

Selective Hydrogenation of Diketones on Supported Transition Metal Catalysts

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Abstract

The hydrogenation of α -diketones yields α -hydroxyketones or vic-diols, both compounds of great interest in fine chemistry. The reaction tests were the liquid phase hydrogenation of 2,3-butanedione and 2,3-pentanedione at mild conditions. The objectives of this work were evaluating the effect over the activity and selectivity of: (a) different transition metallic phase based catalysts supported on activated carbon, (b) the symmetry of the reactants and (c) solvents. The physicochemical characterization of the catalysts was carried out by ICP, XRD, TEM, N₂ adsorption and XPS. The keto-enol equilibrium of diketones was studied by 1H-NMR. All the catalysts were active in both reactions. In terms of activity, Pt and Rh were the best active phases. For both reactants the highest selectivity towards hydroxyketones were achieved with Pd, while Ru was the most selective towards the diol. Both the activity and selectivity followed similar patterns in the hydrogenation of both diketones. The greater activity of Pt was attributed to the high dispersion of the active metal phase in this catalyst and the high efficiency of Pt for C=O bond reduction. The high selectivity of the Pd catalysts towards the intermediate product was attributed to many effects: (i) a lower interaction of the hydroxyketone with the active site as compared to the diketone, (ii) the easy reducibility of the C=C double bond on Pd, provided by the keto-enol tautomerism of diketones.

Graphic Abstract



Keywords Selective hydrogenation $\cdot \alpha$ -Diketones \cdot Transition metals \cdot Palladium \cdot Hydroxyketones

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1 Introduction

The hydrogenation of α -diketones is a reaction of great interest in the industries of fine chemicals and chemical specialties. The products are α -hydroxyketones and/or vic-diols as shown in Fig. 1. The α -hydroxyketones (e.g. acetoin, acetyl ethyl carbinol, propionyl methyl carbinol, etc.) are usually employed as chemical intermediates or as active components in the industry or scents and fragrances [1, 2]. Vic-Diols (e.g. 2,3-butanediol, 2,3-pentanediol, 2,3-hexanediol, etc.) are usually employed as solvents and humidifiers in the cosmetics industry, and as plasticizers or intermediates for the polymers industry (Vulkollan) [3]. Though currently being of great interest, only a few reports on the simple hydrogenation of α -diketones [4–6] or their chiral hydrogenation [7–9] can be found in the open literature.

Duan et al. [4] hydrogenated butanedione and acetoin in the gas phase, obtaining selectivity of 99.9% towards 2,3-butanediol when using Ni/SiO₂ catalysts. Zuo et al. [10] studied the hydrogenation of 2,3-butanedione in the liquid phase employing Pt/Al₂O₃ catalysts modified with different transition metal promoters.

The platinum VIII group (Ru, Rh, Pd, Os, Ir and Pt) have been used as hydrogenation catalysts. During catalytic hydrogenation, the second-row group VIII metals (Ru, Rh, Pd) often show behavior different from that of the third-row group (Os, Ir, Pt), e.g. the former give substantial isomerization in olefin hydrogenation, while the second group no [11]. Besides Ru and Rh are highly active and selective catalysts, particularly, for the hydrogenation of aromatic compounds [12]. On the other hand, Os and Ir have found much less use as hydrogenation catalysts, although their high selectivity but very low activity in a few processes as the hydrogenation of α , β -unsaturated aldehydes to allylic alcohols [11] or the hydrogenation of crotonaldehyde [13], besides, at mild conditions Ir is a well-known hydrogenolysis catalyst of carbon carbon bonds [14].



