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Efficient one-pot production of 1,2-propanediol and ethylene glycol from microalgae (*Chlorococcum sp.*) in water

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The catalytic valorization of microalgae, a sustainable feedstock to alleviate dependence on fossil fuel and offset greenhouse gases emissions, is of great significance for production of biofuels and value-added chemicals from aquatic plants. Here, an interesting catalytic process is reported to convert microalgae (*Chlorococcum sp.*) into 1,2-propanediol (1,2-PDO) and ethylene glycol (EG) in water over nickel-based catalysts. The influences of reaction temperature, initial H_2 pressure and reaction time on the product distribution were systematically investigated by using a batch reactor. Under optimal reaction conditions (at 250 °C for 3 h with 6.0 MPa of H_2 pressure), microalgae were directly and efficiently converted over a Ni–MgO–ZnO catalyst and the total yield of polyols was up to 41.5%. The excellent catalytic activity was attributed to the smaller size and better dispersion of Ni particles on the MgO–ZnO supporter based on the characterization results as well as its tolerance to nitrogen-containing compounds. Besides, the reaction pathway was proposed based on the formation of reaction intermediates and the results of model compound conversion.

1. Introduction

With fossil fuel reserves declining and the environment deteriorating, catalytic valorization of renewable energy sources for the production of value-added chemicals or liquid biofuels from these biomass resources has attracted increasing attention. As one of the existing solid organic carbon resources biomass has several advantages, such as ease of storage and transportation, wide distribution and short growth duration.[1–4] Among them, catalytic conversion of biomass to polyols (such as 1,2-PDO and EG) is particularly noteworthy because of their versatile uses as important bulk chemicals directly or precursors in the synthesis of fuels and value-added compounds.[5–9]

Sugars, pure cellulose and pretreated terrestrial raw biomass can be used as feedstock for the production of EG and 1,2-PDO.[10–17] In 2008, Zhang *et al*. reported a one-pot conversion of pure cellulose to EG over Ni-promoted tungsten carbide catalyst.[10] Such process opened a novel route for green EG production, and the EG yield could be enhanced to 75% over these tungsten-based catalysts, while 38.5% yield (calculated based on saccharides in Jerusalem Artichole Tubers, JAT) of 1,2-PDO was achieved from JAT containing high percentage of saccharides in it over a similar catalyst.[12] However, in the process of complex raw biomass conversion for polyols production, pretreatment processes should be involved to reduce the formation of unexpected byproducts.[15,16] For example, starting from miscanthus, a base solvent should be first used to remove epidermal protectors and lignin fractions, which could preferentially poison the Ni–W_2C/AC catalyst due to the formation of organic acids and unsaturated compounds.[16] Similarly, corn stalk was pretreated with 1,4-butanediol, NaOH, H_2O_2 and ammonia first, and much higher yields of ethylene glycol and 1,2-propylene glycol could be achieved over the same catalyst compared with that from untreated raw corn stalk. In view of higher cost of tungsten catalysts, Mu *et al*. reported a catalytic production process of 1,2-alkanediols from cellulose over Ni-supported catalysts, and that the total yield of glycols reached up to 70.4%.[17] However, pure cellulose was only used as reaction substrate in this process, and the activities of such catalyst for raw feedstock conversion were not reported.

Microalgae, a kind of aquatic plants with high efficiency in capturing light, were one of the fastest growing light-driven cell factories. They were considered as appropriate sources for hydrocarbons due to their higher percentage of carbohydrates and lipid components.[18,19] Recently, research on microalgae mainly focused on the biofuel production, eutrophic wastewater purification and usage on food industry.[20–25] However, the efficient conversion of microalgae to high value-added

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chemicals, such as alkanediols was rarely reported. Since the percentage of moisture in microalgae is very high, microalgae with its nutrient solution can be directly used as reaction system, avoiding the addition of other reaction solvents and complicated separation and purification processes compared with terrestrial raw biomass. Therefore, selective conversion of microalgae into high value-added polyols, especially alkanediols (*e.g.*, EG and 1,2-PDO) was of great interest.

