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# Hydrogenolysis of biomass-derived sorbitol over La-promoted Ni/ZrO<sub>2</sub> catalysts†

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Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts were prepared by a step-by-step impregnation method through regulation of the contents of the active component and alkali. The introduction of an alkaline promoter not only enhanced the alkalinity of the catalyst but also improved the dispersion of Ni on the catalyst owing to the strong interaction between Ni<sup>2+</sup> and alkali promoter. The synergistic effect between Ni and La<sub>2</sub>O<sub>3</sub> was beneficial to selective hydrogenolysis of sorbitol. Under the optimal reaction conditions, sorbitol conversion reached nearly 100% and target products (ethylene glycol, 1,2-propanediol, and glycerol) selectivity reached 74.8%. Metal–alkali coordination mechanism and possible pathways for target products formation were proposed.

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## 1. Introduction

On account of excessive exploitation of fossil fuel sources and serious contaminative environmental problems, worldwide efforts have been devoted to exploiting new energy sources, especially clean and renewable energy sources.<sup>1–3</sup> As a clean and renewable resource, biomass energy is an ideal alternative resource with its advantages of high reserves, renewability, and non-greenhouse-gas emission.<sup>4–6</sup> Sugar alcohols (sorbitol and xylitol) are the important platform compounds produced from biomass and can be converted into high-value-added chemicals through hydrogenolysis, oxidation, or selective reduction.<sup>7–10</sup>

It is widely believed that hydrogenolysis of polyols to glycols involves three key steps:<sup>11,12</sup> First, some hydroxyl groups on the molecule of polyols are dehydrogenated at the metal active sites. Subsequently, C–C bond cleavage of intermediates occurs by an alkaline catalyst *via* retro-aldol condensation. Finally, the carbonyl intermediates are hydrogenated to target glycols on the metal surfaces.<sup>13</sup> For sorbitol conversion into small-molecule alcohols, researchers have mainly focused on the synergistic regulation of metal active sites and alkaline sites, which are useful for selective cleavage of C–C and C–O

bonds.<sup>14,15</sup> According to previous reports,<sup>11–17</sup> owing to their high activity for C–C bond cleavage, Ni- and Ru-based catalysts have been often applied in experiments. Unfortunately, they also catalyse excessive C–C bond scission to produce by-products. In contrast, Cu-based catalysts exhibit good activities for C–O, C=O, and C=C bond hydrogenation and C–OH dehydrogenation but poor reactivity activity for C–C bond cleavage.<sup>18</sup> Huang *et al.*<sup>19</sup> observed that, by using Cu–SiO<sub>2</sub> catalysts, one could obtain ~60% yield of glycols and glycerol (GLY) in the presence of Ca(OH)<sub>2</sub>. Ni–NaY and Pt–NaY catalysts were used in the presence of Ca(OH)<sub>2</sub>. It was found that the main products on Ni–NaY and Pt–NaY catalysts were 1,2-propylene glycol (1,2-PG) and GLY, respectively.<sup>20</sup>

Composite catalysts combining with metallic sites and basic sites have been used in this reaction.<sup>21</sup> A Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst can promote C–C and C–O bonds cleavage, leading to the conversion of glucose to glycols (with a selectivity of 67%).<sup>22</sup> Ordered mesoporous 10.9% Ni/6.3% CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> showed better catalytic performance in the hydrogenolysis of sorbitol, obtaining a 56.9% yield of ethylene glycol (EG) and 1,2-PG.<sup>23</sup> A Cu–Ni/ZrO<sub>2</sub> catalyst was efficient for xylitol conversion to EG and 1,2-PG with a 65% total selectivity in water without a base additive.<sup>24</sup> Recently, researchers<sup>25</sup> found that Ru–(Mn–Al)O<sub>x</sub> solid base catalysts exhibited high performance (with 58% selectivity of glycols) in the hydrogenolysis of xylitol under base-free conditions. This catalyst, however, was not stable during the reaction because the Mn species were converted to other compounds. 3% Ru/4.5% MnO/C also showed good activity with 70% selectivity of glycols in a water–alcohol mixture solvent, avoiding competitive decarbonylation at the Ru sites. However, the catalyst exhibited poor hydrothermal stability in the hydrogenolysis of xylitol.<sup>26</sup> Zhang<sup>27</sup> reported the use of 10% Ni–0.5%

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Ir/La<sub>2</sub>O<sub>3</sub> catalyst for the conversion of cellulose to EG and 1,2-PG in a higher yield of 63.7%.

Although the catalytic system reported in the previous literature can efficiently realize sorbitol hydrogenolysis, the commonly used alkaline additives are slightly soluble CaO or Ca(OH)<sub>2</sub>, which can easily corrode equipment and cause poor product separation.<sup>28,29</sup> Therefore, the development of new solid-alkali-supported metal catalysts can effectively solve this problem. In this paper, using the inexpensive alkaline additive La<sub>2</sub>O<sub>3</sub> and inexpensive active Ni, we prepared Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts with different Ni/La ratios by using the initial wetness impregnation method. The physicochemical properties of the catalysts were characterized by X-ray diffraction, scanning electron microscopy, H<sub>2</sub> and CO<sub>2</sub> temperature-programmed reduction techniques, inductively coupled plasma atomic emission spectrometry, X-ray photoelectron spectroscopy and Transmission Electron Microscopy. The catalytic performance was investigated in sorbitol hydrogenolysis *via* different reaction parameters. The synergistic effect between the metal and the base of the catalysts was discussed and the possible pathways for target products formation were also proposed during sorbitol hydrogenolysis.

## 2. Experimental section

### 2.1. Catalyst preparation

The Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts were prepared by initial wetness impregnation. ZrO<sub>2</sub> was added to a La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution with different La contents, and the mixture was stirred for 4 h at room temperature. The excess H<sub>2</sub>O was evaporated at 80 °C for 12 h. Subsequently, the obtained powder was dried overnight at 100 °C. Finally, the powder was calcined at 550 °C for 4 h at a heating rate of 5 °C min<sup>-1</sup> to obtain the La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>.

The obtained La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> was added to a Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution with a certain Ni amount, followed by rigorous stirring at room temperature at 4 h. Then the sample was dried and calcined following the same procedure mentioned above. Finally, the Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts were reduced in the H<sub>2</sub> atmosphere at 500 °C for 4 h before reaction.

