

# Selective C-O hydrogenolysis of erythritol over supported Rh-ReO<sub>x</sub> catalysts in aqueous phase.

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Scissors for C-O bonds. Selective C-O hydrogenolysis is a challenging strategy to remove the hydroxyl groups of oxygenated biomass-derived molecules. Reaction pathways for erythritol in water were studied over  $TiO_2$ - and  $ZrO_2$ -supported Rh-ReOx catalysts. Using  $ZrO_2$  as support, a selectivity up to 66% butanetriols and butanediols was achieved at 80% conversion.

#### Abstract

Bimetallic Rh–ReO<sub>x</sub> (Re/Rh molar ratio 0.4-0.5) catalysts supported on TiO<sub>2</sub> and ZrO<sub>2</sub> were prepared by successive impregnation of dried and calcined unreduced supported Rh catalysts. Their catalytic performances were evaluated in the hydrogenolysis of erythritol to butanetriols (BTO) and butanediols (BDO) in aqueous solution at 150-240°C under 30-120 bar H<sub>2</sub>. The activity was dependent on the nature of the support and the highest selectivity to BTO and BDO at 80% conversion reached 37 and 29%, respectively, in the presence of 3.7wt%Rh–3.5wt%ReO<sub>x</sub>/ZrO<sub>2</sub> catalyst at 200°C under 120 bar. Characterizations of the catalysts by CO chemisorption, TEM-EDX, TGA-MS, XPS suggest a different distribution and reducibility of Re species over the supported Rh nanoparticles depending on the support.

# Keywords

Biomass; aqueous phase; butanetriols and butanediols; erythritol hydrogenolysis; supported Rh-ReOx catalysts

# 1. Introduction

Over the last few decades, society has been moving toward the use of lignocellulosic biomass on a large scale for the production of chemicals and fuels.<sup>[1–4]</sup> Indeed, platform chemicals derived from the carbohydrate fraction (cellulose and hemicellulose), such as sugars (e.g. glucose), sugar alcohols (e.g. sorbitol) and cyclic ethers (e.g. tetrahydrofurfuryl alcohol via furfural) are promising alternatives to unsustainable fossil resources for the production of highvalue added chemicals. The platform molecules are highly functionalized and contain an O/C ratio higher than most of the commodity chemicals, thus, their transformation requires to lower the O content. Among the deoxygenation methods, hydrogenolysis of alcoholic C-O bond is of particular significance. Performing this reaction efficiently, and also selectively eliminating either a primary or a secondary alcohol, is necessary, however C-O bond hydrogenolysis is not an easy reaction to achieve. A number of supported catalytic systems have been studied and reported to be selective for the partial dehydroxylation of glycerol towards 1,2-propanediol<sup>[5,6]</sup> (up to 98%) and 1,3-propanediol<sup>[7–9]</sup> (up to 67%). Nevertheless, the efficient and selective removal of OH groups in superior polyols with more OH groups such as erythritol, xylitol, and sorbitol remains very challenging.<sup>[10–12]</sup>

Erythritol (ERY) is a promising platform chemical for the production of butanetriols and diols as C4 building blocks. Chemical<sup>[13]</sup> and fermentative<sup>[14,15]</sup> processes have been investigated for its production in large-scale. ERY can be produced by catalytic hydrogenation of dialdehyde starch over nickel catalyst at 160-200°C under 140 bar of H<sub>2</sub>, but this process has not been industrialized due to safety and environmental reasons.<sup>[13]</sup> The standard industrial production routes involve the microbial fermentation of sugar and sugar alcohols such as glucose and glycerol using various yeasts. The highest yields reported for the production of ERY are of 61% from glucose<sup>[14]</sup> and 56% from glycerol.<sup>[15]</sup>

The literature dealing with the production of C4-triols and diols from sugar alcohols is limited.<sup>[10–12]</sup> During erythritol hydrogenolysis, four types of reactions can occur: C-O bond hydrogenolysis, C-C bond hydrogenolysis, dehydration and epimerization as shown in Scheme 1. Erythritol is converted to the desired butanetriols (1,2,3-BTO, 1,2,4-BTO) and the series of butanediols (BDO) by C-O bond cleavage. Over-hydrogenolysis of butanediols yields 1-butanol (1-BuOH)<sup>[16]</sup> and 2-butanol (2-BuOH).<sup>[17]</sup> In addition, dehydration of erythritol can occur and yields 1,4-anhydroerythritol (1,4-AE); the successive C-O hydrogenolysis generates the formation of 3-hydroxytetratydrofuran (3OH-THF) and tetrahydrofuran (THF). C-C

hydrogenolysis reactions lead to many types of C2 and C3 products such as ethylene glycol (EG), glycerol (GLY), propylene glycol (PG) and propanol (PrOH). Finally, erythritol can also undergo epimerization reaction and form threitol.

The butanetriols and butanediols are all valuable products. 1,2,4-BTO, currently obtained industrially by catalytic hydrogenation of malic esters, is used in the production of polyurethane foams, butanetriol trinitrate (a propellant), pharmaceuticals, and high quality inks.<sup>[18,19]</sup> 1,4-BDO is employed as solvent, in the manufacture of various polymers, and for the synthesis of  $\gamma$ -butyrolactone and THF. 1,2-BDO is generated as a by-product during the fabrication of 1,4-butanediol from butadiene. It is a precursor for the production of low viscous polyester and plasticizers.<sup>[20]</sup> 2,3-BDO has many applications in the printing inks, pharmaceuticals, perfumes, and pesticides industries. It is produced via pyruvate from the microbial fermentation of monosaccharides (hexoses or pentoses).<sup>[21]</sup>



Scheme 1. Possible reaction routes associated with the conversion of erythritol under hydrogenolysis conditions.

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The first studies dealing with the conversion of erythritol were conducted over conventional hydrogenolysis catalysts such as supported Ru and Cu.<sup>[22,23]</sup> Montassier et al<sup>[22]</sup> reported that Cu-Ru/C catalyst favored predominantly dehydration reaction, with formation of 1,4-anhydroerythritol, and traces of C2-C3 products by C-C bond hydrogenolysis, when working at 260°C under 40 bar of H<sub>2</sub>. Moreover, under similar reaction conditions, Ru/S-modified carbon (S/Ru=1) and Raney Cu exhibited initial selectivities towards butanediols (1,2-BDO+2,3-BDO) of 33% and 54%, respectively.<sup>[23]</sup>

Since, it has been shown that the combination of an oxophilic promoter (Re, Mo or W) and a highly reducible noble metal (Ir, Rh, or Ru) enhanced the catalytic performance in the selective C-O bond hydrogenolysis of polyols or cyclic ethers (tetrahydrofurfuryl alcohol and tetrahydropyran-2-methanol).<sup>[24–28]</sup> For example, C and SiO<sub>2</sub>-supported Rh-ReO<sub>x</sub> catalysts were shown to be active and selective in C-O hydrogenolysis of 1,2,6-hexanetriol to 1,6hexanediol<sup>[27]</sup> and 1,2,4-butanetriol to 1,4-butanediol.<sup>[28]</sup> In Dumesic's group work, Rh-ReO<sub>x</sub>/C proved to be selective in the hydrogenolysis of secondary C-O bonds during hydrogenolysis of polyols and cyclic ethers derived from biomass.<sup>[28]</sup> There are fewer studies dealing with the use of these supported bimetallic catalysts for hydrogenolysis of erythritol. Tomishige's group studied the effect of the nature of the noble metal (Ir and Rh) and of the oxophilic promoter (Re, W, and Mo) over SiO<sub>2</sub> support.<sup>[10]</sup> They also investigated the effect of reaction parameters including H<sub>2</sub> pressure (20-80 bar), temperature (80-140°C), erythritol concentration (5-67wt%) aqueous solution), acid additive  $(n_{H+}/n_{Ir} = 1)$ , and metal particle size, on the selectivity towards butanediols over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalysts. Under optimum conditions (100°C, 80 bar of H<sub>2</sub>,  $n_{H+}/n_{Ir}=1$ ), the maximum selectivity towards butanediols in water reached 48% at 74% conversion. In another study, a selectivity of 40% towards butanediols was observed at 91% conversion when using Ir-ReO<sub>x</sub>/SiO<sub>2</sub> combined with H-ZSM-5 in water, at short reaction time (120°C, 80 bar of H<sub>2</sub>).<sup>[12]</sup> Really high selectivity in butanediols was reported in the presence of ReOx-Pd/CeO2 (93% selectivity at 98% conversion), however the reaction was conducted with dioxane as solvent.<sup>[11]</sup>

In this work, mesoporous TiO<sub>2</sub> and ZrO<sub>2</sub> were chosen as the supports because of their stability in water under hydrogenolysis conditions.<sup>[29,30]</sup> Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> were investigated for the selective hydrogenolysis of erythritol to butanetriols and diols in batch reactor. The influence of reaction conditions (e.g. temperature, pressure of H<sub>2</sub>, acid additive, effect of support) were studied in details. We also tried to get better insight on the reaction mechanism associated with the formation of butane- triols and diols.

# 2. Results and discussion

# 2.1. Catalyst characterization

The properties (chemical composition, BET surface area, CO chemisorption) of the synthesized catalysts are presented in Table 1.

