Bimetallic Effects of Silver-Modified Nickel Catalysts and their Synergy in Glycerol Hydrogenolysis

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A series of Ag-modified Ni catalysts was prepared, and the role of bimetallic effects on the selective cleavage of C–O and C–C bonds was investigated in glycerol hydrogenolysis, a model reaction for the utilization of biomass-derived polyols. Compared to Raney Ni, the optimal Raney Ni₆Ag catalyst was more active in glycerol conversion and efficient for C–O bond cleavage to afford a higher selectivity toward C₃ products (1,2-propanediol and lactic acid; 88%) at the same ~70% conversion of glycerol, especially 1,2-propanediol (73%). On Ni catalysts, the hydroge-

Introduction

The selective hydrogenolysis of glycerol, the main byproduct of biodiesel production by transesterification,^[1] to useful chemicals (i.e., propanediols (1,2- and 1,3-PD)) has been significant industrially.^[2,3] This reaction is also very important as an appropriate model reaction to study the selective cleavage of C-O and C-C bonds in the catalytic dehydroxylation of biomass-derived polyols,^[4-6] which is regarded as an important process for future biorefineries.^[7,8] To better understand the reaction mechanism of hydrogenolysis as a guideline to select suitable metal catalysts and cocatalysts to improve the product selectivity, intensive studies on various metal catalysts, which mainly include Ru-,^[9-14] Cu-,^[12,15-19] Pt-,^[9,12,20,21] and Pd-based catalysts,^[22,23] for glycerol hydrogenolysis have been conducted. Ni is a promising catalyst for hydrogenolysis because of its low cost, high activity, and resistance to poisoning^[24,25] but it shows poor hydrothermal stability compared to noble-metal catalysts^[26] and low hydrogenolytic activity toward C-O bond compared to Cu catalysts.^[12]

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nation of adsorbed species was the most likely rate-limiting step in glycerol hydrogenolysis under alkaline conditions. The Ag additive enhanced the hydrogenation ability of Ni catalysts, which should be related to the higher strength of the adsorption of hydrogen and the lower strength of the adsorption of substrates on Ni sites because of the formation of Ni-Ag alloys. A mechanistic interpretation was presented for the excellent catalytic behavior.

Numerous strategies for the stabilization of Ni particles in hydrothermal processes, such as aqueous-phase reforming (APR), have been investigated. Raney Ni (R-Ni) is a prominent hydrogenation catalyst in industrial application, not only for its activity^[27,28] but also for its dramatic stability and insolubility in aqueous-phase reactions as it loses only \approx 50% of its initial activity for APR over 48 h at 225 °C for which the catalysts composed of Ni supported on Al_2O_3 , SiO_2 , or ZrO_2 lost $\approx 90\%$ of their initial activity (deactivation because of Ni sintering and leaching).^[29] The adjustment of the pH of the solutions with base (i.e., KOH) is an elegant strategy to stabilize the Ni nanoparticles under aqueous solution conditions, and at pH > 8, achieved by the addition of at least 0.5 M base, the Ni sintering (particle growth) through Ostwald ripening as a result of the acidic APR conditions was almost prevented, which corresponds to the suppression of Ni leaching.^[30]

As C-O bond breaking is avoided by using Ni- and Ru-based catalysts, which exhibit high hydrogenolysis activity for the C-C bond in comparison with Cu-based catalysts and are ideal for H₂ production from biomass-derived feedstocks through the APR process, the main difficulty in using Ni catalysts for the production of desired C₃ chemicals (i.e., 1,2-PD) through C-O bond rupture from glycerol hydrogenolysis is the selective cleavage of C-O and C-C bonds over Ni sites.^[12, 29-31] One alternative to enhance the efficiency of Ni-based catalysts for the formation of C₃ products is to engineer the metal function in the catalysts. This objective can be realized by the alloying of Ni with other transition metals. Previous studies demonstrated that bimetallic catalysts exhibited a decreased tendency for C-C bond hydrogenolysis than the respective monometallic ones.^[15,32] Thus, the investigation of second metal components that promote C-O bond cleavage or inhibit C-C bond cleavage is regarded as the key to accomplish a complete cleavage

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ratio of C–O/C–C bonds in glycerol hydrogenolysis over Nibased catalysts.

