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Efficient one-pot production of 1,2-propanediol and ethylene glycolfrom 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 was 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 ºC for 3 h with 6.0 MPa of H_2 pressure), microalgae was directly and efficiently converted over Ni-MgO-ZnO catalyst and a total yield of polyols was up to 41.5%. Such excellent catalytic activity was attributed to the smaller size and better dispersion of Ni particles on MgO-ZnO supporter based on the characterization results as well as its tolerance to nitrogen-contained 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 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 easy for storage and transportation, widely 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 the versatile uses of them 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 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 can 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 the 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 the unexpected byproducts[15,16]. For example, starting from miscanthus, base solvent should be firstly used to remove epidermal protectors and lignin fractions, which could preferentially poisoned theNi-W_2C/AC catalyst due to the formation of organic acids and unsaturated compounds[16]. Similarly, corn stalk was pretreated with 1,4-butannediol, NaOH, H_2O_2 and ammonia firstly, and much higher yields of ethylene glycol and 1,2-propylene glycol can be achieved over the same catalyst compared with that from untreated raw corn stalk. In view of higher cost of tungstic 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. It was considered as an appropriate source for hydrocarbons due to its higher percentage of carbohydrates and lipid components[18,19]. Recently, researches of microalgae were 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 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.

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On the other hand, the percentage of nitrogen-contained components in microalgae was 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* 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-contained 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 green feedstock and 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 bubbled with the compressed air enriched with 1% CO_2(v/v)and BG11 nutrients. The temperature was kept at 26±2ºC and light intensity was ~200μmol photons $m^{-2}\cdot s^{-1}$.The pH value was maintained at the range of 7.0-8.0. The initial inoculum was about 0.1-0.2 g/L. The microalgae cells were harvested by centrifugation at 5000rpm for 5min at day 6 or day 7 when the biomass concentration reached about 5.0 g/L. The microalgae cells were washed three times with deionized water and then lyophilized. The lyophilized microalgae were ground into powders and stored under the temperature below 273K.

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

2.2 Catalyst preparation

Ni-MgO-ZnO catalyst was prepared by 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 in the prepared solution under vigorous stirring at 343 K and maintained the pH value of 8.0. The resultant precipitate was aged under continuous stirring in 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 into the drying vessel. The resultant dry cake was grounded into powders, followed by calcination at 673K under N_2. The synthesized catalysts were reduced at 673K for 300 min in 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 with the 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 conducted on Rigaku Ultima IVX-Ray diffractometer with a CuKα Radiation. The CO-Chemisorption was carried out at room temperature on Micromeritics ASAP 2020 instrument. Prior to the measurements, the samples were degassed at 350 ºC for 300min. The metal dispersion was obtained through the differences 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 ºC prior to acquiring the adsorption isotherm. Element analysis of feedstock was performed at 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 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, 50mL) 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 changed into 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 microalgae totally conversed, the liquid products were also analyzed by HPLC (Shimadzu LC-20AD, Aminex HPX-87H Ion Exclusion Column: 300mm×7.8mm) with differential refraction detector (RID-10A). These products were quantified by gas chromatograph (GC, Shimadzu GC2010 Plus, HP-INNOWax column: 30m×0.25mm; film thickness,0.25μm)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%. Besides, 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 were shown in Table 1. It can be seen that the content of moisture 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 a little of sulfur component 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.

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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.

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 such microalgae used in this study was a special carbohydrate-rich species which was much more different from traditional ones. Therefore, the hydrothermal processes of these cultured microalgae conversion 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 condition in hydrogen-rich atmosphere, and the distributions of products were shown in Fig. 1. It can be seen that microalgae can be efficiently one-pot converted into polyols over Ni-based catalyst under mild conditions, and 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 asisobutanol, 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-contained compounds stayed in the reaction solution and did not adsorb on the surface of catalyst.

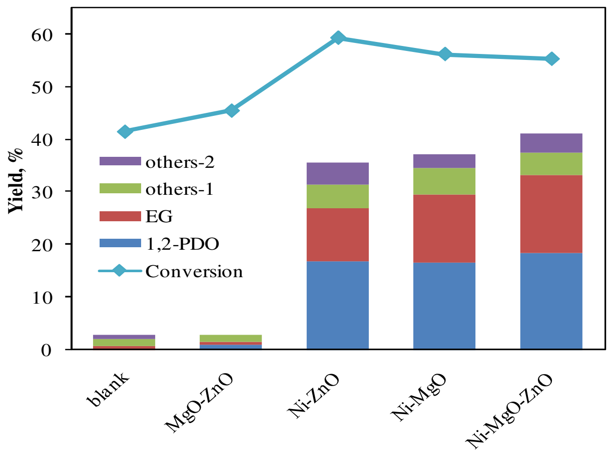


Fig. 1 Catalytic conversion of microalgae into polyols over various catalysts .*Reaction conditions: 250 ºC, 3 h, 6MPa of H_2.*