Catalyst	Rh-Re loading <sup>[a]</sup>	n <sub>Re</sub> /n <sub>Rh</sub>	S <sub>BET</sub> <sup>[b]</sup>	CO/Rh
	(wt%)	$(mol_{Re}/mol_{Rh})$	$(m^2.g^{-1})$	(mol/mol) <sup>[c]</sup>
Rh/TiO <sub>2</sub>	3.7-0.0	-	83	0.27
Rh/ZrO <sub>2</sub>	3.6-0.0	-	97	0.74
Rh-ReO <sub>x</sub> /SiO <sub>2</sub>	3.2-2.5	0.4	200	-
Rh-ReO <sub>x</sub> /TiO <sub>2</sub>	3.7-2.6	0.4	85	0.25
Rh-ReO <sub>x</sub> /ZrO <sub>2</sub>	3.7-3.5	0.5	98	0.80

Table 1. Physicochemical properties of the synthesized catalysts

<sup>[a]</sup> based on ICP-OES analysis

<sup>[b]</sup> from N<sub>2</sub> physisorption,  $S_{BET}$  TiO<sub>2</sub> = 91m<sup>2</sup>.g<sup>-1</sup>,  $S_{BET}$  ZrO<sub>2</sub> = 129 m<sup>2</sup>.g<sup>-1</sup>,  $S_{BET}$  SiO<sub>2</sub> = 200 m<sup>2</sup>.g<sup>-1</sup>

<sup>[c]</sup>Calculated from CO chemisorption measurements

The analysis of the metal and promoter contents of the catalysts showed that complete deposition occurred. The Rh and Re loadings were in the range 3.2-3.7wt% and 2.5-3.5wt%, respectively. The molar ratio between metallic Rh and oxophilic promoter (Re) was fixed at 0.4-0.5 based on the literature. Indeed, the catalytic performances of Re promoted catalysts for hydrogenolysis reactions have been shown to depend on Re content; the curve usually exhibits a volcano shaped trend, where the maximum depends on the nature of the noble metal. For the conversions of glycerol to 1,3-propanediol<sup>[31]</sup> and tetrahydrofurfuryl alcohol to 1,5-pentanediol,<sup>[32]</sup> optimum Rh/Re ratios of 0.5 were determined; the presence of high amount of Re can decrease the amount of Rh surface atoms, hence the catalytic activity.

The BET surface area of mesoporous (TiO<sub>2</sub> and ZrO<sub>2</sub>) and non-porous (SiO<sub>2</sub>-Aerosil) supports were of 91, 129 and 200 m<sup>2</sup> g<sup>-1</sup>, respectively; the BET surface area of the catalysts were not significantly changed after incorporation of the metals.

Figure 1 shows the diffraction patterns of Rh/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalysts compared to the pristine support. The two patterns exhibited no peaks other than those associated to the anatase TiO<sub>2</sub> support, i.e. no discrete Rh and Re containing phases were observed suggesting high dispersion. Figure 2 shows the patterns of Rh/ZrO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalysts. No size of Rh metal crystallites could be estimated due to the overlap between peaks of ZrO<sub>2</sub> and the main peak of metallic Rh at 41°, whereas no diffraction peak assignable to Re metal or oxide was observed. Finally, the XRD pattern associated with Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Figure S1) exhibited a wide and weak diffraction peak at 2-Theta = 41°. The crystallite size of metallic Rh was approximately 5 nm as determined by using the Scherrer equation from the half-width of the XRD broadening peak.



Figure 1. XRD patterns for  $TiO_2$  (1), Rh/TiO\_2 (2), Rh-ReO<sub>x</sub>/TiO<sub>2</sub> (3).



Figure 2. XRD patterns for ZrO<sub>2</sub> (1), Rh/ZrO<sub>2</sub> (2), Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> (3).

Figure 3 shows TEM images of the mono- and bi-metallic catalysts supported on  $TiO_2$  and the corresponding size histograms. The images for the  $ZrO_2$ -supported catalysts are shown in Figure S2. For each sample, approximately 250 particles were measured for estimation of the average particle sizes. The average particle size in Rh/TiO<sub>2</sub> was 1.6 nm. On the other hand, the Rh/ZrO<sub>2</sub> sample showed no evidence of any particles, indicating the presence of tiny nanoparticles of Rh, below ca. 1 nm. After deposition of rhenium (Fig. 3(b) and Fig. S2(b)), particles were detected on both supports. However, the particle size distribution of these particles showed that the mean size on  $ZrO_2$  (3.1 nm) was larger than on  $TiO_2$  (1.5 nm).



**Figure 3.** Representative TEM images and size distribution associated with (a) Rh/TiO<sub>2</sub> and (b) Rh-ReO<sub>x</sub>/TiO<sub>2</sub>.

Using energy dispersive X-ray spectroscopy (EDS) analysis over several randomly selected images of Rh-ReO<sub>x</sub>/TiO<sub>2</sub> both Rh and Re were present with a distribution of Re/Rh atomic ratios within 0.10-0.31, i.e. slightly lower than the ratio of 0.4 determined by ICP-OES analysis.

The difference suggests that some zones are likely to contain very dispersed monometallic Re nanoparticles that are too small to be detected by TEM. This result is consistent with the observation of tiny Re nanoparticles on Pd-ReO<sub>x</sub>/TiO<sub>2</sub> prepared using a similar procedure.<sup>[33]</sup> In turn, in the case of the Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalyst, the Re/Rh ratios measured were mainly in the range 0.33-0.45, i.e. closer to the ratio of 0.5 determined by ICP-OES analysis; some rare zones having a low density of particles contained Rh rich particles. This result rather suggests Re in close proximity to Rh nanoparticles over ZrO<sub>2</sub>. Moreover, the Rh-ReO<sub>x</sub> particles on the ZrO<sub>2</sub> support were larger than on TiO<sub>2</sub>, which would also indicate that the Re species decorate the Rh particles or that small aggregates of Rh nanoparticles and rhenium oxide species with an estimated size of 3.1 nm were formed.

Figure 4 shows the profiles of H<sub>2</sub>O associated with the H<sub>2</sub>-thermogravimetric analysis/mass spectrometry (TGA/MS) of the Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalysts. The mass spectrum of the evolved gas captured was recorded as a function of temperature. The only signals observed were attributed to m/z = 17 and 18 which correspond to the formation of water due to the reduction. In the literature, temperature-programmed reduction (TPR) profiles of a series of Rh catalysts supported on  $TiO_2^{[34]}$  and  $ZrO_2^{[35]}$  showed that a reduction temperature lower than 180°C was high enough to reduce all rhodium oxide to metallic state. The Rh-Re/TiO<sub>2</sub> and ZrO<sub>2</sub> catalysts presented different profiles of reduction temperature. The signal for Rh-ReO<sub>x</sub>/TiO<sub>2</sub> showed three main hydrogen consumption peaks. A large reduction peak centered at 100°C can be ascribed to the reduction of rhodium oxide, but also to the reduction of rhenium oxide in interaction with Rh; this is consistent with previous studies which report the lowering of the reduction of Re in the presence of metallic Rh.<sup>[28,31]</sup> For instance, the temperature-programmed reduction (TPR) profile of a Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Rh = 0.5) showed one reduction peak at  $120^{\circ}$ C, which is close to the values provided here.<sup>[31]</sup> A wide consumption peak exhibited between 300 and 400°C is attributed to the reduction of ReO<sub>x</sub> species; indeed, the peak temperature of Re oxidized species in supported monometallic rhenium catalysts usually appears in the range of 300 to 375°C.<sup>[28,33,36,37]</sup> The broad shoulder up to 500°C corresponds to the reduction of bulk titania support.<sup>[33]</sup> These findings suggest that a large fraction of Re species was present as isolated clusters on the TiO<sub>2</sub> support and reduced without promotion by Rh. On the other hand, Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> displayed a broad peak associated with hydrogen consumption between 50 and 250°C centered at 150°C, with no discernible reduction peak corresponding to isolated ReO<sub>x</sub> species. This observation means that in that solid, the contact between Rh and Re has been established and the presence of metallic Rh promotes the reduction of Re species.

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Figure 4. H<sub>2</sub>O MS signal for (1) Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, (2) Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>

X-ray photoelectron spectroscopy (XPS) analysis was performed on the as-prepared precursors, the solids reduced in situ in the XPS chamber, and then after passivation with flowing 1vol%  $O_2$  in  $N_2$  at room temperature. The Rh 3d and Re 4f spectra of the Rh-ReO<sub>x</sub>/TiO<sub>2</sub> solids are displayed in Figure 5, and those of the Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalyst are depicted in Figure S3. Table 2 compiles the chemical state of the catalyst components and their relative abundance in the different materials.





**Figure 5.** XPS spectra for Rh 3d and Re 4f core levels of the  $TiO_2$ -supported Rh/ReO<sub>x</sub> materials: (a) in catalyst precursor, (b) after reduction, and (c) after passivation.

Treatment	Distribution of oxidation states (%)								
	Rh <sup>3+</sup>	$Rh^+$	Rh <sup>0</sup>	Re <sup>7+</sup>	Re <sup>6+</sup>	Re <sup>4+</sup>	Re <sup>3+</sup>	Re <sup>0</sup>	
$Rh-ReO_x/TiO_2 (Re/Rh = 0.4)^{[a]}$									
Precursor	74	26	-	73	27	-	-	-	0.61
In situ reduction	-	19	81	-	26		41	33	0.67
Exposure to air	-	70	30	70	25	5	-	-	0.42
$Rh-ReO_{x}/ZrO_{2}(Re/Rh = 0.5)^{[a]}$									
Precursor	82	18	-	80	20	-	-	-	0.64

Table 2. Distribution of Rh and Re oxidation states and surface atomic ratio by XPS.