### 2.2. Catalyst characterization

The textural properties of the catalysts were determined using an automated surface area and pore size analyzer (Quantachrome Co., USA) at -196 °C.

X-ray powder diffraction patterns were obtained on a Rigaku D/max-rC X-ray diffractometer operated at 40 kV and 40 mA using Cu K $\alpha$  radiation ( $\lambda$  = 0.154 nm) and  $2\theta$  was scanned from 10° to 80° with a step size of 0.0167°.

The surface morphology of the catalyst was observed using a Hitachi S-4800 scanning electron microscope (SEM).

The thermogravimetry (TG) experiments were operated from room temperature to 550 °C at a heating rate of 20 °C min<sup>-1</sup> under an air atmosphere.

CO temperature-programmed desorption (CO-TPD) were measured using a CHEMBET 3000 chemisorption/desorption apparatus (Quantachrome Co., USA). In a typical test, a 50 mg

sample was placed into a U-shaped quartz tube, reduced at 500 °C for 4 h under H<sub>2</sub> flow and purged at the same temperature for 40 min under He flow. After cooling to 50 °C, it was adsorbed with CO for 80 min. The sample was then purged by a He flow to remove the physical adsorbed CO for 1 h. The sample was heated from 50 °C to 850 °C at a heating rate of 10 °C min<sup>-1</sup> and the CO desorption was monitored with a TCD detector.

CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) measurement was conducted on CHEMBET 3000 equipment (Quantachrome, USA). In a typical run, 50 mg sample was put into a U-shaped quartz tube and purged with He at 400 °C for 40 minutes. After cooling to 50 °C, it was adsorbed with CO<sub>2</sub> for 1 h. Finally, He was again introduced to remove the physical adsorbed CO<sub>2</sub> for 1 h. The sample was heated from 50 °C to 900 °C at 10 °C min<sup>-1</sup> heating rate and the CO<sub>2</sub> desorption was monitored with a TCD detector.

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was performed on an Auto Chem II 2920 chemical adsorption instrument. For a typical test, 20 mg sample was purged with He flow at 250 °C for 1 h, then the temperature was decreased to 50 °C. The sample was heated from 50 °C to 900 °C at a heating rate of 10 °C min<sup>-1</sup> under a 5% H<sub>2</sub>/He flow.

The Ni and La leaching after reaction was analyzed by the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement using a PerkinElmer OPTIMA 8000 instrument.

The microstructure of catalysts was analyzed by Transmission Electron Microscopy (TEM) on a JEOL JEM-2100EX electron microscopy and the electron beam accelerating voltage was 200 kV.

X-ray photoelectron spectroscopy (XPS) was performed by using a Thermo Fisher Scientific Escalab 250 Xi photoelectron spectrometer and values were corrected by C 1s (284.8 eV). The spectra was excited using Mg K $\alpha$  (1253.6 eV) radiation (operated at 200 W) of a twin anode in the constant analyzer energy mode with a pass energy of 30 eV.

### 2.3. Sorbitol hydrogenolysis and products analysis

Sorbitol hydrogenolysis was performed in a stainless steel autoclave, into which 20 mL of 100 mg mL<sup>-1</sup> sorbitol aqueous solution and 0.4 g of freshly reduced catalyst were introduced. After eliminating the air residue by H<sub>2</sub> flushing, the reactor was pressurized by H<sub>2</sub> and was heated to a certain temperature for a certain period. During the hydrogenolysis process, the H<sub>2</sub> pressure was kept at a constant 4 MPa by supplying H<sub>2</sub>. After reaction, the reaction system was cooled to collect the products.

The stability experiment procedure was described as follows: after each reaction cycle, the reaction liquid was centrifuged, the upper layer liquid was removed for product analysis, and the lower catalysts continued to be used in the next cycle reaction without any treatment. This cycle was repeated five times. For catalyst regeneration, the used catalysts were calcined in an air atmosphere at 500 °C for 1 h and then were reduced in an H<sub>2</sub> atmosphere at 500 °C for 4 h.

The aqueous products were analysed with a Waters 2695 HPLC containing a refraction index and UV detector (RID-2414)



and SH1011 separation column. Sulfuric acid solution ( $0.005 \text{ mol L}^{-1}$ ) was used as the eluent at a  $0.5 \text{ mL min}^{-1}$  flow rate. The gas products were analyzed with a Ke Chuang Gas Chromatography 9800FP with a Porapak Q column.

The sorbitol conversion and selectivity  $S_{(i)}$  of product  $i$  were defined by the following formulas:

$$\text{conversion} = \frac{X_1 - X_2}{X_1} \times 100\%,$$

$$S_{(i)} = \frac{n_i M_0}{6(X_1 - X_2)} \times 100\%,$$

where  $X_1$  expressed the initial sorbitol weight and  $X_2$  expressed the sorbitol weight after reaction,  $n_i$  represented the carbon moles of product  $i$  (GLY, EG, and 1,2-PG) and  $M_0$  was molar weight of sorbitol.

### 3. Results and discussion

#### 3.1. Characterizations of catalysts

Table 1 listed the texture properties of different catalysts. The Brunauer–Emmett–Teller (BET) area and pore volume of  $\text{ZrO}_2$  were  $40.9 \text{ m}^2 \text{ g}^{-1}$  and  $0.20 \text{ mL g}^{-1}$ , respectively, whereas for  $\text{Ni/ZrO}_2$ , with the introduction of Ni, the specific surface area and pore volume of 10%  $\text{Ni/ZrO}_2$  catalyst decreased. However, the average pore size of  $\text{Ni/ZrO}_2$  increased after Ni introduction. This might be because Ni entered into the inner channels of  $\text{ZrO}_2$  after impregnation, causing a decrease of specific surface area. The addition of  $\text{La}_2\text{O}_3$  did not obviously cause the specific surface area and pore volume to decrease, indicating that it could highly disperse on the  $\text{ZrO}_2$  surface.

