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Study of Monometallic Pd/TiO_2 Catalysts for the Hydrogenation of Succinic Acid in Aqueous Phase

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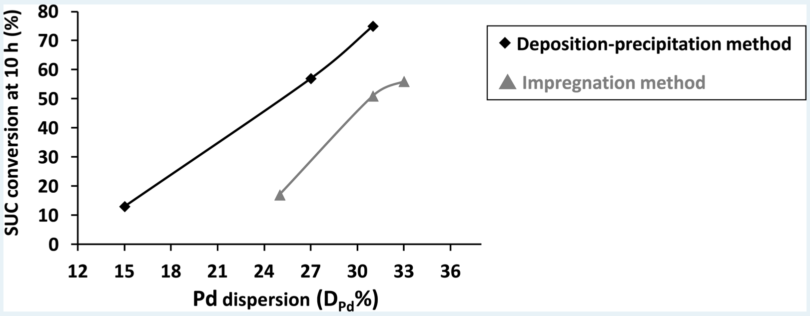
Supporting Information



ABSTRACT: A series of 2 wt % Pd/TiO_2 monometallic catalysts were prepared by varying some parameters, such as the nature of the precursor salt, the titania support, and the preparation method. The structural and textural properties of the catalytic systems were fully characterized by several physical and chemical techniques (inductively coupled plasma optical emission spectrometry, N_2 physisorption, H_2 chemisorption, transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy, powder X-ray diffraction, temperature-programmed reduction, X-ray photoelectron spectroscopy, and gas phase reaction of cyclohexane dehydrogenation). The catalytic performances were further estimated for the hydrogenation of an aqueous solution of succinic acid (SUC) performed in a batch reactor at 160 °C and under 150 bar total pressure. The results showed that all the Pd catalysts are very selective to produce γ-butyrolactone, the first hydrogenated product. However, the rate of succinic acid conversion is a function of both the Pd dispersion and the preparation method. The deposition−precipitation method allows one to obtain the highest performing 2 wt % Pd/TiO_2 samples during SUC hydrogenation in terms of activity and stability.

KEYWORDS: *Pd catalysts, preparation, hydrogenation, succinic acid, γ-butyrolactone*

1. INTRODUCTION

Succinic acid (SUC) (dicarboxylic acid of $C_4H_6O_4$ molecular formula) can be used as a precursor of many industrially important chemicals involved in various applications. The hydrogenation of succinic acid can notably yield 1,4-butanediol (BDO), tetrahydrofuran (THF), succinate salts, and γ-butyrolactone (GBL).[1−4] These compounds are involved in the production of valuable products that find a wide market as pharmaceutical and food products, as solvents, or as starting materials for polymers, such as polybutylene terephthalate (PBT) (high-performance resins for the automotive and electronics industries), polytetramethylene ether glycol (PTMEG), polybutyrate succinate (PBS), and polyamides (Nylonx,4).[5] On the one hand, most of the commercially available succinic acid is currently produced by a chemical process in which petroleum derivative compounds are used as a starting material.[6−10] On the other hand, a lot of research performed in the past decade showed that fermentative production of succinic acid from polysaccharides can be more cost-effective than the petroleum-based processes.[1−5,9−12] However, the fermentation processes are performed in the aqueous phase, which means that it may be economically viable to develop heterogeneous catalysts able to further hydrogenate SUC in this medium.[3,10,13] In fact, most of the reports on the SUC transformation in the liquid phase refer to the use of organic solvents (dioxane, ethanol).[14−19]

The proportion of the desired products issued from the SUC hydrogenation depends on both the type of catalyst and the reaction conditions being applied. Among the various heterogeneous catalysts examined for hydrogenation of

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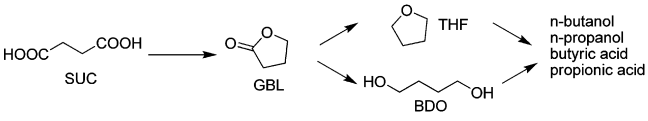
carboxylic acid such as maleic or succinic acid, Cu-, Ru-, and Pd-based catalysts are the most studied as monometallic systems or modified by different metals.[20−39] Due to their stability, noble metals supported on acid-resistant carbons were first considered as ideal for this application. In fact, several patents dealing with the hydrogenation of succinic acid have reported promising catalysts for the selective formation of BDO, THF, or GBL (according to Scheme 1), constituted of bimetallic or trimetallic systems. Examples of this technology include Re-doped Pd/C,[40−43] Re-doped Ru/C,[40,44] Re−Ag-doped Pd/C,[45] and Re−Sn- or Pt−Sn-doped Ru/C.[46] However, little information is provided on the stability or the potential leaching of catalysts during the reaction. During the hydrogenation of carboxylic acids in aqueous medium, a loss of activity was observed for Ru−Sn/C catalysts attributed to an important leaching of tin species.[47] Therefore, the authors showed that Pt addition on these bimetallic catalysts prevented that leaching and significantly improved the catalytic performances. More generally, the effect of the water solvent during the hydrogenation reactions of the carbonyl group was somewhat described in literature, involving different kinds of catalysts and experimental conditions.[48,49]

Scheme 1. Catalytic Hydrogenation of Succinic Acid (SUC) to γ-Butyrolactone (GBL), 1,4-Butanediol (BDO), and Tetrahydrofuran (THF)



In our previous studies dealing with the hydrogenation of an aqueous SUC solution at 160 °C under 150 bar,[50,51] we studied the effect of the addition of Re on 2% Ru and 2% Pd catalysts supported on C or TiO_2. The titania support was investigated due to its efficiency to prepare stable materials under hydrothermal conditions.[52,53] After addition of Re, the bimetallic catalysts become selective in BDO, whereas the monometallic systems lead selectively to the first hydrogenated products (GBL). These first studies were mainly focused on the influence of the Re addition onto the monometallic Pd catalysts, by varying the deposited Re loading and its introduction mode. In the case of Pd−Re/TiO_2 catalysts, two different methods of Re deposition on the monometallic parent catalyst were used: the successive impregnation and the catalytic reduction method. The first step of the preparation of these bimetallic catalysts is therefore based on the synthesis of monometallic parent Pd systems. In the present work, we prepared a series of Pd/TiO_2 catalysts by varying several parameters (preparation method, nature of the precursor salt, nature of the titania support, activation protocol, etc.) in order to examine their influence on the performances during the hydrogenation of an aqueous solution of SUC. The expected aim is to prepare active and stable Pd/TiO_2 catalysts for the transformation of SUC toward GBL under the aqueous phase. The structural and textural properties of the monometallic systems were fully characterized by several physical and chemical techniques (inductively coupled plasma optical emission spectrometry, N_2 physisorption, H_2 chemisorption, transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy, powder X-ray diffraction, temperature-programmed reduction, X-ray photoelectron spectroscopy, gas phase reaction of cyclohexane dehydrogenation). The hydrogenation reaction of SUC was performed in water in a batch reactor, with a 5 wt % SUC aqueous solution, at 160 °C and under 150 bar total pressure.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Two commercial titania (Degussa P25, specific area = 50 m^2 g^{-1}, and Mel Chemicals DT51, specific area = 90 m^2 g^{-1}), noted TiO_2 (P25) and TiO_2 (DT51), respectively, were used as supports. TiO_2, denoted TiO_2 (Synth), was also prepared in the laboratory, by sol−gel method using titanium isopropoxide as precursor and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$, Pluronic P123 from Aldrich) as templating agent.[54] The mixture obtained from these two solutions was maintained under stirring at 40 °C for 1 h, and thereafter treated in a closed Teflon vessel at 40 °C for 5 h. Finally, the solid was recovered by filtration of the obtained suspension and then dried 12 h at 60 °C. Before use, the support was calcined at 400 °C for 4 h.