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In situ reduction	-	16	84	-	33	-	67	-	0.75
Exposure to air	-	57	43	55	45	-	-	-	0.78

<sup>[a]</sup> as measured by ICP-OES analysis

In the two catalyst precursors, the Rh 3d profile fitting showed the characteristic doublets of  $Rh^{3+}$  (BE = 308.2 eV) and  $Rh^+$  (BE = 309.1 eV).<sup>[38]</sup> Further, the Re 4f profile could be decomposed in two doublets with Re 4f<sub>7/2</sub> components appearing at ca. 46.2 eV and 44.2 eV, indicating the presence of Re<sup>7+</sup> and Re<sup>6+</sup> with estimated percentages in the two solids of approximately 75% and 25%, respectively.

After in situ reduction of the bimetallic catalyst precursors, the binding energy of the Rh  $3d_{5/2}$  at 307.6 eV shows that metallic Rh<sup>0</sup> was the major rhodium species (81% and 84% of the Rh was reduced on TiO<sub>2</sub> and ZrO<sub>2</sub>, respectively), although a certain proportion of Rh<sup>+</sup> was still present. However, there was some disparity in Re oxidation state. While over ZrO<sub>2</sub> all Re remained fully oxidized after reduction at 450°C (33% Re<sup>6+</sup> and 67% Re<sup>3+</sup>), over TiO<sub>2</sub> it was partially reduced to Re<sup>0</sup> (33%) in addition to Re<sup>6+</sup> (26%) and Re<sup>3+</sup> (41%), suggesting Rh-Re interactions in the latter material. Surprisingly, in both materials rhodium could not be reduced entirely to Rh<sup>0</sup> after reduction at 450°C. It looks like that the presence of Re oxides prevented the total reduction of Rh.

After subsequent exposure to ambient air of the reduced Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst, Rh<sup>0</sup> was partly re-oxidized (30% Rh<sup>0</sup> and 70% Rh<sup>+</sup> instead of 81% Rh<sup>0</sup>) as well as Re, which was analysed as Re<sup>7+</sup> (70%), Re<sup>6+</sup> (25%) and a small percentage of Re<sup>4+</sup> (5%). In the same way, measurements of the Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> material after reduction and exposure to air revealed that no more than 43% of Rh was present as Rh<sup>0</sup>. Re composition was 55% Re<sup>7+</sup> and 45% Re<sup>6+</sup>. The re-oxidation of Re<sup>0</sup> is consistent with the known oxophilic character of Re.

Finally, no significant change in the Re/Rh atomic ratio of the catalysts was seen by XPS regardless of the nature of the support (TiO<sub>2</sub> or ZrO<sub>2</sub>) and whether the catalyst was the precursor or the reduced material. Moreover, while the XPS Re/Rh ratio was close to 0.6-0.8, the actual global Re/Rh ratio was of 0.4-0.5, which indicates some segregation of Re at the surface of the two catalysts. In contrast, exposure to air of the TiO<sub>2</sub>-supported catalyst decreased this ratio to 0.42, suggesting some redistribution.

The extent of irreversible CO chemisorption was measured for the reduced Rh/TiO<sub>2</sub>, Rh/ZrO<sub>2</sub>, Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalysts. The CO adsorption amounts are shown in Table 1. The monometallic Rh/ZrO<sub>2</sub> displayed a higher CO/Rh ratio (0.74) than Rh/TiO<sub>2</sub> (0.27), indicating a much higher Rh dispersion on zirconia. This is consistent with the TEM characterizations, which showed no detectable Rh nanoparticles on ZrO<sub>2</sub>, while a mean particle size of 1.6 nm was determined on TiO<sub>2</sub> (Fig. 3 and Fig. S2). After deposition of Re on Rh/TiO<sub>2</sub> and Rh/ZrO<sub>2</sub>, the CO uptake did not change significantly compared with the amount of surface metallic atoms was almost the same after addition of Re.

Though part of Re was metallic in the Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst after reduction, the CO/Rh ratio was unaffected by Re loading. The CO chemisorption on TiO<sub>2</sub> may be influenced by different factors. Rh particles may be partly covered by Re species during the preparation method. Decoration or partial encapsulation of Rh particles by the support through a strong metal-support interaction (SMSI) effect known for titania-supported metals exposed to reducing conditions may occur.<sup>[39]</sup> These two factors would lower the number of accessible metallic Rh<sup>0</sup> sites on TiO<sub>2</sub>. On the other hand, the presence of metallic Re<sup>0</sup>, which is able of chemisorbing CO, will positively affect the amount of CO.

On the other hand, considering that Re oxides do not chemisorb CO and the absence of metallic Re<sup>o</sup> in the reduced Rh-ReO<sub>\*</sub>/ZrO<sub>2</sub> (Table 2, Fig. S3), this would indicate no covering of Rh surface with Re species over ZrO<sub>2</sub>. This observation is not in line with the TGA-MS results (Fig. 4) and the EDS data which rather indicated an interaction between Rh and Re in the Rh-ReO<sub>\*</sub>/ZrO<sub>2</sub> catalyst. Furthermore, it is to be noted that the ZrO<sub>2</sub> support needs much higher temperatures than TiO<sub>2</sub> to be reduced, and no SMSI effect is expected Regarding Rh-ReO<sub>\*</sub>/ZrO<sub>2</sub> the reader should keep in mind that there is no metallic Re<sup>°</sup>, that Re oxides do not chemisorb CO, and that ZrO<sub>2</sub> support needs much higher temperatures than TiO<sub>2</sub> to be reduced. <sup>[40]</sup> Therefrom, considering that (i) the same CO/Rh ratio was obtained for Rh/ZrO<sub>2</sub> and Rh-ReO<sub>\*</sub>/ZrO<sub>2</sub> despite different particle sizes estimated from TEM, (ii) the TGA-MS results (Fig. 4) and the EDS data indicated an interaction between Rh and Re, it is proposed that Rh might aggregate with Re oxide species.

Overall, the different characterizations of the materials suggest differences in the distribution of Rh and Re and in the reducibility of Re species on  $TiO_2$  and  $ZrO_2$ , though a detailed structure could not be proposed.

#### 2.2. Catalytic results

# 2.2.1. Typical evolution of products as a function of time in the hydrogenolysis of erythritol

First, the effect of the amount of catalyst (expressed as mmol of Rh introduced) on initial reaction rate associated with erythritol disappearance (based on the first two hours of the reaction) was studied under 80 bar of hydrogen at 200°C in the presence of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>. Without catalyst, the reaction did not take place. As the amount of rhodium increased from 0.07 to 0.18 mmol (7.2 mg to 18.5 mg), the initial rate of disappearance of ERY increased from 0.005 to 0.015 mol<sub>ERY</sub> h<sup>-1</sup>. The linear relationship (Figure S4) confirms that the reaction rates were obtained in kinetic region without mass transfer resistance.

Figure 6 shows a typical example of the temporal dependence of product concentrations when the reaction (0.4 mol L<sup>-1</sup> erythritol) was performed under 80 bar of hydrogen at 200°C, over 0.3 g Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst. Erythritol was converted smoothly to reach 81% conversion after 25 h. Butanetriols and butanediols were the main products obtained. They all appeared from the initial stage of the reaction and their concentration attained 0.07 mol L<sup>-1</sup> and 0.11 mol L<sup>-1</sup>, respectively; the time course of the reaction suggests that it is not necessary to go through 1,4anhydroerythritol to produce the triols and diols. Threitol concentration progressively increased to reach a plateau at 0.04 mol L<sup>-1</sup> from 9.5 h; this indicates a lower reactivity of the threitol isomer compared with erythritol. Cyclic products (1,4-AE, 3OH-THF, THF), butanol (BuOH), C3 products (GLY, PG, 1-PrOH), and ethyleneglycol (EG, the latter is not shown) were formed continuously in very low concentrations (< 0.04 mol L<sup>-1</sup>).



**Figure 6.** Evolution of the concentrations of the different categories of products as a function of time during erythritol hydrogenolysis. ( $\blacklozenge$ ) Erythritol; ( $\times$ ) Cycles; (-) C3 products; (+) Threitol; ( $\circ$ ) BuOH; ( $\Box$ ) BDO; ( $\nabla$ ) BTO.

Reaction conditions: ERY 0.4 mol L<sup>-1</sup>, 120 mL H<sub>2</sub>O, 200°C, 80 bar of H<sub>2</sub>, 0.3 g Rh-ReO<sub>x</sub>/TiO<sub>2</sub>.

Figure S5 presents the temporal evolution of the TOC values calculated from HPLC analysis in the liquid phase (TOC calculated), on one hand, and obtained from direct analysis using the TOC analyzer (TOC measured), on the other hand. At time zero, the calculated and measured TOC values of prepared solution were 19.0 and 18.8  $g_C L^{-1}$ , respectively. During the hydrogenolysis reaction, no difference was observed between the two values indicating that all the products in aqueous phase were analysed by HPLC. These values decreased slightly during reaction (4% loss after 25 h), meaning that a small amount of gaseous products was formed due to over-hydrogenolysis.

# 2.2.2. Screening of rhodium catalysts for hydrogenolysis of erythritol at 200°C under 80 bar H<sub>2</sub>

The catalytic performances of the various supported mono- and bimetallic catalysts are summarized in Table 3.

The bare supports (TiO<sub>2</sub>, ZrO<sub>2</sub>) showed negligible activity for hydrogenolysis of erythritol (8% and 1% conversion after 24 h, respectively); only cyclic compounds (1,4-AE, 3OH-THF and THF) were formed presumably because of some intrinsic acidity of the supports. The absence of metallic rhodium for  $H_2$  dissociation explains that no C-O and C-C bond cleavage occurred.

**Table 3.** Conversion (Conv.) and carbon selectivities observed for the hydrogenolysis of erythritol over rhodium-based catalysts. Selectivities are given at final conversion.

