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Short Communication

Hydrogenolysis of biomass-derived sorbitol to glycols and glycerol over Ni-MgO catalysts

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ABSTRACT

Ni-MgO catalysts with varying Ni/Mg ratios were prepared by co-precipitation and tested in sorbitol hydrogenolysis. At 473 K and 4 MPa H_2, the best catalyst with Ni/Mg ratio of 3:7 exhibited 67.8% conversion and 80.8% total selectivity of ethylene glycol, 1,2-propylene glycol and glycerol. These catalysts were characterized by XRD, CO_2-TPD and H_2 chemisorption, revealing that the activity depended strongly on the basicity and Ni surface area. The reaction conditions were optimized, which were relatively mild for this chemoselective conversion.

1. Introduction

Glycerol and C2–C3 glycols containing ethylene glycol (EG) and propylene glycol (PG) are important commodity chemicals widely used in the manufacture of polyesters resins, surfactants, pharmaceuticals and functional fluids. Sugars and sugar alcohols, which can be derived largely from the renewable lignocellulosic biomass instead of fossil resources, are considered to be potential feedstocks for the production of lower glycols through hydrogenolysis because of their rich oxygen-containing functional groups [1]. Previously, the catalytic hydrogenolysis of sorbitol and other polyols was usually conducted using a metal catalyst and a basic promoter, and those promoters like NaOH and $Ca(OH)_2$ have proved a positive influence on the C–C scission where a widely accepted mechanism was the retro-aldol condensation [2–6]. However, such problems as accelerated degradation and glycol products separation would occur when the alkali was dissolved in the reaction solution. Without alkalis, MgO supported Cu, Co and Pt catalysts showed bifunctional effects and excellent performances in the aqueous-phase hydrogenolysis of glycerol to glycols [7–9], which should be also efficient for sorbitol hydrogenolysis. Considering the high cost of noble metal catalysts, some non-noble metal catalysts with excellent C–C bond breaking ability, like Ni, have attracted great attention in polyols hydrogenolysis [5,10,11].

Herein, the bifunctional Ni-MgO catalysts were prepared by co-precipitation and used for sorbitol hydrogenolysis under mild conditions and without alkaline additives. The catalysts were characterized to study the relationship between the structure and their catalytic performance. We also discussed the effects of temperature, H_2 pressure and reaction time.

2. Experiment

2.1. Catalyst preparation and characterization

A series of Ni-MgO catalysts with varying Ni/Mg molar ratios were prepared by co-precipitation [12,13]. A mixed solution (1 M total metal) of $Ni(NO_3)_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ was deposited by a Na_2CO_3 solution (1.2 M) at an adding rate of 1 mL/min at room temperature (RT). After aged overnight, isolated and washed by vacuum filtration until pH < 8, the precipitates were dried at 383 K for 12 h and calcined at 773 K for 3 h in static air, followed by reduction with pure H_2 at 773 K for 3 h at a ramp rate of 3 K/min. Ni-Al_2O_3 catalyst was also prepared by the same procedures but with reduction temperature of 1073 K. The NiOx sample was obtained by co-precipitation and using only $Ni(NO_3)_2 \cdot 6H_2O$ as precursor. All the catalysts were identified as Ni-Mg(x:y) or Ni-Al(x:y), where x:y referred to the atomic ratio. The catalysts were characterized by ICP-AES, N_2-TPD, CO_2-TPD, XRD, H_2-TPR and H_2 chemisorption to study their physico–chemical properties and the technical details were provided in the Supporting Information (SI).

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2.2. Catalytic test and product analysis

Sorbitol hydrogenolysis was carried out in a batch system with a 100 mL 316 L stainless steel autoclave reactor. After 50 mL aqueous solution of 20% sorbitol and 0.5 g catalyst were loaded, the reactor was purged with hydrogen for four times, aerated to the desired pressure and then heated to the defined temperature for a given period at 600 rpm stirring speed. All the experiments were carried out in triplicate. After reaction, the unconsumed sorbitol and products were quantified by both gas chromatography (GC) and ion chromatography (IC). The byproducts were analyzed by GC coupled with a mass spectrometer (MS), and the total carbon balance (TC) was also measured. The analytical methods were shown in the SI [13].