In this work, a commercial R-Ni catalyst was modified with Ag to develop a water-tolerant catalyst, which had better selectivity toward C₃ products (1,2-PD) and lactic acid (LA) through C–O bond cleavage. A certain amount of NaOH (0.5 M) was added to obtain stable Ni catalysts. The results of catalyst characterization studies and catalytic activity measurements allow us to elucidate the reaction mechanism in glycerol hydrogenolysis and document the influence of Ag to control the cleavage of C–O and C–C bonds over the Ni-based catalysts.

Results and Discussion

Catalyst characterization

The characteristics of the catalysts used in this study are summarized in Table 1. H₂ temperature-programmed reduction (TPR) profiles were measured to investigate the redox properties and phase composition of the catalysts. Four distinct peaks appeared in the TPR profile of Ag/Al₂O₃ (Figure 1). The reduction peaks in the temperature range of 100-400 °C were assigned to large Ag oxide particles located outside the Al₂O₃ matrix, and the other peaks at above 620°C were possibly caused by the interaction of Ag with the AI_2O_3 support.^[33] Compared to Ag/Al₂O₃, R-Ni was reduced at ~235°C, which shifted toward a higher temperature at around 254 °C with the addition of Ag. This indicated that a close interaction between Ni and Ag could lead to the decrease of the reducibility of Ni. The peak at above 333 °C was assigned to the reduction of Ag oxide, which was ascribed to Ag₂O by Jeong and Kang.^[34] If the Ni/Ag ratio decreased from 34:1 to 6:1, the reduction peak for Ag₂O was shifted toward a higher temperature;^[35] however, the reduction peak for Ag₂O shifted toward a lower temperature as more Ag was added (Ni/Ag = 1:1).^[36] This could be attributed to the size shift of the Ag₂O particles.^[33]

XRD measurements were conducted to verify the metal crystallites of the catalysts. The unmodified R-Ni that contained Sn and AI showed typical diffraction peaks near $2\theta = 44$, 45, and 51° , which were characteristic of Ni-Sn alloys,^[29] Ni-Al alloy,^[37,38] and metallic Ni (200),^[38] respectively (Figure 2A). The addition of Ag to R-Ni had significant effects on the XRD pattern of the catalysts. All the XRD patterns of R-Ni_xAg catalysts had four main characteristic peaks of face-centered cubic (fcc) crystalline





Figure 1. H₂-TPR profiles of a) Ag/Al₂O₃ calcined at 400 °C, b) R-NiAg reduced at 700 °C, c) R-Ni₆Ag reduced at 700 °C, d) R-Ni₃₄Ag reduced at 700 °C, and e) R-Ni reduced at 260 °C.



Figure 2. XRD patterns of catalysts; A) wide-scan XRD pattern and B) fine scan of the Ag(111) peak: a) Ag/Al₂O₃ calcined at 400 °C, b) R-NiAg reduced at 700 °C, c) R-Ni₆Ag reduced at 700 °C, d) R-Ni₃₄Ag reduced at 700 °C, and e) R-Ni reduced at 260 °C.

Table 1. Characterization of catalysts.										
Catalyst	$Ni^{[a]}$ [wt%]	$AI^{\scriptscriptstyle[a]}\left[wt\%\right]$	$Sn^{\scriptscriptstyle{[a]}}\left[wt\% ight]$	$Ag^{[a]}[wt\%]$	Ag/Ni bulk atomic ratio ^[b]	Ag/Ni surface atomic ratio ^[c]	BET surface area $[m^2g^{-1}]$			
R-Ni ^[d]	64.1	12.7	20.4	0	0	0	21.1			
R-Ni ₃₄ Ag	50.2	16.6	30.5	2.7	0.03	2.30	42.4			
R-Ni ₆ Ag	45.6	14.3	27.6	12.6	0.15	2.71	40.2			
R-NiAg	30.8	13.2	21.5	34.5	0.61	4.87	32.6			
17.5 % Ag/Al ₂ O ₃ ^[e]	-	-	-	-	-	-	103.7			
[a] Determined by using ICP-OES. Others: Na, Sm, Mo (in trace amounts), which were not considered in Raney Ni-based catalysts. [b] Determined by using ICP-OES. [c] Determined by using XPS. [d] Raney Ni prereduced at 260 °C. [e] Catalyst from Ref. [58].										

