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Selective butadiene hydrogenation by Pd nanoparticles deposed onto nano-sized oxide supports by CVD of Pd-hexafluoroacetylacetonate

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ABSTRACT

The organometallics chemical vapor deposition (OM-CVD) technique, using $Pd(hfac)_2$ as a precursor, was employed for the preparation of a series of heterogeneous catalysts based on Pd nanoparticles supported on nanometric oxides (CeO₂, ZnO and TiO₂). The properties of metal nanoparticles were tuned by proper pretreatment of the oxidic support.

Complete decomposition of Pd precursor during formation of the metal phase by hydrogen reduction was investigated by TPRD-mass spectrometry analysis, and the obtained nanoparticles were characterized by CO-DRIFT spectroscopy and HR-TEM microscopy.

Butadiene selective hydrogenation to butene, a well known structure-sensitive reaction, was used to test the performances of the systems prepared.

 Pd/CeO_2 catalyst showed the best selectivity to butene with the lowest amount of undesired butane, result ascribable to the morphology of palladium nanoparticles.

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1. Introduction

In the field of heterogeneous catalysis operated by supported metal nanoparticles (hereinafter referred to as NPs) it is well established that the catalytic properties exerted by NPs are size dependent [1], and moreover, when structure sensitive reactions are considered, performances, as activity and selectivity to desired products, are strongly dependent on the morphology of supported NPs [2].

Thus, size, composition, morphology and crystal structure of the metal NPs can largely influence the rate of several elementary steps and control the selectivity to desired products, as well as to undesired ones.

Tuning the shape, i.e. the ratio between edges, corners and different exposed crystal planes (facets) and keeping the size in the nanometric range is one of the key point in the development of supported NPs based catalysts.

Chemical vapor deposition (CVD) techniques [3] can be fruitfully exploited for the preparation of *ad hoc* materials, as they normally yield quite narrow particle size distribution and cleaner precursor decomposition pathways [4]. CVD based methodologies have found many applications in the field of nanoparticles and films deposition on powder supports [5]. Volatile metal precursors are nowadays products commercially available and less exotic than they were in the past, some of them being largely used in the microelectronics industry [6].

We have recently reported that CVD allows the easy tuning of structural properties of metal nanoparticles [7] and that can be successfully applied to the preparation of NPs supported on oxidic materials with different properties [8]. In particular, multistep methodology provides supported well formed, crystalline, homogeneously dispersed nanoparticles that show superior catalytic performances if compared to "standard" catalysts [9].

Partial hydrogenation of dienes and alkynes is a reaction of great industrial importance [10]. Butadiene is an impurity in C4 alkenes produced by cracking and butane/butadiene mixtures have to be purified before butene transformations, such as polymerization or alkylation processes.

Butene purification is actually performed by selective hydrogenation of butadiene. A good process will consequently work in such a way that the complete hydrogenation of butadiene into butenes takes place, while avoiding any butane formation. Palladium is still the reference catalytic metal for butadiene hydrogenation. However, it has been shown that its activity and selectivity can be strongly influenced by many factors like the metal dispersion, the nature of the support, and the preparation method. The improvement of selectivity still remains an important issue.

Butadiene selective hydrogenation is sensitive to the surface structure; the hydrogenation rate has been found to be more rapid with the more open (111) Pd face than with the close-packed (100) surface [11].



Keywords: Palladium Cerium oxide Zinc oxide Titanium dioxide 1,3-Butadiene hydrogenation Nanoparticles

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For these reasons this transformation can be considered as a good test reaction due to its sensitivity to the size and the shape of supported metal nanoparticles and as an important reaction in its industrial applications at the same time.

Recently was reported the catalysts design, i.e. the optimized preparation, of palladium supported nanoparticles exposing the desired (111) faces, however such nanoparticles were in the tens of nanometers dimensional range [12].