Monometallic 2.0 wt % Pd/TiO_2 catalysts were prepared either by impregnation or deposition−precipitation method. For the impregnation technique (IMP), several palladium precursor salts were used: $Pd(NH_3)_4Cl_2$ (denoted $Pd_{N\text{-}Cl}$), $Pd(NH_3)_4(NO_3)_2$ (denoted $Pd_{N\text{-}NO}$), $PdCl_2$ (denoted Pd_{Cl}), K_2PdCl_4 (denoted $Pd_{K\text{-}Cl}$), and $Pd(C_5O_7O_2)_2$ (denoted Pd_{ac}). In the latter case, impregnation was performed using acetone as solvent. From other precursor salts, an aqueous solution was prepared with a defined pH value (1 or 11, controlled by addition of 32 wt % chlorhydric acid or 28 wt % ammonia, respectively) in order to favor ionic interactions (of $PdCl_4^{2-}$ or $Pd(NH_3)_4^{2+}$ complex, respectively) with the support during impregnation. After the impregnation step, the solvent was evaporated and the catalysts were further dried overnight in an oven at 120 °C. The supported catalysts were calcined under an artificial air flow (80% N_2 + 20% O_2, 3.6 L h^{-1}) at 300 or 400 °C for 4 h. Finally, they were reduced for 4 h in flowing H_2 (3.6 L h^{-1}) at 300 or 400 °C. For the deposition−precipitation method (DP), K_2PdCl_4 was exclusively used. The support was slurried with water, and an appropriate amount of this precursor salt was added to the suspension. Afterward, pH was adjusted and maintained at 11 by addition of solid KOH. The suspension was refluxed for 1 h, after which the mixture was cooled, filtered, washed, dried, and reduced with H_2 flow (3.6 L h^{-1}) at 300 °C for 3 h and finally passivated in 1% O_2/N_2 (1.8 L h^{-1}, 30 min).

A specific nomenclature was used to identify each catalyst, based on the following: (i) the nature of the used precursor salt, (ii) the pH value of the preparation medium, (iii) the temperature during calcination (C) and/or reduction (R) activation steps, and (iv) the nature of the TiO_2 support (P25, DT51, or Synth). For example, a monometallic 2 wt % Pd catalyst supported on TiO_2 (P25) prepared by impregnation from the $PdCl_2$ salt (at pH = 1), calcined, and reduced at 300 °C is associated with the following nomenclature: $Pd_{Cl(pH=1)}$C300R300/TiO_2 (P25).

Catalysts were characterized by several techniques according protocols described in the Supporting Information.

2.2. Hydrogenation of Succinic Acid. All experiments were performed in a Hastelloy Parr 4560 high-pressure reactor of 300 mL equipped with an electrically heated jacket, a turbine agitator with a magnetic driver, and a liquid sample line. In a typical reaction, the reactor was loaded with 120 g of a 5 wt %

succinic acid aqueous solution prepared by adding 6 g of solid SUC to 114 g of water and sonication (420 mmol L^{-1}) and 1 g of catalyst (molar ratio SUC/Pd ~250). After being purged with Ar, the reactor was heated to 160 °C and hydrogen was added to 150 bar. The reaction was performed in the absence of external and internal mass transfer.

The aqueous samples taken from the reactor at regular intervals were analyzed using both gas chromatography (HP-5 column, 30 m × 0.25 mm column, thickness 0.25 μm) and a high-performance liquid chromatography instrument equipped with UV and RI detection (ICSep Coregel 107H column at 40 °C, 0.005 N H_2SO_4 as mobile phase at a flow rate of 0.5 mL min^{-1}). The main reaction products consisted of γ-butyrolactone, tetrahydrofuran, and 1,4-butanediol. Byproducts analyzed in the liquid phase were *n*-butanol, *n*-propanol, butyric acid, and propionic acid (Scheme 1). The mass balance was checked by measuring total organic carbon (TOC) in the liquid phase using a Shimadzu TOC-V_{CSH} analyzer. This measure indicates if significant C−C cracking reactions occurred, transferring compounds from the aqueous phase to the gas phase. Indeed, the difference in the TOC concentration introduced into the reactor and the measured TOC in the product solutions was an estimation of formed gaseous products. Some experiments were performed twice; the reaction rates and selectivity to the various products were reproducible (differences between values inferior to 5%).

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Catalysts. The characteristics of the supports are summarized in Table 1.

Table 1. Characteristics of the TiO_2 Supports (P25, DT51, and Synth)

	S_p[a] (m^2 g^{-1})	V_p[a] (cm^3 g^{-1})	d_p[a] (nm)	average crystallite size[b] (nm)	sulfur (wt %)
TiO_2 (P25)	52	0.13	14.5	21 (anatase), 38 (rutile)	<0.1
TiO_2 (DT51)	88	0.30	12.2	18 (anatase)	2.4
TiO_2 (Synth)	195	0.34	6.3	6 (anatase)	<0.1

[a] Specific surface area (S_p), pore volume (V_p), and pore diameter (d_p) determined by N_2-sorption. [b] Average crystallite size determined by XRD analysis.

Table 2 gives the list of the monometallic 2 wt % Pd/TiO_2 catalysts prepared either by impregnation method (IMP, entries 1−12) or by deposition−precipitation (DP, entries 13−15), as well as their main characteristics. In addition to the preparation method, several parameters were modulated in the course of the catalyst synthesis, with the aim of optimizing the palladium dispersion on the TiO_2 support. This table shows that the dispersion, determined by H_2 chemisorption, varies from 0 to 33%, depending on the characteristics of the support, the precursor salt, and the activation treatment (see discussion in Supporting Information). The best dispersion values are achieved for the following formulations: $Pd_{Cl(pH=1)}$C300R300/TiO_2 (P25) (D = 33%), $Pd_{Cl(pH=1)}$C300R300/TiO_2 (Synth), and $Pd_{K-Cl(pH=11)}$R300/TiO_2 (Synth) (D = 31%), and $Pd_{K-Cl(pH=11)}$R300/TiO_2 (DT51) (D = 27%). On P25 and Synth TiO_2 supports, the impregnation of the $PdCl_2$ salt leads to high values of dispersion, whereas, on DT51, the DP method involving K_2PdCl_4 salt seems to be more adapted.

Some surprising results are obtained, such as the change in the turnover frequency (TOF) for cyclohexane dehydrogenation with the palladium dispersion (entries 1−4 and 5−7) and the low hydrogen chemisorption capability associated with a low hydrogenation activity (entries 9−11), which may be due to the presence of sulfur on the DT51 support. These specific behaviors are discussed hereafter.

