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Selective hydrogenolysis of biomass-derived xylitol to ethylene glycol and propylene glycol on Ni/C and basic oxide-promoted Ni/C catalysts

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ABSTRACT

The selective hydrogenolysis of xylitol to ethylene glycol and propylene glycol was examined on Ni/C catalysts in the presence of solid bases, e.g. Ca(OH)₂ and CeO₂, physically mixed with or co-supported with Ni on C. Compared with Ru/C, the Ni/C catalysts were more selective to the two target glycols under identical conditions, apparently as a result of their lower hydrogenation activity and consequently favored the C—C cleavage of xylose intermediate by the base catalyst over its competitive hydrogenation on the Ni particles. Noticeably, the presence of the solid bases rendered the Ni particles resistant to leaching and sintering, and thus stable in the xylitol hydrogenolysis. Supporting the solid bases, especially CeO₂ and CaO, with the Ni particles on C led not only to a reduction in the amount of solid bases required, but also efficient formation of the two glycols with negligible lactic acid. For instance, on Ni-CaO/C (at a CaO/Ni molar ratio of 0.66), the combined selectivity to ethylene glycol and propylene glycol, together with glycerol, reached 69.5% at nearly 100% xylitol conversion at 473 K, 4.0 MPa H₂. These features of the basic oxide-promoted Ni catalysts show their promising advantages over the noble Ru catalysts, upon optimization of their compositions and structures, and the reaction parameters, for the efficient hydrogenolysis of xylitol and other lignocellulose-derived polyols to produce the two target glycols.

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1. Introduction

Naturally occurring biomass provides the only practical source of renewable liquid fuels and organic chemicals [1–4]. In this context, due to their rich chemistry and large availability from non-edible hemicellulose and cellulose, xylitol and sorbitol are considered the key primary building blocks in the synthesis of various value-added chemicals [5–8]. One such example is their catalytic hydrogenolysis to ethylene glycol and propylene glycol, which provides a promising route for the sustainable production of the two important commodity glycols that are manufactured today in industry from petroleum-based ethylene and propylene via their epoxide intermediates [9–17].

Recent efforts have demonstrated the efficacy of supported Ru and Ni catalysts in the presence of basic promoters (e.g. $Ca(OH)_2$) for the hydrogenolysis of xylitol and sorbitol to ethylene glycol and propylene glycol [9–15]. Zhou et al. [9] reported an 85.7% sorbitol conversion and 51.3% selectivity to the two glycols on a carbon nanofiber-supported Ru catalyst at 493 K and 8.0 MPa H₂. We previously [10] studied the xylitol hydrogenolysis on Ru/C and achieved a combined selectivity of ~61% to the two glycols at nearly 100%

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0920-5861/\$ - see front matter © 2014 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cattod.2013.12.040 xylitol conversion in the presence of Ca(OH)₂ under relatively mild conditions of 473 K and 4.0 MPa H₂. In term of the Ni catalysts, Yuan and co-workers [11] achieved sorbitol conversion of above 90% and selectivity to the two glycols of 55-60% on Ce-promoted Ni/Al₂O₃ catalysts with Ca(OH)₂ at 513 K and 7.0 MPa. Banu et al. [12] reported that Ni–NaY catalyzes the sorbitol hydrogenolysis in the presence of Ca(OH)₂ to the two glycols with a total selectivity of 76% at 75% sorbitol conversion at 493 K and 6.0 MPa H₂. Sotak et al. [14] found that a Ni₂P/C catalyst in the presence of $Ba(OH)_2$ is efficient for the xylitol hydrogenolysis, providing a 71.4% selectivity to the two glycols at 99% conversion under relatively mild conditions (473 K and 4.0 MPa H₂). Chen et al. [15] used a bifunctional co-precipitated Ni-MgO catalyst with a Ni/Mg molar ratio of 3/7 in sorbitol hydrogenolysis, and at 473 K and 6.0 MPa H₂, obtained 80.8% selectivity to ethylene glycol, propylene glycol and glycerol at 67.8% conversion.

These previous studies show that the Ni catalysts exhibit comparable selectivities to the two target glycols to those on the Ru catalysts. However their potential as efficient polyol hydrogenolysis catalysts is limited due to their inferior activities as they require harsher reaction conditions (*i.e.*, higher reaction temperatures or H₂ pressures) and show lower stabilities that need to be further improved. Meanwhile, these studies apparently encounter low selectivities to the two glycols particularly from the viewpoint of industrial practice, which is maybe related, at least partly, to the

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Table 1

Activities and selectivities in xylitol hydrogenolysis on Ni/C with different loadings in the presence of Ca(OH)2, and average diameters of Ni particles on Ni/C.