Reaction conditions: ERY 0.4 mol L<sup>-1</sup>, 120 ml H<sub>2</sub>O, T=200°C, 80 bar of H<sub>2</sub>, 0.3 g catalyst, BTO = butanetriols, BDO = butanediols, BuOH = butanols, Cycles = 1,4-AE+3OH-THF+THF, C3 = GLY+PG+PrOH.

Catalyst	Molar ratio	Time	Conv.	Carbon selectivity (%)					
	Re/Rh	[h]	[%]	BTO	BDO	BuOH	Threitol	Cycles	C3
Rh/TiO <sub>2</sub>	-	25	10	1	11	0	0	88	0
Rh/ZrO <sub>2</sub>	-	24	70	17	11	2	3	44	12
Rh-ReO <sub>x</sub> /SiO <sub>2</sub>	0.4	31	67	28	17	1	40	3	7

Rh-ReO <sub>x</sub> /TiO <sub>2</sub>	0.4	25	80	24	36	5	11	11	8
Rh-ReO <sub>x</sub> /ZrO <sub>2</sub>	0.5	8	82	28	26	4	8	12	11

Rh/TiO<sub>2</sub> exhibited a very low activity, resulting in only 10% conversion after 25 h; the products analyzed were mainly cyclic compounds (88% selectivity). In contrast, the deposition of Rh on ZrO<sub>2</sub> was associated with an increase in activity (70% conversion after 24 h); the cyclization reaction was still predominant with a 44% selectivity to cyclic compounds at final conversion. C3 compounds (selectivity of 12%), BTO (selectivity of 17%) and BDO (selectivity of 11%) products were also generated. The lower conversion over Rh/TiO<sub>2</sub> than over Rh/ZrO<sub>2</sub> can be explained by the different metallic dispersion of Rh over the supports as shown in Table 1, in which the CO adsorption amounts on Rh/ZrO<sub>2</sub> was higher than that on Rh/TiO<sub>2</sub> (CO/Rh was 0.74 and 0.27, respectively). The difference of dispersion was confirmed by TEM analysis (Fig. 3 and Fig. S2a).

It was reported in the literature that the addition of  $\text{ReO}_x$  species to supported rhodium metal (Rh/SiO<sub>2</sub>) enhanced the catalytic activity of glycerol hydrogenolysis in water and promoted the formation of deoxygenated products (1,2- and 1,3-propanediol).<sup>[31]</sup> In the present investigation, erythritol conversion attained 67% over Rh-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst, after 31 h. The epimerization of erythritol to threitol was observed with a selectivity of 40%. The selectivity to linear deoxygenated products (BTO + BDO + BuOH) by C-O hydrogenolysis attained 46%. However the silica support was unstable under the hydrothermal conditions used (200°C); leaching of 24% of Si was detected by ICP-OES analysis of the final solution. For that reason we moved to supports known to be stable in water at high temperature (TiO<sub>2</sub>, ZrO<sub>2</sub>).<sup>[29,30]</sup>

Modification of Rh/TiO<sub>2</sub> with ReO<sub>x</sub> ( $n_{Re}/n_{Rh}=0.4$ ) enhanced the activity for the hydrogenolysis of erythritol; the conversion increased from 10% over Rh/TiO<sub>2</sub> to 80% over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> after 25 h. The selectivity to deoxygenated products (BTO + BDO + BuOH) was of 65% at final conversion. The hydrogenolysis activity was also enhanced when working with ZrO<sub>2</sub> as support; the reaction time needed for attaining 82% conversion was only of 8 h over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> and the final selectivity to the deoxygenated products was 58%. These corroborate the efficiency of the combination of Rh and ReO<sub>x</sub> for activity and selectivity to deoxygenated products. The results are in agreement with reports on hydrogenolysis of tetrahydropyran-2-

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methanol to 1,6-hexanediol in which the catalytic activity as well as the selectivity were enhanced over metal oxide modified supported Rh catalysts.<sup>[26–28]</sup>

# 2.2.3. Temperature effect over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>

The effect of reaction temperature was studied over the range 150-240°C under 80 bar of  $H_2$  in the presence of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>. The evolution of erythritol concentration as a function of time is shown in Figure 7a, the selectivities to the different products at 80% conversion are shown in Figure 7b.



**Figure 7.** Effect of temperature a) on temporal evolution of erythritol concentration b) on selectivity to the reaction products at 80% conversion. ( $\nabla$ ) 240°C; (0) 200°C; ( $\Box$ ) 150°C; ( $\blacksquare$ ) Cycles; ( $\blacksquare$ ) C3; ( $\blacksquare$ ) Threitol; ( $\blacksquare$ ) BuOH; ( $\blacksquare$ ) BDO; ( $\blacksquare$ ) BTO. Reaction conditions: ERY 0.4 mol L<sup>-1</sup>, 120 ml H<sub>2</sub>O, 80 bar of H<sub>2</sub>, 0.3g Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalyst,

C-O cleavage: BuOH+BDO+BTO.

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As expected, the higher the temperature, the more rapid the reaction. At 240°C erythritol was sharply converted to attain full conversion after 5 h, while at 200°C erythritol conversion reached 92% after 10 h and full conversion after 24 h. Finally, at 150°C erythritol conversion was 27% after 9 h and 80% after 48 h.

Upon decreasing the reaction temperature from 240 to 150°C, the selectivity to linear deoxygenated products increased from 33 to 79% (Fig. 7b). The results show that the selectivity towards C-O bond cleavage was enhanced with decreasing temperature. The same trend was observed in the dehydroxylation of sorbitol over CuO-ZnO catalyst<sup>[41]</sup> in which the selectivity to linear deoxygenated products increased from 35 to 63% as temperature decreased from 240 to 180°C. In parallel, the selectivity to C2-C3 compounds, produced from the C-C cleavage in the middle-carbon chain through decarbonylation or retro-aldol condensation reactions, increased from 5 to 16% with an increase in temperature from 150°C to 240°C. This tendency agrees with that found for transformation of sorbitol into liquid alkanes over a bifunctional catalytic system  $Pt/ZrO_2 + TiO_2-WO_x$ ,<sup>[42]</sup> in which the number of C-C cleavages increased as temperature increased from 200°C to 240°C. In addition, the highest selectivity towards cycles was observed at  $240^{\circ}$ C (selectivity = 24%), suggesting that dehydration reactions are favored at high temperature; the heterocyclic compounds are thermodynamically-stable. A similar progression was noted by Sato et al,<sup>[43]</sup> for the dehydration of 1,4-butanediol over conventional acid catalysts such as zirconia, alumina, and silica-alumina. They observed that the conversion increased along with the temperature and the dehydration compound (tetrahydrofuran) was the main product.

The % loss of TOC measured at the end of the reaction over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> increased from 3 to 13% as temperature increased from 150 to 240°C, due to the formation of gaseous products. It is worth noting that CO<sub>2</sub> has been reported as the main product during the aqueous-phase hydrodeoxygenation of sorbitol over Pt-ReO<sub>x</sub>/C (245°C, 62 bar of H<sub>2</sub>);<sup>[44]</sup> the formation of CO<sub>2</sub> was due to the decarbonylation of the intermediate aldehyde over the metallic surface, followed by water-gas shift reaction. In addition to CO<sub>2</sub>, C1-C4 alkanes in gas phase had also been detected. In the present erythritol hydrogenolysis reaction, the selectivity to C3 products such as glycerol (formed by decarbonylation reaction) increased from 5 to 12% as temperature increased from 150 to 240°C, which can explain the increase in % loss of TOC measured. The temperature was chosen at 200°C for further experiments to minimize the possible formation of gaseous products and keep a reasonable activity.

# 2.2.4. Effect of support (TiO<sub>2</sub> or ZrO<sub>2</sub>) and H<sub>2</sub> pressure during erythritol hydrogenolysis.

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The effect of  $H_2$  pressure (in the range 30-120 bar) on initial rate (Figure S6) and product selectivity (Figure 8) was investigated for erythritol hydrogenolysis at 200°C, over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> and Rh-ReO<sub>x</sub>/TiO<sub>2</sub>.

At low pressure (30 bar), the two catalysts showed similar initial reaction rates of  $220\pm10$  mmol<sub>ERY</sub> g<sub>Rh</sub><sup>-1</sup> h<sup>-1</sup>. However, as pressure increased from 30 to 120 bar, the initial rate over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> increased slowly to 461 mmol<sub>ERY</sub> g<sub>Rh</sub><sup>-1</sup> h<sup>-1</sup>, whereas it increased nearly linearly over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> up to 1583 mmol<sub>ERY</sub> g<sub>Rh</sub><sup>-1</sup> h<sup>-1</sup>. These results show a nearly first order kinetics in H<sub>2</sub> pressure over the ZrO<sub>2</sub>-supported catalyst in the range of pressure considered; which indicates that the hydrogen is involved in the rate-determining step and suggesting that one active hydrogen species is produced from one hydrogen molecule.<sup>[17,45]</sup> In contrast, the order was positive but close to zero over the TiO<sub>2</sub>-supported one. This suggests that the attack of hydrogen active species is not the rate-determining step, but the C-O bond cleavage in the substrate can be the rate-determining reaction.<sup>[17]</sup> These observations in initial rates over two catalysts under 80 bar H<sub>2</sub> (8 h *vs.* 25 h, Table 3). Differences in dispersion and in interactions between rhodium, rhenium and the support suggested by the characterizations of the solids (see above) may explain the different behaviors on the two supports.

The carbon selectivity to the different categories of products and the TOC values measured at 80 % conversion are presented in Figure 8 for the two supported-catalysts under different pressures. As examples, Figure S7 illustrates the evolution of selectivity as a function of erythritol conversion at 200°C under 80 bar or 120 bar.



