overall reactivity and on the nature of the species adsorbed on the silica support, but not on the metallic phases, because of the metal/surface selection rule.

Acknowledgement

Thanks are due to Regione Piemonte (projects B18 and E28) for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.05.011.

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