

Bimetallic synergy effects of phyllosilicate-derived NiCu@SiO₂ catalysts for 1,4-butynediol direct hydrogenation to 1,4-butanediol

Changzhen Wang^{*[a]}, Yani Tian^[a], Ruifang Wu^[a], Haitao Li^[a], Benzhen Yao^[b], Yongxiang Zhao^{*[a]} and Tiancun Xiao^{*[b]}

Abstract: Hydrogenation of 1,4-butynediol (BYD) to 1,4-butanediol (BDO) is a two-step process, with an initial hydrogenation of BYD to 1,4-butenediol (BED) and the subsequent hydrogenation of BED to BDO. However, the BYD hydrogenation also involves many side reactions originated from the isomerization of BED. In order to inhibit isomerization pathways, phyllosilicate-derived bimetallic the NiCu@SiO₂ catalysts have been developed for efficient $C \equiv C/C = C$ hydrogenation in this work. Due to the formation of phyllosilicate matrix and highly dispersed metal nanoparticles, NiCu@SiO₂ showed total BYD conversion with extremely high BDO selectivity compared to a conventional impregnated Ni/SiO2 catalyst. A remarkable result of NiCu@SiO₂ catalysts is that a new type of bimetallic catalytic sites responsible for the high hydrogenation activity can be differentiated from the Ni phyllosilicate matrix by the induction of Cu species, and these neighboring bimetallic sites with the help of weak acid phyllosilicate interface, can realize to stabilize the activated BED species (allyl alcohol form) adsorbed on the cooperative active sites, thus to avoid its isomerization to aldehyde form and unexpected C=O hydrogenolysis. Consequently, it enhanced the selectivity to the diol products BDO significantly. Owing to the benign improvement of three center synergy effect, 9Ni1Cu@SiO₂ possesses the optimum BYD direct hydrogenation ability with a rarely reported high selectivity of 90.5-94.5% at 50°C and 1MPa.

Introduction

BDO, eg.,1,4-butanediol, is a bulk fine chemical raw material and feedstock used in the production of commercialized chemicals in industry, which can extend its industrial chain to produce high-value-added downstream chemicals such as tetrahydrofuran (THF), γ -butyrolactone (GBL) etc^[1-2] in the fields of polyester materials, paper, medicine, automotive, pesticide, textile and household industries^[3]. By far, the most important BDO production method in industry is 1,4-butynediol (BYD) hydrogenation, and based on this reaction system, noble metals (Pd, Pt etc.) ^[4-7] and Raney Ni catalysts^[1, 8] have been widely used.

Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, UK. E-mail: xiao.tiancun@chem.ox.ac.uk

Supporting information for this article is given via a link at the end of the document.

Amongst them, although Ni has the advantage of low cost and easy availability, the Raney Ni catalysts themselves still have the problems of environment pollution and security risk due to their high bulk metal content. As an alteration, dispersed Ni-based supported catalysts have been reported [9-10], however, the present Ni-based catalysts are also not ideal for BYD direct hydrogenation due to their low activity/selectivity and deactivation^[11]. As revealed by Campelo et al^[12], since the traditional Ni-based catalysts had a poor metal support interaction, the active metal site is usually liable to migrate under high temperature or liquid-phase conditions, thus resulting in the rapid structural or textural destructive of catalysts. In order to enhance the structural stability of Ni-based catalysts, we intended to apply a recently developed phyllosilicate-derived core-shell catalyst^{[13-} ^{14]}, to the BYD liquid-phase hydrogenation. Compared with the traditional catalysts, this core-shell nanomaterial has the advantage of mono-layer dispersity and tunability, which increases the availability of the active sites. Moreover, due to the generation of robust metal phyllosilicate shell with high exposure of metal surface, this type of catalyst is expected to possess extremely high liquid-phase stability due to the strong metal support interactions and geometric confinement structure^[15-16], which seems to be more applicable to catalytic hydrogenation reactions, but have seldom been reported by other researchers^[17].

