Aqueous phase hydrogenation of β-hydroxybutyric acid to 1,3-Butanediol over Ru catalysts: effect of temperature, support, and mechanistic investigation

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Resumo/Abstract

RESUMO – Esta contribuição reporta a hidrogenação em fase aquosa do ácido β-hidróxibutírico (HBA) para 1,3-Butanodiol (1,3-BDO) sobre catalisadores de Ru. A reação foi estudada com catalisadores 5,0%Ru/C comercial e 0,3%Ru/TiO2, 1,7%Ru/TiO2 e 0,2%Ru/SiO2 sintetizados. Difração de Raios X sugere maior tamanho de partículas de Ru suportadas em SiO2 do que em TiO2. Sobre o Ru/C, a conversão de HBA e seletividade a 1,3-BDO aumentou e diminuiu drasticamente, respectivamente, aumentando a temperatura de 130 para 170 ºC. Os catalisadores sintetizados apresentaram melhor seletividade do que o comercial, atingindo 73,8% sobre o 1,7%Ru/TiO2. O catalisador 0,2%Ru/SiO2 mostrou número de *turnover* de conversão aproximadamente seis vezes maior do que as demais amostras, porém reações laterais produzindo 2-Propanol e 2-Butanol em quantidades significativas foram mais pronunciadas no material suportado em SiO2, sugerindo efeito da interação metal-óxido. Um estudo mecanístico foi realizado modificando condições reacionais. Os resultados indicam que o 1,3-BDO sofre desidratação a 2-Butanol e desidrogenação a 4-Hidróxi-2-Butanona, possivelmente intermediário na produção de 2-Propanol a partir da quebra C-C.

*Palavras-chave: PHB, ácido 3-hidróxibutírico, Butanodiol, catalisadores de Ru*

ABSTRACT – This contribution reports the aqueous-phase hydrogenation of the PHB monomer β-hydroxybutyric acid (HBA) to 1,3-Butanediol (1,3-BDO), a high value-added product, over Ru catalysts. The reaction was studied with a commercial 5.0%Ru/C catalyst and 0.3%Ru/TiO2, 1.7%Ru/TiO2 and 0.2%Ru/SiO2 synthesized catalysts. X-Ray Diffraction analyses suggest larger Ru particles on SiO2 than on TiO2. Over Ru/C, HBA conversion and 1,3-BDO selectivity increased and decreased harshly, respectively, with temperature increase from 130 to 170 ºC. The synthesized catalysts presented improved selectivity in comparison to the commercial one, reaching 73.8% over 1.7%Ru/TiO2. Even though the 0.2Ru%/SiO2 catalyst showed conversion turnover number about six times higher than the other samples, side reactions producing 2-Propanol and 2-Butanol in significant amounts, were more pronounced on the SiO2 supported material, suggesting an effect of interaction metal-oxide. A mechanistic study was conducted by modifying reaction conditions. Results indicate that 1,3-BDO undergoes dehydration to 2-Butanol and dehydrogenation to 4-Hydroxy-2-Butanone, possibly an intermediate in the production of 2-Propanol by a C-C cleavage pathway.

*Keywords: PHB, 3-hydroxybutyric acid, Butanediol, Ru catalysts*

## Introduction

Among the biodegradable polymers currently being studied, the Poly(β-hydroxybutirate) (PHB) rises as promising bioplastic, due to its ease of production from renewable sources and fast degradation on several environmental conditions. In this sense, the PHB monomer β-hydroxybutyric acid (HBA), may be readily produced from the polymer through microbial, enzymatic, and chemical methods (1).

HBA possesses interesting properties such as antiviral activity, besides a wide range of applications in the synthesis of chemicals (2). However, studies on the catalytic hydrogenation of HBA to 1,3-Butanediol (1,3-BDO) are scarce (3).

1,3-Butanediol is a high value-added product, with known nutritional properties, being currently studied in food ingredient research. Furthermore, it may be used as building block for several chemicals (4). Thus, given the environmental-friendly nature of PHB, the development of active and selective catalysts for the hydrogenation of HBA to 1,3-BDO is highly desirable (3).

