



Hydrogenolysis of 2-Tosyloxy-1,3-propanediol into 1,3-Propanediol over Raney Ni Catalyst

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2-Tosyloxy-1,3-propanediol (TPD), um potencial precursor para produção de 1,3-propanodiol (1,3-PD), é produzido através da tosilção do glicerol com a ajuda de uma técnica de proteção de grupos. Neste trabalho, discutiu-se a hidrogenólise do TPD em 1,3-PD sobre catalisador de Raney Ni através de diferentes parâmetros de reação para otimizar as condições de reação para formação seletiva do 1,3-PD. O mecanismo de hidrogenólise do TPD e reações laterais também foram confirmados pela técnica de cromatografia em fase gasosa acoplada à espectrometria de massas (GC-MS).

2-Tosyloxy-1,3-propanediol (TPD), a potential precursor for 1,3-propanediol (1,3-PD) production, is produced by the tosylation of glycerol with the help of protecting group techniques. In this work, the hydrogenolysis of TPD into 1,3-PD over Raney Ni catalyst is discussed at different reaction parameters to optimize the reaction conditions for selective formation of 1,3-PD. The mechanisms of the hydrogenolysis of TPD and the side reactions were also confirmed by gas chromatography-mass spectrometry (GC-MS) technique.

Keywords: glycerol, 2-tosyloxy-1,3-propanediol, 1,3-propanediol, hydrogenolysis, Raney Ni

Introduction

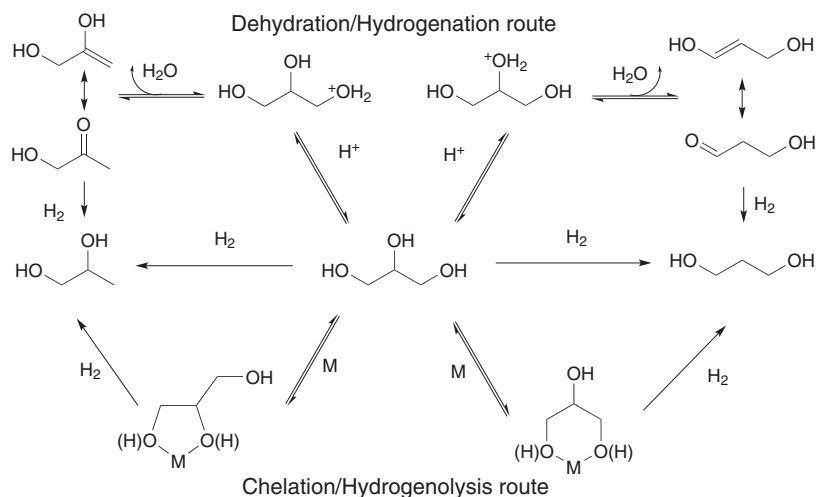
Glycerol, a promising biomass-derived compound, is available as a major byproduct (10% in weight) in the manufacturing of biodiesel.¹⁻³ Because of the recent escalating production and the utilization of biodiesel worldwide, large quantities of glycerol have been produced.^{4,5} The rich availability makes it an important raw material for the manufacture of some valuable chemicals (diols, epoxides, esters, ethers, etc.), thereby facilitating the replacement of petroleum-based products, and also benefiting the emerging biodiesel industry.⁶⁻⁸

1,3-Propanediol (1,3-PD), currently produced from petroleum derivatives, such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route), is an important precursor for the synthesis of polymethylene terephthalate and polyurethanes.⁸ Recent advances in the hydrogenolysis of glycerol into 1,3-PD have produced a range of possible hydrogenolysis products, such as 1,3-PD, 1,2-propanediol (1,2-PD), 1-propanol (1-PrOH), 2-propanol (2-PrOH), and some other degradation products (ethylene glycerol, ethanol, methanol and methane), but few catalysts are

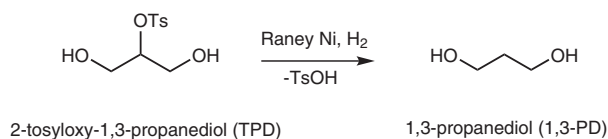
selective for 1,3-PD.⁹⁻¹⁴ Kurosaka *et al.*¹¹ found that the yield of 1,3-PD was up to 24% by the hydrogenolysis of glycerol over Pt/WO₃/ZrO₂ catalyst. Most recently, Nakagawa *et al.*¹³ made a break through when they obtained 38% yield of 1,3-PD by running the reaction using Ir-ReO_x/SiO₂ as a catalyst.