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Ag at around $2\theta = 38.2$, 44.4, 64.6, and 77.6°, which can be indexed to the (111), (200), (220), and (311) planes, respective-ly.^[39] Moreover, the peak of the Ag(111) plane shifted to a higher angle, which indicated the formation of Ni-Ag alloys after reduction (Figure 2B). This result was consistent with the H₂-TPR study that confirms the close interaction of Ni-Ag (Figure 1).

X-ray photoelectron spectroscopy (XPS) was performed to clarify the chemical state of the Ni and Ag species on the surface of Ag-modified R-Ni, catalysts and the corresponding Ni2p, Al2p, and Ag3d spectra of the R-Ni-based catalysts are given in Figure 3. The Ni 2p_{3/2} peak could be mainly deconvoluted into two peaks at binding energies (BEs) of 852.5 and 855.7 eV, which correspond well to Ni⁰ and Ni²⁺ species, respectively.^[37,40,41] However, the spectra presented in Figure 3A suggested that a small amount of Ni species was concentrated on the surface of the R-Ni_xAg samples as there was no noticeable peak in the XPS spectra. This can be attributed to three situations: (a) the pronounced Al₂O₃ enrichment (which existed as hydrated alumina before calcination)^[42] on the surface of catalysts, as supported by the spectra shown in Figure 3B, which was removed under reaction conditions (Figure S1), the Al 2p core-level BEs measured at around 74.4 and 72.6 were typically ascribed to AI_2O_3 (AI^{3+}) and metallic AI (AI^0) species, respectively, $^{[37,41]}_{l}$ (b) the metallic Al (Al⁰) enrichment on the surface of Ni-Al alloys (because of the lower surface energy of Al with respect to Ni^[37] (Figure S1); (c) the Ag species enrichment on the surface of Ni-Ag alloys, which was because of the lower surface energy of Ag with respect to Ni and reported to be thermodynamically favorable by DFT studies and Monte Carlo simulations,^[43-46] whereas for other metal dopants such as Pt there was Ni enrichment on the surface of the Ni-based alloys (see Figure S2). The surface Ag/Ni atomic ratio of R-Ni₆Ag catalyst was 2.71, which was dramatically higher than the bulk Ag/Ni atomic ratio of 0.15 and slightly increased as more Ag was added (Table 1). Herein, all the cases above must coexist. As the BE of bulk metallic Ag (Ag⁰) was 368.1 eV and that of Ag_2O (Ag⁺) was 367.7 eV,^[47] the Ag present in the highvalence state (Figure 3C) should be attributed to the passivation treatment, and an interaction between Ni and Ag could not be ruled out (as supported by H₂-TPR and XRD results).

H₂ and NH₃ temperature-programmed desorption (TPD) were performed, and the results were compared for the R-Ni and R-Ni₆Ag catalysts to further analyze the changes of the hydrogenation activity and the acidity of the Ag-modified Ni catalysts, respectively. The H₂-TPD profiles showed that the addition of Ag increased the desorption temperature, which indicates a stronger metal-H bond on the surface of the R-Ni₆Ag catalysts than that on R-Ni as the temperature of desorption is related to the metal-H bond strength (Figure 4).^[48] The shift of electronic effects that results from the formation of Ni-Ag alloys may lead to this decreasing desorption behavior. R-Ni is known as a Ni-based alloy with few acidic functional groups. The NH₃-TPD profiles exhibited that the desorption peak shifted to lower temperature, which indicated a weaker acid strength on the surface of R-Ni₆Ag catalysts than R-Ni, which was attributed to a new acid site occurrence, likely Aq₂O (Ag⁺),

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Figure 3. XPS spectra of A) Ni2p, B) Al2p, and C) Ag3d: a) R-NiAg reduced at 700 °C, b) R-Ni₆Ag reduced at 700 °C, c) R-Ni₃₄Ag reduced at 700 °C, and d) R-Ni reduced at 260 °C.

as shown by XPS (Figure 3C), on the surface of Ag-modified R-Ni catalysts.