On the other hand, the percentage of nitrogen-containing components in microalgae is quite high, and it would poison the hydrogenation or hydrogenolysis catalysts during the reaction process.[26,27] Herein, a nickel-based catalyst, which was easily prepared *via* a traditional co-precipitation method in our group, was used to convert microalgae (*Chlorococcum sp*.) into polyols directly. It was found that such as-synthesized nickel-based catalyst exhibited excellent tolerance of nitrogen-containing components, and the total yields of polyols from microalgae hydrogenation were approximately 41.5% under mild conditions. Meanwhile, the influences of reaction conditions were systematically investigated and the reaction pathway of microalgae conversion was proposed. Because of the use of green feedstock and the process being free of organic solvent, such catalytic utilization of microalgae for polyols production would provide a potential route for the production of valuable chemicals from renewable biomass.

2. Experimental

2.1. Materials

Microalgae (*Chlorococcum sp*.) were self-cultured by our co-workers. Typically, the cells of *Chlorococcum sp*. were cultured in a 550 mL glass column (43 mm diameter, 390 mm height) with a working volume of 400 mL and treated with compressed air enriched with 1% CO_2 (v/v) and BG11 nutrients. The temperature was kept at 26 ± 2 °C and the light intensity was ~200 μmol photons m^{-2} s^{-1}. The pH value was maintained at the range of 7.0–8.0. The initial inoculum was about 0.1–0.2 g L^{-1}. The microalgae cells were harvested by centrifugation at 5000 rpm for 5 min at day 6 or day 7 when the biomass concentration reached about 5.0 g L^{-1}. The microalgae cells were washed three times with deionized water and then lyophilized. The lyophilized microalgae were ground into powders and stored at a temperature below 273 K.

All the other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and used as received without further purification.

2.2. Catalyst preparation

The Ni–MgO–ZnO catalyst was prepared by a co-precipitation method. In a typical process, the metal salt solution was prepared by mixing nickel nitrates, zinc nitrates and magnesium nitrates with a certain molar ratio. Then, a solution of Na_2CO_3 was added dropwise to the prepared solution under vigorous stirring at 343 K and the pH was maintained at 8.0. The resultant precipitate was aged under continuous stirring at the same temperature for 3–4 h. The suspension was poured out of the reactor and separated by vacuum filtration. The filter cake was washed thoroughly and then transferred to the drying vessel. The resultant dry cake was ground into a powder, followed by calcination at 673 K under N_2. The synthesized catalysts were reduced at 673 K for 300 min under a H_2 flow. Prior to exposure to air, the catalysts were passivated in a flow of 0.5% O_2/N_2 for 5 h at room temperature. Other catalysts (such as Ni–ZnO, Ni–MgO and MgO–ZnO) were prepared using similar methods, just changing the types and molar ratios of metal nitrates.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) patterns of catalysts were performed on a Rigaku Ultima IV X-ray diffractometer with a CuKα Radiation. The CO-chemisorption was carried out at room temperature on a Micromeritics ASAP 2020 instrument. Prior to the measurements, the samples were degassed at 350 °C for 300 min. The metal dispersion was obtained through difference calculation. The BET surface areas were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using Micromeritics TriStar II equipment. Samples were degassed at 200 °C prior to acquiring the adsorption isotherm. Element analysis of feedstock was performed using a CHNS Analyzer (Thermo scientific Flash 2000). The total organic carbons (TOC) of liquid products were achieved on Shimadzu TOC-L. The contents of each metal in the synthesized catalyst were determined by ICP on an Optimal Emission Spectrometer (Perkin Elmer Optima 8000).

2.4. Catalytic experiments and product analysis

The catalytic conversion of microalgae without any treatment was carried out in a stainless steel autoclave (Parr, 50 mL) with an initial H_2 pressure of 2–6 MPa at 423–533 K for 60–240 min. Typically, 0.25 g of microalgae (1.0 wt%) and 0.15 g of catalyst and 25 mL of deionized water were placed in the autoclave and stirred at a speed of 600 rpm. After the reaction step, the autoclave was cooled automatically, and the liquid solution was separated from the solid mixture by centrifugation. The solid catalyst was collected and washed with deionized water and ethanol for several times, following with desiccation at 353 K overnight.