The hydrogenolysis of glycerol might proceed through different pathways, depending on whether the primary or secondary hydroxyl is more easily reduced (Scheme 1).¹⁰ Because of the glycerol molecule with hydroxyl groups of similar reactivity, it is difficult to produce the desired 1,3-PD in a high selectivity. 2-Tosyloxy-1,3-propanediol (TPD), a potential precursor for the production of 1,3-PD, is produced by the tosylation of glycerol with the help of a group protection technique (acetalization).¹⁵⁻¹⁷ Compared with hydroxyl group, the tosyloxyl group is a better living group, and is easier to be replaced with a hydride ion. Therefore, 1,3-PD can be obtained in a high selectivity by the subsequent removal of the tosyloxyl group of TPD (Scheme 2). In this work, instead of expensive reducing reagent lithium hydride, the detosyloxylation of TPD was carried out by catalytic hydrogenolysis over the non-expensive Raney Ni catalyst, and studied at different reaction parameters to optimize the reaction conditions for selective formation of 1,3-PD.

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Scheme 1. Illustration of the pathways of glycerol hydrogenolysis (adapted from reference 10).



Scheme 2. Illustration of the hydrogenolysis of TPD into 1,3-PD.

Experimental

Reagents and materials

Glycerol ($\geq 99\%$) was supplied by Ningbo Jiesen Biodiesel Co., Ltd. Benzaldehyde ($> 98.5\%$) and *p*-toluenesulfonyl chloride ($\geq 98.5\%$) were brought from Sinopharm Chemical Reagent Co., Ltd. 1,3-PD ($\geq 99.6\%$) and 1-PrOH ($\geq 99.7\%$) were purchased from Sigma-Aldrich Chemical Co. 1,4-Butanediol ($\geq 99.0\%$) was provided by Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants. High purity grade hydrogen was obtained from Hangzhou Electrochemical Group Co., Ltd. Raney Ni (Ni $\geq 90\%$, activity $\text{min}^{-1} \text{ g}^{-1} \geq 5 \text{ mL H}_2$) was bought from Dalian General Chemical Industry Co., Ltd.

Synthesis of TPD

TPD was prepared from glycerol in a three-step sequence (acetalisation with benzaldehyde-tosylation-deacetalisation) (see in the Supplementary Information (SI) section).^{15,17,18} The overall yield of TPD was 90%. No further experiment was performed to maximize the yield of TPD. The chemical structure of TPD was confirmed by ^1H and ^{13}C NMR (nuclear magnetic resonance, Bruker AVANCE III 500MHz, Switzerland) spectra. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.82 (d, 2H, J 8.3 Hz), 7.35 (d,

2H, J 8.1 Hz), 4.56 (p, 1H, J 4.7 Hz), 3.78 (m, 4H), 2.80 (s, 2H, OH), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ / ppm 145.2, 133.1, 130.0, 127.9, 82.7, 61.1, 21.6.

Hydrogenolysis of TPD

The hydrogenolysis of TPD was carried out in a 200 mL stainless steel autoclave. The autoclave was charged with 100 mL TPD dioxane solution (2 wt.%), 0.32-0.96 g Raney Ni. After being sealed and purged repeatedly with 2 MPa H_2 to eliminate air, the autoclave was heated to the required temperature and then pressurized with H_2 to a given value. The stirring speed was set constant at 750 rpm. The reactions were conducted at the following conditions: 110-150 $^\circ\text{C}$, 0.4-4 MPa H_2 , 2-8 h. After reaction, the autoclave was cooled to room temperature. The products were analyzed by gas chromatograph, (GC, Shimadzu GC-17A, HP-FFAP 30 m $\times$ 0.25 mm $\times$ 0.25 μm , flame ionization detector), and identified by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A/5875C, HP-5SM 30 m $\times$ 0.25 mm $\times$ 0.25 μm). Quantifications were achieved by using 1,4-butanediol as an internal standard. The unreacted TPD was confirmed by high performance liquid chromatography (HPLC, Varian Prostar 210, kromasil 100-5 C_{18} column: Φ 4.6 mm $\times$ 250 mm, UV-Vis detector).

