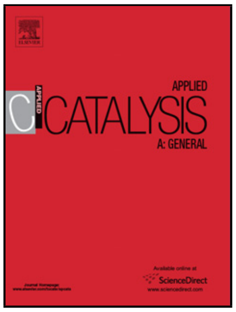

Selective hydrogenolysis of biomass-derived sorbitol to propylene glycol and ethylene glycol on *in-situ* formed PdZn alloy catalysts

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Selective hydrogenolysis of biomass-derived sorbitol to propylene glycol and ethylene glycol on *in-situ* formed PdZn alloy catalysts

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Graphical Abstract

Highlights

- In-situ formed PdZn alloy catalyst is efficient and stable for sorbitol hydrogenolysis to propylene glycol and ethylene glycol.
- The presence of ZnO facilitates the in-situ formation of PdZn alloys on ZrO_2 and their stability.
- The primary kinetic isotope effects with different deuterated sorbitol molecules validate the kinetically-relevant step in sorbitol hydrogenolysis.

Abstract: Sorbitol hydrogenolysis to industrially important propylene glycol and ethylene glycol receives increasing attention, recently. Here, we developed an efficient and stable PdZn alloy catalyst, *in-situ* formed from a physical mixture of Pd/ZrO_2 and ZnO, for the sorbitol hydrogenolysis with Mg_3AlO_x as a solid base, and obtained a 54.6% yield of the two target glycols (493 K and 5.0 MPa H_2). The amounts of ZnO and Mg_3AlO_x strongly influenced the activity and selectivity, due to their effects on the formation of the PdZn alloys and the competitive metal-catalyzed dehydrogenation/hydrogenation and base-catalyzed retro-aldol condensation steps. The kinetic isotope effects, combined with the inhibiting effects of H_2 pressure on the activity in a broad range (3.0-8.0 MPa), confirm that the sorbitol dehydrogenation to hexose intermediates is the kinetically-relevant step in the sorbitol hydrogenolysis. This study provides insights into the catalytic functions and reaction parameters for the hydrogenolysis of polyols to the target glycols.

Keywords: Sorbitol; Selective hydrogenolysis; PdZn alloy; Propylene glycol; Ethylene glycol; Reaction mechanism

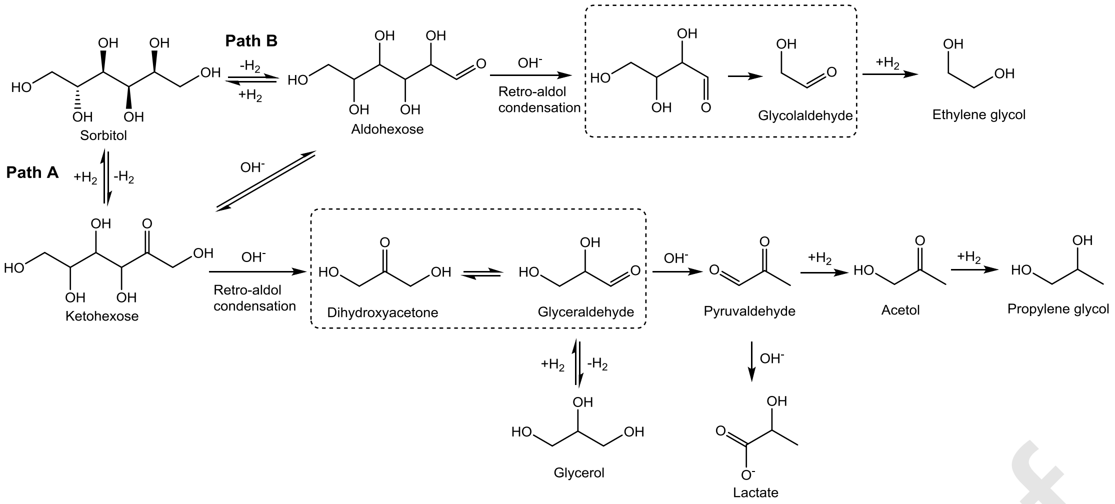
1. Introduction

Polyols, represented by sorbitol and xylitol, are renewable and largely available from non-edible cellulose and hemicellulose. Their transformation to propylene glycol and ethylene glycol via catalytic hydrogenolysis provides an economically viable route to the two important glycols, widely used as functional fluids and for the synthesis of polyester resins, fibers, and pharmaceuticals.[1-8] Currently, the two glycols are manufactured mainly by multi-step transformations from petroleum-based propylene and ethylene.

Because of such importance, the selective hydrogenolysis of sorbitol and xylitol has been intensively studied on various metal catalysts in the presence of base promoters.[9-21] Zhou *et al.* used carbon nanofiber-supported Ru catalyst with CaO for the sorbitol hydrogenolysis, achieving 85.7% sorbitol conversion and 60.8% combined selectivity to ethylene glycol, propylene glycol and glycerol at 493 K and 8.0 MPa H_2.[16] Using NaOH as the base promoter, a total yield of 61.4% for ethylene glycol and propylene glycol was obtained over the amine-functionalized carbon nanotubes supported Ru catalysts at 483 K and 6 MPa H_2.[17] Palkovits and coworkers found that Cu/C in the presence of $Ca(OH)_2$ efficiently catalyzed the full conversion of sorbitol to ethylene glycol and propylene glycol in a selectivity of as high as 84.5% at 513 K and 5 MPa H_2.[18] Sun *et al.* reported the hydrogenolysis of xylitol to ethylene glycol and propylene glycol in a 67.3% yield at 473 K and 4 MPa on Ni/C in the presence of $Ca(OH)_2$.[19] Liu *et al.* observed up to 81.0% yield to ethylene glycol and propylene glycol in xylitol hydrogenolysis on bimetallic NiCu-SiO_2 catalysts with $Ca(OH)_2$ at 473 K and 8 MPa H_2.[20]