Figure 8. Dependence of product selectivities and %TOC measured at 80% conversion of erythritol. (▲) % TOC measured; (■) Cycles; (■) C3; (■) Threitol; (■) BuOH; (■) BDO;
(■) BTO.

Reaction conditions: 200°C, 0.3g catalyst, ERY 0.4 mol  $L^{-1}$ , 120 ml H<sub>2</sub>O.

First, regarding the carbon balance, there was no difference between TOC measured and TOC calculated. In the presence of both catalysts, the mass balance was > 90% except under 30 bar of hydrogen. The loss of carbon in liquid phase is due to the formation of short-chain compounds which have been transferred from the liquid phase to the gas phase, such as  $CO_2$  or alkanes.

At the temperature of 200°C, whatever the support (TiO<sub>2</sub> or ZrO<sub>2</sub>) and the pressure (P<sub>H2</sub> in the range 30-120 bar), the selectivity to butanols (in the range 4-6%) and to C3 compounds (in the range 7-11%) remained roughly constant. Cyclic compounds (mainly 1,4-AE) resulting from internal dehydration of erythritol in the presence of Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalysts were favored under 30 bar of H<sub>2</sub> (13% and 21%, respectively). These data are consistent with observations during the hydrogenolysis of sorbitol to hexane over Pt/NbOPO<sub>4</sub> at 250°C, in aqueous medium: it was shown that the oxygenated compounds resulting from dehydration of sorbitol (1,4-sorbitan, isosorbide, and 2-(tetrahydrofuran-2-yl) ethan-1-ol) were the main products under low hydrogen pressure.<sup>[46]</sup>

Moreover, the epimerization of erythritol to threitol was higher under 120 bar of H<sub>2</sub> over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> (selectivity 14%) and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> (selectivity of 9%), than under 30 bar (selectivity of 5%). It was also observed in the literature that the presence of ReO<sub>x</sub> species enhanced the selective 1,3-isomerization of allylic alcohols<sup>[47]</sup> and isomerisation of sorbitol to mannitol over Pt-ReO<sub>x</sub>/C.<sup>[44]</sup> A mechanism similar to that described for epimerization of xylitol to arabitol may be suggested via dehydrogenation-hydrogenation route.<sup>[48]</sup> It was proposed that the reaction starts with reversible dehydrogenation of xylitol to xylose on the metal surface; the isomerization of xyluose is catalyzed by base<sup>[49]</sup> or Lewis acid sites<sup>[50]</sup> and then xylulose undergoes hydrogenation reaction over the metal surface to arabitol. So, as hydrogen pressure increased, the dissolved hydrogen concentration in aqueous medium will increase and result in more hydrogen molecules that access the metal active site; thus, the final hydrogenation step of unsaturated intermediates will be favored. This behavior is also in accordance with results for selective hydrogenolysis of xylitol to ethylene glycol and propylene

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glycol over Cu/SiO<sub>2</sub> at 200°C, which showed that the selectivity to arabitol increased as hydrogen pressure increased.<sup>[51]</sup>

Furthermore, the selectivity to BTO over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> catalysts increased from 10 and 13% to 35 and 37%, respectively, when the pressure increased from 30 to 120 bar. This enhancement was accompanied with the decrease in selectivity to BDO (from 43 to 28%) over Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, while no drastic changes were noticed in the presence of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>, i.e. the selectivity to BDO remained constant around 26-29%.

Owing to the multiple hydroxyl groups on the polyols, a number of different products are obtained, depending on which hydroxyl groups are eliminated. A more detailed examination of the selectivity to the different triols (1,2,3- and 1,2,4-BTO) and diols (1,2-, 2,3-, 1,3- and 1,4-BDO) obtained during erythritol hydrogenolysis over both supported catalysts under varied pressures was undertaken. The temporal concentration of the butanetriols and butanediols observed over the Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst under 80 bar H<sub>2</sub> are presented (Figure 9a) as a representative example.



**Figure 9.** (a) Concentration of the different butanetriols and butanediols as a function of time. ( $\Delta$ ) 1,2,3-BTO; ( $\blacktriangle$ ) 1,2,4-BTO; ( $\diamondsuit$ ) 1,2-BDO; ( $\bigstar$ ) 2,3-BDO; (\*) 1,4-BDO. Reaction conditions: ERY 0.4 mol.L<sup>-1</sup>, 120 mL H<sub>2</sub>O, 200°C, 80 bar of H<sub>2</sub>, 0.3 g Rh-ReO<sub>x</sub>/TiO<sub>2</sub>. (b) n<sub>1,2,3-BTO</sub>/n<sub>1,2,4-BTO</sub> ratio as a function of pressure and support; ( $\bigstar$ ) Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>, ( $\Delta$ ) Rh-ReO<sub>x</sub>/TiO<sub>2</sub>.

The triol and diol compounds were formed from the beginning of the reaction as primary products; their concentrations kept increasing until the end of the reaction, i.e. 80% conversion of erythritol. The molar ratio between the two butanetriols ( $n_{1,2,3-BTO}/n_{1,2,4-BTO}$ ) are shown in Figure 9(b). They were dependent on the catalyst (Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>) and the pressure. The ratio was close to 1 over Rh-ReO<sub>x</sub>/TiO<sub>2</sub>; this suggests that there is no preferential removing of the primary or secondary hydroxyl group from erythritol, which yield 1,2,3-BTO and 1,2,4-BTO, respectively. However the removal of the primary hydroxyl is favored over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> at low pressure (ratio ~ 1.6).

In regards to the diols, both 1,2-BDO and 2,3-BDO were the main diols formed, while 1,4-BDO was always formed in lower concentrations, and 1,3-BDO was only detected in traces or not at all.

The selectivities over TiO<sub>2</sub>- or ZrO<sub>2</sub>-supported Rh-ReO<sub>x</sub> catalysts were then compared to the ones observed by the group of Tomishige for erythritol hydrogenolysis over various Ir- and Rh-based catalysts at lower temperature.<sup>[10]</sup> They found that at 50% conversion, the Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Rh molar ratio 0.5) catalyst formed preferably butanols (selectivity 46%) than butanediols (selectivity 8%). In contrast, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir molar ratio 1) catalyst promoted the formation of butanediols (at 74% conversion, the selectivity to BDO was 48%). However, these authors observed that 1,4-BDO, and at a lesser extent 1,3-BDO, were by far the major diols formed. On the contrary, when the present Rh-ReO<sub>x</sub> catalysts were applied to erythritol at 200°C, 1,2-BDO and 2,3-BDO, the diols with two adjacent hydroxyl groups, were obtained as the major diols. The discrepancy between both studies must result from the nature of the metal (Rh or Ir), and support (SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>), and the different temperature used (200°C in the present work instead of 120°C). This point will be discussed later in this paper.

Lastly, 1-BuOH and 2-BuOH were always formed with low selectivity; the trend is towards the formation of a slightly higher concentration of 1-BuOH.

# 2.2.5. Hydrogenolysis of butanetriols over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> at different pressures

In order to understand the trends of selectivity to BTO, BDO and BuOH as a function of pressure over the two catalysts during hydrogenolysis of erythritol, some catalytic tests were performed starting from butanetriols (1,2,3- or 1,2,4-BTO) at the initial concentration of 0.12 mol  $L^{-1}$ . The initial reaction rates are summarized in Table 4.

**Table 4.** Initial reaction rates as a function of catalyst and pressure for hydrogenolysis of ERY, 1,2,3-BTO, 1,2,4-BTO, and 1,4-AE.

Catalyst	Pressure H <sub>2</sub>	ubstrate g <sub>Rh</sub> <sup>-1</sup> h <sup>-1</sup>	$g_{Rh}^{-1} h^{-1}$ ]		
Catalysi	[bar]	ERY	1,2,3-BTO	1,2,4-BTO	1,4-AE
	30	210	78	263	-
Rh-ReO <sub>x</sub> /TiO <sub>2</sub>	80	281	87	247	-
	120	461	-	240	-
	30	232	97	281	212
Rh-ReO <sub>x</sub> /ZrO <sub>2</sub>	80	888	398	738	845
	120	1583	-	-	-

Reaction conditions: 200°C, BTO 0.122 mol L<sup>-1</sup>, 120 mL H<sub>2</sub>O, 0.075g catalyst

Over Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, the initial reaction rate of conversion of 1,2,3-BTO (78-87 mmol<sub>BTO</sub>  $g_{Rh}^{-1}$   $h^{-1}$ ) and 1,2,4-BTO (247-263 mmol<sub>BTO</sub>  $g_{Rh}^{-1}$   $h^{-1}$ ) was not significantly modified by the H<sub>2</sub> pressure applied (30 to 80 or 120 bar). On the contrary, in the presence of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>, the initial rate for the conversion of 1,2,3-BTO and 1,2,4-BTO increased from 97 and 281 mmol<sub>BTO</sub>  $g_{Rh}^{-1}$   $h^{-1}$ , respectively, to 398 and 738 mmol<sub>BTO</sub>  $g_{Rh}^{-1}$   $h^{-1}$ , respectively, as H<sub>2</sub> pressure was varied from 30 to 80 bar. As for erythritol hydrogenolysis, almost a zero order reaction with respect to H<sub>2</sub> pressure was observed for BTOs hydrogenolysis over the TiO<sub>2</sub> supported catalyst, whereas a first-order kinetics in H<sub>2</sub> pressure was noted for the ZrO<sub>2</sub> supported catalyst (Figure S6). These results suggest different mechanisms of activation of H<sub>2</sub> on both promoted catalysts. In comparison, Chia et al<sup>[28]</sup> and Tomishige et al<sup>[31,52]</sup> reported a first-order reaction for cyclic ethers and glycerol hydrogenolysis for Rh-Re supported on carbon and Rh-Re and Ir-Re supported on silica, respectively.