Loading	Activity (h^{-1})	Selectivity (on a ca	Selectivity (on a carbon basis, %)					Diameter (nm)	
		Ethylene glycol	Propylene glycol	Glycerol	Lactic acid	Arabitol	Threitol	d _{XRD}	d_{TEM}
2.4%	11.4	21.7	24.7	n.d. ^b	16.4	n.d.	n.d.	_c	11.2 ± 3.4
4.6%	17.2	32.0	33.7	n.d.	17.3	3.2	n.d.	7.9	9.1 ± 1.9
7.3%	24.4	30.8	32.5	1.0	17.6	3.9	1.5	6.8	8.5 ± 1.5
10.5%	31.3	31.1	31.8	2.6	15.0	5.4	2.2	6.6	$\textbf{8.8}\pm\textbf{1.5}$

^a Reaction conditions: 473 K, 4.0 MPa H₂, 40 g 10 wt% xylitol aqueous solution, 0.06–1 g Ni/C, 0.26 g Ca(OH)₂, 1 h, ~20% conversion.

^b Not detected.

^c The diffraction peak is too weak for estimating Ni particle size.

use of relatively large amount of the basic promoters, facilitating the competitive formation of lactic acid in the form of lactate and consumption of the bases [10,16]. These issues are strongly relevant to the polyol hydrogenolysis mechanism [10,18]. We recently proposed that the xylitol hydrogenolysis to ethylene glycol and propylene glycol proceeds by its kinetically relevant dehydrogenation of xylitol to xylose intermediate on the metal surfaces, and subsequent base-catalyzed retro-aldol condensation of xylose to form glycolaldehyde and glyceraldehyde, the intermediates for the two glycols [10]. The selectivity to the two glycols is therefore ultimately controlled by the relative rates between the hydrogenation of the aldehyde intermediates and their competitive reactions with the bases, reflecting the bifunctional nature of the xylitol hydrogenolysis.

In this work, we studied the Ni/C catalyst for the xylitol hydrogenolysis in the presence of a different solid bases such as Ca(OH)₂ and CeO₂, aimed at tuning the relative rates between the aforementioned competitive reactions on the metal surfaces and basic sites. We found that the basic oxides (e.g. CaO and CeO₂)-promoted Ni/C catalysts exhibit high selectivities to ethylene glycol and propylene glycol while the amount of the solid bases required is significantly reduced and lactic acid is essentially not formed.

2. Experimental methods

The Ni/C and basic oxide-modified Ni/C (denoted as Ni-Oxide/C) catalysts were prepared using the incipient wetness impregnation method. After impregnation of C (AR, Beijing Dali Fine Chemical, dried at 373 K in air for 12 h) with aqueous solutions of Ni(NO₃)₂ and, for Ni-Oxide/C catalysts, another metal nitrate (Ce(NO₃)₃, La(NO₃)₃, Mg(NO₃)₂, Ca(NO₃)₂, Ba(NO₃)₂, NaNO₃, Al(NO₃)₃, or ZrO(NO₃)₂), the slurry was dried at room temperature until large amount of water was evaporated and then the resulting sample was dried at 383 K for at least 12 h. The catalyst precursor was reduced in a flow of 20% H₂/N₂ at 673 K for 3 h.

 ZrO_2 was prepared hydrothermally as reported by Li et al. [19]. CeO₂ was synthesized hydrothermally in a similar way. Briefly, a Teflon inner vessel containing an aqueous solution of 0.4M (NH₄)₂Ce(NO₃)₆ (AR, Sinopharm Chemicals) and ~4.0 M urea in a stainless steel jacket was heated at 413 K for 24 h. The resulting precipitates were filtered and washed thoroughly with deionized water until the filtrate was neutral, followed by drying at 383 K for 12 h. The as-prepared ZrO₂, CeO₂ and purchased Al₂O₃ (Condea Chemie Gmbh) were calcinated at 673 K under a flowing air before use as additives.

The catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and inductive coupled plasma emission spectroscopy (ICP). The XRD patterns were obtained on a Rigaku D/MAX-2400 diffractometer using Cu Ka1 radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 100 mA. The TEM images were taken on a Philips Tecnai F30 FEGTEM operated at 300 kV. Samples were prepared by uniformly dispersing the catalysts in ethanol and then placing them onto carbon-coated copper

grids. The average sizes of Ni particles were calculated by averaging of more than 300 particles randomly distributed in the TEM images. Ni loadings and the amount of Ni leaching into the reaction solution were examined by ICP.