Besides, concerning on the structural feature of BYD which has various unsaturated bonds, the hydrogenation of BYD will not only include the C=C and C=C hydrogenation process, but also involved by many side reactions such as isomerization, aldol condensation and C=O hydrogenolysis because of the unsaturated feature of C-O bonds (C-OH or C=O). To be concise, there are a series of reactions during BYD hydrogenation process as shown in Scheme 1^[18-20]. BYD is usually first semihydrogenated to form unsaturated BED, which can be then hydrogenated to BDO. However, the accompanying BED intermediate with allyl alcohol structure is preferably converted to its highly-unstable isomerization product γ -hydroxybutanal (γ -HALD), which results in the formation of aldol condensation byproducts such as 2-hydroxytetrahydrofuran (HTHF) and acetal (HBOTHF); similarly, it can also be excessively hydrogenolysis to form n-butanol (BOL) or crotyl alcohol (CROL). [21] Even worse, some of these byproducts (HTHF and acetal) could form an azeotrope within BDO, thus will not only reduce the hydrogenation efficiency, but also lower the BDO yield quality. In our opinion, an efficient way to inhibit the isomerization of BED intermediate is to enhance its adsorption stability, thus promising its further

 [[]a] Dr C Wang, Dr Y Tian, Ms R Wu, Dr H Li and Prof Y Zhao Engineering Research Center of Ministry of Education for Fine Chemicals, Shanxi University, Taiyuan, 030006, China Department E-mail: czwang@sxu.edu.cn ; yxzhao@sxu.edu.cn
 [b] Dr B Yao and Dr T Xiao

FULL PAPER

10.1002/cctc.201901052

WILEY-VCH

cis-BED OH Hydrogenati Hydrogenati но OH BDO BYD но trans-BED Hydrogenolysis Isomerizatio Cyclizati Hydrogenolysis OН но CROL y-HALD HTHF Hydrogenolysis Condensation он OH BOL HBOTHE

Scheme 1. Proposed reaction pathways for the production of BDO and byproducts through BYD hydrogenation.

hydrogenation. A simple way to boost the adsorption of C=C bond (electron clouds above the carbon chains) over BED is to modify the active metal site surface properties and surrounding electronic environment via second metal promoters ^[22-24]. In the orthoelements of Ni, Cu has a similar inner electronic distribution with Ni, but with different outer electron cloud, which can form bimetallic synergistic effect with nickel and enhance the hydrogen overflow/transfer ability of the surrounding metal surface ^[15], thus stabilizing the adsorption state of allyl alcohol form ^[25]. On the other hand, since the essence of isomerization of BED is the electron clouds shift from the C-OH to the C-C chains^[21], we may use some assistant sites to distract electron cloud density over terminal –OH group, thus retard its dominant isomerization pathway.

Bear these ideas in mind, we proposed a novel phyllosilicate derived Ni-Cu core-shell catalyst. To our knowledge, the BYD direct hydrogenation has never been reported over a phyllosilicate derived Ni-Cu core-shell catalysts combined with both the phyllosilicate shell structure and the bimetallic synergy effect, which may play vital roles on the BYD direct hydrogenation activity and BDO target product selectivity. Based on our characterization results, the importance of bimetallic synergy effect with phyllosilicate structure were thoroughly studied to illustrate the different reaction pathways of BYD hydrogenation, and the optimal Ni-Cu catalyst was developed to the application of the direct hydrogenation of BYD to BDO.

Results and Discussion

Textrual properties of the NiCuphy@SiO2 core-shell framework

Phyllosilicate-derived NiCu@SiO₂ core-shell catalysts were prepared via a hydrothermal method using SiO₂ nanosphere as the mono-dispersed core template for the growing of Ni-Cu phyllosilicate shell (Figure S1). The actual metal elemental

composition of as-prepared bimetallic materials was determined by ICP-AES and the results are presented in Table 1. The total metal content of different bimetallic catalysts is at ca.18 wt% and the Ni/Cu ratios of the obtained samples were close to the nominal values, which indicated the well dispersion of the dual metal.