The XRD patterns of different catalysts were presented in Fig. 1. The diffraction patterns of NiO found in 10%  $\text{Ni/ZrO}_2$  had diffraction peaks at  $37.3^\circ$  and  $43.3^\circ$ , corresponding to the (111) and (200) crystal planes of NiO, respectively. With  $\text{La}_2\text{O}_3$  introduction, the intensity of NiO decreased, which indicated that  $\text{La}_2\text{O}_3$  improved the dispersion of NiO by the enhanced interaction between  $\text{Ni}^{2+}$  and  $\text{La}_2\text{O}_3$ .<sup>30</sup> With increasing  $\text{La}_2\text{O}_3$  in the catalysts, no obvious changes in NiO diffraction patterns could be observed. However, with further increasing  $\text{La}_2\text{O}_3$  loading to

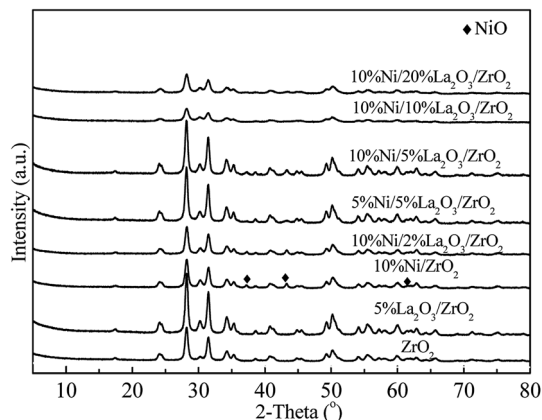


Fig. 1 XRD patterns of La-promoted  $\text{Ni/ZrO}_2$  catalysts by different Ni and La loadings.

>10%, the intensity of  $\text{ZrO}_2$  and NiO decreased remarkably. The reduction of the diffraction peaks was possibly attributed to the decrease of the relative content of  $\text{ZrO}_2$  on the catalysts. No  $\text{La}_2\text{O}_3$  diffraction peaks were observed even the loading was as high as 20%, indicating that  $\text{La}_2\text{O}_3$  existed as an amorphous form and highly dispersed on  $\text{ZrO}_2$  surface. The weakness of the NiO diffraction peak should be due to the good dispersion of NiO on the catalyst surface, which was promoted by  $\text{La}_2\text{O}_3$ . Compared to  $\text{Ni/ZrO}_2$ , the NiO particle sizes in the  $\text{Ni/La}_2\text{O}_3/\text{ZrO}_2$  catalysts were significantly reduced, again evidencing Ni stabilization by  $\text{La}_2\text{O}_3$  addition. Fig. 1 and 2 also showed that the catalysts had a good crystalline phase before reaction, indicating that the support and Ni particles were unchanged and demonstrating high hydrothermal stability.

To investigate the effect of  $\text{La}_2\text{O}_3$  on the reduction characteristics of catalysts, we investigated the  $\text{H}_2$  reduction behavior through the  $\text{H}_2$ -TPR technique (Fig. 3). There was a single peak at  $\sim 500^\circ \text{C}$  for 10%  $\text{Ni/ZrO}_2$ , which corresponded to the reduction of NiO particles. After adding  $\text{La}_2\text{O}_3$ , the reduction peaks of NiO shifted to lower temperatures, showing that  $\text{La}_2\text{O}_3$  weakened the interaction between Ni species and the  $\text{ZrO}_2$  support. Upon further increase of the  $\text{La}_2\text{O}_3$  loadings, the reduction peak of NiO was further reduced to  $\sim 400^\circ \text{C}$ .

Table 1 Textural properties and  $\text{H}_2$ -chemisorption of La-promoted  $\text{Ni/ZrO}_2$  catalysts

Catalyst	$S_{\text{BET}}^a$ ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume <sup>b</sup> ( $\text{mL g}^{-1}$ )	Pore diameter <sup>c</sup> (nm)	$D_{\text{Ni}}^d$ (%)	$d_{\text{NiO}}^e$ (nm)
$\text{ZrO}_2$	40.9	0.20	16.7	—	—
10% $\text{Ni/ZrO}_2$	36.8	0.17	19.8	5.3	25
10% $\text{Ni/2\% La}_2\text{O}_3/\text{ZrO}_2$	35.2	0.18	18.2	10.7	8
10% $\text{Ni/5\% La}_2\text{O}_3/\text{ZrO}_2$	36.4	0.17	20.1	9.6	11
10% $\text{Ni/10\% La}_2\text{O}_3/\text{ZrO}_2$	33.5	0.17	18.8	10.8	7
10% $\text{Ni/20\% La}_2\text{O}_3/\text{ZrO}_2$	30.9	0.16	19.0	10.7	8
5% $\text{Ni/5\% La}_2\text{O}_3/\text{ZrO}_2$	37.9	0.19	19.6	12.6	5
7.5% $\text{Ni/5\% La}_2\text{O}_3/\text{ZrO}_2$	35.7	0.17	20.3	11.0	9
12.5% $\text{Ni/5\% La}_2\text{O}_3/\text{ZrO}_2$	31.8	0.12	22.4	7.9	15

<sup>a</sup> Calculated by using the BET method. <sup>b</sup> Determined by the cumulative volume between  $P/P_0 = 0.03$ –0.99. <sup>c</sup> Calculated from the desorption branch by using the Barrett–Joyner–Halenda (BJH) method. <sup>d</sup> Ni dispersion values were obtained by CO-TPD. <sup>e</sup> Diameters of NiO particles were calculated by using the Scherrer formula ((111) crystal plane).



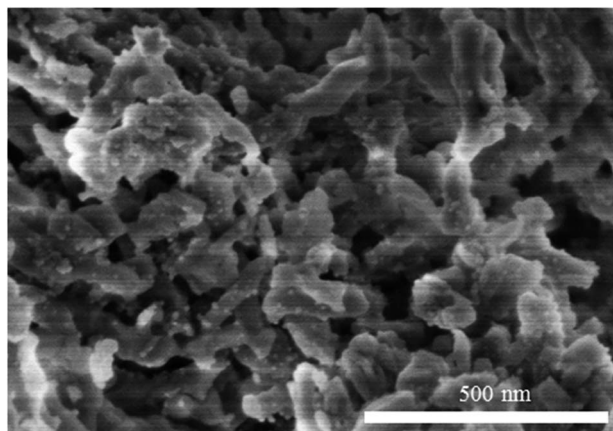


Fig. 2 SEM image of 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst before reaction.

