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Sorbitol hydrogenolysis to glycerol and glycols over M-MgO (M = Ni, Co, Cu) nanocomposite: A comparative study of active metals

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ABSTRACT

The activities and selectivities of MgO-supported Ni, Cu, and Co catalysts have been compared in aqueous-phase hydrogenolysis of sorbitol to glycerol and glycols. All catalysts effectively catalyzed the sorbitol conversion into C2 and C3 polyols like glycerol, 1,2-propylene glycol, and ethylene glycol, but with different product distributions. The differences in activities and selectivities are ascribed to their different dehydrogenation/hydrogenation activities. The influences of base promoter, temperature, H₂ pressure, and reaction time were also studied. Added base promoter and prolonged reaction time enhanced sorbitol conversion for the three catalysts, but led to product degradation and decreased selectivity over Ni-MgO and Co-MgO, whereas selectivity maintained almost unchanged over Cu-MgO.

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1. Introduction

With the scarcity of fossil resources, there is a pressing need for the development of renewable fuels and chemicals to meet future economic and environmental requirements [1,2]. Biomass, which is currently regarded as the only sustainable and carbon-neutral source to produce chemicals, is rich in oxygen and is thus preferable for transformation into oxygenated chemicals [3]. Biomass-derived compounds like sorbitol and xylitol have carbon skeletons that are ideal for transformation and have abundant hydroxyl groups. Hydrogenolysis of sorbitol with selective C–C and C–O cleavage is a promising pathway for the production of glycerol (GL), 1,2-propylene glycol (PG), and

ethylene glycol (EG), which are commodity chemicals widely used in the polyester industry [4]. Recently, catalytic hydrogenolysis of sorbitol into PG and EG has been widely reported [5,6].

Sorbitol is a C6 polyol and can generate C2 and C3 lower glycols by selective C–C and C–O cleavage. The reported procedures for sorbitol hydrogenolysis generally occur over a metal catalyst promoted by base at 433–523 K and elevated H₂ atmosphere [1]. Ru, Ni, and Pt have superior hydrogenation activities and are considered to be very effective for sorbitol transformation [5]. For example, Banu et al. [7,8] found that NaY-supported Ni and Pt catalyzed sorbitol hydrogenolysis to PG and EG, and Ca(OH)₂ promoted sorbitol conversion without

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significantly affecting glycol selectivity. Zhou et al. [9,10] reported sorbitol hydrogenolysis to glycols over carbon nano-fiber-supported Ru catalyst and examined the influences of different bases on the reaction. They found that sorbitol conversion was greatly enhanced by promotion with bases, and CaO was the best base promoter in terms of excellent selectivity toward glycols. Leo et al. [11] examined the influences of supports and found that acidity promoted dehydration of the intermediates from retro-aldol condensation and thus improved glycol selectivity. Sun et al. [12,13] investigated xylitol hydrogenolysis to EG and PG over Ru, Pd, Rh, and Pt on different supports in the presence of $\text{Ca}(\text{OH})_2$; they found that Ru/C was the most effective catalyst when compared with Ru supported on metal oxides (TiO_2 , ZrO_2 , Al_2O_3 , and Mg_2AlO_x). They proposed that key reactions to generate EG and PG for xylitol hydrogenolysis involved dehydrogenation, retro-aldol condensation, dehydration, and hydrogenation. In summary, catalytic hydrogenolysis of sorbitol and xylitol can be achieved with a noble metal catalyst promoted by a basic additive. Promoters like NaOH and $\text{Ca}(\text{OH})_2$ have proved a positive influence on C–C scission where a widely accepted mechanism is the retro-aldol condensation as proposed by Wang et al. [14], which involves C–C cleavage in hydrogenolysis through retro-aldol and C–O bond cleavage through dehydration of a β -hydroxyl carbonyl.

However, excessive use of base is counteractive because of contaminants and problems like accelerated degradation of glycol products and separation difficulties, which occur when the alkali dissolves in the reaction solution. Our previous work demonstrated that the bifunctional Ni-MgO catalyst was very efficient in sorbitol conversion and facilitated chemoselective C–C cleavage for the formation of EG, PG, and GL [15]. Without the addition of alkali, MgO-supported Cu, Co, and Pt catalysts also showed bifunctional effects and were highly active for aqueous-phase glycerol hydrogenolysis to PG [16–19]. Considering the high costs of noble metal catalysts, it is desirable to develop efficient catalysts based on nonprecious metals for polyol hydrogenolysis. To the best of our knowledge, the use of supported Cu and Co to catalyze sorbitol hydrogenolysis has not been reported, and few studies using Ni-, Cu-, or Co-based catalysts have compared their activities and selectivities in sorbitol hydrogenolysis.

