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Hydrogenation of 2-butyne-1,4-diol in supercritical carbon dioxide promoted by stainless steel reactor wall

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Abstract

Hydrogenation of 2-butyne-1,4-diol to 1,4-butanediol promoted by stainless steel reactor wall has been investigated in supercritical carbon dioxide ($scCO_2$) as well as in conventional organic solvents in the absence of catalysts at 50 °C. $scCO_2$ was found to be an effective medium at pressures higher than supercritical region (7.3 MPa). The influence of phase behavior, pressure and reaction time has been discussed. The first step hydrogenation of butynediol (C≡C) to butenediol (C=C) is slower but the second-step hydrogenation of butenediol (C=C) to butanediol (C–C) is faster in $scCO_2$ compared with the case of ethanol.
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1. Introduction

Butane-1,4-diol (butanediol) is a useful intermediate in the manufacture of fine chemicals, such as polybutylene and polyurethane polymers, tetrahydrofuran and so on [1,2]. Practical use of butanediol may be greatly increased if it could be produced more cheaply. Traditional methods are based on catalytic hydrogenation of 2-butyne-1,4-diol (butynediol) with transition metal catalysts in aqueous solution or organic solvents [1–5]. Earlier processes for butynediol hydrogenation to butanediol used Raney type nickel catalysts at 60–100 °C [3] or Ni-Cu-Mn supported on γ-alumina at 100–160 °C [4]. The use of noble metal supported catalysts such as Ru-Pd/C, $Pt/CaCO_3$, Pd/C and Pd/Al_2O_3 were also reported. High activity and selectivity to butanediol were found with Ru-Pd/C (Ru:Pd = 4:1) at 70–180 °C [1] as well as Pd/C and Pd/Al_2O_3 at 60–80 °C [5]. $Pt/CaCO_3$ was reported to be an efficient catalyst for producing butanediol with 100% selectivity in a fixed bed reactor at 40 °C [2]. Due to the presence of catalysts, promoters and organic solvents, additional separation step is necessary and the catalysts would suffer from fast deactivation at high temperatures.

Increasing interest in global environmental problems requires the reduced utilization of organic solvents and their replacement with environmental friendly alternative media. Much effort has been paid to avoid organic solvents in chemical reactions and supercritical fluids as a replacement for organic solvents have been used for various organic/inorganic, homogeneous/heterogeneous chemical reactions [6–9]. Their physicochemical properties may be manipulated by relatively small changes in operating pressure and temperature. The advantages of supercritical fluids as solvents have led to their increased use in chemical reactions because it is possible to tune solubilities, mass transfer, solvent strength, and reaction kinetics of reacting species present in them. Recently supercritical carbon dioxide ($scCO_2$) is playing an important role in the development of green chemical industrial processes for its environmentally benign nature, nontoxicity, abundance, low cost and wide tuning ability of solvent properties. $scCO_2$ has widely been used as a green reaction medium in chemical reactions such as Diels–Alder reaction [10,11], Heck coupling [12,13], polymerization [14,15], hydroformylation [16–18],

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oxidation [19], and hydrogenation reactions [20–25]. As a reaction medium $scCO_2$ is most attractive in hydrogenation due to the complete miscibility between hydrogen and $scCO_2$, because the reactions in conventional solvents depend on hydrogen concentration and are sometimes limited by the rate of diffusion of hydrogen from gas to the liquid phase. Previously, we have reported that the hydrogenation of unsaturated aldehydes could be performed successfully in $scCO_2$ with a significant improvement in activity and product selectivity [21–25]. We also found that the hydrogenation of butynediol in $scCO_2$ medium can be promoted by a steel-stainless reactor (SUS 316) wall without any catalyst [26]. In the present work, we have discussed the influence of several parameters such as pressure, solvent, reaction time, and phase behavior and the reaction mechanism of butynediol hydrogenation in stainless steel reactor without adding any catalysts. The present hydrogenation is an environmentally benign green process as it is free of organic solvents, catalysts and additives.

2. Experimental

2.1. Hydrogenation

The hydrogenation reactions were carried out in a 50 mL SUS 316 stainless steel autoclave. Five millimole butynediol (0.1 mmol/1 mL reactor) was charged into the reactor and the reactor was flushed with 2.0 MPa CO_2 three times. The reactor was then heated up to the desired temperature of 50 °C and H_2 and compressed liquid CO_2 were introduced to the desired pressure with a high-pressure liquid pump. The reaction runs were conducted while stirring with a magnetic stirrer. The composition of reaction mixture was analyzed by a gas chromatograph using a flame ionization detector.