Considering the above, this contribution reports the aqueous-phase hydrogenation of HBA to 1,3-BDO over Ru catalysts supported on carbon, TiO2 and SiO2. The effect of temperature, support and Ru content were evaluated. Also, mechanistic insight of side reactions was obtained by modifying reactions conditions and HPLC analyses.

## Experimental

*Catalysts synthesis*

The Ru/TiO2 catalysts were prepared by incipient wetness impregnation, following a protocol adapted from Liu et al (5). Initially a commercial TiO2 (Degussa P25) was dried in oven at 110 ºC for 24 h. An aqueous solution of the precursor RuCl3.xH2O (Sigma) was then added to the dried support. The slurry mixture was stirred at 250 rpm for 4.5 h. Afterwards, the product was dried at 80 ºC for 2.0 h, then at 110 ºC overnight. The prepared material was activated under H2 flow (30 mL/min) for 2.0 h at 350 ºC.

The SiO2 support was prepared from treatment of tetraethylorthosilicate with HNO3, followed by calcination under air at 500 ºC (3 ºC/min) for 5 h. The Ru/SiO2 catalyst was prepared by incipient impregnation, following the same protocol described. The commercial 5.0% Ru/C (Sigma) catalyst was used without any pre-treatments.

*Characterization*

X-Ray Diffraction (XRD) analyses were performed using CuKα radiation with 2θ = 10 – 80º (2º step), the diffractograms were collected by an XRD 6000 (Shimadzu). For the chemical composition analysis, X-Ray Fluorescence (XRF) was employed in an EDX-720 (Shimadzu).

*Catalytic tests*

The experiments were conducted in a stainless-steel batch reactor (70 mL). In an usual experiment, the equipment was loaded with 20 mL of a reactant aqueous solution (0.1 mol.L-1) and 150 mg of catalyst. The reactor was then pressurized with pure H2 to obtain reaction pressure of 70 bar, according to the reaction temperature (130 – 170 ºC). The system was then inserted in thermal oil bath at the desired temperature. After the transient period, the reaction was kept at this condition for 5h. Finally, the resulting mixture was analyzed by HPLC (Shimadzu) equipped with Refractive Index Detector (RID), the usual analyses were performed with column oven at 65 ºC.

## Results and Discussion

*Characterization*

Phase identification and chemical composition analyses were performed through XRD and XRF, respectively, the results are presented in Figure 1. TiO2 presents high crystallinity and contains the Anatase and Rutile phases. Incorporating Ru on TiO2 did not cause any observable changes in the diffractogram, regardless of Ru amount, which suggests highly dispersed nanoparticles, or simply the crystalline lines of Rutile overlap Ru peaks. The Ru/C diffractogram is characteristic of activated carbon, with no peaks attributable to Ru as well. Conversely, metallic Ru (2θ = 43.5º) was identified on 0.2%Ru/SiO2, indicating larger Ru particle size than on TiO2, possibly caused by lower specific surface area of SiO2, however, N2 physisorption analyses are yet to be performed to confirm the effect.

No lines related to Ru oxides were detected, pointing that reduction occurred successfully, and the metallic phase is stable at storage conditions.



**Figure 1.** XRD patterns obtained for the samples and chemical composition estimated by XRF.

*Effect of temperature, support, and Ru content*

Initially, the effect of reaction temperature on HBA conversion and 1,3-BDO selectivity and yield was evaluated with the commercial 5.0%Ru/C catalyst, the results are exhibited in Figure 2. Increasing reaction temperature had a positive effect on HBA conversion, as expected, however, it was observed drastic 1,3-BDO selectivity drop, resulting in poor yields. In all experiments, the main subproducts detected were 2-Propanol and 2-Butanol, with concentration increasing with temperature. 2-Butanol is known to be formed through 1,3-BDO dehydration (6), and 2-Propanol was detected in small amounts in the conversion of 1,3-BDO over rare earth oxides (7), in small amounts and at much higher temperatures (~300 ºC) though.