Fig. 1 Scheme of consecutive hydrogenation of a $\alpha\text{-diketone}$ to b $\alpha\text{-hydroxyketone}$ and c vic-diol

For the reaction sequence $A \rightarrow B \rightarrow C$ it can be deduced that in order to produce B with high selectivity the following aspects must be considered:

- The reaction should be performed under chemical control in order to the intrapellet diffusion resistance. If the residence time inside the pellet is reduced, desorption of the intermediate B product is favored and so, total hydrogenation to C is disfavored.
- Mild reaction conditions are preferred so that the energy barrier for deep hydrogenation is not surpassed and C formation is disfavored. High temperatures (T > 398 K) and pressures (P > 100 bar) favor the reactions of overhydrogenation and hydrogenolysis, thus reducing the yields to the desired products [15]. Some side reactions are also responsible for catalyst deactivation.
- Low hydrogen concentrations are preferred in order to disfavor the consecutive reaction intermediates leading to deep saturation.

Carbonaceous catalysts are widely used in industrial reactions, especially for hydrogenation processes [16]. In a recent review Campisciano et al. [12] focused the attention on the carbon nanoforms in metal-based reactions, among them hydrogenation reactions of ketones. These catalysts have several advantages in comparison to alumina and silica supported catalysts, e.g. low cost, inertness, high superficial area and stability. Also these catalysts show low deactivation; it is possible to modify the chemical surface during the catalyst preparation and it is easy to recover the metallic phase from the spent catalysts [16].

So the objectives of this work were evaluating the effect over the activity and selectivity during the hydrogenation of α -diketones of: (a) different commercial and synthesized transition metallic phase based catalysts supported on activated carbon, (b) the symmetry of the reactants and (c) several solvents. The reaction tests were the liquid phase hydrogenation of symmetrical 2,3-butanedione (BD) and non-symmetrical 2,3-pentanedione (PD). In the hydrogenation of BD, the main products are acetoin (AC) and/ or 2,3-butanediol (BDO). In the hydrogenation of PD the products are 2-hydroxy-3-pentanone (2H3P), 3-hydroxy-2-pentanone (3H2P) and/or 2,3-pentanediol (PDO).

2 Experimental

2.1 Catalysts Preparation

The method of incipient wetness impregnation was used for preparing the Pt catalyst. The chosen activated carbon was Norit RX3. This was impregnated with an acidic solution of the H_2PtCl_6 precursor at pH=1 with HCl. After the impregnation with the acidic solution, the catalyst was dried overnight at 373 K. The theoretical mass percentage of Pt in the final catalyst was 5% (5Pt-C).

The Pd, Ru and Rh activated carbon supported catalysts were of commercial type: BASF 5Pd-C, 5Ru-C and 5Rh-C.

Before the catalytic tests, all catalysts were reduced in a flow of hydrogen (20 mL min⁻¹) at 673 K for 4 h.

2.2 Catalysts Characterization

The catalysts were characterized by ICP, XRD, XPS, TEM and nitrogen physisorption.

The metal loading of catalysts was obtained by digesting the sample and then analyzing the solution by ICP technique, in Perkin Elmer Optima 2100DV ICP-OES equipment.

X-ray diffractograms were obtained in a Shimadzu XD-1 equipment, using CuK_{α} radiation (λ =1.5405 Å) filtered with Ni. The 2 θ range between 10 and 90° was scanned at a rate of 1° min⁻¹. The samples of catalysts and a typical carbon support (RX3) were prepared by milling the material to a fine powder and treating it in hydrogen.

The particle size of the supported metals was studied by transmission electron microscopy (TEM). Samples of the reduced ex situ catalyst were milled and then dispersed in a 50% v/v ethanol:water solution for further analysis. The measurements were performed in JEOL 100CX Transmission Electron Microscope, operated at 100 kV. For each catalyst, a set of digital images were taken in order to measure particle diameters. The Digital Micrograph software was used. Then, size particles distributions were obtained.

XPS measurements were carried out with a Multitech UniSpecs equipment, with a MgK (hv: 1253.6 eV) radiation source and a pass energy of 50 eV. The XPS system analysis pressure was kept at 5.10^{-7} Pa. Catalyst samples were reduced ex situ for 1 h with H₂ at 673 K and treated in situ for 10 min in the instrument chamber before recording the spectrum. A careful deconvolution of the spectra was made. The areas of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30–70% proportions. The reference binding energy (BE) was the C1s peak at 284.5 eV.