2.2. Phase behavior

The examination of phase behavior is important to study whether the reaction in $scCO_2$ is taking place homogeneously in a single phase or heterogeneously in two or more phases. A 10 mL high-pressure sapphire-windowed view cell was used to observe the phases present at different pressures of CO_2. The phase behavior observation was also used to estimate the solubility of substrate in compressed CO_2 [21]. A certain amount of butynediol or butenediol was added to the view cell followed by introduction of CO_2. Then, stirring of the mixture was started and the state of the reaction mixture was examined by naked eyes from the windows after 5 min.

3. Results and discussion

The hydrogenation of butynediol in the conventional organic solvents produced several intermediates and by-products [26]. Under the present conditions, butanediol and butenediol were main products in most cases, with a minor product of *n*-butanol. Our concerns are total conversion and selectivity to these two main products in the following sections.

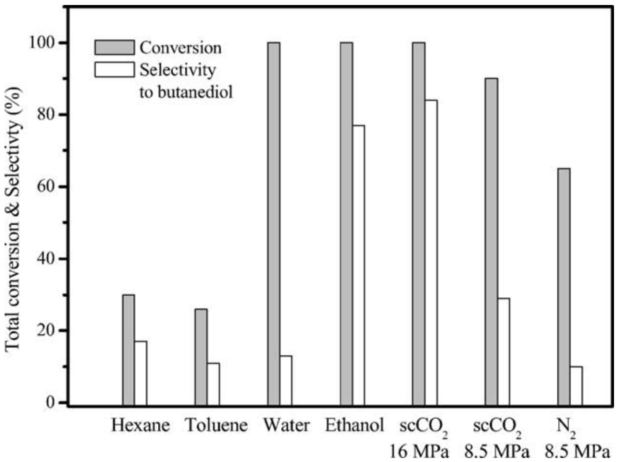

Fig. 1. Influence of solvents on the total conversion and selectivity to butanediol. Reaction conditions: butynediol 5 mmol (0.1 mmol/1 mL of reactor; 0.5 mmol/1 mL of organic solvents or water); H_2 4.0 MPa; organic solvent or water 10 mL; temperature 50 °C; reaction time 180 min.

3.1. Influence of solvents

The conversion of butynediol in different solvents has been compared and the results obtained are shown in Fig. 1. Polar solvents like ethanol and water are more effective compared with hexane and toluene. An apolar solvent of CO_2 was found to be an effective medium at pressures higher than supercritical region (7.3 MPa), which is effective similar to ethanol and water under the reaction conditions used. The conversion decreased when N_2 (8.5 MPa) was used instead of CO_2, indicating that the conversion depends on not only the total pressure but also the nature of reaction medium. In the organic solvents, higher selectivity to butanediol was observed in ethanol; note, however, the selectivity to butanediol is higher in $scCO_2$ than in ethanol at 100% conversion.

The higher reaction conversion obtained in the apolar solvent of $scCO_2$ compared with nonpolar solvents such as toluene and hexane may be due to the difference in hydrogen concentration in the different reaction media. The hydrogenation in conventional solvents depends on hydrogen concentration dissolved and are sometimes limited by the rate of diffusion of hydrogen from gas to the liquid phase. When $scCO_2$ was used as reaction medium in the hydrogenation, the process of phase transfer between gas and liquid could be eliminated due to completely miscible ability of hydrogen with $scCO_2$. Table 1 shows the hydrogen solubility in different solvents near the reaction conditions used in the present reactions. The solubilities in organic solvents have been estimated with Henry's law with the data of literatures [27,28], and the concentrations in compressed CO_2 have been estimated from the density of CO_2 at partial pressures of 16

Table 1
Solubility of hydrogen in different solvents at 50 °C

Solvent	Solubility (mole fraction)
Hexane	–
Toluene	0.0025 [27]
Ethanol	0.0091 [28]
Water	0.0005 [28]
CO_2 16 MPa	0.09
CO_2 8.5 MPa	0.26

The solubility of H_2 in organic solvents was estimated by Henry's law H_2 4.0 MPa. That in $scCO_2$ was estimated as follows: moles of H_2 (4 MPa) charged first into the reactor was estimated by the equation of state for ideal gases. Moles of CO_2 subsequently introduced up to a total pressure of 20 MPa, for example, was estimated assuming the partial pressure of CO_2 was 16 MPa; a density of pure CO_2 at this pressure was used to estimate the moles of CO_2 in $H_2 + CO_2$ mixture.

and 8.5 MPa and at 50 °C [29]. The concentration of H_2 in CO_2 is about 10–100 times higher than these in organic solvents, which could contribute to the higher total conversion in $scCO_2$ compared with those in organic solvents.