To avoid the use of soluble base promoters and reduce the formation of carboxylic acids, typically lactic acid, known competitively via the same intermediates for the target glycols, bifunctional catalysts with integrated metallic and basic sites have been explored in hydrogenolysis of sorbitol and xylitol.[22-31] Chaudhari and coworkers investigated the performance of Cu/CaO-Al_2O_3 in sorbitol hydrogenolysis without addition of any other bases at 503 K and 6 MPa H_2, and observed a high combined selectivity to ethylene glycol, propylene glycol and glycerol (73.3% at 98.1% conversion).[22] Wang *et al.* applied MgO-supported Ni, Cu, and Co catalysts in sorbitol hydrogenolysis, and showed a 66% combined selectivity for ethylene glycol, propylene glycol and glycerol at 57.2% conversion on Ni/MgO at 473 K and 6.0 MPa H_2.[23] Shanthi *et al.* reported 62% selectivity for ethylene glycol and propylene glycol at 64% sorbitol conversion on Ni/Ca(Sr)-hydroxyapatites at 473 K and 6.0 MPa H_2.[24] Rivière *et al.* carried out xylitol hydrogenolysis on Ru-(Mn-Al)O_x solid base catalysts, and achieved 58% combined selectivity to the two glycols and glycerol at 80% xylitol conversion under conditions of 473 K and 6.0 MPa H_2.[25] Recently, Ni/La_2O_3/ZrO_2 catalyst was found to be efficient for sorbitol hydrogenolysis to propylene glycol and ethylene glycol with a 47.1% total selectivity at 96.8% sorbitol conversion (at 493 K and 4.0 MPa).[26] Notwithstanding these significant progresses, the solid bases-containing bifunctional catalysts generally suffer from deactivation, mainly due to the leaching or transformation of the basic components under the hydrothermal conditions.[22, 25, 27, 29] Therefore, a careful design of stable catalysts is required with improved hydrogenolysis activity and selectivities to propylene glycol and ethylene glycol.

As for the reaction mechanism, the dehydrogenation of sorbitol and xylitol is widely accepted as the first step, for their hydrogenolysis to propylene glycol and ethylene glycol on different metal catalysts with bases.[15, 22, 32-35] As shown in Scheme 1, sorbitol is first dehydrogenated to hexose intermediates, including ketohexose (Path A) and aldohexose (Path B), on the metal surfaces. In the Path A, ketohexose undergoes selective cleavage of its C(3)–C(4) bond via retro-aldol condensation with bases to form tautomeric dihydroxyacetone and glyceraldehyde, which are further hydrogenated to glycerol on metal surfaces. Competitively, glyceraldehyde can be also dehydrated to pyruvaldehyde, which then undergoes either hydrogenation to acetol and propylene glycol or base-involved benzilic acid rearrangement to lactic acid. In the parallel Path B, the C(2)–C(3) and C(4)–C(5) bonds of aldohexose are successively cleaved via retro-aldol condensation by bases to form three molecules of glycolaldehyde, which is then hydrogenated to ethylene glycol on metal surfaces. In this mechanism, the first dehydrogenation step of sorbitol on metal surface has been generally proposed as the kinetically-relevant step.[15, 22, 32-35] However, few studies have reported on the kinetic and particularly isotopic evidences to unequivocally validate such hydrogenolysis mechanism.



Scheme 1. Proposed reaction pathways for sorbitol hydrogenolysis to C_2 and C_3 products on metal catalysts in the presence of bases.[15]

Considering the aforementioned progresses and existing problems, this work aims to develop new catalysts with improved activity and selectivity to propylene glycol and ethylene glycol in the sorbitol hydrogenolysis, and provide further insights into the reaction mechanism. Recently, Pd-based catalysts, coupling with ZnO, have shown promising performance in selective hydrogenolysis of glycerol, which is also kinetically limited, similar to the sorbitol reaction, by a primary dehydrogenation step.[36-38] For example, we found that physical mixtures of Pd/ZrO_2 and ZnO efficiently catalyze glycerol hydrogenolysis to propylene glycol, as a result of *in-situ* facile formation of PdZn alloys on ZrO_2. In this work, we present an in-depth study on the selective hydrogenolysis of sorbitol to propylene glycol and ethylene glycol on the PdZn alloys in the presence of solid bases. The effects of reaction parameters, including amount of solid base, temperature and H_2 pressure, are examined within the kinetically-controlled regime. Kinetic isotope effects for different deuterated sorbitol molecules are measured under actual reaction conditions to probe the kinetic relevance of C-H bond activation involved in the sorbitol hydrogenolysis.

2. Experimental

Monoclinic ZrO_2-supported Pd (Pd/ZrO_2) catalysts were prepared by a deposition–

precipitation method. Briefly, ZrO_2 powder (Alfa Aesar) was dispersed into an aqueous solution of $PdCl_2$ (Sinopharm Chemical), containing 3 wt% palladium with respect to ZrO_2. Under vigorous stirring, a Na_2CO_3 solution (1.0 mol/L) was added to the palladium solution dropwise until the pH value of the final solution reached 10, which was then maintained for 1.5 h. The resulting precipitates were centrifugally separated, thoroughly washed with deionized water until no Cl^- ions were detected, and then dried subsequently in ambient air at 333 K for 12 h and at 393 K for 12 h. Afterwards, the resulting powders were calcined in flowing air at 773 K for 3 h, and then were reduced in a 20% H_2/N_2 (Beijing Haipu) flow at 673 K for 3 h. Following the similar procedure for Pd/ZrO_2, Al_2O_3 (Alfa Aesar) and TiO_2 (Alfa Aesar) supported Pd catalysts were also prepared. The Pd content in these catalysts was fixed at 3 wt% when prepared. The actual Pd loadings of Pd/ZrO_2, Pd/Al_2O_3 and Pd/TiO_2 catalyst were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Teledyne Leeman Laboratories), being 2.57%, 3.15% and 2.58%, respectively.

Mg_3AlO_x (Mg/Al molar ratio of 3/1), was prepared by a co-precipitation method. Briefly, an aqueous solution (40 mL) of $Mg(NO_3)_2 \cdot 6\ H_2O$ (1.125 mol/L, Beijing Yili Fine Chemical) and $Al(NO_3)_3 \cdot 9\ H_2O$ (0.375 mol/L, Beijing Yili Fine Chemical) was dropwisely added simultaneously with another solution containing NaOH (0.34 mol/L, Beijing Yili Fine Chemical) and Na_2CO_3 (0.060 mol/L, Beijing Yili Fine Chemical) into 20 mL deionized water under vigorous stirring, keeping the pH value of the solution at 9–10. The resulting precipitates were aged overnight, filtered, and washed thoroughly with deionized water. The hydroxycarbonate precursor was dried at 383 K overnight and then calcined in ambient air at 673 K for 4 h to obtain the corresponding Mg_3AlO_x. CeO_2 was prepared hydrothermally by hydrolysis of an aqueous solution of $(NH4)_2Ce(NO_3)_6$ (Sinopharm Chemical) with urea at 413 K for 24 h in a Teflon-lined stainless-steel autoclave. The resulting yellow precipitates were centrifugally separated and thoroughly washed with deionized, followed by drying in air at 393 K overnight and subsequent calcination at 673 K for 3 h.