In this study, MgO-supported Ni, Co, and Cu catalysts were prepared by co-precipitation and their activities were compared in sorbitol hydrogenolysis to EG, PG, and GL. The effects of the active metal on the activity and selectivity as a function of base promoter, temperature, H_2 pressure, and reaction time were studied.

2. Experimental

2.1. Catalyst preparation and characterization

Ni-MgO, Co-MgO, and Cu-MgO catalysts were prepared by co-precipitation as reported previously [15]. The aqueous mixture solution of $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cu}$) and $\text{Mg}(\text{NO}_3)_2$ with total metal concentration of 1 mol/L was stirred vigorously at 323 K while Na_2CO_3 solution (1.2 mol/L) was added dropwise until the pH reached 8 with a titration velocity of 1 mL/min. After precipitation, the suspension was stirred for 8 h, thoroughly washed with deionized water, and dried at 323 K for 12 h. The precipitate was then calcined at 773 K for 3 h in air and reduced in H_2 for another 3 h. Co-MgO and Cu-MgO were similarly prepared by co-precipitation except that the calcining and reduction temperatures for Co and Cu were 873 and 573 K, respectively. The molar ratio of Mg/M was fixed at 3. For comparison, MgO was prepared with the same method. All precursors used in the preparation were purchased from Sinopharm Chemical Reagent and were used as received. Raney Ni, Raney Co, and Raney Cu were purchased from Dalian Tongyong Chemical.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffraction spectrometer using $\text{Cu K}\alpha$ radiation at 80 kV and 40 mA. Transmission electron microscopy (TEM) was performed using an H-7650 Hitachi transmission electron microscope operating at 160 kV. N_2 adsorption-desorption experiments were performed with a Micromeritics ASAP 2020 surface area and porosity analyzer. The surface area calculation was based on the BET method.

2.2. Catalytic test

The conversion of sorbitol was performed in a 50-mL stain-

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less steel autoclave. In a typical experiment, 25 mL of 10 wt% sorbitol aqueous solution and 0.25 g of catalyst were charged to the reactor, which was then flushed five times with flowing H₂ to remove air, and pressurized with H₂ to the desired pressure. The reactor was heated to 473 K, and the mixture was stirred at 1000 r/min. After reaction, the autoclave was cooled to room temperature. The product mixture was then filtered on a 0.22-μm membrane, collected, and analyzed.

The products were identified by gas chromatography–mass spectrometry (GC–MS) using a 7890A gas chromatograph (Agilent, USA) coupled with a 5975C mass spectrometer (Agilent). Chromatographic separation was achieved on an HP-INNOWax column (30 m × 0.25 mm; film thickness 0.25 μm). The injection temperature was 523 K for an injection volume of 1 μL with a split ratio of 30:1. The column temperature program was 353 K for 10 min with a rise to 493 K at a rate of 2 K/min with a hold time of 30 min. The peaks were matched according to the NIST11 database. Glycols such as EG, PG, and other low-boiling compounds were analyzed by GC coupled with flame ionization detection (FID) with a CP-Wax 58 column (FFAP, 25 m × 0.25 mm × 0.2 μm film thickness, Chrompack). The temperature program of the column oven was from 333 K (2 min) to 523 K (8 min) at a rate of 20 K/min. The injector and detector temperatures were 523 and 553 K, respectively. The FID detector used H₂ (30 mL/min) and N₂ was applied as the carrier gas (1 mL/min). High-boiling substances like GL, erythritol, mannitol, and sorbitol were analyzed by ion chromatography (IC) with a Dionex CarboPac MA1 column (4 mm × 250 mm). The IC column temperature was 303 K, and the mobile phase was 250 mmol/L NaOH solution (0.4 mL/min). The combination of GC and IC techniques is very efficient to quantify the reaction as reported previously [20]. The gas products were collected in air bags and measured by GC coupled with a thermal conductivity detector. The total organic carbons (TOC) were determined using a liquiTOC II analyzer. The conversion and selectivity were calculated using the equations:

$$\text{Conversion (\%)} = \frac{\text{(moles converted sorbitol)}}{\text{(moles charged sorbitol)}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{(moles carbon in specific product)}}{\text{(moles carbon in converted sorbitol)}} \times 100\%.$$