Results and Discussion

Reaction scheme and product identification

The hydrogenolysis of glycerol is suggested to proceed via dehydration of glycerol into acetol and 3-hydroxypropanal (3-HPA) intermediate, and followed by

the subsequent hydrogenation to produce the corresponding 1,2-PD and 1,3-PD, respectively.^{9-14,19,20} Hence, as shown in Scheme 3, the selective transformation of glycerol to 1,3-PD requires a catalyst system with the ability to not only promote the coupled glycerol dehydration (equilibria: $K_{\text{glycerol dehydration}}$)/3-HPA hydrogenation (equilibria: K_{diol}) reactions, but also minimize the 3-HPA dehydration (equilibria: K_{eq}). However, as stated by Taher *et al.*,¹⁹ the activation barrier of initial dehydration of glycerol was much higher than the dehydration/hydrogenation of 3-HPA, that is:

$$\Delta G^\ddagger (K_{\text{glycerol dehydration}}) \gg \Delta G^\ddagger (K_{\text{diol}}) > \Delta G^\ddagger (K_{\text{eq}}).$$

To overcome the $\Delta G^\ddagger (K_{\text{glycerol dehydration}})$, the dehydration of 3-HPA to acrolein (AO) is highly favored at higher temperature ($> 175^\circ\text{C}$).

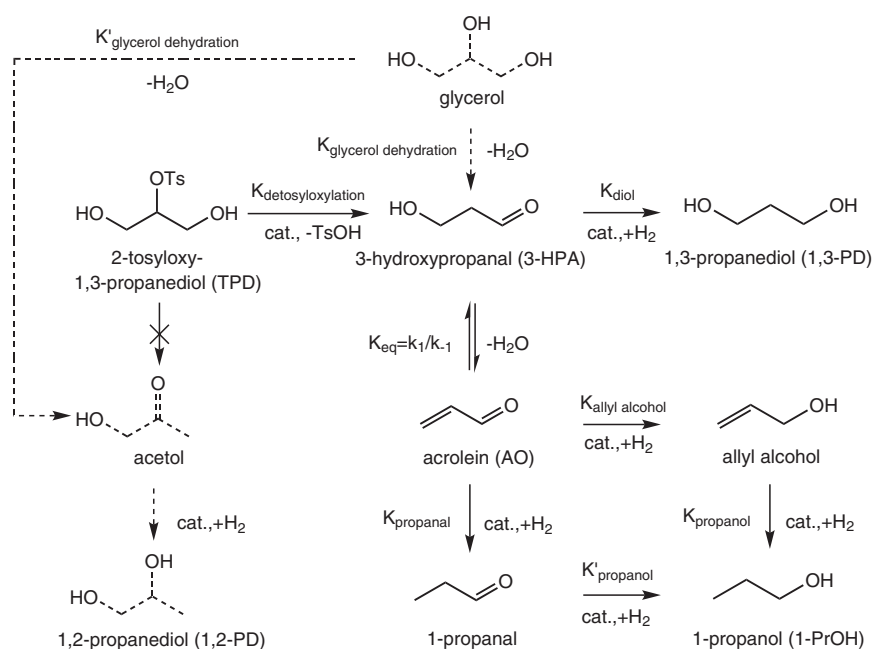
In our investigation, by using GC-MS as a qualitative assay, the dominative TPD hydrogenolysis products were 1,3-PD and 1-PrOH. Based on these proposed mechanism of 1,3-PD formation in glycerol hydrogenolysis,¹⁹⁻²³ the hydrogenolysis of TPD might occur as shown in Scheme 3. TPD undergoes a detosyloxylation to give 3-HPA and TsOH, the subsequent reaction of 3-HPA proceed via the following routes: (i) hydrogenation of 3-HPA to produce 1,3-PD, and (ii) dehydration of 3-HPA to form AO intermediate, and followed by the subsequent hydrogenation to produce 1-PrOH. Compared with the hydroxyl group of glycerol, the tosyloxyl group of TPD is a better leaving group, and can easily undergo a detosyloxylation to give the exclusive