3.1.1. Change in TOF Value with Dispersion. On Pd/TiO_2 (P25) prepared by IMP (entries 1−8 in Table 2), the results obtained for the model reaction of cyclohexane dehydrogenation, occurring on the metallic phase only and considered as structure insensitive,[55−57] are not in direct agreement with the values of dispersion. Despite the different dispersion values of the various Pd/TiO_2 (P25) catalysts, the specific activities (A_s) given in Table 2 are similar, around 3 mol h^{-1} $g_{Pd}{}^{-1}$, except for the catalyst prepared from K_2PdCl_4 precursor (entry 8 in Table 2). TOF values are therefore somewhat different for these samples, especially for those presenting dispersion around 10%.

The TOF values determined on all samples are not constant and vary in the 0.26−0.77 s^{-1} range, depending on the dispersion of the catalyst, contrary to what is usually observed for various metallic functions deposited on different classical oxide supports (C, Al_2O_3, and SiO_2 especially).[55,57] This singular behavior is not observed on Pd/TiO_2 catalysts prepared by DP (entries 13−15 in Table 2), which exhibit no chlorine. The presence of chlorine is known to induce a negative effect on the activity of the catalysts during cyclohexane dehydrogenation to benzene.[58] By their electron-attracting inducting effect, the chloride ions in the vicinity of the metal decrease its electron density and thus tend to increase the strength of the benzene−metal bond. This is a disadvantage to the benzene desorption and thus results in a lower activity for this reaction. However, the chlorine contents of the catalysts prepared from chlorinated precursor salt at pH = 11 (entries 1−4) are quite similar, ranging from 0.4 to 0.6 wt %, and not directly correlated with the TOF changes, but the number of Pd atoms in contact or close to the chlorine species on the support should decrease with the increase in the metal particle size, in accordance with the observed trend: TOF values increase with the increase in the particle size. More generally, it is admitted that the smallest particles interact more with the support. Then, electron transfers can take place from palladium atoms to the support, thus leading to an electronic depletion of the metal and therefore to a lower dehydrogenating activity.[59,60]

Thus, the change of TOF with the palladium dispersion on TiO_2 may be attributed to the nature of metal−support interactions, and TOF measurements for cyclohexane dehydrogenation may allow an indirect comparison of the metal−support interactions between different samples. In Figure 1, presenting the change in TOF values vs Pd particle size, obtained from the whole results of Table 2, one point is not located on the tendency curve; it corresponds to the $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (P25) catalyst prepared by the deposition−precipitation method (Table 2, entry 13), which presents a relatively low TOF value (0.38 s^{-1}) for a rather high average Pd particle size (6.2 nm). Then, it seems that the DP preparation on TiO_2 (P25) leads to large particles in stronger interaction with the support compared to that with the IMP method. Besides, Corma et al.[61] have found that the specific activity of palladium-supported catalysts for methylcyclohexane dehydrogenation could depend on the surface orientations.

3.1.2. Effect of the Presence of Sulfur on the Support. On the TiO_2 (DT51) support, three Pd catalysts were prepared by

Table 2. Characteristics of All the Prepared 2 wt % Pd/TiO_2 Monometallic Catalysts

entry	preparation method[a]	catalysts	$D_{Pd}{}^{b}$ (%)	$d_{Pd}{}^{c}$ (nm)	$A_s{}^{d}$ (mol h^{-1} $g_{Pd}{}^{-1}$)	TOF[d] (s^{-1})	Cl[e] (wt %)
1	IMP	$Pd_{N\text{-}Cl(pH=11)}R300/TiO_2$ (P25)	13	7.2	3.1	0.71	0.5
2	IMP	$Pd_{N\text{-}Cl(pH=11)}C300R300/TiO_2$ (P25)	25	3.7	3.1	0.37	0.6
3	IMP	$Pd_{N\text{-}Cl(pH=11)}C400R300/TiO_2$ (P25)	21	4.4	3.0	0.42	0.6
4	IMP	$Pd_{N\text{-}Cl(pH=11)}C300R400/TiO_2$ (P25)	20	4.7	3.2	0.47	0.4
5	IMP	$Pd_{ac}C300R300/TiO_2$ (P25)	28	3.3	2.6	0.27	0
6	IMP	$Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25)	33	2.8	3.2	0.28	0.4
7	IMP	$Pd_{N\text{-}NO(pH=11)}C300R300/TiO_2$ (P25)	11	8.5	2.9	0.77	0
8	IMP	$Pd_{K\text{-}Cl(pH=1)}C300R300/TiO_2$ (P25)	2	f	0.6	f	1.4
9	IMP	$Pd_{Cl(pH=1)}C300R300/TiO_2$ (DT51)	≈0	f	0.3	f	0.7
10	IMP	$Pd_{N\text{-}Cl(pH=11)}C300R300/TiO_2$ (DT51)	≈0	f	0.1	f	0.8
11	IMP	$Pd_{K\text{-}Cl(pH=1)}C300R300/TiO_2$ (DT51)	3	f	0	f	1.4
12	IMP	$Pd_{Cl(pH=1)}C300R300/TiO_2$ (Synth)	31	3.0	2.8	0.26	1.3
13	DP	$Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (P25)	15	6.2	1.9	0.38	<0.1
14	DP	$Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51)	27	3.5	2.9	0.32	<0.1
15	DP	$Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (Synth)	31	3.0	3.1	0.30	<0.1
16	used	$Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25)	20	4.6	2.5	0.37	nd[g]
17	used	$Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51)	28	3.3	2.3	0.24	nd[g]

[a] IMP, impregnation method; DP, deposition−precipitation method; used, catalyst after the catalytic test of succinic acid hydrogenation (160 °C, 150 bar, 50 h). [b] Dispersion determined by H_2 chemisorption at 70 °C. [c] Average Pd particle size deduced from dispersion value. [d] Specific activity (A_s) and turnover frequency (TOF) for the cyclohexane dehydrogenation at 270 °C. [e] Chlorine content determined by ICP-OES. [f] Dispersion value is too low to be used for valuable calculation. [g] Not determined.

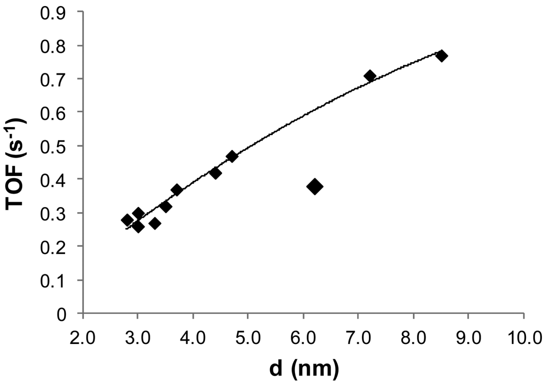


Figure 1. TOF value obtained during cyclohexane dehydrogenation as function of the average Pd particle size of the 2 wt % Pd/TiO_2 monometallic catalysts.

the IMP method with various precursor salts (Table 2, entries 9−11). For all samples, dispersion (determined by hydrogen chemisorption) and specific activity values in cyclohexane hydrogenation are surprisingly almost zero. As presented in Table 1, the DT51 support contains sulfur, which may poison the metallic phase.[62,63] The diffractogram of the 2 wt % $Pd_{N\text{-}Cl(pH=11)}C300R300/TiO_2$ (DT51) catalyst (entry 10, Figure S2d in Supporting Information) showed peaks characteristic of a Pd_4S phase, in addition to the anatase structure. Palladium sulfide was also detected by TEM combined with EDX analysis on $Pd_{Cl(pH=1)}C300R300/TiO_2$ (DT51) (Figure S1c in Supporting Information), which presents a homogeneous distribution on the support with an average particle size of 1.7 nm.

