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Physically mixed ZnO and skeletal NiMo for one-pot reforming-hydrogenolysis of glycerol to 1,2-propanediol

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ABSTRACT

The one-pot aqueous phase reforming (APR) and hydrogenolysis of glycerol to 1,2-propanediol (PDO) was catalyzed by physically mixed skeletal NiMo and zinc oxide catalysts in a continuous flow fixed-bed reactor without the aid of added H₂. The skeletal NiMo catalyst alone is highly active towards glycerol but the selectivity for 1,2-PDO is only moderate. Physically mixing of MgO, SiO₂, Al₂O₃, HZSM-5, TiO₂, ZrO₂, or CeO₂ as a cocatalyst with skeletal NiMo was detrimental to the conversion of glycerol and yield of 1,2-PDO. However, physically mixing with ZnO gave an advantageous promoting effect on both the catalytic activity and selectivity for 1,2-PDO, and gave a 1,2-PDO yield of 52.0%, which is higher than that obtained with noble metal catalysts for the APR-hydrogenolysis of glycerol. The synergistic effect between physically mixed ZnO and skeletal NiMo was attributed to in situ enhancement of the Lewis acidity of ZnO by chemisorbed CO₂ from the APR of glycerol on skeletal NiMo, which benefited both the dehydration of glycerol to acetol on ZnO and the hydrogenation of acetol to 1,2-PDO on skeletal NiMo.

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1. Introduction

1,2-Propanediol (PDO) has extensive applications as a functional fluid, and in the production of daily essential tools, polyesters, and polyurethanes [1,2]. It is currently manufactured by the catalytic hydration of propylene oxide [3], which is a process that uses rapidly depleting fossil fuels. Many researchers have studied the catalytic transformation of glycerol to 1,2-PDO under H₂ in a batch reactor [4–6]. This process is regarded as more promising than the traditional petrochemical route because glycerol is now abundantly available as the main by-

product in the production of biodiesel [7–9]. In general, the production of 10 ton of biodiesel is accompanied by the production of 1 ton of glycerol. However, due to the low solubility of H₂ in a glycerol/water solution [10], a relatively high H₂ pressure (5–8 MPa) is needed to achieve a high yield of 1,2-PDO [11–13].

In recent years, researchers have explored the production of 1,2-PDO from glycerol under an inert atmosphere [14–17] using H₂ generated by the aqueous phase reforming (APR) of some of the glycerol as a hydrogen source for the hydrogenolysis of glycerol (Scheme 1). The advantages of this one-pot APR-

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Scheme 1. Reaction pathway of the one-pot APR-hydrogenolysis of glycerol to 1,2-PDO.

hydrogenolysis are: (1) the reaction is performed under an inert atmosphere, which avoids the use of highly flammable H_2 produced from fossil fuels, thus ensuring a safer and more sustainable process; and (2) the reaction pressure is lower than that which use externally supplied H_2 as the reactant, thus leading to improved operation safety and economics [16]. In this way, a greener production of 1,2-PDO from glycerol and water is obtained.

In a pioneering work, Wawrzetz et al. [17] explored the one-pot APR-hydrogenolysis of glycerol in a continuous flow fixed-bed reactor over a Pt/ Al_2O_3 catalyst. They investigated the detailed reaction network by systematic experimental design. The continuous production of 1,2-PDO from glycerol without externally supplied H_2 is highly attractive from an industrial point of view. However, concerning its practical application, hardly any work has been devoted to enhancing the selectivity for 1,2-PDO. Moreover, there has been a surprising dearth of the development of an inexpensive non-noble metal catalyst for this promising one-pot reaction process [18].