The results indicate that 1,3-BDO is produced but undergoes side reactions that are promoted by temperature increase, thus causing the selectivity loss observed. At 170 ºC, almost no 1,3-BDO was detected, hence this condition may not be suited for the reaction. HBA may have also undergone side reaction, but the mechanisms are unknown. With an initial knowledge of suitable reaction conditions, the performance of the synthesized catalysts was evaluated.

The HBA conversion (XHBA) and 1,3-BDO selectivity (S1,3-BDO) obtained with the Ru/TiO2 and Ru/SiO2 catalysts highlight the effect of Ru content and nature of support. The results are presented in Figure 3. The TiO2 supported materials presented increasing XHBA and S1,3-BDO with Ru content, reaching 17.1 and 73.8% with the 1.7%Ru/TiO2 sample, respectively at 130 ºC (Fig. 3a). The Ru/SiO2 catalyst showed similar activity to 1.7%Ru/TiO2, even with much lower Ru content, even though it was less selective towards 1,3-BDO.



**Figure 2.** Effect of reaction temperature on HBA conversion (XHBA), 1,3-BDO selectivity (S1,3-BDO) and 1,3-BDO yield (Y1,3-BDO) over 5.0%Ru/C. Parameters: P = 70 bar, mcat = 150 mg, t = 5 h.

By increasing the reaction temperature to 150 ºC (Fig. 3b), conversion rose almost proportionally in all samples, as was observed with Ru/C, but the selectivity profile changed significantly. In this case, the highest selectivity obtained was 51.8% with 0.3%Ru/TiO2, while in the other samples it dropped harshly. Considering all tests at 150 ºC, a pattern was observed in which the most active samples were also the least selective, further indicating side reactions taking place during the experiments. At both temperatures, the main subproducts detected were also 2-Propanol and 2-Butanol.

In addition, blank tests confirmed the stability of HBA in the reaction conditions in the absence of catalysts. Experiments with the supports TiO2 and SiO2 were also performed, showing no effect on HBA. Therefore, it appears that metallic Ru is the active site in the hydrogenation of 1,3-BDO but is also participating in the side reactions. Comparing the results obtained with the 0.2%Ru/SiO2 and 0.3%Ru/TiO2 samples, possessing very similar Ru content, the support may also influence HBA hydrogenation, possibly due to the interaction of Ru and oxide, which may generate different sites according to the support nature. At both temperatures, Ru on SiO2 seems to be more active than on TiO2. Nonetheless, the selectivity drop with temperature was much more significant in the SiO2 supported catalysts, pointing that the material promotes side reactions to a greater extent than Ru/TiO2.



**Figure 3.** Effect of Ru content on HBA conversion (XHBA), 1,3-BDO selectivity (S1,3-BDO) and 1,3-BDO yield (Y1,3-BDO) over 5.0%Ru/C at a) 130 ºC and b) 150 ºC. Parameters: P= 70 bar, mcat = 150 mg, t = 5 h.

To investigate side reactions occurring with 1,3-BDO, product degradation experiments over the supports and catalysts were performed by 1,3-BDO hydrogenation maintaining the reaction parameters, the results are shown in Figure 4. In the absence of catalyst or support (blank tests), 1,3-BDO showed high stability in the reaction conditions, even at 200 ºC. Curiously, while pure SiO2 had no effect, TiO2 converted approximately 10% of 1,3-BDO, which is the opposite effect than the observed in the catalysts (Fig. 3). This suggests that over 0.2%Ru/SiO2 the formation of subproducts originates only from the cooperation of Ru and SiO2. On the other hand, impregnation of small amount of Ru (0.3%) on TiO2 only caused a slight increase (7%) in 1,3-BDO degradation (Fig. 4), corroborating the hypothesis of different active sites according to the support.

