Ni₂P/SiO₂ 和 Ni/SiO₂ 催化剂甘油氢解反应性能比较: 催化剂活性及产物选择性影响因素的探讨

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摘要: 采用浸渍法及程序升温还原法制备了 Ni₂P/SiO₂ 和 Ni/SiO₂ 催化剂, 利用 N₂ 吸附-脱附、X 射线衍射、X 射线荧光、CO 化学吸附、氢气程序升温脱附及氨气程序升温脱附等手段对催化剂进行了表征并用于甘油氢解反应。结果表明, Ni₂P/SiO₂ 和 Ni/SiO₂ 具有相近的表面 Ni 密度, 但前者表面酸中心和表面氢物种 (包括吸附氢和溢流氢) 密度明显更高, 且在甘油氢解反应中的活性也更高, 这与其酸性中心与金属中心之间的协同作用有关。Ni₂P/SiO₂ 催化剂上主要产物为 1,2-丙二醇及 1-丙醇, 而 Ni/SiO₂ 催化剂上主要产物为 1,2-丙二醇、乙二醇和乙醇。提高反应温度和 H₂ 压力不能促进 Ni₂P/SiO₂ 上乙醇和乙二醇的生成, 但促进了 1,2-丙二醇进一步氢解转化为 1-丙醇。由此可见, Ni₂P/SiO₂ 具有较强的 C—O 键断裂活性及较弱的 C—C 键断裂活性, 这可能分别与其较多酸性中心和电子及几何结构性质密切相关。

关键词: 甘油氢解; 磷化镍; 镍; 酸性; 电子和几何性质

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Comparison of Ni₂P/SiO₂ and Ni/SiO₂ for Hydrogenolysis of Glycerol: A Consideration of Factors Influencing Catalyst Activity and Product Selectivity

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Abstract: Ni₂P/SiO₂ and Ni/SiO₂ catalysts were prepared for the hydrogenolysis of glycerol, and their structural properties were characterized by N₂ sorption, X-ray diffraction, X-ray fluorescence, CO chemisorption, H₂ temperature-programmed desorption, and NH₃ temperature-programmed desorption. It was found that Ni₂P/SiO₂ had a similar density of exposed Ni sites as Ni/SiO₂, while Ni₂P/SiO₂ had much larger amount of acid sites and surface hydrogen species than Ni/SiO₂. Ni₂P/SiO₂ was more active than Ni/SiO₂ in the hydrogenolysis of glycerol. This is attributed to the synergism between acid and metal sites on Ni₂P/SiO₂. Glycerol was mainly converted to 1,2-propanediol over Ni₂P/SiO₂, while it was mostly converted to not only 1,2-propanediol but also ethylene glycol and ethanol over Ni/SiO₂. The formation of ethylene glycol and ethanol on Ni/SiO₂ is attributed to the C—C bond cleavage catalyzed by metallic Ni rather than weak acidity. In addition, temperature and H₂ pressure increase did not promote the formation of ethylene glycol and ethanol on Ni₂P/SiO₂. Instead they mainly promoted the further conversion of 1,2-propanediol to form 1-propanol. Thus, Ni₂P/SiO₂ was more active for the cleavage of C—O bonds and less active for the cleavage of C—C bonds than Ni/SiO₂. We suggest that the higher activity of Ni₂P/SiO₂ for the cleavage of C—O bonds can be ascribed to its acidity, while its lower activity for the cleavage of C—C bonds may be mainly related to its electronic and geometrical properties.

Key words: glycerol hydrogenolysis; nickel phosphide; nickel; acidity; electronic and geometrical properties

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Biomass is an environmentally friendly renewable resource, from which various useful chemicals and fuels can be produced [1]. Now, the transesterification of vegetable oils and animal fats with methanol to biodiesel has been commercialized, during which glycerol is co-produced. A rapid development of biodiesel processes leads to an over-supply of glycerol in the market. It is very significant to convert glycerol to more valuable chemicals. The hydrogenolysis of glycerol into high-value diols (1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), and ethylene glycol (EG)) is very attractive among the routes for using glycerol [2,3].