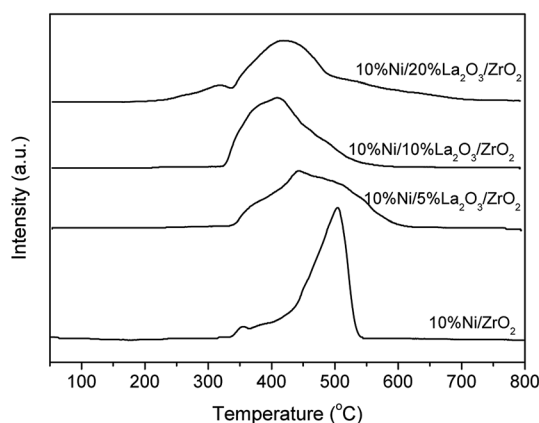


Fig. 3 H<sub>2</sub>-TPR profiles of catalysts with different La promoters.

The basicities of the Ni-based catalysts with different La<sub>2</sub>O<sub>3</sub> loadings were displayed in Fig. 4. The desorption peak of CO<sub>2</sub> at 150 °C for ZrO<sub>2</sub> and those obtained at 750 °C and 850 °C for La<sub>2</sub>O<sub>3</sub> indicated that ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> presented weak basicity and strong basicity, respectively. Because Ni was supported on ZrO<sub>2</sub> without La<sub>2</sub>O<sub>3</sub>, the weak basicity was kept but the total

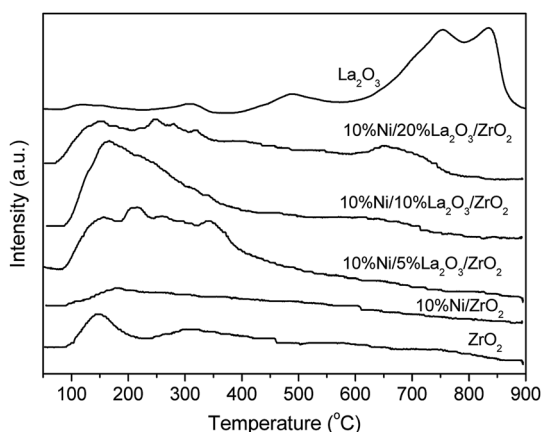


Fig. 4 CO<sub>2</sub>-TPD profiles of catalysts with different La loadings.

number of basic sites was reduced. However, for the Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts, the number of weak basic sites remarkably increased, suggesting that the La<sub>2</sub>O<sub>3</sub> additive strengthened the weak basicity.

### 3.2. Catalytic performance

Table 2 listed the results of sorbitol hydrogenolysis over Ni-based catalysts with different contents of La<sub>2</sub>O<sub>3</sub> under the conditions of 220 °C and 4 MPa H<sub>2</sub> pressure. Throughout the process, sorbitol was mostly converted to the target products. By-products such as erythritol, xylitol, *etc.* were also observed, and the data for those were not shown here. When a 10% Ni/ZrO<sub>2</sub> catalyst was used, a 66.6% sorbitol conversion with a 23.7% total selectivity containing GLY, EG, and 1,2-PG was achieved. With the addition of La<sub>2</sub>O<sub>3</sub>, sorbitol conversion and total glycol selectivity were obviously increased. With increasing La<sub>2</sub>O<sub>3</sub> content from 2 wt% to 5 wt%, the sorbitol conversion sharply rose from 63.5% to 96.8%. Meanwhile, the total selectivity for the target products also rose from 37.3% to 74.8%.

However, when we continued to increase the La<sub>2</sub>O<sub>3</sub> content to 20 wt%, the sorbitol conversion and total selectivity dropped to 87.5% and 62.2%, respectively. The above results indicated that the alkaline La<sub>2</sub>O<sub>3</sub> promoted catalytic performance for obtaining the target products, which was conducive to C–C scission in the retro-aldol condensation and also helpful for improving the desired product selectivity. Sorbitol and intermediates might also be adsorbed on the alkaline sites to improve the reaction.<sup>31</sup> However, the excessive La<sub>2</sub>O<sub>3</sub> promoted abundant reverse C–C scission and formed other by-products, which led to a decrease in the selectivity of the desired product. Therefore, it could be concluded that 5% La<sub>2</sub>O<sub>3</sub> content was appropriate for optimizing the reaction (entries 2–5). In addition, different contents of Ni were investigated by using 5% La<sub>2</sub>O<sub>3</sub> as a base (entries 6–9). Increasing the Ni content from 5% to 12.5% led to increased sorbitol conversion but the total selectivity of target products remained at ~66%. It was obvious that the basic La<sub>2</sub>O<sub>3</sub> plays a more profound role in glycol formation from sorbitol hydrogenolysis than Ni. Given the best performance in sorbitol hydrogenolysis to the target products, the optimized 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst was chosen to investigate the influence of temperature, reaction time, and H<sub>2</sub> pressure.

As shown in Fig. 5A, the sorbitol conversion increased from 26% to 100% as the reaction temperature increased from 200 °C to 240 °C, which indicated that temperature had an important effect on sorbitol conversion. The selectivity of GLY, EG, and 1,2-PG increased as the reaction temperature increased from 200 °C to 220 °C. However, when the reaction temperature was higher than 220 °C, the selectivity of GLY and target products total selectivity decreased while the selectivity of EG and 1,2-PG still increased, this result demonstrated that GLY acted as the key intermediate for further conversion to EG and 1,2-PG possibly through dehydration and hydrogenation.

Fig. 5B showed the effect of H<sub>2</sub> pressure. The conversion of sorbitol slightly reduced with the increase of H<sub>2</sub> pressure, while the selectivities of the target products were almost unchanged.