This paper reports our endeavors to improve the selectivity for 1,2-PDO at a high conversion of glycerol using a physically mixed bifunctional catalyst system in a continuous flow fixed-bed reactor in the absence of external H_2 . A skeletal NiMo catalyst described in our previous work [19,20] was employed as the primary catalyst since this catalyst is active in both the APR of polyol [19,21] and the saturation of the C=O group [20,22]. On the other hand, it has been reported that metal oxides, resins, or sulphated zirconia as cocatalyst can improve the catalytic performance of some supported metal catalysts in the hydrogenolysis of glycerol under H_2 [8,9,11]. In this work, we first evaluated the catalytic performance of a physical mixture of skeletal NiMo with various conventional oxides for the one-pot APR-hydrogenolysis of glycerol. After identifying ZnO as effective in enhancing the production of 1,2-PDO, we then optimized the ZnO/NiMo ratio and investigated its role in the mechanism. An interpretation of the synergistic effect between ZnO and skeletal NiMo in the one-pot APR-hydrogenolysis of glycerol to 1,2-PDO is presented.

2. Experimental

2.1. Catalyst preparation

A mixture of metallic Ni (40%), Mo (10%), and Al (50%) powders, with the weight percents shown in the brackets, was melted at 1573 K under Ar. A $Ni_{40}Mo_{10}Al_{50}$ alloy ribbon with a cross section of 0.02 mm $\times$ 5 mm was obtained by a single roller melt-spinning method. The brittle alloy ribbon was ground to 60–80 mesh for alkali leaching. Then, 1.0 g of the alloy powder was dealuminated by 10 ml of 5 mol/L NaOH aqueous solution at 363 K for 1 h under gentle stirring [23]. The resulting

black NiMo powder was washed to neutrality with deionized water. For activity testing, the freshly prepared catalyst was loaded into a tubular reactor with the protection of deionized water to avoid oxidation. The mass ratio of Ni to Mo in the skeletal NiMo catalyst was 37:1, which was determined by inductively coupled plasma atomic emission spectroscopy. Its specific surface area, pore volume, and pore diameter determined by N_2 physisorption were 92 m^2/g , 0.096 cm^3/g , and 4.18 nm, respectively.

SiO_2 (S5505-100G, Sigma-Aldrich), Al_2O_3 (AR, Sinopharm), and TiO_2 (P25, AR, Sinopharm) were used as received. MgO, CeO_2 , and ZnO were prepared by the thermal decomposition of pre-dried $Mg(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ (AR, Sinopharm), respectively, in air at a heating rate of 10 K/min from room temperature to 773 K and held for 4 h. ZrO_2 was prepared by adding 25 wt% ammonia (AR, Sinopharm) aqueous solution to 0.5 mol/L $ZrOCl_2$ (AR, Sinopharm) aqueous solution and refluxing for 48 h. The resulting white powder was calcined in air at a heating rate of 10 K/min from room temperature to 873 K and held for 5 h. HZSM-5 was prepared by the procedure described by Haw et al. [24] with a Si/Al molar ratio of 20.

2.2. Characterization

X-ray diffraction patterns (XRD) were acquired on a Bruker D8 Advance X-ray diffractometer using Ni-filtered $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm) with a scanning range (2θ) of 30° – 90° . The tube voltage was 40 kV and the current was 40 mA.

X-ray photoelectron spectroscopy (XPS) was performed on a Perkin Elmer PHI5000C spectrometer with Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV) as the excitation source. The sample, protected by absolute ethanol, was pressed into a self-supporting disc, mounted on the sample plate, and degassed in the pretreatment chamber under vacuum for 4 h at room temperature. The sample was then transferred to the analysis chamber with a background pressure better than 3×10^{-7} Pa. Binding energy (BE) values were referenced to the C 1s level of contaminant carbon at 284.6 eV.

The active surface area of the skeletal NiMo was determined by pulsed H_2 adsorption. After it was treated at 508 K for 2 h under flowing Ar, the sample was cooled down to room temperature under Ar. Then, H_2 pulses were injected until the eluted peak areas of consecutive pulses monitored by a thermal conductivity detector (TCD) became constant. The active surface area of the skeletal NiMo, 21 m^2/g , was derived from the amount of H_2 adsorbed by assuming a H/Ni_s stoichiometry of 1 and a surface area of 6.5×10^{-20} m^2 per Ni atom [25], which falls well within the values reported for Raney-type Ni catalysts [26].