Low- and high-magnification SEM images of the R-Ni-based catalysts demonstrated a predominant porous region (Figure 5) in agreement with previous studies that showed that fresh R-Ni is a high-surface-area catalyst that consists of reduced Ni particles.^[29] After drying and passivation, R-Ni had a BET surface area of $21.1 \text{ m}^2 \text{g}_{cat}^{-1}$, which increased to $42.4 \text{ m}^2 \text{g}_{cat}^{-1}$ as a small amount of Ag was added to R-Ni and decreased slightly as more Ag was added (Table 1). In addition, the BET results of R-NiAg suggested that the loading of large amounts of Ag to R-Ni does not decrease the surface area of the catalysts by pore blockage dramatically.



Figure 4. $\rm H_{2^-}$ and $\rm NH_3\text{-}TPD$ profiles of a) R-Ni_6Ag reduced at 700 $^\circ C$ and b) R-Ni reduced at 260 $^\circ C.$



Figure 5. SEM images of catalysts shown at low and high magnification (insets): A) R-Ni reduced at 260 $^{\circ}$ C and B) R-Ni_eAg reduced at 700 $^{\circ}$ C.

Catalytic performance

The effect of the addition of Ag to R-Ni catalyst on the catalytic activity and C₃ products selectivity is shown in Table 2. In comparison with that over R-Ni, the conversion of glycerol was promoted by the addition of small amount of Ag at a Ni/Ag ratio of 34:1, which indicates that the addition of Ag improves the overall rate of glycerol consumption (Table 2, entry 2). Importantly, R-Ni₆Ag showed a higher carbon balance than R-Ni in the hydrogenolysis of glycerol, which increased from 85.7 to 96.1%, and maintained a higher conversion at \approx 78.0%. An increase of the Ag content, however, had a negative effect on the conversion, which decreased slightly from 78.8 to 69.2% (Table 2, entries 2–4).

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Notably, the Ag-modified R-Ni catalysts exhibited a higher selectivity for the production of total C₃ products, especially 1,2-PD, than R-Ni for glycerol hydrogenolysis after calcination at 700 °C (Table S1), which improved from 70.9 and 48.4% to 87.6 and 65.9% at a Ni/Ag ratio of 6:1 (Table 2, entries 1 and 3), respectively, and a LA selectivity of ~22% was maintained. Actually, 1,2-PD can be generated from the hydrogenation of 2-hydroxyacrolein over metal sites, whereas LA must derive from the cooperative production of metal and hydroxyl ions through the Cannizzaro reaction from pyruvaldehyde, the keto-form of 2-hydroxyacrolein (Table S2).^[9,13,49,50]

As the product distribution is sensitive to the level of conversion, the influence of the reaction time on glycerol hydrogenolysis over R-Ni₆Ag was investigated (Figure 6). At around 70% conversion of glycerol in the presence of base, R-Ni₆Ag promoted approximately 88 and 73% selectivity to total C₃ products and 1,2-PD after 1 h, respectively. As the conversion of glycerol neared completion, ethanol was observed as the product of the further degradation of diols, which was consistent with the findings of Montassier et al.^[9,28,51] Methanation was the main side reaction of glycerol hydrogenolysis, and trace amounts of 1-propanol and methanol were observed in the liquid phase.



Figure 6. Glycerol conversion and product selectivity over R-Ni₆Ag as a function of reaction time. Reaction conditions: 20 wt % glycerol, 0.5 M NaOH, substrate/catalyst=8 (weight ratio), $p_{H_2} = 4$ MPa (RT), T = 210 °C.

Table 2. Effect of Ag addition to Raney Ni catalysts. ^[a]										
Entry	Catalyst	Conversion ^[b] [%]	Carbon ba [%]	llance ^[c]		Carbon selectivity [%]				
					1,2-PD	^[b] LA ^[d]	EG ^[b]	Ethanol ^[b]		
1	R-Ni ^[e]	66.1	85.7		48.4	22.5	4.9	2.5		
2	R-Ni ₃₄ Ag	78.8	87.2		54.2	22.0	5.9	1.6		
3	R-Ni₅Ag	78.0	96.1		65.9	21.7	5.9	1.5		
4	R-NiAg	69.2	84.4		47.0	23.6	5.5	1.3		
5	Ag/Al_2O_3	18.3	99.4		53.1	33.7	7.3	2.7		
[a] Reaction conditions: 20 wt% glycerol 0.5 M NaOH substrate/catalyst (weight										

[a] Reaction conditions: 20 wt% glycerol, 0.5 M NaOH, substrate/catalyst (weight ratio) = 8, p_{H_2} = 4 MPa (RT), T = 210 °C, t = 6 h; 1,2-PD: 1,2-propanediol; EG: ethylene glycol; LA: lactic acid (in the form of lactate). [b] Quantified by using GC-FID. Error represents 95% confidence limits. [c] Others: methane, methanol, 1-propanol. [d] Quantified by using HPLC. Error represents 95% confidence limits. [e] Raney Ni pre-reduced under 260 °C.