Noble metals (such as Ru [4–8], Ni [9–11], and Cu [12]) catalysts have been applied to the hydrogenolysis of glycerol. Cu-based catalysts gave the products 1,2-PDO and 1,3-PDO via the cleavage of C–O, while Ru and Ni-based catalysts also gave the degradation products (EG and ethanol) via the cleavage of C–C bonds. When Ru and Ni-based catalysts were combined with acid catalysts, the cleavage of C–O bonds via dehydration/hydrogenation was promoted while the cleavage of C–C bonds was partially restrained.

It is known that the Ni_2P phase has both acid and metal functions [13]. There is an electron transfer from Ni to P in Ni_2P , which leads to the Ni site possessing a small positive charge [14]. Thus, the structural properties of Ni_2P are very different from that of metallic Ni. This may result in different performance of Ni and Ni_2P catalysts in the hydrogenolysis of glycerol, and the study of this difference can provide information about the relationship between the catalyst structure and reactivity. To our knowledge, there are no related reports on the application of Ni_2P in the hydrogenolysis of glycerol.

SiO_2 was used as support to prepare $\text{Ni}_2\text{P}/\text{SiO}_2$ in this work to reduce the effect of the support. For comparison Ni/SiO_2 was also prepared. The factors that influence the catalyst performance in the hydrogenolysis of glycerol are discussed in association with the structural properties of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 .

1 Experimental

1.1 Catalyst preparation

Commercial spherical silica (B-type, Qingdao Haiyang Chemicals Co., Ltd., China. BET specific surface area = $548 \text{ m}^2/\text{g}$) was used as support. Before using, silica particles with 20–40 mesh were obtained by triturating and sieving. $\text{Ni}_2\text{P}/\text{SiO}_2$ was prepared by the temperature-programmed reduction (TPR) method [15]. Firstly, the precursor of

$\text{Ni}_2\text{P}/\text{SiO}_2$ was prepared by the impregnation method. Silica was incipiently impregnated with an aqueous solution of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ni}(\text{NO}_3)_2$, followed by drying at 393 K for 12 h and calcination at 823 K for 5 h. Secondly, $\text{Ni}_2\text{P}/\text{SiO}_2$ was prepared from the precursor by TPR using the following program: heating from 293 to 523 K at 10 K/min and from 523 to 923 K at 1 K/min and then maintaining 923 K for 3 h. The H_2 (> 99.9%) flow was set at 290 ml/min per gram of precursor. The prepared catalyst was passivated in a 0.5% O_2/N_2 flow for 10 h. Ni/SiO_2 was prepared by the impregnation method. Silica was incipiently impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2$, followed by drying at 393 K for 12 h and calcination at 823 K for 5 h. The prepared Ni/SiO_2 precursor was reduced at 723 K for 40 min to prepare Ni/SiO_2 .

1.2 Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a D8 Focus powder diffractometer operated at 40 kV and 40 mA using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). N_2 adsorption-desorption isotherms were obtained on a Quantachrome NOVA-2000 apparatus at 77 K. The Brunauer Emmett Teller (BET) equation was used to calculate the specific surface area (A_{BET}). The Barrett Joyner Halenda (BJH) method was used to calculate the average pore diameter and pore volume from the desorption branch of the isotherm. The contents of Ni and P were measured by a Bruker S4 Pioneer X-ray fluorescence (XRF) instrument. CO chemisorption was used to measure the density of exposed Ni sites of the catalysts, and H_2 temperature-programmed desorption (H_2 -TPD) and NH_3 temperature-programmed desorption (NH_3 -TPD) were used to measure the states of hydrogen species and the acidity of the catalysts, respectively. CO chemisorption, H_2 -TPD, and NH_3 -TPD were carried out in a homemade device and the procedures were same as those in previous work [15].

