

Article

## Effect of Phosphine Doping and the Surface Metal State of Ni on the Catalytic Performance of Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst

Xiaoru Li <sup>1,2,3</sup>, Haiyang Cheng <sup>1,2,\*</sup>, Guanfeng Liang <sup>1,2</sup>, Limin He <sup>1,2</sup>, Weiwei Lin <sup>1,2</sup>, Yancun Yu <sup>1,2</sup> and Fengyu Zhao <sup>1,2,\*</sup>

<sup>1</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China; E-Mails: lixiaoru@ciac.ac.cn (X.L.); lianggf@ciac.ac.cn (G.L.); helm12@163.com (L.H.); linwei@ciac.ac.cn (W.L.); yuyc@ciac.ac.cn (Y.Y.)

<sup>2</sup> Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

<sup>3</sup> University of Chinese Academy of Sciences, Beijing 100049, China

\* Authors to whom correspondence should be addressed; E-Mails: zhaofy@ciac.ac.cn (F.Y.Z.); hycyl@ciac.ac.cn (H.Y.C.); Tel./Fax: +86-431-8526-2410 (F.Y.Z.); +86-431-8526-2454 (H.Y.C.).

Academic Editor: Masahiko Arai

Received: 12 February 2015 / Accepted: 15 April 2015 / Published: 23 April 2015

---

**Abstract:** Ni-based catalysts as replacement for noble metal catalysts are of particular interest in the catalytic conversion of biomass due to their cheap and satisfactory catalytic activity. The Ni/SiO<sub>2</sub> catalyst has been studied for the hydrogenolysis of glycerol, and doping with phosphorus (P) found to improve the catalytic performance significantly because of the formation of Ni<sub>2</sub>P alloys. However, in the present work we disclose a different catalytic phenomenon for the P-doped Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. We found that doping with P has a significant effect on the state of the active Ni species, and thus improves the selectivity to 1,2-propanediol (1,2-PDO) significantly in the hydrogenolysis of glycerol, although Ni-P alloys were not observed in our catalytic system. The structure and selectivity correlations were determined from the experimental data, combining the results of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) and ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD). The presence of NiO species, formed from P-doped Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, was shown to benefit the formation of 1,2-PDO. This was supported by the results of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst containing NiO species with incomplete reduction. Furthermore, the

role the NiO species played in the reaction and the potential reaction mechanism over the P-doped Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is discussed. The new findings in the present work open a new vision for Ni catalysis and will benefit researchers in designing Ni-based catalysts.

**Keywords:** glycerol; hydrogenolysis; Ni/Al<sub>2</sub>O<sub>3</sub>; phosphorus-doping; metal state

---

## 1. Introduction

Over the last decade, biodiesel, a potential fuel, has attracted much attention. However, high cost in production makes it difficult for plants to take a step forward. In order to help overcome the problems, glycerol, a by-product in the manufacture of biodiesel fuel by transesterification (10% in weight), was used as a low-cost feedstock to produce valued fine chemicals [1,2]. The substance 1,2-propanediol (1,2-PDO), a hydrogenolysis product of glycerol, is widely applied in polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, functional fluids (antifreeze, de-icing, and heat transfer) and its market share is expected to expand owing to the growing concern of the toxicity of ethylene glycol-based antifreeze to humans and animals on de-icing. Traditionally, 1,2-PDO is produced by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process, but these processes bring about many environmental problems [3]. As a green process, the hydrogenolysis of glycerol is an industrially relevant route for the production of 1,2-PDO.

Until now, great efforts have been made in the hydrogenolysis of glycerol [4–9]. Noble metals such as Ru, Rh, Pt have been much explored for the hydrogenolysis of glycerol. Although the noble metal catalysts are effective for the hydrogenolysis of glycerol at a relatively low temperature, they do not fit the requirements of industrial application due to their lower selectivity and high cost. By contrast, a non-noble metal has an advantages in price. Some catalysts such as Cu-based, Co-based, and Ni-based catalysts have been explored for the hydrogenolysis of glycerol. Ni-based catalysts have had a great deal of attention due to their moderate activity.

Perosa *et al.*, reported their primary research on the hydrogenolysis of glycerol without solvent over Raney nickel catalyst, and they obtained 12% conversion of glycerol and 93% selectivity to 1,2-PDO at 150 °C, 8.0 MPa H<sub>2</sub>. The selectivity to 1,2-PDO decreased on enhancing the reaction temperature, reducing to 70%–80% and 48% at 190 °C and 210 °C, respectively [10]. Ryneveld *et al.*, investigated the transformation of glycerol to lower alcohols in a fixed-bed reactor over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, and they obtained 1,2-PDO with a high selectivity of 80% at 230 °C. As the temperature increased to 320 °C, the 1,2-PDO selectivity decreased to 2%, while the selectivity for ethanol and propanol increased to 52% [11]. Yu *et al.*, used KBH<sub>4</sub> treated carbon thermal reduced Ni/AC catalyst to catalyze the hydrogenolysis of glycerol; they obtained 76.1% selectivity to 1,2-PDO in water at 200 °C [12]. Huang *et al.*, reported that the Ni/Al<sub>2</sub>O<sub>3</sub> showed high selectivity to CH<sub>4</sub> and CO for vapor phase glycerol hydrogenolysis in a fixed-bed reactor [13]. The selectivity of the desired product of 1,2-PDO is not always satisfactory over the Ni-based catalysts.

Doping a second element to the metal catalysts is considered to be an efficient means as well as being widely used to adjust the catalytic performance. Morales *et al.*, reported that selectivity to 1,2-PDO was enhanced significantly over Ni-Ce/SBA catalyst compared with that of the Ni/SBA due to the increase

of surface acidity on the addition of Ce [14]. Huang *et al.*, reported that the addition of phosphorus to Ni/SiO<sub>2</sub> catalyst could increase the selectivity to 1,2-PDO to 85.9% from 49.9% at 220 °C, they suggested that the formation of a Ni<sub>2</sub>P alloy phase and its electronic and geometrical properties could affect the hydrogenolysis of C–O and C–C bonds [15]. Montassier *et al.*, found that Ru/C catalyst doped with sulfur could increase the selectivity of 1,2-PDO from 12%–80% because doping of sulfur could prevent the carbonyl hydrogenation and C–C and C–O hydrogenolysis based on electron transfer from Ru to S [16]. Moreover, the effects of promoters like Al, Ba and Zn on the Cu-Cr catalysts in the hydrogenolysis of glycerol was investigated in 2-propanol at 220 °C, in the presence of Ba, the highest selectivity to 1,2-PDO reached 85% at 34% conversion, it was suggested that the increased acid sites and the BaCrO<sub>4</sub> phase might be responsible for the improved activity and selectivity [17].