Temperature-programmed desorption of NH_3 (NH_3 -TPD)

was conducted as follows. The oxide was activated in He flow at 673 K for 1 h and then saturated by flowing a 10 vol% NH_3 -90 vol% He mixed gas at 393 K for 1 h. The sample was purged with He for 2 h to remove gaseous and physisorbed NH_3 and then heated at a ramping rate of 20 K/min. The desorbed NH_3 was monitored by TCD.

2.3. Activity testing and product analysis

The continuous flow fixed-bed reactor for the one-pot APR-hydrogenolysis of glycerol was used following the procedure of Shabaker et al. [27]. An aqueous solution containing 10 wt% glycerol was fed into the reactor in an upflow configuration. The reaction was conducted at 508 K and pressure of 3.1 MPa regulated by Ar, which was lower than the H_2 pressure required for the hydrogenolysis of glycerol using external H_2 [11–13]. During the reaction, the gas products were analyzed by an online gas chromatograph (GC102M). H_2 and CO_2 were separated by a 0.5 nm molecular sieve packed column and measured by a TCD. Light alkanes were separated by a Porapak R packed column and measured by a flame ionization detector (FID). Liquid phase products were condensed and analyzed on a GC9560 gas chromatograph fitted with a CP-Wax 52 CB capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm) and an FID. The liquid products were also measured by GC-MS (Finnigan Voyager) with an HP-5 capillary column. The carbon balance was within $\pm 5\%$ for all reaction runs.

3. Results and discussion

3.1. APR-hydrogenolysis of glycerol over skeletal NiMo catalyst

Figure 1 presents the XRD pattern of the skeletal NiMo catalyst. There were diagnostic (111), (200), and (220) reflections of Ni at 2θ of 44.3° , 51.8° , and 76.3° (JCPDS 04-0850), respectively. Based on the Scherrer equation and the broadening of the Ni(111) peak, the average crystallite size of Ni was estimated to be 3.7 nm. No feature due to an Mo species was found, indicating their high dispersion in the catalyst.

Figure 2 shows the Ni 2p and Mo 3d XPS profiles of the skeletal NiMo catalyst. Ni was predominantly in the metallic state shown by the Ni $2p_{3/2}$ BE of 852.7 eV [28]. The Mo 3d profile was deconvoluted into three components with $3d_{5/2}$ BEs of 228.0, 229.3, and 232.6 eV, which were assigned to metallic Mo,

Fig. 1. XRD pattern of the skeletal NiMo catalyst.

Fig. 2. Ni 2p (a) and Mo 3d (b) XPS profiles of the skeletal NiMo catalyst.

MoO_2 , and MoO_3 , respectively [28]. The molybdenum oxides were formed during the alkali leaching [29].

Entry 1 in Table 1 shows the catalytic activity of the one-pot APR-hydrogenolysis of glycerol over the skeletal NiMo catalyst. Glycerol was almost completely converted under the reaction condition used. There were both APR products (H_2 , CO_2 , and light alkanes) and dehydration/hydrogenation (hydrogenolysis) products (acetol and 1,2-PDO) of glycerol. Ethanol and other liquid products were detected in smaller amounts. On this catalyst, the carbon-based selectivities to gas products, acetol, and 1,2-PDO were 40.9%, 8.5%, and 32.0%, respectively. Since the skeletal NiMo catalyst is not only active in converting glycerol, but also moderately selective for 1,2-PDO, it gives a solid basis for the development of a more selective catalyst by suitable catalyst modification.