The collected liquid solution was filtered through 0.22 μm pore-size filters prior to analysis. The main products in the resultant solution were identified based on the standard compounds and the structures of them were further confirmed by GCMS. To guarantee the carbohydrates in the microalgae had been totally converted, the liquid products were also analyzed by HPLC (Shimadzu LC-20AD, Aminex HPX-87H Ion Exclusion Column: 300 mm × 7.8 mm) with differential refraction detector (RID-10A). These products were quantified by gas chromatography (GC, Shimadzu GC2010 Plus, HP-INNOWax column: 30 m × 0.25 mm; film thickness, 0.25 μm) with a flame ionization detector (FID). The conversion of microalgae was calculated based on TOC data using the equation: Conversion = (moles of carbon in the resultant liquid determined by

TOC) ÷ (moles of carbon in microalgae determined by a CHNS analyzer) × 100%. The yield of polyols was calculated based on carbon *via* the equations: Yield = (moles of carbon in the products determined) ÷ (mole of carbon in the carbohydrates components of microalgae) × 100%. The yields of gas products were too low to be quantified in this work.

3. Results and discussion

3.1. Chemical compositions of microalgae

The results of microalgae composition characterization are shown in Table 1. It can be seen that the moisture content in the freeze-dried microalgae was 4.7% and the ash content was 1.2%, indicating that the content of the organic components was more than 90%. The percentages of carbon, hydrogen and nitrogen component in microalgae were 48.4, 7.6 and 1.9%, respectively, while some sulfur components can also be detected. Different from the structure of lignocellulose biomass, lignin was not detected in microalgae, and the main components of microalgae were carbohydrate, lipids and protein. The content of carbohydrates almost accounted for half of the total mass as well as 32.6% of lipid and 11.9% of protein.

Generally, the major component of microalgae was protein, and the contents of lipid and carbohydrate were quite low.[28] However, the content of protein in our self-cultured microalgae was only 11.9%, and the main component was carbohydrate, indicating that the microalgae used in this study was a special carbohydrate-rich species which was quite different from traditional ones. Therefore, the hydrothermal processes of these cultured microalgae conversions for the production of polyols were of great interest and systematically investigated in our work.

3.2. Catalytic conversion of microalgae into polyols

The catalytic activities of microalgae (*Chlorococcum sp.*) conversion for polyols production over these as-synthesized catalysts were investigated under hydrothermal conditions in a hydrogen-rich atmosphere, and the distributions of products are shown in Fig. 1. It can be seen that microalgae can be efficiently converted in a one-pot process into polyols over Ni-based catalyst under mild conditions, and the total yield of polyols was up to 41.5%. Especially, the yields of 1,2-PDO and EG reached 30.7% as well as a little amount of monohydric alcohols (others-1, such as isobutanol, isoamylol, cyclopentanol and 3-hexanol) and long-carbon-chain diols (others-2, such as 1,2-butanediol, 1,2-butyl glycol, 1,3-propanediol, 1,2-adipic alcohol) at 250 °C for 3 h in water with 6 MPa of initial H_2 pressure, indicating that aquatic microalgae could be directly used as sustainable feedstock for the production of high value-added alkanediols. Besides, using wet microalgae directly obtained from nutrient solution without pretreatment as reaction substrate, the total yields of polyols were also up to 40.5% and the yields of 1,2-PDO and EG reached 29.8% as well, indicating that complicated separation and purification processes of microalgae from nutrient solution can be avoided and the cost of alkanediols production would further decrease. The results of TOC and CHNS Analyzer demonstrated that these nitrogen-containing compounds stayed in the reaction solution and did not adsorb on the surface of catalyst.

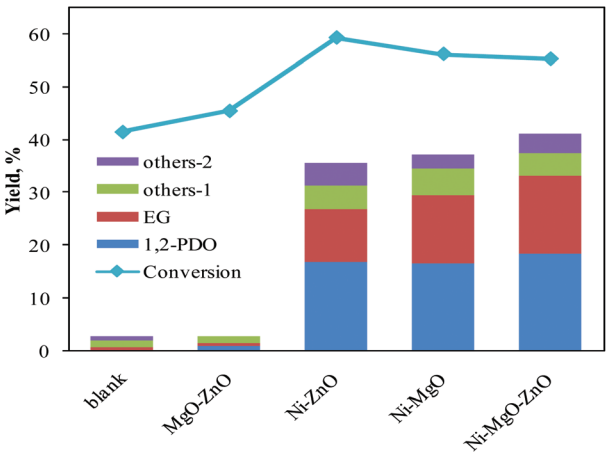


Fig. 1 Catalytic conversion of microalgae into polyols over various catalysts. Reaction conditions: 250 °C, 3 h, 6 MPa of H_2.