Transmission electron microscope (TEM) morphologies of the fresh NiCuphy@SiO₂ materials before reduction are shown in Figure 1. Uniform spherical silica cores (~700 nm) with characteristic layer-like phyllosilicate shell (15-80 nm) were successfully synthesized for all samples, and it is interesting to note that different shell structures were manifested for NiCuphy@SiO₂ with various Ni/Cu ratios. For monometallic 10Niphy@SiO₂, nanoscale lamella structure is uniformly distributed on the outer layer of the silica nanosphere (Figure 1a), which can be ascribed to the typical structure of Niphy (Ni phyllosilicate) phase^[26]. By comparison, a regularly long and fluffy encapsulation structure, which is attributed to the Cuphy (Cu phyllosilicate) phase^[17], is formed on the core surface of the monometallic 10Cuphy@SiO2. While for the bimetallic NiCuphy@SiO₂, it is seen that along with the introduction of Cu, the lamella phyllosilicate shell is gradually altered to fluffy structure with the persistence of their core-shell framework.

In order to highlight the importance of phyllosilicate-derived core-shell structure, we also characterized a reference Ni/SiO₂-im catalyst, which was prepared by using impregnation method (Figure 1f). Different from 10Niphy@SiO₂ which displays highly dispersed phyllosilicate shell inlaid on the outside of the SiO₂ nanosphere^[27], the Ni/SiO₂-im sample shows big metal aggregates poorly attaching on the silica surface without coreshell structure. The existence of phyllosilicate structured shell of NiCuphy@SiO₂ can be also confirmed by FT-IR results in Figure S2 in the Supporting Information.

The crystalline structures of calcined bimetallic NiCuphy $@SiO_2$ samples were determined using X-ray diffraction

FULL PAPER



Figure 1. TEM images of the calcined NiCuphy@SiO₂ materials. a) 10Niphy@SiO₂, b) 9NiCuphy@SiO₂, c) 7Ni3Cuphy@SiO₂, d) 5Ni5Cuphy@SiO₂, e) 10Cuphy@SiO₂ and f) Ni/SiO₂-im.

(XRD) in Figure 2a. A broad diffraction peak centered at 20=22.5° is visible for all the patterns which is ascribed to the SiO₂ (JCPDS 39-1425) cores. For various xNiyCuphy@SiO₂ samples, small peaks concentrated at 30.8° and 35.0° emerged in 10Cuphy@SiO₂ and 5Ni5Cuphy@SiO₂, which can be attributed to the amorphous copper phyllosilicate (Cu₂Si₂O₅(OH)₂, JCPDS 27-0188). While, differently, two weak diffraction peaks that appeared at 34.1° and 60.5° attributing to the poorly-crystallized nickel phyllosilicate (Ni $_3$ Si $_2O_5$ (OH) $_4$, JCPDS 49-1859) were formed for the Ni-containing samples. By the way, for all the Nicontaining NiCuphy@SiO2 samples, a series of minor diffraction peaks centered at 20=37.3°, 43.3°, and 62.9° corresponding to NiO (JCPDS 47-1049) were detected, indicating the co-existence of amorphous NiO in the nickel phyllosilicate framework. This may result from the lack of hydroxyl groups and the interlamellar spacing after calcination, which is consistent with the previous reports^[14].

The related surface area (SA) and pore volume (Vp) of different NiCuphy@SiO₂ materials were characterized by N₂ adsorption in Figure S3 and the results are shown in Table 1. NiCuphy@SiO₂ samples have much higher surface area and pore volume (SA>100 m² g⁻¹ and Vp>0.16 cm³ g⁻¹) than the impregnated Ni/SiO₂-im (SA=8 m² g⁻¹and Vp=0.02 cm³ g⁻¹). Together with the distinct isotherms plot of Ni/SiO₂-im which shows no hysteresis loop in Figure S3, these phenomena confirmed that the mesoporous phyllosilicate shell structure of NiCuphy@SiO₂ samples^[14]. We believe these shell pores can help the bimetallic Ni-Cu catalysts provide more accessible active sites for liquid-phase hydrogenation.