In this paper, the catalytic performance of Ni/Al<sub>2</sub>O<sub>3</sub> and phosphorus doping Ni/Al<sub>2</sub>O<sub>3</sub> (Ni-P/Al<sub>2</sub>O<sub>3</sub>) catalysts were studied and compared for the hydrogenolysis of pure glycerol. The effect of phosphorus doping on the catalytic performance was determined based on the variation of the structure and electronic state of the Ni species. It was confirmed that the doping of phosphorus could induce the formation of NiO species in Ni-P/Al<sub>2</sub>O<sub>3</sub> catalysts, which was found to be responsible for the improved selectivity to 1,2-PDO (91%).

## 2. Results and Discussion

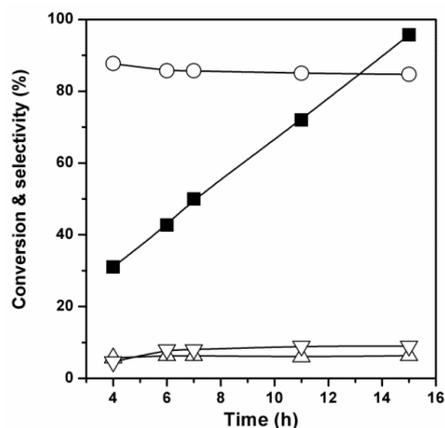
### 2.1. Influence of P Doping on the Catalytic Performance

The catalytic activity of a series of 17.5% Ni-yP/Al<sub>2</sub>O<sub>3</sub>-500 catalysts was determined for the hydrogenolysis of glycerol in the absence of solvent. Usually, 1,2-PDO and ethylene glycol (EG) were produced as the main products over the Ni-based catalysts accompanied by minor amounts of byproducts of 1-propanol, ethanol, methanol, and acetol in the hydrogenolysis of glycerol; herein we mainly discuss the factors which affected the selectivity to 1,2-PDO and EG. The influence of P doping on the hydrogenolysis of glycerol is listed in Table 1. It is clear that the activity did not change with the P doping initially but it declined remarkably after the P content was increased up to 4.4%. However, the selectivity to 1,2-PDO increased linearly with the content of P, and it reached 91.1% over the 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500, which was much higher than the value (66.5%) of 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500. Figure 1 shows the changes of the conversion and product selectivity with reaction time over the 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500. The conversion increased linearly with reaction time, indicating that the present hydrogenolysis of glycerol is zero order with respect to glycerol. The selectivity to 1,2-PDO remained around 85%, and changed very slightly with conversion of glycerol up to 95.7%.

**Table 1.** Effect of P-doping on the catalytic performance in hydrogenolysis of glycerol.

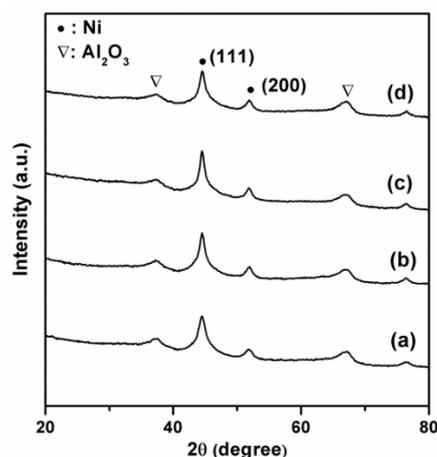
Entry	Catalyst	Conversion (%)	Selectivity (%)		
			1,2-PDO <sup>a</sup>	EG <sup>a</sup>	Others <sup>b</sup>
1	17.5% Ni/Al <sub>2</sub> O <sub>3</sub> -500	42.4	66.5	21.6	11.9
2	17.5% Ni-1.7% P/Al <sub>2</sub> O <sub>3</sub> -500	42.6	77.5	11.9	10.6
3	17.5% Ni-2.9% P/Al <sub>2</sub> O <sub>3</sub> -500	42.7	85.7	6.3	8.0
4	17.5% Ni-4.4% P/Al <sub>2</sub> O <sub>3</sub> -500	25.8	91.1	3.2	5.7

Reaction conditions: glycerol 38.0 mmol, catalyst 0.25 g, 230 °C, 5 MPa H<sub>2</sub>, reaction time 6 h. <sup>a</sup>: 1,2-PDO: 1,2-propylene glycol, EG: ethylene glycol. <sup>b</sup>: The others include 1-propanol, ethanol, methanol and acetol.



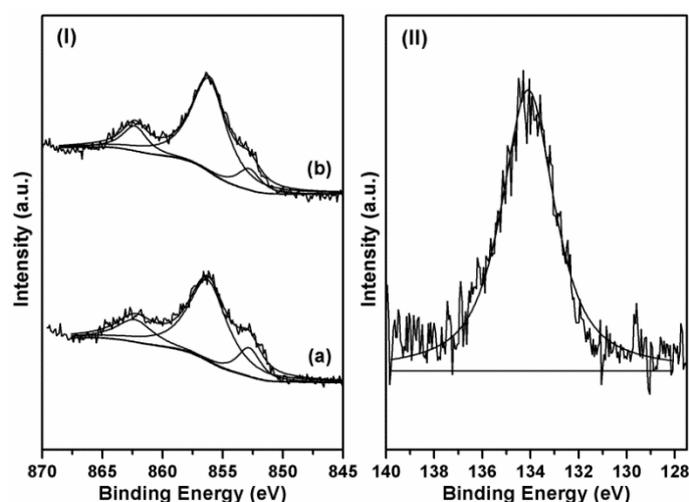
**Figure 1.** Glycerol conversion and product selectivity as a function of reaction time over 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500. Reaction conditions: glycerol 38.0 mmol, catalyst 0.25 g, 230 °C, 5 MPa H<sub>2</sub>. (■) conversion of glycerol, selectivity to (○)1,2-Propylene Glycol (1,2-PDO), (△)Ethylene Glycol (EG), and (▽) other byproducts include 1-propanol, ethanol, methanol and acetol.