3. Results and discussion

3.1. Chemical and physical properties of catalysts

Table 1 summarized the physico–chemical properties of Ni-MgO catalysts with Ni/Mg molar ratio ranging from 1/9 to 5/5. A high surface area accompanied with a strong basicity was obtained for MgO sample. As Ni was introduced and increased, both the BET surface areas and the basicities of catalysts continuously decreased. The actual content of Ni was very close to the theoretical loading, which increased with the increasing Ni/Mg ratio. Based on H_2-TPR results, only a small fraction of nickel oxides could be reduced at the temperature below 700 K for Ni-MgO catalysts, while the unsupported NiOx sample could be completely reduced at 700 K. The Ni oxides loaded on MgO were more difficult to reduce than the unsupported NiOx and the reduction temperature rose with the increase of Ni/Mg ratio (Fig. S1 in the SI). When the Ni/Mg ratio increased from 1/9 to 3/7, the Ni surface area reached a maximum of 6.2 m^2/g, and subsequently dropped as the ratio continuously increased. This decrease could be attributed to the decline in catalyst reducibility and the aggregation of Ni particles [12]. As identified in Fig. 1, the diffraction lines at 44.5°, 51.8° and 76.4° for 2θ were attributed to the Ni(111), Ni(200) and Ni(220) crystal planes (JCPDS No. 87-0712), which showed stronger intensity as Ni content increased. On the other hand, the MgO characteristic diffraction peaks at 36.9°, 42.9°, 62.3°, 74.7° and 78.6° for 2θ (JCPDS No. 77-2179) became weaker when Ni was introduced. The angles of $MgNiO_2$ characteristic diffraction peaks (JCPDS No. 24-0712) were a little higher than those of MgO and NiO (JCPDS No. 89-7130), and a gradual shift of peaks at about 37°, 43° and 62° for 2θ to the higher diffraction angles was observed after increasing partial substitution of Mg with Ni [14,15]. The phenomenon indicated that the amount of $MgNiO_2$ solid solution increased, which brought about higher reduction temperature and poorer reducibility in Ni-MgO catalysts with the increasing Ni content [12,16]. Ni nanoparticles grew slowly as Ni content increased. The degree of reduction was rapidly lessened from 52.4% to 18.9% and the average size of Ni particles was about 10 nm.

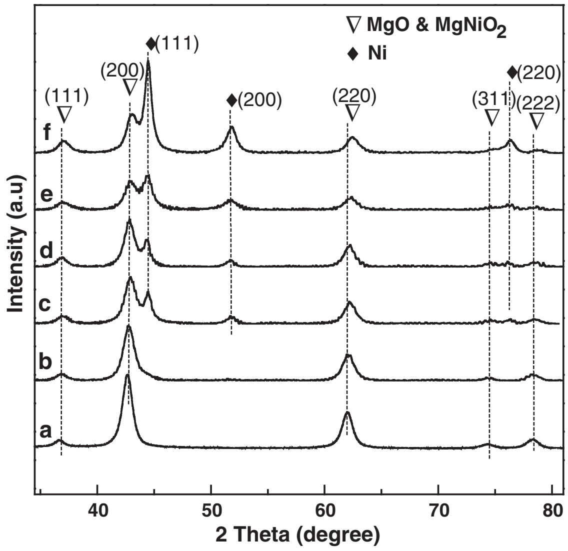

Fig. 1. XRD patterns of MgO (a), Ni-Mg(1:9) (b), Ni-Mg(2:8) (c), Ni-Mg(3:7) (d), Ni-Mg(4:6) (e) and Ni-Mg(5:5) (f) samples.