Here, we wish to report about the development of Pd catalysts by Pd(hfac)₂ OM-CVD as an easy preparation method for palladium nanoparticles, falling in the nanometric dimensional range, supported on different nanometric oxides, namely ZnO, CeO₂ and TiO₂. Appropriate thermal pretreatments were used to tune the surface properties of the oxides with the aim of control the dispersion and, in some extent, the morphology of the supported Pd NPs. Surface and structural properties of the NPs were then characterized by means of infrared spectroscopy of adsorbed CO, a typical surface sensitive technique and by HR-TEM, which is instead a bulk technique. The catalysts were then tested in butadiene traces selective hydrogenation, a typical surface-sensitive reaction, in order to reveal the different properties of supported metal nanoparticles (dimension, morphology, i.e. exposed facets, etc.). Finally some structure-properties relationships were drawn and discussed.

2. Experimental

2.1. Materials

The nanometric oxides (NanoactiveTM TiO₂, ZnO, and CeO₂) were used as received (NanoScale Materials Inc.). Palladium hexafluoroacetylacetonate (hereinafter denoted as $Pd(hfac)_2$) was purchased from Strem Chemicals and used as received. All the gases were purchased from SIAD S.p.A. (Bergamo, Italy) and were research grade (at least 99.995% purity), gases were used as received, only He was purified by passing through a gas-purifier (Supelco).

2.2. Catalysts preparation and characterization

Around 500 mg of support (TiO₂, ZnO, CeO₂) were calcined 1 h at 300 °C in O₂ flow, and then cooled down to RT in a inert gas flow. These materials were denoted as TiO₂, ZnO₂, CeO₂A samples.

On the other hand TiO₂, ZnO_, CeO₂B samples were simply evacuated (turbo-molecular pump and liquid N₂ trap, final vacuum 10^{-5} mbar) at RT for 2 h in order to remove most of physisorbed water.

Specific surface area after heat treatments was measured by single point method nitrogen physisorption under flow conditions with a PulseChemisorb2700 apparatus (Micromeritics).

CVD of Pd(hfac)₂ was conducted in static mode as already reported elsewhere [8]: the appropriate amount of Pd precursor (namely 24.5 mg) was thoroughly mixed, by a magnetic stirring bar, with the activated supports (0.5 g) in a Schlenk flask under Ar atmosphere at RT, then the sealed flask was kept at 80 °C overnight in a oven.

All the samples were then transferred in a U-shaped Pyrex reactor and reduced at 300 °C under H_2 flow (flow of 50 mL min⁻¹) for 1 h, then cooled down to RT in Ar flow (50 mL min⁻¹).

Pd loading was determined by ICP-MS (X Series II, Thermo Electron) after microwave digestion of reduced catalysts in 3:1 HCl/ HNO_3 mixture. The measurements largely confirmed the nominal 1% wt. load (real Pd loadings are comprised between 0.9% and 1.1% wt.).

TPRD analysis and CO chemisorption tests were performed using a home-made reactor stand/DRIFTS reaction chamber. Apparatus details are described elsewhere [13]. TPRD analysis was performed under H₂ 5% by vol. in He (flow = 20 mL min⁻¹) with a heating rate of 5 °C min⁻¹ from RT to 550 °C. The samples (20 mg *ca.*, diluted in quartz powder) were held on the glass frit of a U-shaped Pyrex reactor and selected mass channels (HF (m/z = 20); methane (m/z = 15); H₂O (m/z = 18); CF₃ (m/z = 69); 2-propanone (m/z = 58); CF₃CO fragment (m/z = 97); CO (m/z = 28); CO₂ (m/z = 44); CF₃COCH₃ (m/z = 112); 2,4-pentandione (m/z = 200)) were monitored by an on-line mass spectrometer.