Xylitol hydrogenolysis reactions were carried out in a stainless steel autoclave (100 ml) at a stirring speed of 800 rpm. Typically, 40 g of 10 wt% xylitol (99%, Alfa Aesar) aqueous solution, proper amount of Ni catalysts (varied depending on xylitol conversion) and also for the Ni/C case, solid base were introduced to the autoclave. Afterwards, the reactor was purged with H₂ (>99.99%, Beijing Huayuan) three times, and pressurized with H₂ to 4.0 MPa and heated to 473 K, which was kept constant during the reaction. The reactant and liquid products, after silylation with hexamethyldisilazane (HDMS) and trimethylchlorosilane (TMSCl) (both ≥98.0%, Sinopharm Chemical) in pyridine (AR, Shantou Xilong Chemical), were analyzed by gas chromatography (Agilent 7890A) using a capillary column HP-1ms ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$) and a flame ionization detector. The detected liquid products included ethylene glycol, propylene glycol, glycerol, lactic acid, threitol, arabitol, and dehydroxy-pentitols (mainly 1,2,5-pentanetriol and 1,2,4,5-pentanetetraol), and dehydrated product hydroxyl furan. Gas products, *i.e.* CH_4 and CO_2 , were also detected in trace amounts, and thus not discussed in this work. Xylitol conversion and product selectivity are reported on a carbon basis, and xylitol reaction activity is reported as molar xylitol conversion rate per mole of metal loaded per hour (h^{-1}) .

3. Results and discussion

Table 1 shows the activity and selectivity of the xylitol hydrogenolysis at 473 K and 4.0 MPa H₂ on four Ni/C catalysts with different Ni loadings in the range 2.4-10.5 wt% in the presence of Ca(OH)₂. The xylitol conversion was kept around 20% in the kinetic-controlled regime. These catalysts were characterized by XRD and TEM, as shown in Figs. S1 and 2 (in Supporting data), respectively, and their Ni particle sizes were accordingly estimated. As listed in Table 1, the average sizes estimated from the XRD patterns (6-8 nm) were comparable to the data derived from the TEM images (8-11 nm), revealing the similar sizes of the Ni particles on the Ni/C catalysts especially with Ni loadings of 4.6 wt%, 7.3 wt% and 10.5 wt%. As the Ni loadings increased from 2.4 wt% to 10.5 wt%, the activity (normalized per Ni atom) increased linearly from $11.4 \, h^{-1}$ to 31.3 h⁻¹. Such increase in the activities with the Ni loadings are due clearly not to the change in the Ni particle sizes, but most likely to the increase in the surface density of the Ni particles on C, i.e. the higher Ni particle density favors the dehydrogenation of xylitol, the previously proposed rate-determining step involved in the polyol hydrogenolysis reactions [10,16]. This Ni density effect on the activity, although the underlying reason is not clear, might be relevant to the effect on the adsorption configurations of xylitol and its C-H bond activation on the Ni particles.

The Ni loadings also strongly influence the product selectivities in the xylitol hydrogenolysis. On 2.4 wt% Ni/C, the selectivities

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Fig. 1. Dependence of product selectivities on xylitol conversions on Ni/C. Reaction conditions: 473 K, 4.0 MPa H_2 , 1–3 h, 40 g 10 wt% xylitol aqueous solution, 0.05–0.8 g 7.3 wt% Ni/C, 0.26–0.6 g Ca(OH)₂.

to the two target glycols, ethylene glycol and propylene glycol, were 21.7% and 24.7%, respectively, which largely increased to 32.0% and 33.7% with increasing the Ni loading from 2.4 wt% to 4.6 wt%, and then remained almost unchanged at higher Ni loadings of 7.3 and 10.5% at similar xyiltol conversions (\sim 20%). Glycerol was detected always at low selectivities, which increased to 2.6% at the Ni loading of 10.5 wt%, while the selectivities to lactic acid slightly varied between 15.0% and 17.6% in the whole range of the Ni loadings. Accordingly, the combined selectivities to ethylene glycol, propylene glycol, and glycerol increased from 46.4% to 65.7% with increasing the Ni loadings from 2.4% to 10.5 wt%. Such change is consistent with the enhanced activities of the Ni/C catalysts at higher Ni loadings and the consequent effect on the xylitol reaction pathways. Ethylene glycol, propylene glycol and glycerol are derived, according to the proposed xylitol hydrogenolysis mechanism [10], from glycolaldehyde and glyceraldehyde intermediates that are formed involving the kinetically relevant dehydrogenation of xylitol to xylose on the metal surfaces, and its subsequent retro-aldol condensation with bases. The higher activities of the Ni/C catalysts at higher Ni loadings favor the hydrogenation of the glycolaldehyde and glyceraldehyde intermediates and their derivatives (e.g. pyruvaldehyde), which would otherwise undergo condensation reactions to form unidentified products or react to form glycolic acid and lactic acid under the basic conditions [10]. The enhanced activities also led to the increase in the selectivities to arabitol and threitol monotonically from nearly zero to 7.6% with increasing the Ni loading from 2.4 wt% to 10.5 wt%, as a result of the improved hydrogenation and decarbonylation of the xylose intermediate relative to its C–C cleavage via retro-aldol condensation.