3. Results and discussion

3.1. Properties of catalysts

The properties of the metal catalysts are shown in Table 1. Because of a lack of contrast between the support and the metal particles (Fig. 1), no meaningful particle size distribution of the catalysts was obtained. Therefore, we calculated the crystallite size based on XRD patterns (Fig. 2) using Scherrer's equation. The results demonstrated that the Ni-, Co-, and Cu-based composites prepared by co-precipitation possessed similar MgO and metal crystallite size, which was in accordance with the TEM images. The crystallite size of MgO was 5.2 nm, whereas these of MgO support and active metals in all catalysts were around 10 nm. Cu-MgO showed the largest crystallite size. Low-contrast metal crystallites on MgO observed in the TEM

Table 1
Properties of MgO, Ni-MgO, Co-MgO, and Cu-MgO catalysts.

Catalyst	Crystallite size ^a (nm)				Surface area ^b (m ² /g)	Pore volume ^c (mL/g)	Pore diameter ^c (nm)
	MgO	Ni	Co	Cu			
MgO	5.2	—	—	—	266	0.22	3.4
Ni-MgO	10.6	9.6	—	—	109	0.17	6.1
Co-MgO	10.5	—	11.4	—	43	0.10	10.0
Cu-MgO	13.6	—	—	14.8	37	0.13	14.2

^a Calculated from XRD characterization using Scherrer's equation.

^b Based on BET method.

^c Quantified from N₂ sorption.

micrographs indicated that Ni, Co, and Cu may might with a raft-like morphology on the MgO support. The desorption spectra determined by N₂ physisorption and pore diameter distribution for the three catalysts are given in Fig. 3. The MgO showed typical IV-type isotherms where the adsorbed volume was up to 0.4 relative pressures with H₂-type hysteresis loop. With Ni, Co, and Co loaded on MgO, the hysteresis loop became narrow, and the pore structure of MgO was shifted because of the introduction of metal onto the MgO. As shown in Table 1, the surface area of MgO decreased dramatically from 266 to 109 m²/g for Ni-MgO, whereas the surface areas of Co-MgO and

Fig. 1. TEM images of MgO, Ni-MgO, Co-MgO, and Cu-MgO catalysts.

Fig. 2. XRD patterns of MgO, Ni-MgO, Co-MgO, and Cu-MgO catalysts.

Fig. 3. Nitrogen sorption isotherms (a) and pore distribution (b) of MgO, Ni-MgO, Co-MgO, and Cu-MgO catalysts.

Cu-MgO were less than 50 m²/g. The average pore volume of MgO was larger than those of the catalysts with metal loading, but the pore sizes of Ni-MgO, Cu-MgO, and Co-MgO were much bigger than that of MgO.

3.2. Hydrogenolysis of sorbitol on Ni, Co, and Cu based catalysts

Table 2 shows the results of sorbitol hydrogenolysis over MgO-supported Ni, Co, and Cu nanocomposites and over the corresponding skeleton catalysts with and without a base promoter at 473 K and 6 MPa H₂. All catalysts were effective for sorbitol hydrogenolysis. Previously, the catalytic hydrogenolysis of sorbitol, xylitol, and glycerol was usually conducted with a noble metal catalyst and a base promoter, where promoters like NaOH and Ca(OH)₂ have proved a positive influence on C–C scission. Table 2 shows satisfactory results for the bifunctional MgO-supported Ni, Co, and Cu catalysts. Qualitative results

show that the products mainly included EG, PG, GL, erythritol, and mannitol as a result of dehydroxylation reaction (C–O hydrogenolysis), retro-aldol condensation (C–C hydrogenolysis), and isomerization (Scheme 1). Other compounds like methanol, 2-propanol, ethanol, *n*-propanol, *n*-butanol, sorbitan, acetylacetone, acetol, and lactic acid were also observed. The total carbon balance ranged from 91% to 98%; Ni-MgO showed the poorest carbon balance, followed by Co-MgO and Cu-MgO. From Table 2, it is apparent that different metal catalysts on MgO performed differently in terms of sorbitol conversion and product selectivity. The Ni-MgO catalyst was observably more effective and selective in producing C2 and C3 polyols, giving markedly higher selectivity toward EG, PG, and GL than Co-MgO and Cu-MgO. After 4 h at 473 K under 6 MPa H₂, the Ni-MgO catalyst gave 57.2% conversion of sorbitol with a total C2/C3 polyol selectivity of 66.0%. PG (33.5%), EG (17.1%), and GL (15.4%) were the main products, followed by sorbitan and

Table 2

Hydrogenolysis of sorbitol over Ni, Co, and Cu catalysts.