On the contrary, when Pd is deposited by DP on the TiO_2 (DT51) support (Table 2, entry 14), the presence of sulfur on the support seems not to hinder the hydrogen chemisorption, whereas the sulfur content is equal to 2.4 wt %. The sulfur species are therefore probably located differently depending on the preparation method.

3.2. Study of the Monometallic Pd Catalysts by TPR and XPS Analysis.

TPR experiments were performed to study the reduction state of catalysts as a function of temperature. For that purpose, the catalysts underwent a reoxidation under pure O_2 at 300 °C for 1 h, before the temperature-programmed reduction until 700 °C. TPR profiles of the 2 wt % $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25), 2 wt % $Pd_{Cl(pH=1)}C300R300/TiO_2$ (Synth), and 2 wt % $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51) catalysts are shown in Figure 2.

For all the Pd catalysts, H_2 consumption occurs from room temperature attributed to the reduction of oxidized palladium. A single peak is observed for the catalysts supported on TiO_2 (P25) and TiO_2 (DT51) (Figure 2a,c), consumption being completed at 40 °C, whereas three peaks are present in the case of the TiO_2 (Synth) supported sample (Figure 2b) for which the palladium reduction ends at higher temperatures (around 60 °C). That particular profile may correspond to the reduction of palladium particles with various metal−support interactions, palladium in stronger interaction being reduced at higher temperatures. It is known that the palladium absorbs hydrogen to form a β-PdH phase, where decomposition is generally characterized by a hydrogen desorption peak between 70 and 100 °C. However, no desorption peak was observed in this study. A number of studies reported that the formation of this hydride phase depends on the size of palladium particles and would be favored on larger particles.[64,65]

In the case of the $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51) catalyst (Figure 2c), an additional hydrogen consumption is observed at higher temperatures, between 240 and 510 °C, attributed to the reduction of support species in contact with palladium. The TiO_2 (DT51) support tested without Pd (Figure 2d) shows also a consumption peak at high temperature, with a more important intensity and which begins only from 465 °C, with the reduction of Ti^{4+} ions being more difficult in the absence of metal sites.[66] In the presence of palladium, hydrogen chemisorbed after dissociation on metal diffused to the support, allowing the reduction of Ti^{4+} ions toward Ti^{3+}.[67,68] However,

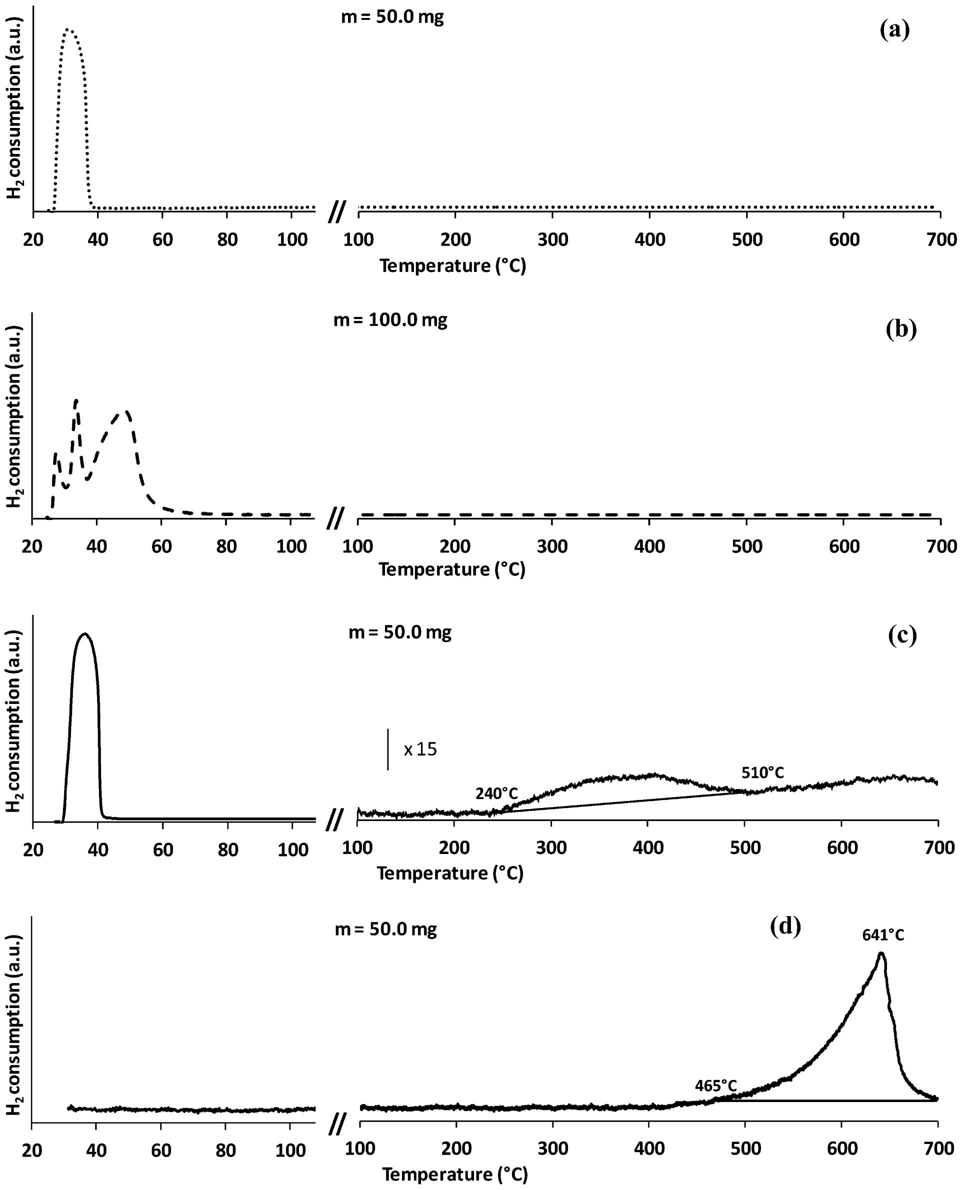


Figure 2. TPR profiles of the monometallic catalysts and TiO_2 (DT51) support after an in situ oxidation at 300 °C of the samples (mass used for each test indicated on figures): (a) $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25), (b) $Pd_{Cl(pH=1)}C300R300/TiO_2$ (Synth), (c) $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51), (d) TiO_2 (DT51).

the hydrogen consumption at high temperature is nearly three times greater on the TiO_2 (DT51) support only than that on the Pd-based catalyst, with the elimination of sulfur (from support) in H_2S form during the reduction at high temperature perhaps contributing to this behavior.