3.2. Hydrogenolysis of sorbitol on Ni-MgO catalysts

Table 2 presented the results of sorbitol hydrogenolysis over Ni-MgO catalysts under relatively mild conditions of 473 K and 4 MPa H_2, and sorbitol was mostly converted to glycerol and lower glycols mainly containing EG and 1,2-PG. Other compounds like sorbitans, mannitol, acetylacetone and lactic acid were also observed. The total carbon balance ranged from 92.3% to 100.3% for all the tests. When the Ni-Mg(1:9) catalyst was used, a 47.4% sorbitol conversion with a 66.2% total selectivity of glycols and glycerol was obtained. With Ni content increasing, the sorbitol conversion was improved to the biggest value of 67.8% over Ni-Mg(3:7) catalyst, and then dropped as the Ni loading continued to increase. The total selectivity of EG, 1,2-PG and glycerol, also reached the maximum of 80.8% on Ni-Mg(3:7) catalyst. The activity deterioration for the Ni-Mg(4:6) and Ni-Mg(5:5) catalysts compared with the catalysts with lower Ni-Mg ratios could be ascribed to the decrease of basicity and Ni surface area which were critical in the C–C bond cleavage and the subsequent hydrogenation [3,6].

From the reaction mechanism, the strong basicity of catalyst was conducive to the C–C scission in the retro-aldol condensation. Sorbitol and intermediates might also be abundantly adsorbed on the plentiful

Table 1
Characterization results of Ni-MgO catalysts.

Catalyst	Ni[a] (wt.%)	$D_{reduc.}$[b] (%)	S_{BET}[c] ($m^2\ g^{-1}$)	S_{Ni}[d] ($m^2\ g^{-1}$)	Basic.[e] ($\times10^{-6}$ mol g^{-1})	PS[f] (nm)	
						Ni	MgO
Ni-Mg(1:9)	14.6	52.4	193.5	2.3	362.2	7.0	7.1
Ni-Mg(2:8)	28.5	40.1	141.6	4.8	285.7	8.5	6.8
Ni-Mg(3:7)	38.4	36.2	106.9	6.2	257.9	9.1	6.7
Ni-Mg(4:6)	47.2	27.3	99.2	5.6	229.9	10.5	6.8
Ni-Mg(5:5)	56.7	18.9	79.0	3.8	175.8	10.8	6.4
MgO	–	–	262.0	–	380.8	–	9.8

[a] Ni loading, determined by ICP analysis.
[b] Degree of reduction, quantified from H_2-TPR data.
[c] BET surface area, measured by N_2-TPD.
[d] Ni surface area, characterized with H_2 chemisorption.
[e] Basicity, measured by CO_2-TPD.
[f] Particle size, calculated in XRD characterization from the Scherrer equation.

Table 2
Hydrogenolysis of sorbitol over Ni-MgO catalysts.[a]

Enter	Catalyst	Sorbitol	Product selectivity (%)					TC[d]
		Conv. (%)	EG	1,2 -PG	Glycerol	Gas products[b]	Others[c]	(%)
1	Ni-Mg(1:9)	47.4	16.6	24.5	25.1	15.2	14.0	97.2
2	Ni-Mg(2:8)	61.4	18.6	30.8	23.7	12.9	11.9	98.3
3	Ni-Mg(3:7)	67.8	26.0	33.7	21.1	9.7	8.1	99.6
4	Ni-Mg(4:6)	41.9	15.6	34.1	11.7	6.3	25.8	94.7
5	Ni-Mg(5:5)	33.0	10.3	28.6	10.9	10.4	29.9	93.4

[a] Reaction conditions: 20% aqueous sorbitol solution, 50 mL; catalyst amount, 0.5 g; reaction time, 4 h; H_2 pressure, 4 MPa; temperature, 473 K; stirring speed, 600 rpm.
[b] Gas products include CH_4, CO_2 and hexane.
[c] Others include acetone, methanol, ethanol, lactic acid, hydroxyacetone, butanediol, hexanediol, acetonyl acetone, mannitol, erythritol, sorbitans, isosorbide, etc.
[d] Total carbons, includes total organic carbons and total inorganic carbons.

alkaline sites to improve the reaction rate [17]. The addition of MgO or NaOH promoted the sorbitol conversion, however, the glycol selectivities decreased in spite of the extra alkaline sites introduced by MgO added (Table S1 in the SI). It could be concluded that the basicity of Ni-MgO was strong enough to perfectly facilitate this chemoselective reaction and such alkaline additives were hardly necessary [3]. For the Ni-Al(3:7) catalyst, NaOH significantly enhanced the sorbitol conversion and the product selectivity, though the resultant conversion was only 48.1%. The result indicated that the acidic carrier Al_2O_3 supported metal catalysts should proceed under harsher conditions and with an appropriate amount of basic additives to reduce the byproducts in sorbitol conversion [5,18].