Generally, nitrogen-contained 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 had good tolerance of nitrogen. Adding a certain amount of glutamic acid into initial reaction mixture, the total yields of polyols and alkanediols maintained, 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 of 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 addition of catalyst, where only a little amount of acetol was detected in liquid solution. However, the conversion of microalgae was up to 41.5%, indicating that the structure of microalgae can be destroyed at this condition and converted into other by-products undetected. Similarly, MgO-ZnO catalyst did not exhibit a satisfying catalytic activity for the conversion of microalgae at the same condition as well, and only some acetol was produced in the hydrogenolysis process. Besides, a certain amount of carbonaceous by-products was generated since black solids gradually deposited at the bottom of the vessel after being used for one or two days. However, acetol's yield obtained over 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 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 39.8m^2/g, 20.7m^2/g and 10.2m^2/g 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 large-scale used for polyols production since the amount of obtained catalyst was much less than that of Ni-ZnO and Ni-MgO-ZnO in the same preparation condition, suffering from leaching in the catalyst-synthesized process due to hardly formation of 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. This results indicated that most of Mg precursor was drained, leading to the higher content of Ni than that in Ni-ZnO catalyst. From the XRD spectra of the synthesized catalyst shown in Fig. 2, the peaks of ZnO and Ni can be obviously observed, in contrast to the weak peaks of MgO in Ni-MgO-ZnO catalyst. Similarly, the peaks of MgO in Ni-MgO catalyst were quite weak and it almost cannot be distinguished in the spectrum of MgO-ZnO catalyst, consistent with the results of ICP analysis. Because of high content of Ni in Ni-MgO catalyst, the activity of Ni-MgO catalyst had a little increase than that of Ni-ZnO catalyst. However, the high Ni loading in Ni-MgO could result in the particle agglomeration and decrease the amount of the exposed active sites. The calculated particle sizes of nickel on ZnO, MgO, and MgO-ZnO through Scherrer Equation were 10.03nm, 11.25nm and 7.32nm, 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 the inferior activity of Ni-MgO catalyst compared with 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 the better dispersion and smaller size of Ni particles on 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 ZnO-contained catalyst, probably resulting from lattice distortion of Ni when added ZnO[29]. For Ni-MgO catalyst, there was little chance for the competition of the other atoms, since the main component was Ni particles.

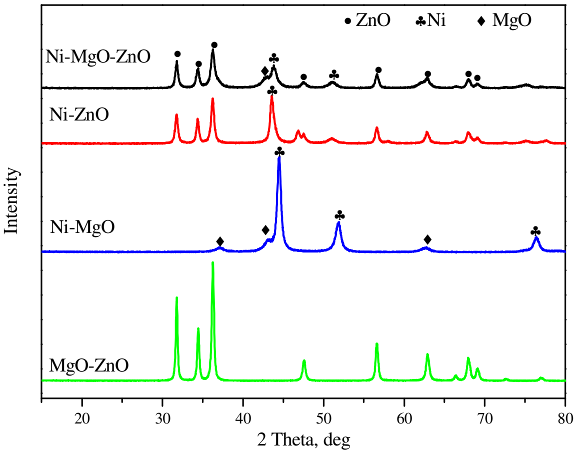


Fig. 2 XRD patterns of the as-synthesized catalysts.

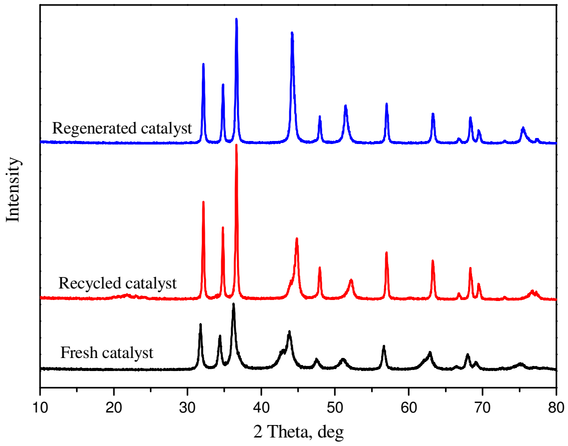


Fig. 3 XRD patterns of the recycled and regenerated Ni-MgO-ZnO catalysts.

