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# ***In situ* preparation of bimetallic ReO<sub>x</sub>-Pd/TiO<sub>2</sub> catalysts for selective aqueous-phase hydrogenation of succinic acid to 1,4-butanediol.**

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## **Abstract**

TiO<sub>2</sub>-supported Re-Pd catalysts were evaluated for the selective hydrogenation of succinic acid (SUC) to 1,4-butanediol (BDO) in aqueous solution at 160 °C under 150 bar of H<sub>2</sub>. Rhenium immobilized on Pd/TiO<sub>2</sub> catalysts by *ex situ* preparation methods, namely successive impregnation (SI) or deposition by catalytic reduction (CR), was partially leached after handling in air and introduction into the SUC aqueous solution in the batch reactor; it was then re-deposited under H<sub>2</sub> pressure. It was demonstrated in this study that Re can be deposited by CR on a monometallic Pd catalyst directly *in situ* in the autoclave under hydrogen pressure before the catalytic test. The Re loading and the activation time under reducing atmosphere in the autoclave were optimized. Finally, the best bimetallic catalysts synthesized *in situ* demonstrated an intermediate selectivity to BDO compared to the systems prepared *ex situ* from the same parent monometallic catalyst, in the following order: *ex situ* CR < *in situ* CR < *ex situ* SI.

## **Keywords**

succinic acid hydrogenation; butanediol; aqueous phase; RePd catalysts; *in situ* catalyst preparation.

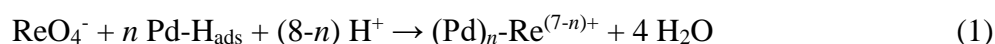
## 1. Introduction

Biomass and the platform molecules derived from it have been identified as an important source to renewable feedstocks [1,2]. An example is succinic acid (SUC), which up to recently has mostly been produced by chemical processes from petroleum based maleic acid or maleic anhydride. It is now well established that bio-based SUC can be produced by fermenting carbohydrates using natural producers or engineered bacteria or yeast [3-7]. This platform molecule was listed in 2004 by the US Department of Energy as one of the 12 Top Value Added Chemicals produced from sugars [8]. Later, it was attested to be a renewable precursor in replacement for petroleum-based SUC, with a market potential for products based on SUC estimated to be around 250 000 t per year [9]. Further conversion of bio-SUC to its derivatives mostly relies on chemical transformations [10]. Bio-SUC has a large potential in the production of  $\gamma$ -butyrolactone (GBL), 1,4-butanediol (BDO), and tetrahydrofuran (THF) via catalytic hydrogenation. Especially, BDO is a raw material for a number of synthesis, including polybutylene terephthalate (PBT) thermoplastic polyesters, polybutylene succinate (PBS) resins, and polyurethane polymers, with large downstream applications. The global market for BDO is growing and numerous companies and industrial consortia have started to develop the industrial production of bio-SUC on a large scale [11].

Various mono and bimetallic catalysts have been examined in the literature for the liquid phase hydrogenation of succinic acid to GBL, BDO and THF [10,12-31]. The most active catalysts for the synthesis of BDO or THF contain a first component, which is a noble metal (Pd, Ru, or Pt) and a second component which is rhenium, tin, or cobalt. They are usually prepared before the catalytic test from *ex situ* classical preparation methods involving deposition of the metal precursors on a support (carbon, TiO<sub>2</sub>).

Most of the studies firstly reported in the literature were conducted in 1,4-dioxane as solvent [18-22,24,26]. Water, which is the solvent of production of bio-SUC [10], has been used to a limited extent for this reaction until recently [12-17,23,25,27-30]. Moreover, the direct transformation of SUC in aqueous solutions contributes to decrease the high cost of purification from organic media, increasing the competitiveness of the global production process [10]. Liang *et al* showed that Re-2wt%Pd/C catalysts (1, 2, or 3.8 wt% Re) prepared by incipient-wetness co-impregnation with an aqueous solution of both metal precursors, favored the conversion of the intermediate GBL towards THF during the reaction of SUC in water at 240 °C under 80 bar H<sub>2</sub> [23]. The SUC transformation was in favor of THF formation owing to the high temperature used in this study. Previously, we also developed Re-2wt%Pd heterogeneous catalysts supported on carbon or TiO<sub>2</sub> and studied their efficiency for the hydrogenation of SUC in

aqueous phase with the aim of optimizing the formation of BDO [13-17]. Several series of Re-2wt%Pd/TiO<sub>2</sub> catalysts with various Re loadings were synthesized *via ex situ* preparation methods starting from 2wt%Pd/TiO<sub>2</sub> parent systems modified by sequential deposition of rhenium according to two protocols: a successive impregnation (SI) or a deposition by catalytic reduction (CR), followed by reduction under H<sub>2</sub> flow at 450 °C. For that purpose, we systematically used an aqueous solution of ammonium perrhenate, and compared series issued from two commercial supports, *i.e.* TiO<sub>2</sub> DT51 (from Cristal) and TiO<sub>2</sub> P25 (from Degussa), and two Pd precursor salts, *i.e.* PdCl<sub>2</sub> and K<sub>2</sub>PdCl<sub>4</sub>. The CR deposition method is based on a surface redox reaction between adsorbed atomic hydrogen on Pd (Pd-H<sub>ads</sub>) of the parent catalyst and the Re precursor according to the overall reaction:



By means of various analysis techniques (X-ray diffraction, transmission electron microscopy coupled with energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, temperature programmed reduction...), we performed an extensive characterization of the structure of all the bimetallic catalysts after their *ex situ* preparation. Whatever the preparation method, the nature of the TiO<sub>2</sub> support, and the Pd precursor salt, we observed significant interactions between Pd and Re [17] and the characteristics of the various catalysts were not so different. Nevertheless, during the hydrogenation of succinic acid performed in water in a batch reactor at 160 °C under 150 bar H<sub>2</sub>, a significant disparity in selectivity was observed, depending mainly on the method employed for the Re deposition. The results showed that catalysts prepared by SI required a higher loading of Re to reach the highest yield of BDO compared to catalysts prepared by CR. However, the yield of BDO was the highest (90 %) over 3.4wt%Re-2wt%Pd/TiO<sub>2</sub> prepared by SI method and on the TiO<sub>2</sub> DT51 support [14-17]. This discrepancy between the relatively similar characteristics of the various samples and the catalytic performances suggested that some modifications may occur during the catalytic test. Thus, it seemed then crucial to us to complete this study by evaluating the stability of the *ex situ* bimetallic catalysts during the catalytic test (immersed in water, under high pressure and temperature).

Consequently, the present paper will focus on the Re-2wt%Pd/TiO<sub>2</sub> series from TiO<sub>2</sub> DT51 support, leading to the highest yield to BDO, with the aim of evaluating the stability of the catalysts after handling in air and transfer in the batch reactor for the catalytic test. It will demonstrate that rhenium species are leached in water during the heating of the solution under inert gas whereas no Re is present in solution at the end of the reaction. For this reason, the second part of the study will be devoted to the potential of *in situ* Re deposition onto Pd/TiO<sub>2</sub>

directly in the batch reactor, before performing the SUC hydrogenation reaction. This method can be considered as an *in situ* CR preparation. Once optimized, the catalytic performances of the bimetallic systems obtained by this *in situ* preparation protocol will be compared to those observed previously from the *ex situ* syntheses (CR and SI).

## 2. Experimental

### 2.1. Monometallic catalysts preparation

The monometallic 2wt%Pd/TiO<sub>2</sub> catalyst was prepared by deposition-precipitation using K<sub>2</sub>PdCl<sub>4</sub> as the precursor and TiO<sub>2</sub> DT51 (Cristal, 88 m<sup>2</sup> g<sup>-1</sup>), as described previously [12].