As shown in Table 2, the Ni-Mg(3:7) catalyst with the highest nickel surface area exhibited the best catalytic performance, which suggested that the available active Ni sites were also essential for this conversion. During the recycling process, MgO was partly eroded by H_2O, reacted with CO_2 and transformed into $MgCO_3$. Therefore, the Ni nanoparticles aggregated (Fig. S3 in the SI) [9,19]. Based on the XRD and H_2 chemisorption analysis, the recycled Ni-Mg(3:7) catalyst in the second run possessed 19.4 nm average-sized Ni clusters with an only 3.5 m^2/g Ni surface area, over which the sorbitol conversion dropped to 58.7% along with a 63.5% total selectivity of EG, 1,2-PG and glycerol (Fig. S2 in the SI). Besides, the products with chelating groups would facilitate leaching and poisoning of Ni catalyst, which also led to the loss of catalytic activity [20]. Over Ni-MgO catalysts, the 1,2-PG selectivity increased and glycerol selectivity decreased with the Ni/Mg ratio ranging from 1/9 to 4/6, revealing that the catalysts with higher metal loading also enhanced the glycerol dehydration with C–O bond breaking [3,5,19,21]. The optimized Ni/Mg atomic ratio was 3/7 and the Ni-Mg(3:7) catalyst was chosen to investigate the influences of temperature, H_2 pressure and reaction time on the sorbitol hydrogenolysis.

3.3. The effects of reaction conditions on sorbitol hydrogenolysis

As revealed in Fig. 2, the sorbitol conversion increased rapidly with temperature increasing from 433 K to 453 K and then remained at about 70%, whereas the total selectivity of EG, 1,2-PG and glycerol reached 80.8% at 473 K followed by a significant decrease. So, polyols could be considerably converted under a lower temperature, while the further hydrogenation of intermediates into lower glycols would be favorable at the higher appropriate temperature [4]. Product distribution showed that the selectivity towards glycerol was reduced, but the total selectivity of C3 products including glycerol and 1,2-PG remained almost unchanged with reaction temperature increasing to 473 K. The increasing temperature could accelerate the glycerol hydrogenolysis to 1,2-PG with promoted C–O bond scission [19]. At the temperature higher than 473 K, further degradation of all the glycols was strongly enhanced, resulting in a sharp decline of product selectivity.

Fig. 3 showed that the sorbitol conversion increased significantly with higher H_2 pressure, together with a steady growth of glycerol selectivity. In contrast, the selectivity of EG and 1,2-PG reached the maxima of 33.7% and 26.0% under 4 MPa, and then dropped with the continuously increasing H_2 pressure. Thus, the higher H_2 pressure could promote the hydrogenation of unsaturated intermediates as well as the further degradation of glycols [21,22]. To our knowledge, the optimized H_2 pressure of 4 MPa was the lowest, suggesting that the Ni-MgO catalysts were indeed efficient.

As the reaction proceeded, both the sorbitol conversion and the glycerol selectivity gradually increased (Fig. 4). After 8 h, sorbitol was completely converted and the highest glycerol selectivity of 28.1% was acquired. However, the total selectivity of EG, 1,2-PG and glycerol reached the maximum when the reaction time was extended to 4 h, and subsequently dropped with time. GC analysis indicated that the deep degradation products generally increased over a prolonged period of time, like alcohols, CO_2, CH_4, and other alkanes.