BYD hydrogenation performance of the reduced NiCu@SiO₂ bimetallic catalysts

Figure 3 and Table S1 show the catalytic performance of different catalysts reduced at 500 °C for hydrogenation of 10 wt.% BYD at 50 °C for 3 h in a batch reactor. Referential Ni/SiO₂-im catalyst presented both low BYD activity (<46.5%, not shown) and BDO yield (<8.0%) due to its bad hydrogenation ability. In contrast, 10Ni@SiO₂ catalyst exhibited a complete BYD conversion while maintaining 75.6% BDO selectivity. This shows the overwhelming advantage of phyllosilicate derived core shell structure in BYD direct hydrogenation. However, although great enhancement can be achieved on the activity, an unpleasant result showing in Figure 3 is that the monometallic Ni catalysts, e.g., 10Ni@SiO₂ catalyst cannot effectively prevent the γ -HALD-pathway products like harmful semi-acetal byproduct such as HTHF (HTHF selectivity was maintained at ca. 20% for both Ni-SiO₂ catalysts as shown in Table S1).



Figure 2. XRD patterns of the a) calcined NiCuphy@SiO₂ and b) reduced NiCu@SiO₂ catalysts.

FULL PAPER

Table 1. Physico-chemical properties of the phyllosilicate-derived NiCuphy@SiO₂ samples.

Catalyst	Metal content ^[a]		BET results ^[b]			Metal	Metal particle
	Ni / wt%	Cu / wt%	SA/m ² g ⁻¹	Vp/cm ³ g ⁻¹	Dp/nm	crystallite size ^[c] /nm	size ^[d] /nm
10Cuphy@SiO ₂	-	17.5	114	0.18	4.9	4.3	5.2
5Ni5Cuphy@SiO2	8.8	7.4	111	0.19	6.4	4.4	5.6
7Ni3Cuphy@SiO ₂	13.8	3.9	113	0.27	6.7	7.7	6.5
9Ni1Cuphy@SiO ₂	16.5	1.3	115	0.30	9.5	9.5	8.8
10Niphy@SiO ₂	18.0	-	103	0.29	9.2	10.1	10.1
Ni/SiO ₂ -im	18.2	-	8	0.02	10.3	18.2	40.0

^[a] The metal content was calculcated by ICP-AES.

^[b] The BET results were calculated by N₂ adsorption.

^[c] The metal crystallite size was calculated based on the reduced XRD diffractions via Scherrer equation.

^[d] The average metal particle size was determined in TEM images of the reduced catalysts.



Figure 3. Catalyst activity tests for BYD direct hydrogenation over NiCu@SiO₂ catalysts (reaction conditions: catalyst 0.2 g, BYD 10 wt.% in 40 mL methanol, reaction temperature 50 °C, reaction pressure 1 MPa, reaction time 3h

Interestingly, the addition of Cu into Ni@SiO₂ catalyst can greatly inhibit the formation of such byproducts, but the direct hydrogenation ability of NiCu@SiO₂ is gradually decrease with the increase of Cu content, and the BYD conversion over monometallic 10Cu@SiO₂ is only 12.3%, indicating that individual Cu site might not be suitable for BYD hydrogenation and Ni site is the main active center over Ni-Cu catalysts. However, this does not mean that Ni-Cu catalysts, 9Ni1Cu@SiO₂ exhibit the highest BDO selectivity up to 90.5% with a low byproduct yield of 8.1%. While for other reported noble and Raney Ni catalysts, lower or similar BDO selectivity (<86%) was always obtained under higher reaction temperature/pressure conditions with higher semi-acetal byproduct percentage (>13%)^[1, 28-30].

Insight of the bimetallic synergy effects of the phyllosilicatederived NiCu $@SiO_2$ catalysts In order to insight the promotion roles induced by the bimetallic synergy effects over phyllosilicate-derived NiCu@SiO₂ catalysts for BYD direct hydrogenation to BDO, comprehensive characterizations were thoroughly employed focusing on the cooperation of different active centers.