### 2.2. Bimetallic catalysts prepared by *ex situ* SI and CR methods

#### 2.2.1. Description of the preparation methods

Supported bimetallic Re-Pd/TiO<sub>2</sub> catalysts were prepared *ex situ* from the parent Pd catalyst by the addition of different amounts of Re from aqueous solution of ammonium perrhenate using the SI or the CR procedures, as described elsewhere [14-17]. Briefly, in the SI procedure, an aqueous solution of a predetermined amount of the Re salt was added to a suspension of the Pd/TiO<sub>2</sub> catalyst at room temperature. After 5 h the excess water was evaporated under vacuum for 30 min and the solid was dried overnight at 50 °C under vacuum. After reduction in H<sub>2</sub> flow at 450 °C, the SI catalysts were passivated at room temperature in 1 % v/v O<sub>2</sub>/N<sub>2</sub> for 30 min, and stored under Ar before catalytic testing. In the CR procedure based on a surface redox reaction, the parent Pd catalyst placed in a fixed-bed reactor was activated under a flow of H<sub>2</sub> at 300 °C. After cooling, the Re solution (acidified and degassed) was poured onto the Pd/TiO<sub>2</sub> catalyst. The mixture was maintained for 1 h under H<sub>2</sub> bubbling; after filtration, the solid was dried under H<sub>2</sub> and reduced at 450 °C. The reduced solid was allowed to cool, and was slowly exposed to air after N<sub>2</sub> flushing. The catalysts prepared by CR were stored in ambient air.

#### 2.2.2. SUC hydrogenation

The aqueous-phase catalytic hydrogenation experiments were carried out at 160 °C under 150 bar of hydrogen pressure in a 300 mL high-pressure batch reactor (Parr Instrument 4560, Hastelloy C276) equipped with a magnetically driven impeller (1200 rpm) and a liquid sampling system described previously [13-15]. The reactor was loaded with 120 g of a 5 wt% SUC aqueous solution and 1 g of catalyst (molar ratio SUC/Pd ca. 250). After purging with Ar, the reactor was heated under Ar to 160 °C, then hydrogen was adjusted to 150 bar which corresponds to time zero.

### **2.3. Bimetallic catalysts prepared by *in situ* method**

For the *in situ* synthesis of bimetallic catalysts, the batch reactor used for the catalytic test was loaded with 1 g of monometallic Pd/TiO<sub>2</sub> catalyst in 100 g of a NH<sub>4</sub>ReO<sub>4</sub> aqueous solution containing a predetermined amount of Re to give a final 1.0 wt%, 2.0 wt%, 3.0 wt% or 4.0 wt% Re loading on the catalyst. After purging with Ar, the suspension was heated to 160 °C, the reactor was pressurized under 150 bar H<sub>2</sub> and maintained under these conditions for a given time (named thereafter “activation duration”) to activate the catalyst. After cooling and release of the pressure, 6 g succinic acid and 14 g water were added to the autoclave reactor to get 120 g of a solution containing 5 wt% SUC. Finally, after purging with Ar, the reactor was heated under Ar to 160 °C, then hydrogen was adjusted to 150 bar which corresponds to time zero of the reaction.

### **2.4. Analytical methods**

During the SUC hydrogenation reaction, quantitative analyses of organic compounds present in the liquid samples and withdrawn from the reactor at regular intervals were performed using both a Shimadzu high performance liquid chromatography instrument equipped with a ICSEp Coregel 107H column and a differential refractometer and a UV detection in series, and a gas chromatography equipped with a HP-5 column, as previously described [12-17]. The carbon mass balance in liquid phase was examined by measuring total organic carbon (TOC) using a Shimadzu TOC-V<sub>CSH</sub> analyzer.

The elemental analysis of Re and Pd in the aqueous phase samplings withdrawn from the batch reactor was also performed to: (1) evaluate the possible presence in solution of metallic species leached from *ex situ* bimetallic catalysts during the SUC hydrogenation, and (2) follow the *in situ* deposition of Re onto the Pd/TiO<sub>2</sub> catalyst. These analyses were carried out by using inductively coupled plasma-optical emission spectrometry (ICP-OES, Activa Jobin-Yvon).

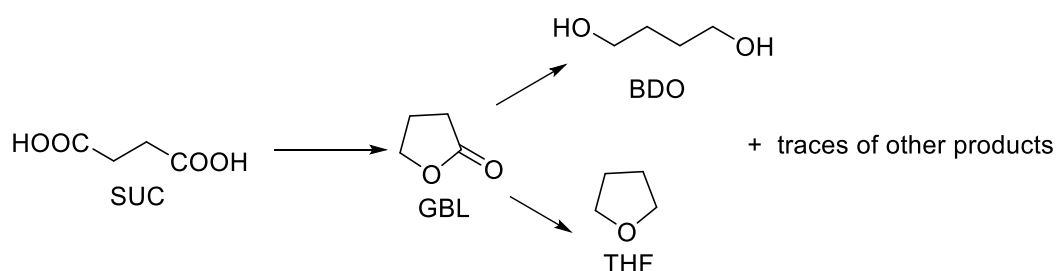
### **2.5. TEM analysis**

Transmission Electron Microscopy (TEM) was conducted using a JEOL 2010 instrument with a LaB<sub>6</sub> source operated at 200 kV coupled to an Oxford Link ISIS instrument for Microanalysis Energy Dispersive X-ray spectroscopy, and according to an experimental protocol described in detailed elsewhere [17]. The bimetallic catalysts were dispersed dry with a syringe on the carbon film coated over the copper grid.

### 3. Results and discussion

#### 3.1. Hydrogenation of SUC in the presence of *ex situ* SI and CR prepared catalysts

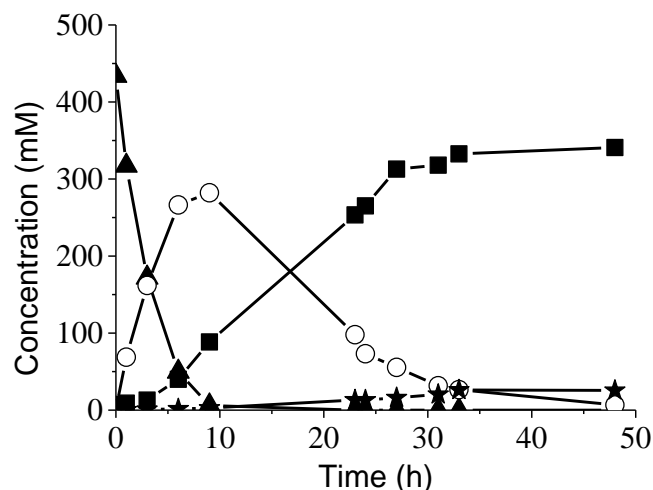
Under the experimental conditions used in our studies (160 °C, 150 bar of hydrogen pressure), hydrogenation of succinic acid (SUC) generated  $\gamma$ -butyrolactone (GBL), 1,4-butanediol (BDO), and tetrahydrofuran (THF) as the main products (Scheme 1). n-Butyric acid, n-butanol and n-propanol were also detected, but since the used temperature was relatively low for hydrogenolysis reactions, only traces were measured (< 1 %) [15,23].