To make uttermost use of the synthesized catalyst, the recycle and regeneration of the Ni-MgO-ZnO were investigated. The main products of the recycle experiments 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 was conducted shown in Fig. 3. It can be seen that the ZnO and Ni peaks of the catalysts after recycling and regenerating become sharper than that of fresh catalyst. However, the MgO peak was weaker after once recycle, even disappeared after regenerated process. It indicates the catalysts after reaction the crystal size of ZnO and Ni increased after recycle and regeneration, and that the MgO were drained in the reaction, leading to the original structure of Ni-MgO-ZnO collaps.

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

3.3Reaction pathway of microalgae conversion

The conversion for microalgae was conducted in the temperature of 200-250°C with the 4-6 MPa of initial H_2 pressure as shown in Fig. 4. To balance 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 carbon and hydrogen content were 74% and 12%, maybe most of them was the released lipids after the hydrothermal process. Quantifying this part of products, it 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%, then some little furans, ketones and organic acids.

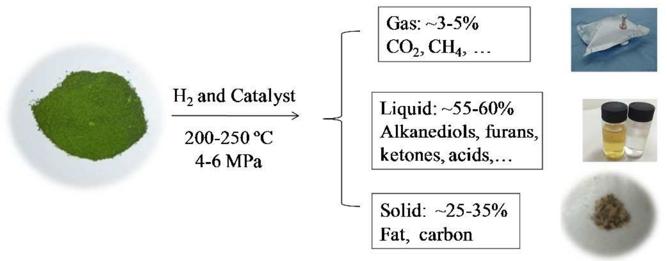
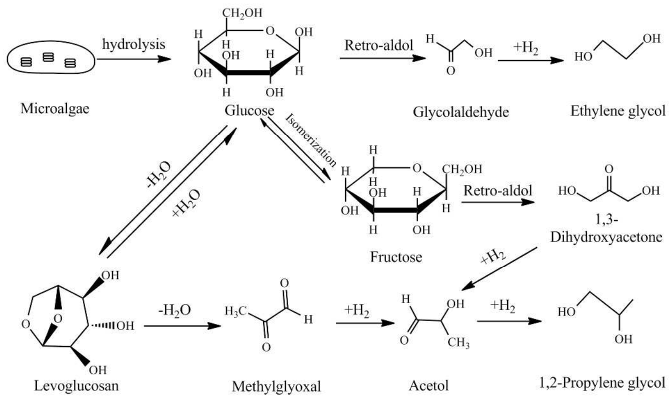


Fig. 4 The reaction process for microalgae conversion and distribution of various products.

As mentioned above, the feedstock used in this work was a special kind of microalgae with high content of carbohydrates. In the conversion process, carbohydrates in microalgae were firstly hydrolyzed to glucose in the hydrothermal condition. Then generated glucose was hydrogenated over nickel-based catalysts. Transformation of glucose into short chain alcohols should undergo the cleavage of C-C bonds. One of the proposed paths for C-C bond cleavage was from glucose to glycolaldehyde via 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 short time through dehydration and no formation of sorbitol was detected in the reaction solution via hydrogenation process[31]. Then the generated levoglucosan underwent the cleavage of C-C and C-O bonds and was converted into methylglyoxal. In the H_2 atmosphere, methylgloxal 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 literatures, it was also reported that glucose would be isomerized into fructose, then producing 1,3-dihydroxyacetone via the retro-aldol reaction[4,11,16,17]. 1,3-dihydroxyacetone is rather unstable and was apt 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.



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

Such reaction pathway can be confirmed by the results of model compound conversion. As shown in Table 2, glucose 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 and sequential hydrolysis of carbohydrates 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 rate-determined 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-PDOwith the 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 the 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 reacted 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 was can be selectively hydrogenated into 1,2-PDO in a quite short time, while prolonging the reaction time would just lead to excessive C-C breakage.

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, 3h, 6MPa	26.0	12.8	1.9	40.7
2	glucose	250 °C, 3h, 6MPa	47.2	11.0	10.3	68.5
3	levoglucosan	250 °C, 3h, 6MPa	25.4	13.0	6.7	45.1
4	acetol	250 °C, 1h, 6MPa	70.6	0.0	22.3	92.9
5	acetol	250 °C, 2h, 6MPa	60.4	0.0	31.4	91.8
6	acetol	250 °C, 3h, 6MPa	28.8	0.0	53.9	82.7

3.4 Influences of reaction conditions

Since 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 firstly investigated and the results were shown in Fig. 5a. It can be seen that the yields of polyols increased at the temperature 140-250 °C. Further increasing of the reaction temperature, yields of EG and others-2 decreased 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 ºC, 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 polyols of 41.5% was obtained. The concentration of acetol was too low to be detected in the conversion process of microalgae over Ni-MgO-ZnO catalyst, due to its rapid hydrogenation rate to 1,2-PDO. Since further increasing reaction temperature to 260ºC led to the degradation of polyols, the reaction temperature of 250 ºC was employed as the reaction conditions hereafter.