Generally, nitrogen-containing compounds would poison hydrogenation catalysts. Surprisingly, although the content of nitrogen was up to 1.9%, such Ni–ZnO–MgO catalyst exhibited excellent catalytic activities as well and showed a good tolerance for nitrogen. Adding a certain amount of glutamic acid into the initial reaction mixture, the total yields of polyols and alkanediols were consistent at about 43.7 and 32.1%, respectively. Besides, increasing microalgae from 1.0 wt% to 4.0 wt%, such catalyst also showed good performance in the conversion of microalgae, and the yields of polyols and alkanediols were about 41.5 and 30.8%, respectively. Therefore, this aqueous catalytic process for alkanediols production from aquatic raw biomass was much more promising since cheaper microalgae can be directly used without any additional pretreatment for the production of alkanediols and the as-synthesized catalyst had an excellent tolerance for toxic components in microalgae cells.

To investigate the influence of the catalyst composition on the yields of polyols, conversions of microalgae over the other metal-based catalysts synthesized with a similar method were also performed. From Fig. 1, it can be seen that the yield of polyols was very low in the blank experiment without any

Table 1 Characterization of microalgae (*Chlorococcum sp.*)

Method	Component	Percentage (%)
Proximate analysis	Moisture	4.7
	Ashes	1.2
Element analysis	C	48.4
	H	7.6
	N	1.9
	S	0.1
Biochemical composition	Carbohydrate	49.6
	Lipid	32.6
	Protein	11.9
	Lignin	N.D.

addition of catalyst, where only a little amount of acetol was detected in solution. However, the conversion of microalgae was up to 41.5%, indicating that the structure of microalgae can be destroyed at these conditions and converted into other by-products undetected. Similarly, the MgO–ZnO catalyst did not exhibit a satisfying catalytic activity for the conversion of microalgae under the same conditions either, and only some acetol was produced in the hydrogenolysis process. Besides, some carbonaceous by-products were generated since black solids gradually deposited at the bottom of the vessel after being used for one or two days. However, the acetol yield obtained over the MgO–ZnO catalyst was a little higher than that from the blank experiment, indicating that MgO–ZnO could promote the microalgae converting to liquid products or reaction intermediates.

With the introduction of Ni particles onto the supporter (such as MgO, ZnO and MgO–ZnO), it can be clearly seen that microalgae can be almost completely converted. The highest polyols yield (41.5%) can be achieved over the Ni–MgO–ZnO catalyst compared with that of 37.0% and 37.5% catalyzed by Ni–ZnO and Ni–MgO under the same conditions. The BET surface area of Ni–MgO–ZnO, Ni–ZnO and Ni–MgO were 39.8 $m^2\ g^{-1}$, 20.7 $m^2\ g^{-1}$ and 10.2 $m^2\ g^{-1}$ respectively. Ni–MgO–ZnO with the largest surface area depicts the best catalytic activity. Catalytic activity of Ni–MgO and Ni–ZnO are almost equal, both showing quite excellent activity for polyols production, but Ni–MgO cannot be used on a large scale for polyols production since the amount of obtained catalyst was much less than that of Ni–ZnO and Ni–MgO–ZnO under the same preparation conditions, suffering from leaching in the catalyst-synthesized process due to virtually no MgO precipitation at the pH value of 7.5–8.0. The ICP analysis showed that the actual content of Mg in Ni–MgO–ZnO catalyst (theoretical molar content of Mg in Ni–MgO–ZnO was 10%) was only 2.0%, and the actual elemental ratio of Ni and Mg in the synthesized Ni–MgO catalyst was just 15 : 1 with the feed intake of Ni and Mg in molar ratio of 4/6. These results indicated that most of the Mg precursor was drained, leading to a higher content of Ni than that in the Ni–ZnO catalyst. From the XRD spectra of the synthesized catalyst shown in Fig. 2, the peaks of ZnO and Ni can be observed clearly, in contrast to the weak peaks of MgO in the Ni–MgO–ZnO catalyst. Similarly, the peaks of MgO in the Ni–MgO catalyst were quite weak and it almost cannot be distinguished in the spectrum of the MgO–ZnO catalyst, consistent with the results of ICP analysis. Because of high Ni content in the Ni–MgO catalyst, the activity of the Ni–MgO catalyst had a little increase compared to that of the Ni–ZnO catalyst. However, the high Ni loading in Ni–MgO could result in particle agglomeration and decrease the amount of the exposed active sites. The calculated particle sizes of nickel on ZnO, MgO, and MgO–ZnO using the Scherrer equation were 10.03 nm, 11.25 nm and 7.32 nm, respectively. And the Ni dispersion on ZnO, MgO, and MgO–ZnO obtained by difference calculation through CO-chemisorption characterization was 1.23%, 1.16% and 1.25%. Therefore, the high content of Ni cannot compensate for the agglomeration of Ni, resulting in