3.2. Phase behavior and solubility

Phase behavior plays an important role in the reactions in $scCO_2$. To confirm whether the reaction in $scCO_2$ is taking place homogeneously in a single phase or heterogeneously in two or more phases, a 10 mL stainless steel sapphire-windowed was used to observe the phase behavior and to estimate solubility. Fig. 2 shows the phase behavior in CO_2 in the absence of H_2 for estimating of the solubility of butynediol and butenediol at 50 °C. The solid marks indicate the presence of a single phase. Namely, all the substrate was completely dissolved in $scCO_2$ and a homogeneous phase was formed under these conditions. The open marks indicate the presence of two phases. Although, we do not know the solubility exactly under the present conditions, we can say that the solubility of both butynediol and butenediol increases with the increase in CO_2 pressure. The solubility of butynediol is lower than 1.6×10^{-3} mmol/mL at 16.0 MPa, while, the solubility of butenediol is about 2.7×10^{-3} mmol/mL at 16.0 MPa; the solubility of butenediol is higher than that of butynediol in $scCO_2$.

3.3. Pressure effects

Fig. 3 shows changes of the total conversion and selectivity to butanediol with CO_2 pressures. Both the total conversion and selectivity increase with increasing CO_2 pressure. Under the present conditions the reaction can occur in two phases since we used a larger amount of reactant (0.1 mmol/mL) than the solubility of butynediol in 16 MPa CO_2 lower than 1.6×10^{-3} mmol/mL as estimated from Fig. 2(a). At low CO_2 pressures, the substrate should exist mostly in the liquid phase. With increasing CO_2 pressure the solubility of the substrate can be increased as shown in

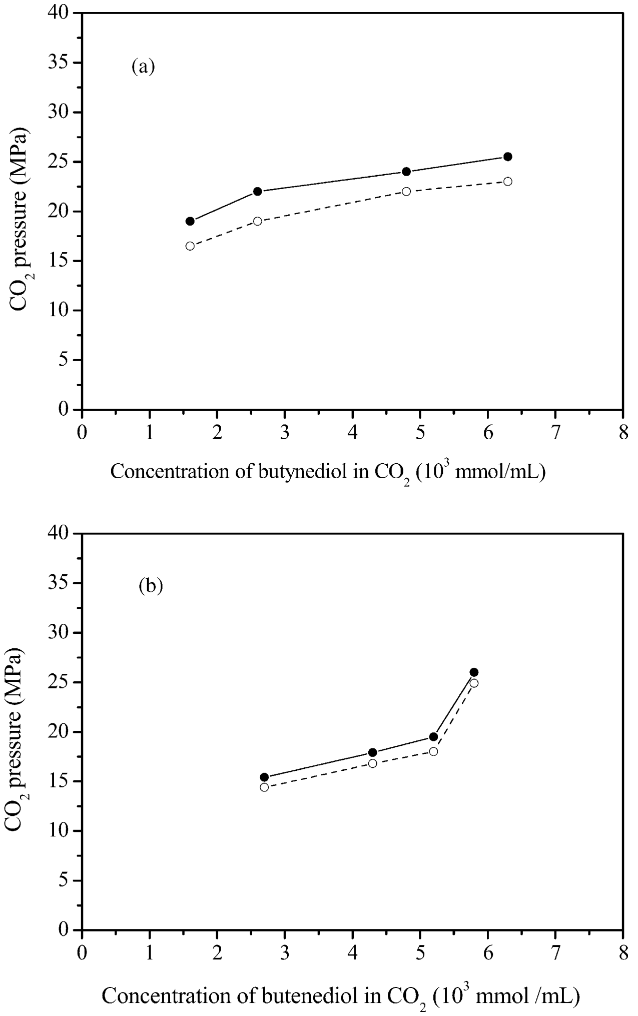

Fig. 2. The phase behavior in CO_2 for the estimation of solubility of butynediol (a) and butenediol (b) at 50 °C. The solid and open marks indicate the presence of a single phase (gas) and two phases (gas and liquid), respectively.