One may also note that the reaction of 1,2,4-BTO hydrogenolysis proceeded twice or three times more rapidly than the reaction of 1,2,3-BTO in the same conditions. This difference in reactivity was also observed by Amada et al over Ir-ReOx/SiO<sub>2</sub>.<sup>[10]</sup> The reactivity of 1,2,4-BTO was approximately equal to that of erythritol, and 1,2,3-BTO showed much lower activity. We

propose that the cause of these differences may rely on the ability to form cyclic ethers. Indeed, 1,2,3-BTO cannot be dehydrated to form a cyclic ether, whereas 3-hydroxytetrahydrofuran (3OH-THF) and THF were produced from 1,2,4-BTO with a global selectivity of 11-12% at 50% conversion over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and 21-25% at 80% conversion over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> (Figure 10).

Figure S8 gives an example of hydrogenolysis of 1,2,3-BTO and 1,2,4-BTO under 80 bar of H<sub>2</sub> over the ZrO<sub>2</sub>-supported catalyst. Figure 10 summarizes the influence of the support (TiO<sub>2</sub> or ZrO<sub>2</sub>) and the pressure applied (30 or 80 bar) on the selectivity to the different products during hydrogenolysis of both triols. The results are given at 80% conversion for Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> and at 50% conversion for Rh-ReO<sub>x</sub>/TiO<sub>2</sub> as the latter was less active. The selectivity to BDO for the hydrogenation of a given triol in the presence of Rh-ReO<sub>x</sub>/TiO<sub>2</sub> was constant with H<sub>2</sub> pressure; however, the values were drastically different (92% from 1,2,3-BTO and 52-56% from 1,2,4-BTO). Over-hydrogenolysis to butanol remained low (< 5%) and selectivity to C3 compounds slightly increased as pressure increased (8-11%). As for the results in the presence of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>, at 80% conversion, the selectivity to BDO was also not significantly affected by the pressure; again, the selectivity to BDO was higher from 1,2,3-BTO (62-69%) than 1,2,4-BTO (30-33%). The selectivity to BDO was higher from 1,2,3-BTO and increased with the pressure (Figure 10).



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**Figure 10.** Dependence of product selectivities as a function of the pressure and the support in hydrogenolysis of 1,2,3-BTO and 1,2,4-BTO. The results are given at 50% conversion over Rh-ReO<sub>x</sub>/TiO<sub>2</sub>, 80% conversion over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>. ( $\blacksquare$ ) BDO; ( $\blacksquare$ ) Cycles; ( $\blacksquare$ ) C3; ( $\blacksquare$ ) BuOH. Reaction conditions: 200°C, BTO 0.122 mol L<sup>-1</sup>, 120 mL H<sub>2</sub>O, 0.075g catalyst.

# 2.2.6. Selectivity to butanediols and butanols

The diols may be formed from erythritol through different routes: (i) erythritol may be first hydrogenolysed to the two butanetriols and subsequently to the diols; hydrogenolysis of 1,2,3-BTO will produce 2,3-BDO, 1,2-BDO, and 1,3-BDO, whereas hydrogenolysis of 1,2,4-BTO will produce 1,2-BDO, 1,3-BDO, and 1,4-BDO (Scheme 2), (ii) they may also be formed via the ring opening hydrogenolysis of 1,4-AE via 3OH-THF; however, only 1,2- and 2,3-BDO will be produced by this route, (iii) elimination of two hydroxyl groups directly from erythritol; as shown in Fig. 6, BDO are formed from the start of the reaction which suggests the feasibility of this last route ; moreover this mechanism agrees well with the proposition of Arai et al on the possibility of the direct hydrogenolysis of 1,4-AE to 2-BuOH without the desorption of intermediates from the active site over a Rh-MoO<sub>x</sub> catalyst.<sup>[17]</sup> As an attempt to identify the preferential mechanism (i, ii, iii), we looked at the selectivity to the different butanediols and butanols during the hydrogenolysis of the butanetriols and 1,4-anhydroerythritol.



Scheme 2. Reaction pathways associated with the formation of BDO and BuOH from BTO.

#### 2.2.7. Hydrogenolysis of butanetriols

As an example, Table 5 includes the detailed selectivity towards butanediols and butanols obtained during the hydrogenolysis of butanetriols over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> under 80 bar. The same trends were observed at lower pressure. The difference in selectivity towards one or another BDO can be linked to the existence of preferential C-O bond cleavage. (Scheme 2). It is usually recognized<sup>[53]</sup> that in acid catalyzed dehydration, the selectivity is driven by the stability of ions formed in the reaction, leading to dehydration of substituted C bearing a secondary alcohol first. In contrast, selectivity for hydrogenolysis using a heterogeneous metallic catalyst is often driven by steric hindrance, leading to cleavage of the primary alcohol first.

**Table 5.** Carbon selectivity to BDO or BuOH at 50% conversion over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and 80% conversion over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> during hydrogenolysis of BTO.

			Carbon selectivity%						
Catalyst	Susbtrate	2,3-BDO	1,2-BDO	1,4-BDO	1,3-BDO	1-BuOH	2-BuOH		
	1,2,3-BTO	72	20	n.a	0	1	3		
Rh-ReO <sub>x</sub> /TiO <sub>2</sub>	1,2,4-BTO	n.a	34	15	3	2	2		
	1,2,3-BTO	48	14	n.a	0	2	4		
Rh-ReO <sub>x</sub> /ZrO <sub>2</sub>	1,2,4-BTO	n.a	23	4	< 1	4	2		

Reaction conditions: 200°C, 80 bar of H<sub>2</sub>, BTO 0.122 mol L<sup>-1</sup>, 120 mL H<sub>2</sub>O,  $n_{BTO}/n_{Rh}$ = 530, 0.075g catalyst.

n.a.: not applicable

Starting from 1,2,3-BTO as the reactant, whether the Rh-ReO<sub>x</sub> nanoparticles were supported on TiO<sub>2</sub> or ZrO<sub>2</sub>, the selectivity towards 2,3-BDO (72%; 48%) was clearly much higher than that to 1,2-BDO (20%; 14%) and 1,3-BDO (not detected), indicating that the reactivity of the terminal primary -OH group in position 1 in 1,2,3-BTO is higher than that of the secondary – OH groups in positions 2 and 3 (Scheme 2). A ratio 2,3-BDO/1,2-BDO of c.a. 3.5 was calculated for the two catalysts. In addition, 1,3-BDO was not observed, meaning that removal of the most hindered secondary hydroxyl group in position 2 did not occur.

On the other hand, starting from 1,2,4-BTO as the reactant, 1,2-BDO was the major product with 34% and 23% selectivity over Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub>, respectively. Lower amounts of 1,4-BDO (15%; 4%) and negligible amounts of 1,3-BDO (3%; <1%) were detected. So the reactivity of the terminal primary –OH group at position 4, the one with the less steric hindrance, is higher than that of the two other OH-groups (positions 1 and 2). Moreover, the reactivity of the secondary –OH group (position 2) is higher than the one of the adjacent primary OH-group (position 1); this latter reactivity trend is different from that observed from 1,2,3-BTO, where the elimination of the primary OH group was favored over the cleavage of either of the two secondary OH-groups. The ratio 1,2-BDO/1,4-BDO was ca. 2.3 and 5.7 over TiO<sub>2</sub> and ZrO<sub>2</sub>, respectively.

It should also be noted that unlike from 1,2,3-BTO, cyclic compounds (3OH-THF and THF) were formed from 1,2,4-BTO. The amount of C3 products is higher from hydrogenolysis of 1,2,4-BTO than from 1,2,3-BTO.

These results are different from those analysed by Amada et al over an Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst at  $100^{\circ}$ C.<sup>[10]</sup> These authors observed the preferential formation of 1,3-BDO from 1,2,3-BTO (47 % selectivity at 1% conversion only), whereas the main product from 1,2,4-BTO was 1,4-BDO (selectivity 73% at 22% conversion), formed by dissociation of the C-O bond neighboring the CH<sub>2</sub>OH group. 1,4-BDO was also obtained with the highest selectivity (63%) compared to 1,3-BDO and 1,2-BDO (14% and 9%, respectively) at 13% conversion in 1,2,4-BTO hydrogenolysis by Chia et al, over a Rh-ReO<sub>x</sub>/C catalyst at 100°C under 34 bar H<sub>2</sub>.<sup>[28]</sup> These studies highlighted the high reactivity of a secondary hydroxyl group adjacent to a primary OH-group. These results also demonstrate the crucial role of the support.

Finally, the selectivity at 80% conversion towards the butanols formed by elimination of two hydroxyl groups over both catalysts was examined. In the hydrogenolysis of 1,2,3-BTO, the selectivity to 2-BuOH (3% and 4%, respectively) was slightly higher than that to 1-BuOH (1% and 2%; Table 5). This is due to the fact that 2-BuOH can be formed from the major 2,3-BDO via cleavage of any of the secondary –OH group (positions 2 and 3) and from cleavage of the primary –OH group of 1,2-BDO (position 1, Scheme 2), while 1-BuOH can be obtained solely through cleavage of secondary –OH group of 1,2-BDO (the less favored BDO from 1,2,3-BTO). However the observation of a non-negligible amount of 1-BuOH suggests a high reactivity of the secondary OH in comparison with the primary OH in 1,2-BDO. In contrast, in the hydrogenolysis of 1,2,4-BTO, the selectivity to 1-BuOH (2%; 4%) was higher than that to 2-BuOH (2%; 2%). 1-BuOH was obtained from cleavage of secondary –OH group in 1,4-BDO, whereas 2-BuOH was obtained only from 1,2-BDO through elimination of the primary –OH groups. As mentioned above, C-O cleavage from 1,2-BDO occurs preferentially on the secondary OH-group yielding 1-BuOH.