Nevertheless, the catalysts 1.7%Ru/TiO2, 0.2%Ru/SiO2 and 5.0%Ru/C presented striking activity on 1,3-BDO degradation, reaching almost 100% conversion at 150 ºC. The significant difference between the tests with 0.2%Ru/SiO2 and 0.3%Ru/TiO2 once again suggests the Ru incorporation on SiO2 has a predominant effect on side reactions with 1,3-BDO, even in small Ru amounts. Regarding the TiO2 supported samples, increasing the Ru content from 0.3 to 1.7% had a remarkable effect on 1,3-BDO conversion, showing that metallic sites are the main cause for product degradation, and the Ru amount should be selected carefully, if one aims at maximizing 1,3-BDO yield.

It is noteworthy that the main subproducts detected were once again 2-Propanol and 2-Butanol, suggesting that the side reactions involving 1,3-BDO have significant impact on the selectivity loss during HBA hydrogenation. Nonetheless, for now nothing can be said regarding side reactions with HBA, which may also be occurring.



**Figure 4.** 1,3-BDO conversion over the supports and catalysts on the product degradation experiments. Parameters: T = 150 ºC (except for the blank tests), P= 70 bar, mcat = 150 mg, t = 5 h.

The data discussed so far point that metallic Ru particles are the only active sites in the HBA hydrogenation, given that the supports had no activity by themselves. With this assumption and using the Ru content estimated by XRF, the HBA conversion and 1,3-BDO production Turnover Numbers, given by TONX and TONP, respectively, were determined for the catalysts (Figure 5). TONX and TON­P relate to mols of HBA converted and mols of 1,3-BDO produced, respectively per active site. TONX and TONP increased with decreasing Ru content, pointing that small amounts of metallic sites are desirable to maximize 1,3-BDO yield. The TONs also highlight the effect of Ru particles supported on SiO2, being about six times more active than the other materials at 150 ºC, the sample also presented the highest TONP among the studied catalysts at both temperatures. Overall, raising reaction temperature from 130 to 150 ºC caused TONP values to decrease, except with the 0.3%Ru/TiO2 catalyst, reaching production turnover similar to the SiO2 supported sample (about 40 mol1,3-BDO/molRu).

Due to lack of characterization of the synthesized catalysts, the only assumption that can be made at the moment is that the observed activity effect of Ru on SiO2 may be caused by larger particle sizes (Fig. 1).

Hence, understanding the mechanisms of HBA hydrogenation to 1,3-BDO and side reactions occurring is critical for the development of more selective catalysts. With the current equipment available, a mechanistic study of reactions involving 1,3-BDO was carried out. The next section details the procedures employed and results obtained.



**Figure 5.** Turnover numbers of HBA conversion (TONX) and 1,3-BDO production (TONP) determined at 130 and 150 ºC. Parameters: P= 70 bar, mcat = 150 mg, t = 5 h.

*Mechanistic investigation of 1,3-BDO side reactions*

The investigation consisted in modifying reaction conditions to control 1,3-BDO degradation and prevent intermediates to be further converted. The goal was to identify the pathway leading 1,3-BDO to 2-Propanol and 2-Butanol. Ideally, the identification of unknown substances should be conducted with mass spectrometry, however, at the time of research, only the HPLC equipment was available.

Thus, from theory and literature on 1,3-BDO conversion (7-9), standard solutions of the possible intermediates were analyzed by HPLC to identify each retention time (tR), which depends on the molecule structure, then correlate with the signals obtained in the procedures to be described below. However, the identification may be misleading, as different compounds may present similar retention time, hence, additional analyses were performed in the HPLC by changing the oven temperature (Toven) from 65 ºC (temperature used in typical analyses) to 30 ºC to confirm assignments by observing the retention time shift of the samples. In other words, the assignment was only made if the signal matched the standard solution at both temperatures.

Therefore, three additional experiments were performed: a) 1,3-BDO conversion under inert atmosphere (pure Argon) at 1 bar; b) 1,3-BDO hydrogenation at 1 bar; and c) 4-Hydroxy-2-Butanone (4H2B) hydrogenation at 70 bar. The results are presented in Table 1 in terms of conversion and product distribution and the obtained chromatograms are shown in Figure 6 (solid line and dotted line: Toven = 65 ºC and Toven = 30 ºC, respectively). The selected catalyst for the tests was the commercial 5.0%Ru/C. The retention times of the standard solutions at both analysis temperatures are given in Table 2.