**Scheme 1.** Catalytic hydrogenation of SUC to BDO.

##### 3.1.1. Summary of the morphology and catalytic performances of the *ex situ* SI and CR bimetallic catalysts

As mentioned in the introduction, the catalytic performances for SUC transformation of Re-Pd/TiO<sub>2</sub> systems prepared *ex situ* by SI and CR methods were studied in depth in our previous studies. For that purpose, several series of Re-2wt%Pd/TiO<sub>2</sub> catalysts with various Re loadings and using the same Re precursor salt (NH<sub>4</sub>ReO<sub>4</sub>), but two types of TiO<sub>2</sub> supports (named DT51 and P25, respectively) and of Pd precursor salts (PdCl<sub>2</sub> and K<sub>2</sub>PdCl<sub>4</sub>) were prepared and characterized [12-17]. Firstly, it was shown that monometallic Pd/TiO<sub>2</sub> catalysts gave GBL with excellent selectivity (> 90 %) [12]. In the presence of these catalysts, after SUC was fully converted, yields of BDO and THF were lower than 5 % and GBL formed was not further converted upon prolonged reaction times. Conversely, it was highlighted that the incorporation of Re by the SI or CR procedures made the hydrogenation of GBL to BDO possible and high yield to BDO was obtained (up to 90 %) [14-17]. Figure 1 shows a typical reaction profile as a function of time obtained at 160 °C under 150 bar H<sub>2</sub> in the presence of the bimetallic 3.4wt%Re-2wt%Pd/TiO<sub>2</sub>-SI catalyst prepared by *ex situ* SI method from TiO<sub>2</sub> DT51 support and K<sub>2</sub>PdCl<sub>4</sub> precursor salt.



**Fig. 1.** Hydrogenation of succinic acid in the presence of 3.4wt%Re-2wt%Pd/TiO<sub>2</sub> prepared by *ex situ* SI method: (▲) SUC, (○) GBL, (■) BDO, (★) THF. Reaction conditions: 6 g SUC in 114 g water (0.43 mol L<sup>-1</sup>), P<sub>H<sub>2</sub></sub> = 150 bar, T = 160 °C, 1 g catalyst.

Compared with the experiment in the presence of the parent monometallic Pd/TiO<sub>2</sub> catalyst (not shown, [12]), the catalytic activity of the Re-Pd/TiO<sub>2</sub> catalyst for conversion of SUC to GBL was increased (total conversion of SUC was obtained after 10 h compared with 48 h in the presence of the monometallic parent catalyst). The hydrogenation of GBL was greatly in favor of BDO while a very little amount of THF was formed (ca. 10 mmol L<sup>-1</sup>, yield < 2.4 %). After 48 h, the GBL was totally converted and the selectivity towards BDO was 90 %. The mechanism illustrating the essential role of Re species in the step of ring opening of GBL intermediate was described and discussed in depth in ref [17].

Table 1 gathers the main characteristics of these catalysts deduced from the numerous techniques employed to evaluate their morphology after the *ex situ* preparation. Significant interactions between Pd and Re entities were highlighted on all catalysts and rhenium was not completely reduced to the metal state, with a large proportion of Re<sup>3+</sup> species corresponding to the formation of ReO<sub>x</sub>-type clusters on the catalyst surface.



**Table 1.** Summary of the main characteristics and catalytic performances of Re-2wt%Pd/TiO<sub>2</sub> bimetallic catalyst series prepared by *ex situ* CR (deposition by catalytic reduction) and SI (successive impregnation) methods and reported in previous references.

Bimetallic catalyst series	Pd salt	Synthesis method	Characterization methods <sup>a</sup>	Main characteristics of reduced samples <sup>b</sup>	Maximum BDO yield (%) <sup>c</sup>	Ref .
Re-Pd <sub>Cl</sub> /TiO <sub>2</sub> P25	PdCl <sub>2</sub>	CR	ICP-OES +	Re <sup>3+</sup> species mainly located at the interface Pd-support	53 % for 0.9wt%Re	[16] [17]
		SI	H <sub>2</sub> chemisorption +	Re <sup>3+</sup> and Re <sup>0</sup> species located on the Pd particles and the support	67 % for 3.4wt%Re	[16] [17]
Re-Pd <sub>KCl</sub> /TiO <sub>2</sub> P25	K <sub>2</sub> PdCl <sub>4</sub>	CR	TEM- STEM- EDX +	Re <sup>3+</sup> species mainly located at the interface Pd-support	30 % for 0.6wt%Re	[14] [17]
		SI	TPR +	Re <sup>3+</sup> and Re <sup>0</sup> species located on the Pd particles and the support	67 % for 3.6wt%Re	[14] [17]
Re-Pd <sub>KCl</sub> /TiO <sub>2</sub> DT51	K <sub>2</sub> PdCl <sub>4</sub>	CR	+ XPS +	Inhomogeneous Re deposition due to experimental limitations <sup>d</sup>	56 % for 0.8wt%Re	[14] [17]
		SI	Model reaction	Re <sup>3+</sup> and Re <sup>0</sup> species located on the Pd particles and the support	90 % for 3.4wt%Re	[14] [17]

<sup>a</sup> ICP-OES: analysis by inductively coupled plasma optical-emission spectrophotometer of Pd and Re contents on solids at the end of their preparation

H<sub>2</sub> chemisorption: determination of the metallic accessibility to hydrogen of the pre-reduced catalysts

TEM-STEM-EDX: observation of the bimetallic particles and of their composition

TPR: study of the reduction profile of the catalysts after *in situ* oxidation

XPS: determination of the chemical nature of the Re and Pd species on the catalysts at various stages of their preparation (before reduction, after *ex situ* reduction, after *in situ* reduction in XPS chamber)

Model reaction: cyclohexane dehydrogenation performed in gas phase to evaluate the metal function

<sup>b</sup> Chemical state determined by XPS after *in situ* reduction in the XPS chamber

<sup>c</sup> Reactions conditions: 6 g SUC in 114 g water, P<sub>H<sub>2</sub></sub> = 150 bar, T = 160 °C, 1 g catalyst, 48 h reaction time

<sup>d</sup> The very fine granulation of the DT51 support caused plugging of the frit of the reactor used for the CR preparation method, leading to an inhomogeneous hydrogen flow limiting the catalytic reduction process

At the outcome of our previous works, many questions remain unresolved regarding the differences of catalytic performances in water of the bimetallic Re-Pd/TiO<sub>2</sub> systems prepared

*ex situ* (Table 1), complicated by the fact that it is impossible to *in situ* characterize the samples, *i.e.* under 150 bar of H<sub>2</sub> pressure at 160 °C. All characterizations performed *ex situ* might not be an exact representation of the working catalyst under hydrothermal conditions under hydrogen pressure. Moreover, it was shown that a simple contact with air of the reduced bimetallic catalysts leads to the oxidation of a part of Pd and all the Re species, for which Re<sup>3+</sup>, Re<sup>4+</sup>, Re<sup>6+</sup> and Re<sup>7+</sup> were observed [32]. As some rhenium oxides are known to be soluble in water, the stability in aqueous solution of the Re-Pd/TiO<sub>2</sub> bimetallic catalysts prepared *ex situ* has to be verified.

### 3.1.2. Study of the stability during the catalytic test of the Re-2wt%Pd/TiO<sub>2</sub> bimetallic catalysts prepared *ex situ*

#### \* After catalytic test

At the end of the catalytic tests, after sampling of the hot final solutions from the autoclave containing the *ex situ* prepared bimetallic catalysts, no Re or Pd was detected in solution at the limit concentrations of the ICP-OES method (Re, Pd < 0.2 ppm). It is important to mention that if the catalyst is maintained in the solution and filtrated in ambient condition, leaching of Re species is observed. Consequently, a modification of the catalyst occurred during the transfer from the medium of the catalytic test to the ambient condition. Thus, the temperature, the reaction medium as well as the H<sub>2</sub> pressure may play a major role in the stability of the catalyst. The characterization of the used catalyst necessitates to depressurize H<sub>2</sub>, filtrate and dry the catalyst and then will not give any information on its chemical state during the catalytic test. Thus, to gain a deeper understanding of the characteristics of the catalyst during the catalytic test, it is of major importance to characterize the catalyst stability throughout the whole catalytic test.