Transmission electron microscopy (TEM) measurements were carried out on Philips Tecnai F30 FEG-TEM operating at an acceleration voltage of 300 kV. Before the TEM measurement, the samples were ultrasonically dispersed in ethanol and the suspensions were deposited on carbon-coated copper grids. The average sizes of Pd particles and their size distributions were calculated by measuring at least 300 particles randomly distributed in the TEM images. XRD patterns were obtained on a Rigaku D/MAX-2400 diffractometer using Cu K□ radiation (λ = 1.5406 Å) operated at 40 kV and 100 mA. The 2θ angle was scanned in the range of 20-60° at a rate of 2°/min. X-ray photoelectron spectra (XPS) were collected on an Axis Ultra spectrometer (Kratos, UK) using an Al anode (Al Kα, hv =1486.6 eV) operated at 150 W. The samples were treated in flowing 20% H_2/N_2 (50 mL/min) at 493 K for 2 h in a process chamber before the XPS measurement to eliminate possible oxidation of the metal catalysts caused by the unavoidable exposure to ambient air. The binding energies were calibrated by referring to the Zr $3d_{5/2}$ signal of ZrO_2 at 182.1 eV.[38]

Sorbitol hydrogenolysis reactions were carried out in a stainless steel autoclave (100 mL) with vigorous stirring at 750 rpm. Typically, 5 g sorbitol (98%, Alfa Aesar), 0.15 g of catalyst, 0.1 g Mg_3AlO_x and the specified amount of ZnO (Alfa Aesar) were introduced into the autoclave containing 45 g H_2O. After fully purged with 1.0 MPa H_2 (>99.99%, Beijing Haike Yuanchang), the reactor was pressurized with H_2 to 5.0 MPa and then heated to the target reaction temperatures (473-513 K). After the reactor cooled to room temperature, the catalysts and liquid phase were simply separated by filtration. The reactants and products in the liquid phase were analyzed by high-performance liquid chromatography (HPLC, Shimadzu LC-20A) using Bio-Rad Aminex HPX-87H and HPX-87C columns connected to a RID detector. The activities of Pd catalysts were calculated by the molar sorbitol conversion rates per mole of Pd loaded per hour (h^{-1}), while the product selectivities were reported on a carbon basis.

Kinetic isotope effects on the sorbitol hydrogenolysis were examined using different deuterated sorbitols (including sorbitol-1,1,2,3,4,5,6,6-d_8, sorbitol-1,6,6-d_3, sorbitol-1,1-d_2, sorbitol-2-d_1 and sorbitol-5-d_1), in comparison with undeuterated sorbitol under the same conditions. These deuterated sorbitols were obtained by the same method described in the literature.[15] These hydrogenolysis reactions were carried out in a Teflon-lined stainless steel autoclave (50 mL) with magnetic stirring at 800 rpm.

In a typical run, 0.05 g of Pd/ZrO_2, 0.005 g of ZnO, 0.05 g of Mg_3AlOx and 0.22 g of sorbitol (the same molar amount for deuterated sorbitols) were loaded into the autoclave containing 15.8 g of H_2O. Then, the reactor was charged with 4.0 MPa H_2 and heated to 453 K, which was maintained for 1.5 h.

3. Results and discussion

3.1 Activity and selectivity of sorbitol hydrogenolysis on Pd/ZrO_2 and ZnO

Table 1 shows the activities and selectivities in the sorbitol hydrogenolysis on Pd-based catalysts in the presence of different solid bases at 493 K and 5.0 MPa H_2. The activities and selectivities were compared at similar sorbitol conversions (~30%) within the kinetically-controlled regime (detailed conversions and reaction time shown in Table S1, SI). Propylene glycol, ethylene glycol and also glycerol were detected as the target products, together with by products including lactic acid and C_4- C_6 polyols (1,2-butanediol, erythritol, threitol, xylitol, arabitol, mannitol and iditol). As shown in Table 1, physically mixed with a small amount of ZnO (5 mg), Pd/ZrO_2 actively catalyzed the sorbitol hydrogenolysis with an activity of 152.2 h^{-1}, as previously observed for glycerol hydrogenolysis.[38] However, its selectivity for the sum of propylene glycol, ethylene glycol and glycerol was only 36.8%, while the selectivity for the C_6 polyols (including mannitol and iditol), formed from the hydrogenation of the hexose intermediates, were as high as 21.4%. Such selectivity trend is consistent with the absence of stronger basic sites on ZnO, required for catalyzing the retro-aldol condensation of the hexose intermediates to the C_2-C_3 products (as shown in Scheme 1). After replacing ZnO with a stronger solid base, Mg_3AlO_x, the combined selectivity for the C_2-C_3 products increased obviously to 64.8%, concurrently with a large decrease in the selectivity for the C_6 polyols (12.1%, Table 1). However, the hydrogenolysis activity was only 12.2 h^{-1} on Pd/ZrO_2+Mg_3AlO_x, much lower than that on Pd/ZrO_2+ZnO, demonstrating the promoting effect of ZnO on Pd catalyst in the sorbitol hydrogenolysis, via the *in-situ* formation of active PdZn alloys, as previously reported for glycerol hydrogenolysis,[38] which will be further discussed below. Further, physically mixing Mg_3AlO_x with Pd/ZrO_2 and ZnO led to a significant increase in the selectivities for propylene glycol and ethylene glycol to 38.9% and 12.7%, respectively, and a total selectivity of the two polyols and glycerol to 60.1%, while the hydrogenolysis activity remained to be as high as 136.2 h^{-1} (Table 1).

