

Effect of CO₂ on conversion of inulin to 5-hydroxymethylfurfural and propylene oxide to 1,2-propanediol in water

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The CO₂–water system has the potential to serve as a substitute for mineral acids for some reactions in acidic media. In this work, two reactions under hydrothermal conditions with and without CO₂ were studied – the conversion of inulin to 5-hydroxymethylfurfural (5-HMF), and the hydrolysis of propylene oxide to 1,2-propanediol (1,2-PDO). The effects of CO₂ pressure, reaction temperature and reactant concentration on the yield of 5-HMF and 1,2-PDO were examined. It was demonstrated that CO₂ could increase the yields of 5-HMF and 1,2-PDO considerably under optimized conditions. The methods to prepare 5-HMF and 1,2-PDO are greener, in that conventional acids are not required and the solution is neutralized automatically after depressurization.

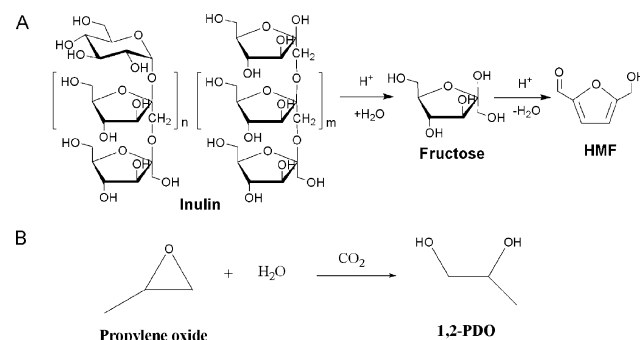
Introduction

Green chemistry has attracted more and more attention in recent years.¹ Efficient utilization of greener solvents is an important aspect of green chemistry because most chemical processes use solvents, and many of them are toxic and volatile. CO₂ and H₂O are very attractive because they have some unique features such as being non-toxic, non-flammable, abundant, cheap and easy to obtain. In the last two decades, many studies have been focused on chemical reactions in CO₂² and water.³ It is well known that CO₂ can react with water, leading to the formation and dissociation of carbonic acid.⁴ The CO₂–water system can replace conventional hazardous acids such as HCl and H₂SO₄ for the catalysis of some chemical reactions, and the solution can be easily neutralized by depressurization without requiring salt disposal.⁵ Much research has been reported on acid-catalyzed organic reactions in high-temperature water in the presence of CO₂, such as: the dehydration of cyclohexanol to form cyclohexene, and the alkylation of *p*-cresol with *tert*-butyl alcohol to produce 2-*tert*-butyl-4-methylphenol;⁶ the hydrolysis of ethers, methylbenzoate and diphenylcarbonate;⁷ the dehydration of 1,4-butanediol to form tetrahydrofuran;⁸ and the cyclization of citronellal to *p*-menthane-3,8-diols.⁹ The CO₂–water system has also been used in the selective reduction of nitroarenes to *N*-arylhydroxylamines,¹⁰ the reduction of aldehydes to alcohols,¹¹ the synthesis of vicinal diamines,¹² polysaccharide hydrolysis reactions,¹³ diazotization reactions,¹⁴ and some other reactions.¹⁵ The results indicate that the CO₂–water system can accelerate many reactions.

The development of sustainable sources for the production of chemicals is another interesting topic in green chemistry, and biomass is promising renewable resource.¹⁶ As a key platform molecule from biomass, 5-hydroxymethylfurfural

(5-HMF) is considered to be a versatile and valuable intermediate for plastics, pharmaceuticals, fine chemicals, and liquid fuels.¹⁷ Many value-added compounds, such as 2,5-furandicarboxylic acid, 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl)tetrahydrofuran, dimethylfuran and liquid alkanes, can be derived from 5-HMF by oxidation, hydrogenation, hydrogenolysis or aldol condensation.^{17a,17b,18} It is therefore not surprising that preparation of 5-HMF has been studied extensively in recent years using different renewable feedstocks and reaction media. For example, 5-HMF has been prepared by dehydration of fructose in polar organic solvents,¹⁹ high-temperature water²⁰ and ionic liquids,²¹ from glucose in ionic liquids catalyzed by salts,^{21a,22} from inulin in various solvents,²³ and from cellulose²⁴ in various media.