#### \* During catalytic test

Elemental analysis of the liquid samples withdrawn from the reaction medium during the heating period under Ar to the temperature of 160 °C showed a very significant leaching of Re: 60 % for 3.4wt%Re-2wt%Pd/TiO<sub>2</sub>-SI catalyst and 100 % in the case of the 0.8wt%Re-2wt%Pd/TiO<sub>2</sub>-CR sample with a lower initial Re loading. In contrast, as soon as the reactor was pressurized under 150 bar H<sub>2</sub> at time zero, only 0.5 % of the initial Re loading of the 3.4wt%Re-2wt%Pd/TiO<sub>2</sub>-SI catalyst was analyzed in solution. Rapidly, no Re could be detected anymore in solution during the hydrogenation reaction, which indicates that rhenium leached during heating under Ar could be re-immobilized on the solid under H<sub>2</sub> pressure. In these conditions,

the differences of catalytic performances exhibited by the *ex situ* SI and CR catalysts can originate from various proportions of Re in strong interaction with Pd after *ex situ* preparation, which was not leached. Also the distribution of  $\text{ReO}_x$  oxidized species in the catalysts resulting from the SI or CR protocol may not be the same; dissolved rhenium species may have different oxidation degrees and may be re-adsorbed and reduced differently.

These observations can be connected with reports in the literature on Re-Pd heterogeneous bimetallic catalysts, which were developed for the reduction of aqueous perchlorate in contaminated water, using hydrogen at ambient temperature and pressure [33-35]. First, the authors prepared a Re-Pd catalyst by  $\text{H}_2$  reduction of ammonium perrhenate precursor added to an acidic aqueous suspension of a carbon supported Pd catalyst at room temperature. They observed that the catalyst stored and handled in air showed significant leaching of Re when used in subsequent batch reactions [33]. About half of the Re originally immobilized on the catalyst surface leached at the initial stage of the batch reaction, but this solubilized Re was re-deposited on the solid upon exposure in  $\text{H}_2$ -saturated water. Consequently, the Re-Pd catalysts were prepared *in situ* by deposition of the rhenium salt at room temperature under  $\text{H}_2$  sparging for 5 h; the solids were filtrated and dried in an anaerobic glovebox (95 %  $\text{N}_2$ , 5 %  $\text{H}_2$ ) prior to the addition of perchlorate [34]. Secondly, by subjecting a perrhenate aqueous suspension of Pd/C to cycles of air- and  $\text{H}_2$ -sparging, the authors showed that the amount of  $\text{ReO}_4^-$  immobilized was heavily dependent on the redox chemistry of the overlying aqueous conditions (*i.e.*, air-sparged vs  $\text{H}_2$ -sparged solutions). Under  $\text{H}_2$  reducing environment, the  $\text{ReO}_4^-$  precursor was immobilized on the catalyst surface; under oxidizing conditions, only electrostatic reversible sorption of rhenium was observed.

Also, in a patent dealing with the hydrogenation of aqueous solutions of maleic acid to THF and/or BDO, a bimetallic catalyst was prepared *in situ* in water by addition of 4 wt% Re as  $\text{HReO}_4$  to an aqueous suspension containing a pre-reduced 1wt%Pd/C catalyst, and treatment in  $\text{H}_2$  prior to introduction of substrate or during the reaction [36]. This catalyst showed as good performance as a 4wt%Re-1wt%Pd/C catalyst prepared *ex situ*. For the synthesis of this latter, a 1wt%Pd/C catalyst was impregnated with aqueous perrhenic acid  $\text{HReO}_4$  and dried, and then activated in the reactor used for the reaction at ambient temperature in water in flowing  $\text{H}_2$  at 140 bar.

In conclusion, during the catalytic test performed on the Re-Pd/ $\text{TiO}_2$  bimetallic catalysts prepared *ex situ* then handled in air, a very significant fraction of Re deposited on the catalysts (> 50 %) was solubilized in the batch reactor during the heating period under Ar, this fraction was immediately re-deposited on the solid after pressurization under hydrogen at 160 °C before

the introduction of the SUC aqueous solution. To further elucidate the speciation of rhenium and enable improvements in catalyst performance, the study was further focused on the *in situ* deposition of Re onto the monometallic Pd/TiO<sub>2</sub> catalyst performed in the batch reactor under H<sub>2</sub> before the SUC hydrogenation reaction. This *in situ* preparation method will be described exclusively on the TiO<sub>2</sub> DT51 support, the Re-2wt%Pd/TiO<sub>2</sub> series synthesized *ex situ* on this support having led to the highest yield to BDO.

### **3.2. *In situ* synthesis of bimetallic catalysts**

In view of our previous observations and based on the literature, we assumed that it would be possible to deposit catalytically active rhenium on the monometallic catalysts *in situ* in the autoclave in a way similar to the *ex situ* CR deposition method, before performing the SUC hydrogenation experiment. The detailed protocol of the *in situ* synthesis of bimetallic Re-Pd/TiO<sub>2</sub> catalysts was described in the experimental section. During the *in situ* preparation, some exchange of rhenium with the TiO<sub>2</sub> support cannot be ruled out. Anyway, it was interesting to explore this new method of Re-Pd bimetallic systems preparation and compare the catalytic performances.

First, in the course of the *in situ* preparation, the extent of Re immobilization was followed by analyzing the amount of rhenium remaining in the liquid phase as a function of time in the samples periodically withdrawn from the reactor during heating under Ar, and then under H<sub>2</sub> pressure. The reactor was loaded with 1 g of 2wt%Pd/TiO<sub>2</sub> and 102 ppm or 427 ppm of Re<sup>7+</sup> (introduced as NH<sub>4</sub>ReO<sub>4</sub>), respectively. If all Re was deposited, this should correspond to solids containing 1.0 wt% Re or 4.3 wt% Re, respectively. Table 2 summarizes the extent of Re deposition as a function of reaction conditions and time.

**Table 2.** Immobilization of Re during *in situ* synthesis of bimetallic catalysts from 2wt%Pd/TiO<sub>2</sub> in aqueous solution, under Ar, then under H<sub>2</sub> pressure.

Re <sup>7+</sup> introduced in the reactor (ppm)	Test conditions upon sampling	Re analyzed in the liquid phase (ppm)	Re deposited on the solid (%)
102 ppm	Ar, 25 °C	98	0
	Ar, 100 °C	102	0
	Ar, 160 °C	91	10
	150 bar H <sub>2</sub> , 180 °C <sup>a</sup> , t ~ 0	4	96
	150 bar H <sub>2</sub> , 160 °C, t = 30 min	3	97
	Final solution after filtration	0.9	99
427 ppm	Ar, 70 °C	456	0
	Ar, 100 °C	455	0
	Ar, 120 °C	404	5
	150 bar H <sub>2</sub> , 180 °C <sup>a</sup> , t ~ 0	9	98
	150 bar H <sub>2</sub> , 160 °C, t = 1 h	4	99
	Ar, 25 °C, 5 bar <sup>b</sup>	4	99
	Final solution after filtration	5	99

<sup>a</sup> Upon introduction of H<sub>2</sub>, since the reaction is exothermic, temperature increased to 180 °C

<sup>b</sup> After cooling, flushing under Ar, and reactor maintained under Ar overnight