It is noted that the two target glycols, ethylene glycol and propylene glycol, are stable in the xylitol hydrogenolysis, as shown by the representative results on 7.3 wt% Ni/C in Fig. 1. At 473 K and 4.0 MPa H₂, the selectivities to ethylene glycol and propylene glycol increased slightly from 29.7% and 34.8% to 31.9% and 35.4%, respectively, as the conversions increased from 5% to 100%, corresponding to a 67.3% yield for the two target glycols on Ni/C, which was higher than the yield of 60.0% on Ru/C reported recently under the identical reaction conditions [10]. Glycerol was always detected at very low



Fig. 2. Activities and selectivities to ethylene glycol, propylene glycol and lactic acid for the five reaction cycles of xylitol hydrogenolysis on Ni/C. Reaction conditions: 473 K, 4.0 MPa H_2 , 1 h, 40 g 10 wt% xylitol aqueous solution, 0.2 g 7.3 wt% Ni/C, 0.26 g Ca(OH)₂.

selectivities (~1%, not shown in Fig. 1). The lactic acid selectivities kept essentially constant, being around 18.3% even at 100% conversion, which was lower by about 10% than the value (~28%) on Ru/C. The higher yields for the target glycols and lower yields for lactic acid on Ni/C show its advantage over Ru/C for the selective xylitol hydrogenolysis, together with its good stability and reusability, as discussed below.

It is known that Ni particles are apt to leach and agglomerate leading to their deactivation. The stability and recyclability of Ni/C was thus examined at ca. 20% xylitol conversion in the kinetic-control regime. In the recycling experiments, the catalyst was washed thoroughly with deionized water and acetone, and then filtered for the next cycle. As shown in Fig. 2, no significant decline in the activities and selectivities was observed on 7.3 wt% Ni/C after five successive cycles. This is consistent with the characterization results for this catalyst. The Ni contents in aqueous reaction solutions after each cycle were measured by ICP and no Ni leaching was detected. TEM images in Fig. 3 show that the mean diameters of the Ni particles and their size distributions remained essentially unchanged (8.5 \pm 1.5 nm vs. 8.3 \pm 1.3 nm) after recycling the 7.3 wt% Ni/C catalyst over 5 times. These results demonstrate that the Ni/C catalysts are stable and reusable under the reaction conditions employed in this work.

It is worth mentioning that the observed stability of the Ni/C catalysts must be related to the presence of Ca(OH)₂ and its basicity. Under neutral conditions, the Ni particles on 7.3 wt% Ni/C agglomerated rapidly from 6.8 nm into 30–40 nm in diameter in the reaction solutions, as characterized by XRD (Fig. 4), and leached significantly during the xylitol conversion. Obviously, Ca(OH)₂ protected the Ni particles from agglomeration and leaching. Such a protecting effect was also observed in the presence of other bases, Mg(OH)₂ and CaCO₃, as shown in Fig. 4, maintaining the sizes of the Ni particles (being around 6–7 nm) almost unchanged after the xylitol hydrogenolysis, compared to the size (6.8 nm) before the reaction. When CeO₂ was used, the diffraction peak at $2\theta = 44.8^{\circ}$ became very weak, indicative of the dispersion of the Ni particles on the C support surface although the underlying reason needs to

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be clarified. However, the Ni particles aggregated dramatically in the presence of acidic Al₂O₃ or amphoteric ZrO₂ with weak acidbasicity, resembling the result under the neutral conditions. These XRD results confirm the protecting role of bases in stabilizing the Ni particles under the reaction conditions.

Upon the promotion of Mg(OH)₂, CaCO₃ and CeO₂ as well as Al₂O₃ and ZrO₂, the xylitol hydrogenolysis was also examined at 473 K and 4.0 MPa H₂ on 7.3 wt% Ni/C, for comparison with Ca(OH)₂. As shown in Table 2, the activity was 4.8 h⁻¹ on Ni/C under neutral condition, i.e. without addition of any promoter, which was similar to that in the presence of acidic Al₂O₃ and ZrO₂, being 4.0 h⁻¹ and 3.5 h⁻¹, respectively. The activity was not enhanced even in the presence of basic Mg(OH)₂, CaCO₃ and CeO₂, which was 3.5 h⁻¹,

4.1 h^{-1} and 4.2 h^{-1} , respectively, and much lower than the value (24.4 h^{-1}) in the presence of Ca(OH)₂ although the sizes of the Ni particles were similar or for the case of CeO₂ even smaller during the reactions. Such inferior activities, compared to that in the presence of Ca(OH)₂, are due to the low pH values in the aqueous reaction solutions, analogous to the phenomenon observed on Ru/C.