Inulin is a non-digestible oligosaccharide consisting of glucose–(fructose)_{*n*} or (fructose)_{*m*} which is available in large quantity.²⁵ It exists in many plants, such as in the roots of chicory. Preparation of 5-HMF from inulin involves the hydrolysis of inulin to form fructose, which further dehydrates to form 5-HMF (Scheme 1); both reactions can be catalyzed by acids.^{23b}



Scheme 1 The pathways for acid-catalyzed production of 5-HMF from inulin (A) and hydrolysis of propylene oxide to form 1,2-PDO (B).

1,2-Propanediol (1,2-PDO) is a useful chemical that can be used directly as an intermediate or additive to produce antifreezing agents, pharmaceuticals, lubricants, foods, cosmetics,

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and polyester resins.²⁶ It can be produced from the catalytic hydrolysis of propylene oxide in water with acids or bases as the catalysts, a reaction that has been studied widely.²⁷

Greener methods to prepare 5-HMF from inulin and 1,2-propanediol from propylene oxide are highly desirable. In this work, we have studied the effect of CO₂ on conversion of inulin to produce 5-HMF and the hydrolysis of propylene oxide to form 1,2-PDO in a CO₂-water system (Scheme 1). We demonstrate that CO₂ is effective at enhancing the yields of the reactions under optimized conditions.

Experimental

Materials

Inulin (99%) from dahlia tubers was purchased from Fluka, and had an average molecular weight of 5000 g mol⁻¹. 5-HMF (99%) was purchased from Aldrich. CO₂ was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Propylene oxide and other materials (A. R. grade) were purchased from Beijing Chemical Reagent Company. All chemicals were used without further purification. Doubly distilled water was used in all the experiments.

Conversion of inulin to 5-HMF

We conducted experiments to convert inulin to 5-HMF in water with and without CO₂. In a typical experiment, inulin and water were added to a 6.0 mL stainless steel batch reactor, and the oxygen in the reactor replaced by nitrogen. The reactor was placed into a constant-temperature air bath of the desired temperature. The reactor was then charged with CO₂ (if being used) until the desired pressure was reached, and the stirrer was started. After a certain time, the reactor was placed into an ice-water bath to cool it quickly, and then CO₂ was released slowly, passing it through a trap containing water to absorb the trace amount of product released with the CO₂. After depressurization, the reaction mixture in the reactor and the liquid in the trap were transferred to a 10 mL vessel. The mixture was centrifuged to separate insoluble products and the solution was analyzed by HPLC. The analytical method was similar to that used previously.^{23b} The HPLC setup used a Shimadzu LC-20AT pump, a Hypersil ODS2 5 μm column, and a Soma UV-Vis LC-830 detector at 282 nm. Methanol-water (50:50 v/v) solution was used as the mobile phase with a flow rate of 0.8 mL min⁻¹. A Shimadzu RID-10A detector and a Hypersil NH2 5 mm column were also used with water as the mobile phase at 0.5 mL min⁻¹. The amount of 5-HMF was calculated by using an external standard (5-HMF). Each sample was analyzed at least three times, and the repeatability was better than ±1%.

Hydrolysis of propylene oxide

The reactor used was the same as that described above. In the experiment, propylene oxide and water were added to the reactor. The air in the reactor was replaced by nitrogen, and the reactor was then put into a constant temperature air bath of desired temperature. CO₂ was added until a suitable pressure was reached, and the reaction mixture was stirred for the desired time. The reactor was placed into an ice-water bath and CO₂ was released slowly, passing it through a cold-trap containing *N,N*-

dimethylacetamide to absorb the reactant and product released with the CO₂. The *N,N*-dimethylacetamide in the cold-trap and an internal standard (1-butanol) were added to the reactor. The reaction mixture was analyzed by GC (Agilent 4890D) equipped with a flame-ionized detector. The purity and structure of the product at some typical experimental conditions were also checked by ¹H NMR and GC-MS (SHIMADZU-QP2010).