**Table 1.** Conversion and products distribution obtained in the tests: a) 1,3-BDO conversion under inert atmosphere at 1 bar, b) 1,3-BDO hydrogenation at 1 bar and c) 4H2B hydrogenation at 70 bar. X is the 1,3-BDO or 4H2B conversion.

|  |  |  |
| --- | --- | --- |
|  |  | **Product distribution (mol.L-1)** |
| **Test** | **X (%)** | **4H2B** | **1,3-BDO** | **2-PropOH** | **2-ButOH** |
| a) | 27.7 | 0.00693 | 0.0723 | 0.000389 | 0.000895 |
| b) | 53.4 | 0.000318 | 0.0476 | 0.0308 | 0.00210 |
| c) | 100 | 0 | 0.0164 | 0.0518 | 0.0119 |

Parameters: 5.0%Ru/C, T = 130 ºC, mcat = 150 mg, t = 5 h. r

**Table 2.** Retention time (tR) of the standard solutions analyzed with HPLC through RID at Toven = 30 and 65 ºC. Chromatograms are shown in Figure 6.

|  |  |  |
| --- | --- | --- |
| **Compound** | **tR­\_65 ºC (min)** | **tR­\_30 ºC (min)** |
| **4H2B** | (l) 18.17 | (l) 23.27 |
| **1,3-BDO** | (z) 19.25 | (z) 22.05 |
| **Acetone** | (n) 21.40 | (n) 27.84 |
| **2-Propanol** | (o) 24.30 | (o) 26.80 |
| **Butanone** | (v) 26.30 | (v) 35.50 |
| **2-Butanol** | (t) 31.08 | (t) 35.20 |

Firstly, test a) of 1,3-BDO conversion in the absence of hydrogen resulted in several products (Fig. 6a), which were assigned to: 4-Hydroxy-2-Butanone (4H2B), Acetone, Butanone and 2-Butanol, the retention time of the substances matched the standards at both oven temperatures (Table 2). Butanone and 2-Butanol have similar retention times at 30 ºC (Table 2), however, the higher intensity of the peak in comparison to the 65 ºC, point the presence of both compounds. The intense peaks at tR = 19.2 min (solid line: Toven = 65 ºC) and tR = 22.05 min (dotted line: Toven = 30 ºC) relate to 1,3-BDO, which was the reactant in this case. Interestingly, Ru/C converted 27.7% of 1,3-BDO (Table 1a) in the absence of H2, producing acetone and 4H2B, which were not observed in any previous experiment so far. 4H2B may be produced by dehydrogenation of the secondary hydroxyl group of 1,3-BDO, but it is also prone to dehydration or even C-C bond cleavage on the presence of metallic sites. Butanone is likely to have been produced mainly from dehydration of the secondary hydroxyl of 1,3-BDO. The presence of a small acetone signal suggests that, in fact, C-C cleavage of 4H2B took place to a lesser extent (8,9). Nevertheless, only very small 2-Propanol and 2-Butanol signals were identified, so with test a) alone it was still unclear whether 4H2B and Butanone are intermediates of 1,3-BDO conversion during hydrogenation of HBA.



**Figure 6.** Chromatograms obtained in the tests: a) 1,3-BDO conversion under inert atmosphere at 1bar, b) 1,3-BDO hydrogenation at 1 bar and c) 4-Hydroxy-2-Butanone (4H2B) hydrogenation at 70 bar. Solid lines: analyses at Toven = 65 ºC, dotted lines: analyses at Toven = 30 ºC. Icons are also presented in Table 2. Parameters: 5.0%Ru/C, T = 130 ºC, mcat = 150 mg, t = 5 h.