Table 2 Hydrogenolysis of sorbitol to glycols over different Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts<sup>a</sup>

Entry	Catalyst	Conversion (%)	Product selectivity (C mol%)			Total selectivity (%)
			GLY	EG	1,2-PG	
1	10% Ni/ZrO <sub>2</sub>	66.6	13.1	3.9	6.7	23.7
2	10% Ni/2% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	63.5	18.3	5.2	13.8	37.3
3	10% Ni/5% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	96.8	27.7	20.3	26.8	74.8
4	10% Ni/10% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	94.2	24.5	17.9	28.4	70.8
5	10% Ni/20% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	87.5	21.2	14.2	26.8	62.2
6	5% Ni/5% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	55.8	30.2	13.3	21.7	65.3
7	7.5% Ni/5% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	75.4	30.3	14.3	21.8	66.4
8	10% Ni/5% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	76.6	32.1	13.6	20.4	66.1
9	12.5% Ni/5% La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	71.3	31.6	13.9	20.8	66.3

<sup>a</sup> Reaction conditions: 10% sorbitol contained in an aqueous solution of 40 mL; catalyst amount = 1 g; temperature = 220 °C; initial H<sub>2</sub> pressure = 4 MPa. Entries 1–5 are for 4 h; entries 6–9 are for 2 h. GLY = glycerol; EG = ethylene glycol; 1,2-PG = 1,2-propylene glycol.

This indicated that the target products obtained by sorbitol hydrogenolysis were insensitive to the H<sub>2</sub> pressure.

The effect of reaction time on sorbitol conversion and product selectivity was presented in Fig. 5C. The sorbitol conversion increased with the reaction time, reaching almost 100% at 4 h. Meanwhile, the selectivity of GLY decreased from

31% to 10% as reaction time increased from 0.5 h to 8 h. At 4 h, the selectivities of EG and 1,2-PG reached the maximum values. At the same time, xylitol and erythritol were also detected in the liquid phase, obtaining the selectivity of 5.6% and 1.8%, respectively. Trace ethanol was also detected in the liquid phase. There were also a certain amount of gas products such as

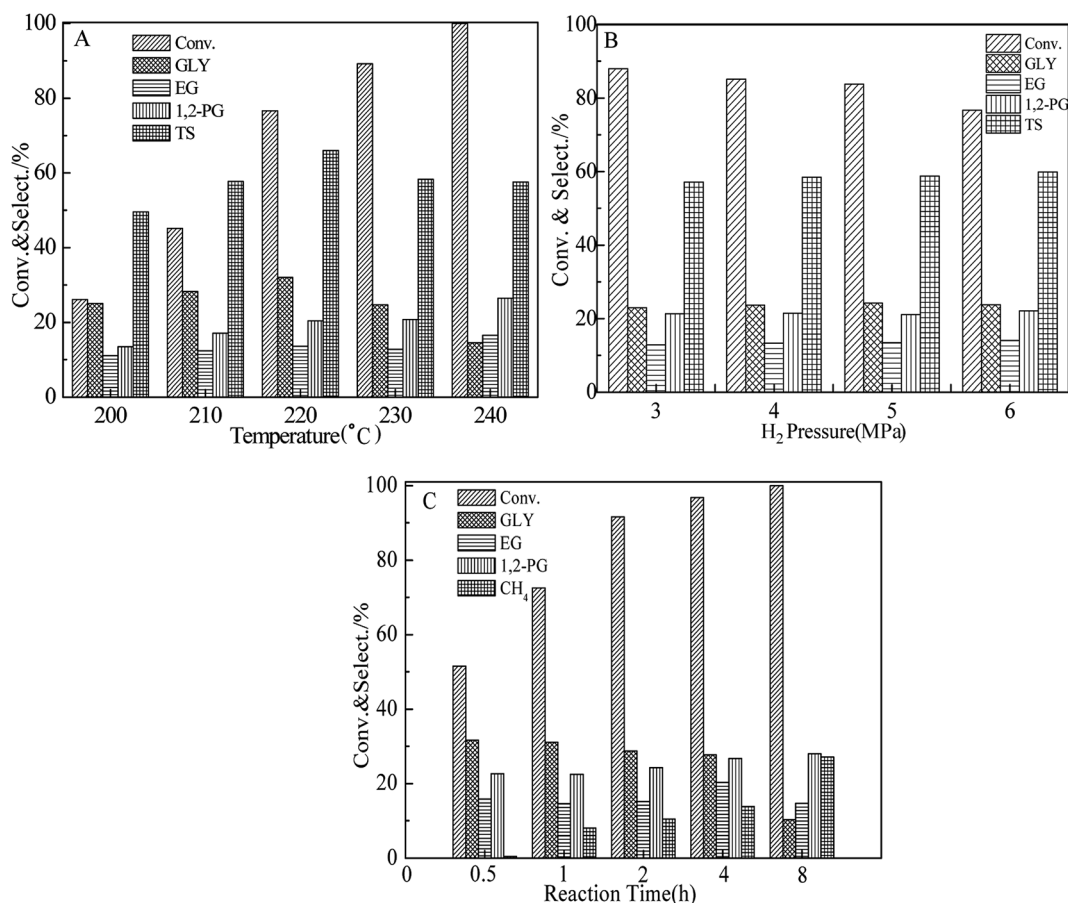


Fig. 5 Influence of reaction temperature (A), initial H<sub>2</sub> pressure (B), and reaction time (C) on sorbitol hydrogenolysis to glycols over 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>. Reaction conditions: 10% sorbitol contained in an aqueous solution of 40 mL; catalyst amount = 1 g; temperature = 220 °C; initial H<sub>2</sub> pressure = 4 MPa; time = 2 h. "TS" means total selectivity of GLY, EG, and 1,2-PG.



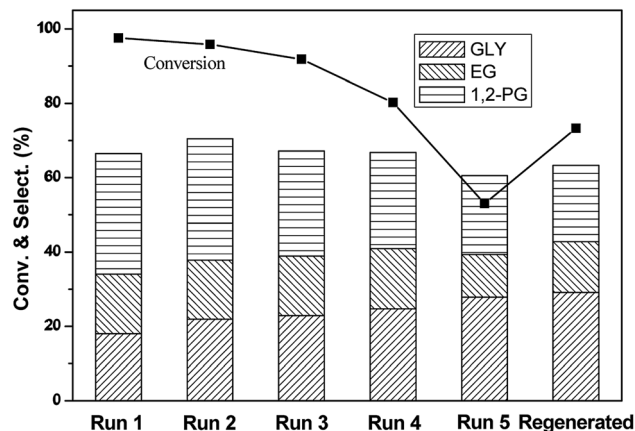


Fig. 6 Stability and regeneration test of 10% Ni/5%  $\text{La}_2\text{O}_3/\text{ZrO}_2$  in sorbitol hydrogenolysis to glycols. Reaction conditions: 10% sorbitol contained in an aqueous solution of 40 mL; catalyst amount = 1 g; temperature = 220 °C; initial  $\text{H}_2$  pressure = 4 MPa; time = 4 h.