Effects of Ag dopant: Understanding the network of glycerol hydrogenolysis over Ni catalysts

On Ni-based catalysts, hydrogenolysis activity is highly exhibited in the C–C bond and C–O bond breaking is avoided.^[12,31] One way to design a better Ni catalyst for the catalytic dehydroxylation of biomass-derived polyols is to realize a higher cleavage ratio of C–O/C–C bonds. The investigation of second metal components for Ni-based catalysts is a promising option to influence the tendency for C–O and C–C bond breaking.^[15,32] The addition of Ag to R-Ni caused an increase in activity and superior selectivity toward C₃ products through C–O bond rupture, especially 1,2-PD, for glycerol hydrogenolysis at a Ni/Ag ratio of 6:1.

Proposed reaction mechanisms and selectivity challenges for the dehydration products in glycerol hydrogenolysis at high pH are outlined in Scheme 1. In the presence of base, the de-



Scheme 1. Proposed mechanism for the hydrogenolysis of glycerol over Nibased catalysts under alkaline conditions.^[7]

hydrogenation of glycerol to glyceraldehyde intermediate on the metal catalyst was suggested as the initial step and was enhanced as more base was added.^[9] Previous studies revealed that Ag addition inhibited the dehydrogenation ability of Ni catalysts because of the higher activation energy of Ag for alcohol dehydrogenation in comparison with Ni.^[52,53] This was consistent with the improved carbon balance and higher glycols yield (1,2-PD and ethylene glycol; Table 2), which was attributed to the suppression of further hydrogenolysis of products by inhibiting the dehydrogenation step.^[54] However, from the catalytic results, Ag-modified R-Ni catalysts were more active in glycerol conversion, which suggests that the dehydrogenation activity of R-Ni-based catalysts was not the key factor to control the rate of glycerol conversion in the presence of base.

The production of C₃ products through C–O bond rupture was caused by the dehydration of glyceraldehyde before hydrogenation (for 1,2-PD production) or the Cannizzaro reaction (for LA production; Scheme 1). Although undesirable C-C bond rupture occurred through Ni-catalyzed retro-aldol condensation that acted as the crucial barrier to obtain a high C₃ product selectivity. Strategies to enhance the efficiency of Ni catalysts in this study for catalytic dehydroxylation reaction can be either metal function modification for the inhibition of retro-aldol condensation or acid/base sites adjustment for the enhancement of dehydration. As revealed by the H₂-TPR, XRD, and XPS results, a portion of the Ag species interacted with the Ni moieties to form Ni-Ag alloys after reduction, whereas other Ag species, likely Ag₂O (Ag⁺), were present on the surface of R-Ni_xAg catalysts. Consequently, contiguous Ni ensembles on the catalyst surface were diluted with Ag species, which led to less contiguous Ni ensembles and more Ni monomer sites on the surface. Contiguous Ni ensembles were reported to be more active in C-C bond cleavage than Ni monomer sites, whereas Ni monomer sites were more suitable for hydrogenation reactions.^[55, 56] Additionally, as suggested by the weakened dehydrogenation properties of Ni catalysts with the addition of Ag, the formation of Ni-Ag alloys may also inhibit undesired C-C bond cleavage by effectively decreasing the strength of adsorption of the intermediates on Ni sites as the bond energy of the CO–H bond ($E_{O-H} \approx 104 \text{ kcal mol}^{-1}$) is generally higher than that of the C–C bond ($E_{C-C} \approx 83$ kcal mol⁻¹).^[57] However, the Ag catalyst was effective for the cleavage of the C–O bond,^[58] and the surface Ag species likely act as new acid sites to promote the dehydration activity as R-Ni is known as a Ni-based catalysts with few acidic functional groups. Thus, it was significant that both the Ni metal function and catalyst acidity were altered by the formation of Ni-Ag alloys, and the synergistic effect of the Ni metal function and catalyst acidity was proposed to be responsible for the improved C₃ product selectivity. However, Montassier et al. concluded that C-O bond cleavage proceeded through a basecatalyzed instead of acid-catalyzed dehydration.^[9,51] If this assumption is reasonable, the dehydration process must be totally directed by the added base. To confirm the role of catalyst acidity on catalytic properties in the presence of base, in this work, ZnO-modified R-Ni catalysts were prepared by an incipient impregnation method as the addition of ZnO to NiMo catalysts could improve the catalytic activity and selectivity because of the Lewis acidity of ZnO.^[59] The acidity of the catalysts played a critical role to promote dehydration products but had little effect on the rate of glycerol conversion in the presence of base (Table S3).