Entry	Catalyst	Conversion (%)	C2 and C3 polyol selectivity (%)				Others ^a (%)	TOC balance (%)
			EG	PG	GL	Sum		
1	Ni-MgO	57.2	17.1	33.5	15.4	66.0	19.6	91
2	Co-MgO	39.4	12.3	23.9	12.1	48.3	33.5	93
3	Cu-MgO	37.0	4.9	35.8	16.3	57.0	19.0	98
4	Ni-MgO + Ca(OH) ₂ ^b	85.6	20.2	31.9	3.2	55.3	9.1	85
5	Co-MgO + Ca(OH) ₂ ^b	80.2	16.4	20.8	0.9	38.1	19.9	88
6	Cu-MgO + Ca(OH) ₂ ^b	78.7	23.7	32.6	4.0	60.3	19.5	97
7	Raney Ni	33.4	8.1	17.0	10.5	35.6	25.6	84
8	Raney Co	22.9	5.4	11.3	18.8	35.5	27.9	89
9	Raney Cu	18.2	4.3	15.1	20.6	40.0	31.2	95
10	Raney Ni + MgO ^c	45.7	13.8	23.9	6.8	44.5	19.7	79
11	Raney Co + MgO ^c	36.6	12.0	18.9	9.9	40.8	25.7	81
12	Raney Cu + MgO ^c	30.3	17.8	25.1	13.4	56.3	24.8	93
13	Raney Ni + Ca(OH) ₂ ^b	72.9	16.7	25.8	1.5	44.0	11.2	76
14	Raney Co + Ca(OH) ₂ ^b	67.2	12.5	16.0	2.4	30.9	17.0	87
15	Raney Cu + Ca(OH) ₂ ^b	59.3	18.5	29.0	0.2	47.7	22.3	95
16	None	2.0	—	—	—	—	—	100
17	MgO	6.3	—	—	—	—	—	98
18	Ca(OH) ₂	12.1	—	—	—	—	—	96

Reaction conditions: Aqueous solution of 10 wt% sorbitol 25 mL, catalyst 0.25 g, H₂ pressure 6 MPa, 473 K, 4 h, stirring speed 1000 r/min.

^a Others include acetone, methanol, ethanol, lactic acid, butanediol, hexanediol, mannitol, erythritol, and sorbitans.

^b 1 g Ca(OH)₂ was added as a co-catalyst.

^c Equivalent amount of MgO was added.

erythritol (Table 2, entry 1). The conversion of sorbitol over Co-MgO was similar to Cu-MgO with only 2.4% slightly higher conversion. The product distribution of Co-MgO was basically the same as Ni-MgO, whereas Cu-MgO showed superior selectivity to PG. The ratios of PG to EG were about 2 over Ni-MgO and Co-MgO, whereas this value was almost 7 over Cu-MgO. When additional base promoter was used, obvious enhancement of activity was observed (Table 2, entries 4–6). A decrease of selectivity to PG and GL was observed on Ni-MgO and Co-MgO catalyst, suggesting that the added base led to excessive hydrogenolysis and the generation of more gaseous product, as indicated by the poor TOC balance. However, an increase in selectivity for C2 and C3 polyols was obtained over Cu-MgO but with a different product distribution. For Cu-MgO catalyst, base promoter cooperated with the catalyst and enhanced conversion without dramatically affecting the inherent selectivity toward PG. The influences of active metal and added base were consistent with previously reported results [4,21]. With added $\text{Ca}(\text{OH})_2$, the selectivity toward EG increased, which suggests that $\text{Ca}(\text{OH})_2$ enhanced the C–C cleavage at the C2–C3 position via retro-aldol condensation. Ye et al. [22] reported that glycerol could be obtained over Ni- Al_2O_3 with a selectivity of 44.9%, suggesting that Ni on an acidic support followed a reaction pathway different from that when on a basic support. The TOC balance indicated that Ni and Co were much more active in the deep degradation with the generation of gaseous products.