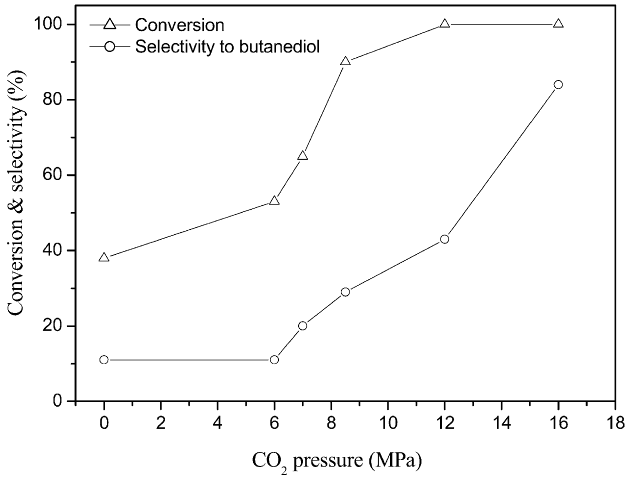

Fig. 3. Influence of CO_2 pressure on the total conversion and selectivity. Reaction conditions: butynediol 5 mmol (0.1 mmol/1 mL of reactor); H_2 4.0 MPa; temperature 50 °C; reaction time 180 min.

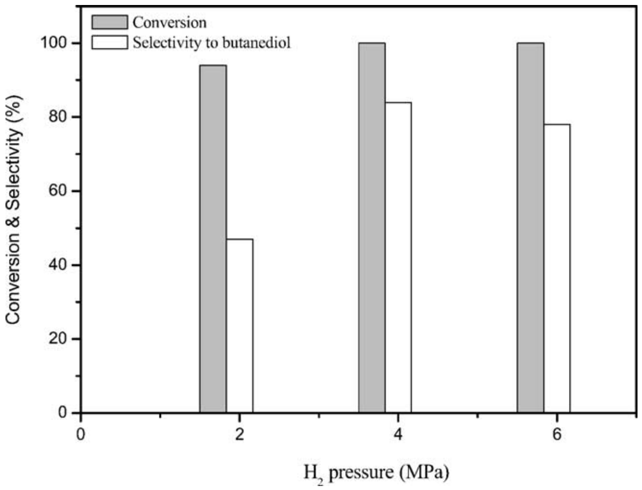

Fig. 4. Effects of H_2 pressure on the conversion and selectivity. Reaction conditions: butynediol 5 mmol (0.1 mmol/1 mL of reactor); CO_2 pressure 16 MPa; temperature 50 °C; time 120 min.

Fig. 2(a) and so the substrate should also exist in the CO_2 gas phase at elevated pressures. As reported previously, the present hydrogenation is catalyzed by the reactor wall and so the contact between the wall and the reaction mixture is of significance for determining the overall rate of reaction. The contact of the reactor wall with the liquid phase at low CO_2 pressures is worse than that with the CO_2 gas phase at elevated pressures, resulting in the larger conversion with increasing CO_2 pressure as observed.

Fig. 4 shows the influence of H_2 pressure on the total conversion and selectivity when the reaction was carried out under such conditions: CO_2, 16 MPa; butynediol, 5 mmol; temperature, 50 °C; time, 120 min. The total conversion increased with H_2 pressure increasing and 100% conversion was obtained at a H_2 pressure of 4.0 MPa or above; while, selectivity to butanediol has a maximal value at 4.0 MPa. These results are similar to those obtained in solvent free conditions. The total conversion is enhanced by using $scCO_2$ as reaction medium, the conversion obtained in 16 MPa CO_2 being 10 times higher than that in solvent free conditions at 2.0 MPa H_2.

3.4. Hydrogenation in $scCO_2$ and ethanol

The total conversion and selectivity to butanediol increased for longer reaction times in both $scCO_2$ and ethanol as shown in Fig. 5. The initial conversion in ethanol was higher than that in $scCO_2$; however, the selectivity to butanediol in $scCO_2$ increased faster with reaction time than that in ethanol, which means that in $scCO_2$ the first step hydrogenation of C≡C to C=C is slower but the second-step hydrogenation of C=C to C–C is faster compared with the case of ethanol. This will be discussed in detail in the following hydrogenation of butenediol in $scCO_2$ as well as in ethanol.