Results and discussion

The effect of CO₂ on the conversion of inulin to 5-HMF and propylene oxide to 1,2-PDO was studied and the results are discussed below.

Influence of CO₂ pressure and reaction time on 5-HMF yield

Fig. 1 shows the effect of reaction time on the yield of 5-HMF at 180 °C under different CO₂ pressures. It can be observed that addition of CO₂ to the reaction system enhances the yield considerably. For example, with a reaction time of 1.5 h, the yield of 5-HMF was 53% at a CO₂ pressure of 6 MPa, while the yield was 38% in the absence of CO₂. The main reason is that CO₂ in aqueous solution can generate carbonic acid *in situ*, which acts as the catalyst for the reaction.

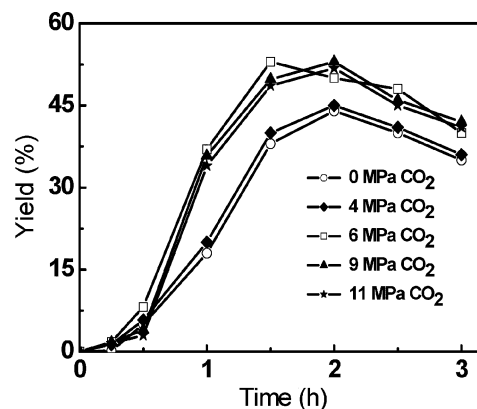


Fig. 1 Yields of 5-HMF at 180 °C under different CO₂ pressures. Reaction conditions: inulin 0.1 g, water 2 mL.

Fig. 1 also demonstrates that at all the pressures, with increasing reaction time the yield of 5-HMF first increased and then decreased. In other words, each yield-time curve has a maximum. The main reason is that 5-HMF can be converted to polymeric by-products or further hydrolysed to levulinic acid and formic acid.^{23a} With a sufficiently long reaction time, most of the inulin is converted and the by-products became dominant.

In order to show the effect of CO₂ pressure on the yield, Fig. 2 illustrates the dependence of the maximum yield of 5-HMF on CO₂ pressure at a reaction time of 1.5 h, which was obtained from the data in Fig. 1. The yield of 5-HMF increased with CO₂ pressure below 6.0 MPa, and then decreased significantly as the pressure exceeded 6 MPa. It is known that the pH value of the CO₂-water system decreases with increasing CO₂ pressure,²⁸ which influences the reaction. In order to obtain some information about how the pH affects the yield, we investigated the yield of 5-HMF in the pH range of 2 to 6 using HCl as the catalyst, and present the results in Fig. 3. It can be seen that there is a maximum in the yield-pH curve at a pH of about

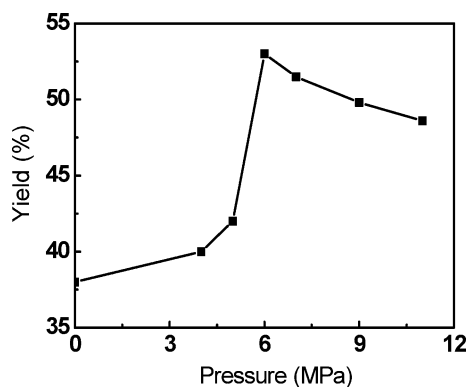


Fig. 2 The maximum yields of 5-HMF at different CO₂ pressures. Reaction conditions: inulin 0.1 g, water 2 mL, 180 °C, 1.5 h.