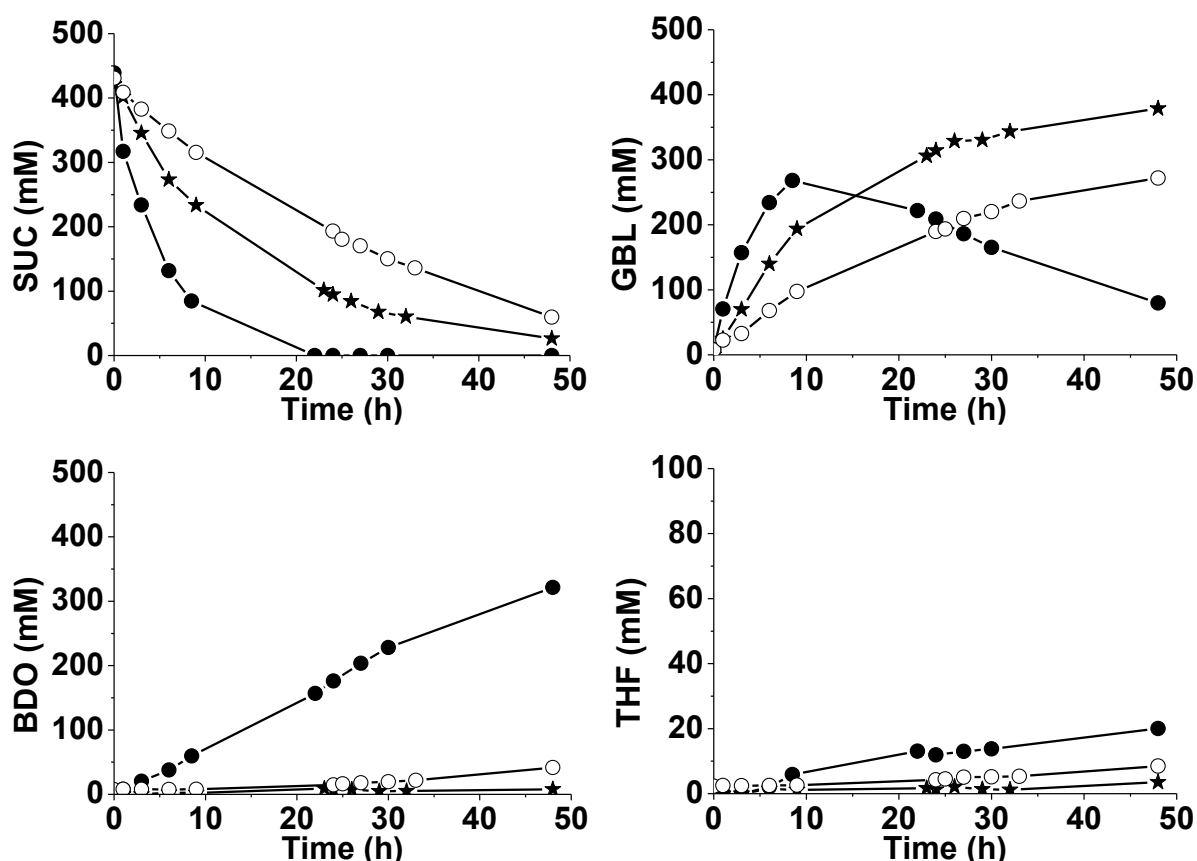
During the heating period under Ar atmosphere, the immobilization of Re species was rather limited, less than 10 % of Re introduced in the reactor was deposited on the Pd catalyst after 20 min. This is consistent with the observations of Choe *et al* [35] on the sorption of ReO<sub>4</sub><sup>-</sup> on a 5wt%Pd catalyst supported on active carbon (AC). In their experiments ca. 45 % of the ReO<sub>4</sub><sup>-</sup> ions introduced to give 5 wt% Re on the solid were sorbed onto Pd/C under air-sparging. Compared to the conditions in the present study, the load of Pd was higher and the specific surface area of the AC support was also much higher than the one of TiO<sub>2</sub>, which explains the larger amount of immobilized Re observed by these authors. Besides, in our experiments, we observed that as soon as the Pd/TiO<sub>2</sub> catalyst in contact with 102 ppm or 427 ppm Re-containing solutions was exposed to reducing conditions (by pressurization of the reactor with H<sub>2</sub> to 150 bar at 160 °C), the Re concentration present in the liquid phase became very low and represented below 4 % and 2 % of the initial amount, respectively (Table 2). After a longer period under H<sub>2</sub> (30 min or 1 h) nearly complete immobilization of Re on the Pd parent catalyst was observed (while according to Choe *et al* [34], the immobilization of 5 wt% ReO<sub>4</sub><sup>-</sup> on Pd/C

required 2.5 h at room temperature under atmospheric pressure of H<sub>2</sub> to be complete). Finally, the end solution recovered after filtration of the catalyst contained only a few ppm of Re (0.9 and 5 ppm, respectively). In addition, the ICP-OES analysis of the solids recovered after filtration of the final suspension gave 0.9 wt% Re and 4.1 wt% Re, respectively, *i.e.* very close to the expected values for total deposition of rhenium, ca. 1.0 wt.% and 4.3 wt.%.

These results strongly support that the *in situ* deposition of solubilized oxidized Re species occurs mainly by a redox reaction ( $\text{Re}^{7+} \rightarrow \text{Re}^{(7-n)+}$ ) between hydrogen activated on Pd and rhenium ions in solution. As long as the catalyst is maintained under H<sub>2</sub> or is not exposed to air, leaching is not observed.

### ***3.3. Influence of activation duration during the in situ preparation***

As shown previously, during the *in situ* preparation of Re-Pd/TiO<sub>2</sub> catalysts, the ReO<sub>4</sub><sup>-</sup> species were immediately immobilized on the Pd/TiO<sub>2</sub> catalyst once upon pressurization of the reactor under hydrogen and we attributed this deposition to a partial reduction of ReO<sub>4</sub><sup>-</sup> into Re<sup>n+</sup> by Pd-H. The time attributed to this step under H<sub>2</sub> pressure will be named the “activation duration”. We firstly investigated the influence of this activation duration, by preparing *in situ* bimetallic Re-Pd/TiO<sub>2</sub> catalysts by addition of ammonium perrhenate salt amounts as to get ca. 2.0 wt% or 4.0 wt% Re loading in the final bimetallic catalysts, with an activation duration of either 1 h or 15 h. Figures 2 and 3 show the performances for the SUC hydrogenation at 160 °C under 150 bar H<sub>2</sub> obtained with the two bimetallic catalysts, respectively, after both activation times.