The next experiment, test b) (Fig. 6b), was performed in the same conditions as test a), but with 1 bar of pure H2 instead of Ar. In this case, 1,3-BDO conversion reached 53.7% and 4H2B was observed in a very small quantity (Table 1b), indicating that it was formed and further converted into other products. The intense 2-Propanol peak (Fig. 6b tR = 24.3 min) point to C-C bond cleavage of 4H2B to acetone (present in small quantity), followed by hydrogenation to 2-Propanol. Given that it was not observed in test a), this may explain the 2-Propanol formation in the catalytic tests with HBA, in the presence of 70 bar of H2. Moreover, the absence of Butanone indicates that it was further hydrogenated to 2-Butanol, which was detected in significant amount (Table 1b). The result shows 4H2B and Butanone being highly unstable in the presence of H2, which would be the reason as to why both were not detected previously in the HBA hydrogenation.

To confirm 2-Propanol formation from 4H2B, test c) was carried out using 4H2B as reactant, under 70 bar of H2 (Fig. 6c). As expected, 4H2B is highly active, being completely converted over 5 h of reaction, forming 2-Propanol mainly. This corroborates the idea that 4H2B is in fact an intermediate in the degradation of 1,3-BDO to 2-Propanol. Interestingly, 1,3-BDO was observed in the reaction product, which is expected to occur by hydrogenation of the 4H2B carbonyl, however, it was at a concentration about three times lower than 2-Propanol, suggesting that C-C bond cleavage is predominant over hydrogenation to 1,3-BDO, even in H2 atmosphere at 70 bar. Furthermore, 2-Butanol was detected in significant amount, likely formed by 1,3-BDO dehydration to butanone and further hydrogenation to 2-Butanol or even by dehydration of 4H2B to methyl vinyl ketone, then successive hydrogenations to Butanone and 2-Butanol. Despite the formation of 2-Propanol, no acetone was detected in this test, therefore it is probably readily hydrogenated to the alcohol (9).

Furthermore, a single 2-Butanol hydrogenation experiment performed at P = 70 bar over the Ru/C catalyst showed low conversion (15%), indicating higher stability of the compound in comparison with 4H2B (Table 1c) and Butanone, which appears to be readily hydrogenated even at P = 1 bar.

Overall, the investigation suggests that 1,3-BDO degradation starts from the secondary hydroxyl dehydrogenation to 4H2B, followed by C-C cleavage to acetone and further hydrogenation to 2-Propanol. The pathway leading to 2-Butanol is still unclear, but it is probably formed either by dehydration of 1,3-BDO to butanone followed by hydrogenation, dehydration of 4H2B then successive hydrogenations, or a combination of both.

It is also noteworthy that the literature in which the ideas for the tests were based shows the mechanisms of 1,3-BDO conversion in gas-phase and higher temperatures, so this results not only corroborates these finding, but also suggests that a similar pathway takes place on aqueous phase. All the products identified here come from reactions starting from the secondary hydroxyl of 1,3-BDO, however, it was already shown that the primary hydroxyl may also undergo side reactions (7,8). Nevertheless, in this study it was observed that, in HBA hydrogenation conditions, the secondary 1,3-BDO hydroxyl is much more unstable than the primary.

With the data presented here, it was possible to evaluate the effect of temperature, support, and Ru content on the HBA hydrogenation to 1,3-BDO, as well as identify the main mechanism of side reactions involved the product. This work may serve as a starting point in more profound investigations regarding HBA hydrogenation and the development of selective catalysts towards 1,3-BDO.

## Conclusions

Aqueous-phase hydrogenation of β-hydroxybutyric acid was studied over Ru catalysts supported on carbon, TiO2 and SiO2. Increasing reaction temperature increased and decreased HBA conversion and 1,3-Butanediol selectivity, respectively. Synthesized catalysts showed higher selectivity than the commercial. The Ru/SiO2 catalyst presented the highest conversion and production turnover numbers, but side reactions were more pronounced, indicating and effect of support nature. All catalysts were also active in the degradation of 1,3-Butanediol. The mechanistic investigation suggests that side reactions start at dehydration to 2-Butanol or dehydrogenation to 4-Hydroxy-2-Butanone, which is converted into 2-Propanol by a C-C cleavage mechanism. The data presented here serve as basis for the development of active and selective catalysts for the hydrogenation of β-hydroxybutyric acid to 1,3-Butanediol.

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