3.2. APR-hydrogenolysis of glycerol over the ZnO-NiMo mixture catalyst

Guided by the findings that the mixing of a catalyst with a second component can greatly influence the product distribution [8,30–32], we physically mixed the NiMo catalyst with MgO , SiO_2 , Al_2O_3 , HZSM-5, TiO_2 , ZrO_2 , CeO_2 , or ZnO , with their diverse acid properties, as a cocatalyst for the one-pot APR-hydrogenolysis of glycerol to 1,2-PDO. Figure 3 presents the NH_3 -TPD profiles of these oxides. The total acid amounts are summarized in Table 2. As shown in Fig. 4, except for ZnO , the conversion of glycerol decreased to varying degrees with these oxide-NiMo mixture catalysts, and consequently the yields of 1,2-PDO were also decreased. In contrast, when ZnO was used as the cocatalyst, there was a promoting effect on the catalytic performance. Entries 2–4 in Table 1 show that the conversion of glycerol with the ZnO -NiMo mixture catalysts remained essentially the same as that with just the skeletal NiMo catalyst, while the selectivity for 1,2-PDO was increased significantly and the selectivity for gas products was decreased remarkably. When the ZnO /NiMo mass ratio was increased from 0 to 2.0, the yield of 1,2-PDO increased from 31.7% to

Table 1

Catalytic activity in one-pot APR-hydrogenolysis of glycerol.

Entry	Catalyst	Conversion (%)	Yield of 1,2-PDO (%)	Carbon-based product selectivity ^a (%)				
				Gas ^b	Ethanol	Acetol	1,2-PDO	Others ^c
1	NiMo	99.1	31.7	40.9	13.5	8.5	32.0	5.1
2	ZnO–NiMo(0.5) ^d	98.7	38.3	30.8	8.3	12.6	38.8	9.5
3	ZnO–NiMo(1.0) ^d	99.4	46.1	23.1	6.8	15.5	46.4	8.2
4	ZnO–NiMo(2.0) ^d	98.9	49.6	16.5	5.3	17.1	50.2	10.9
5	ZnO–NiMo(2.0) ^{d,e}	98.7	52.0	12.9	4.6	18.8	52.7	11.0
6	ZnO ^f	0.0	—	—	—	—	—	—
7	ZnO + NiMo ^g	98.5	30.2	38.3	14.7	8.9	30.7	7.4
8	NiMo + ZnO ^h	99.3	33.3	39.4	12.3	7.6	33.5	7.2
9	Pt/Al ₂ O ₃ –Ru/Al ₂ O ₃ (1.0) ⁱ	51.2	20.1	28.1	7.2	12.4	39.2	13.1

Reaction conditions: $T = 508$ K, $p_{Ar} = 3.1$ MPa, weight hourly space velocity (WHSV) = 1.2 h⁻¹ (relative to NiMo if not specified), and $t = 8$ h.^a Defined according to Ref. [16].^b Including CO₂ and light alkanes.^c Including CH₃CHO, CH₃COCH₃, CH₃OH, CH₃CHOHCH₃, CH₃CH₂CH₂OH, CH₃COOH, CH₃CH₂COOH, CH₂OHCH₂OH, and trace amount of undefined products.^d ZnO was evenly mixed with NiMo as a mixture catalyst. Mass ratio of ZnO to NiMo in bracket.^e WHSV = 1.44 h⁻¹.^f WHSV = 0.6 h⁻¹ (relative to ZnO).^g ZnO was loaded into the reactor first followed by NiMo, allowing the reactant to contact with ZnO first.^h Loading order was reverse to entry 7.ⁱ Prepared according to Ref. [16]. Mass ratio of Pt/Al₂O₃ to Ru/Al₂O₃ in bracket. WHSV = 1.2 h⁻¹ (relative to Pt/Al₂O₃ and Ru/Al₂O₃).

49.6% with a fall of the selectivity for gas products from 40.9% to 16.5%. Meanwhile, the selectivity for ethanol decreased from 13.5% to 5.3%. These results clearly demonstrated that the APR of glycerol was suppressed and the hydrogenolysis of glycerol was promoted with the aid of the physically mixed ZnO. The yield of 1,2-PDO can be further improved to 52.0% at the WHSV of 1.44 h⁻¹ (entry 5, Table 1), which exceeded substantially the results documented in the literature from the APR-hydrogenolysis of glycerol on some other catalysts [14–17,33].