$\text{CH}_4$ , CO, and  $\text{CO}_2$ . Unfortunately, the  $\text{CH}_4$  selectivity increased to 27% at 8 h. With increasing of reaction time, the yields of small molecule monohydric alcohols and gas-phase products increased. In a word, the optimized conditions were determined as: initial  $\text{H}_2$  pressure of 4 MPa, reaction temperature of 220 °C and reaction time of 2 h.

The stability of the catalyst was of great importance for industrial applications. A stability test was conducted using a 10% Ni/5%  $\text{La}_2\text{O}_3/\text{ZrO}_2$  catalyst and the optimized reaction conditions (Fig. 6). After reaction, the catalyst was separated *via* filtration and directly used for the next run without any treatment. As shown in Fig. 6, the sorbitol conversion decreased rapidly from 98% to 52% after five cycles, while the target products total selectivity slightly decreased to 60%. After regeneration of the used catalyst by calcination and reduction, the catalytic performance could be regenerated partially based on the sorbitol conversion and glycols selectivity. The leaching of  $\text{Ni}^{2+}$  was 1.5 wt%, 0.8 wt%, 0.3 wt%, 0.1 wt%, 0.03 wt%, respectively, after each run. For  $\text{La}^{3+}$ , the leaching was 1.9 wt%, 1.2 wt%, 0.8 wt%, 0.6 wt%, 0.3 wt%, respectively. It was inferred that metal elution might be one factor of catalyst deactivation.<sup>26</sup>

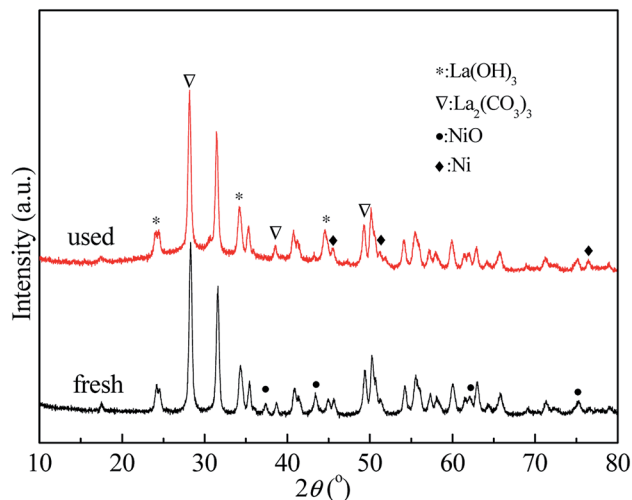


Fig. 8 XRD patterns of the fresh and the used 10% Ni/5%  $\text{La}_2\text{O}_3/\text{ZrO}_2$  after the fifth used.

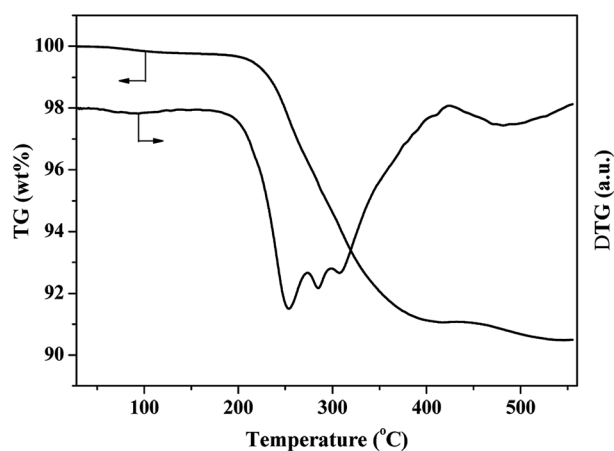


Fig. 9 TG-DTG profiles of 10% Ni/5%  $\text{La}_2\text{O}_3/\text{ZrO}_2$  catalyst after sorbitol hydrogenolysis and drying at 100 °C.

According to Fig. 7, the La XPS spectra of the fresh and used catalysts indicated that their chemical valence was almost the same, showing the stable La species under the current

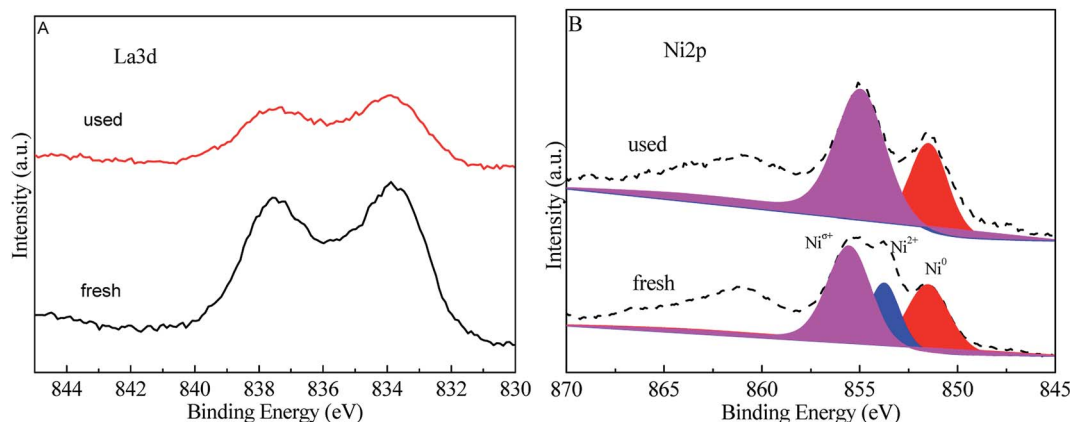


Fig. 7 XPS spectra of La 3d (A) and Ni 2p (B) in the fresh and the fifth used 10% Ni/5%  $\text{La}_2\text{O}_3/\text{ZrO}_2$  catalysts.