It was reported that transition-metal phosphides such as Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P can be formed on high temperature treatment under the reducing atmosphere of hydrogen [18,19]. In addition, Huang *et al.*, reported that the formation of the Ni<sub>2</sub>P alloy phase could improve the selectivity to 1,2-PDO in the glycerol hydrogenolysis over P-doped Ni/SiO<sub>2</sub> catalyst [15]. Thus, powder X-ray diffraction measurements of 17.5% Ni-γP/Al<sub>2</sub>O<sub>3</sub>-500 catalysts were carried out to check the formation of Ni-P alloys. As seen in Figure 2, the diffraction peaks appearing at 37.3° and 67.1° were attributed to γ-Al<sub>2</sub>O<sub>3</sub> (JCPDS, 13-0373), and the peaks at 44.5°, 51.9°, and 76.4° were assigned to metallic Ni<sup>0</sup> (JCPDS, 04-0850). The intensity of the Ni diffraction peaks changed slightly with doping of P, and all the sizes of the Ni particles were about 10.9 nm as calculated from the half-width of Ni (111) by the Scherrer equation, thus indicating that doping and increasing P content affect slightly the dispersion of crystalline Ni particles. However, the diffraction peaks of Ni<sub>2</sub>P (at 40.8°, 44.6° and 47.3°, (JCPDS, 65-3544)), and Ni<sub>12</sub>P<sub>5</sub> (at 48.9°, 43.9° and 41.7°, (JCPDS, 65-1623)) were not found.



**Figure 2.** X-ray diffraction patterns of (a) 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500, (b) 17.5% Ni-1.7% P/Al<sub>2</sub>O<sub>3</sub>-500, (c) 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500, and (d) 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500.

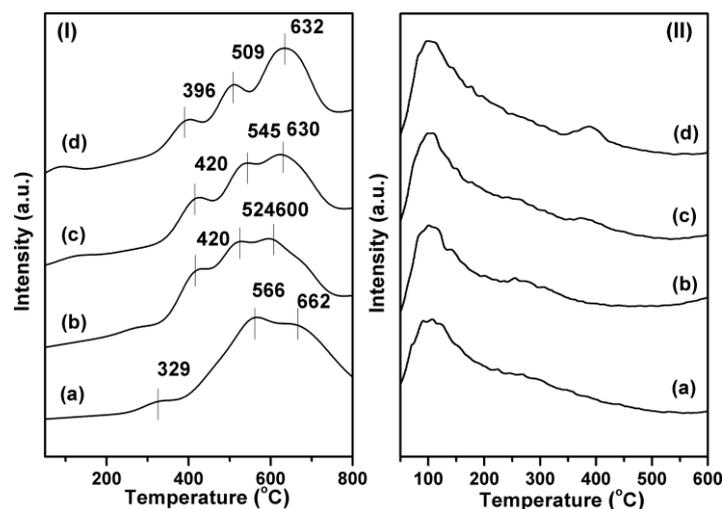
Moreover, the valence state and the chemical environment of Ni and P were examined by XPS, Figure 3I lists the XPS profiles of the Ni 2p<sub>3/2</sub> level for the comparative samples of 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500 and 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500. The peaks appeared at binding energy of 850–870 eV, regions could be deconvoluted into three peaks: 852.8 eV corresponds to the metallic Ni [20], 856.3 eV corresponds to nickel oxide/hydroxide [21,22], besides, shake-up satellites can be seen at the higher binding energy of 6.1 eV. The electronic binding energy of Ni 2p<sub>2/3</sub> in 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500 was the same as that in 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500. The XPS spectra of P 2p presented at binding energy of 134.2 eV was assigned to the oxidized P species (P<sup>5+</sup>) [23,24]. However, both the reduced phosphides (element P) at 129.5 eV and AlPO<sub>4</sub> at binding energy of 134.7 eV were not detected [19,23,24]. The above XPS results indicated that, in 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500, Ni species existed as Ni<sup>0</sup> and NiO, and P species existed as PO<sub>4</sub><sup>3-</sup>. Huang and Sawhill reported that Ni-P alloys such as Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P were formed with the addition of phosphorus to Ni/Al<sub>2</sub>O<sub>3</sub> at a reduction temperature of 850 °C [15,19]. However, in the present work, Ni-P alloys were not formed due to a lower reduction temperature based on the results of XRD and XPS.



**Figure 3.** XPS spectra of (I) Ni 2p<sub>3/2</sub> levels for 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500 (a) and 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500 (b); and (II) P 2p levels for 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500.

Therefore, in order to figure out the exact reasons for the improvement of the selectivity to 1,2-PDO over the 17.5% Ni-yP/Al<sub>2</sub>O<sub>3</sub>-500 catalysts, H<sub>2</sub>-Temperature Programmed Reduction (H<sub>2</sub>-TPR) and NH<sub>3</sub>-Temperature Programmed Desorption (NH<sub>3</sub>-TPD) measurements were studied. It is clear that the reduction peaks changed largely after doping of P ( H<sub>2</sub>-TPR profiles in Figure 4I). For all the samples, there are three reduction peaks. With the doping of P, the reduction peak at the lower temperature (329 °C) moved to the higher temperature (390–420 °C), and the peak at 662 °C moved to the lower ones but the peak areas at the high reduction temperature increased greatly. It suggested that three kinds of NiO species were formed and that P doping could influence the interaction between these NiO species with Al<sub>2</sub>O<sub>3</sub> support. At the reduction temperature of 580 °C, the NiO species could not be completely reduced to Ni<sup>0</sup>. But no diffraction peaks of NiO were detected in the reduced 17.5% Ni-yP/Al<sub>2</sub>O<sub>3</sub>-500 catalysts because of its low amount and poor crystallinity. In addition, the doping of P has an effect on

the acidity of the catalyst, as seen in Figure 4II. The total acid sites increased with the increase in P content, and a new acid site presented at around 380–400 °C for the catalysts with higher P content.



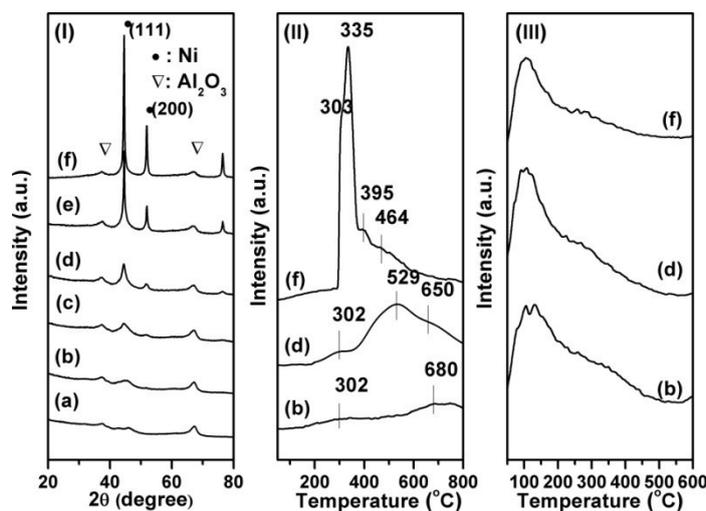
**Figure 4.** The H<sub>2</sub>-TPR (I) and NH<sub>3</sub>-TPD (II) of 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500 (a), 17.5% Ni-1.7% P/Al<sub>2</sub>O<sub>3</sub>-500 (b), 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500 (c), and 17.5% Ni-4.4% P/Al<sub>2</sub>O<sub>3</sub>-500 (d).