Brunauer–Emmett–Teller surface area (S_{BET}) of the prepared catalysts was determined by means of nitrogen physisorption at 77 K following the BET model in a Quantachrome Corporation NOVA-1000 equipment. Before the measurement, the samples were degassed at 573 K in a vacuum.

1H-NMR were obtained in a Bruker Avance II 300 MHz spectrometer using CDCl_3 as solvent. Chemical shifts are reported in δ units and are referenced to the residual solvent signal (7.26 ppm).

2.3 Catalytic Activity Tests

The catalysts were tested with the hydrogenation reactions of 2,3-butanedione (BD) and 2,3-pentanedione (PD). The catalytic tests were performed in a stirred tank reactor (100 mL Parr type) with PTFE-coated internals. The used solvents were isopropanol (Cicarelli, 99.5%) and cyclohexane (Cicarelli, 99.5%). BD was supplied by Sigma-Aldrich (Cat. N°11038, purity 99%) and PD by Fluka (Cat. N°69043, purity 99%). Reactants and solvents were distilled before the catalytic tests. The catalysts were ground to a particle size lower than 10 µm and the stirring rate was 1200 rpm in order to eliminate internal and external mass transfer resistances. The reactor was operated under the following experimental conditions: 353 K, 20 bar hydrogen pressure, 0.188 M initial reactant concentration (BD or PD), 61 mL reaction media volume, 50 mg catalyst mass. The catalysts were previously reduced for 4 h at 673 K. Reactants and products were analyzed by means of gas chromatography in a Shimadzu GC-2010 equipped with a flame ionization detector and a 30 m long J&W InnoWax 19091 N-213 column.

3 Results and Discussion

3.1 Characterization Results

Table 1 shows the results of metal load as determined by ICP, the metal dispersion (D) as calculated from particle size information obtained by TEM (dp_{TEM}), and the XPS results. The ICP results indicate that the metal load is in most cases close to the theoretical value, with an error margin of 2%.

The results of TEM can be seen in Figs. 2 and 3. Figure 2 shows the micrographs of the catalyst samples in which the different phases of the catalyst can be clearly distinguished. Metals (black dots) and support (light color particles). It can be seen in Fig. 2 that metallic particles had a spherical shape and were dispersed throughout the support homogeneously.

Table 1 ICP, TEM and XPS results

Catalyst	Metal load (wt%)	dp _{TEM} (nm)	D (%)	XPS	
				Region	BE (eV)
5Pt-C	5.1	4.1	30	4f _{7/2}	71.3 (56.4%) 73.2 (43.6%)
5Pd-C	4.9	5.2	24	3d _{5/2}	335.4 (54.1%) 336.7 (45.9%)
5Rh-C	5.0	4.5	28	3d _{5/2}	307.0 (46.4%) 308.8 (53.6%)
5Ru-C	4.9	11.1	11	3 <i>p</i> _{3/2}	461.6 (44.3%) 463.1 (55.7%)





Fig. 3 Distribution of metal particle size for different activated carbon supported catalysts



$$I_{TEM} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2} \tag{1}$$

where dp_i is the particle diameter and n_i is the number of particles of diameter dp_i . Table 1 shows the results of the calculation of the average metal particle size.

The metal dispersion (D) of the catalysts was calculated from the TEM particle size values using Eq. (2).

$$D(\%) = \frac{\left(6 \cdot \sigma \left[\frac{at}{m^2}\right] \cdot PA\left[\frac{g}{mol}\right] \cdot 10^{10}\right)}{\rho \left[\frac{g}{m^3}\right] \cdot dp \left[\mathring{A}\right] \cdot NA} \cdot 100\%$$
(2)

where σ : atomic surface density [at m⁻²]; PA: atomic weight of the metal [g mol⁻¹]; ρ : density of the metal [g m⁻³]; dp: particle diameter (average) [Å]; NA: Avogadro's Number [17]. The model particle of Sundquist [18] was used, with a mixture of 70% < 111 > planes, 25% < 100 > planes and 5% < 110 > planes. This model gives surface densities of 14.2, 14.5 and 15.5 atoms nm⁻² for Pt, Pd and Rh, considering fully centered cubic structures (fcc). These values were mainly taken from the review of Scholten et al. [17]. In the case of Ru the most common crystal habitat is hexagonal close packed (hcp) though fully centered cubic crystals are also found in supported systems [19]. Calculating for fcc Ru (cell size a=3.83 Å) with Sundquist's model gives an atomic surface density of 14.91 atoms nm⁻².