CO chemisorption experiments were made according the following procedure: before chemisorption, the samples (20 mg *ca*. deposed on a KBr bed) were reduced in situ at 300 °C for 30 min under 20 mL of hydrogen flow. A mass spectrometer-monitored pulsed CO chemisorption was performed at RT until the saturation of carbonyl adsorbed on Pd bands was reached (injected volume 50 μ L, CO 50%, Ar 50%) [8].

The morphology and size distribution of the supported metal particles were evaluated by HR-TEM micrographs. The powder samples have been further grinded and dispersed in isopropanol in an ultrasound bath. A drop of the suspension has been deposited on the carbon grid which, after solvent evaporation under vacuum, has been inserted in the column of the JEOL Jem-2010 EX high resolution transmission electron microscope.

Pictures were taken at $250,000-800,000 \times$ magnifications, spanning wide regions of several support grains in order to provide a well representative map of the catalyst system.

Distribution histograms of metal particles numbers and volumes versus diameters were evaluated from about 300 to 550 counts per sample.

2.2.1. 1,3-Butadiene hydrogenation catalytic tests

Catalysts, 10 mg *ca.*, dispersed in 450 mg quartz powder, were loaded in a U-shaped Pyrex reactor, and reduced at 300 °C under H₂ flow for 1 h (H₂ flow 20 mL/min, heating rate 5 °C/min). Catalytic tests were conducted on the reduced catalysts by feeding a reaction mixture of 1000 ppm of H₂ and 500 ppm of 1,3-butadiene diluted in He. The reaction was monitored from RT to 400 °C (heating rate 5 °C/min) by an online quadrupole mass spectrometer (HPR-20 QIC gas analysis mass spectrometer system/Hiden Analytical Ltd.) connected downstream to the reactor. The QMS was calibrated with a mixture of 1,3-butadiene, 500 ppm; 1-butene, 500 ppm; *n*-butane, 500 ppm diluted in He. Since MS does not allow to distinguish the three butene isomers (1-butene, *cis*-2-butene and *trans*-2-butene) hereinafter we will generally refer to "butene".

3. Results and discussion

3.1. Catalysts preparation

Two series of three supported Pd catalysts, one on activated TiO_2 , ZnO and CeO_2 supports (A series) and one on non-activates oxidic supports (B series), were prepared by the OM-CVD of the volatile Pd precursor Pd(hfac)₂. A general scheme of the experimental set-up has been described elsewhere [13].

The OM-CVD was carried out at 80 °C overnight, this temperature was chosen in order to ensure the complete sublimation of Pd precursor avoiding any residue to be left in the support powder. As a result of the interaction (adsorption) of Pd precursor the support materials originally white (TiO_2 and ZnO, whereas CeO₂ is pale yellow) turned to a vivid yellow color. Finally, the adsorbed Pd precursor on oxide powder was converted in supported metal nanoparticles by a reductive treatment at 300 °C under H₂ flow and at the end of this treatment all the catalysts turned to gray color due to the formation of supported Pd NPs.

This preparation method was simple and effective, since the use of solvents and operations such as filtration, washings typical of

Table 1

Selected properties of Pd catalysts, oxide pretreatment temperature and Pd loading (measured by ICP-MS).

Catalyst	Pretreatment T of support (°C)	Pd loading (wt.%)
Pd/TiO ₂ _A	300	1.0
Pd/ZnO_A	300	0.9
Pd/CeO2_A	300	1.1
Pd/TiO ₂ _B	RT	1.1
Pd/ZnO_B	RT	1.0
Pd/CeO ₂ _B	RT	0.9

the preparations by traditional "wet methods" were avoided. The final properties of the catalysts obtained are summarized in Table 1.

3.2. TPRD characterization

The decomposition of adsorbed Pd(hfac)₂ was investigated by TPRD experiments, by means of an on-line QMS, in order to follow the evolution of adsorbed molecules and of gas phase decomposition products. The aim was to find out temperature and conditions suitable in order to obtain supported palladium metal particles starting from the adsorbed Pd precursor.