Generally, the C–C hydrogenolysis ability of Cu and Co is considered weak, whereas C–O cleavage over Ni and Co is rather strong. This means that Cu and Co are suitable candidates

for the conversion of glycerol to PG with high selectivity without C–C scission. Liu et al. [23] recently reported selective hydrogenolysis of xylitol to EG and PG on Cu- SiO_2 nanocomposite, indicating that well-dispersed Cu is effective in the hydrogenation of intermediates.

To illuminate the effects of MgO and the influences of base promoter on sorbitol hydrogenolysis over Ni-MgO, Co-MgO, and Cu-MgO nanocomposites, the conversions of sorbitol with Raney Ni, Raney Co, and Raney Cu were investigated. Raney Ni and Raney Co showed slightly lower conversion of sorbitol with poorer selectivity to target products than Raney Cu. Raney Ni exhibited distinct activity in sorbitol hydrogenolysis; the conversion reached 33.4% and the sum of C2 and C3 polyol selectivity was 35.6%. When MgO was added, both the activity and selectivity toward the lower polyols were improved over all the skeleton catalysts, suggesting that the metal and MgO played synergistic roles in promoting sorbitol transformation. When $\text{Ca}(\text{OH})_2$ was added, performance was significantly enhanced. The TOC balances over Ni-MgO and Co-MgO further indicated the difference in the degradation of polyols in the reaction. The results also suggested that bulk metals favored deep hydrogenolysis with more gaseous product generated under the investigated reaction conditions, as demonstrated by poor TOC balance (Table 2).

Wang et al. [14] reported a mechanistic study of polyol hydrogenolysis, and proposed C–C cleavage in hydrogenolysis through retro-aldol and C–O bond cleavage through dehydration of a β -hydroxyl carbonyl. Montassier et al. [24] found that for hydrogenolysis, C–O cleavage depended on dehydrogenation, which was catalyzed by the metal catalyst. The catalyst

Scheme 1. Reaction pathway for sorbitol hydrogenolysis to C2/C3 polyols and the degradation reaction of C2/C3 polyols under hydrothermal hydrogenation conditions over M-MgO catalysts (M = Ni, Co, Cu).

also catalyzes hydrogenation, whereas base promoters accelerate the dehydration of the former dehydrogenated species. Therefore, the overall selectivity of sorbitol hydrogenolysis was determined by both the nature of the active metal and the acidic or basic nature of the reaction system. In view of the activity and selectivity of sorbitol conversion presented in Table 2, it is advisable to tune the metal species and basicity to obtain a selective catalyst for polyol transformation to lower polyols. The reaction pathway for sorbitol hydrogenolysis to C2/C3 polyols and further degradation of the C2/C3 polyols under hydrothermal hydrogenation conditions over M-MgO catalyst are shown in Scheme 1.

3.3. Effects of reaction conditions on sorbitol hydrogenolysis

As shown in Fig. 4, sorbitol conversion over Ni-MgO, Co-MgO, and Cu-MgO increased rapidly with temperature increasing from 433 to 493 K, whereas the selectivity of EG, PG, and GL differed greatly for the different catalysts. The selectivity of both EG and PG over all catalysts increased as a result of elevating the reaction temperature, suggesting that polyols could be converted at lower temperature, whereas further hydrogenation of intermediates into lower glycols would be favorable at appropriate higher temperatures. However, at temperatures above 473 K, further degradation of the glycols and GL were enhanced, leading to a decline in product selectivity. Product distribution over Cu-MgO showed that the selectivity toward GL reduced as the temperature increased, but the total selectivity of EG, PG, and GL remained almost unchanged as the reaction temperature increased from 433 to 453 K. Selectivity as high as 35.5% toward PG was achieved at 473 K. At 493 K, the combined selectivity of EG, PG, and GL dropped by 24% when compared with the reaction at 433 K. This difference was ascribed to excessive hydrogenolysis at elevated temperatures.