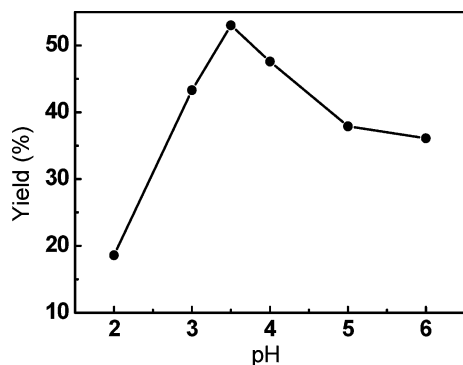


Fig. 3 5-HMF yield of the reaction catalyzed by HCl. Reaction conditions: inulin 0.1 g, HCl solution 2 mL, 180 °C, 1.5 h.

3.5. The maximum yield was about 53%, which was the same as the maximum yield of 5-HMF in the CO₂-water system. This suggests that the change of pH originates from addition of CO₂, which was the main cause of the maxima in Fig. 1. It is known that in the acid-catalyzed reaction, inulin is broken down to the fructofuranosyl cation in the first step, and this cation reacts with water to form fructose,²⁹ which is further dehydrated to produce 5-HMF. This is a complex reaction system and many by-products can be formed. For example, levulinic acid and formic acid can be formed from 5-HMF under acidic conditions.^{23a,30,31} Stronger acidity can enhance the reactions to produce 5-HMF from inulin and also accelerate the production of by-products. These competing factors result in the optimized CO₂ pressure.

Effect of temperature on the yield of 5-HMF

The transformation of inulin to 5-HMF was also conducted in water at 160 °C and 200 °C with and without CO₂. Fig. 4 shows the yields of 5-HMF at 160 °C in neat water and in water at different CO₂ pressures. CO₂ also affected the yield of 5-HMF at this temperature. Similarly, a maximum can also be observed in each yield-time curve at a reaction time of about 4 h. This further demonstrates that addition of CO₂ to high-temperature water can promote the reaction. CO₂ with a pressure of 6 MPa was also most effective at producing 5-HMF at this temperature.

The yield of 5-HMF as a function of reaction time at 200 °C with and without the addition of CO₂ is shown in Fig. 5. In pure water, 5-HMF yield increased from 0 to 48% in 1 h. Addition of CO₂ could also increase the yield of the product, and the

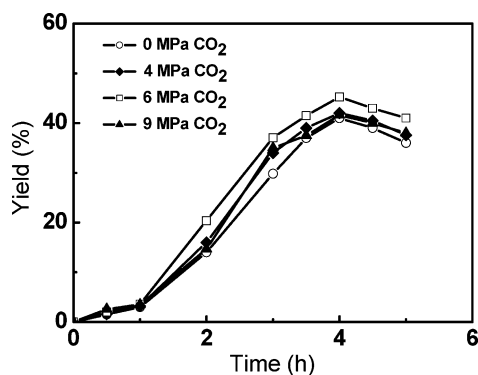


Fig. 4 Yields of 5-HMF at 160 °C at different CO₂ pressures. Reaction conditions: inulin 0.1 g, water 2 mL.

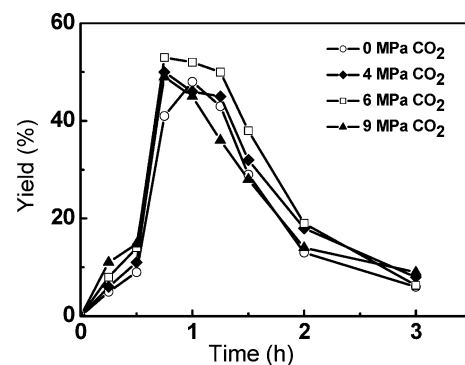


Fig. 5 Yields of 5-HMF at 200 °C at different CO₂ pressures. Reaction conditions: inulin 0.1 g, water 2 mL.

optimized pressure was about 6 MPa. 5-HMF yield increased to 53% in 0.75 h at 6 MPa.