QMS analysis of evolved gas products (see Fig. 1, only the decomposition profiles of Pd(hfac)₂/ZnO_A was reported as an example) shows, as the main feature, a series of intense peaks of several decomposition products fragments located between 200 and 300 °C. More in detail the following peaks were evident: methane (m/z = 15) and CF₃ fragment (m/z = 69) show two peaks at 205 and 265 °C; 2-propanone (m/z = 58) and CF₃CO fragment (m/z = 97) show only one peak at 265 °C. CO (m/z = 28) and CO₂ (m/z = 44)evolution occurs with a very intense peak located respectively at 225 and 219 °C with weak shoulders at 270 °C. Minor peaks can be detected at lower temperature (<150 °C) during the initial stages of ligand decomposition. It should be stressed that above 300 °C all the mass channel profiles monitored became flat and the evolution of any decomposition products is totally absent, thus confirming that ligands decomposition results to be complete just below this temperature. For these reasons the reduction under hydrogen flow at 300 °C is an appropriate method to obtain clean supported Pd metal (nano)particles, since no residues of the hfac ligand are left on support and/or metal surface that can be further eliminated at higher temperatures. Usually, in such cases, an evo-



Fig. 1. TPRD profiles of Pd(hfac)₂/ZnO_A sample; curve with open squares: $m/z = 15(CH_3)$; curve with open triangles: m/z = 58 (CH₃CO); curve with open circles: m/z = 69 (CF₃); black curve with no markers: m/z = 97 (CF₃CO).



Fig. 2. HR-TEM micrograph and particle size distribution histogram of Pd/TiO $_2$ A sample.

lution of methane at higher temperatures, resulting from hydrogenation of carbon containing adsorbed compounds, occurs [14].

3.3. HR-TEM characterization

Samples of the A series, which are expected to have the smaller Pd NPs, were analyzed by HR-TEM microscopy.

The registered micrographs show that the support oxidic materials are present as aggregates of nanometric particles with different dimension and structure: titania consists in crystalline grains with irregular shape and a mean diameter of 10 nm; ZnO is again in the form of agglomerated crystalline grains but of spherical shape and mean diameter of 13 nm; finally cerium oxide is in the form of agglomerates of well formed nanocrystallites with mean diameter as small as 5 nm.

Supported Pd NPs fall in the nanometer range for all the investigated samples and, more in detail, Pd/TiO_2 _A sample shows the presence of Pd NPs with a mean diameter of 1.2 nm (see Fig. 2), whereas in Pd/ZO_A sample NPs are even smaller having a mean diameter of 0.8 nm (see Fig. 3). For Pd/CeO₂_A sample Pd NPs were not detectable by standard HR-TEM measurements, because of the high electron density of CeO₂ as already reported [15].

3.4. CO-DRIFTS characterization

Infrared spectroscopy of adsorbed CO is a powerful technique for the identification of almost all the metal surface sites present on the catalysts surface: CO adsorbed on Pd^0 metallic particles or on Pd^{n+} oxidized sites show distinctive absorption bands whose



Fig. 3. HR-TEM micrograph and particle size distribution histogram of Pd/ZnO_A sample.

attribution can be easily performed according to the existing literature as reported in Table 2 [16–18].

The exposed faces and low coordination sites (corners and edges) of metal nanoparticles, and also their defectivity can be derived from the analysis of the pattern (bands shape and wavenumbers) of adsorbed CO spectra.

As a general consideration, in the spectra of CO adsorbed on palladium nanoparticles, four main components can be revealed and they can be assigned on the basis of the existing literature (passing from high to low wavenumbers): (a) linear carbonyls on Pd(111)faces and/or on defects; (b) twofold bridged carbonyls on Pd(100) faces; (c) twofold bridged carbonyls on Pd(111) faces; (d) threefold bridged carbonyls on Pd(111) faces.