Table 1 shows the results of the calculation of the average particle diameter (dp_{TEM}) and the metal dispersion (D), of the different catalyst samples. The order found for the particle sizes was: 5Pt-C < 5Rh-C < 5Pd-C < 5Ru-C. The Pt

catalyst has the lowest particle size (dp = 4.1 nm) and hence the highest dispersion (D = 30%). The Ru catalyst has the biggest particle size (dp = 11.1 nm) and the lowest dispersion (D=11%). Rh and Pd have intermediate values, with dp = 4.5 nm (D = 28%) and 5.2 nm (D = 24%), respectively. The differences in the metal particle size and metal dispersion could be attributed at least in part to the interaction between the precursor and the surface groups of the carbonaceous support during the catalyst preparation procedure. The metal precursors salts in solution are present as metal complexes. These complexes can be tetrahedral or octahedral. The magnitude of the molecules could affect the magnitude of the dispersion forces between them during the impregnation. If the dispersion forces are proportional to the size of the complexes, bigger complexes would give higher dispersion [3]. Besides, due to electronic or geometrical effects, different carboxylic groups on the carbonaceous supports could interfere and give higher dispersion of the metallic phase.

Figure 4 shows the XPS spectra of the Pd and Rh 3d regions of the 5Pd-C and 5Rh-C catalysts, the Ru 3p region of the 5Ru-C catalyst and the Pt 4f region of the 5Pt-C catalyst pretreated in hydrogen at 673 K. Figure 4 shows the Pd and Rh $3d_{5/2}$ and $3d_{3/2}$ signals separated by approximately 5.25 and 4.75 eV, and the $4f_{5/2}$ and $4f_{7/2}$ signals of Pt separated by 3.35 eV, in total accordance with literature values [20, 21]. The points are the experimental data and the curves beneath are the corresponding deconvoluted peaks. The XPS results of the catalysts can be found in Table 1.







Fig. 5 X-ray diffractograms of the RX3 support and the metal catalysts

The deconvolution of the metal (Me) $3d_{5/2}$, $3p_{3/2}$ and $4f_{7/2}$ spectra resulted in two peaks for all the samples, indicating the presence of two different Me species on the catalysts: a metal reduced Me° specie and other electrodeficient one Me^{δ +}, with δ =2 for Pd or Pt, while δ =3 for Rh and Ru [3, 21]. For the cases of Pt and Pd, the major species was the reduced one, with values of 56.4% and 54.1%, respectively. In the case of Rh and Ru, the concentrations of reduced species (46.4 and 44.3%) were the lowest.

The X-ray diffractograms of the support and catalysts are shown in Fig. 5. In all the diffractograms a large peak at 26.4° is seen, that corresponds to C < 002 > phase of graphite [16]. Then an intense peak at $2\theta = 39.9^{\circ}$ of the 5Pd-C catalyst was attributed to the < 111 > plane of metallic Pd° [22]. In the 5Pt-C catalyst a small peak appears at $2\theta = 39.7^{\circ}$, which would correspond to the < 111 > plane of Pt [23–25]. For 5Rh-C catalyst, a peak of the < 111 > plane of Rh was observed at $2\theta = 41.2^{\circ}$. In the case of the 5Ru-C catalyst, an intense peak of the < 101 > main plane of Ru was observed at $2\theta = 43.3^{\circ}$, as reported by other authors [26]. The low intensity in 5Pt-C and 5Rh-C catalyst difractograms could be attributed to the small metal particle size observed by TEM.