Increasing temperature can accelerate sorbitol and glycerol hydrogenolysis to PG. At 473 K above, further degradation of PG was strongly enhanced, resulting in a significant decline of PG selectivity over Ni-MgO and Co-MgO. This suggests that the temperature had profound effects on the bond cleavage over Ni-MgO and Co-MgO. Satisfactory selectivity of EG and PG was

obtained at 473 K, so this temperature was selected to study the effects of H₂ pressure and reaction time on the activities and selectivities for sorbitol hydrogenolysis over Ni-MgO, Co-MgO, and Cu-MgO.

The influence of H₂ partial pressure on hydrogenolysis was studied at 473 K with a reaction time of 4 h. Figure 5 shows the effects of H₂ pressure on the activities and selectivities for sorbitol hydrogenolysis over Ni-MgO, Co-MgO, and Cu-MgO. The selectivity behavior with increased H₂ pressure was different for the three catalysts. Sorbitol conversion increased significantly with higher H₂ pressure, together with a steady growth of EG selectivity for all catalysts. In contrast, the selectivity of GL dropped with increasing H₂ pressure. For Ni-MgO catalyst, the PG selectivity reached a maximum of 35.8% under 6 MPa and then dropped as the H₂ pressure increased. High H₂ pressure is considered to promote the hydrogenolysis and thus had a negative effect on PG and GL selectivity. A steady increase of PG selectivity was observed over Co-MgO with as the H₂ pressure increased. Interestingly, the selectivity of PG over Cu-MgO remained high under different H₂ pressures.

Increased H₂ pressure promoted the hydrogenation of unsaturated intermediates and further degradation of products. The differences in the effects of H₂ pressure over different metals may be a result of the varying abilities of Ni, Co, and Cu in C–C and C–O hydrogenolysis, which suggests that Cu was weakest in the degradation of glycols. The changes in product distribution with different H₂ pressure may be explained by the different rates of formation of the lower polyol products, as well as the rates of consumption of the intermediates. The product selectivity of Ni-MgO was more sensitive to the pressure than Co-MgO and Cu-MgO. In light of these results, it is clear that Ni particles are more active in the hydrogenolysis of sorbitol with C–C and C–O cleavage, whereas Cu provided good activity in C–O cleavage rather than in C–C bond cleavage.

Figure 6 illustrates the influence of reaction time on sorbitol conversion and selectivity over Ni-MgO, Co-MgO, and Cu-MgO. As the reaction proceeded from 2 to 4 h, both the sorbitol conversion and the C2 and C3 polyol selectivity gradually increased. The C2 and C3 polyol selectivity over Ni-MgO reached a maximum when the reaction time was extended to 4 h, and

Fig. 4. Effects of temperature on activities and selectivities for sorbitol hydrogenolysis over Ni-MgO (a), Co-MgO (b), and Cu-MgO (c). Reaction conditions: 10 wt% sorbitol aqueous solution 25 mL, 6.0 MPa H₂, 4 h.

Fig. 5. Effects of H₂ pressure on activities and selectivities for sorbitol hydrogenolysis over Ni-MgO (a), Co-MgO (b), and Cu-MgO (c). Reaction conditions: 10 wt% sorbitol aqueous solution 25 mL, 473 K, 4 h.

Fig. 6. Influence of reaction time on activities and selectivities over Ni-MgO (a), Co-MgO (b), and Cu-MgO (c). Reaction conditions: 10 wt% sorbitol aqueous solution 25 mL, 473 K, 6 MPa H₂.

subsequently dropped with time. GC analysis and TOC balance indicated that deep degradation products like alcohols, CO₂, CH₄, and other alkanes generally increased over prolonged periods on Ni-MgO. The selectivity toward EG and PG grew slowly with increased reaction time, whereas a slight decrease of GL selectivity was observed over Co-MgO. However, Cu-MgO showed different character; the selectivity of PG remained significantly high (above 30%) irrespective of the reaction time. Thus, it appears that the presence of Cu was necessary to achieve high PG selectivity. This is in accordance with results observed for the conversion of glycerol over Cu catalysts with a long reaction time, where PG selectivity was maintained as high as 97% [18].

4. Conclusions

Ni-MgO, Co-MgO, and Cu-MgO nanocomposites showed different activities and selectivities in sorbitol hydrogenolysis. The experimentally observed activities of the metal catalysts were in the order of Ni-MgO > Co-MgO > Cu-MgO, whereas the reaction conditions had profound influence on the selectivity of Ni-MgO-catalyzed sorbitol conversion. Co-MgO and Cu-MgO,

with relatively poor activities in C–C hydrogenolysis, maintained high selectivities toward the target glycols and glycerol. Ni-MgO and Co-MgO favored the formation of PG and EG, whereas PG was the predominant product over Cu-MgO. This study provides direction toward the efficient design of bimetallic multifunctional catalysts capable of rational tuning of the product distribution in sorbitol hydrogenolysis.