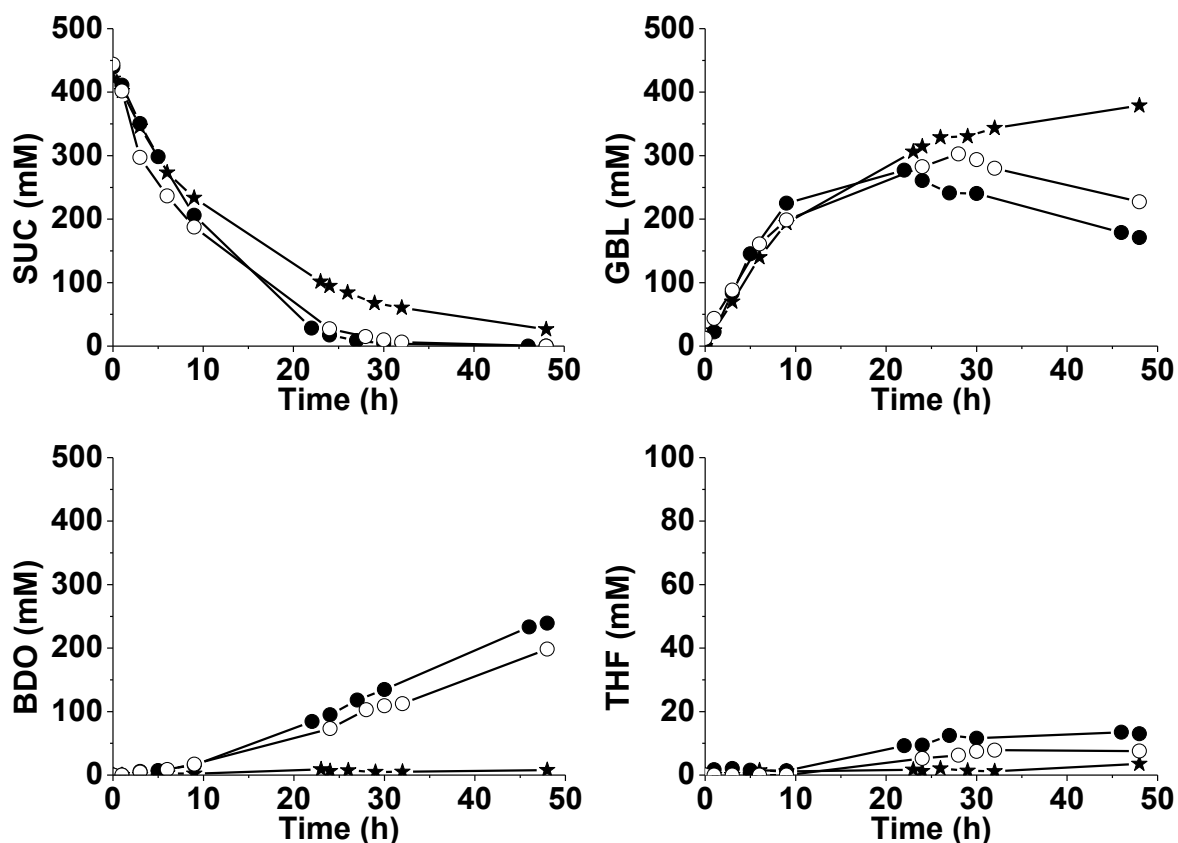


**Fig. 2.** Influence of the activation time (1 h or 15 h) on the performances for SUC hydrogenation of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 2.0 wt% Re loading. (★) 2wt%Pd/TiO<sub>2</sub>, (●) 2wt%Pd/TiO<sub>2</sub> + 1.8wt%Re, 1 h-activation, (○) 2wt%Pd/TiO<sub>2</sub> + 2.0wt%Re, 15 h-activation.

Figure 2 shows that an activation duration of 1 h led to a bimetallic catalyst containing 1.8wt%Re on 2wt%Pd/TiO<sub>2</sub> that converted SUC within 20 h, and the final selectivity to BDO was 73 % after 48 h. Surprisingly the solid pretreated during a longer period of 15 h became less active. Only 87 % SUC were converted after 48 h with selectivity to GBL and BDO of 70 % and 10 %, respectively. This suggests a different reduction degree of Re on the catalyst surface, that would be far from the optimum required for a good selectivity to BDO. Unfortunately it remains difficult to get information on the oxidation degree of Re under experimental conditions representative of the *in situ* preparation medium (*i.e.* under H<sub>2</sub> pressure at 160 °C) and thus corresponding to the Re state during the reaction. However in our previous study, TPR analysis of the 1.9wt%Re-Pd/TiO<sub>2</sub> catalyst prepared *ex situ* by CR and then oxidized at 300 °C evidenced that 88 % of H<sub>2</sub> consumption was reached before 50 °C [17]. XPS studies on the same sample showed that after reduction under H<sub>2</sub> at 450 °C and atmospheric pressure, Re is mainly at the +3 oxidation degree, with only 30 % in the metallic state. In the present study, we suppose that under our experimental conditions, Re species should be in lower

reduction states overall, depending on the activation duration and probably on the Re content introduced.

Figure 3 shows the results obtained in the case of the catalysts loaded with ca. 4.0 wt% Re prepared with an activation duration of 1 h or 15 h.

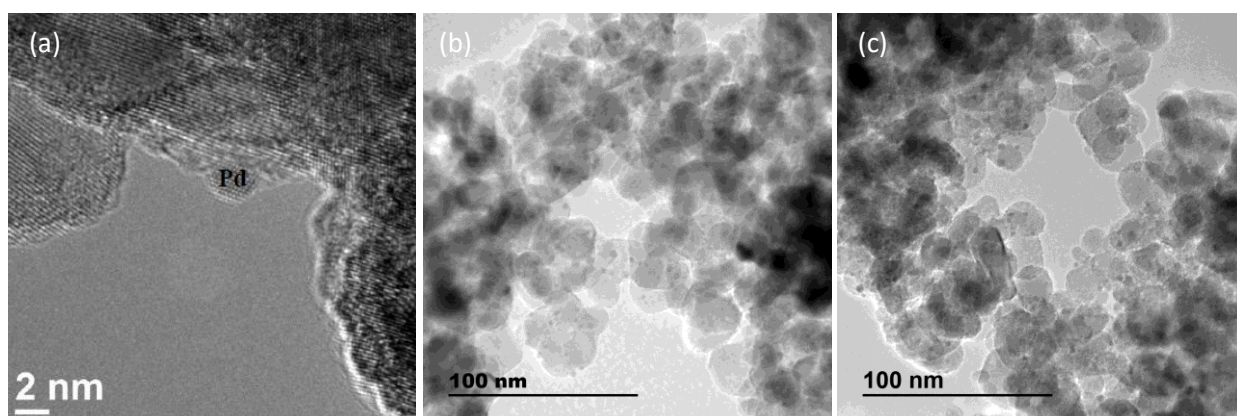


**Fig. 3.** Influence of the activation time (1 h or 15 h) on the performances for SUC hydrogenation of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 4.0 wt% Re loading. (★) 2wt%Pd/TiO<sub>2</sub>, (●) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re, 1 h-activation, (○) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re, 15 h-activation.

Compared with the *in situ* bimetallic 2.0wt%Re-2wt%Pd/TiO<sub>2</sub> catalysts for which a beneficial effect of 1 h-activation was obtained (Figure 2), the influence of the activation duration (1 h or 15 h) on the reaction rate of SUC hydrogenation was moderate for *in situ* loading of 4.0 wt% Re (Figure 3). Nearly the same activity for SUC conversion was observed for the solids prepared from 2wt%Pd/TiO<sub>2</sub> and 4wt%Re loading, after one hour or one night pre-treatment. The reaction of SUC was slightly faster than in the presence of the monometallic parent solid. Yet, GBL was converted more efficiently after only 1 h-activation. After 48 h reaction, 41 % GBL and 51 % GBL remained in the reaction medium, respectively, depending on the activation duration.



In order to attempt explaining the different performances of the *in situ* bimetallic catalysts depending on the duration of activation, the used catalysts containing ca. 4 wt% Re were recovered after reaction and characterized by transmission electron microscopy TEM-EDX. Figures 4b and 4c show representative images of these catalysts which have undergone an activation duration of 1 h or 15 h, respectively. For comparison, Figure 4a gives an example of TEM images obtained for the monometallic 2wt%Pd/TiO<sub>2</sub> used as parent sample for this *in situ* preparation. In our previous studies, this monometallic parent catalysts has been deeply characterized by X-ray diffraction (XRD), H<sub>2</sub> chemisorption and TEM [12,17]. No XRD peak other than those of TiO<sub>2</sub> supports were detected suggesting small Pd particle sizes. By H<sub>2</sub> chemisorption performed at 70 °C, the metal dispersion was determined to be 27 %, the average metal particle size that was deduced (3.5 nm) was slightly smaller than determined by TEM (2.4 nm, Fig. 4a).