1.3 Activity test

The hydrogenolysis of glycerol was carried out in a stainless-steel fixed-bed reactor. For comparison, the hydrogenolysis of 1,2-PDO, the hydrogenation of acetol and the hydrogenolysis of glycol were also tested. The passivated $\text{Ni}_2\text{P}/\text{SiO}_2$ was pre-reduced at 723 K for 40 min in a H_2 flow (> 99.9%, 150 ml/min), while Ni/SiO_2 was in-situ prepared via reduction with H_2 at 723 K for 40 min. After the reduction, the temperature and H_2 pressure were adjusted to the desired values. The glycerol, 1,2-PDO, acetol

or glycol aqueous solution was continuously fed to the reactor using a pump. The reactant mass concentration was 60%. The liquid products were analyzed on an SP-3420 gas chromatograph equipped with an FID and a commercial PEG-20M capillary column. Gas products were analyzed by a 102 gas chromatograph equipped with a TCD and a TDX-101 packed column.

2 Results and discussion

2.1 Catalyst characterization

Figure 1 shows the XRD patterns of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 . Apart from the support, only a metallic Ni phase was detected in Ni/SiO_2 while only a Ni_2P phase was detected in $\text{Ni}_2\text{P}/\text{SiO}_2$. The average sizes of Ni_2P and metallic Ni crystallites were 13.5 and 10.7 nm (Table 1), calculated with the Scherrer equation from the $\text{Ni}_2\text{P}(111)$ and $\text{Ni}(111)$ peaks, respectively.

Fig. 1. XRD patterns of $\text{Ni}_2\text{P}/\text{SiO}_2$ (1) and Ni/SiO_2 (2).

Table 1 shows the Ni and P contents and textural properties of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 . The Ni mass contents in Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ were 16.7% and 14.7%, respectively. The Ni/P molar ratio in the $\text{Ni}_2\text{P}/\text{SiO}_2$ was calculated as 1.6:1, which was higher than that (1:1) in the precursor and lower than that (2:1) in pure Ni_2P . This indicates that there was a P loss during the preparation of $\text{Ni}_2\text{P}/\text{SiO}_2$ [16] and there were still excess, unreduced P species (such as $\text{H}_n\text{PO}_4^{(3-n)-}$ and $\text{P}_2\text{O}_7^{4-}$ [17]) in the $\text{Ni}_2\text{P}/\text{SiO}_2$. Compared with Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$ had a lower specific surface area and a smaller average pore diameter, and pore volume. This

may be ascribed to its higher preparation temperature and the blockage of pores with the excess unreduced P species. In addition, the CO uptakes of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 were 27 and 25 $\mu\text{mol/g}$, respectively, indicating that Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ had similar densities of exposed Ni sites.

Figure 2 shows the H_2 -TPD profiles. Generally the peaks below 700 K are ascribed to the desorption of hydrogen species on the surface of the metal phase, while the peaks above 700 K are attributed to spilt-over hydrogen species [18]. $\text{Ni}_2\text{P}/\text{SiO}_2$ had three desorption peaks below 700 K, indicating that there were hydrogen species in different states adsorbed on the Ni_2P particles. Ni/SiO_2 gave a distinct and a broad peak below 700 K. Above 700 K $\text{Ni}_2\text{P}/\text{SiO}_2$ had more spilt-over hydrogen than Ni/SiO_2 . $\text{Ni}_2\text{P}/\text{SiO}_2$ had a similar density of the exposed Ni sites as Ni/SiO_2 as measured by CO chemisorption while it yielded a much larger amount of desorbed H_2 than Ni/SiO_2 . This was likely due to the contribution of P–OH groups on $\text{Ni}_2\text{P}/\text{SiO}_2$ [15]. On one hand P–OH groups could be formed on Ni_2P particles via the passivation and re-reduction processes [13] and may have contributed to the H_2 desorption below 700 K. On the other hand P–OH groups may exist in the unreduced P species on the support, which may account for the larger amount of spilt-over hydrogen on $\text{Ni}_2\text{P}/\text{SiO}_2$. Indeed, it has been proposed that –OH groups (which also act as Brønsted acid sites) can stabilize spilt-over hydrogen [19].