Table 1 Effects of solid base and support on activities and selectivities in sorbitol hydrogenolysis on ZnO-promoted Pd catalysts [a]

Catalyst	Activity (h^{-1})	Selectivity (on a carbon basis, %)					
		Propylene glycol	Ethylene glycol	Glycerol	Lactic acid	C_4 polyols[b]	C_5 polyols[c]	C_6 polyols[d]
Pd/ZrO_2+ZnO	152.2	20.2	6.6	10.0	1.5	3.5	7.3	21.4
$Pd/ZrO_2+Mg_3AlO_x$	12.2	31.4	17.1	7.6	8.7	6.5	8.5	12.1
$Pd/ZrO_2+ZnO+Mg_3AlO_x$	136.2	38.9	12.7	8.5	3.5	6.9	1.2	12.7
$Pd/ZrO_2+ZnO+La(OH)_3$	143.7	36.9	13.7	12.1	1.9	6.2	1.3	8.8
$Pd/ZrO_2+ZnO+CeO_2$	136.6	35.9	15.4	9.3	3.9	6.0	1.0	9.2
$Pd/Al_2O_3+ZnO+Mg_3AlO_x$	52.3	40.4	13.8	7.5	4.3	6.1	1.3	9.8
$Pd/TiO_2+ZnO+Mg_3AlO_x$	34.4	41.6	12.8	3.6	3.7	5.9	0.8	8.9

[a] Reaction conditions: 50 g of 10 wt% aqueous sorbitol solution, 0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005 g of ZnO or none, 0.1 g of solid base, 493 K, 5.0 MPa H_2, ~30% sorbitol conversion (obtained by varying reaction time). [b] C_4 polyols include 1,2-butanediol, erythritol and threitol, [c] C_5 polyols include xylitol and arabitol, [d] C_6 polyols include mannitol and iditol.

Resembling Mg_3AlO_x, other solid bases, such as $La(OH)_3$ and CeO_2, can also efficiently catalyze the retro-aldol condensation involved in the sorbitol hydrogenolysis. When they were used with Pd/ZrO_2+ZnO, the activities were 143.7 and 136.6 h^{-1}, and the combined selectivities to the two target glycols were 50.6 % and 51.3%, respectively (Table 1), both essentially identical to those when Mg_3AlO_x was present. Notably, the selectivities to lactic acid were about 2-4% in the presence of the three solid bases, which were much lower than those on other catalysts, for example, Ru/C in the presence of $Ca(OH)_2$ (~25%)[15], implying the superiority of these solid bases to soluble bases in minimizing the benzilic acid rearrangement of glyceraldehyde-derived pyruvaldehyde intermediate to lactic acid in the sorbitol hydrogenolysis (Scheme 1). It is also worthwhile to note that the presence of the solid bases led to very low selectivities (~1%) for the C_5 polyols (Table 1), reflecting another advantage of such catalytic components in discouraging the metal catalyzed C-C cleavage via decarbonylation of the carbonyl intermediates to C5 and C_1 byproducts in the sorbitol hydrogenolysis, as reported on Ru-based catalyst[15].

For the Pd catalysts, the support effects were also examined with a similar particle size of Pd sites (~3 nm, see Figs. S1 and S2, SI) at 493 K and 5.0 MPa H_2. As shown in Table 1, the product distributions on the three supported Pd catalysts (i.e. Pd/ZrO_2, Pd/Al_2O_3 and Pd/TiO_2) were similar at similar sorbitol conversions (~ 30%), showing about 60% combined selectivities to propylene glycol, ethylene glycol and glycerol and ~4% selectivities to lactic acid. But Pd/ZrO_2 exhibited a much higher activity (136.2 h^{-1}) than Pd/Al_2O_3 (52.3 h^{-1}) and Pd/TiO_2 (34.4 h^{-1}), mainly attributed to their different metal-support interaction and the consequent effect on their sorbitol dehydrogenation activity[39, 40].

The promoting effect of ZnO on the sorbitol hydrogenolysis was further examined with its varying amounts, physically mixing with Pd/ZrO_2 and Mg_3AlO_x (Fig.1, detailed conversions and reaction time shown in Table S2, SI). Without addition of ZnO, the activity was as low as 12.2 h^{-1} , and the selectivities to propylene glycol, ethylene glycol, glycerol and lactic acid were 31.4%, 17.1%, 7.6% and 8.7%, respectively, as discussed above (Table 1). As the amount of ZnO increased to 5 mg, the activity increased sharply to 136.2 h^{-1}, and then decreased slightly to 96.3 h^{-1} with increasing the ZnO amount to 20 mg. Within this range of the ZnO amounts, the selectivity to propylene glycol first increased to 40.8% at 2.5 mg ZnO, and then gradually decreased to a constant value of 37.5% with increasing the amount to above 7.5 mg. The selectivity to ethylene glycol declined from 19.1% to 12.2% when the amount of ZnO increased from 1.0 mg to 7.5 mg, which then remained essentially constant. Meanwhile, the selectivity to glycerol varied in a narrow range of 7.0%~9.1%. Differently, the selectivity to lactic acid decreased to the minimum value of 3.5% at 5 mg ZnO, and then slightly increased to

~5.0% at the larger amounts. Notably, the catalytic performance of Pd/ZrO_2 can be largely improved by optimizing the amount of ZnO in the sorbitol hydrogenolysis.

Such trends of the activities and also selectivities to C_2-C_3 products are very similar to those previously observed in glycerol hydrogenolysis on Pd/ZrO_2+ZnO, where PdZn alloys were formed on ZrO_2, via the *in-situ* reduction of dissolved Zn^{2+} ions on Pd surfaces under the similar hydrogenolysis conditions, and found to be very effective in the kinetically-relevant step of glycerol dehydrogenation[38]. The Pd/ZrO_2+ZnO mixture was characterized by XPS before and after the sorbitol hydrogenolysis. Relative to the binding energies of the Pd $3d_{3/2}$ and $3d_{5/2}$ signals for Pd/ZrO_2 (340.6 and 335.3 eV, Fig. 2a), the values for the used catalyst after the sorbitol hydrogenolysis shifted by 0.7 eV to 341.3 and 336.0 eV, respectively (Fig. 2b), reflecting electronic transfer from Pd to Zn and their strong interaction. These values are identical to those for the as-prepared PdZn alloys on ZrO_2 (Fig. 2c).[38, 41] Taken together, these results suggest that the PdZn alloys were also formed *in-situ* on ZrO_2 from the mixture of Pd/ZrO_2+ZnO during the sorbitol hydrogenolysis in the presence of Mg_3AlO_x, which acted as the active dehydrogenation sites and contributed to the observed higher activities.