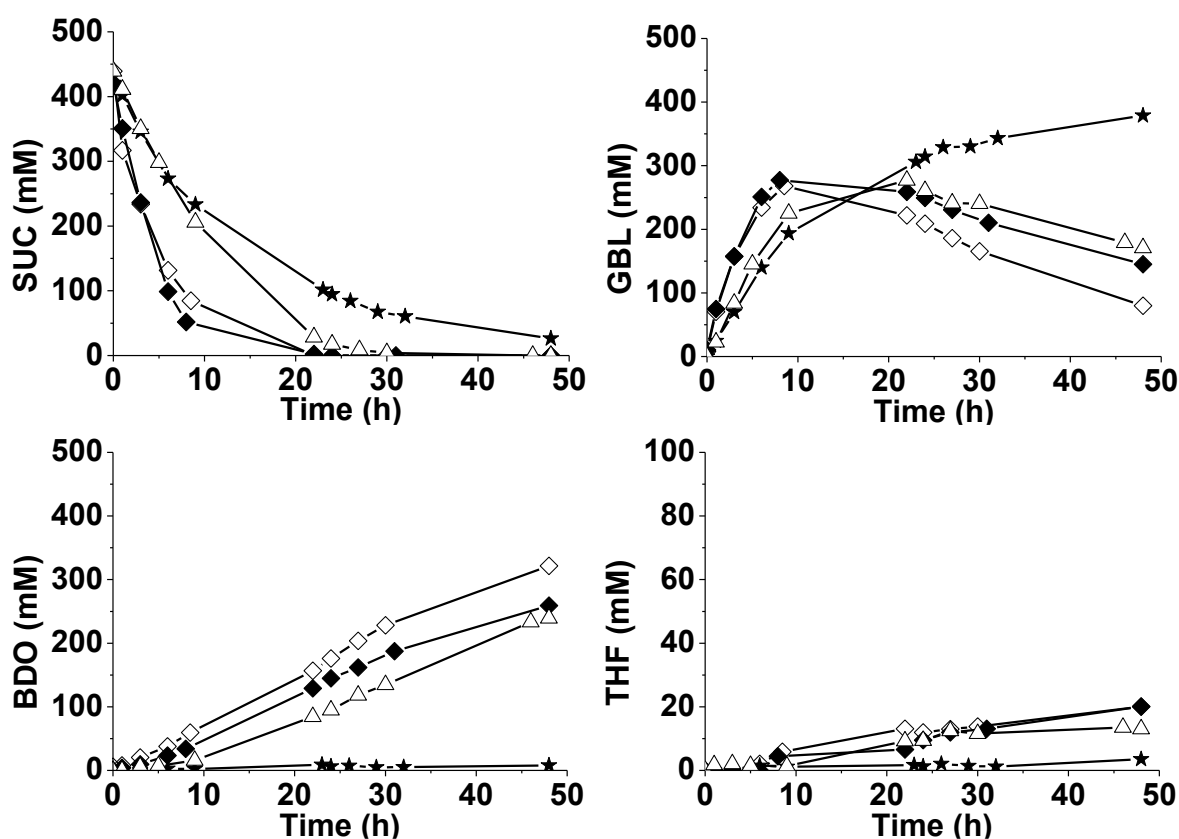
**Fig. 4.** Representative TEM images of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 4 wt% Re loading. (a) Pd/TiO<sub>2</sub> parent catalyst before *in situ* preparation, (b) used Re-Pd/TiO<sub>2</sub> catalyst obtained after 1 h-activation, (c) used Re-Pd/TiO<sub>2</sub> catalyst obtained after 15 h-activation.

For the *in situ* bimetallic catalysts recovered after reaction, attention was focused on the EDX analysis and the location of Re species. For both activation durations (1 h-Fig. 4b or 15 h-Fig. 4c), small metallic particles constituted of Pd and Re were observed dispersed all over the support. A few very large particles, consisting mainly of Pd in the 1 h-activated solid, and with high Re concentrations in the 15 h-activated solid, were also detected. TEM-EDX analysis was not able to show obviously if the *in situ* deposition of Re occurred as different forms according to the duration of activation, since the observations were finally quite comparable, in agreement with the comparable performances displayed by these two catalysts for the SUC hydrogenation.

Finally, these screening experiments for an estimation of the optimum activation period indicate that a duration of 1 h should be sufficient and the best for the catalytic performance.

### 3.4. Determination of the optimum Re loading for *in situ* bimetallic catalysts

As observed earlier for the catalysts prepared by the *ex situ* CR and SI method [13-15], an optimum of Re loading was also expected for the *in situ* preparation. The effect of Re loading was further investigated leading to the catalytic results for SUC transformation shown in Figure 5 (the *in situ* activation duration was maintained to 1 h).

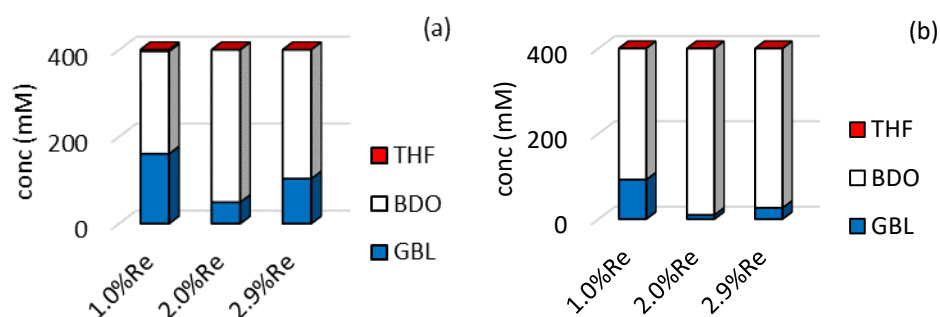


**Fig. 5.** Influence of the Re loading introduced *in situ* on the 2wt%Pd/TiO<sub>2</sub> catalyst on the performances for SUC hydrogenation (activation duration of 1 h). (★) 2wt%Pd/TiO<sub>2</sub>, (◆) 2wt%Pd/TiO<sub>2</sub> + 1.0wt%Re, (◇) 2wt%Pd/TiO<sub>2</sub> + 1.8wt%Re, (△) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re.

The deposition of Re in the 1-4wt% range clearly improved the catalytic activity compared with that of the parent catalyst: SUC was completely hydrogenated within 24 h instead of more than 48 h, and GBL was mainly converted to BDO. Among the catalysts studied, the one containing 4.1 wt% Re was the least active giving only 48 % SUC conversion after 9 h, compared to 90 % conversion over the catalyst loaded with 1.8 wt% Re. In the subsequent hydrogenation of GBL, which determines the final yield in BDO, the solid containing 1.8 wt% Re was the most active

and gave a 73 % selectivity to BDO. This selectivity was only 62 % and 54 %, respectively, in the presence of 1.0 wt% and 4.1 wt% Re.

For this *in situ* bimetallic catalysts series, the highest activity of the sample containing 2.0 wt% Re was confirmed in the hydrogenation of the GBL substrate performed under the same conditions, as shown in Figure 6. Compared with the *in situ* bimetallic catalysts loaded with 1.0 wt% Re or 2.9 wt% Re, the one loaded with 2.0 wt% Re was the most active in converting GBL to BDO with a 97 % selectivity to BDO.



**Fig. 6.** Influence of the Re loading introduced *in situ* on the 2wt%Pd/TiO<sub>2</sub> catalyst on the performances for GBL hydrogenation (activation duration of 1 h) after (a) 24 h and (b) 48 h. ([GBL]<sub>0</sub> = 420 mmol L<sup>-1</sup>)

Another experiment for the direct hydrogenation of GBL was performed over a 3.1 wt%Re/TiO<sub>2</sub> monometallic rhenium catalyst. This catalyst was very little active (< 5 % conversion after 24 h) in this reaction, which was explained by the leaching of rhenium while the catalyst was in contact with water. In that case, in the absence of Pd on the catalyst, oxidized rhenium species could not be re-immobilized on the solid under H<sub>2</sub> pressure. In the literature, Re/C catalysts prepared using a microwave-assisted thermolytic method were shown to perform 91 % conversion after 10 h starting from a 10 wt% aqueous solution of SUC at 240 °C under 80 bar, with selectivity to GBL and THF of 59.2 % and 33.0 %, respectively [25]. The catalysts were relatively stable upon recycling provided care was taken to protect them from oxidation. Also, mesoporous carbon-supported Re catalysts were active for succinic acid conversion to THF in dioxane at 240 °C, with negligible leaching of Re [20].

Finally, we compared the catalytic performances of the bimetallic Re-Pd/TiO<sub>2</sub> catalysts containing the optimal Re content introduced by each studied preparation method: *ex situ* CR, *ex situ* SI, and *in situ* method. The optimum loading of Re deposited by *in situ* method for the selectivity to BDO was around 1.8 wt% Re, which is a value between the optimum loadings

using the *ex situ* SI (3.4 wt%) and *ex situ* CR (0.8 wt%) protocols. Table 3 summarizes the final selectivity attained over the best catalyst of each series.