Fig. 2. H_2 -TPD profiles of Ni/SiO_2 (1) and $\text{Ni}_2\text{P}/\text{SiO}_2$ (2).

Figure 3 shows the NH_3 -TPD profiles. Ni/SiO_2 had two peaks at 480 and 623 K, while $\text{Ni}_2\text{P}/\text{SiO}_2$ gave a main peak at 488 K with a shoulder peak at higher temperature. Obviously, $\text{Ni}_2\text{P}/\text{SiO}_2$ had more acid sites than Ni/SiO_2 , while the strength of acid sites on $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 was weak

Table 1 Ni and P contents and textural properties of Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$

Sample	Ni content (%)	P content (%)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Average pore diameter (nm)	Pore volume (cm^3/g)	CO uptake ($\mu\text{mol/g}$)	Crystallite size (nm)
Ni/SiO_2	16.7	—	444	5.7	0.654	25	10.7
$\text{Ni}_2\text{P}/\text{SiO}_2$	14.7	4.8	356	4.9	0.514	27	13.5

Fig. 3. NH_3 -TPD profiles of Ni/SiO_2 (1) and $\text{Ni}_2\text{P}/\text{SiO}_2$ (2).

and medium. Base on peak areas the number of acid sites on $\text{Ni}_2\text{P}/\text{SiO}_2$ was about three times as large as that on Ni/SiO_2 . Using Fourier transform infrared (FT-IR) analysis with the probe molecule pyridine, Brönsted and Lewis acid sites have been detected on $\text{Ni}_2\text{P}/\text{SiO}_2$ [13]. The Brönsted acid sites are attributed to P–OH groups. The Lewis acid sites may be related to the Ni sites on the surface of Ni_2P particles. As indicated by a density functional theory (DFT) calculation, the Ni–P bond in Ni_2P is covalent [20], while there is an electron transfer from Ni to P [14]. The electron-deficiency of Ni sites may account for the Lewis acidity of Ni_2P . This is not the case for the metallic Ni. Thus, the

acidity of $\text{Ni}_2\text{P}/\text{SiO}_2$ can ascribed to electron-deficient Ni sites (Lewis acid sites) and P–OH groups (Brönsted acid sites) [13,15], while that of Ni/SiO_2 is only due to the unreduced nickel silicate that leads to Lewis acidity [21]. Phosphorous may account for the larger amount of acid sites as well as surface hydrogen (including spilt-over one) on $\text{Ni}_2\text{P}/\text{SiO}_2$.

2.2 Catalytic performance of Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$

Table 2 shows the reactivity of Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ in different reactions. The glycerol conversions over $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 were 95.1% and 73.2% in hydrogenolysis of glycerol, respectively. Thus, $\text{Ni}_2\text{P}/\text{SiO}_2$ was more active than Ni/SiO_2 in the hydrogenolysis of glycerol. Also, there was a remarkable difference in the product selectivities on $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 . On $\text{Ni}_2\text{P}/\text{SiO}_2$ the main products were 1,2-PDO and 1-propanol with selectivities of 85.9% and 7.2%, respectively, and the total selectivity of glycol and ethanol was only about 2.3%. On Ni/SiO_2 , however, the selectivity to 1,2-PDO was only 49.9%, while the selectivities for EG and ethanol were 30.4% and 12.8%, respectively. In the effluent gas only CH_4 was detected using Ni/SiO_2 , while it was not produced over $\text{Ni}_2\text{P}/\text{SiO}_2$. In addition neither CO nor CO_2 was produced over Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$. Clearly the cleavage of C–O bonds mainly occurred on $\text{Ni}_2\text{P}/\text{SiO}_2$ while the cleavage of both C–O and C–C bonds took place on Ni/SiO_2 .