Based on the above results of the H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD, doping of P could influence the electronic environment of the Ni species and the surface acidity of Ni/Al<sub>2</sub>O<sub>3</sub>, which may have been responsible for the improved selectivity to 1,2-PDO over the Ni-P/Al<sub>2</sub>O<sub>3</sub> catalysts. Therefore, we designed experiments to discuss the effects of the Ni species on the catalytic properties as follows.

## 2.2. Influence of Ni Metal State on the Catalytic Performance

As already known, the loading of metal and calcination temperature could change the redox properties and surface acidity of the catalysts. Thus, a series of *x*Ni/Al<sub>2</sub>O<sub>3</sub>-450 catalysts with different Ni loadings were prepared first of all and their properties were examined, as shown in Figure 5I; the diffraction peaks of Ni became sharper with increasing Ni loading, indicating that the Ni particles increased with increase in Ni content. As calculated from the half-width of Ni (111) by the Scherrer equation, the average particle size of Ni increased from 7.1–16.6 nm when Ni loading increased from 5%–40%. It was found that when Ni loading was 5%, the main reduction peak appeared at 680 °C as shown in Figure 5II. While, on increasing Ni loading, the main reduction peak shifted to lower temperature, and moved to 335 °C at Ni loading of 40%. The change of reduction temperature with different loadings revealed that NiO has a strong interaction with Al<sub>2</sub>O<sub>3</sub> [25,26]. The interaction decreased with increasing Ni loading because the NiO crystallites aggregated or grew to large ones, inducing a weak interaction with Al<sub>2</sub>O<sub>3</sub> [27,28]. Therefore, the reduction temperature changed to the low one with increasing Ni loading. In addition, NH<sub>3</sub>-TPD examination was performed to compare the acidity of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with different loadings (Figure 5III); there existed a main desorption peak at about 100 °C. The amount of surface acid sites decreased with increasing Ni loading because the acid sites of Al<sub>2</sub>O<sub>3</sub> were overlaid by Ni particles. Furthermore, the influence of Ni loading on product selectivity was compared at a similar conversion around 50% as shown in Table 2. The selectivity to 1,2-PDO decreased and the selectivity to EG increased initially with increasing Ni

loading, then it changed slightly at Ni loading above 17.5%, which may correlate with the surface properties such as the Ni state and the acidity of the catalysts.



**Figure 5.** The XRD (I); H<sub>2</sub>-TPR(II); and NH<sub>3</sub>-TPD (III) of Ni/Al<sub>2</sub>O<sub>3</sub>-450 with different loadings of Ni. (I) Al<sub>2</sub>O<sub>3</sub> (a), and 5% (b), 9.5% (c), 17.5% (d), 29.6% (e) and 40% (f).

**Table 2.** Influence of Ni loading on the hydrolysis of glycerol over Ni/Al<sub>2</sub>O<sub>3</sub>-450 catalysts.

Ni loading (%)	Time (h)	Conversion (%)	Selectivity (%)		
			1,2-PDO	EG	Others
5	12	50.6	84.2	4.8	11.0
9.5	7.3	51.5	75.8	14.3	9.9
17.5	5	52.8	61.4	25.1	13.5
29.6	4	47.2	60.5	26.2	13.3
40	7	45.9	59.1	27.0	13.9

Reaction conditions: glycerol 38.0 mmol, catalyst 0.25 g, 230 °C, 5 MPa H<sub>2</sub>.

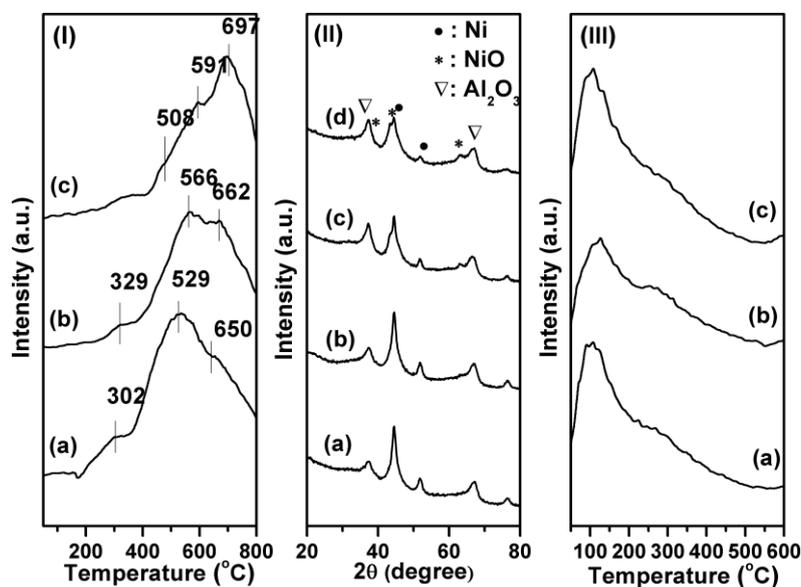
Following this, the influence of the calcinating temperature was determined based on the results of TPR, XRD, and the NH<sub>3</sub>-TPD results of the 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-T catalysts. From the H<sub>2</sub>-TPR results, three reduction peaks were found for all the samples checked. With increasing calcination temperature from 450–600 °C, the reduction peaks moved to higher temperatures (Figure 6I), which was ascribed to the increasing interaction of the NiO crystal with the support during higher calcination [29,30]. Therefore, the complete reduction of NiO needs a much higher temperature. It is in agreement with the results of XRD patterns in Figure 6II, in which the NiO species was found in the 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-T catalysts calcined at 600 °C. Furthermore, when the Ni/Al<sub>2</sub>O<sub>3</sub> was partially reduced via a shorter reduction time (17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-450-PR), the diffraction peaks of NiO at 43.1° appeared clearly. The reduction degree decreased with increasing calcination temperature due to the stronger interaction between NiO and Al<sub>2</sub>O<sub>3</sub> support. An increase in the amount of NiO species on the surface of the catalyst contributed to the high selectivity to 1,2-PDO in the hydrogenolysis of glycerol. As seen in Table 3, on increasing the calcination temperature from 450–600 °C, it is obvious that the conversion decreased gradually from 59.8%–27.1%, but the selectivity to 1,2-PDO increased from 61.4%–78.6% (Entries 1,3,4), and a similar result was also obtained for the 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-450-PR catalyst; with