It is clear from Fig. 1, 4 and 5 that reaction temperature influences the maximum yield of 5-HMF at a given CO₂ pressure. For example, as temperature changed from 160 °C to 200 °C the maximum yield increased from 41% to 48% in the absence of CO₂. At 6 MPa the maximum yield of 5-HMF at 180 °C and 200 °C were nearly the same (53%), which was considerably higher than that at 160 °C. A yield of 53% is higher than that in aqueous solution using iron vanadyl phosphate as the catalyst (39.9%),^{23a} but is lower than that in ionic liquid (56%)^{23b} and in water catalyzed by γ -titanium phosphate (65%).^{23c} However, the CO₂-water system used in this work is advantageous in that both water and CO₂ are cheaper, greener, and easily recycled.

Temperature has a pronounced effect on the reaction time needed to reach the maximum yield of 5-HMF. At a CO₂ pressure of 6 MPa, the times to reach the maximum yield at 160 °C, 180 °C and 200 °C were 4 h, 1.5 h and 0.75 h, respectively. As expected, the reaction rate also increased with increasing temperature in the absence of CO₂. The reason is that increasing temperature favors acceleration of the reaction. The other reason is that increasing temperature enhances the acidity of water in the temperature range studied in this work, but the pH is larger than 5,³² and the yield increased with the acidity of the solution in the weak acidic region, as shown in Fig. 3.

Effect of initial inulin concentration on 5-HMF yield

The conversion of inulin to 5-HMF at different initial inulin concentrations was studied in neat water and at a CO₂ pressure of 6 MPa. The results are given in Fig. 6. In the concentration range studied, the yield of the reaction with CO₂ was always considerably higher than that without CO₂. In both cases, the yield of 5-HMF first increased with increasing inulin concentration, and then decreased with further increasing of the feedstock concentration. The reason for this is discussed below.

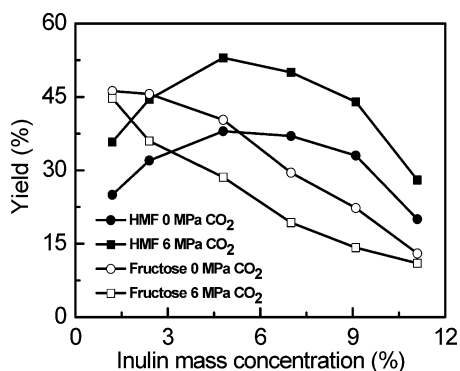


Fig. 6 Dependence of yields of 5-HMF and fructose on initial inulin concentration. *Reaction conditions:* water 2 mL, 180 °C, 1.5 h.

Our experiments showed that conversion of inulin was 100% under all conditions. As discussed above, in the reaction process, inulin is first converted into fructose by hydrolysis, which is then dehydrated to form 5-HMF. Fructose can be converted to humins and polymers, and 5-HMF can be further converted to by-products such as levulinic acid.^{17c,23a} Fig. 6 also gives the yield of fructose under different conditions, and it can be seen that the yield of fructose decreases with increasing inulin concentration. It can be deduced from Fig. 6 that the reaction rate for the conversion of fructose to 5-HMF increases with increasing inulin concentration, which favors enhancement of the yield of 5-HMF. The same results also suggest that the reaction rate for the conversion of fructose into the by-products increases as the concentration of inulin is increased, which disfavors high yields of 5-HMF. Competition between these two opposing factors results in the maximum in each curve.

The figure also demonstrates that in the inulin concentration range studied, the yield of fructose in the presence of CO₂ was lower than that in the absence of CO₂, and the yield of 5-HMF was higher when CO₂ was added. This indicates that addition of CO₂ can enhance the conversion of fructose into 5-HMF, giving higher yields of 5-HMF as more CO₂ was added.