3-HPA at low temperature (ca. $100\text{--}140^\circ\text{C}$). This means that the activation barrier

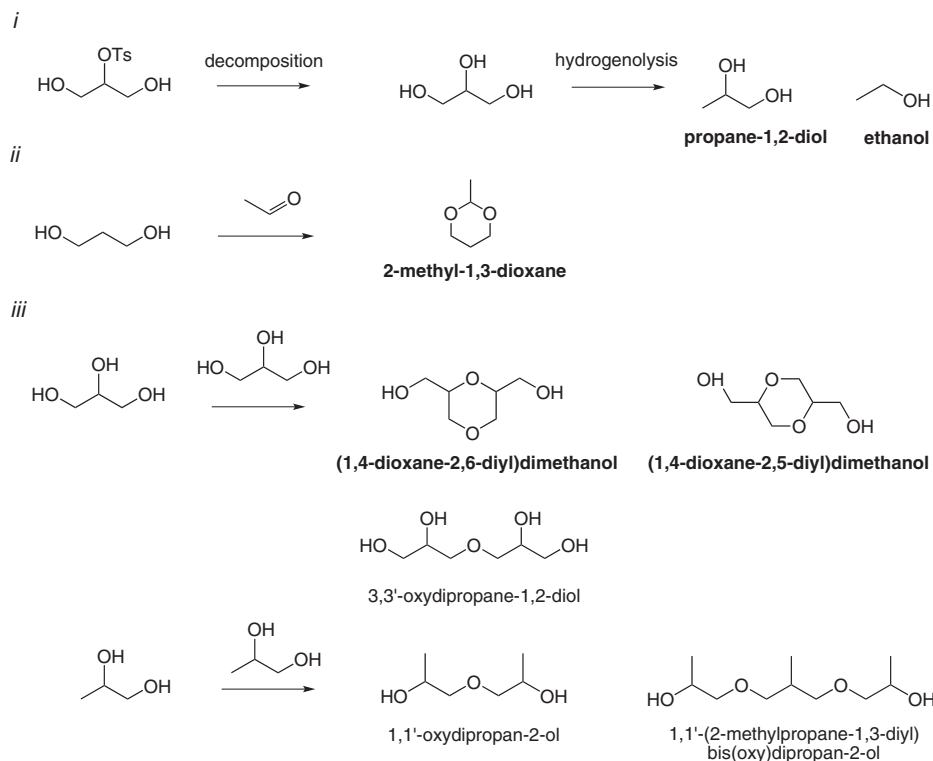
$$\Delta G^\ddagger (K_{\text{glycerol dehydration}}) \gg \Delta G^\ddagger (K_{\text{detosyloxylation}}) > \Delta G^\ddagger (K_{\text{diol}}) > \Delta G^\ddagger (K_{\text{eq}}),$$

thereby minimizing the dehydration route of the 3-HPA to produce 1-PrOH. The determination of the optimum reaction conditions of Scheme 3 for selective formation of 1,3-PD, therefore, mainly depends on the adjustment of two equilibria of 3-HPA/AO (K_{eq}) and 3-HPA/1,3-PD (K_{diol}).

Moreover, with the exception of the 1,3-PD and 1-PrOH, about 15 kinds of chemicals were also separated by GC, and half of them can be possibly identified via MS by the comparison with the standard mass spectrum in the NIST data base (see MS spectra comparison in the SI section). As stated by Huang *et al.*²⁰ and Schlaf *et al.*,²⁴ the alcohol and aldehyde can be easily condensed over acid catalysts in the hydrogenolysis of glycerol; da Silva *et al.*²⁵ and Medeiros *et al.*²⁶ have demonstrated that the condensation reaction between the glycerol and assorted alcohols, and the self-condensation of glycerol can be readily achieved over acid catalyst. Based on these proposed mechanism of formation, as shown in Scheme 4, in the present of TsOH, these identified byproducts can be supposed from the following reactions: (i) the decomposition of TPD to produce glycerol, and followed by the subsequent hydrogenolysis reaction, (ii) the condensation of 1,3-PD and acetaldehyde, and (iii) the self-condensation of glycerol or 1,2-PD.