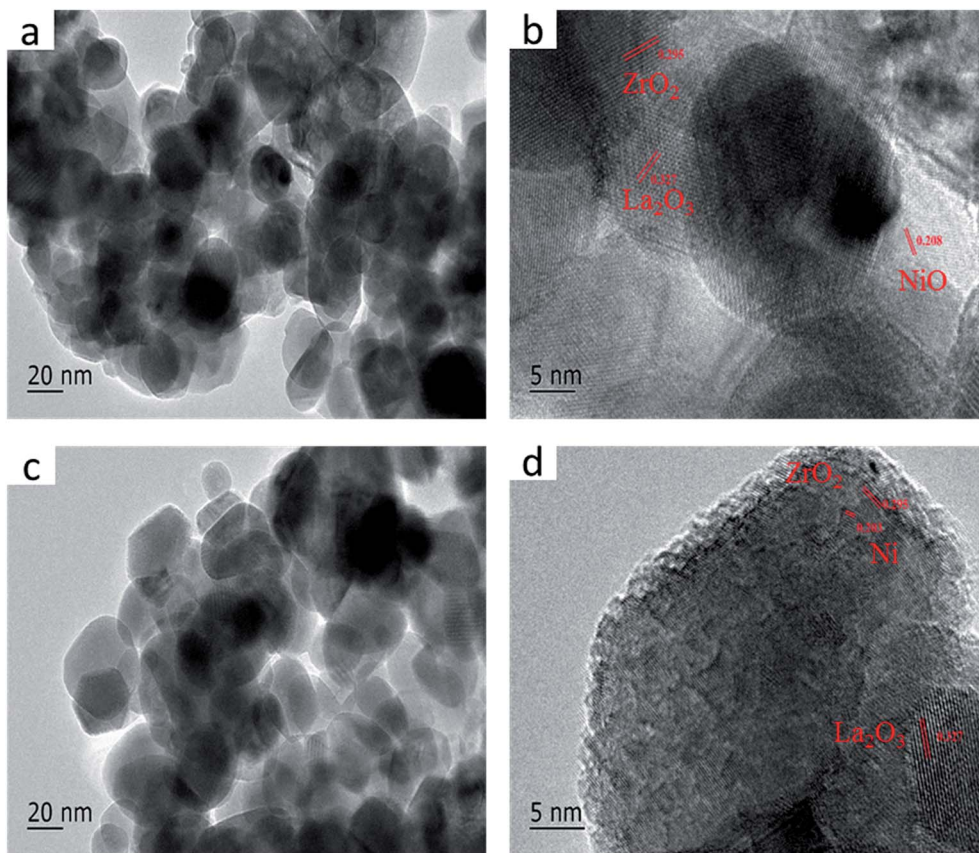


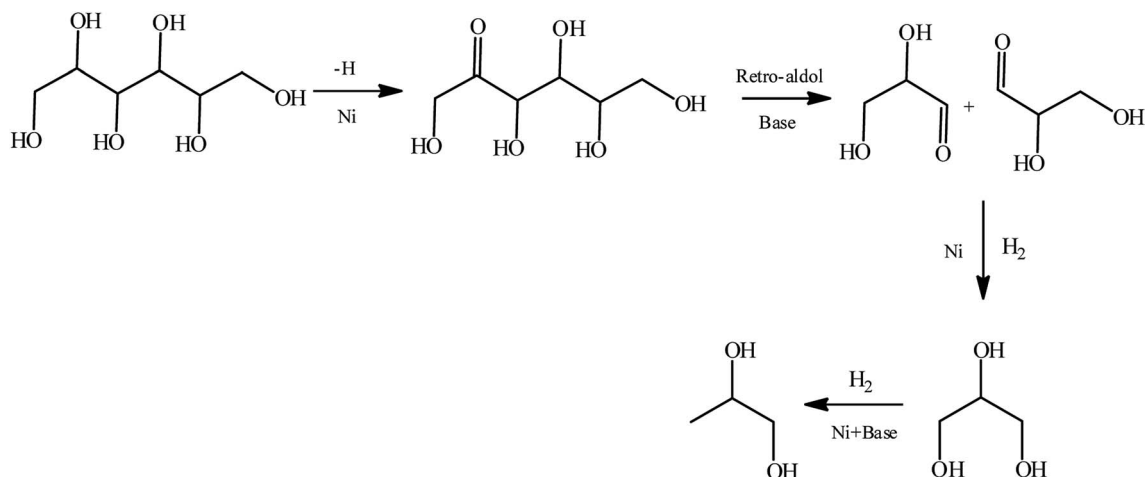
Fig. 10 TEM images of fresh and used catalysts: (a and b) fresh and (c and d) after the fifth used 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>.

hydrothermal conditions. For the Ni species, partial oxidation took place after the fifth cycle. It also could be seen from XRD pattern (Fig. 8) that the catalyst after the fifth cycle was mainly contained La(OH)<sub>3</sub> and La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> phase.<sup>32,33</sup>