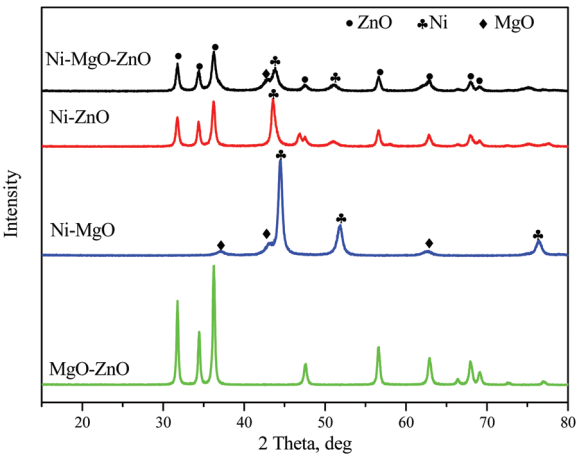


Fig. 2 XRD patterns of the as-synthesized catalysts.

inferior activity of the Ni–MgO catalyst compared with the Ni–MgO–ZnO catalyst. On the other hand, the addition of a small amount of MgO into Ni–ZnO could enhance the yield of polyols, which would be due to a better dispersion and smaller size of Ni particles on the Ni–MgO–ZnO catalyst from the broader peaks of Ni compared to the other two catalysts. Besides, the main peak of Ni shifted slightly in the XRD pattern of the ZnO-contained catalyst, probably resulting from lattice distortion of Ni when added ZnO.[29] For the Ni–MgO catalyst, there was little chance for the competition of the other atoms, since the main component was Ni particles.

To make uttermost use of the synthesized catalyst, the recycling and regeneration of the Ni–MgO–ZnO catalyst were investigated. The main products of the recycling and regenerating experiments were glycerols and acetols. The activity of the catalysts decreased when recycled. Even through regenerated, the catalytic activity of Ni–MgO–ZnO could not be recovered. For exploring the reason of deactivation of the recycled and regenerated catalysts, XRD characterization of Ni–MgO–ZnO was conducted as shown in Fig. 3. It can be seen that the ZnO and Ni peaks of the catalysts after recycling and regenerating

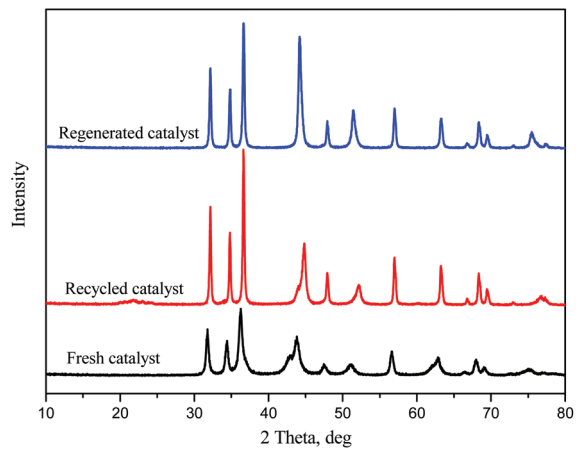


Fig. 3 XRD patterns of the recycled and regenerated Ni–MgO–ZnO catalysts.

become sharper than that of fresh catalyst. However, the MgO peak was weaker after once recycle, and even disappeared after the regeneration process. This indicates that the crystal size of ZnO and Ni increased after the recycling and regeneration processes, and that MgO content was drained in the reaction, leading to a collapse of the original structure of Ni–MgO–ZnO.