# 2.2.8. Hydrogenolysis of 1,4-anhydroerythritol

Furthermore, some reactions were performed starting from 1,4-anhydroerythritol. The effect of  $H_2$  pressure (30 and 80 bar) on the evolution of product selectivity is presented over Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> at 200°C (Figure S9). The initial conversion rates of 1,4-AE were 213 and 845 mmol<sub>1,4-AE</sub> g<sub>Rh</sub><sup>-1</sup> h<sup>-1</sup> (Table 4), i.e. a positive order of ca. 1 with respect with H<sub>2</sub> pressure over this catalyst.

First, the ring opening hydrogenolysis of 1,4-AE via 3OH-THF yielded 1,2,3-BTO, which was further converted to BDO and butanol. Under 30 bar, the selectivity to 1,2,3-BTO decreased

from 25 to 7% as conversion increased from 20 to 65%, while at the same time the selectivity to BDO increased from 20 to 26%; differently, under 80 bar, the selectivity to 1,2,3-BTO decreased from 21 to 4% as conversion increased from 32 to 82%, and the selectivity to BDO increased from 16 to 26%. The butanediols produced were 2,3-BDO and 1,2-BDO and the 2,3-BDO/1,2-BDO ratio was estimated to be approximately 2 all along the reaction, i.e. a preferential C-O cleavage of the primary CH<sub>2</sub>OH group. Notably, 1,3-BDO was not detected. The same trends were observed, when starting from 1,2,3-BTO (Table 5). Differently, over a Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Rh = 0.13) operating at 120°C under 80 bar H<sub>2</sub>, 1,2-BDO, 2,3-BDO, and 1,3-BDO were obtained with selectivity of 13%, 6%, and 3%, respectively, at 29% conversion of 1,4-AE.<sup>[17]</sup> Ir-ReO<sub>x</sub>/SiO<sub>2</sub> yielded even higher selectivity to 1,3-BDO was formed both by hydrogenolysis of 1,2,3-BTO by successive C-OH hydrogenolysis of 1,4-AE via the intermediate 3OH-THF. In contrast, they observed a relatively higher selectivity to 2,3-BDO over a Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst. The selectivity to the butanediols is thus very dependent on the reaction conditions and the catalyst used.

In addition, 1,4-AE underwent successive C-O bond hydrogenolysis to 3OH-THF and THF. However, the selectivity to cycles remained low and constant (8-9% under 30 bar and slightly higher at 14% under 80 bar) as a function of conversion. This suggests that ring opening hydrogenolysis of 1,4-AE to 1,2,3-BTO is leading over C-O hydrogenolysis to 3OH-THF. An interesting point is the absence of formation of 1,3-BDO during 1,4-AE hydrogenolysis, which suggests that no hydrogenolysis of 3OH-THF to 1,3-BDO took place during the reaction. 3OH-THF has already been found to be poorly reactive.<sup>[54]</sup>

The C-C cleavage of 1,4-AE yielded C3 products (glycerol which is then converted to 1,2propanediol, 1-PrOH, and 2-PrOH). The selectivity to C3 remained constant (32% under 30 bar, slightly lower at ca. 24% under 80 bar) as a function of conversion. Finally, there was no effect of  $H_2$  pressure on the selectivity to butanol which remained constant and low (0-4%) as a function of conversion.

# 2.2.9. Comparison of evolution of selectivity to BDO during erythritol, and BTO or 1,4-AE hydrogenolysis

The results from the hydrogenolysis of the butanetriols (Fig. S8, Table 5) and of 1,4anhydroerythritol (Fig. S9) were then compared with the evolution of the selectivity to the butanediols observed previously during hydrogenolysis of erythritol at different pressures (Fig. 8).

Taking into consideration that 1,2,4- and 1,2,3-BTO were formed in approximately equivalent amounts during erythritol hydrogenolysis, and that hydrogenolysis of the cyclic compound 1,4- anhydroerythritol only generates 1,2,3-BTO, the presence of 1,2,4-BTO from erythritol signifies that the two triols are mainly formed by elimination of an hydroxyl group from erythritol. They are then hydrogenolysed to the diols, and further to butanols. The selectivity to the butanediols should be governed by the selectivity of the hydrogenolysis of the butanetriols. Accordingly, the molar ratio 2,3-BDO/1,2-BDO and 1,2-BDO/1,4-BDO during erythritol reaction are well in accordance with the ratios obtained from the hydrogenolysis of both triols formed. 1,4-AE which is formed, may also contribute to the formation of 1,2,3-BTO, and the further transformation to 2,3- and 1,2-BDO; however, the contribution of this pathway must be negligible according to the low selectivity in cycles.

However, it is clear that 1,4-AE, once formed, tend to be transformed to C3 compounds. Indeed, we observed a high initial selectivity to C3 compounds when starting from 1,4-anhydroerythritol. The results obtained during the hydrogenolysis of BTO and 1,4-AE, and in particular the absence of 1,3-BDO, strongly support that butanediols are mainly produced from butanetriols than from cyclic compound such as 3-OH-THF.

# 2.2.10. Stability of bimetallic catalysts

It was reported that the addition of  $H_2SO_4$  to the reaction medium inhibited the leaching of metal components during hydrogenolysis of erythritol to butanediols over Ir-ReO<sub>x</sub>/SiO<sub>2</sub>.<sup>[10]</sup> It enhanced the stability and activity of the catalyst and also increased selectivity to 1,3-propanediol in the aqueous hydrogenolysis of glycerol.<sup>[7]</sup> However, we could not find any report dealing with the effect of acid on Rh-ReO<sub>x</sub> catalysts, therefore we decided to study the addition of  $H_2SO_4$  on Rh-ReO<sub>x</sub>/TiO<sub>2</sub>. The amount of acid added was fixed at a molar ratio H<sup>+</sup>/Rh=1 as the optimal  $n_{H+}/n_{Ir}$  ratio during hydrogenolysis of glycerol to 1,3-propanediol had been determined to be 1.<sup>[52]</sup>

Figure 11 shows the effect of  $H_2SO_4$  additive on erythritol conversion and pH evolution at 200°C, 80 bar pressure of hydrogen, in the presence of the Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst. The activity of Rh-ReO<sub>x</sub>/TiO<sub>2</sub> was not affected by the addition of acid: 46% of ERY conversion was attained after 9.5 h in comparison to 50% in the absence of  $H_2SO_4$  (Fig. 11a). In the absence of the acid,

the initial pH value of the solution was 5.8. During the heating period up to 200°C, the value sharply decreased to 3.4; then, it increased slightly to reach 3.7 after 9.5 h (Fig. 11b). After addition of the acid, the initial pH was 3.2; as reaction proceeded, it increased to 4.2 after 9.5 h. ICP analysis of the solution after filtration of catalyst showed that the leaching of rhenium metal decreased from 6 to 2% after the addition of H<sub>2</sub>SO<sub>4</sub>, whereas no appreciable leaching of Rh and Ti metals was detected in the presence and absence of acid (<0.1% and 0.01% respectively).



**Figure 11.** Temporal (a) erythritol conversion and (b) pH variation with ( $\blacktriangle$ , H<sup>+</sup>/Rh=1) or without ( $\Delta$ ) acid (H<sub>2</sub>SO<sub>4</sub>) addition.

Reaction conditions: ERY 0.4 mol  $L^{-1}$ , 120 ml H<sub>2</sub>O, 80 bar of H<sub>2</sub>, 200°C, 0.3 g of Rh-ReO<sub>x</sub>/TiO<sub>2</sub> catalyst.

Figure 12 presents the carbon selectivity to the products at ca. 50% conversion after 9.5 h. The addition of  $H_2SO_4$  had hardly no effect, as similar selectivities ( $\pm$  1%) towards deoxygenated products (BTO + BDO + BuOH) were obtained. Further experiments were performed without mineral acid addition.

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**Figure 12.** Dependence of product selectivities at ca. 50% conversion of erythritol.  $(\blacksquare, H^+/Rh=1); (\Box, without acid).$ 

The recyclability of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> (Figure 13) was examined. The catalyst was collected, washed with water, and dried over the night at  $110^{\circ}$ C. Before catalytic testing, the catalyst was re-activated under H<sub>2</sub> as for the fresh catalyst.

The catalytic activity declined slightly during the second test; indeed 74% of erythritol conversion was attained after 10 h, while in the presence of fresh catalyst (run 1), the conversion was of 82% after 8 h. In order to investigate the reason of this small deactivation, the amount of Rh and Re dissolved was analyzed by ICP-OES. No rhodium was detected in solution and 1% of rhenium had leached after the first run, just after filtration of the solid. Subsequent washing of the filtrated solid in ambient air might have leached some rhenium more, which might be responsible for the small deactivation. Concerning the selectivity to desired products, no significant changes were observed as 58% and 56% to deoxygenated products were obtained during run 1 and 2 respectively.



**Figure 13.** Catalyst recycling study. ( $\blacksquare$ ) Run 1; ( $\square$ ) Run 2.

Reaction conditions: 120 mL of 4.75% wt ERY, 0.3 g of Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> (nRe/nRh=0.5), T=200°C, 80 bar of H<sub>2</sub>.