this the conversion decreased to 23.4% but the selectivity to 1,2-PDO increased to 78.0% (Entry 2). Thus, we can conclude that the existence of NiO could enhance the selectivity to 1,2-PDO, but decrease the reaction conversion. In addition, the acidity of the catalysts calcined at different temperatures was also examined. As shown in Figure 6III the amount of surface acid sites decreased with increasing calcination temperature, which may be attributed to the reduction of the surface hydroxyl density and specific surface. It is worth noting that the surface acid sites decreased but the selectivity to 1,2-PDO increased, which is different from the 17.5% Ni-yP/Al<sub>2</sub>O<sub>3</sub>-500 catalysts, in which the acidity increased with doping of P, and the selectivity to 1,2-PDO increased as well.

**Table 3.** Effect of calcination temperature on the catalytic performance of 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-T catalysts.

Entry	Calcination temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)		
				1,2-PDO	EG	Others
1	450	6	59.8	61.4	25.1	13.5
2 <sup>a</sup>	450	6	23.4	78.0	9.3	12.7
3	500	6	42.4	66.5	21.6	11.9
4	600	6	27.1	78.6	9.4	12.0

Reaction conditions: glycerol 38.0 mmol; catalyst 0.25 g, 230 °C, 5 MPa H<sub>2</sub>. <sup>a</sup> 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-450-PR.

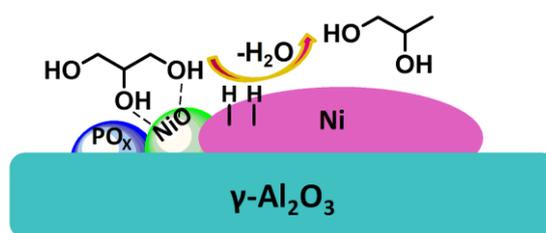


**Figure 6.** (I) H<sub>2</sub>-TPR; (II) XRD and (III) NH<sub>3</sub>-TPD of fresh reduced 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-T with different calcination temperatures: 450 °C (a), 500 °C (b), 600 °C (c), and calcinated at 450 °C but reduced from room temperature to 580 °C without maintaining at 580 °C (17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-450-PR) (d).

The effects of acidity have been widely discussed for the hydrogenolysis of glycerol. It was suggested that the surface acid site could benefit from the formation of an intermediate acetol, which is then converted to 1,2-PDO [5,17,31,32]. In other words, the selectivity to 1,2-PDO may depend on the amount of surface acid sites. Herein, with decreasing of Ni loading and the doping of P, the amount of surface acid sites increased, resulting in an enhancement of the selectivity to 1,2-PDO. However, with rising calcination temperature, the surface acid sites decreased but the selectivity to 1,2-PDO still

increased. Based on the above results, we propose that both the acidity and NiO species have an influence on the production of 1,2-PDO; the amount of surface acid sites is not the decisive factor, but the NiO species is the main factor for the enhancement of selectivity to 1,2-PDO and the decrease in the reaction conversion in the hydrogenolysis of glycerol.

When the reaction was conducted in the absence of hydrogen over Ni/Al<sub>2</sub>O<sub>3</sub>-500 and Ni-1.7%P/Al<sub>2</sub>O<sub>3</sub>-500 catalysts even though acetol was detected, both the reactions gave very low conversion <1% under 230 °C for 10 h, thus direct dehydration of glycerol to acetol is very difficult with the present catalysis system. However, when acetol was used as the starting reactant, it was converted completely to 1,2-PDO within 20 min at same reaction conditions. So we deduced that the hydrogenolysis of glycerol in the present catalysis system follows the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism [33–35] in which the adjacent two hydroxyls of glycerol adsorbed on the NiO surface, react with atomic hydrogen on the Ni surface, and the C-O bond cleavage and hydrogen atom addition occur simultaneously to produce 1,2-PDO, as shown in Scheme 1. For the formation of EG, glycerol first of all dehydrogenates to glyceraldehydes, then decarbonylates through retro-aldolization to produce EG [16]. The NiO on the Ni-base catalysts reduced the active sites for dehydrogenation which was the first step in producing EG, so the selectivity to EG decreased.



**Scheme 1.** Illustration of the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) over Ni-P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The NiO benefits for the adsorption of glycerol, and activates the hydroxyl groups, eventually accelerating the hydrogenolysis and lowering the rate of dehydrogenation. The surface acid sites are also a benefit for the hydrogenolysis of glycerol to 1,2-PDO. Thus the selectivity to 1,2-PDO increased when the NiO species and acid sites were at higher levels on the surface of the catalysts. Therefore, 17.5% Ni- $\gamma$ P/Al<sub>2</sub>O<sub>3</sub>-500 catalysts presented a higher selectivity to 1,2-PDO compared with 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500 because doping of P could induce an increase in the amount of surface NiO and acid sites.

For the activity and selectivity of 17.5% Ni- $\gamma$ P/Al<sub>2</sub>O<sub>3</sub>-500 catalysts in the glycerol hydrogenolysis, two factors need to be considered. The first one is the active site for the adsorption of hydroxyl of glycerol, which is related to the NiO and acid sites, and the second one is the active site of Ni<sup>0</sup> species for cleavage of hydrogen. With doping of P and raising of the calcination temperature or shortening reduction time (partially reduction), the amount of the catalytic active sites of Ni<sup>0</sup> decreased and NiO increased, resulting in a decrease in reaction rate and an increase in the selectivity to 1,2-PDO.

The stability of 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500 was compared with 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500, the results are shown in Table 4. Due to the catalyst being susceptible to air, the stability was measured by increasing the ratio of substrate to catalyst and extending the reaction time simultaneously. It is

obvious that the reaction rate decreased slightly for both catalysts, it decreased to 0.79 from 0.99 h<sup>-1</sup> for 17.5% Ni/Al<sub>2</sub>O<sub>3</sub>-500, and decreased to 0.73 from 1.00 h<sup>-1</sup> for 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500. However, the selectivity to the main product 1,2-PDO did not change, it was 66% for 17.5% Ni /Al<sub>2</sub>O<sub>3</sub>-500, and >85% for 17.5% Ni-2.9% P/Al<sub>2</sub>O<sub>3</sub>-500. Ni leaching was not detected in the filtrate based on the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis with a detection limit of 0.1 ppm. The loss in activity may be caused by the surface coverage and the pore blockage with carbonaceous deposition on the surface of the catalyst.