H₂-TPR profiles in Figure 4 provide the information about the Ni-Cu bimetallic interaction as well as the metal support interaction. Due to the distinct phyllosilicate structures of Niphy and Cuphy, the reduction behaviors of monometallic 10Niphy@SiO₂ and 10Cuphy@SiO₂ are significantly different. 10Cuphy@SiO₂ only displayed a sharp peak centered at 290 °C attributing to the reduction of Cuphy species ^[31]. Whereas 10Niphy@SiO₂ displayed a sluggish reduction peak of Niphy at a rather high and broad reduction temperature range centered at 745 °C ^[26]. Another comparison between 10Niphy@SiO₂ and Ni/SiO2-im also indicated that the Niphy species are relatively hard to reduce and even some Ni species cannot be reduced

FULL PAPER

during reduction treatment, thus remaining to the tough framework. This phenomenon is acceptable since the Ni species is existed in the form of strong chemical bond Si-O-Ni in phyllosilicate structure^[25, 27].

For the bimetallic NiCuphy@SiO₂ catalysts, an obvious three stages reduction behavior was observed. Identical to the monometallic catalysts, the first reduction stage at approx. 260 $^{\circ}$ C



Figure 4. H_2 -TPR plots of the NiCuphy@SiO₂ catalysts.

is attributed to the reduction of copper species to metallic Cu, and another wide and high temperature reduction stage in the range of 550-800 °C can be designated to the reduction of Niphy from the bimetallic Ni-Cu, indicating the stronger metal-support interactions in the phyllosilicate-derived NiCuphy@SiO₂, which can lead to higher metal dispersion and solvothermal-stability of the core shell catalysts^[26]. Besides, the reduction peak areas of the above two stages showed regular variation trends with the alteration of Ni/Cu content in the bimetallic NiCuphy@SiO₂.

Interestingly, there was a new emerged reduction peak at 330-450 °C of all bimetallic catalysts which can be hardly ascribed to the above two metal species. We believe this new formed metal species is responsible for the highly active Ni species that differentiated from the Niphy matrix by the induction of promoting Cu species. In general, Cu2+ is more easily reducible than Ni2+ under similar conditions since it has much lower standard reduction potential^[32], and over the Ni-Cu catalyst surface, the presence of Cu species can produce a large amount of spillover hydrogen which is able to migrate to the adjacent Ni²⁺ sites and consequently accelerates the reduction/nucleation of the nearby Ni site and improves the reducibility of Ni2+ species at considerably lower temperatures^[22]. As a result, the Ni species bonding to the nearby Cu site has a strong bimetallic synergy effect, and is easy to be reduced at a rather low temperature of 330-450 °C for NiCuphy@SiO2. Furthermore, since Cu site acts as the spillover hydrogen donator between Ni-Cu, the increase of Cu/Ni ratios in bimetallic NiCuphy@SiO₂ samples can effectively elevate the H₂ spillover intensity, and thus decreasing the differentiated nickel reduction temperature. Importantly, as the increase of Cu/Ni ratios will by no means lead to the decline of total active Ni sites number, and considering the dual factors of spillover hydrogen donator (Cu site) and receptor (Ni site) amongst the bimetallic catalysts, 9Ni1Cu@SiO₂ showed the largest amount of Cu-induced NiO species differentiated from the Niphy matrix as shown in Figure 4, which may be responsible for the superior hydrogenation activity of NiCu@SiO₂ catalysts.