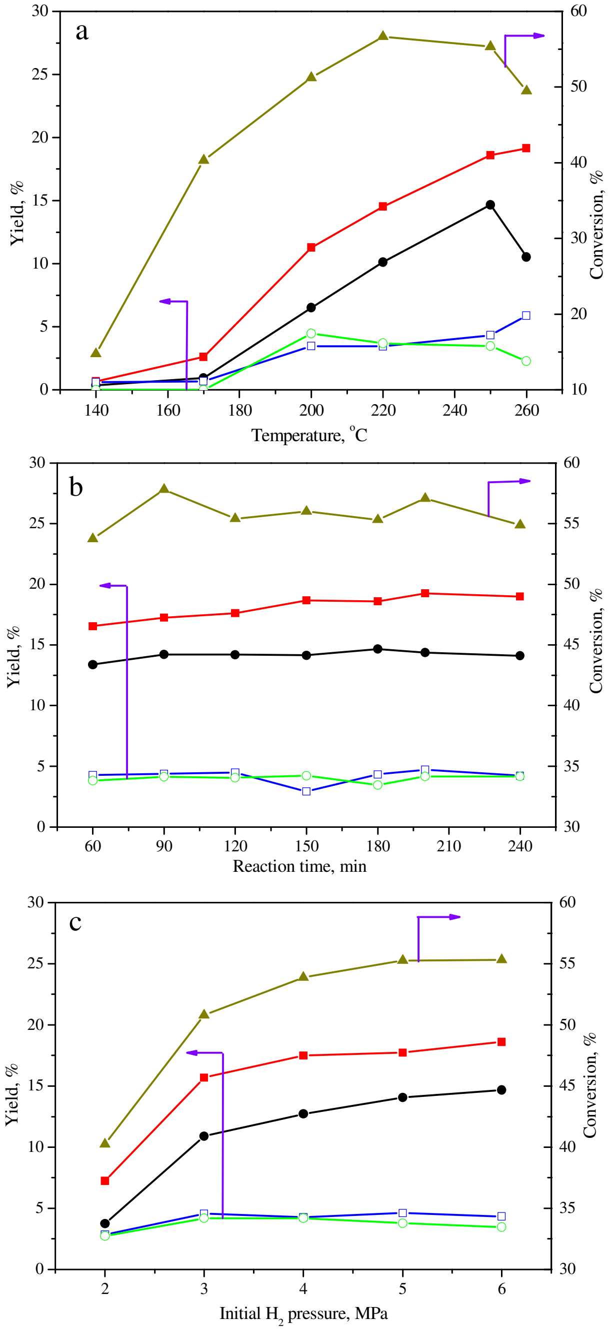


Fig. 5 Product distributions for microalgae conversion over Ni-MgO-ZnO catalyst (■represents 1,2-PDO; ● represents EG; □ represents others-1, including isobutanol, isoamylol, cyclopentanol and 3-hexanol; ○represents others-2, including 1,2-butanediol, 1,2-butyl glycol, 1,3-propanediol, 1,2-adipic alcohol;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

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 reaction time was prolonged from 60 min to 240 min gradually. At 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 at the last 60 min. In the range of entire time, yields of products 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 condition. 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.

Conclusions

In summary, an interesting catalytic process to directly one-pot convert aquatic microalgae into industrially attractive 1,2-PDO and EG 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-contained components as well as a smaller particle size and well dispersion of Ni on 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 green feedstock and 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.

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Notes and references

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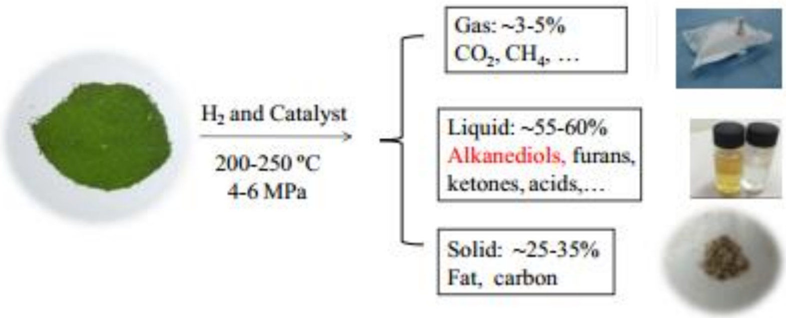
Graphical Abstract



Directly one-pot valorization of aquatic microalgae for high yield production of alkanediols over an easily prepared Ni-based catalyst with excellent tolerance of nitrogen-contained components was demonstrated.