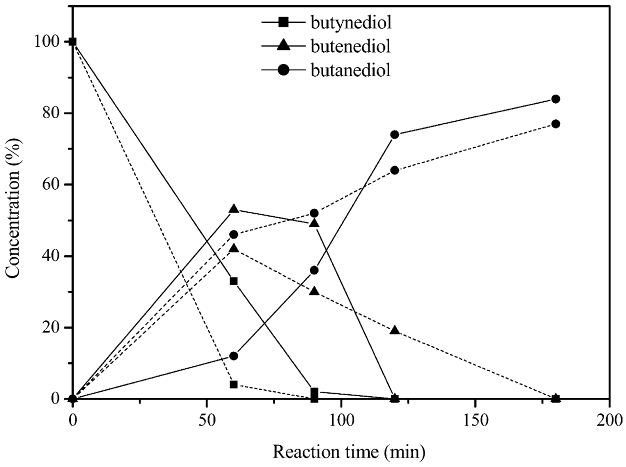

Fig. 5. Changes of the concentration of butynediol, butenediol and butanediol with reaction time in $scCO_2$ as well as in ethanol, the solid lines show the results in $scCO_2$, dash lines show the results in ethanol. Reaction conditions: butynediol 5 mmol (0.1 mmol/1 mL of reactor, 0.5 mmol/1 mL of ethanol); CO_2 16 MPa; H_2 4.0 MPa; temperature 50 °C.

3.5. Hydrogenation of butenediol in $scCO_2$ and ethanol

A lower initial concentration of butenediol of 2.0×10^{-3} mmol/mL was used in the butenediol hydrogenation, which is lower than the solubility at 16.0 MPa. The butenediol hydrogenation is a single phase in $scCO_2$ and two phases in ethanol. Fig. 6 indicates that the total conversion in 16 MPa CO_2 is about four times higher than that obtained in ethanol and a higher selectivity to butanediol was also obtained in $scCO_2$. These improved high total conversion and selectivity could be explained by the following factors. (1) Effective surface area of reactor wall is larger in $scCO_2$ than that in ethanol. In $scCO_2$, all the reactants of butenediol and hydrogen are dissolved in CO_2. Only this

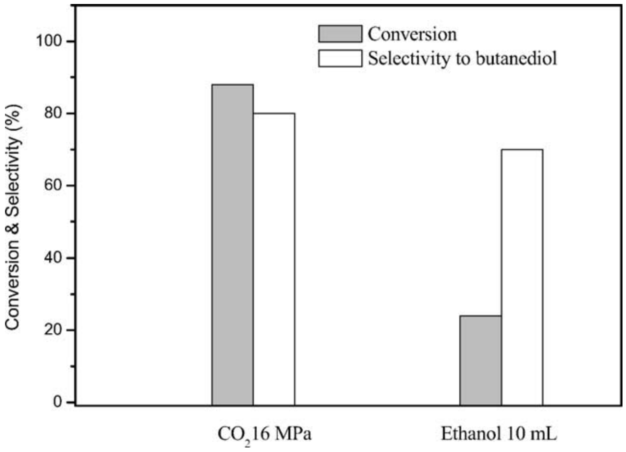

Fig. 6. Hydrogenation of butenediol in $scCO_2$ and ethanol. Reaction conditions: butenediol 0.10 mmol (2.0×10^{-3} mmol/mL in $scCO_2$, 0.01 mmol/mL in ethanol); H_2 4.0 MPa; temperature 50 °C; time 10 min. A single phase (CO_2 phase containing a mixture of dissolved butenediol and H_2) existed in $scCO_2$, while two phases (liquid (butenediol and partial H_2 dissolved in ethanol)–gas (H_2)) in ethanol.

gas phase existed in the reactor and so the reaction was promoted by all the inner surface of the reactor wall. In ethanol, butenediol was dissolved in 10 mL ethanol, so that the effective surface area of the reactor wall is less than one-forth of that in $scCO_2$ (the total inner surface area of the reactor). (2) Higher hydrogen concentration in $scCO_2$ due to the complete miscible ability of H_2 with $scCO_2$. (3) The mass transfer (hydrogen transfer from gas to liquid phase) resistance is eliminated in $scCO_2$.

4. Conclusions

Butynediol hydrogenation promoted by stainless steel reactor wall has been investigated in $scCO_2$ as well as in organic solvents in the absence of any catalysts. The conversion depends on not only the total pressure but also the nature of reaction medium. Among the organic solvents examined, higher selectivity to butanediol appeared in ethanol; however, the selectivity to butanediol is much higher in $scCO_2$ than in ethanol at 100% conversion. Higher concentration of hydrogen dissolved in the $scCO_2$ solvent has been considered to be a reason for improving the reaction rate. The total conversion increases with increasing CO_2 and H_2 pressures. However, selectivity to butanediol showed a maximal value at H_2 4.0 MPa. Butenediol hydrogenation in a single $scCO_2$ phase is about four times faster than that in ethanol. This may be due to effective contact between the reactor wall and the reaction mixture, larger hydrogen concentration and absence of mass transfer resistance in $scCO_2$.

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