As for the product selectivity, Ni/C under neutral conditions was selective to ethylene glycol (18.3%), propylene glycol (12.5%) and glycerol (11.0%) with a combined selectivity of 41.8%, which was much higher than that on Ru/C with only trace amounts of the C_2 and C_3 products under identical conditions. Instead, xylitol dominantly converted to other C_5 polyols, e.g. arabitol, with a

Table 2	2
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Effects of different basic and acidic additives on activities and selectivities in xylitol hydrogenolysis on Ni/C.ª

Additive	Activity (h ⁻¹)	Selectivity (on a carbon basis, %)							
		Ethylene glycol	Propylene glycol	Glycerol	Lactic acid	Arabitol	Threitol	Deoxy- pentitols ^b	
_	4.8	18.3	12.5	11.0	n.d.	15.9	2.7	5.8	
ZrO_2	3.5	17.0	13.4	13.9	n.d.	12.0	2.0	6.5	
Al_2O_3	4.0	16.9	12.2	13.9	n.d.	15.7	2.0	6.7	
CeO ₂	4.2	26.3	30.9	4.0	3.6	5.6	2.8	6.5	
CaCO ₃	4.1	26.6	31.1	6.0	3.0	6.3	2.3	5.4	
Mg(OH) ₂	3.5	27.3	32.7	6.0	5.4	4.0	2.0	4.7	

^a Reaction conditions: 473 K, 4.0 MPa H₂, 3 h, 40 g 10 wt% xylitol aqueous solution, 0.2 g 7.3 wt% Ni/C, 0.1 g additive, ~15% xylitol conversion. ^b Including 1,2,5-pentanetriol and 1,2,4,5-pentanetetrol.

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Fig. 4. XRD patterns of Ni/C (7.3 wt% Ni loading) catalysts before and after xylitol hydrogenolysis in the absence and presence of $Ca(OH)_2$, $Mg(OH)_2$, $CaCO_3$, CeO_2 , ZrO_2 and Al_2O_3 at 473 K and 4.0 MPa H_2 .

selectivity of 80.4% on Ru/C [10], which was much higher than the result (15.9%) on Ni/C, reflecting the lower activity of Ni/C than Ru/C and the consequent effect on the reaction pathways. According to the proposed reaction mechanism, the lower hydrogenation activity of Ni/C favored the retro-aldol condensation of the xylose intermediate over its competitive hydrogenation reaction, leading to higher extent of its C–C bond cleavage to ultimately form the C₂ and C₃ products. Deoxypentitols, mainly pentane-1,2,5-triol and pentane-1,2,4,5-tetrol, were also detected on Ni/C, which were likely formed, by referring to the similar reaction of glycerol conversion to propylene glycol [20], involving dehydration of the xylose intermediate and subsequent hydrogenation, in competition with the retro-aldol condensation of xylose. Addition of both ZrO2 and Al₂O₃ exerted negligible effect on the product distributions on Ni/C, as shown in Table 2. However, when CeO₂ was added, even with known weak basicity, the total selectivity to ethylene glycol (26.3%), propylene glycol (30.9%) and glycerol (4.0%) increased sharply from 41.8% to 61.2%, which further increased to 63.7% and 66.0% in the presence of CaCO₃ and Mg(OH)₂, respectively. Concurrently, the selectivities to arabitol and threitol decreased significantly from 18.6% to 6.0-8.6% in the presence of CeO₂, CaCO₃ and Mg(OH)₂. The combined selectivities to ethylene glycol, propylene glycol and glycerol are comparable to the data (64.3%) in the presence of Ca(OH)₂, but use of CeO₂, CaCO₃ and Mg(OH)₂, due to their weaker basicity, led to a dramatic decline in the selectivities to lactic acid by 3-5 folds (3.0-5.4% vs. 17.6\%), showing the feasibility for controlling the product distributions by tuning the basicity in the xylitol hydrogenolysis. Based on these results, we next further reduced the use of the solid bases by directly modifying the Ni/C catalysts with basic oxides and tune the product selectivities.