Based on the above results, it can be inferred that Ni particles were the main active sites for the hydrogenolysis of microalgae, and the MgO–ZnO supporter had played an important role in the catalytic activities of polyols production. Although Ni particles dispersed on a single ZnO supporter exhibited a good activity as well, the addition of MgO could decrease the size of Ni particles, leading to its superior activities over the Ni–MgO–ZnO catalyst. However, the recycling and regeneration of the catalysts needs to be improved in future studies.

3.3. Reaction pathway of microalgae conversion

The conversion for microalgae was conducted at a temperature of 200–250 °C with 4–6 MPa of initial H_2 pressure as shown in Fig. 4. To balance the carbon of the raw material and products, it was calculated that about 3–5% of raw materials were conversed to gaseous products, including CH_4, CO_2 and CO. The solid products, in which the carbon and hydrogen contents were 74% and 12%, respectively, it was thought that most of it was released as lipids after the hydrothermal process. It was found that this part of products was between 25% and 35%. In this process, more than half of solid carbon in the raw materials was turned to liquids. From GC-MS analysis, total peak area of the alkanediols was more than 70%, and also some little furans, ketones and organic acids.

As mentioned above, the feedstock used in this work was a special kind of microalgae with a high carbohydrates content. In the conversion process, carbohydrates in the microalgae were firstly hydrolyzed to glucose under hydrothermal conditions. Then the generated glucose was hydrogenated over nickel-based catalysts. Transformation of glucose into short chain alcohols is due to cleavage of C–C bonds. One of the proposed paths for C–C bond cleavage was from glucose to glycolaldehyde *via* a retro-aldol reaction, followed by the production of ethylene glycol from glycolaldehyde by hydrogenation.[30] On the other hand, as the heating rate was very fast, the glucose was also transformed into levoglucosan in a short time through dehydration and no formation of sorbitol *via* a hydrogenation process was detected in the reaction solution.[31] Then the generated levoglucosan underwent cleavage of C–C and C–O bonds and was converted into methylglyoxal. In the H_2 atmosphere, methylglyoxal was further hydrogenated into acetol, which could be detected in the reaction system when the feedstock did not hydrogenate thoroughly over MgO–ZnO catalysts or without catalysts. In some literature, it has also been reported that glucose would be isomerized into fructose, then producing 1,3-dihydroxyacetone *via* a retro-aldol reaction.[4,11,16,17] 1,3-Dihydroxyacetone is rather unstable and was likely to be converted into acetol under our reaction condition. In the presence of Ni–MgO–ZnO catalysts, acetol was completely hydrogenated into 1,2-PDO. Therefore, it could be inferred that the main reaction pathway for microalgae hydrogenolysis for polyols production was direct cleavage of C–C bonds in glucose, as shown in Scheme 1.

Such reaction pathway can be confirmed by the results of model compound conversion. As shown in Table 2, glucose

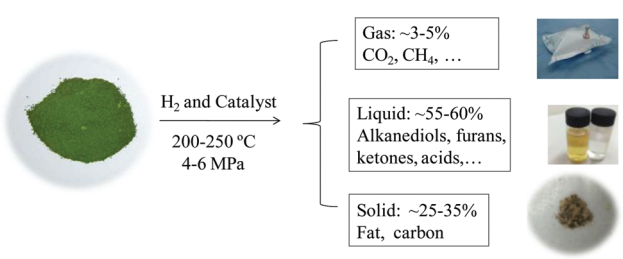
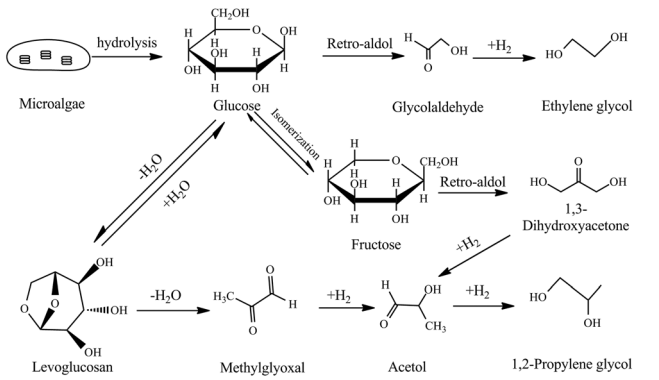


Fig. 4 The reaction process for microalgae conversion and distribution of various products.