**Table 4.** The stability of the catalysts.

Entry	Catalysts	Time (h)	Conv. (%)	Selectivity (%)			Rate (h <sup>-1</sup> ) <sup>a</sup>
				1,2-PDO	EG	Others	
1 <sup>b</sup>	17.5% Ni/ Al <sub>2</sub> O <sub>3</sub> -500	6	42.4	66.5	21.6	11.9	0.99
2 <sup>c</sup>	17.5% Ni/ Al <sub>2</sub> O <sub>3</sub> -500	18	33.9	66.1	20.8	13.1	0.79
3 <sup>b</sup>	17.5% Ni-2.9% P/Al <sub>2</sub> O <sub>3</sub> -500	6	42.7	85.7	6.3	8.0	1.00
4 <sup>c</sup>	17.5% Ni-2.9% P/Al <sub>2</sub> O <sub>3</sub> -500	18	31.2	89.7	5.7	4.6	0.73

Reaction conditions: 38.0 mmol glycerol, 230 °C, 5 MPa H<sub>2</sub>. <sup>a</sup> The rate was calculated with converted gram of glycerol divided by gram of catalyst used and reaction time. <sup>b</sup> 0.25g catalyst, <sup>c</sup> 0.083 g catalyst.

The hydrogenolysis of glycerol with a supported Ni catalyst has been reported in several literature works and the results are compared in Table 5. Ni<sub>2</sub>P/SiO<sub>2</sub> was reported to be the most efficient catalyst with 95.1% conversion and 85.9% selectivity to 1,2-PDO; the formation of Ni<sub>2</sub>P alloy phase and its electronic and geometrical properties should have an effect on the hydrogenolysis of C–O and C–C bonds [15]. Herein, P doping Ni/Al<sub>2</sub>O<sub>3</sub> exhibited a comparable conversion and selectivity to 1,2-PDO. However, Ni<sub>2</sub>P alloy phase was not formed, but the existence of amorphous and/or crystal NiO was responsible for the high selectivity to 1,2-PDO at a comparable conversion.

**Table 5.** Comparison of the Ni-based catalysts in the hydrogenolysis of glycerol.

Catalyst	Reaction condition	Conversion (%)	S <sub>1,2-PDO</sub> (%)	Ref.
Raney Ni	190 °C, 1 MPa, 44 h	97	71	[10]
Ni/AC-CB	200 °C, 5 MPa, 24 h	63.2	77.4	[12]
7.5%Ce-Ni/SBA	200 °C, 2.4 MPa, 8 h	51	29	[14]
Ni <sub>2</sub> P/SiO <sub>2</sub>	220 °C, 3 MPa, 1.13 h	95.1	85.9	[15]
17.5% Ni-2.9% P/Al <sub>2</sub> O <sub>3</sub>	230 °C, 3 MPa, 15 h	95.7	84.7	This work

### 3. Experimental Section

#### 3.1. Materials

γ-Alumina (Sinopharm Chemical Reagent Co., Shanghai, China) was used as the support without special treatment. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Beijing Yili Fine Chemicals Co., Beijing, China, 98%), NH<sub>4</sub>·H<sub>2</sub>PO<sub>4</sub> (Beijing Chemicals, Beijing, China, 98%), glycerol (Xilong Chemicals, Guangzhou, China, 99%) were used directly without any treatment. Deionized water and the gases of H<sub>2</sub> (99.999%), N<sub>2</sub> (99.999%) and NH<sub>3</sub> (99.999%) were used as delivered.

### 3.2. Catalysts Preparation

A series of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with different Ni loadings of 5%, 9.5%, 17.5%, 29.6% and 40% were prepared by the incipient wetness impregnation method. A solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added dropwise to a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slurry, and then the mixture was dried at 80 °C overnight, followed by calcination in air at different temperatures (450 °C, 500 °C and 600 °C) for 5 h. The samples were labeled as xNi/Al<sub>2</sub>O<sub>3</sub>-T, where x denotes the loading of Ni and T denotes the calcined temperature.

In addition, the P-doped Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with a Ni loading of 17.5% were prepared with the method as described above, except for dropwise addition of NH<sub>4</sub>·H<sub>2</sub>PO<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O together in the first impregnating step. After calcination (500 °C, 5 h), the samples were stored in a vessel and labeled as 17.5% Ni-yP/Al<sub>2</sub>O<sub>3</sub>-500, y denotes the loading of phosphine. To eliminate the diffusion effect, the catalysts were ground and screen separated by 180 (<80  $\mu$ m) and 200 mesh (<75  $\mu$ m). The results show that the reaction rate kept at a constant value with a particle size smaller than 180 mesh, indicating that the inner transfer resistance was removed with a catalyst smaller than 180 mesh in size. As a result the catalysts used in the reactions were ground and separated by 180 mesh.

### 3.3. Characterization

XRD patterns of all involved catalysts were performed on Bruker D8 ADVANCE diffractometer, using Cu-K $\alpha$  radiation ( $\lambda = 0.154$  nm). Prior to the test, samples were pre-reduced at 580 °C for 2 h. Crystallite sizes of Ni particles were determined from the most intense peaks at  $2\theta = 44.5^\circ$  (h k l = 1 1 1) using the Scherrer equation, *i.e.*,  $D_c = K \lambda / \beta \cos\theta$ , where the constant K here is 0.9,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the width of the peak at half-maximum, and  $\theta$  is the Bragg angle.

H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD were carried on TP-5080 (Tianjin Xianquan Industry and Trade Development Co. Ltd, Tianjin, China), with a thermal conductivity detector. Before a H<sub>2</sub>-TPR run, 30 mg of the catalyst was loaded in the quartz tube and pretreated with nitrogen at 150 °C for 10 min. After cooling to room temperature, the sample cell was heated to 800 °C with a ramping rate of 10 °C/min in flow gases of H<sub>2</sub>/N<sub>2</sub> with a flow rate of 30 mL/min. For the NH<sub>3</sub>-TPD test, 100 mg of the sample was pre-reduced in pure H<sub>2</sub> at 580 °C for 1 h. After the catalyst had cooled to room temperature, the absorption was conducted by flushing the sample with NH<sub>3</sub> for 30 min, and then sweeping with N<sub>2</sub> for 1 h to remove physisorbed and/or weakly bound species. Desorption of NH<sub>3</sub> was carried out at 800 °C with a heating rate of 10 °C/min in a nitrogen flow.