Table 3 displayed the activities and selectivities of the xylitol hydrogenolysis at ca. 15% conversion on a series of 2.4 wt% Ni/C catalysts modified with equimolar amounts of oxides (designated as Ni-Oxide/C) at 473 K and 4.0 MPa H₂. Ni-CaO/C was selective to ethylene glycol, propylene glycol and glycerol with a combined selectivity of 72.8%, which was higher than the aforementioned best result (around 65%) on Ni/C in the presence of Ca(OH)₂ at similar conversions (Table 1). Moreover, less than 1% selectivity of lactic acid was produced, in contrast to about 17% of lactic acid on Ni/C when Ca(OH)₂ was separately added into the reaction solutions, although the activity of Ni-CaO/C was lower $(7.0 h^{-1} vs. 11.4 h^{-1})$, as expected by its lower amount of CaO used. Since CaO is slightly soluble in water, two control experiments were performed to examine whether CaO on Ni-CaO/C worked homogeneously or heterogeneously. The equal amount of CaO (\sim 0.02 g) was used by physically mixing with 2.4 wt% Ni/C, as done in the experiments described in Table 1. The activity decreased to $1.6 \, h^{-1}$, and more significantly, the selectivity to ethylene glycol, propylene glycol and glycerol decreased to 48% with a much higher selectivity to lactic acid, similar to the result in Table 1. In contrast, when extra 0.02 g of CaO was added together with Ni-CaO/C into the reaction solution, the activity and product selectivity did not altered significantly, except that the selectivity to glycerol declined from 11.0% to 8% concurrently with the increase in the selectivity to lactic acid to about 3%. These control experiments confirm that CaO on Ni-CaO/C acts as a solid base in the xylitol hydrogenolysis. For comparison, Ru-CaO/C was also examined, showing that xylitol was transformed mainly into arabitol and threitol with a combined selectivity of 54.5%, and only trace amounts the target glycols were detected, as a result of the prevailing hydrogenation of the xylose intermediate on the very active Ru surface over its C-C bond cleavage via the retro-aldol condensation on CaO base, reflecting the competition between the two steps [10].

Similar promoting effects on the xylitol hydrogenolysis were also observed for the other basic oxides, including MgO, BaO, CeO₂ and La₂O₃ (Table 3). Characterization of these Ni-Oxide/C catalysts by XRD before and after the reactions, as shown in Fig. 5 reveals that

Table 3

Activities and selectivities in xylitol hydrogenolysis on oxide-modified Ni/C and CaO-modified Ru/C.^a

Catalyst	Activity (h ⁻¹)	Selectivity (on a car					
		Ethylene glycol	Propylene glycol	Glycerol	Arabitol	Threitol	Deoxy-pentitols ^b
Ni-CaO/C	7.0	28.3	33.5	11.0	6.7	trace	6.3
Ru-CaO/C	103	trace	trace	trace	45.2	9.3	n.d.
Ni-BaO/C	8.2	26.7	30.7	9.6	7.4	trace	6.9
Ni-CeO ₂ /C	9.7	25.6	31.6	3.8	5.0	3.6	8.7
Ni-La ₂ O ₃ /C	6.6	23.2	29.8	4.2	5.6	4.3	8.0
Ni-MgO/C	2.6 ^c	22.4	27.3	3.7	n.d.	n.d.	n.d.
Ni-Al ₂ O ₃ /C	1.8 ^c	n.d.	n.d.	n.d.	trace	n.d.	n.d. (40.0) ^d
Ni-ZrO ₂ /C	1.9 ^c	n.d.	n.d.	n.d.	12.6	trace	n.d.(34.0) ^d
Ni/C	1.0 ^c	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

^a Reaction conditions: 473 K, 4.0 MPa H₂, 40 g 10 wt% xylitol aqueous solution, 0.4 g 2.4 wt% Ni/C modified with equal mol of different oxides, 3 h; 0.1 g 4 wt% Ru/C modified with equal mol of CaO, 1 h. ~15% xylitol conversion.

^b Including 1,2,5-pentanetriol and 1,2,4,5-pentanetetrol.

^c At <4% xylitol conversion.

^d Data in the parenthesis represents the selectivity to hydroxyl furan.