Effect of water–propylene oxide molar ratio on 1,2-PDO yield

The effect of the molar ratio of water to propylene oxide on the hydrolysis of propylene oxide to prepare 1,2-PDO was studied at 70 °C in the molar ratio range of 1:1 to 8:1. Fig. 7 demonstrates dependence of the yield of 1,2-PDO on the molar ratio at CO₂ pressures of 0 MPa, 2 MPa, 5 MPa, and 8 MPa with a reaction time of 6 h. The yield of 1,2-PDO increased with increasing water–propylene oxide molar ratio at all the pressures. One of the main reasons for this is that the concentration of propylene

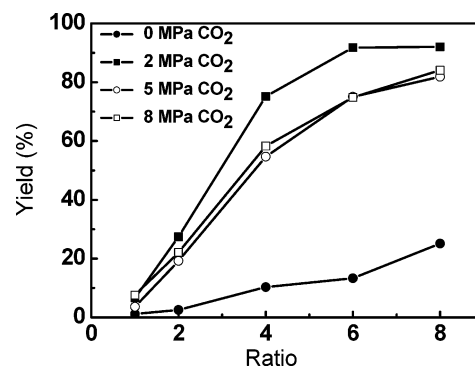


Fig. 7 Effect of molar ratio of water to propylene oxide on the yield of 1,2-PDO at different CO₂ pressures. *Reaction conditions:* propylene oxide 1.452 g (25 mmol), 70 °C, 6 h.

oxide was fixed in the experiment, while that of water, which was a reactant, increased with the molar ratio.

In the absence of CO₂ the yield of 1,2-PDO increased from 1.1% to 25.1% when the water–propylene oxide molar ratio changed from 1:1 to 8:1. Clearly, CO₂ enhanced the yield of the reaction significantly even the pressure was as low as 2 MPa. The strong effect of CO₂ on the yield resulted mainly from the change of pH of the solution.

At CO₂ pressure of 2 MPa, the yield of 1,2-PDO increased from 6.6% to 92% as the molar ratio changed from 1:1 to 6:1, but did not change with further increase of the molar ratio. The yield did not reach 100% because by-products dipropanediol and 1,2-propanediol were produced (as identified by GC-MS), formed from intermolecular dehydration of 1,2-PDO and the reaction of propylene oxide with 1,2-propanediol, respectively.³³

At 5 MPa and 8 MPa, the yield was lower than that at 2 MPa, an effect that may be attributed to two opposing effects of increasing the CO₂ pressure: although increasing CO₂ pressure should accelerate the reaction because of the stronger acidity of water, the larger amount of propylene oxide in the vapor phase is not favorable to the reaction.

Effect of CO₂ pressure on the hydrolysis of propylene oxide

The effect of CO₂ pressure on the hydrolysis of the propylene oxide to produce 1,2-PDO was studied at 70 °C with a reaction time of 4 h, and the results are presented in Fig. 8. The yield increased with increasing pressure in the low pressure region, stayed nearly unchanged between 4 and 8 MPa, and then decreased considerably with further increase of pressure. Changing the CO₂ pressure influences the reaction in two opposite ways. Firstly, the acidity of the aqueous phase becomes stronger with increasing CO₂ pressure, which is favorable to the reaction. Secondly, the reactant propylene oxide is distributed between the CO₂-rich phase and the aqueous phase. The amount of propylene oxide in the CO₂-rich phase should be larger at higher CO₂ pressure because the solvating power of CO₂ is greater at higher pressure. Dissolution of the reactant in the CO₂ phase is not favorable to the reaction because of the vapor–liquid interface mass transfer. Therefore, in the lower pressure region, the first factor is dominant and the yield increases with pressure. In the pressure range 4–8 MPa, the effects cancel out, and therefore the yield is nearly independent of CO₂ pressure. At higher pressures, the second factor dominates because the

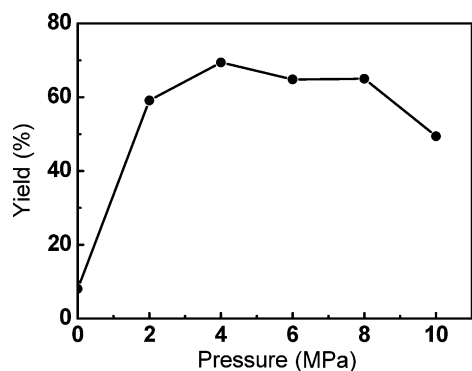


Fig. 8 Effect of CO₂ pressure on the yield of 1,2-PDO. Reaction conditions: propylene oxide 1.452 g (25 mmol), water 1.8 g (100 mmol), 70 °C, 4 h.

solvating power of CO₂ is more sensitive to pressure in the supercritical region.