For XPS measurements, a VG Microtech 3000 Multilab was used. Prior to measurement, samples were pre-reduced at 580 °C for 2 h. The electronic properties of Ni and P on the surface of the catalysts were determined. All XPS spectra were corrected to the C 1s peak at 284.6 eV.

### 3.4. Hydrogenolysis of Glycerol

The hydrogenolysis of glycerol was performed in a 50 mL stainless steel reactor with an inner Teflon tube in solvent-free conditions. The calcinated catalysts were pre-reduced under a H<sub>2</sub> flow at 580 °C for 2 h, and kept without exposing to air before use. The reduced catalysts were added to an autoclave containing 38.0 mmol pure glycerol and pre-heated at 80 °C for about 5 min. The autoclave was then flushed with H<sub>2</sub> more than three times and pressured to 5.0 MPa of H<sub>2</sub>. After the reactor had

been preheated to 230 °C, the reaction time was counted by starting stirring with an agitation speed of 1200 rpm, under these conditions the mass and heat transfer limitations were verified to be negligible. After reaction, the reactor was cooled to room temperature, and the gas phase was collected by a gas-bag and analyzed using a gas chromatograph (Shimadzu, Kyoto, Japan, GC-14C) equipped with an active carbon column and a thermal conductivity detector (TCD). The liquid phase was diluted with water and centrifuged to remove the catalyst and analyzed using a gas chromatograph (Shimadzu, Kyoto, Japan, GC-14C) equipped with a capillary column (Restek Stabilwax, Bellefonte, PA, USA, 30 m × 0.53 mm × 1 μm, carrier: N<sub>2</sub>) and a flame ionization detector (FID). The carbon balance of the present reaction was about 90% as calculated, in which the gas products were not included as it was difficult to detect the exact content at the high concentration of H<sub>2</sub>. For the specific system, the conversion of glycerol and the selectivity of each liquid product were calculated based on the following Equations (1) [5].

$$\begin{aligned} \text{Conversion (\%)} &= \frac{\text{Sum of C – based moles of all liquid products}}{\text{Sum of C – based moles of reactant and all products}} \times 100\% \\ \text{Selectivity (\%)} &= \frac{\text{C – based moles of each liquid products}}{\text{Sum of C – based moles of all liquid products}} \times 100\% \end{aligned} \quad (1)$$

#### 4. Conclusions

This work explored the hydrogenolysis of pure glycerol over P-doping Ni/Al<sub>2</sub>O<sub>3</sub>. It was found that doping of P to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst decreased the reaction rate slightly but increased the selectivity to 1,2-PDO greatly. It was confirmed that the doping of P lowered the reduction degree of Ni/Al<sub>2</sub>O<sub>3</sub>, and left some NiO species on the reduced Ni-P/Al<sub>2</sub>O<sub>3</sub> which improved selectivity to 1,2-PDO. The role of NiO was proven by designed experiments including Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with NiO species, obtained by shortening reduction time and enhancing calcination temperature. Thus, a possible function of NiO was proposed, in that the hydroxyl of glycerol favored adsorption onto the NiO species and then dehydroxylation and hydrogenation occurred to produce 1,2-PDO. Moreover, doping of P induced an increase in the amount of surface acid sites, resulting in an enhancement of the selectivity to 1,2-PDO. The results described here provide an important reference on the rational design of Ni-based catalysts for glycerol hydrogenolysis.

#### Acknowledgments

This work was financial supported by the National Natural Science Foundation of China (21273222).

#### Author Contributions

Xiaoru Li did the experiment and wrote the paper, Haiyang Cheng discussed the results and revised the paper, Limin He, Guanfeng Liang, Yancun Yu, Weiwei Lin, Fengyu Zhao supervised this work.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, C.D. From Glycerol to Value-Added Products. *Angew. Chem. Int. Ed.* **2007**, *46*, 4434–4440.
2. Jerzykiewicz, M.; Cwiela, I.; Jerzykiewicz, W. The antioxidant and anticorrosive properties of crude glycerol fraction from biodiesel production. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 1196–1201.
3. Zhou, C.H.C.; Beltramini, J.N.; Fan, Y.X.; Lu, G.Q.M. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549.
4. Dasari, M.A.; Kiatsimkul, P.P.; Sutterlin, W.R.; Suppes, G.J. Low-pressure hydrogenolysis of glycerol to propylene glycol. *Appl. Catal. A* **2005**, *281*, 225–231.
5. Miyazawa, T.; Kusunoki, Y.; Kunimori, K.; Tomishige, K. Glycerol conversion in the aqueous solution under hydrogen over Ru/C + an ion-exchange resin and its reaction mechanism. *J. Catal.* **2006**, *240*, 213–221.
6. Yuan, Z.L.; Wang, L.N.; Wang, J.H.; Xia, S.X.; Chen, P.; Hou, Z.Y.; Zheng, X.M. Hydrogenolysis of glycerol over homogeneously dispersed copper on solid base catalysts. *Appl. Catal. B* **2011**, *101*, 431–440.
7. Hao, S.L.; Peng, W.C.; Zhao, N.; Xiao, F.K.; Wei, W.; Sun, Y.H. Hydrogenolysis of glycerol to 1,2-propanediol catalyzed by Cu-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub> in liquid phase. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 1499–1503.
8. Akiyama, M.; Sato, S.; Takahashi, R.; Inui, K.; Yokota, M. Dehydration-hydrogenation of glycerol into 1,2-propanediol at ambient hydrogen pressure. *Appl. Catal. A* **2009**, *371*, 60–66.
9. Mizugaki, T.; Arundhati, R.; Mitsudome, T.; Jitsukawa, K.; Kaneda, K. Selective Hydrogenolysis of Glycerol to 1,2-Propanediol Using Heterogeneous Copper Nanoparticle Catalyst Derived from Cu–Al Hydrotalcite. *Chem. Lett.* **2013**, *42*, 729–731.
10. Perosa, A.; Tundo, P. Selective hydrogenolysis of glycerol with Raney nickel. *Ind. Eng. Chem. Res.* **2005**, *44*, 8535–8537.
11. Van Ryneveld, E.; Mahomed, A.S.; van Heerden, P.S.; Green, M.J.; Friedrich, H.B. A catalytic route to lower alcohols from glycerol using Ni-supported catalysts. *Green Chem.* **2011**, *13*, 1819–1827.
12. Yu, W.Q.; Xu, J.; Ma, H.; Chen, C.; Zhao, J.; Miao, H.Q. Song, A remarkable enhancement of catalytic activity for KBH<sub>4</sub> treating the carbothermal reduced Ni/AC catalyst in glycerol hydrogenolysis. *Catal. Commun.* **2010**, *11*, 493–497.
13. Huang, L.; Zhu, Y.L.; Zheng, H.Y.; Li, Y.W.; Zeng, Z.Y. Continuous production of 1,2-propanediol by the selective hydrogenolysis of solvent-free glycerol under mild conditions. *J. Chem. Technol. Biotechnol.* **2008**, *83*, 1670–1675.
14. Jimenez-Morales, I.; Vila, F.; Mariscal, R.; Jimenez-Lopez, A. Hydrogenolysis of glycerol to obtain 1,2-propanediol on Ce-promoted Ni/SBA-15 catalysts. *Appl. Catal. B* **2012**, *117*, 253–259.