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Fig. 5. XRD patterns of Ni/C catalysts modified with different oxides of Al₂O₃, ZrO₂, CaO, MgO, La₂O₃, CeO₂, BaO before (a) and after (b) xylitol hydrogenolysis at 473 K and 4.0 MPa H₂.

the Ni particles modified with the basic oxides did not agglomerate essentially, reflecting the protecting role of the bases on the Ni particles dispersed on C, as found for Ni/C physically mixed with the bases (Fig. 4). Including Ni-CaO/C, their activities were much higher than the un-promoted Ni/C $(1.0 h^{-1})$, and they decreased in the order of Ni-CeO₂/C > Ni-BaO/C > Ni-CaO/C > Ni-La₂O₃/C > Ni-MgO/C, being 9.7 h⁻¹, 8.2 h⁻¹, 7.0 h⁻¹, 6.6 h⁻¹, and 2.6 h⁻¹, respectively. This order, except CeO₂, agrees approximately with the decrease in their relative basicity, demonstrating the basicity effects on the Ni activities for the kinetically-relevant xylitol dehydrogenation. It is noted that the formation of lactic acid was negligible (with < 1% selectivity) on these basic oxide-modified Ni/C catalysts. The selectivity to the sum of C_2 and C_3 products (i.e. ethylene glycol, propylene glycol and glycerol) was 67.0% on Ni-BaO/C, similar to the value (i.e. 72.8%) on Ni-CaO/C, higher than the value on Ni-CeO $_2$ /C, Ni-La₂O₃/C and Ni-MgO/C, being 61.0%, 57.2% and 53.4% respectively. Clearly, all these basic oxides are efficient for catalyzing the retro-aldol condensation reaction and the C--C bond cleavage to form the C_2 and C_3 products, notwithstanding the difference in their selectivities. For comparison, acidic oxide such as Al₂O₃ and amphoteric oxide such as ZrO₂ were also supported together with

Ni on C to examine their effects. However, ZrO_2 and Al_2O_3 failed to stabilize the Ni particles on C, as evidenced from the narrow and sharp Ni diffraction peaks after the reaction (Fig. 5), similar to the phenomenon when they were added physically with Ni/C (Fig. 4). ZrO_2 and Al_2O_3 promoted the Ni activities $(1.9 h^{-1} \text{ for Ni-}$ $ZrO_2/C and <math>1.8 h^{-1}$ for Ni- Al_2O_3/C vs. $1.0 h^{-1}$ for Ni/C), but they led to no detectable formation of the C₂ and C₃ products. A dehydrated product, hydroxyl furan, was mainly detected on Ni- ZrO_2/C and Ni- Al_2O_3/C , apparently as a result of the sequential dehydration and hydrogenation reactions of the xylose intermediate on the Ni surface.

To further understand the promoting effects of the basic oxides, their contents on the Ni-Oxide/C catalysts were varied. Table 4 shows the activities and selectivities of the xylitol hydrogenolysis at 473 K and 4.0 MPa H₂ on the representative CeO₂ and CaO-modified 7.3 wt% Ni/C catalysts (noted as Ni-xCeO₂/C and Ni-xCaO/C, in which x stands for the molar ratio of CeO₂ and CaO to Ni). As the CeO₂/Ni molar ratio increased from 0.1 to 2.0, the activities increased by about two folds from $9.2 h^{-1}$ to $18.3 h^{-1}$. In this range of CeO₂/Ni ratios, the Ni particles remained similar in sizes. Fig. 6 shows the STEM images of the representative Ni-xCeO₂/C

Table 4

Effects of CeO2 and CaO contents on activities and selectivities in xylitol hydrogenolysis on Ni-CeO2/C and Ni-CaO/C.ª

Catalyst ^b	Activity (h ⁻¹)	Selectivity (on a carbon basis, %)						
		Ethylene glycol	Propylene glycol	Glycerol	Arabitol	Threitol	Deoxy-pentitols ^c	
Ni-0.1CeO ₂ /C	9.2	22.5	12.3	20.0	15.7	4.0	2.9	
Ni-0.22CeO ₂ /C	11.2	23.1	18.0	15.4	8.6	3.4	5.7	
Ni-0.45CeO ₂ /C	11.5	24.4	26.1	7.6	5.6	4.0	7.6	
Ni-0.66CeO ₂ /C	12.9	25.1	26.3	7.5	5.3	3.3	6.8	
Ni-1CeO ₂ /C	14.4	25.2	26.5	8.0	5.8	3.6	5.5	
Ni-1.5CeO ₂ /C	20.5	25.4	25.4	9.0	6.9	3.4	4.5	
Ni-2CeO ₂ /C	18.3	26.0	26.1	8.2	7.6	4.2	3.8	
Ni-0.33CaO/C	6.4	22.4	18.3	16.3	15.1	2.1	6.8	
Ni-0.66CaO/C	6.4	27.6	25.8	15.2	8.6	1.3	6.0	
Ni-1CaO/C	6.7	27.7	25.2	16.4	8.3	1.3	5.3	
Ni-0.66CaO/C	_d	28.4	26.0	15.1	2.7	0.9	5.0	

^a Reaction conditions: 473 K, 4.0 MPa H₂, 2 h, 7.3 wt% Ni loading, 0.1–0.4 g catalyst, 40 g 10 wt% xylitol aqueous solution, 20–30% xylitol conversion.