Scheme 3. The potential pathways of TPD hydrogenolysis. Adapted from references 9-14,19-23.



Scheme 4. The potential side reactions of TPD hydrogenolysis (the products identified via GC-MS were highlighted in bold). Adapted from references 20, 24-26.

Effect of reaction temperature

Figure 1 shows the effect of temperature on TPD conversion and product selectivity. As the temperature elevated from 110 to 150 °C, there was a proportional increase in TPD conversion from 16.7 to 84.1%. The selectivity of 1,3-PD increased until 140 °C and began to decrease from 57.1 to 55.2%, as the temperature further elevated to 150 °C. Conversely, when the temperature was above 140 °C, the selectivity of 1-PrOH increased from 24.8 to 42.7%. It is to prove that the dehydration of 3-HPA to form AO is highly favored at high temperature (> 140 °C) to drive the reaction towards the side of 1-PrOH formation. As stated in Huang *et al.*,²⁰ it was found a similar conclusion that high operating temperature (180-230 °C) resulted in low selectivity of 1,3-PD (25-13%).

Effect of catalyst weight

Figure 2 provides the effect of catalyst weight on TPD hydrogenolysis. The conversion of TPD increased obviously within the catalyst weight range of 0.32-0.96 g. In the absence of Raney Ni, TPD was found to be inactive at 140 °C, indicating that the function of Raney Ni is not only limited to 3-HPA and AO hydrogenation, but also involved in detosyloxylate step as well. The selectivity of 1,3-PD increased from 57.1 to 73.9% with the increasing

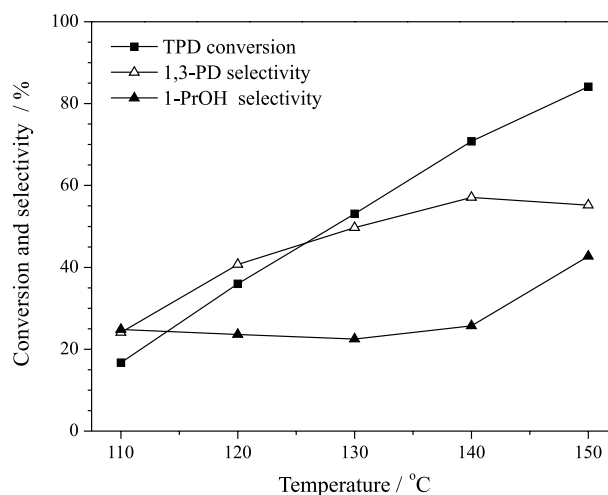


Figure 1. The effect of temperature on TPD hydrogenolysis (2 wt.% of TPD in dioxane, 3 MPa H₂, 0.32 g Raney Ni, 4 h).

catalyst weight from 0.32 to 0.80 g, and slowly increased to 74.5% as the catalyst weight further increased to 0.96 g. Conversely, the selectivity towards 1-PrOH presented a distinct decrease (25.6-15.0%) within the catalyst weight range of 0.32-0.80 g. It is to validate the hypothesis that, as illustrated in Scheme 3, the 1,3-PD and 1-PrOH are formed in parallel, and the selectivity of 1,3-PD and 1-PrOH can be controlled by the relative hydrogenation/dehydration rate of 3-HPA. Thus, increasing Raney Ni weight can fasten the hydrogenation rate of 3-HPA and the selectivity of

1,3-PD increased correspondingly. Opposite to the work presented by Dasari *et al.*,²⁷ the excess catalyst did not further promote the excessive hydrogenolysis of 1,3-PD to lower alcohol and gas.