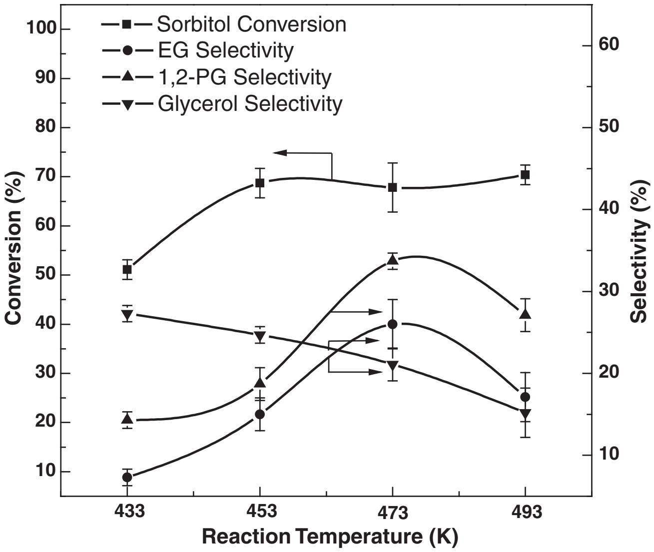

Fig. 2. Effect of reaction temperature on the sorbitol hydrogenolysis over Ni-Mg(3:7) catalyst under 4 MPa H_2 for 4 h.

4. Conclusions

Ni-MgO catalysts were very efficient for sorbitol hydrogenolysis to lower glycols, even under mild conditions and without basic promoters. Characterization results suggested that catalytic performance largely hinged upon the basicity and active metal sites. The poor hydrothermal stability of Ni-MgO catalyst would lead to the loss of activity in repeated runs. Under harsh conditions, the deep degradation was accelerated resulting in more byproducts and lower yield of glycols although the sorbitol conversion increased.

Acknowledgements

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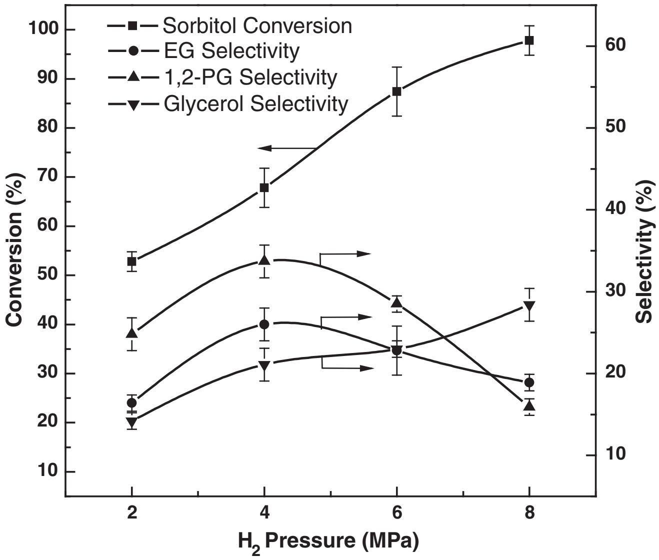

Fig. 3. Effect of H_2 pressure on the sorbitol hydrogenolysis over Ni-Mg(3:7) catalyst at 473 K for 4 h.

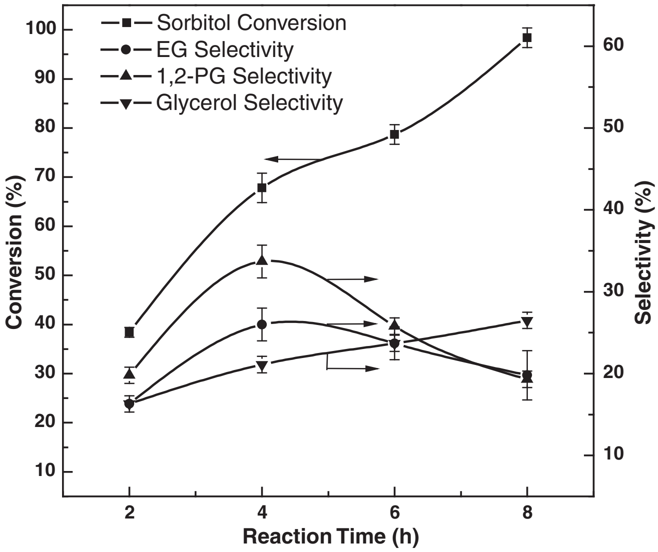

Fig. 4. Effect of reaction time on the sorbitol hydrogenolysis over Ni-Mg(3:7) catalyst under 4 MPa H_2 at 473 K.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.05.012.

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