Figure 2b shows the XRD patterns of phyllosilicate-derived NiCu@SiO₂ core-shell catalysts reduced at 500 °C. In contrast to the XRD patterns of fresh NiCuphy@SiO2, the presence of metallic Ni (44.5°, 51.8° and 76.3°) and/or Cu (43.2°, 50.4° and 74.1°) phases can be expected from the reduced catalysts. Furthermore, only one single diffraction peak in the intermittent position between those assigned to the characteristic diffraction of metallic Cu (43.2°) and Ni (44.5°) could be distinguished as shown in the narrow scanning plots for the bimetallic NiCu@SiO₂, and the peak summit is shifting to lower degree with the increase of Cu content. This shift is interpreted by the generation of defective sites in the metallic Ni phase via the addition of Cu species, thus resulting in the formation of a homogeneous Ni-Cu intermetallic mixture/alloy in the phyllosilicate-derived catalyst system, similar conclusion was also reported for other bimetallic catalysts ^[22, 33-35]. Predictably, as labeled in Figure 2b, some illcrystallized nickel phyllosilicate phase was still present for all the Ni containing NiCu@SiO₂. This phenomenon is in accordance with the H₂-TPR results that a reduction temperature of 500 °C cannot reduce all the Niphy phase. Consistent with this deduction, the FT-IR and HR-TEM results of the reduced NiCu@SiO2 catalysts (Figure S2 and Figure S4) also show the partially survival of phyllosilicate structure.

As stated above, we inferred that the portion of Ni species interacting with the neighboring Cu species in the NiCu@SiO₂ catalysts, namely the metal species corresponding to the second stage (330-450 °C) of H₂-TPR profiles was more likely to be reduced to form the bimetallic Ni-Cu alloy sites, which could also



Figure 5. TEM images of the reduced NiCu@SiO₂ catalysts. a) $10Ni@SiO_2$, b) $9Ni1Cu@SiO_2$, c) $7Ni3Cu@SiO_2$, d) $5Ni5Cu@SiO_2$, e) $10Cu@SiO_2$, and f) Ni/SiO_2 -im.

FULL PAPER



Figure 6. a) Ni 2P_{3/2} and b) Cu 2p_{3/2} XPS spectra of the reduced NiCu@SiO₂ catalysts; c) H₂-TPD and d) NH₃-TPD profiles of the reduced NiCu@SiO₂ catalysts.

be reflected by the derivative lattice fringes of reduced Ni-Cu alloy (0.206 nm) the in the HR-TEM image of $9Ni1Cu@SiO_2$ catalyst (Figure S4) from the standard Ni lattice distance of 0.204 nm^[36-37].

The metal crystallite sizes of reduced NiCu@SiO₂ catalysts calculated via Scherrer equation are also listed in Table 1. Different from the referential Ni/SiO₂-im catalyst which shows a large Ni crystallite size of 18 nm, all the NiCu@SiO₂ catalysts have highly nano-crystallized metal sizes smaller than 10 nm. It is reasonable since all the reduced Ni-Cu particles are derived from the Ni/Cuphy nanocomposite, they can be fine embedded in the phyllosilicate shell framework or the core-shell interface with a strong structural confinement effect, thus keeping well nano-crystallization.

TEM morphologies of the reduced NiCu@SiO₂ catalysts can further support our argument. The reduced NiCu@SiO₂ samples still kept core-shell structures similar to their pristine in Figure 1, but with large amounts of homogeneously dispersed metal nanoparticles decorating either on the core-shell interface or inside the shell (Figure 5 inset). The average metal particle size counted from their TEM images (Table 1) showed the similar evolution trend as reflected by XRD results. The survival of lamella shell structure of NiCu@SiO₂ catalysts reaffirms the persistence of Niphy matrix after reduction, and this structure is of vital importance for the high dispersion and well confinement of the generated metal nanoparticles ^[26]. Without the confined phyllosilicate matrix structure, the reduced Ni/SiO₂-im catalyst showed much bigger metal particle sizes.

XPS was used to study the surface chemistry properties and synergy effect of Ni-Cu in the reduced catalysts. Figure 6a shows the Ni $2P_{3/2}$ core level spectra of the reduced Ni-containing catalysts. For the Ni/SiO₂-im catalyst, the binding energy (BE) of Ni⁰ is shown at 852.3 eV and that of Ni²⁺ is at 855.3 eV, which are close to the standard BE values of common Ni species^[32]. While for the xNiyCu@SiO₂ catalysts, due to the stronger metal support interaction of phyllosilicate phase ^[22, 38], the chemical shift for Ni⁰ and Ni²⁺ species are moved to higher BE values of 852.6 and 856.4 eV, this promotion effect of electropositive metal sites may be benefit for the stabilization of adsorbed configuration of BED which will be discussed later.