Table 2 Reactivity of Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ in different reactions

Reaction	Conversion (%)		$S_{1,2\text{-PDO}}/\%$		$S_{\text{EG}}/\%$		$S_{\text{ethanol}}/\%$		$S_{1\text{-propanol}}/\%$		$S_{\text{others}}/\%$	
	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$	Ni/SiO_2	$\text{Ni}_2\text{P}/\text{SiO}_2$
Glycerol hydrogenolysis	73.2	95.1	49.9	85.9	30.4	1.3	12.8	1.0	1.4	7.2	5.5	4.6
Acetol hydrogenation	99.9	99.3	13.1	84.3	1.0	0.9	78.8	0.8	4.8	13.2	2.3	0.8
1,2-PDO hydrogenolysis	62.9	23.7	—	—	—	—	93.4	4.4	4.6	94.6	2.0	1.0
EG hydrogenolysis	46.5	—	—	—	—	—	18.1	—	—	—	81.9 ^a	—

Reaction conditions: 493 K, 3.0 MPa, WHSV of 1.13 h^{-1} , H_2 /reactant molar ratio of 20.

^aMethanol selectivity.

$S_{1,2\text{-PDO}}$: 1,2-PDO selectivity; S_{ethanol} : ethanol selectivity; S_{EG} : glycol selectivity; $S_{1\text{-propanol}}$: 1-propanol selectivity; Others: including methanol, acetol, 1,3-PDO, and 2-propanol.

As shown in Table 1 Ni/SiO_2 had a larger specific surface area than $\text{Ni}_2\text{P}/\text{SiO}_2$, and Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ had similar densities of exposed Ni sites. Thus, the higher activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in the hydrogenolysis of glycerol and the different product selectivities on $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 should be related to other structural properties. As indicated by the NH_3 -TPD results (Fig. 3) $\text{Ni}_2\text{P}/\text{SiO}_2$ possessed more acid sites than Ni/SiO_2 . The acid sites can promote the dehydration of glycerol to form acetol that is then hydrogenated to 1,2-PDO. A similar promoting effect has also been proposed in the literatures [4–9]. Miyazawa et al. [4] proposed that

compared with Ru/C alone the combination of Ru/C with an acid catalyst promoted the hydrogenolysis of glycerol and led to the increased selectivity for 1,2-PDO and the decreased selectivity for EG. Zhao et al. [9] reported that unsupported Ni powders can catalyze the hydrogenolysis of glycerol to form 1,2-PDO and EG. This indicates that metallic Ni can catalyze the cleavage of both C–C and C–O bonds. When metallic Ni was supported on NaX zeolite, the selectivity for 1,2-PDO was enhanced and the selectivity for EG was decreased. This was attributed to the acidity of NaX that catalyzed the dehydration of glycerol to acetol [9]. Ma

et al. [6] and Balaraju et al. [7] have also proposed that there is a synergism between acid and metal sites in the hydrogenolysis of glycerol (via dehydration and hydrogenation) to form 1,2-PDO. Different from supported metallic catalysts whose acidity is derived from the supports, Ni_2P can provide itself acid sites as well as Ni sites, and the synergism between acid and Ni sites for the hydrogenolysis of glycerol to form 1,2-PDO may be more effective. In addition, following the suggestion of Liu et al. [22] that O atom preferentially interacted with the P atom rather than the Ni atom on Ni_2P (001), we speculate that the interaction between the P sites in Ni_2P and the O atom in glycerol might also favor the activation and cleavage of C–O bonds. Therefore, the more acidic sites and the preferential interaction of P with O may account for the higher activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in the hydrogenolysis of glycerol in comparison with that of Ni/SiO_2 . Moreover, the acidity may restrain the cleavage of C–C bonds through promoting the cleavage of C–O bonds. In other words, there may be a competition of cleavage between the C–O bonds and C–C bonds. Metallic Ni is active for the cleavages of both C–C and C–O bonds, while the acidity can promote the cleavage of C–O bonds via dehydration forming acetol that can actively be hydrogenated (shown below). However, metallic Ni or Ru catalysts still gave a certain amount of EG and ethanol even if they were combined with acidic components [4,9]. Therefore the restraining effect of acidity on the cleavage of C–C bonds is limited. Thus, the smaller activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ compared with that of Ni/SiO_2 for the cleavage of C–C bonds may not be only attributed to the role of the acidity. It is also likely related to the different structural properties of bulk Ni_2P and Ni.