Table 2 N₂ physisorption results

Catalyst	BET surface $(m^2 g^{-1})$	d _{pore} (nm)	$V_{pore} (cm^3 g^{-1})$
5Pt-C	896	2.4	0.59
5Pd-C	809	2.6	0.56
5Rh-C	360	7.3	0.54
5Ru-C	797	2.8	0.57

The textural properties of the support and the catalysts were also assessed by means of nitrogen physisorption. Type IV isotherms were got indicating the presence of hysteresis phenomena, typical of microporous solids. The pore distribution was obtained by means of the method Barrett-Joyner-Halenda method. The specific surface area, the pore size and the pore volume are indicated in Table 2. All metal catalysts had similar textural properties and only the Rh catalyst had a lower surface area and bigger average pore diameter than



Fig. 6 Results for BD hydrogenation. a Total conversion, b Selectivity to AC and c Selectivity to BDO

Table 3 Turnover frequencies (TOF) in the hydrogenation of BD and PD $\,$

	BD		PI	PD		
Catalyst	TOF (s ⁻¹)	r^{o} (mol. min ⁻¹ g _{cat} ⁻¹)	T	$OF(s^{-1})$	r^{o} (mol min ⁻¹ g _{cat} ⁻¹)	
5Pt-C	0.67	0.0031	0.	57	0.0027	
5Rh-C	0.38	0.0031	0.	34	0.0028	
5Ru-C	0.66	0.0021	0.	39	0.0013	
5Pd-C	0.37	0.0026	0,	31	0.0021	

Reaction conditions: $C_{diketone}^{\circ}$ =0.188 M, Wcat=50 mg, V=61 mL, T=353 K, P_{H2}=20 bar, Solvent: Isopropanol

the others, this could be attributed to different carbonaceous supports of the commercial catalysts tested.

3.2 Catalytic Activity Results

Some blank tests of BD and PD hydrogenation without catalyst were made in order to check any interference from the reaction vessel and pipelines. Conversion was lower than 1% after 8 h reaction time.

Results of BD catalytic hydrogenation can be seen in Fig. 6 and Table 3. As seen in Figure 6a, all catalysts were active in BD hydrogenation. The total conversion followed the order: Pt > Rh > Pd > Ru. The activity pattern matches the results of obtained metal dispersion, or metal particle size. With high dispersion and the small diameter particle, the total conversion of BD was increased, eventhough electronical or geometrical effects of the carbonaceous support could not be discarded as the support specific properties, such as the superficial groups or texture and porous structure could also modify the adsorption–desorption equilibrium of the reactants and products, and so forth.

Values of turn over frequencies (TOF) are presented in Table 3. They were calculated using values of metal dispersion and the initial reaction rates. The specific activity of a catalytic center per unit time for BD hydrogenation indicates that the order was $Pt \gg Ru > Rh \approx Pd$. Despite Ru catalyst has the poor dispersion, the good performance per site was attributed to the high interaction with C=O bond, in coincidence with Pt [27]. Pd and Rh catalysts showed lower levels of activity per site for BD hydrogenation.

In Fig. 6b the selectivity to AC for the different catalysts was observed. The most selective catalyst was Pd. It can be seen that for this catalyst the selectivity is high in the first 120 min of reaction (S_{AC} =98%) and then it slightly decreases to 95% up to 8 h. Pt and Rh catalysts were less selective to AC, especially after 8 h reaction time, they had selectivity values of 59% and 45%, respectively. The Ru catalyst was the least selective to AC.