On increasing the WHSV, Fig. 5(a) illustrates that the conversion of glycerol over the skeletal NiMo catalyst decreased drastically when the WHSV exceeded 1.2 h⁻¹, while it decreased more slowly over the ZnO–NiMo(2.0) mixture catalyst (Fig. 5(b)). In addition, before the maximum selectivity for 1,2-PDO (52.7%) was reached at the WHSV of 1.44 h⁻¹ over the ZnO–NiMo(2.0) mixture catalyst, the selectivities for both acetol

and 1,2-PDO increased more with the WHSV than was the case with just the skeletal NiMo catalyst. This showed that the presence of ZnO favored both the dehydration of glycerol and the hydrogenation of acetol.

Table 2Acid amounts on the oxides determined by NH₃-TPD.

Sample	Acid amount (mmol/g)
HZSM-5	0.67
TiO ₂	0.53
Al ₂ O ₃	0.44
ZnO	0.32
ZrO ₂	0.12
CeO ₂	~0
SiO ₂	0
MgO	0

Fig. 3. NH₃-TPD profiles of the oxides. **Fig. 4.** Conversion of glycerol and yield of 1,2-PDO over oxide–NiMo mixture catalysts. Reaction conditions: oxide/NiMo mass ratio = 0.5, $T = 508$ K, $p_{Ar} = 3.1$ MPa, WHSV = 1.2 h⁻¹ (relative to NiMo), and $t = 8$ h.

Fig. 5. Effect of WHSV (relative to NiMo) on the conversion of glycerol and product selectivity over skeletal NiMo catalyst (a) and ZnO-NiMo(2.0) mixture catalyst (b). Reaction conditions: 0.50 g NiMo, $T = 508$ K, and $p_{Ar} = 3.1$ MPa. The mass ratio of ZnO/NiMo is 2.0 for the ZnO-NiMo(2.0) mixture catalyst.

In order to further confirm the promoting effect of the physically mixed ZnO on the catalytic activity, comparative kinetic experiments at conversions of glycerol below 15% were conducted on the skeletal NiMo catalyst and the ZnO-NiMo(2.0) mixture catalyst. As shown previously [34], transport limitation can be excluded under the present reaction conditions. Figure 6 presents the intrinsic activities of these two catalysts expressed as the turnover frequencies (TOFs) of glycerol conversion and 1,2-PDO production on the metallic Ni active sites. It should be emphasized that since the exact nature of the active sites on these catalysts is unclear, this comparison is only qualitative [35]. In Fig. 6, the higher TOF of glycerol over the ZnO-NiMo(2.0) mixture catalyst than the skeletal NiMo catalyst (3.5 vs. 2.0 min⁻¹) is consistent with the data in Fig. 5 that the former had a higher conversion of glycerol at higher WHSVs. The TOF of 1,2-PDO is 1.6 min⁻¹ over the ZnO-NiMo(2.0) mixture catalyst, which is more than twice that over the skeletal NiMo catalyst (0.72 min⁻¹). It is notable that the TOF of 1,2-PDO on the ZnO-NiMo(2.0) mixture catalyst is comparable to that over a noble Pt/Al₂O₃ catalyst [17].

In a recent work [16], a noble Pt/Al₂O₃-Ru/Al₂O₃ mixture catalyst (1:1, mass ratio) was found to be effective in the APR-hydrogenolysis of glycerol in a batch autoclave under N₂.

Fig. 6. TOFs of glycerol conversion and 1,2-PDO production for the skeletal NiMo catalyst and the ZnO-NiMo(2.0) mixture catalyst in the APR-hydrogenolysis of glycerol. Reaction conditions: $T = 508$ K, $p_{Ar} = 3.1$ MPa, and WHSV (relative to NiMo) of 7.2 h⁻¹ for the skeletal NiMo catalyst and 10.8 h⁻¹ for the ZnO-NiMo(2.0) admixture catalyst.