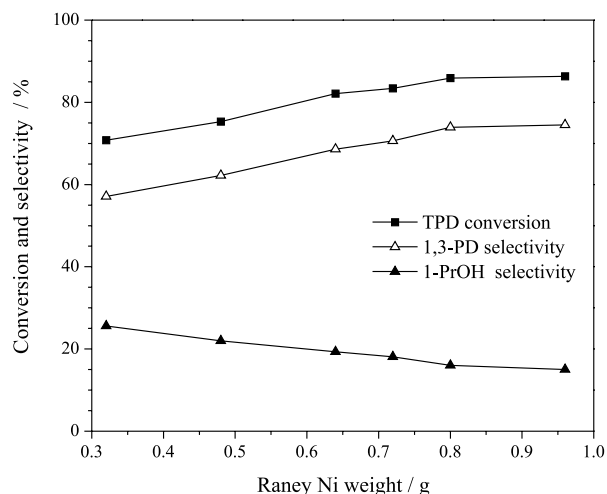


Figure 2. The effect of Raney Ni weight on TPD hydrogenolysis (2 wt.% of TPD in dioxane, 140 °C, 3 MPa H₂, 4 h).

Effect of hydrogen pressure

Figure 3 summarizes the TPD conversion and product selectivity at different H₂ pressure. The conversion of TPD was independent with H₂ pressure. Enhancing the H₂ pressure from 0.4 to 1.0 MPa lead to an increase in the selectivity of 1,3-PD from 63.6 to 74.0%, whereas the selectivity of 1-PrOH declined from 17.8 to 15.0%. These results imply that the high H₂ pressure could fasten the hydrogenation rate of 3-HPA, and drive the reaction equilibrium towards 1,3-PD formation. As the H₂ pressure further enhanced from 1.0 to 4.0 MPa, there was no further increase in the selectivity of 1,3-PD (74.0-73.9%), and the excess H₂ pressure did not cause considerable change in the selectivity of 1-PrOH either, suggesting that 1-PrOH is produced through the dehydration of 3-HPA rather than the excessive hydrogenolysis of 1,3-PD. To validate this speculation, the hydrogenolysis of 1,3-PD was carried out in dioxane at 140 °C under 5.0 MPa H₂, after reaction for 4 h, the conversion of 1,3-PD was low, no *n*-PrOH was produced (Figure S12 in the SI section).

Effect of reaction time

The effect of reaction time on TPD conversion and product selectivity was studied, and the results are tabulated in Figure 4. With the reaction time prolonged from 2 to 8 h, the conversion of TPD increased from 67.8 to 91.2%, meanwhile the selectivity of 1,3-PD raised from 76.7 to

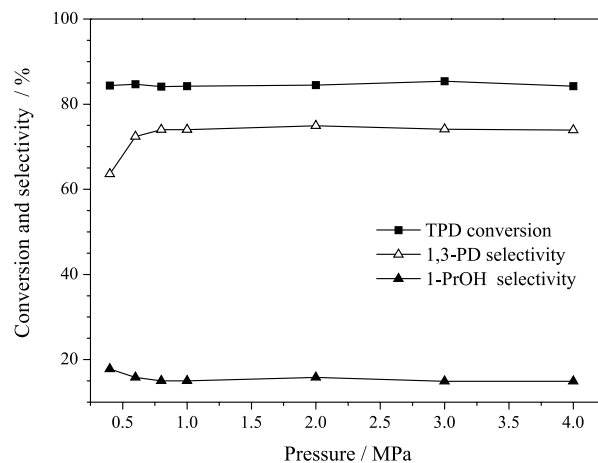


Figure 3. The effect of hydrogen pressure on TPD hydrogenolysis (2 wt.% of TPD in dioxane, 140 °C, 0.8 g Raney Ni, 0.4-4 MPa H₂, 4 h).