 Table 4
 PD hydrogenation results. Selectivity values at an isoconversion condition of 50%

Catalyst	Solvent	Time (min)	S _(2H3P + 3H2P) (%)	S _{others} (%)
5Pt-C	Cyclohexane	38	81	19
5Rh-C	Cyclohexane	43	75	25
5Ru-C	Cyclohexane	145	66	34
5Pd-C	Cyclohexane	50	90	10
5Pd-C	Isopropanol	80	85	15

Others: PDO, esters, heavy products

Figure 6c shows values of selectivity to the vic-diol BDO during the hydrogenation of BD. The most selective catalyst was Ru, with ca. 80% at 8 h reaction time. This high selectivity was attributed in part to the high amount of surface Ru³⁺ species, that favors the adsorption of AC and to the capacity or Ru for hydrogenating C=O bonds [3]. Ru³⁺ is a hard Lewis acidic site and due to its high density charge would favour the adsorption of a carboxylic group of the α -diketone (Lewis basic site) and would favors its total hydrogenation to the butanediol. In the case of Pt and Rh, a growing selectivity can be seen. Pd was the least selective to the over hydrogenated product.

These results for BD hydrogenation are similar to those obtained previously with metal catalysts based on composite polymer-alumina supports [3, 5, 6]. They also correlate with other reports in the literature [9]. The Pd seems to be the most appropriated phase for obtaining self-hydrogenation product AC, while the other favors the over hydrogenation, especially Ru.

Tables 3 and 4 show the results of PD hydrogenation. In Table 3 TOF values for PD hydrogenation can be seen. Table 4 has selectivity values corresponding to points with 50% conversion. Since PD is an asymmetric diketone, the product of partial hydrogenation can be 3-hydroxy-2-pentanone (3H2P) or 2-hydroxy-3-pentanone (2H3P). In our analysis we have considered the selectivity to the intermediate products as the sum of the selectivity to these two isomers ($S_{(2H3P+3H2P)}$). The selectivity to other reaction products was indicated as Southers. The results indicate that the selectivity to the intermediate products followed the order Pd > Pt > Rh > Ru. These results show that the most promising active phase for producing the intermediate products is Pd. At 50% of PD total conversion, S_(2H3P+3H2P) for Pd was 90% when cyclohexane was the solvent and 85% when isopropanol was used, indicating a slight negative influence of the polarity of the solvent over the selectivity, but a notable negative influence on the conversion.

The conversion order was identical during the hydrogenation of BD or PD, irrelevant of the simetry of the substrate, suggesting that in part small metal particle sizes favor the hydrogenation rate. In terms of activity, Pt and Rh were the most active, followed by Pd, and finally, Ru. When the effect of the solvent is analyzed it can be seen that the reaction proceeds with a higher rate when cyclohexane is used as solvent. The effect of solvent in reaction rate could be attributed to solvent polarity. The polar solvents could be absorb over metal active sites, and compete with substrate and H_2 adsorption, reducing the reaction rate [3].

Table 3 shows TOF values of PD hydrogenation for the different catalysts. The order obtained was $Pt \gg Rh > Ru \approx Pd$. Just like BD hydrogenation, Pt shows the high activity per site. Rh, Pd and Ru present lower values. Gertosio et al. [28] found similar results when hydrogenating a reactant with alpha-diketonic functional groups in a C_{11} - C_{12} position. They used novel metal supported on SiO₂ and carbon, and found that the order of activity when comparing the initial rate was: Pt > Rh > Ru > Pd. In that work the Pd catalyst had an induction time higher than other metals: after activating, the metal conversion was complete. In our work, similar results were obtained, but no induction time was observed for any catalyst. This could be due to many reasons, like solvent effect, catalyst properties and/or differences in the thermal reduction treatment [29]. In our case, using a carbonaceous support favors the reduction of metallic active sites.

The dissociative chemisorption H_2 is done on reduced metallic sites Me°. The amount of available *d* electrons in the catalyst set was: Pd (d^{10}) > Pt (d^9) > Rh (d^8) > Ru (d^7). The rupture of H–H bond is favorable on sites with more *d* available electrons [30]. The selectivity pattern achieved in the hydrogenation of the diketones BD and PD could be associated to the electronic density in the external *d* orbital. It has been reported that the hydrogenation of BD on Pd supported over composite supports, gives high selectivities to the hydroxyketone product, being the addition of an H atom the rate limiting step [5].