Due to the different pretreatments of the oxidic supports, the degree of interaction between Pd precursor and the support can vary between the A and B series, and, in turn, also the final structural and morphological properties of supported Pd nanoparticles are expected to be different. A similar effect was reported for Pd/MgO catalysts, prepared by impregnation of Pd(acac)₂ of differently pretreated magnesia. In that case Pd nanoparticles on activated MgO showed uniform size distribution in the sub-nanometer range, whilst the nanoparticles supported on non-activated magnesia were larger and with a broader size distribution [14].

The HR-TEM characterization, reported above, substantially confirms the presence of (sub)-nanometric Pd NPs in the samples obtained from activated oxidic support materials (the A series).

 Pd/TiO_2 A shows three main bands (see Fig. 4 (a)), two of them appearing just after the first CO pulse: one, very sharp and intense, is located at 2112 cm⁻¹ and can be ascribed to terminal CO the

Table 1	2

Frequency (cm ⁻¹)	Assignment	Reference
2080 2060 1980–1994 1864–1936	Linear CO on exposed (111) Pd faces Linear CO on Pd defects Twofold bridged CO on (100) Pd faces Twofold bridged CO on (111) Pd faces	[16]
1967–1977 <1960 1932	Twofold bridged CO on (100) Pd faces Hollow bonded CO(111) Pd faces Threefold hollow and bridge bonded CO(111) Pd faces	[17]
2091 2085 1986 1937	Linear CO on defects Pd sites CO linearly bonded to Pd atoms Bridge-bonded CO on Pd (100) planes Bridge-bonded CO on Pd (111) planes	[18]

second band is located at 1973 cm⁻¹ and it is typical of CO adsorbed on highly defective Pd (111) planes, as commonly found in TiO₂ supported palladium sites.

The third band, located at 1898 cm^{-1} , starts to develop only after the third CO pulse and can be ascribed to three-folded CO. The first two bands undergo a small blue shift to higher wavenumbers increasing the CO coverage (from the 1st to the 5th CO pulse) passing, respectively, from 2107 to 2112 cm⁻¹ and from 1963 to 1973 cm⁻¹.

Pd/TiO₂_B sample shows similar bands (see Fig. 4(b)), with some exceptions: the high frequency band is red-shifted to 2067 cm⁻¹, and low frequency bands are more convoluted, but two peaks can be recognized and are located at 1934 and 1870 cm⁻¹. It should be noted that CO absorption bands in this sample do not suffer any relevant change during CO pulses (wavenumbers shifts and/or intensity changes). Such data agree with the presence of Pd nanoparticles with more extended planes (i.e. larger nanoparticles) where lateral interaction between adsorbed CO are less important, resulting in negligible frequency shifts of the bands [19].

Ceria supported Palladium NPs show a more complex CO absorption bands pattern: high frequency band is broader and in one sample two components are clearly present, also in the low frequency region at least three or four bands are present.

Pd/CeO₂_A sample shows a peculiar behavior in the high frequency region (see Fig. 5(a)): at low CO coverage (1st CO pulse) an intense band located at 2045 cm⁻¹ readily appears and progressively blue-shifts to higher wavenumbers up to 2067 cm⁻¹. In the meanwhile a shoulder, located at 2042 cm⁻¹, becomes apparent at high CO coverage (after 4th pulse).

In the low frequency region of two- to three-folded adsorbed CO two bands are present, one located at 1922 cm^{-1} ascribable to two-folded CO and another one at 1845 cm^{-1} ascribable to three-folded CO. The 1745 cm^{-1} band can be attributed to bridged carbonates adsorbed on oxidic support [20]. According to the literature [21] the band at higher wavenumbers can be attributed to linear CO on Pd nanoparticles and the band located at 2042 cm⁻¹ to multibonded CO on Pd atoms [22,23] that are formed only at high coverage.