**Table 3.** Comparison of performances for SUC hydrogenation of best bimetallic catalysts prepared by *ex situ* CR and SI methods, and *in situ* deposition. Reactions conditions: 160 °C, 150 bar H<sub>2</sub>, 48 h reaction time.

Catalyst	Selectivity GBL (%)	Selectivity BDO (%)	Selectivity THF (%)
0.8wt%Re-Pd/TiO <sub>2</sub> -CR <i>ex situ</i>	23	56	16
1.8wt%Re-Pd/TiO <sub>2</sub> - <i>in situ</i> 1 h-activation	18	73	5
3.4wt%Re-Pd/TiO <sub>2</sub> -SI <i>ex situ</i>	0	90	5

The *ex situ* CR method or the *in situ* preparation are both based on reductive immobilization in water of ReO<sub>4</sub><sup>-</sup> ions on Pd/TiO<sub>2</sub> parent catalyst, by means of the dissociation of molecular hydrogen to yield Pd-adsorbed atomic hydrogen (Pd-H<sub>ads</sub>) and then allow reduction of oxidized Re species. The different performances of the bimetallic catalysts obtained by these two preparation protocols suggests that the distributions of the Re species should differ on the catalysts. We tried to understand the differences.

In the former case, the 0.8wt%Re-Pd/TiO<sub>2</sub>-CR bimetallic catalyst was prepared *ex situ* under reducing conditions, and then exposed to and stored in air after reduction under flowing H<sub>2</sub>, and loaded in the batch reactor without special care. As shown, nearly complete leaching of the Re species occurred in the autoclave, before Re was again totally immobilized on the solid under H<sub>2</sub> pressurization.

In the latter case, to prepare the 1.8wt%Re-Pd/TiO<sub>2</sub> *in situ* catalyst, ReO<sub>4</sub><sup>-</sup> precursor was immobilized on the Pd/TiO<sub>2</sub> catalyst suspended in an aqueous solution into the autoclave under 40 bar H<sub>2</sub> pressure at 160 °C during 1 h activation duration. Some ReO<sub>4</sub><sup>-</sup> sorption onto the Pd/TiO<sub>2</sub> solid occurred during the heating period under Ar, however it was limited (Table 2). After introduction of hydrogen pressure, H<sub>2</sub> dissociates on Pd to yield Pd-adsorbed atomic hydrogen (Pd-H<sub>ads</sub>). In the literature, Re-5wt%Pd/AC catalysts prepared in aqueous solution under reducing conditions (sparging H<sub>2</sub> at ambient condition for 5 h) were analyzed by XPS, after taking care to handle the synthesized catalyst in an anaerobic glovebox without exposure to air [34,35]. Pd was present predominantly in the metallic state. The presence of two Re species was observed on the surface corresponding to monomeric Re<sup>+</sup> and Re<sup>5+</sup> entities associated to Re 4f<sub>7/2</sub> binding energies (BE) equal to 41.5 eV and 43.9 eV, respectively. The

proportion of both species varied with Re content: at low Re content (< 5 wt%) the  $\text{Re}^+$  species was observed in majority, formed by direct contact with Pd according to the suggested mechanism  $\text{ReO}_4^-_{(\text{ads})} + 6 \text{Pd-H}_{\text{ads}} + \text{H}^+ \rightarrow \text{Re}^{\text{I}}\text{OH}_{(\text{ads},\text{Pd})} + 6 \text{Pd} + 3 \text{H}_2\text{O}$ . This species was described as more resistant to re-oxidation. As Re loading increased, the authors explained the formation of oxorhenium (V) clusters on the carbon support *via* atomic hydrogen spillover. Back to the systems described in this work and taking into account that the Pd content was 2 wt% only, the shift of Re speciation with Re loading in the above cited literature may explain that the performances of the bimetallic catalysts depend on the Re content. We may assume that upon increasing the Re content introduced in the autoclave, lower extent of reduction takes place for the Re species, which is less favorable for the selective SUC hydrogenation to BDO. XPS analysis of catalysts prepared *in situ* has not been performed to demonstrate such hypothesis, due to the harsh challenging preparation conditions ( $P_{\text{H}_2} = 150 \text{ bar}$ ,  $T = 160 \text{ }^\circ\text{C}$ ).

#### 4. Conclusions

The first conclusion of this work is that one has to pay attention when Re-based bimetallic catalysts are used in aqueous phase, since we demonstrated an important Re leaching in solution on the samples after their exposure to air. Consequently, care must be taken to maintain the catalysts under anoxic or reducing conditions to immobilize Re species on their surface.

Following the finding that Re leaching from the *ex situ* prepared Re-Pd/TiO<sub>2</sub> bimetallic catalysts exposed to air was important when introduced in an aqueous solution, but that Re was again very rapidly re-immobilized on the solid under H<sub>2</sub> atmosphere, we studied a new way to prepare *in situ* Re-Pd/TiO<sub>2</sub> bimetallic systems into the autoclave used for SUC transformation. This *in situ* preparation was assumed to be comparable to an *in situ* deposition of Re by catalytic reduction (CR). An optimum activation period (1 h) under H<sub>2</sub> atmosphere before SUC introduction in the batch reactor and an optimum loading of Re were determined. The as-prepared catalyst exhibited an intermediate selectivity to BDO compared to the catalysts prepared *ex situ* from the same parent monometallic catalysts, according to the following order: *ex situ* CR < *in situ* CR < *ex-situ* SI (successive impregnation).

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## Captions to illustrations

### Scheme 1. Catalytic hydrogenation of SUC to BDO.

**Fig. 1.** Hydrogenation of succinic acid in the presence of 3.4wt%Re-2wt%Pd/TiO<sub>2</sub> catalyst prepared by *ex situ* SI method: (▲) SUC, (○) GBL, (■) BDO, (★) THF. Reaction conditions: 6 g SUC in 114 g water (0.43 mol L<sup>-1</sup>), P<sub>H2</sub> = 150 bar, T = 160 °C, 1 g catalyst.

**Fig. 2.** Influence of the activation time (1 h or 15 h) on the performances for SUC hydrogenation of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 2.0 wt% Re loading. (★) 2wt%Pd/TiO<sub>2</sub>, (●) 2wt%Pd/TiO<sub>2</sub> + 1.8wt%Re, 1 h-activation, (○) 2wt%Pd/TiO<sub>2</sub> + 2.0wt%Re, 15 h-activation.

**Fig. 3.** Influence of the activation time (1 h or 15 h) on the performances for SUC hydrogenation of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 4.0 wt% Re loading. (★) 2wt%Pd/TiO<sub>2</sub>, (●) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re, 1 h-activation, (○) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re, 15 h-activation.

**Fig. 4.** Representative TEM images of Re-2wt%Pd/TiO<sub>2</sub> prepared *in situ* with ca. 4 wt% Re loading. (a) Pd/TiO<sub>2</sub> parent catalyst before *in situ* preparation, (b) used Re-Pd/TiO<sub>2</sub> catalyst obtained after 1 h-activation, (c) used Re-Pd/TiO<sub>2</sub> catalyst obtained after 15 h-activation.

**Fig. 5.** Influence of the Re loading introduced *in situ* on the 2wt%Pd/TiO<sub>2</sub> catalyst on the performances for SUC hydrogenation (activation duration of 1 h). (★) 2wt%Pd/TiO<sub>2</sub>, (◆) 2wt%Pd/TiO<sub>2</sub> + 1.0wt%Re, (◇) 2wt%Pd/TiO<sub>2</sub> + 1.8wt%Re, (△) 2wt%Pd/TiO<sub>2</sub> + 4.1wt%Re.

**Fig. 6.** Influence of the Re loading introduced *in situ* on the 2wt%Pd/TiO<sub>2</sub> catalyst on the performances for GBL hydrogenation (activation duration of 1 h) after (a) 24 h and (b) 48 h. ([GBL]<sub>0</sub> = 420 mmol L<sup>-1</sup>)