#### 3. Conclusion

In summary, the addition of Re to TiO<sub>2</sub> and ZrO<sub>2</sub>-supported Rh catalysts remarkably enhanced the catalytic activity for the hydrogenolysis of erythritol and their selectivity towards BTO and BDO. Characterization techniques demonstrated the existence of interaction between the two metals, which, however, were different for both supports. Rh-ReO<sub>x</sub>/TiO<sub>2</sub> contained simultaneously nanoparticles of Rh and Re and very dispersed monometallic Re nanoparticles. The strong interaction between Rh and Re in Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> probably results from the formation of aggregates of Rh nanoparticles and ReO<sub>x</sub> species. They were more easily obtained over ZrO<sub>2</sub> than on TiO<sub>2</sub>, resulting in a higher activity. The Therefore, the activity was dependent on the nature of the support and the highest selectivity to BTO and BDO reached 37 and 29%, respectively, at 80% conversion in the presence of 3.7wt%Rh–3.5wt%ReO<sub>x</sub>/ZrO<sub>2</sub> catalyst at 200°C under 120 bar.

### 4. Experimental section

#### 4.1. Preparation of catalysts

Commercial TiO<sub>2</sub> (DT-51D, Cristal) and ZrO<sub>2</sub> (MEL chemicals) were used as supports. Rh-ReO<sub>x</sub>/TiO<sub>2</sub> and Rh-ReO<sub>x</sub>/ZrO<sub>2</sub> were prepared by consecutive impregnation. The first impregnation step was conducted by introducing the support and an aqueous solution (ca. 10 g L<sup>-1</sup>) of RhCl<sub>3</sub> (Alfa Aesar) precursor salt in a flask; the solution was stirred at room temperature for 7 h. After evaporation of the solvent, the material was dried overnight in an oven at 110°C and calcinated under air (60 mL min<sup>-1</sup>) at 4 °C min<sup>-1</sup> to 500 °C for 3 h. The second impregnation was conducted with an aqueous solution of NH<sub>4</sub>ReO<sub>4</sub> (Alfa Aesar), using the same conditions as in the first step. After calcination, the solids were reduced under pure H<sub>2</sub> (30 mL min<sup>-1</sup>) at  $3.5^{\circ}$  C min<sup>-1</sup> to 450 °C for 3 h; they were then passivated under 1% v/v O<sub>2</sub>/N<sub>2</sub> (30 mL min<sup>-1</sup>) at room temperature for 30 min. The monometallic Rh/TiO<sub>2</sub> and Rh/ZrO<sub>2</sub> were reduced directly after the first impregnation and calcination steps and then passivated.

#### 4.2. Characterization of catalysts

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Powder X-ray diffraction patterns (XRD) of the samples were recorded using a Bruker Advance Diffractometer D8A25 equipped with a nickel filter, a copper tube ( $\lambda K\alpha$  (Cu) = 1.54184 Å) and a multi-channel fast detector (LynxEye 192 channels an active length of 2.947 °). Samples were scanned at 0.04 ° s<sup>-1</sup> over the range  $5 \le 2\theta \le 80^{\circ}$ . Phase identification was achieved by using the JCPDS files as reference, i.e. TiO<sub>2</sub> anatase structure (JCPDS 21-1272),<sup>[55]</sup> ZrO<sub>2</sub> monoclinic phase (JCPDS 37-1484),<sup>[56]</sup> metallic Rh (JCPDS 05-0685),<sup>[57]</sup> and metallic Re (JCPDS 05-0702).<sup>[58]</sup> The mean crystallite sizes (d<sub>M</sub>) were estimated using the Scherrer equation from the half-width of the XRD broadening peak in a diffraction pattern,

$$d_{\rm M} = \frac{0.9\lambda}{\beta cos\theta}$$

where  $\lambda$  is the X-ray wavelength ( $\lambda$ = 1.54184 Å),  $\theta$  is the Bragg angle,  $\beta$  is the line broadening at half-maximum of diffraction peak, in radians.

The chemical analysis of Rh, Re, Ti, and Zr of the catalysts was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Jobin Yvon instrument of ACTIVA. Previously to analysis, the solid samples were digested in an acid mixture.

The BET specific surface area of the samples was determined by  $N_2$  physisorption at -196°C, using an ASAP 2020 Micromeritics apparatus. Prior to the measurements, catalysts were degassed at 250°C for 3 h under ultra-high vacuum (10<sup>-4</sup> mbar).

Transmission electron microscopy (TEM) images were obtained in a JEOL 2010 instrument operated at an acceleration voltage of 200 kV and equipped with a LaB6 filament and an Oxford Link Isis EDX microanalysis system. Rhenium is oxophilic and some of its oxides are soluble in water. To avoid the leaching of the Re oxides into the ethanol solution usually used for preparing the grids. The samples were dispersed dry on a carbon-coated copper grid with a syringe.<sup>[33]</sup>

X-ray photoelectron spectroscopy (XPS) was performed using monochromatized Al K $\alpha$  source (hv = 1486.6 eV) in a commercial instrument (AXIS Ultra DLD KRATOS) and revealed well-resolved peaks corresponding to Zr3d, Ti 2p, Rh 3d and Re 4f core levels. Each high-resolution spectrum was decomposed into a combination of Voigt functions. The XPS spectra of the reduced samples were recorded after reduction treatment in an auxiliary reaction chamber and transfer into the XPS chamber, avoiding exposure to air. The binding energies were referred to

the C 1s line set at 284.5 eV. Peak decomposition and fitting, and quantitative determinations were performed using the Vision Kratos softaware.

Thermogravimetric Analysis coupled with Mass Spectrometry (TGA-MS) was conducted using 0.05 g of the bimetallic solids obtained after impregnations and calcination. The samples were reduced in a 50 mL min<sup>-1</sup> 6% v/v H<sub>2</sub>/N<sub>2</sub> at 10°C min<sup>-1</sup> to 900°C.

CO chemisorption was performed using a 3 Flex instrument (Micromeritics). Prior to the CO uptake measurements, the samples were reduced at  $450^{\circ}$ C under H<sub>2</sub> for 4 h, and evacuated under vacuum at 300°C for 4 h. After that, CO uptakes were measured at 35°C. Re oxides present in the solids do not adsorb CO.<sup>[26]</sup>

### 4.3. Catalytic testing

Erythritol (Alfa Aesar) hydrogenolysis was performed in a 300 mL batch Hastelloy Parr 4560 autoclave set-up. In a typical experiment, 120 mL of erythritol aqueous solution (4.75 wt% ERY) and 0.3 g of catalyst were loaded into the reactor. After sealing, the autoclave was purged 3 times with argon, pressurized with H<sub>2</sub> to the required pressure ( $P_{H2}$  =30-120 bar), and heated to reaction temperature (T = 150-240°C) under stirring (1000 rpm). During reaction, the H<sub>2</sub> pressure was kept constant by periodic addition of small amounts of hydrogen. Liquid samples were periodically collected during the course of the reaction. At the end of the reaction, the autoclave was cooled down and after release of pressure, the suspension was collected and filtered. A blank experiment was done where no conversion of erythritol was observed.

Liquid reaction samples were analyzed using a Shimadzu LC 20A HPLC connected to a refractive index detector (RID-10A). The separation of the products was achieved using a column with a stationary phase (PS/DVB with  $SO_3^-$ , Rezex ROA-Organic Acid H<sup>+</sup>, L300, ID7.8mm) heated at 40°C. A solution of H<sub>2</sub>SO<sub>4</sub> (0.005 mol L<sup>-1</sup>) in ultra-pure ELGA water was used as a mobile phase at a flow rate of 0.5 mL min<sup>-1</sup>. The products were identified by their retention time in comparison with available standards. Butanetriols (1,2,3- and 1,2,4-BTO), butanediols (1,2-, 2,3-, 1,3-, and 1,4-BDO) and butanols (1- and 2-BuOH) are the main products obtained during hydrogenolysis of erythritol. Cyclic molecules (1,4-anhydroerythritol 1,4-AE, 3-hydroxytetrahydrofuran, 3-OH-THF and THF), glycerol, propylene glycol and ethylene glycol are minor products. A typical chromatogram, included in the supplementary information (Figure S10), shows that the hydrogenolysis products are well separated on the HPLC column.

Total Organic Carbon (TOC) in aqueous solution, was measured using a Shimadzu TOC- $V_{CSH}$  analyzer in order to check the carbon mass balance in the liquid phase and the possible formation of gaseous products. The samples were diluted by a factor of 100 before TOC analysis.

The pH value was measured for each sample using a pH meter M240 MeterLab® brand Radiometer Analytical equipped with an electrode XC 161. The pH meter was calibrated before each series of measurements with buffers pH 1.679, 4.005 and 7.000 solutions.

The erythritol conversion was calculated from equation (1):

Conversion (%) = 
$$\frac{[Erythritol]_0 - [Erythritol]_t}{[Erythritol]_0} \times 100$$
 (1)

where [erythritol]<sub>0</sub> is the initial concentration of the substrate, and [erythritol]<sub>t</sub> is the concentration at time t. The carbon selectivity  $S_t^i$  to a desired product was calculated according to equation (2) :

$$S_t^i(\%) = \frac{[\text{Product}]_{t \times n_c^{\text{product i}}}}{([\text{Erythrtiol}]_0 - [\text{Erythrtiol}]_t) \times n_c^{\text{erythrtiol}}} \times 100$$
(2)

where  $[Product]_t^i$  is the concentration of product i formed at time t and  $n_C^{product i}$  is the number of carbon atoms in the product i.

The initial reaction rate was calculated using equation (3):

$$V_0\left(\text{mmol}_{\text{ERY}} g_{\text{Rh}}^{-1} h^{-1}\right) = \frac{\text{mmole of erythritol}}{\text{mass of noble metal} \times \text{time}}$$
(3)

A number of repeated runs under the same conditions were performed to ensure satisfactory reproducibility of the data.

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