Ag-modified R-Ni catalysts were efficient for 1,2-PD production and maintained a LA selectivity of ~22% compared to R-Ni (Table 2). As the formation of 1,2-PD proceeds through two consecutive steps: dehydration of the glyceraldehyde on the acid sites followed by hydrogenation of the produced 2-hydroxyacrolein/pyruvaldehyde intermediates on the Ni metal (or bimetallic Ni-Ag), whereas LA is produced by the Cannizzaro reaction from pyruvaldehyde and well controlled by base (Table S2),^[9,13,49,50] as depicted in Scheme 1, the activity of hy-



drogenolysis and the selectivities to 1,2-PD and LA in C₃ products were proposed to be sensitive to the hydrogenation activity of the Ni-based catalysts with controlled base addition. To verify this point of view, herein, Pt-modified R-Ni catalysts were prepared similarly according to the method for Raney Ni-Ag catalysts as supported bimetallic Ni-Pt catalysts exhibited a lower dehydrogenation activity,^[60] but higher hydrogenation activity than the monometallic Ni catalysts.^[61,62] Compared to R-Ni, at a higher conversion of glycerol around 90%, Pt-modified R-Ni catalysts promoted 62.5% selectivity to 1,2-PD and inhibited the selectivity to LA, which decreased from 22.5 to 14.3% at a Ni/Pt ratio of 17:1 (Table S4, entry 5). This indicated that, instead of dehydrogenation or dehydration reactions, hydrogenation reactions over the Ni-based catalysts were the most likely rate-limiting step in glycerol hydrogenolysis under alkaline conditions. Moreover, the hydrogenation activity of the Ni-based catalysts was crucial to control the selectivities to 1,2-PD and LA in C₃ products. As reported previously, glycerol hydrogenolysis performed over a Cu/SiO₂ catalyst under basic conditions (1 M NaOH) yielded LA as the main product (85%).^[51] A Ru catalyst modified with sulfur yielded 75% of 1,2-PD and 13% of LA in the presence of NaOH after 2 h at 240 $^{\circ}\text{C.}^{\text{[63]}}$ A 64% selectivity to LA was obtained at a low conversion over a Pt/C catalyst at 180°C and 4 MPa in the presence of CaO or NaOH.^[9,51] Notably, the Ag additive can enhance the hydrogenation ability of Ni catalysts because of the alloying of Ni with Ag. As suggested by surface science studies and DFT calculations, the binding energies of unsaturated hydrocarbons on metals correlate with hydrogenation activity. The formation of Ni-Ag alloys may not only decrease the strength of the adsorption of unsaturated intermediates effectively (indicated by the inferior dehydrogenation activity of Agmodified Ni catalysts) but it also enhances the strength of the adsorption of hydrogen on Ni active sites (supported by H₂-TPD; Figure 4), which leads to an increased amount of adsorbed hydrogen on the Ni metal for hydrogenation reactions.