^b Numbers represents molar ratios of CeO₂ or CaO to Ni at constant Ni contents.

^c Including 1,2,5-pentanetriol and 1,2,4,5-pentanetetrol.

 $^d~$ At $\sim\!100\%$ conversion.

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Fig. 6. STEM micrographs and histograms of Ni particle size distribution of 7.3 wt% Ni-xCeO₂/C (x=0.22, 0.45, 1) (scale bar=20 nm). (a) Ni-0.22CeO₂/C, 8.1 ± 1.2 nm; (b) Ni-0.45CeO₂/C, 9.0 ± 1.5 nm; (c) Ni-1CeO₂/C, 7.8 ± 1.3 nm.

samples with CeO₂/Ni ratios of 0.22, 0.45, and 1, which possessed Ni particle sizes of 8.1 ± 1.2 nm, 9.0 ± 1.5 nm and 7.8 ± 1.3 nm, respectively. Meanwhile, elemental analysis of the isolated Ni particles for these three samples by energy dispersive X-ray spectroscopy (EDS) shows their Ce/Ni molar ratios increased linearly from 0.05 to 0.25. implying close contact between CeO₂ and the Ni particles. By referring to the Ni-xCaO/C catalysts to be discussed below, the higher activities at the higher CeO₂/Ni ratios is not solely related to the increase in the basicity, but may be due to other reasons, such as electronic effect of CeO₂ on Ni, as proposed by Xu et al. [21] and Yuan et al. [11]. The selectivities to the sum of the C₂ and C₃ products increased from 54.8% to 58.1%, and the selectivities to deoxypentitols (mainly pentane-1,2,5-triol and pentane-1,2,4,5-tetrol) increased from 2.9% to 7.6%, concurrently with the decrease

in the selectivities to C₅ and C₄ products from 19.7% to 9.6%, as the CeO₂/Ni ratios increased from 0.1 to 0.45. In this ratio range, specifically, the propylene glycol selectivities increased from 12.3% to 26.1% with the concurrent decrease of the glycerol selectivities from 20% to 7.6%. By further increasing the CeO₂/Ni ratios from 0.45 to 2.0, the selectivities to the C₂ and C₃ products kept nearly constant (~59%); the selectivities to the C₄ and C₅ products increased from 9.6% to 11.8% while the selectivities to deoxypentitols declined from 7.6% to 3.8%. Moreover, lactic acid was not detectable, irrespective of the CeO₂/Ni ratios.

As for the Ni-xCaO/C catalysts, their activities clustered around a value of $6.5 \, h^{-1}$, independent of the CaO/Ni ratios in the range 0.33 to 1.0. However, similar to the effect of CeO₂ on selectivity, with increasing the Ca/Ni ratios from 0.33 to 1.0, the selectivities to

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the sum of C_2 and C_3 products increased from 57.0% to 69.3%, and the selectivities to the C_4 and C_5 products decreased from 17.2% to 9.6% with an slight decline in the selectivities to deoxypentitols from 6.8% to 5.3%. This selectivity trend reflects the favorable retro-aldol condensation at higher CaO contents and consequently higher basicity. On these catalysts, lactic acid formed at negligible amounts (<1%). Noticeably, the high selectivity to the C_2 and C_3 products can be obtained even at high xylitol conversions. For example, on Ni-0.66CaO/C, the combined selectivity to ethylene glycol, propylene glycol and glycerol reached 69.5% at nearly 100% xylitol conversion with less than 1% selectivity to lactic acid. This selectivity can be potentially further improved upon optimization of the reaction parameters and the catalyst compositions, showing the potential advantages of such modified Ni catalysts for the selective hydrogenolysis of xylitol and other polyols.

4. Conclusions

Ni/C catalysts in the presence of solid bases, e.g. $Ca(OH)_2$ and CeO_2 , physically mixed with or co-supported with Ni on C, can efficiently catalyze the xylitol hydrogenolysis into ethylene glycol and propylene glycol. The presence of the solid bases prevents the agglomeration and leaching of Ni particles on C, and renders them stable under the reaction conditions. Supporting the solid bases, especially CeO_2 and CaO, with Ni on C reduces the amount of solid bases required and leads to negligible formation of lactic acid. The observed efficiency of the Ni catalysts and the reduction in the use of the solid bases are apparently correlated to the appropriate hydrogenation activity of the Ni catalysts and consequently the favorable C–C cleavage of xylose intermediate with the bases, over its competitive hydrogenation on Ni surfaces, to form glycolalde-hyde and glyceraldehyde, the proposed intermediates for the two target glycols.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2013. 12.040.

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