We also prepared this mixed catalyst and evaluated it on our flow reactor under reaction condition identical to that for the ZnO-NiMo mixture catalysts. As compared to the Pt/Al₂O₃-Ru/Al₂O₃ mixture catalyst (entry 9, Table 1), the skeletal NiMo catalyst and all three ZnO-NiMo catalysts were more active, and the selectivities for 1,2-PDO on the ZnO-NiMo(1.0) and ZnO-NiMo(2.0) catalysts were also substantially higher at much higher conversions of glycerol.

3.3. The promotion mechanism of ZnO

To study the promoting effect of ZnO in the ZnO-NiMo mixture catalysts, control experiments were designed and conducted. First, we confirmed that ZnO alone was inactive in the transformation of glycerol (entry 6, Table 1). Second, instead of homogeneously mixing ZnO with NiMo, we placed them in two different sequences in the tubular reactor. In one situation, NiMo was loaded first, followed by ZnO. In the other situation, a reversed loading sequence was adopted. The differences in terms of both glycerol conversion and product distribution between these two situations (entries 7 and 8, Table 1) and when just the skeletal NiMo catalyst was used (entry 1, Table 1) were negligible. This clearly demonstrated that ZnO was effective only when it was homogeneously mixed with NiMo, suggesting a synergistic effect between these two catalyst components.

In the literature, the Lewis acid catalyzed dehydration of glycerol to acetol is well documented [36–38]. Metal oxides such as Zn(II)-Cr(III) mixed oxides [37] and Nb₂O₅ [9] are good catalyst/cocatalyst for the dehydration/hydrogenolysis of glycerol to acetol/1,2-PDO. Moreover, as proposed by Gallezot et al. [39], the Lewis acid polarizes the C=O group by accepting the lone pair electron on the oxygen end of the C=O group. This polarization favors a nucleophilic attack on the carbon atom in C=O by hydrogen dissociatively adsorbed on an adjacent metallic Ni site, which facilitates the hydrogenation of acetol to 1,2-PDO. Thus, the Lewis acid sites are believed to be active in the hydrogenolysis of glycerol in both the dehydration and hydrogenation steps.

However, according to the NH_3 -TPD profiles of the oxides (Fig. 3) and the acid amounts derived from the NH_3 -TPD profiles (Table 2), both the acid amount and acid strength of ZnO are only average among these oxides. On the other hand, it is worth noting that in a combined surface chemistry and theoretical study, Wang et al. [40,41] substantiated that the Lewis acidity of ZnO can be enhanced in the presence of CO_2 . CO_2 is chemisorbed on ZnO and forms a stable tridentate carbonate on the nonpolar (10 $\bar{1}$ 0) surface of ZnO, in which the carbon atom of CO_2 bonds to one surface oxygen anion, and both oxygen atoms of CO_2 form equivalent bonds with neighboring zinc cations. This adsorption mode occurs on every second zinc cation, resulting in both occupied and unoccupied surface zinc sites. The charge-accepting chemisorbed CO_2 makes the unoccupied Zn cation more positive, thus enhancing the Lewis acidity of the unoccupied surface zinc cations [29]. The enhancement of Lewis acidity by CO_2 chemisorption has also been observed on polycrystalline ZnO powder [40–43]. In the one-pot APR-hydrogenolysis of glycerol over the ZnO-NiMo mixture catalysts, CO_2 is one of the main APR products. So, it can be proposed that a CO_2 -enhanced Lewis acidity of ZnO occurred on the ZnO-NiMo mixture catalysts, and that this was responsible for the synergistic effect between ZnO and NiMo and the enhanced conversion of glycerol and selectivity to 1,2-PDO.