Therefore, the addition of Ag to Ni catalysts introduced Ag species on the surface of R-Ni-based catalysts and formed Ni-Ag alloys after reduction, which led to a superior catalytic performance (Scheme 2). However, the atomic ratio of Ni/Ag in R-Ni_xAg should be properly balanced in terms of catalytic activity and C₃ product selectivity. If the Ag-modified Ni catalysts were prepared with the appropriate Ni/Ag atomic ratio of 6:1, a higher selectivity to C₃ products, especially 1,2-PD, was achieved, which increased from 70 and 48% to 88 and 73%, respectively. Notably, for the production of C₃ products through C–O bond breaking, especially 1,2-PD, a desirable Ni catalyst



Scheme 2. A schematic for preparation of R-Ni-Ag catalysts and their catalytic behavior in glycerol hydrogenolysis.

should not only promote the hydrogenation activity of unsaturated bonds (C=O and C=C) but also inhibit the dehydrogenation activity to retard further hydrogenolysis and/or parallel side reactions such as APR. The higher hydrogenation and inferior dehydrogenation ability of Ni-based catalysts was crucial to obtain a superior catalytic activity and yield of C₃ products, especially 1,2-PD, in glycerol hydrogenolysis, consistent with a previous study on cellulose.^[54] The effects of the doping of Ag to Ni catalysts on the improvements of activity and selectivity in glycerol hydrogenolysis can be concluded as follows: (1) ensemble effect, Ni atoms were substituted by Ag atoms during preparation to form Ag species enrichment on the surface of Ni-Ag alloys after calcination, which led to the dilution of contiguous Ni sites that were more favorable for the cleavage of C-C bonds than Ni monomer sites; (2) electronic effect, the formation of Ni-Ag alloys increased the amounts of adsorbed hydrogen through the decreased strength of adsorption of the substrates and/or the increased strength of adsorption of hydrogen on Ni sites, which resulted in the improved hydrogenation ability but inhibited dehydrogenation ability of Ni catalysts.

Conclusions

Raney Ni-Ag catalysts can be selected to achieve a good activity and selectivity for the production of C₃ products, especially 1,2-propanediol, by the aqueous-phase hydrogenolysis of biomass-derived glycerol. Ag-modified Raney Ni catalysts exhibited an increased activity for glycerol hydrogenolysis and enhanced selectivity to C₃ products compared to the unmodified Raney Ni catalyst. The most suitable Ni-based catalyst for C-O bond cleavage in glycerol hydrogenolysis was obtained at a Ni/Ag atomic ratio of 6:1. Characterization of the catalysts by using H₂ temperature-programmed reduction, XRD, and X-ray photoelectron spectroscopy indicated that the dilution of Ni active sites and the existence of Ni-Ag alloys on the surface of Ag-modified Ni catalysts were crucial for the excellent catalytic performance. It is likely that further advances in the insitu characterization of catalysts will lead to a deeper understanding of reaction mechanisms and the generation of new catalysts for the selective hydrogenolysis of C-O and C-C bonds in the catalytic dehydroxylation of biomass-derived polyols.

Experimental Section

Catalyst preparation

The R-Ni_xAg catalysts were prepared similarly according to a method described elsewhere.^[64,65] Briefly, commercial R-Ni (Da Cheng Co., Ltd, China) was pretreated at 260 °C for 2 h in a flowing 5% H₂/Ar mixture (>99.99%, Changchun Juyang Gas Co., Ltd, China), before the addition of appropriate amounts of AgNO₃ (A.R., Sinopharm Chemical Reagent Co., Ltd, China) in deionized water to reduced R-Ni under a N₂ atmosphere (>99.999%, Changchun Juyang Gas Co., Ltd, China), and subsequent heating in a 100 mL stainless-steel autoclave with an inner Teflon coating to 150 °C for 2 h. After reaction, the solvent was removed by centrifugation. The catalyst was then washed and stored under deionized water.



Before we collected catalytic reaction data or catalyst characterization, all catalysts were reduced in a flowing 5% H₂/Ar mixture for 2 h at 700 °C (heating at 5 °Cmin⁻¹). Before contact with air, the catalysts were passivated by flushing with 0.4% O₂/Ar mixtures for 2 h at RT.