Conclusion

The effect of CO₂ on the conversion of inulin to 5-HMF and the hydrolysis of propylene oxide to 1,2-PDO in water has been investigated at different reaction temperatures, CO₂ pressures, and reactant concentrations. CO₂ can enhance the yields of the products of the two reactions considerably at all the conditions studied. For the transformation of inulin to 5-HMF at 160 °C, 180 °C and 200 °C, the yield can be optimized by CO₂ pressure, and the maximum yield occurs at 6 MPa at all the temperatures. The main reason for this is that there is an optimum pH value for the reaction, and the pH of the reaction can be tuned by CO₂ pressure. For the hydrolysis of propylene oxide to prepare 1,2-PDO, CO₂ can enhance the yield of the reaction significantly even when the pressure is as low as 2 MPa. The strong effect of CO₂ on the yield results mainly from the change of pH of the solution. Under suitable condition, the yield of 1,2-PDO can reach 92%. The combination of CO₂ and water therefore has potential applications in greener transformation of inulin to 5-HMF and propylene oxide to 1,2-PDO.

Acknowledgements

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References

- (a) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren and P. T. Anastas, *Science*, 2002, **297**, 807; (b) M. Toda, A. Takagaki, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen and M. Hara, *Nature*, 2005, **438**, 178; (c) P. Tundo, A. Perosa, and F. Zecchini, *Methods and Reagents for Green Chemistry: An Introduction*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007.
- (a) P. G. Jessop, and W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, Weinheim, Germany 1999; (b) P. Licence, W. K. Gray, M. Sokolova and M. Poliakoff, *J. Am. Chem. Soc.*, 2005, **127**, 293.
- (a) T. Sawada, S. Nakayama, A. Kawai-Nakamura, K. Sue, H. Iwamura and T. Hiaki, *Green Chem.*, 2009, **11**, 1675; (b) C. I.