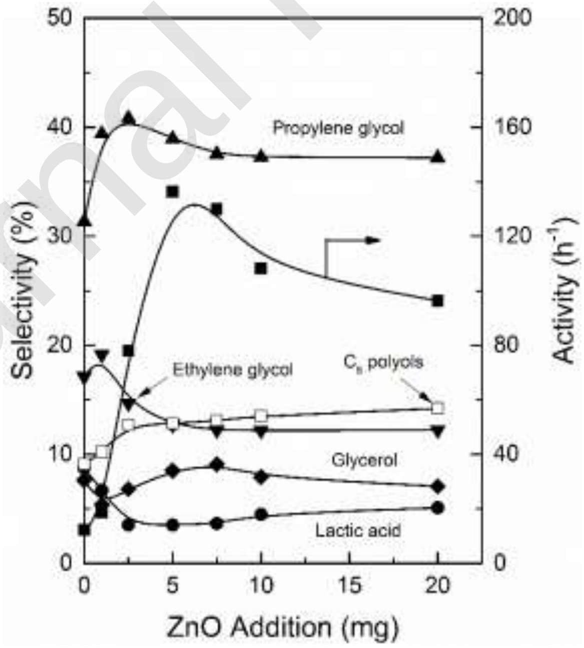


Figure 1. Effects of ZnO addition on selectivities and activities in sorbitol hydrogenolysis on Pd/ZrO_2 with Mg_3AlO_x (50 g of 10 wt% aqueous sorbitol solution,

0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.1 g of Mg_3AlO_x, 493 K, 5.0 MPa H_2, ~30% sorbitol conversion obtained by varying reaction time).

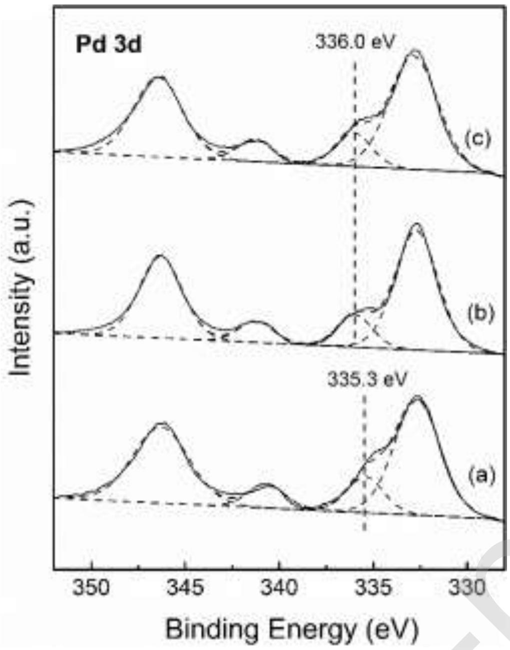


Figure 2 XPS spectra of Pd 3d and Zr 3p signals for (a) Pd/ZrO_2, (b) a physical mixture of 0.15 g 3 wt% Pd/ZrO_2 and 0.1 g ZnO after sorbitol hydrogenolysis reaction (493 K, 5.0 MPa H_2, 2h, 50 g of 10 wt% aqueous sorbitol solution) and (c) fresh $PdZn/ZrO_2$ prepared by the method reported in the Reference [38].

It is noted that the high combined selectivity for the two glycols on Pd/ZrO_2+ZnO with Mg_3AlO_x can be obtained at nearly 100% sorbitol conversions. As shown in Fig. 3, with increasing sorbitol conversion from 20.3% to 96.0% at 493 K and 5.0 MPa H_2, the selectivity for propylene glycol and ethylene glycol increased from 37.6% and 12.6% to 43.3% and 13.6%, respectively, indicative of their high stability under the reaction conditions, leading to a 54.6% yield of the two target glycols on Pd/ZrO_2+ZnO with Mg_3AlO_x. The glycerol selectivity increased slightly from 7.6% to 8.5%, and then declined to 6.8%, while the lactic acid selectivity declined from 3.9% to 2.4%, a very low value at nearly full conversion of sorbitol. In addition, the total selectivity for the C_6 polyols (mannitol and iditol) decreased monotonically from 15.6% to 2.3% with increasing sorbitol conversion in the range of 20.3–96.0%, indicating that the two sorbitol epimers are also reactive to undergo hydrogenolysis to propylene glycol and ethylene glycol under the identical reaction conditions.

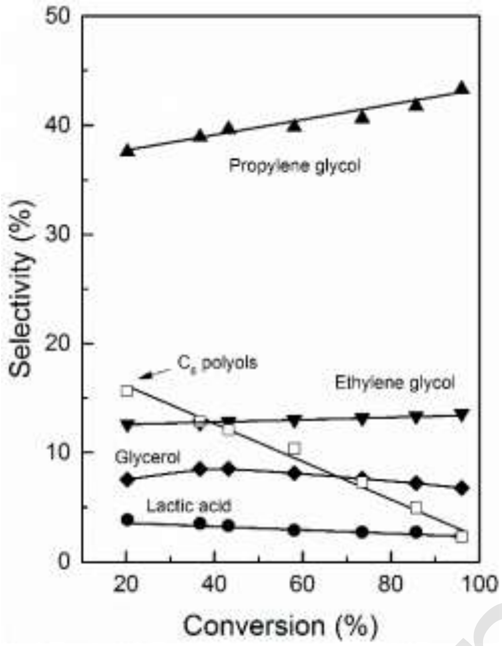


Figure 3. Dependence of product selectivities on sorbitol conversion on Pd/ZrO_2+ZnO with Mg_3AlO_x (50 g of 10 wt% aqueous sorbitol solution, 0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005 g of ZnO, 0.1 g of Mg_3AlO_x, 493 K, 5.0 MPa H_2, 1-17.5 h).

The stability and recyclability of Pd/ZrO_2+ZnO+Mg_3AlO_x were also examined. As shown in Fig. 4, the sorbitol conversions remained essentially unchanged for five successive cycles at 493 K and 5.0 MPa H_2. The selectivities for propylene glycol and ethylene glycol were also stable, being 42.7%-43.6% and 13.3%-13.8%, respectively, while the selectivities for glycerol and lactic acid declined slightly from 6.5% and 2.2% to 5.2% and 1.5%, respectively. Consistently, no leaching of Pd or Zr was detected by ICP-AES in the filtrate after the recycling experiments. These results reveal that the PdZn alloys derived from the physical mixture of Pd/ZrO_2 and ZnO with Mg_3AlO_x is efficient and stable for catalyzing the sorbitol hydrogenolysis under the conditions in this work.