The H_2 consumption values (n_{H_2}) in the first low-temperature range deduced from the TPR profiles (Table 3) are greater than the quantities needed to reduce oxidized palladium to the metallic state (Pd^0) if we exclusively consider the formation of a PdO phase after the preliminary calcination. In these conditions, the reduction of the Pd species would occur according to the following equation: $PdO + H_2 \rightarrow Pd^0 + H_2O$ and the n_{H_2}/n_{Pd} ratio would be equal to 1. In addition, oxidized palladium can also be present in a PdO_2 form.[69]

Table 3. H_2 Consumption from Ambient Temperature until 60 °C Determined from TPR Profiles of the 2 wt % Pd/TiO_2 Monometallic Catalysts

catalysts	n_{H_2} (mol g_{cat}^{-1})	n_{Pd} (mol g_{cat}^{-1})	n_{H_2}/n_{Pd}
$Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25)	2.74×10^{-4}	1.97×10^{-4}	1.4
$Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51)	3.05×10^{-4}	2.07×10^{-4}	1.5
$Pd_{Cl(pH=1)}C300R300/TiO_2$ (Synth)	2.37×10^{-4}	1.88×10^{-4}	1.3

In order to estimate the palladium oxidation state at the end of the oxidation under O_2, XPS analyses were performed on the $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) catalyst after various in situ treatments (Table 4). After oxidation, the decomposition of the Pd $3d_{5/2}$ core level shows the presence of two peaks located at 336.8 and 337.9 eV, corresponding, respectively, to PdO and PdO_2 species.[69,70] A third peak at higher binding energy is also observed at 339.5 eV, which could correspond to palladium in strong interaction with the support. However, no shift toward lower binding energies is observed for the Ti 2p core level (at 458.9 eV), which would indicate an electron transfer from

Table 4. Binding Energies (eV) of Pd $3d_{5/2}$ Core Level and Atomic Ratios Obtained by XPS for the 2 wt % $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) Catalyst after Various In Situ Treatments

	Pd $3d_{5/2}$		Pd/Ti (at/at)	Ti/O (at/at)
without in situ treatment	335.3 eV	Pd^0 (34%)	0.063	0.476
	337.0 eV	Pd^{2+} (66%)		
oxidation under O_2 at 300 °C	336.8 eV	Pd^{2+} (48%)	0.053	0.475
	337.9 eV	Pd^{4+} (48%)		
	339.5 eV	$Pd^{>4+}$ (4%)		
reduction under H_2 at 300 °C	334.9 eV	Pd^0 (96%)	0.038	0.471
	336.7 eV	Pd^{2+} (4%)		
reduction under H_2 at 450 °C	335.0 eV	Pd^0 (100%)	0.036	0.467

palladium to the oxide support, probably due to the low Pd content deposited onto TiO_2. On the other side, XPS data[71] reveal higher binding energies for Pd compounds containing halogenated elements than for Pd. This solid contained chlorine, and this peak was observed after oxidation. This XPS binding energy might then be attributed to a "Pd–Cl–O" compound. With the knowledge that the XPS analysis probes the solid surface at a depth around 10 nm and that the palladium particle size does not exceed 10 nm, the XPS results can be considered as representative of all the metallic phases. Consequently, after oxidation at 300 °C, the $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) catalyst presents 48% of PdO and PdO_2 forms (Table 4). After reduction under H_2 at 300 °C, almost all palladium (96%) is in a metallic state. From these results, the theoretical amount of hydrogen required to reduce the catalyst after oxidation at 300 °C can be evaluated. The obtained value ($2.92.10^{-4}$ mol g_{cat}^{-1}) is in good agreement with that deduced from the TPR analysis ($2.74.10^{-4}$ mol g_{cat}^{-1}, Table 3). Table 4 shows also that the Pd/Ti atomic ratio decreases by a factor of 1.4 between the oxidative and reductive treatment. This result may be explained by the strong metal–support interaction (SMSI effect) which induces a decoration of the metal by TiO_x species, resulting from the partial reduction of the support. This SMSI effect was clearly evidenced many years ago on Pd/TiO_2 catalysts reduced at 500 °C.[72,73] A more recent study showed that this phenomenon begins at much lower reduction temperatures (200 °C) and is very significant at 350 °C.[74] However, results from Table 4 indicate that the Ti/O atomic ratio is similar (0.47) regardless of in situ pretreatment, oxidation, or reduction (at 300 or 450 °C), meaning that the TiO_2 (P25) support is not reduced at 300 and 450 °C, in agreement with the TPR profile that shows that only palladium is reduced in the studied temperature range (20–700 °C). The decrease in Pd/Ti ratio after reduction could rather be explained by a sintering of palladium particles.

3.3. Catalytic Performances of the Pd/TiO_2 Catalysts for Succinic Acid Hydrogenation.

3.3.1. Fresh Catalysts. The succinic acid hydrogenation was performed with a 5 wt % aqueous succinic acid, 1 g of catalyst, at 160 °C and under 150 bar total pressure. Figure 3a shows an example of the evolution in the liquid phase of the concentration of succinic acid and main products formed with the $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) fresh catalyst. Succinic acid is mainly transformed in γ-butyrolactone (issued from the first hydrogenation step, Scheme 1), which is subsequently converted in little quantities of 1,4-butanediol and tetrahydrofuran. After 48 h reaction time, the SUC conversion is total with selectivity to GBL equal to 95%. BDO and THF are produced in concentrations lower than 20 mmol L^{-1}. Comparison of the TOC values obtained from HPLC and GC analysis of solution samplings and from calculation, given in Figure 3b, shows a very satisfactory carbon balance, thus indicating the insignificant presence of gaseous products issued from cracking reactions.

The behavior of the different fresh monometallic Pd/TiO_2 catalysts was compared for the hydrogenation of succinic acid. The disappearance of SUC and the formation of GBL during the reaction are represented in Figure 4a,b, respectively.

All the catalysts are very selective toward GBL (selectivity >90%), but the activity is a function of the catalyst nature. Figure 5 shows that the SUC conversion (value extrapolated after 10 h of reaction) depends on the catalysts' Pd dispersion, the conversion increasing with the Pd accessibility. Furthermore, significant differences are observed according to the preparation methods (DP or IMP). Thus, the $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (P25) and $Pd_{N\text{-}Cl(pH=11)}C300R300/TiO_2$ (P25) catalysts prepared on the same support, but by different methods, DP and IMP, present different dispersions, 15 and 25%, respectively, but show comparable conversion values at 10 h reaction time (around 15%). Similarly, the $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (Synth) and $Pd_{Cl(pH=1)}C300R300/TiO_2$ (Synth) catalysts prepared by the DP and IMP method, respectively, present similar dispersions (31%), but the SUC conversion is significantly higher on the first sample (75%

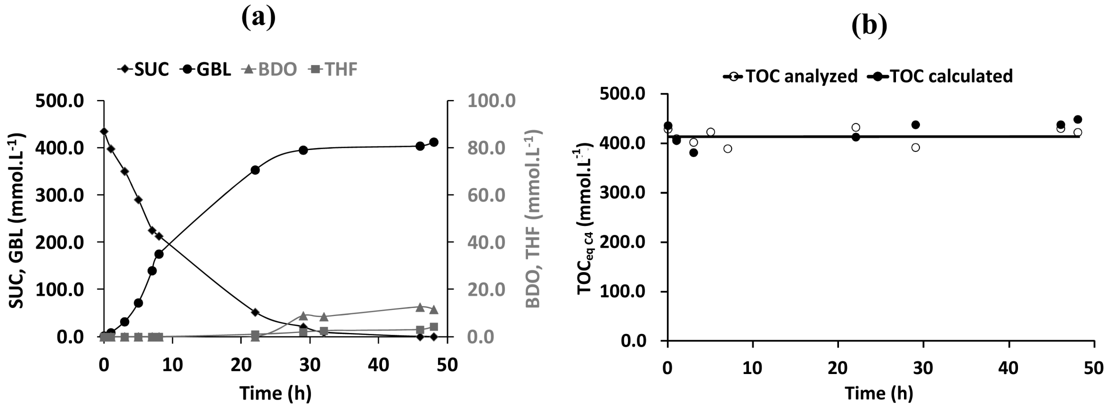


Figure 3. Hydrogenation of succinic acid on the 2 wt % $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) fresh catalyst: (a) evolution of the concentrations of reactant and main products vs time, (b) evolution of TOC in solution vs time.