Pd is a metal frequently recommended for performing the hydrogenation to intermediate products during the reaction of diketones [31, 32]. The loss of selectivity of Pt, Rh and Ru catalyst could be associated to over hydrogenation capacity. The differences found in selectivity during the hydrogenation of BD and PD can be attributed to the different capacities of adsorption of the C=O double bond. Pt, Ru and Rh easily chemisorb C=O through their π electrons. Pd has however a weaker interaction with this type of bonds. The alpha diketones coexist in two isomeric forms: the keto form (with two C=O bonds in the same molecule) and the enol form (with one C=O and one C=C bond) as shown in Fig. 7 [33–35].

In Fig. 8, 1H-NMR spectroscopy results of both diketones BD (Fig. 8a) and PD (Fig. 8b) are presented. The PD spectrum shows a signal between 5 and 5.25 ppm, which corresponds to a quartet; according to the multiplicity and chemical shift, this signal could be assigned to the *enol* form of PD. The absence of this signal for BD is due to enol form is below detection range of the technique. In other words, the *keto-enol* equilibrium of BD is much more displaced to the *keto*-form, and therefore the concentration of *enol* tautomer is below the detection limit of the experiment [36, 37].

The *enol* form has a C = C double bond that can be easily chemisorbed by any of the employed $M^{\delta+}$ active phases, especially Pd, beside sits weaker interaction with C = O bonds, it could explain the high selectivities to α -hydroxyketones [38, 39].

The hydrogenation of alpha- and beta-unsaturated aldehydes and ketones to saturated aldehyde or ketone, using noble metal supported catalysts were reported by Ide et al. [40]. These authors found that in terms of activity Pd was the phase with the best turnover frequencies. The Pd phase

Fig. 7 Keto-enol equilibrium of a generic diketone and proposed mechanism of consecutive reactions





Fig. 8 1H-NMR Spectra of a BD and b PD



Fig. 9 Scheme of the Horiuti–Polanyi reaction mechanism as applied to the hydrogenation of ketones over supported Pd catalysts. Hydrogenation of BD in the enol isomeric forms

was the most active phase for C = C hydrogenation, but failed in the hydrogenation of C = O for producing unsatured alcohols.

The high selectivity of Pd toward the hydroxyketone product can be explained by the occurrence of the Horiuti-Polanyi mechanism [41]. Over the Pd⁰ species dissociative chemisorption of hydrogen first occurs. On nearby Pd electrodeficient atoms (Pd^{δ +}) the C=C moiety in its enol isomeric form gets adsorbed via a π bond. Then one H atom forms a σ bond with one of the carbons (C₂) while the other one (C₁) remains adsorbed forming a σ bond with Pd^{δ +}. In the last step the addition of the H atom to the C_1 atom occurs with the subsequent desorption of the molecule (Fig. 9).

4 Conclusions

The amount of PD in the enol form, observed by 1H-NMR spectroscopy, was ca. 3 wt%; while the keto-enol equilibrium of BD could not be detected because the concentration of the enol form was below the measurement detection limits. The Pd phase has better interaction with C = C than

C = O bonds, besides the synergy of enol presence, good C = C adsorption and H_2 chemisorption leads to a high α -hydroxyketone selectivity for both reactions. On the other hand, the other metal active phases (Pt, Rh and Ru) showed lower selectivity to α -hydroxyketones especially at higher values of reaction time, when the formation of vic-diols were favored. This was especially true for Ru which was the most selective metal catalyst for getting the double hydrogenation product. As similar reaction mechanism occured for BD and PD, the asymmetry structure did not affect the pattern. The kind of solvent seemed to be slightly relevant for the selective hydrogenation of PD with Pd catalysts as the selectivity to the sum of hydroxyketone products in different solvents varied only ca. 5%. In terms of activity, the reaction was faster in cyclohexane phase than in isopropanol, indicating less interaction of the Pd catalyst with apolar solvents.

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Compliance with Ethical Standards

Conflict of interest No conflict of interest are presented for neither of the contributing author.

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