Scheme 1 Proposed pathway for the conversion of microalgae over nickel based catalysts.

Table 2 Conversion results of model compounds over Ni–MgO–ZnO catalyst

Entry	Feedstock	Reaction condition	Yield (%)			
			1,2-PDO	EG	Ethanol	Total
1	Glucose	220 °C, 3 h, 6 MPa	26.0	12.8	1.9	40.7
2	Glucose	250 °C, 3 h, 6 MPa	47.2	11.0	10.3	68.5
3	Levoglucosan	250 °C, 3 h, 6 MPa	25.4	13.0	6.7	45.1
4	Acetol	250 °C, 1 h, 6 MPa	70.6	0.0	22.3	92.9
5	Acetol	250 °C, 2 h, 6 MPa	60.4	0.0	31.4	91.8
6	Acetol	250 °C, 3 h, 6 MPa	28.8	0.0	53.9	82.7

can be efficiently converted as well, and a higher polyols yield of 68.5% was achieved under the same reaction condition, indicating that glucose as one of the reaction intermediates was firstly generated from the depolymerization of microalgae cells with sequential hydrolysis of the carbohydrate components. Meanwhile, the ratio of 1,2-PDO to EG from glucose was higher than that from microalgae under the same conditions, indicating that the depolymerisation process of microalgae was the rate-determining step and acetol was the main reaction intermediate from C–C cleavage of glucose *via* dehydration/hydrogenation reaction. When levoglucosan was used as the feedstock for hydrogenolysis, the main products were 1,2-PDO with a yield of 25.4%, as well as 13.0% of EG. In the process, the transformation between glucose and levoglucosan can be reversible, leading to the production of EG except for 1,2-PDO. To further confirm acetol as reaction intermediate, acetol was directly used as the substrate and the catalytic conversion of it at different reaction time was investigated. From Table 2 it can be seen that half of acetol was transformed to ethanol at 250 °C for 3 h, due to the excessive cleavage of C–C bonds in the intermediates or products. Shortening the reaction time, the formation of ethanol was inhibited and the yield of 1,2-PDO increased. After reaction for only 1 h, the yield of 1,2-PDO production reached up to 70.6%, implying that acetol was the main reaction intermediate and it can be selectively hydrogenated into 1,2-PDO in a short time, while prolonging the reaction time would just lead to excessive C–C breakage.

3.4. Influences of reaction conditions

Since the reaction temperature played an important role in the conversion of microalgae *via* hydrolysis and hydrogenation processes, the influence of reaction temperature on the main product distribution was first investigated and the results are shown in Fig. 5a. It can be seen that the yields of polyols increased at a temperature of 140–250 °C. Further increasing of the reaction temperature, decreased the yields of EG and others-2 in contrast to the slight increase of EG and others-1. Below 170 °C, the yields of the main products were quite low, less than 4%. Above 170 °C, yields of EG and 1,2-PDO increased rapidly and reached up to *ca.* 20% and 15% at 250 °C. At this temperature, the highest yield of polyols of 41.5% was obtained. The concentration of acetol was too low to be detected in the conversion process of microalgae over the Ni–MgO–ZnO catalyst, due to its rapid hydrogenation rate to 1,2-PDO. Since further increasing the reaction temperature to 260 °C led to the degradation of polyols, a reaction temperature of 250 °C was employed in the standard reaction conditions hereafter.

Fig. 5b showed the polyols product distribution as a function of the reaction time at 250 °C. From the figure it can be seen that yields of polyols changed slightly when the reaction time was prolonged from 60 min to 240 min gradually. During the first 120 min, the yields of 1,2-PDO and EG remained almost constant, and then went up slightly until 180 min, and finally kept steady during the last 60 min. During the whole process the yields of products remained almost unchanged. In other words, the reaction time is not a significantly controlling variable on the polyols products distribution. The influences of initial H_2 pressure on the product distribution in Fig. 5c showed that a high initial H_2 pressure was necessary for the sufficient hydrogenolysis of microalgae in the hydrothermal