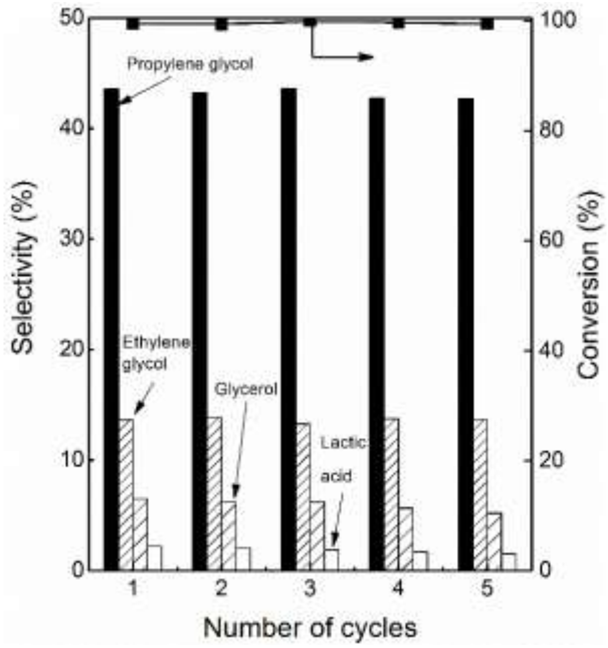


Figure 4. Conversions and selectivities (to propylene glycol, ethylene glycol, glycerol and lactic acid) for the five cycles of sorbitol hydrogenolysis on Pd/ZrO_2+ZnO with Mg_3AlO_x (50 g of 10 wt% aqueous sorbitol solution, 0.50 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.02 g of ZnO and 0.2 g of Mg_3AlO_x in the first cycle, 0.005 g of ZnO and 0.05 g of Mg_3AlO_x in cycles 2-5, 493 K, 5.0 MPa H_2, 10 h).

3.2 Effects of reaction parameters on sorbitol hydrogenolysis

Fig. 5 shows the effects of the Mg_3AlO_x amount on the sorbitol hydrogenolysis activities and selectivities on Pd/ZrO_2+ZnO at 493 K and 5.0 MPa H_2. Mg_3AlO_x, as a mild solid base, plays a key role in providing basicity and catalyzing the retro-aldol condensation of sugar intermediates that leads to the selective cleavage of their C–C bonds. With increasing the amount of Mg_3AlO_x from 0.06 g to 0.3 g, the activity increased from 120.0 to 160.0 h^{-1} (detailed conversions and reaction time shown in Table S3, SI), implying the favored hydrogenolysis at the higher basicity on Pd/ZrO_2+ZnO. This increase in the amount of Mg_3AlO_x led to the slight decrease in the selectivities for propylene glycol and glycerol from 39.4% and 9.1% to 37.5% and 7.8%, respectively, with the concurrent increase in the lactic acid selectivity from 3.1% to 7.5%. Such selectivity change is consistent with the proposed mechanism that the three C_3 products are formed via the same glyceraldehyde intermediate, which undergoes favorable benzilic acid rearrangement to lactic acid over its hydrogenation reaction to glycerol and propylene glycol at higher basicity, as discussed above (Scheme 1). Meanwhile, the selectivity for the C_6 polyols decreased monotonically from 14.5% to 9.2%, apparently as a consequence of the favored base-catalyzed retro-aldol condensation of the hexose intermediates over their epimerization. Such effects show the importance in finely tuning the basicity to maximize the selectivity for the two target glycols.

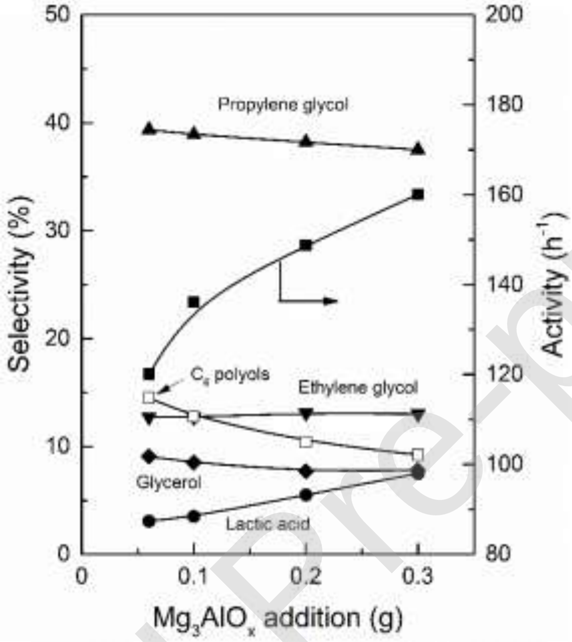


Figure 5. Effect of Mg_3AlO_x addition on selectivities and activities in sorbitol hydrogenolysis on Pd/ZrO_2+ZnO ((50 g of 10 wt% aqueous sorbitol solution, 0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005 g of ZnO, 493 K, 5.0 MPa H_2, ~30% sorbitol conversion obtained by varying reaction time).

Fig. 6 shows the effects of the reaction temperature on the activities and selectivities in sorbitol hydrogenolysis on Pd/ZrO_2+ZnO with Mg_3AlO_x. In the kinetically-controlled regime (at ~30% sorbitol conversions, detailed conversions and reaction time shown in Table S4, SI), as expected, the activities increased dramatically from 48.2 to 392.8 h^{-1} with increasing temperature from 473 to 513 K. Accordingly, estimated by the Arrhenius equation, the apparent activation energy for the sorbitol hydrogenolysis was 105 ± 3 kJ/mol at 473-513 K on PdZn alloy (Fig. S3, SI), close to the value (123±5 kJ/mol, at 463-513 K) for glycerol hydrogenolysis[38], reflecting their similar kinetically-relevant step of the polyol dehydrogenation. In this temperature range, the propylene glycol selectivity increased from 32.5% to the maximum value of 38.9% at around 493 K, and then declined slightly to 35.6%. In contrast, the glycerol selectivity decreased monotonically from 13.3% to 6.2%. The lactic acid selectivity increased slightly from 2.3% to 4.7%, consistent with the fact that the basicity of the Mg_3AlO_x increased at higher temperature and thus facilitated the benzilic acid rearrangement. Meanwhile, the selectivity for C_6 polyols decreased from 14.5% to 11. 2% with the concurrent increase in the selectivity for the C_2-C_3 products, indicating that the retro-aldol condensation reaction of the hexose intermediates is faster than their hydrogenation at higher temperatures. It is also noted that the acetol intermediate was detected above 493 K, and its selectivity increased up to 5.0% at 513 K. Such lower activity for acetol hydrogenation to propylene glycol indicates the structural change of the active PdZn alloys derived from Pd/ZrO_2 and ZnO at the higher temperatures. Such temperature-sensitive activity provides a useful direction for optimizing the parameters in the polyol hydrogenolysis reactions on the PdZn alloy-based catalysts.