It is known that the Ni site in Ni_2P has lower electron density than that in metallic Ni, and the ensemble effect of P leads to the increase of the Ni–Ni distance [17], all of which may be related to the lower activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ for the cleavage of C–C bonds. This supposition is reasonable since the electronic and geometrical property of catalysts may influence the adsorption of glycerol and so influence the selectivity to the cleavage of C–O and C–C bonds. Two series of experiments were designed to test the supposition that Ni_2P is in nature less active than metallic Ni for the cleavage of C–C bonds: (1) The effects of temperature and H_2 pressure on the performance of $\text{Ni}_2\text{P}/\text{SiO}_2$; (2) The hydrogenation of acetol and hydrogenolysis of 1,2-PDO over Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$.

It is well known that the cleavage of C–C bonds is thermodynamically favored at high temperature and H_2 pressure. However, as shown in Figs. 4 and 5, the total selectivity for EG and ethanol (S_{C_2}) did not change obviously as the temperature and H_2 pressure increased, while the selectivity for 1,2-PDO decreased and the selectivity for 1-propanol in-

Fig. 4. Effect of temperature on the reactivity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in hydrogenolysis of glycerol. Reaction conditions: 3.0 MPa, glycerol WHSV of 1.73 h^{-1} , H_2 /glycerol molar ratio of 20.

Fig. 5. Effect of H_2 pressure on reactivity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in hydrogenolysis of glycerol. Reaction conditions: 493 K, glycerol WHSV of 1.13 h^{-1} , H_2 /glycerol molar ratio of 20.

creased. This indicates that the increased temperature and H_2 pressure mainly promoted the further hydrogenolysis of 1,2-PDO to 1-propanol via the cleavage of the C–O bond and had less effect on the cleavage of the C–C bond. However, this case is greatly different from that of Ni-based catalysts combined with acidic sites (for example Ni/NaX [9], Ni/SiO_2 , and $\text{Ni}/\text{Al}_2\text{O}_3$ [10]), on which the cleavage of the C–C bond was greatly promoted by increased temperature and H_2 pressure leading to formation of degradation products.

The reactivities of Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ in the hydrogenation of acetol and hydrogenolysis of 1,2-PDO are shown in Table 2. Acetol was the intermediate product derived from the dehydration of glycerol. In the hydrogenation of acetol, acetol was almost completely converted over both Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$, indicating that acetol was a very active intermediate. However, there was also a difference in the product distribution on Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$.