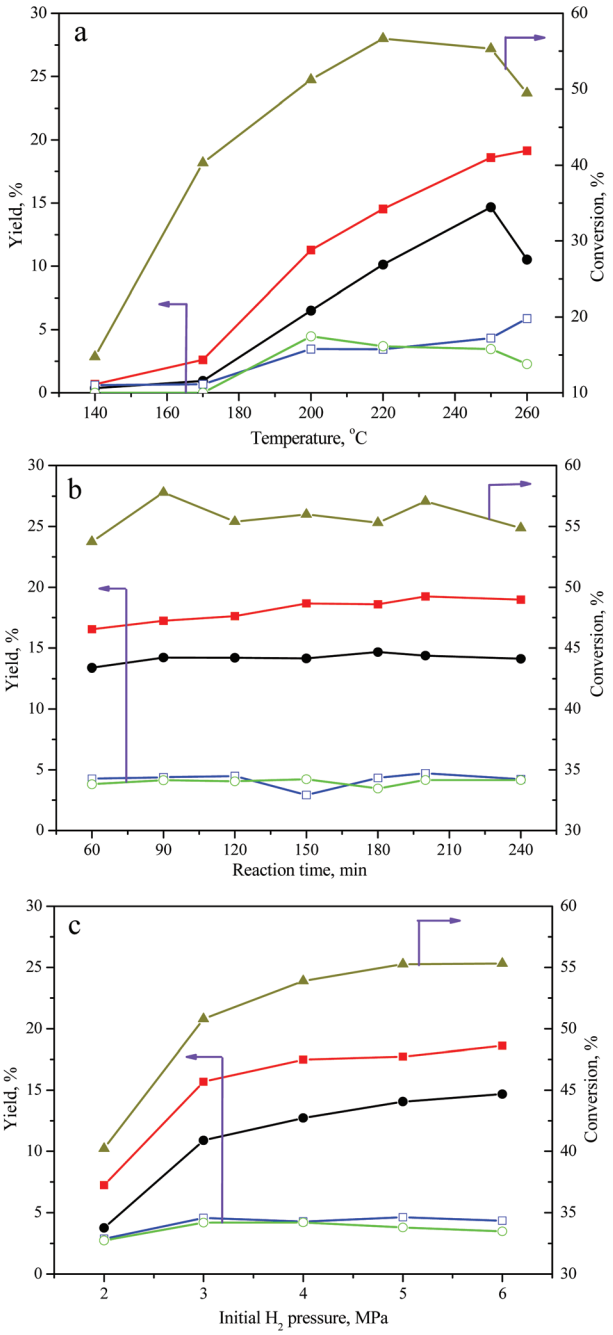


Fig. 5 Product distributions for microalgae conversion over Ni–MgO–ZnO catalyst (■ represents 1,2-PDO; ● represents EG; □ represents others-1, including isobutanol, isoamylol, cyclopentanol and 3-hexanol; ○ represents others-2, including 1,2-butanediol, 1,2-butyl glycol, 1,3-propanediol, 1,2-adipic alcohol; ▲ represents the conversion.): dependence on (a) reaction temperature at 6 MPa H_2 and 180 min; (b) reaction time at 250 °C and 6 MPa; and (c) initial H_2 pressure at 250 °C and 180 min.

conditions. The increase of the initial H_2 pressure from 2 MPa to 6 MPa enhanced the yields of the main products (1,2-PDO and EG). The yields of the 1,2-PDO and EG depicted a rapid growth in the range of 2–4 MPa and mild rise in the other pressure range, whereas the yields of others-1 and others-2 changed slightly all the time.

4. Conclusions

In summary, an interesting catalytic process to directly convert aquatic microalgae into industrially attractive 1,2-PDO and EG in a one-pot procedure with high yields in water over Ni-based catalyst was reported *via* combined steps involving hydrolysis, hydrogenation and hydrogenolysis reactions. Such as-synthesized catalyst exhibited excellent tolerance of N-containingd components as well as a smaller particle size and good dispersion of Ni on the MgO–ZnO supporter, and a 41.5% yield of polyols can be achieved directly from microalgae under optimal reaction conditions. Meanwhile, the reaction pathway for microalgae conversion was proposed based on the formation of intermediate products and the results of model compounds conversion. Because of the use of green feedstock and the process being free of organic solvent, such catalytic utilization of microalgae for polyols production should provide a potential route for the production of valuable chemicals from renewable biomass.

Acknowledgements

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