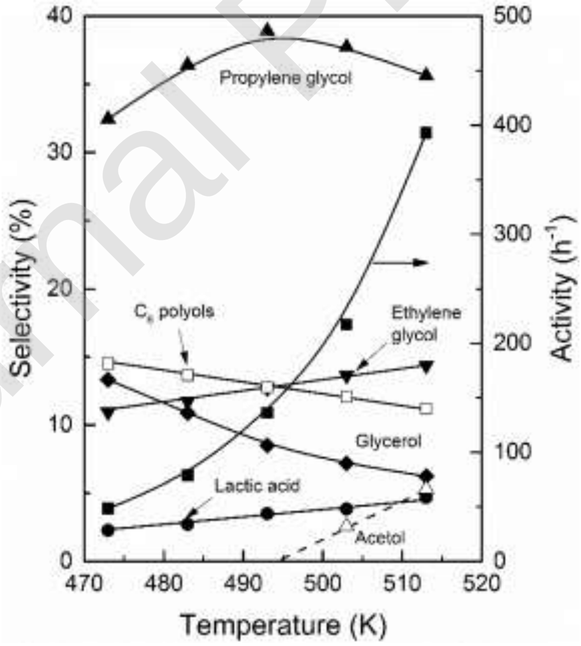


Figure 6. Effect of temperature on selectivities and activities in sorbitol hydrogenolysis on Pd/ZrO_2+ZnO with Mg_3AlO_x (50 g of 10 wt% aqueous sorbitol solution, 0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005 g of ZnO, 0.1 g of Mg_3AlO_x, 5.0 MPa H_2, ~30% sorbitol conversion obtained by varying reaction time).

The effects of H_2 pressure on sorbitol hydrogenolysis activities and selectivities were examined at 493 K on Pd/ZrO_2+ZnO with Mg_3AlO_x in kinetically-controlled regime (at ~30% sorbitol conversions, detailed conversions and reaction time shown in Table S5, SI). As shown in Fig. 7, under a very low H_2 pressure (1.0 MPa), acetol was the main by-product in the reaction with a 20.3% selectivity, very close to the selectivity for propylene glycol (19.1%), because of the inefficient hydrogenation of acetol to propylene glycol. With increasing the H_2 pressure to 8.0 MPa, acetol disappeared, and the selectivities for propylene glycol and ethylene glycol increased significantly to a plateau around 35.9% and 12.7%, respectively. Concurrently, the glycerol selectivity increased monotonically from 2.6% to 12.2% while the lactic acid selectivity decreased slightly from 5.0% to 3.1%. Such a change in the selectivities for the C_3 products reflects their strong dependence on the relative rates of the competitive reactions of the glyceraldehyde intermediate on the PdZn alloy and basic sites (Scheme 1). These results also reflect the accelerated hydrogenation of the unsaturated intermediates at higher H_2 pressures in the sorbitol hydrogenolysis, together with the monotonic increase in the selectivities for the C_6 polyols (from 6.9% to 18.4%).

As for the sorbitol hydrogenolysis activity, it increased from 106.3 to 126.9 h^{-1} with increasing the H_2 pressure from 1.0 to 3.0 MPa, because of the inhibition to the dehydrogenation/hydrogenation activity caused by the strong adsorption of the unsaturated intermediates on the active metal sites at the low H_2 pressures[42]. However, further increasing the H_2 pressure to 8.0 MPa led to a monotonic decrease of the activity to 106.7 h^{-1}. Such inhibiting effect on the sorbitol hydrogenolysis in this broad H_2 pressure range (3.0-8.0 MPa), as also observed on La-promoted Ni/ZrO_2 by Cai *et al.*[26], reflects the proposition that the sorbitol hydrogenolysis is kinetically limited by its dehydrogenation[15], a thermodynamically unfavorable step at higher H_2 pressures. This effect is consistent with the kinetic isotope effects for the sorbitol hydrogenolysis on PdZn alloys, as discussed below.

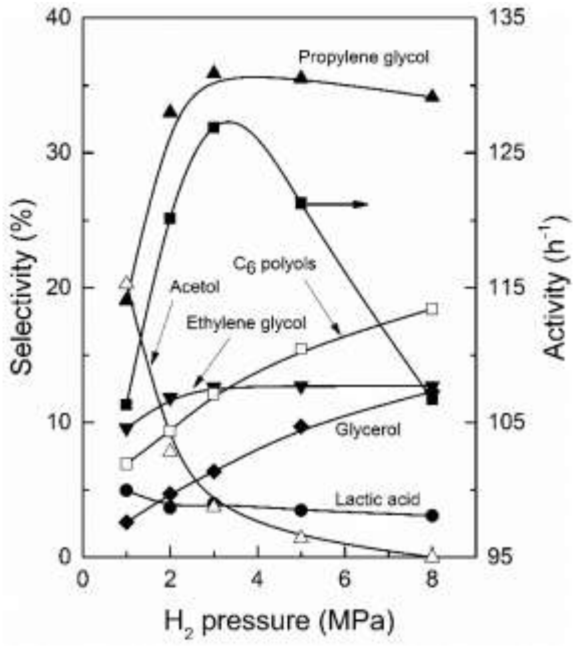


Figure 7. Effect of H_2 pressure on selectivities and activities in sorbitol hydrogenolysis on Pd/ZrO_2+ZnO with Mg_3AlO_x (5 g of sorbitol, pretreated catalysts, 0.1 g of Mg_3AlO_x, 493 K, 8 MPa-balance with N_2, ~30% sorbitol conversion obtained by varying reaction time; Hydrothermal pretreatment conditions of catalysts: 0.15 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005 g of ZnO, 45.0 g of water, 493 K, 5.0 MPa H_2, 1h).