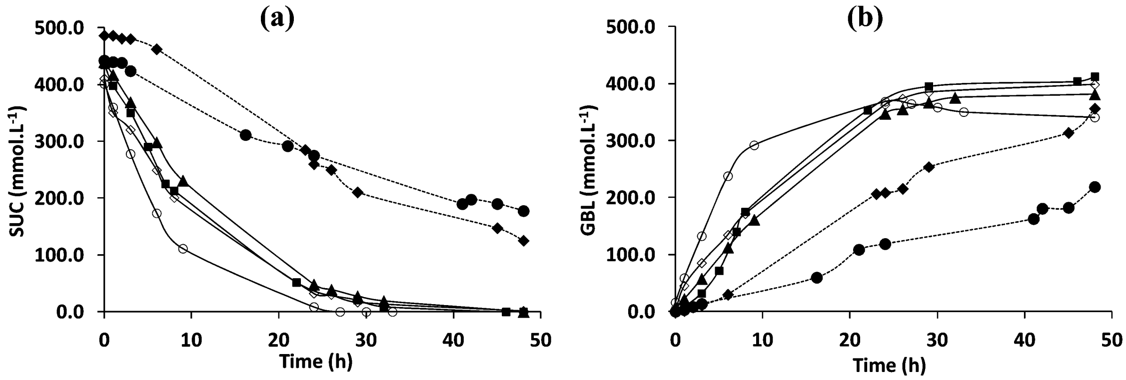


Figure 4. (a) SUC conversion and (b) GBL formation vs time on various fresh 2 wt % Pd/TiO_2 catalysts: (◆) $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (P25); (●) $Pd_{N\text{-}Cl(pH=11)}$C300R300/TiO_2 (P25); (▲) $Pd_{Cl(pH=1)}$C300R300/TiO_2 (Synth); (■) $Pd_{Cl(pH=1)}$C300R300/TiO_2 (P25); (◇) $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (DT51); (○) $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (Synth).

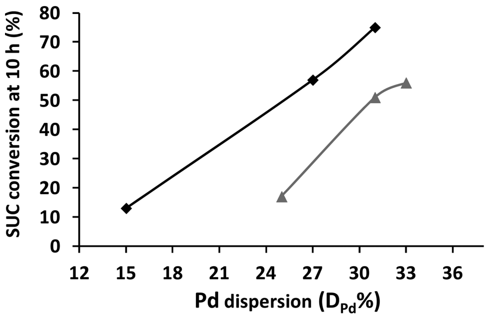


Figure 5. SUC conversion at 10 h reaction time as a function of the Pd dispersion on various fresh 2 wt % Pd/TiO_2 catalysts prepared by: (◆) DP method; (▲) IMP method.

versus 51%). Finally, for a given Pd dispersion (i.e., a given average particle size), the SUC conversion appears to be systematically higher when monometallic Pd/TiO_2 catalysts are prepared according to the DP method. So the particle size is not the only factor governing the catalytic activity during SUC hydrogenation, but the environment of the metallic sites generated in the course of the preparation steps seems to contribute more largely to catalytic performances. It is noteworthy that there is no correlation between the activity of these catalysts in gas phase cyclohexane dehydrogenation and in liquid phase succinic hydrogenation.

3.3.2. Recycling of Catalysts. After the reaction of succinic acid hydrogenation was performed in an autoclave, two representative catalysts ($Pd_{Cl(pH=1)}$C300R300/TiO_2 (P25) and $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (DT51) prepared by IMP and DP method, respectively) were recovered and washed with ultrapure water in order to recycle them (corresponding to entries 16 and 17 in Table 2, respectively). In the fresh state, these two samples present a Pd dispersion of 33 and 27%, respectively (entries 6 and 14, Table 2) and lead to quite similar succinic acid conversions after 10 h reaction time (56−57%, Figure 5). Figure 6 compares the evolutions of the SUC and

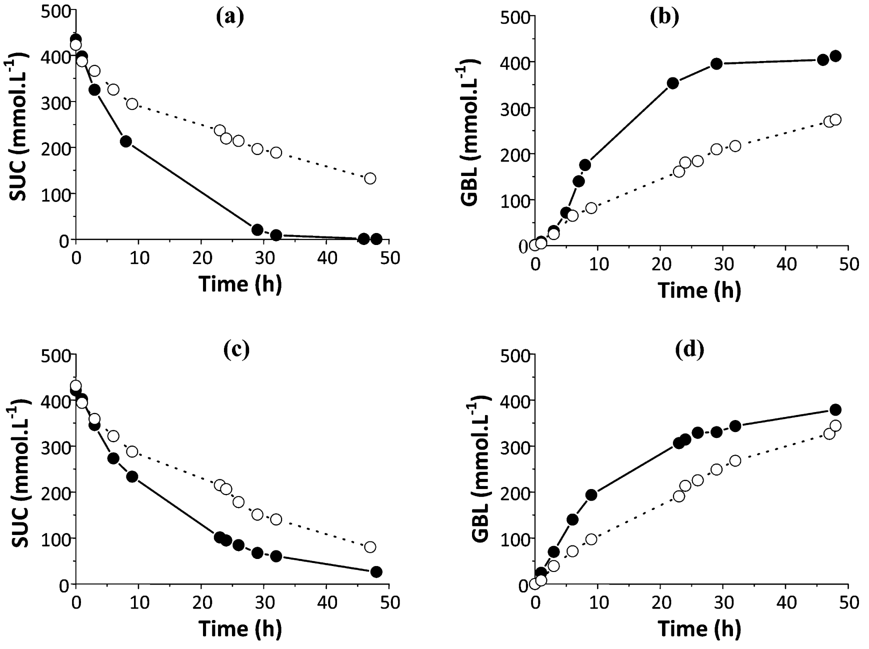


Figure 6. (a,c) SUC conversion, (b,d) GBL formation vs time on two 2 wt % Pd/TiO_2 catalysts in fresh state (filled circles) and after one recycling (open circles): (a,b) $Pd_{Cl(pH=1)}$C300R300/TiO_2 (P25) by IMP method; (c,d) $Pd_{K\text{-}Cl(pH=11)}$R300/TiO_2 (DT51) by DP method.

GBL concentrations as a function of time of these two catalysts in the fresh state and after recycling.