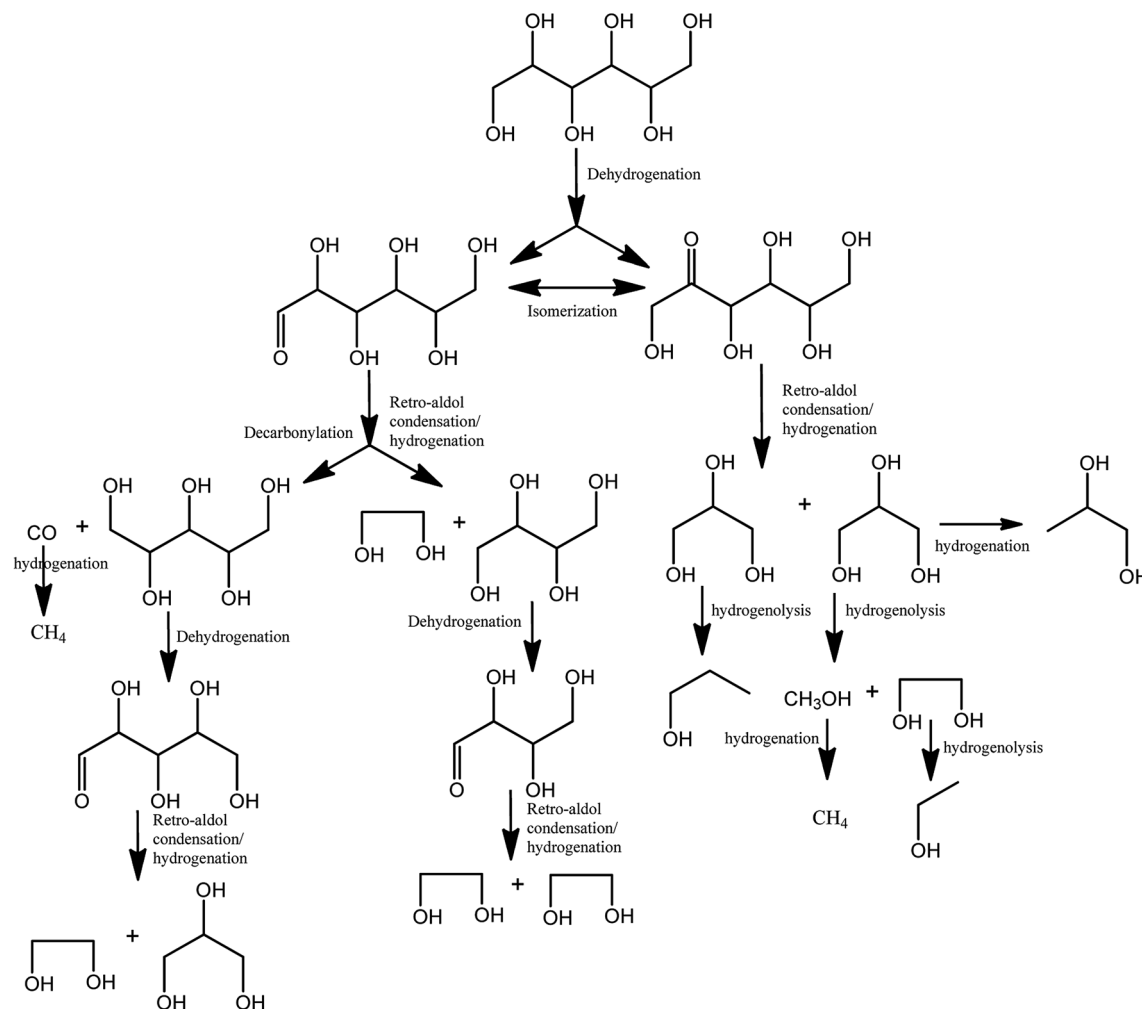
TG analysis<sup>27</sup> (Fig. 9) showed that weight loss at 350 °C was attributed to the removal of surface hydroxyl group and CO<sub>3</sub><sup>2-</sup>. TEM analysis was also carried out for the same catalyst after reaction (Fig. 10), there were no obvious change of the catalysts, so it could be concluded that catalyst deactivation was not

caused by carbon deposition. The main reason for deactivation of the catalyst and decrease of target product selectivity was due to the metal leaching.

Based on the distributions of products in our case and the previous reports,<sup>11–14</sup> we proposed reaction pathway for sorbitol hydrogenolysis to 1,2-PG (Scheme 1) and possible pathways for target products formation from sorbitol hydrogenolysis over 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst in Scheme 2. In Scheme 1, sorbitol was dehydrogenated at C<sub>2</sub>-position, and then



Scheme 1 Reaction pathway for sorbitol hydrogenolysis to 1,2-PG over the Ni based catalyst.<sup>34</sup>



Scheme 2 Possible pathways for sorbitol hydrogenolysis to small molecular glycols.

glyceraldehyde was formed under the action of base. C=O of glyceraldehyde was easily hydrogenated to GLY, and finally 1,2-PG was formed under the action of H<sub>2</sub>, Ni and base.

In the current case, metal Ni and basic La<sub>2</sub>O<sub>3</sub> synergistically promoted the rate-determined sorbitol dehydrogenation to form the corresponding C<sub>6</sub> aldehyde sugar. The C<sub>6</sub> aldehyde sugar could be further isomerized to the relative ketone sugar with the aid of the base La<sub>2</sub>O<sub>3</sub>. Afterward, the aldehyde and ketone sugars were hydrogenolyzed to the C<sub>3</sub>–C<sub>4</sub> aldehyde and a ketone containing polyols intermediates *via* the retro-aldol reaction, where the C<sub>3</sub> counterpart was hydrogenated to GLY and the C<sub>4</sub> intermediate was further converted into the C<sub>2</sub> glycolaldehyde *via* a similar retro-aldol reaction followed by hydrogenation to EG. However, GLY could be further converted into C<sub>1</sub> and C<sub>2</sub> intermediates, which were finally transferred to CH<sub>4</sub> and EG. In addition, decarbonylation and aqueous phase reformation could not be ruled out because trace amounts of CO and CO<sub>2</sub> were detected besides CH<sub>4</sub>. During this process, the synergy between metallic Ni and basic La<sub>2</sub>O<sub>3</sub> in the catalyst played an essential role in obtaining the target C<sub>2</sub>–C<sub>3</sub> polyols with high selectivity.

## 4. Conclusions

Ni/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts were prepared *via* initial wetness impregnation and used as the metal–base bi-functional catalysts for the hydrogenolysis of sorbitol into target small molecular polyol products. The addition of La<sub>2</sub>O<sub>3</sub> improved the basicities of the Ni-based catalyst and promoted dispersion of Ni particles by strong interactions of Ni and La<sub>2</sub>O<sub>3</sub>. By optimizing the sorbitol hydrogenolysis process, we could obtain the highest target products selectivity of 74.8% over 10% Ni/5% La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst, under the conditions of 220 °C, 4 MPa H<sub>2</sub> pressure and 4 h of reaction time. The possible metal–alkali coordination mechanism and possible pathways for target products formation were proposed. Ni metal promoted dehydrogenation and hydrogenation reaction, basic promoter was benefit to C–C bond cleavage, and afterwards polyols were produced by a series of small carbonyl molecules hydrogenation reactions.

## Conflicts of interest

There are no conflicts to declare.





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