Catalyst characterization

XRD studies were conducted by using a Bruker D8 ADVANCE diffractometer with a CuK_a source (40 kV and 10 mA) in the 2 θ range of 20–80° with a scan speed of 1° min⁻¹. The metal loading on the catalysts was investigated by using inductively coupled plasma optical emission spectroscopy (ICP-OES) by using a Thermo iCAP 6300 spectrometer. The BET surface areas of the catalysts were determined by using N₂ adsorption by using a Micromeritics ASAP-2010 apparatus. SEM images were collected by using a Philips XL-30 field-emission scanning electron microscope. XPS data were obtained by using a Thermo ESCALAB 250 spectrometer equipped with an Al source that operates at 15 kV and 150 W. The surface concentrations were analyzed by using the Ni2p_{3/2} and Ag3d_{5/2} peak areas and sensitivities.^[64,66]

TPR was detected by using a TCD-GC (GC-8A, Shimadzu). TPD was measured by using a mass spectrometer (QIC-20, Hiden). Before the H₂-TPR run, 50 mg of the sample was pretreated with air (> 99.99%, Changchun Juyang Gas Co., Ltd, China) at 150°C for 1 h. After cooling to RT, the sample was flushed for 1 h to reach a stable background and then heated to 850°C (heating at 10° C min⁻¹) in flowing 5% H₂/Ar mixtures (50 cm³ (STP) min⁻¹). For the H₂-TPD analysis, 50 mg of the sample was prereduced for 1 h at the appropriate temperature in flowing 5% H₂/Ar mixtures. After cooling to RT, the sample was flushed for 1 h to reach a stable background and then heated to $850\,^\circ\text{C}$ (heating at 10° C min⁻¹) in flowing Ar (>99.999%, Changchun Juyang Gas Co., Ltd, China; 50 cm³ (STP) min⁻¹). For NH₃-TPD, 50 mg of the sample was pretreated with air at 150 $^\circ\text{C}$ for 1 h. After cooling to RT, the sample was flushed with 0.2% NH_3 /Ar mixtures for 30 min and then Ar for 1 h to reach a stable background. Desorption was then performed by heating the sample to 850 °C (heating at 10 °C min⁻¹) in flowing Ar (50 cm^3 (STP) min^{-1}). The TPD curves were related to the monitored ion intensities of m/z=2 (H₂⁺) and 17 (NH₃⁺).

Catalytic reaction

The hydrogenolysis experiments were performed in a stainlesssteel autoclave with a capacity of 50 mL. The reactant solutions (20 wt% glycerol (99%, Aladdin), solvent: H₂O, with base additives) and catalysts were placed in the reactor to give a total volume of \approx 20 mL. Before it was put into a silicone oil bath, the reactor was flushed with H₂ (>99.999%, Changchun Juyang Gas Co., Ltd, China) and pressurized to 4.0 MPa (RT). After the reactor was heated to 210 °C in the oil bath, stirring with a magnetic stirrer at 1200 rpm was started, which was defined as the beginning of the reaction. The reaction was maintained under these conditions for 6 h to ensure that a steady state was achieved.

After the reaction, the reactor was cooled to RT. Gas samples were collected with a gas-bag and analyzed by using GC with a thermal conductivity detector (TCD; GC-8A, Shimadzu) equipped with an active carbon column. Liquid samples from the reaction mixture after centrifugation were analyzed by using GC with flame ionization detection (FID; GC-8A, Shimadzu) and HPLC (LC-20AB, Shimadzu). The GC–FID was equipped with a polyethylene glycol (PEG) column (20 m×0.25 µm×0.25 mm; Dalian Zhonghuida Co., Ltd,

China). The HPLC system was equipped with a refractive index detector (RID; RID-10A, Shimadzu) and an Aminex HPX-87H column ($300 \times 7.8 \text{ mm}$, Bio-Rad) and 5 mm H₂SO₄ was used as the mobile phase with a flow rate of 0.7 mLmin⁻¹ at 60 °C. The major liquid-phase products detected by both GC–FID and HPLC were 1,2-PD, ethylene glycol, and ethanol; other byproducts, which included methanol and 1-propanol, were present in trace amounts. LA was observed by HPLC. Methane was the main gas observed by GC–TCD. The quantification of the liquid products was conducted by using both GC–FID and HPLC based on calibration curves of the standard compounds. The carbon balance was defined as the percentage of carbon accounted for in the liquid phase after 6 h reaction. The conversion of glycerol and selectivity of each product were determined as follows:

$$\begin{array}{l} \mbox{conversion } (\%) = \frac{\mbox{moles of consumed glycerol}}{\mbox{moles of initial glycerol}} \times 100 \\ \mbox{selectivity } (\%) = \frac{\mbox{moles of carbon in specific product}}{\mbox{moles of carbon in consumed glycerol}} \times 100 \\ \end{tabular} \tag{1}$$

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