In both cases, the recycled sample is less active than the fresh one; however, no significant change occurs concerning the selectivity, GBL still being formed mostly with the reused catalyst. Nevertheless, the loss of activity is more drastic for the $Pd_{Cl(pH=1)}C300R300/TiO_2$ (P25) catalyst prepared by the IMP method. For example, at 30 h reaction time, the SUC conversion drops by a factor of 1.8 after recycling of this sample, compared to a factor of 1.3 in the case of the $Pd_{K\text{-}Cl(pH=11)}R300/TiO_2$ (DT51) prepared by the DP method. This loss of activity cannot be explained by a Pd leaching during the first SUC hydrogenation test since no Pd was measured in solution at the end of the reactions (Pd < 0.2 ppm). However, in the case of the Pd/TiO_2 (P25) catalyst, a decrease in the Pd dispersion from 33 to 20% is observed between the fresh and used systems (Table 2), whereas the dispersion state of the metallic phase is not modified for the Pd/TiO_2 (DT51) catalyst (D_{Pd} = 27−28%). The DP preparation method gives more stable catalysts for the aqueous phase hydrogenation of SUC. Finally, the used samples exhibit TOF values for cyclohexane dehydrogenation and average Pd particle sizes in agreement with the tendency curve drawn in Figure 1, though giving slightly lower values.

4. CONCLUSIONS

The objective of this work was to prepare monometallic Pd/TiO_2 catalysts active and stable in aqueous medium during succinic acid hydrogenation to γ-butyrolactone. Pd/TiO_2 catalysts (2 wt %) were prepared by varying several parameters in order to study notably the influence of the preparation method, the chemical nature of Pd precursor salt, and the textural and structural properties of the titania support. The main conclusions derived from this work are the following:

(1) From the impregnation (IMP) method and with the TiO_2 (P25) support, the metallic dispersion depends on the nature of the precursor salt, with $PdCl_2$ salt inducing the smallest average Pd particles size.

(2) The TiO_2 (DT51) leads to very different results depending on the preparation method. Notably, the presence of sulfur issued from the support poisons strongly the Pd particles in the case of the IMP method. This phenomenon does not occur for the catalysts prepared by the deposition−precipitation (DP) supported on TiO_2 (DT51), for which good hydrogen accessibility is obtained. Moreover, the TiO_2 (DT51) support can be partly reduced at high temperature (SMSI effect) as shown by the TPR study.

(3) Characterization of the metallic phase by cyclohexane dehydrogenation has highlighted more or less important Pd support interactions depending on the size of the Pd particles, with particles of smaller sizes being in stronger interaction with the support.

(4) The results obtained during succinic acid hydrogenation showed that all the Pd catalysts are very selective to GBL. However, the rate of succinic acid conversion is a function of both the Pd dispersion and the preparation method. For comparable Pd particle sizes, the catalysts prepared by the DP method are more active that the IMP ones.

Finally, the deposition−precipitation method allows one to obtain the highest performing 2 wt % Pd/TiO_2 samples during SUC hydrogenation in terms of activity and stability. These systems will be subsequently modified by Re addition, in order to improve the selectivity toward 1,4-butanediol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information displaying the experimental protocols of the catalysts characterizations, as well as supplementary characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Werpy, T., Petersen, G., Eds. *Top Value-Added Chemicals from Biomass: Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; Department of Energy: Washington, DC, 2004; Vol. *1*.

(2) Bechthold, I.; Bretz, K.; Kabasci, S.; Kopitzky, R.; Springer, A. *Chem. Eng. Technol.* **2008**, *31*, 647−654.

(3) Werpy, T.; Frye, J.; Holladay, J. In *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions*; Kamm, B., Gruber, P. R., Kamm, M., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2008; Vol. *2*, p 367.

(4) Bozell, J. J.; Petersen, G. R. *Green Chem.* **2010**, *12*, 539−554.

(5) Song, H.; Lee, S. Y. *Enzyme Microb. Technol.* **2006**, *39*, 352−361.

(6) Zeikus, J. G.; Jain, M. K.; Elankovan, P. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 545−552.

(7) Lee, P. C.; Lee, W. G.; Kwon, S.; Lee, S. Y.; Chang, H. N. *Enzyme Microb. Technol.* **1999**, *24*, 549−554.

(8) Varadarajan, S.; Miller, D. J. *Biotechnol. Prog.* **1999**, *15*, 845−854.

(9) Cukalovic, A.; Stevens, C. V. *Biofuels, Bioprod. Biorefin.* **2008**, *2*, 505−529.

(10) Delhomme, C.; Weuster-Botz, D.; Kühn, F. E. *Green Chem.* **2009**, *11*, 13−26.

(11) McKinlay, J. B.; Vieille, C.; Zeikus, G. *Appl. Microbiol. Biotechnol.* **2007**, *76*, 727−740.

(12) Orjuela, A.; Yanez, A. J.; Peereboom, L.; Lira, C. T.; Miller, D. J. *Sep. Purif. Technol.* **2011**, *83*, 31−37.

(13) Chaudhari, R. V.; Rode, C. V.; Deshpande, R. M.; Jaganathan, R.; Leib, T. M.; Mills, P. L. *Chem. Eng. Sci.* **2003**, *58*, 627−632.

(14) Deshpande, R. M.; Buwa, V. V.; Rode, C. V.; Chaudhari, R. V.; Mills, P. L. *Catal. Commun.* **2002**, *3*, 269−274.

(15) Luque, R.; Lin, C. S. K.; Du, C.; Macquarrie, D. J.; Koutinas, A.; Wang, R.; Webb, C.; Clark, J. H. *Green Chem.* **2009**, *11*, 193−200.

(16) Tachibana, Y.; Masuda, T.; Funabashi, M.; Kunioka, M. *Biomacromolecules* **2010**, *11*, 2760−2765.

(17) Hong, U. G.; Lee, J.; Hwang, S.; Song, I. K. *Catal. Lett.* **2011**, *141*, 332−338.

(18) Hong, U. G.; Hwang, S.; Seo, J. G.; Lee, J.; Song, I. K. *J. Ind. Eng. Chem.* **2011**, *17*, 316−320.

(19) Hong, U. G.; Park, H. W.; Lee, J.; Hwang, S.; Yi, J.; Song, I. K. *Appl. Catal., A* **2012**, *415−416*, 141−148.

(20) Messori, M.; Vaccari, A. *J. Catal.* **1994**, *150*, 177−185.

(21) Castiglioni, G. L.; Ferrari, M.; Guercio, A.; Vaccari, A.; Lancia, R.; Fumagalli, C. *Catal. Today* **1996**, *27*, 181−186.

(22) Budge, J. R.; Attig, T. G.; Graham, A. M. U.S. Patent 5 196 602 (1993), Standard Oil Co Ohio.

(23) De Thomas, W., Taylor, P. D., Tomfohrde, H. F. U.S. Patent 5 149 836 (1992), ISP Investments INC.

(24) Budge, J. R. EU Patent 0 404 408 (1990), Standard Oil Co Ohio.

(25) Conway, S. J.; Lunsford, J. H. *J. Catal.* **1991**, *131*, 512−522.

(26) Castiglioni, G. L.; Gazzano, M.; Stefani, G.; Vaccari, A. In *Heterogeneous Catalysis and Fine Chemicals III* Guisnet, M., Barbier, J., Barrault, J., Bouchoule, C., Duprez, D., Perot, G., Montassier, C., Eds.; Elsevier Science Publishers: Amsterdam, 1993.