$\text{Ni}_2\text{P}/\text{SiO}_2$ gave 1,2-PDO and 1-propanol with selectivities of 84.3% and 13.2%, respectively, while Ni/SiO_2 gave 1,2-PDO and ethanol with selectivities of 13.1% and 78.8%, respectively. The conversions of 1,2-PDO over Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$ were 62.9% and 23.7%, respectively, in the hydrogenolysis of 1,2-PDO. Thus, Ni/SiO_2 was more active than $\text{Ni}_2\text{P}/\text{SiO}_2$ in the hydrogenolysis of 1,2-PDO. $\text{Ni}_2\text{P}/\text{SiO}_2$ gave 1-propanol with a selectivity of 94.6%, while Ni/SiO_2 gave ethanol with a selectivity of 93.4%. Clearly, in the reactions above the main product on Ni/SiO_2 was ethanol derived from the cleavage of the C–C bond, while $\text{Ni}_2\text{P}/\text{SiO}_2$ mainly gave the products derived from the cleavage of the C–O bond. This further indicates that Ni/SiO_2 had much higher activity for the cleavage of C–C bonds than $\text{Ni}_2\text{P}/\text{SiO}_2$. A high activity of Ni-based catalysts for the cleavage of C–C bonds has also been found in other reactions such as the hydrogenolysis of saturated hydrocarbons [23] and conversion of triglyceride to hydrocarbons [24]. This higher activity of metallic Ni for the cleavage of C–C bonds might account for the higher conversion of 1,2-PDO over Ni/SiO_2 than over $\text{Ni}_2\text{P}/\text{SiO}_2$. In other words, the conversion of 1,2-PDO on Ni/SiO_2 was realized through the cleavage of both C–C and C–O bonds (especially the cleavage of C–C bonds), while conversion on $\text{Ni}_2\text{P}/\text{SiO}_2$ was mainly realized through the cleavage of C–O bonds. Also, the hydrogenolysis of 1,2-PDO is more difficult than that of glycerol [4]. Thus, the higher activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in the hydrogenolysis of glycerol and lower activity in the hydrogenolysis of 1,2-PDO compared with those of Ni/SiO_2 also indicates that Ni/SiO_2 had a much higher activity for the cleavage of the C–C bond than $\text{Ni}_2\text{P}/\text{SiO}_2$. As another evidence, the hydrogenolysis of EG on Ni/SiO_2 was also tested and the main product was methanol derived from the cleavage of the C–C bond (Table 2). Additionally, it is well known that strong acidity of catalysts also contributes to the cleavage of C–C bonds [25]. Based on the above results we speculate that the acidity of Ni_2P might be too weak to catalyze the cleavage of C–C bonds. Again, Ni/SiO_2 had a much smaller amount of acid sites than $\text{Ni}_2\text{P}/\text{SiO}_2$, while it showed much higher activity for the cleavage of C–C bonds. Therefore, $\text{Ni}_2\text{P}/\text{SiO}_2$ is by nature less active than Ni/SiO_2 for the cleavage of C–C bonds which is probably related to its electronic and geometrical properties.

The reaction mechanism of the glycerol hydrogenolysis has been reported [7,10]. Applied to the present work the main routes on $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 are presented in Scheme 1. On $\text{Ni}_2\text{P}/\text{SiO}_2$ glycerol is mainly converted via the following successive steps: dehydration of glycerol to form acetol on acid sites; hydrogenation of acetol to form 1,2-PDO on metal sites; hydrogenolysis (dehydration/hydrogenation) of 1,2-PDO to 1-propanol. Apart from the above steps there occurred other reactions on Ni/SiO_2 :

Scheme 1. Reaction pathways of glycerol hydrogenolysis.

cleavage of the C–C bond in glycerol to form EG and methanol; hydrogenolysis of 1,2-PDO and EG to form ethanol and methanol; hydrogenation of methanol to form methane. Indeed, methane was formed over Ni/SiO_2 in the hydrogenolysis of glycerol, 1,2-PDO, and EG and the hydrogenation of acetol but was not over $\text{Ni}_2\text{P}/\text{SiO}_2$.

3 Conclusions

The higher activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ than Ni/SiO_2 in the hydrogenolysis of glycerol is attributed to a synergism between acid sites (P–OH) and the metal sites (Ni). Glycerol was dehydrated to acetol on acid sites while acetol was hydrogenated to 1,2-propanediol (1,2-PDO) on Ni sites. $\text{Ni}_2\text{P}/\text{SiO}_2$ had higher activity for the cleavage of C–O bonds and lower activity for the cleavage of C–C bonds than Ni/SiO_2 not only in the hydrogenolysis of glycerol but also in the hydrogenation of acetol and the hydrogenolysis of 1,2-PDO. The former is ascribed to its acidity while the latter may mainly be related to its electronic and geometrical properties.

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