Pd/CeO₂_B sample shows a quite different bands profile (see Fig. 5(b)): the high frequency band shifts from 2061 (1st CO pulse) to 2081 cm⁻¹ (4th CO pulse), while the low frequency ones are strongly convoluted and at least two components of similar intensity can be found and are located at 1945 cm⁻¹ and around 1865 cm⁻¹. The different ratio between the CO adsorbed species with respect to those found for Pd/CeO₂_A sample accounts for a different morphology of palladium nanoparticles (i.e. different relative amounts of Pd sites of different exposed planes, steps, corners and/or different particles size). In particular the lower ratio (two-folded CO)/(three-folded CO) can be related to the presence



Fig. 4. CO-DRIFTS spectra of Pd/TiO2_A (a) and Pd/TiO2_B sample (b) recorded after pulses of CO (numbers indicate the corresponding nth pulse).



Fig. 5. CO-DRIFTS spectra of Pd/CeO2_A (a) and Pd/CeO2_B (b) sample recorded after pulses of CO (numbers indicate the corresponding *n*th pulse).

of less extended exposed planes. Finally the general shift to higher wavenumbers of the whole band system accounts for a more electropositive character of the supported nanoparticles (less back-donation from metal to CO anti-bonding orbitals) or can be explained by geometrical effects (less dipole–dipole coupling due to larger particles).

When measuring ZnO supported samples a strong absorption was noticed over the whole spectral range after in situ reduction of samples, also resulting in a low S/N ratio. In particular for Pd/ ZnO_B sample to record spectra of absorbed CO was not possible, due to the very low S/N ratio and/or to the low intensity of CO absorption bands.

Pd/ZnO_A sample showed three bands (see Fig. 6): linear CO one located at 2073 cm⁻¹ and the second broad one, centered at 1886 cm⁻¹ falling in the region of three-folded CO. The high frequency band can be attributed to linear CO on Pd(111) faces more than to CO on defective Pd sites, since the low wavenumbers band falls in the region typical of twofold bridged CO on (111) Pd faces [16].

CO(linear) to CO(bridged) ratio can be considered an important parameter for the estimation of particles dispersion and/or morphologies in supported metal nanoparticles of different metals [9,17,24] and in general a good agreement between CO-FTIR and HRTEM data was found.

It should be stressed that, due to the different kind of bands present on the different supports, a rigorous comparison between all the catalysts cannot be performed. However, it is possible to compare A and B samples, supported on the same oxide, drawing some reliable conclusions.

In our case A series samples show, in general, the higher CO(lin.)/CO(br.) ratio accounting for more dispersed Pd nanoparticles. The only exception is Pd/CeO₂_B sample which shows a



Fig. 6. CO-DRIFTS spectra of Pd/ZnO_A recorded after pulses of CO (numbers indicate the corresponding *n*th pulse).

CO(lin.)/CO(br.) ratio higher than the corresponding ceria based A sample, thus suggesting a higher dispersion and/or a different shape of supported palladium nanoparticles. Since the more dispersed supported metal nanoparticles are usually the ones derived from precursor adsorbed on activated oxide [14], the CO-DRIFTS data suggest a different shape of Pd NPs.

3.5. Butadiene hydrogenation performances

Butadiene hydrogenation is a consecutive reaction that, according to reaction conditions (temperature, butadiene and hydrogen partial pressures, ratio, etc.) can show very different behavior in terms of conversion and selectivity to butene (the selective hydrogenation product) or to butane (the total, unselective, hydrogenation byproduct) (see Scheme 1). However, if reaction parameters



Scheme 1. 1,3-Butadiene hydrogenation reaction scheme.

are kept constant, as in our case, butadiene hydrogenation can be considered a typical surface sensitive reaction and the selectivity to butene can mainly be related to palladium nanoparticles morphology (i.e. exposed planes) [12].

During our butadiene hydrogenation tests all the A and B series catalysts synthesized show good activity and selectivity in butadiene selective hydrogenation: almost all of them are active at low temperatures (namely $50 \,^{\circ}$ C) and butene selectivity is always higher than 50% (see Fig. 7).