- Herrerias, X. Q. Yao, Z. P. Li and C. J. Li, *Chem. Rev.*, 2007, **107**, 2546.
- J. D. Holmes, K. J. Ziegler, M. Audriani, C. T. J. Lee, P. A. Bhargava, D. C. Steyler and K. P. Johnston, *J. Chem. Phys.*, 1999, **110**, 5703.
- R. R. Weikel, J. P. Hallett, C. L. Liotta and C. A. Eckert, *Top. Catal.*, 2006, **37**, 75.
- S. E. Hunter and P. E. Savage, *Ind. Eng. Chem. Res.*, 2003, **42**, 290.
- C. M. Comisar, S. E. Hunter, A. Walton and P. E. Savage, *Ind. Eng. Chem. Res.*, 2008, **47**, 577.
- S. E. Hunter, C. E. Ehrenberger and P. E. Savage, *J. Org. Chem.*, 2006, **71**, 6229.
- H. Y. Cheng, X. C. Meng, R. X. Liu, Y. F. Hao, Y. C. Yu, S. X. Caia and F. Y. Zhao, *Green Chem.*, 2009, **11**, 1227.
- S. J. Liu, Y. H. Wang, J. Y. Jiang and Z. L. Jina, *Green Chem.*, 2009, **11**, 1397.
- G. P. Li, H. F. Jiang and J. H. Li, *Green Chem.*, 2001, **3**, 250.
- H. F. Jiang and X. Z. Huang, *J. Supercrit. Fluids*, 2007, **43**, 291.
- T. Miyazawa and T. Funazukuri, *Biotechnol. Prog.*, 2005, **21**, 1782.
- P. Tundo, A. Loris and M. Selva, *Green Chem.*, 2007, **9**, 777.
- (a) C. M. Rayner, *Org. Process Res. Dev.*, 2007, **11**, 121; (b) P. A. Aleman, C. Boix and M. Poliakoff, *Green Chem.*, 1999, **1**, 65; (c) A. Yamaguchi, N. Hiyoshi, O. Sato, C. V. Rode and M. Shirai, *Chem. Lett.*, 2008, **37**, 926; (d) A. Yamaguchi, N. Hiyoshi, O. Sato, K. K. Bando and M. Shirai, *Green Chem.*, 2009, **11**, 48; (e) B. Ganchev and W. Leitner, *Green Chem.*, 2007, **9**, 26; (f) G. Gao, Y. Tao and J. Y. Jiang, *Green Chem.*, 2008, **10**, 439.
- (a) B. Kamm, *Angew. Chem., Int. Ed.*, 2007, **46**, 5056; (b) Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933; (c) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
- (a) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982; (b) J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164; (c) J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342.
- G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446.
- (a) K. Seri, Y. Inoue and H. Ishida, *Chem. Lett.*, 2000, 22; (b) X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, Jr., *Ind. Eng. Chem. Res.*, 2008, **47**, 9234; (c) Q. X. Bao, K. Qiao, D. Tomida and C. Yokoyama, *Catal. Commun.*, 2008, **9**, 1383; (d) A. S. Amarasekara, L. D. Williams and C. C. Ebode, *Carbohydr. Res.*, 2008, **343**, 3021.
- (a) F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2006, **45**, 2163; (b) X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2008, **10**, 799.
- (a) G. Yong, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2008, **47**, 9345; (b) X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2009, **11**, 1327; (c) S. Q. Hu, Z. F. Zhang, Y. X. Zhou, B. X. Han, H. L. Fan, W. J. Li, J. L. Song and Y. Xie, *Green Chem.*, 2008, **10**, 1280; (d) C. Moreau, A. Finiels and L. Vanoye, *J. Mol. Catal. A: Chem.*, 2006, **253**, 165.
- H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597.
- (a) C. Carlini, P. Patrono, A. M. R. Galletti and G. Sbrana, *Appl. Catal., A*, 2004, **275**, 111; (b) S. Q. Hu, Z. F. Zhang, Y. X. Zhou, J. L. Song, H. L. Fan and B. X. Han, *Green Chem.*, 2009, **11**, 873; (c) F. Benvenuti, C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, M. A. Massucci and P. Galli, *Appl. Catal., A*, 2000, **193**, 147.
- (a) Y. Su, H. M. Browne, X. Hangar, X. D. Zhou, J. E. Ammonite and Z. C. Zhang, *Appl. Catal., A*, 2009, **361**, 117; (b) J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979; (c) C. Z. Li, Z. H. Zhang and Z. K. Zhao, *Tetrahedron Lett.*, 2009, **50**, 5403.
- A. K. Gupta and I. S. Bhatia, *Phytochemistry*, 1982, **21**, 1249.
- D. C. Cameron, N. E. Altaras, M. L. Hoffman and A. J. Shaw, *Biotechnol. Prog.*, 1998, **14**, 116.
- A. Lundin, I. Panas and E. Ahlberg, *J. Phys. Chem. A*, 2007, **111**, 9087.
- C. Roosen, M. Ansoorge-Schumacher, T. Mang, W. Leitner and L. Greiner, *Green Chem.*, 2007, **9**, 455.
- T. L. Mega and R. L. V. Ethern, *J. Am. Chem. Soc.*, 1988, **110**, 6372.
- T. S. Hansen, J. M. Woodley and A. Riisager, *Carbohydr. Res.*, 2009, **344**, 2568.
- Y. Román-Leshkov and J. A. Dumesic, *Top. Catal.*, 2009, **52**, 297.
- J. P. Hallett, P. Pollet, C. L. Liotta and C. A. Eckert, *Acc. Chem. Res.*, 2008, **41**, 458.
- Z. X. Yu, L. Xu, Y. X. Wei, Y. L. Wang, Y. L. He, Q. H. Xia, X. Z. Zhang and Z. M. Liu, *Chem. Commun.*, 2009, 3934.