Finally, we would like to comment on the atomic economy of the one-pot APR-hydrogenolysis of glycerol to 1,2-PDO over the ZnO-NiMo mixture catalysts. Referring to Scheme 1, the ideal APR/hydrogenolysis ratio of glycerol is 1:7 [15]. Following the classification of the products by Gandarias et al. [14], in Fig. 7 we plotted the evolution of the ratio between the selectivities to hydrogenolysis products and APR products versus the weight ratio of ZnO to NiMo. It is clear that by increasing the ZnO/NiMo ratio from 0 to 2.0, the hydrogenolysis/APR ratio increased from 1.0 to 4.6 at the WHSV of 1.2 h^{-1} . On further increasing the WHSV to 1.44 h^{-1} over the ZnO-NiMo(2.0) mixture catalyst, the hydrogenolysis/APR ratio was 6.3, which approached the ideal ratio. From the product distribution in Table 1, further catalyst or process improvement should focus on suppressing the breaking of the C–C bond in glycerol which

Fig. 7. Effect of mass ratio of ZnO/NiMo on the ratio of hydrogenolysis products to APR products. Reaction conditions: $T = 508 \text{ K}$, $p_{\text{Ar}} = 3.1 \text{ MPa}$, WHSV = 1.2 h^{-1} if not specified, and $t = 8 \text{ h}$. ^aHydrogenolysis products: C_3 products in the liquid phase; APR products: CO_2 and light alkanes. ^bWHSV = 1.44 h^{-1} .

mainly results in ethanol and other C_2 liquid byproducts, and on enhancing the hydrogenation of the dehydration intermediate acetol to 1,2-PDO.

4. Conclusions

In the one-pot APR-hydrogenolysis of glycerol to 1,2-PDO in a continuous flow fixed bed reactor, physically mixed ZnO helps suppress excessive APR of glycerol and enhances the hydrogenolysis of glycerol. With the optimal ZnO-NiMo(2.0) mixture catalyst, a yield of 1,2-PDO of 52.0% was achieved in the absence of externally supplied H_2 , and at a reaction pressure lower than that required for the hydrogenolysis of glycerol under H_2 . The remarkable synergistic effect between the mixed ZnO and NiMo is attributed to CO_2 -enhancement of the Lewis acidity of ZnO, which promotes the dehydration of glycerol to acetol and the hydrogenation of the latter to 1,2-PDO. This work opens a new avenue for the continuous production of 1,2-PDO from glycerol and water over a non-noble metal catalyst under mild reaction conditions.

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Graphical Abstract

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Physically mixed ZnO and skeletal NiMo for one-pot reforming-hydrogenolysis of glycerol to 1,2-propanediol

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Physically mixing ZnO with skeletal Ni₄₀Mo₁₀ gave an excellent catalyst for the hydrogenolysis of glycerol to 1,2-PDO under an inert atmosphere, which was due to CO₂-enhancement of the Lewis acidity of ZnO by CO₂ generated from the reforming of glycerol.

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ZnO与骨架NiMo物理混合用于丙三醇催化重整-氢解制1,2-丙二醇

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摘要: 以骨架NiMo以及氧化物物理混合, 考察了其在连续固定床反应器中无外加氢气条件下的丙三醇一锅法重整-氢解制1,2-丙二醇(1,2-PDO)的性能. 研究发现, 骨架NiMo自身催化活性高, 但对1,2-PDO的选择性一般. 当将其与MgO, SiO₂, Al₂O₃, HZSM-5, TiO₂, ZrO₂或CeO₂机械混合时, 丙三醇转化率和1,2-PDO选择性均发生下降. 但当与ZnO物理混合时, 催化活性和选择性均有所提高, 1,2-PDO得率可达52.0%, 优于贵金属催化剂在该一锅法反应中得到的结果. 物理混合的ZnO与骨架NiMo之间这种独特的协同作用, 归因于重整过程中产生的CO₂在ZnO上发生化学吸附, 原位增强了ZnO的路易斯酸性. 这不仅促进了丙三醇在ZnO上脱水生成中间产物丙酮醇, 也促进了丙酮醇在骨架NiMo上加氢生成1,2-PDO.

关键词: 丙三醇; 氢解; 氧化锌; 镍; 钼; 协同效应

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