3.3 Kinetic isotope effects for sorbitol hydrogenolysis

Recently, we studied the kinetic isotope effects (KIE) with undeuterated and deuterated sorbitol molecules on Ru/C to experimentally confirm the primary dehydrogenation of sorbitol as the kinetically-relevant step in the sorbitol hydrogenolysis[15]. However, because of the interference of the facile H-D exchange between the deuterated sorbitol and H_2O/H_2 molecules on Ru/C under the hydrogenolysis conditions, the measurements of the KIE values were actually conducted under N_2, instead of H_2. Differently, PdZn alloys are inert to the H-D exchange between the C–H bonds of polyols and H_2O/H_2 molecules, as observed in glycerol hydrogenolysis[38], which renders it viable to rigorously measure the intrinsic kinetic isotope effects and probe the kinetically-relevant step in the sorbitol hydrogenolysis.

Undeuterated and deuterated sorbitol molecules (including sorbitol-1,1,2,3,4,5,6,6-d_8, sorbitol-1,6,6-d_3, sorbitol-1,1-d_2, sorbitol-2-d_1 and sorbitol-5-d_1) were used to measure the KIE (k_H/k_D) values on PdZn alloys (Pd/ZrO_2+ZnO) under H_2 (4.0 MPa H_2, 453 K). As shown in Table 2, irrespective of their deuteration degree, these sorbitol molecules showed similar selectivities to the C_2-C_3 products (including propylene glycol, ethylene glycol, glycerol and lactic acid), suggesting that they undergo the hydrogenolysis reactions via the same mechanism on PdZn alloys. At 453 K and 4.0 MPa H_2 in H_2O, the activity of undeuterated sorbitol was 14.7 h^{-1}, while the activity of fully deuterated sorbitol-1,1,2,3,4,5,6,6-d_8 was 6.9 h^{-1} (Table 2). Consequently, the k_H/k_D value between sorbitol and sorbitol-d_8 was 2.13, clearly demonstrating that cleavage of C–H bonds is involved in the kinetically-relevant steps of the sorbitol hydrogenolysis. This normal KIE is consistent with the observed inhibiting effects of H_2 pressure (Fig. 7), and provides an intrinsic evidence for the dehydrogenation mechanism of the sorbitol hydrogenolysis. On the other hand, for the partially deuterated sorbitols (Table 2), the corresponding k_H/k_D values for sorbitol-1,6,6-d_3, sorbitol-1,1-d_2 and sorbitol-2-d_1 were all close to unity (1.03, 1.09 and 1.09, respectively), while sorbitol-5-d_1 showed a higher KIE value of 1.26. Such a comparison implies that the activation of the C(5)–H bond is more preferred when compared to the C(1)–H, C(2)–H and C(6)–H bonds in sorbitol molecules as also found with Ru/C in the presence of $Ca(OH)_2$[15]. This proposed mechanism is consistent with the fact that the selectivities for C_3 products via the retro-aldol condensation of ketohexose intermediate (Path A, Scheme 1) are much higher than that for C_2 product (i.e. ethylene glycol) via aldohexose intermediate from dehydrogenation at the C(1) or C(6) position (Path B, Scheme 1). This mechanism also indicates the significant effects of the configurations of hexitols on their hydrogenolysis activity and the limiting factors for the formation of the two target glycols.

Table 2. Activities and selectivities for hydrogenolysis of undeuterated and different multi-deuterated sorbitols on Pd/ZrO_2+ZnO with Mg_3AlO_x under H_2[a]

Reactant	Conversion (%)	Activity (h^{-1})	KIE (k_H/k_D)	Selectivity (on a carbon basis, %)			
				Propylene glycol	Ethylene glycol	Glycerol	Lactic acid

Sorbitol	22.6	14.7	-	18.6	6.6	11.3	3.6
Sorbitol-1,1,2,3,4,5,6,6-d_8	10.6	6.9	2.13	18.3	7.2	14.2	3.1
Sorbitol-1,6,6-d_3	21.9	14.3	1.03	18.1	6.7	12.7	3.1
Sorbitol-1,1-d_2	20.7	13.5	1.09	20.1	7.2	10.6	3.8
Sorbitol-2-d_1	20.8	13.6	1.09	18.3	8.1	11.3	4.2
Sorbitol-5-d_1	17.9	11.7	1.26	16.7	8.3	9.6	4.2

[a] Reaction conditions: ~1.18 mmol reactant, 15.8 g H_2O, 0.05 g of Pd/ZrO_2 with a 3 wt% Pd loading, 0.005g of ZnO, 0.05 g of Mg_3AlO_x, 453 K, 4.0 MPa H_2, 90 min.

4. Conclusions

Pd/ZrO_2 physically mixed with ZnO is highly active and stable for the sorbitol hydrogenolysis to propylene glycol and ethylene glycol in the presence of Mg_3AlO_x as a solid base, via the efficient dehydrogenation of sorbitol to the hexose intermediates and their retro-aldol condensation, catalyzed respectively by *in-situ* formed PdZn alloys on ZrO_2 and basic sites. The selectivity to the two target glycols reaches 56.9%, with a significantly low selectivity to lactic acid (2.4%) at a nearly full conversion of sorbitol. For this catalyst system of Pd/ZrO_2+ZnO+Mg_3AlO_x, the activities and selectivities depend strongly on the amount of ZnO and solid base, due to their effects on the formation of the active PdZn alloys and the competitive metal- and base-catalyzed steps involved in the sorbitol hydrogenolysis. Together with the observed strong inhibition of H_2 pressure to the hydrogenolysis activity in a broad range (3.0-8.0 MPa), the kinetic isotopic studies confirm that the primary dehydrogenation of sorbitol, via preferential cleavage of its C(5)–H bond to the hexose intermediates, is the kinetically relevant step in the sorbitol hydrogenolysis. This study provides fundamental understanding useful for the design of more effective catalysts and optimization of reaction parameters toward the synthesis of the target propylene glycol and ethylene glycol from different polyols.

CRediT authorship contribution statement

Yuqing Jia: Data curation, Investigation, Writing - original draft.

Qianhui Sun: Data curation, Formal analysis, Writing - original draft.

Haichao Liu: Project administration, Resources, Supervision, Writing - review& editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

TEM micrographs and histograms of Pd particle size distribution for Pd/Al_2O_3 and Pd/TiO_2; XRD patterns of monoclinic ZrO_2 and Pd/ZrO_2; Apparent activation energy for the sorbitol hydrogenolysis on PdZn alloy. Detailed conversion and reaction time for each experiment in Table 1, Figure 1, and Figure 5-7.

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