Hydrogenation performances versus reaction temperature show a general trend for all the catalysts studied: (i) a sudden increase of butadiene conversion at low temperatures, above 100 °C almost total conversion is reached by all systems investigated; (ii) a low selectivity to butene (i.e. total hydrogenation to butene occurring) around 100 °C followed by an increase in butene selectivity that reaches 100% above 200 °C.

The different structural and, in some cases, morphological properties of the supported Pd NPs influence the selectivity of the hydrogenation reaction.

In general A series samples show higher selectivity towards butene, the selective hydrogenation product, coupled to low amounts of butane, the unselective hydrogenation product, at least at low reaction temperatures (below 100 °C). On the other hand B



Fig. 7. Selected catalytic performances at different reaction temperatures of Pd/TiO₂_A (a); Pd/TiO₂_B (b); Pd/CeO₂_A (c); Pd/CeO₂_B (d); Pd/ZnO_A (e); Pd/ ZnO_B (f). Butadiene conversion: very dark gray bar; butene selectivity: light gray bar; butane selectivity: dark gray bar.

series catalysts show lower butene selectivities and corresponding higher butane selectivities at the same reaction temperatures. This difference in the catalytic behavior of the two catalysts series can be explained by the structural/morphological evidences obtained from the characterization data. The higher butene selectivities observed for the A series systems are in good agreement with the presence of more dispersed Pd nanoparticles in A series samples with respect to the B series ones. Indeed CO-DRIFTS and HRTEM data revealed the presence of highly dispersed palladium nanoparticles in A series catalysts as the result of the better interaction between Pd precursor and the activated oxide supports [14].

Moreover, the high butene selectivity can be related also to the morphology of palladium nanoparticles exposing the (111) faces that were reported to be very selective in butadiene hydrogenation to butene [12]. In our case the presence of Pd NPs exposing the (111) faces was clearly revealed for Pd/TiO₂_A and Pd/ZnO_A samples by CO-DRIFT spectra reported in Figs. 4(a) and 6. Namely these two catalysts are the ones showing the higher selectivity.

The only exception to this general picture was represented by Pd/CeO₂_B catalyst, that keeps high selectivity to butene (always higher than 90%) over all the temperature range investigated with a butane selectivity never exceeding 10%. This peculiar behavior can be ascribed to the unique morphology (i.e. exposed planes), among the samples here reported, of palladium nanoparticles.

Also Pd/ZnO_A shows comparable performances, being more active at low temperature but with a slightly lower selectivity to butene (only 73% at 100 $^{\circ}$ C).

Finally the increase of reaction temperature above 300 °C (data not shown) leads to a decrease in butadiene conversion as well as butene selectivity and can be originated from the sintering of Pd nanoparticles, generating less selective low-index planes, as already reported for Pd catalyst reduced at high temperatures [25,26].

4. Conclusions

Pd catalysts supported on different oxides, namely TiO_2 , CeO_2 and ZnO, prepared by CVD of Pd(hfac)₂ precursor show some valuable properties for heterogeneous catalysts like high dispersion of metallic phase, easiness of preparation and generally high activity in the desired reaction (1,3-butadiene hydrogenation). In addition the proper choice of support and the tuning of its surface properties allow one to control the structural and surface properties of the supported Pd NPs. Catalysts obtained from pretreated supports show the presence of highly dispersed NPs; on the contrary, in non pretreated supports larger NPs were present. Moreover, it was also possible to tune the morphology of NPs (the exposed planes). The catalytic behavior was found to depend mainly on these two structural parameters. In particular A series samples showed higher selectivity to butene with respect to B series ones with some exceptions. Indeed Pd/CeO₂_B sample shows a selectivity to butene higher than 90% in a wide range of reaction temperatures that was ascribable to the peculiar morphology of the Pd NPs.

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