81.0%, and the selectivity of 1-PrOH slightly increased from 14.4 to 16.2%. Opposite observations were reported in the literature,²⁸⁻³¹ it was observed that the low selectivity of 1,3-PD formation in glycerol hydrogenolysis could be contributed to the high reactivity of 1,3-PD in water medium catalyzed by Ru/C + Amberlyst, and most 1,3-PD (77.7%) was further hydrogenolysed into 1-PrOH and ethanol. In our experiment, after reaction for 8 h in dioxane, the yield of 1,3-PD was up to 73.8% without obvious degradation.

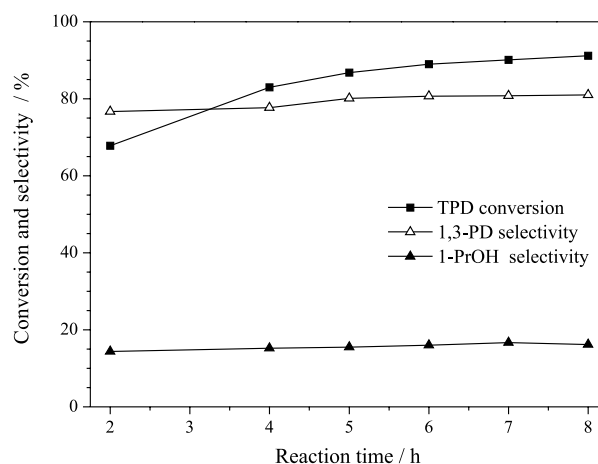


Figure 4. The effect of reaction time on TPD hydrogenolysis (2 wt.% of TPD in dioxane, 140 °C, 0.8 g Raney Ni, 1 MPa H₂).

Effect of TPD concentration

The study was also performed in different TPD concentrations, and the results are presented in Figure 5. The conversion of TPD as well as the selectivity of 1,3-PD and 1-PrOH were kept constant within the TPD concentration range of 2-6 wt.%. As TPD concentration further raised from 6 to 20 wt.%, the conversion of TPD increased from 91.2 to 95.0%, while the selectivity of

1,3-PD decreased from 81.0 to 64.3%, and the selectivity of 1-PrOH declined from 16.2 to 9.3%. As shown in Scheme 4, the decline in the selectivity of 1,3-PD and 1-PrOH was contributed to the TPD decomposition reaction under high concentration of TsOH, and followed by the subsequent hydrogenolysis to produce 1,2-PD and ethanol.

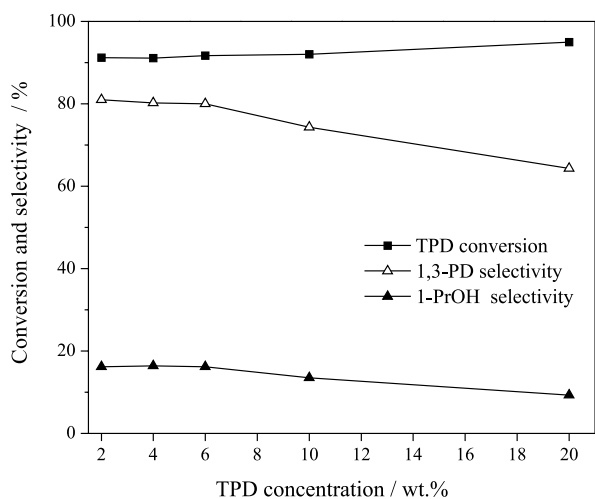


Figure 5. The effect of TPD concentration on TPD hydrogenolysis (140 °C, 40 wt.% Raney Ni of TPD, 1 MPa H₂, 8 h).

Conclusions

Selective formation of 1,3-PD via hydrogenolysis of TPD was achieved at low H₂ pressure using Raney Ni as catalyst. Under the conditions of 140 °C, 1 MPa H₂ and 8 h, 91.2% TPD conversion with 81.0% selectivity for 1,3-PD and 16.7% selectivity for 1-PrOH was obtained. The yield of 1,3-PD was mainly dependent on the reaction temperature, Raney Ni weight and TPD concentration. The proposed mechanism of TPD hydrogenolysis was validated. It was proved that, with the exception of *n*-PrOH formation, the TPD decomposition was another important side reaction under high concentration of TsOH. Further studies aimed at the elimination of TsOH by adding acid binding agent are currently underway.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgments

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