(27) Attig, T. G.; Graham, A. M. U.S. Patent 4 827 001 (1989), Standard Oil Co Ohio.

(28) Wegman, R. W.; Bryant, D. R. U.S. Patent 5 191 091 (1993), Union Carbide Chem. Plastic.

(29) Thakur, D. S.; Roberts, B. D.; Sullivan, T. J.; Vlchek, A. L. U.S. Patent 5 155 086 (1992), Engelhard Corp.

(30) Herrmann, U.; Emig, G. *Chem. Eng. Technol.* **1998**, *21*, 285−295.

(31) Herrmann, U.; Emig, G. *Ind. Eng. Chem. Res.* **1997**, *36*, 2885−2896.

(32) Herrmann, U.; Emig, G. *Ind. Eng. Chem. Res.* **1998**, *37*, 759−769.

(33) Kuksal, A.; Klemm, E.; Emig, G. *Appl. Catal., A* **2002**, *228*, 237−251.

(34) Jeong, H.; Kim, T. H.; Kim, K. I.; Cho, S. H. *Fuel Process. Technol.* **2006**, *87*, 497−503.

(35) Jung, S. M.; Godard, E.; Jung, S. Y.; Park, K. C.; Choi, J. U. *Catal. Today* **2003**, *87*, 171−177.

(36) Jung, S. M.; Godard, E.; Jung, S. Y.; Park, K. C.; Choi, J. U. *J. Mol. Catal. A: Chem.* **2003**, *198*, 297−302.

(37) Hara, Y.; Kusaka, H.; Inagaki, H.; Takahashi, K.; Wada, K. *J. Catal.* **2000**, *194*, 188−197.

(38) Pillai, U. R.; Sahle-Demessie, E. *Chem. Commun.* **2002**, *5*, 422−423.

(39) Pillai, U. R.; Sahle-Demessie, E.; Young, D. *Appl. Catal., B* **2003**, *43*, 131−138.

(40) Dupont E.I. de Nemours and Company, U.S. Patent 5478952 (1995) Ru,Re/carbon catalysts for hydrogenation in aqueous solution.

(41) Dupont E.I. de Nemours and Company, U.S. Patent US 4782167 (1988), process for preparing butyrolactones and butanediols.

(42) Marbry, M. A.; Prichard, W. W.; Ziemecki, S. B. U.S. Patent 4 550 185 (1985), DuPont.

(43) Marbry, M. A.; Prichard, W. W.; Ziemecki, S. B. U.S. Patent 4 609 636 (1986), DuPont.

(44) Schwarz, J. T. U.S. Patent 5 478 952 (1995), DuPont.

(45) Erik, P. S.; Attig, T. G.; Frye, J. G.; Budge, J. R. European Patent 0 881 203 (1997), The Standard Oil Company.

(46) EP 1232789 (2000), Asahi Kasei Kabushiki Kaisha (JP), catalysts for hydrogenation of carboxylic acid.

(47) Hara, Y.; Endou, K. *Appl. Catal., A* **2003**, *239*, 181−195.

(48) Maity, P.; Basu, S.; Bhaduri, S.; Lahiri, G. K. *Adv. Synth. Catal.* **2007**, *349*, 1955−1962.

(49) Indra, A.; Maity, P.; Bhaduri, S.; Lahiri, G. K. *ChemCatChem* **2013**, *5*, 322−330.

(50) Pham Minh, D.; Besson, M.; Pinel, C.; Fuertes, P.; Petitjean, C. *Top. Catal.* **2010**, *53*, 1270−1273.

(51) Khanh, L. B.; Pham Minh, D.; Pinel, C.; Besson, M.; Tapin, B.; Epron, F.; Especel, C. *Top. Catal.* **2012**, *55*, 466−473.

(52) Pintar, A.; Besson, M.; Gallezot, P. *Appl. Catal., B* **2001**, *31*, 275−290.

(53) Balaraju, M.; Rekha, V.; Prabhavathi Devi, B. L. A.; Prasad, R. B. N.; Sai Prasad, P. S.; Lingaiah, N. *Appl. Catal., A* **2010**, *384*, 107−114.

(54) Bidaoui, M.; Especel, C.; Bouchenafa-Saib, N.; Duprez, D.; Mohammedi, O.; Royer, S. *Appl. Catal., A* **2012**, *445−446*, 14−25.

(55) Cusumano, J. A.; Dembinski, G. W.; Sinfeld, J. H. *J. Catal.* **1966**, *5*, 471−475.

(56) Blakely, D. W.; Somorjai, G. A. *J. Catal.* **1976**, *42*, 181−196.

(57) Rodriguez-Ramos, I.; Guerrero-Ruiz, A. *J. Catal.* **1992**, *135*, 458−466.

(58) Pieck, C. L.; Marecot, P.; Parera, J. M.; Barbier, J. *Appl. Catal., A* **1995**, *126*, 153−163.

(59) Benkhaled, M.; Morin, S.; Pichon, C.; Thomazeau, C.; Verdon, C.; Uzio, D. *Appl. Catal., A* **2006**, *312*, 1−11.

(60) Resasco, D. E.; Haller, G. L. *J. Catal.* **1983**, *82*, 279−288.

(61) Corma, A.; Martin, M. A.; Pajares, J. A.; Perez-Pariente, J.; Avalos, M.; Jose Yacaman, M. *J. Mol. Catal.* **1988**, *48*, 199−205.

(62) Pernicone, N.; Cerboni, M.; Prelazzi, G.; Pinna, F.; Fagherazzi, G. *Catal. Today* **1998**, *44*, 129−135.

(63) Pinna, F.; Menegazzo, F.; Signoretto, M.; Canton, P.; Fagherazzi, G.; Pernicone, N. *Appl. Catal., A* **2001**, *219*, 195−200.

(64) Shen, W. J.; Okumura, M.; Matsumura, Y.; Haruta, M. *Appl. Catal., A* **2001**, *213*, 225−232.

(65) Neri, G.; Musolino, M. G.; Milone, C.; Pietropaolo, D.; Glavagno, S. *Appl. Catal., A* **2001**, *208*, 307−316.

(66) Li, Y.; Xu, B.; Fan, Y.; Feng, N.; Qiu, A.; He, J. M. J.; Yang, H.; Chen, Y. *J. Mol. Catal. A: Chem.* **2004**, *216*, 107−114.

(67) Conesa, J. C.; Soria, J. *J. Phys. Chem.* **1982**, *86*, 1392−1395.

(68) Huizinga, T.; Prins, R. *J. Phys. Chem.* **1981**, *85*, 2156−2158.

(69) Kim, K. S.; Grossmann, A. F.; Winograd, N. *Anal. Chem.* **1974**, *46*, 197.

(70) Otto, K.; Haack, L. P.; de Vries, J. E. *Appl. Catal., B* **1992**, *1*, 1−12.

(71) http://srdata.nist.gov/xps/.

(72) Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 170−175.

(73) Tauster, S. J.; Fung, S. C. *J. Catal.* **1978**, *55*, 29−35.

(74) Sá, J.; Bernardi, J.; Anderson, J. A. *Catal. Lett.* **2007**, *114*, 91−95.