15. Huang, J.H.; Chen, J.X. Comparison of Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> for hydrogenolysis of glycerol: A consideration of factors influencing catalyst activity and product selectivity. *Chin. J. Catal.* **2012**, *33*, 790–796.
16. Montassier, C.; Ménézo, J.C.; Hoang, L.C.; Renaud, C.; Barbier, J. Aqueous polyol conversions on ruthenium and on sulfur-modified ruthenium. *J. Mol. Catal.* **1991**, *70*, 99–110.
17. Rode, C.V.; Mane, R.B.; Ghalwadkar, A.A.; Hengne, A.M. Suryawanshi, Y.R. Role of promoters in copper chromite catalysts for hydrogenolysis of glycerol. *Catal. Today* **2011**, *164*, 447–450.
18. Oyama, S.T.; Wang, X.; Lee, Y.K.; Chun, W.J. Active phase of Ni<sub>2</sub>P/SiO<sub>2</sub> in hydroprocessing reactions. *J. Catal.* **2004**, *221*, 263–273.
19. Sawhill, S.; Layman, K.; Vanwyk, D.; Engelhard, M.; Wang, C.; Bussell, M. Thiophene hydrodesulfurization over nickel phosphide catalysts: Effect of the precursor composition and support. *J. Catal.* **2005**, *231*, 300–313.
20. Wang, R.; Li, Y.; Shi, R.; Yang, M. Effect of metal–support interaction on the catalytic performance of Ni/Al<sub>2</sub>O<sub>3</sub> for selective hydrogenation of isoprene. *J. Mol. Catal. A* **2011**, *344*, 122–127.
21. Hoffer, B.W.; van Langeveld, A.D.; Janssens, J.P.; Bonne, R.L.C.; Lok, C.M.; Moulijn, J.A. Stability of highly dispersed Ni/Al<sub>2</sub>O<sub>3</sub> catalysts: Effects of pretreatment. *J. Catal.* **2000**, *192*, 432–440.
22. Mahata, N.; Cunha, A.F.; M. Órfão, J.J.; Figueiredo, J.L. Hydrogenation of nitrobenzene over nickel nanoparticles stabilized by filamentous carbon. *Appl. Catal. A* **2008**, *351*, 204–209.
23. Chen, J.; Ci, D.; Wang, R.; Zhang, J. Hydrodechlorination of chlorobenzene over NiB/SiO<sub>2</sub> and NiP/SiO<sub>2</sub> amorphous catalysts after being partially crystallized: A consideration of electronic and geometrical factors. *Appl. Surf. Sci.* **2008**, *255*, 3300–3309.
24. Abu, I.; Smith, K. The effect of cobalt addition to bulk MoP and Ni<sub>2</sub>P catalysts for the hydrodesulfurization of 4,6-dimethyldibenzothiophene. *J. Catal.* **2006**, *241*, 356–366.
25. Diskin, A.M.; Cunningham, R.H.; Ormerod, R.M. The oxidative chemistry of methane over supported nickel catalysts. *Catal. Today* **1998**, *46*, 147–154.
26. Nagaoka, K.; Sato, K.; Nishiguchi, H.; Takita, Y. Influence of support on catalytic behavior of nickel catalysts in oxidative steam prereforming of *n*-butane for fuel cell applications. *Appl. Catal. A* **2007**, *327*, 139–146.
27. Li, C.P.; Chen, Y.W. Temperature-programmed-reduction studies of nickel oxide/alumina catalysts: Effects of the preparation method. *Thermochim. Acta* **1995**, *256*, 457–465.
28. Lu, H.B.; Yin, H.B.; Liu, Y.M.; Jiang, T.S.; Yu, L.B. Influence of support on catalytic activity of Ni catalysts in *p*-nitrophenol hydrogenation to *p*-aminophenol. *Catal. Commun.* **2008**, *10*, 313–316.
29. Gavalas, G.R.; Phichitkul, C.; Voecks, G.E. Structure and activity of NiO- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and NiO-ZrO<sub>2</sub> calcined at high temperatures: I. Structure. *J. Catal.* **1984**, *88*, 54–64.
30. Chen, Y.G.; Ren, J. Conversion of methane and carbon dioxide into synthesis gas over alumina-supported nickel catalysts: Effect of Ni-Al<sub>2</sub>O<sub>3</sub> interactions. *Catal. Lett.* **1994**, *29*, 39–48.
31. Gandarias, I.; Arias, P.L.; Requies, J.; Guemez, M.B.; Fierro, J.L.G. Hydrogenolysis of glycerol to propanediols over a Pt/ASA catalyst: The role of acid and metal sites on product selectivity and the reaction mechanism. *Appl. Catal. B* **2010**, *97*, 248–256.
32. Nakagawa, Y.; Tomishige, K. Heterogeneous catalysis of the glycerol hydrogenolysis. *Catal. Sci. Technol.* **2011**, *1*, 179–190.

33. Sharma, R.V.; Kumar, P.; Dalai, A.K. Selective hydrogenolysis of glycerol to propylene glycol by using Cu:Zn:Cr:Zr mixed metal oxides catalyst. *Appl. Catal. A* **2014**, *477*, 147–156.
34. Miranda, B.C.; Chimentao, R.J.; Santos, J.B.O.; Gispert-Guirado, F.; Llorca, J.; Medina, F.; Bonillo, F.L.; Sueiras, J.E. Conversion of glycerol over 10% Ni/gamma-Al<sub>2</sub>O<sub>3</sub> catalyst. *Appl. Catal. B* **2014**, *147*, 464–480.
35. Medlin, J.W. Understanding and Controlling Reactivity of Unsaturated Oxygenates and Polyols on Metal Catalysts. *ACS Catal.* **2011**, *1*, 1284–1297.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).