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Graphical Abstract

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Sorbitol hydrogenolysis to glycerol and glycols over M-MgO (M = Ni, Co, Cu) nanocomposite: A comparative study of active metals

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Ni-MgO, Co-MgO, and Cu-MgO bifunctional catalysts prepared by co-precipitation showed diverse activity and selectivity in sorbitol hydrogenolysis to glycerol (GL), 1,2-propylene glycol (PG), and ethylene glycol (EG) under various reaction conditions.

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MgO负载金属双功能催化剂用于生物基山梨醇氢解制丙二醇、乙二醇和甘油

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摘要: 甘油、丙二醇和乙二醇是非常重要的化工原料和合成聚酯类、聚醚类树脂的单体, 也可作为功能化合物直接应用于化妆品、食品及制冷等领域。随着生物炼制行业的发展, 其作为生物基平台化合物在未来可以获得更为广泛的应用。从富含氧原子的纤维素出发制备甘油和二元醇, 符合绿色化学化工的原子经济性、工艺经济性和生产过程清洁等原则, 也是生物质资源化利用的重要途径。因此, 近年来以纤维素及其衍生物糖和糖醇为原料, 通过氢解反应制备甘油和二元醇的研究在国外已广泛开展。在目前已报道的氢解糖和糖醇研究中, 几乎均采用包含金属催化剂和液体碱助剂的耦合催化体系, 所用液体碱为NaOH, KOH和Ca(OH)₂等, 使用量很大。这些碱性助剂可以提高金属催化剂对糖醇加氢和氢解反应的催化活性, 促进底物转化, 但同时也不可避免地加剧了二醇产物进一步氢解和自身缩合反应, 使产物选择性降低。在产物分离和提纯过程中, 过高的碱浓度也会诱导甘油和二醇产品自身缩合, 使分离困难, 提高了分离成本。反应液的强碱性还增加了生产过程的设备成本。本文以固体碱MgO为载体, 分别负载Ni, Co和Cu等金属制备出Ni-MgO, Co-MgO和Cu-MgO等双功能催化剂, 应用于糖醇氢解反应, 从而减少或避免使用液体碱添加剂。木质纤维素降解得到的单糖中含量最大的是六碳糖, 本文以六碳糖加氢衍生物山梨醇为模型底物, 考察了所制MgO负载金属双功能催化剂催化糖醇氢解制甘油和二元醇的活性和选择性, 研究了反应条件对山梨醇氢解生成二醇和甘油的影响。

山梨醇氢解反应在不锈钢反应釜中进行. 采用气相色谱-质谱联用对氢解产物进行定性分析, 采用气相色谱和离子色谱分别对反应中低沸点和高沸点产物进行定量分析. 结果表明, 在Ni-MgO, Co-MgO和Cu-MgO (其中活性金属和载体MgO的比例为1:3) 三种催化剂上山梨醇均能高效转化为乙二醇、1,2-丙二醇和甘油; 无论是否添加Ca(OH)₂, 山梨醇氢解活性顺序均为Ni-MgO > Co-MgO > Cu-MgO. 三种催化剂上产物选择性有较大差异, Ni-MgO和Co-MgO对乙二醇和1,2-丙二醇具有较好的选择性, 其中1,2-丙二醇与乙二醇比例约为2, 而Cu-MgO催化剂对1,2-丙二醇选择性较高, 1,2-丙二醇与乙二醇比例约为7. 同时, 考察了反应温度、压力和反应时间对三种催化剂上山梨醇转化活性和产物选择性的影响. 随着温度升高, 所有催化剂活性均显著增加, 其中Ni-MgO和Cu-MgO催化山梨醇氢解对反应条件较为敏感, 而Co-MgO催化剂对反应条件不敏感. 在Ni-MgO催化剂上, 可以在较低的反应温度下获得较高的产物选择性.

关键词: 生物质; 氢解; 山梨醇; 氧化镁; 负载型金属催化剂; 双功能催化剂

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