The Cu 2p_{3/2} spectra of the reduced catalysts are also illustrated in Figure 6b. In general, the BE values at 932.2-933.0 eV can be assigned to Cu⁰ species while the higher values of 934.2-935.0 eV can be ascribed to the Cuphy derived species^[38]. An obvious phenomenon is that the surface metallic Cu⁰ concentration (>50.0%) is much larger than the corresponding Ni⁰ concentration (Table S2), which indicated again that the Cuphy is more reducible than Niphy. In addition, another apparent change is that the copper BEs gradually shifts to higher values with the decrease of Ni/Cu ratio in Ni-Cu catalysts. The increase in BEs of copper species could be related to the alteration in unfilled-band electron holes arising from the charge transfer from Cu to the

FULL PAPER

adjacent Ni due to the strong electron donating ability of Cu, which contributed to the stronger electronic interaction between the bimetallic Ni-Cu sites, thus facilitating the H₂ spillover/activation during hydrogenation process^[15]. While more importantly, as Cu⁰ site could also act as a strong C=C bond adsorption site^[39-40], we assumed that these electropositive Cu⁰ species adjacent to the active Ni sites could thus stabilize the allyl alcohol adsorption configuration over the Ni-Cu alloy centers.

The activation of hydrogen is essential for hydrogenation reactions ^[15], and H₂-TPD is employed to elucidate the hydrogen activation ability over different Ni-Cu bimetallic catalysts. It can be seen from Figure 6c that 10Ni@SiO₂ has larger H₂ adsorption amount and lower H₂ desorption temperature than the Ni/SiO₂-im, illustrating H₂ activation and dissociation occurred more easily over phyllosilicate derived catalysts, therefore, contributing to its supreme H₂ adsorption capacity and activation ability.

Similarly, intensified H₂ desorption was also seen for all the bimetallic NiCu@SiO₂ catalysts, and the related activating H₂ amounts are depicted in Table S3. With the introduction of Cu into the NiCu@SiO₂ catalysts, the H₂ desorption temperature showed a linear increase while the desorbed H₂ amount possessed a volcano variation, which is consistent with the result reported by Chen et al. ^[41] Amongst them, 9Ni1Cu@SiO₂ had the optimal chemical adsorption hydrogen amount (0.12 mmol/g) with a beneficial lower activation temperature, which may be responsible for its superb H₂ active sites amount/activation ability, thus promoting the hydrogenation capacity.

Table 2 NH $_3$ desorption profiles for NiCu@SiO $_2$ catalysts measured by NH $_3$ -TPD.

	Desorption pea	Total acid	
Catalysts	mmol _{NH3} g ^{−1})	amount	
	α	β	(mmol _{NH3} g ⁻¹)
10Ni@SiO2	93, 0.57	265, 0.25	0.82
9Ni1Cu@SiO2	91, 0.63	231, 0.11	0.75
7Ni3Cu@SiO2	97, 0.49	278, 0.05	0.54
5Ni5Cu@SiO2	98, 0.55	248, 0.12	0.67
10Cu@SiO ₂	82, 0.54	-	0.54

As BYD and BED both had polar hydroxyl groups, we could also use this property to seek for a higher product selectively. For our reduced NiCu@SiO₂ catalysts, due to the rich surface phyllosilicate hydroxyl (M-OH, M=Ni, Cu or Si) group nature of the survived phyllosilicate matrix ^[16, 42], larger surface acidity of reduced NiCu@SiO₂ catalysts was detected by NH₃-TPD and Py-IR comparing with the referential Ni/SiO₂-im catalyst (Figure S5 and Figure S6). It can be seen from Figure 6d that acidity of the catalysts remarkably increases with Ni content increasing thanks to the M-OH structure variation between Niphy and Cuphy. In addition, 10Ni@SiO₂ and xNivCu@SiO₂ catalysts have two obvious peaks at ca. 100 and 250 °C, corresponding to the desorption of NH₃ from the weak (α) and medium (β) acid sites, respectively. In contrast, the NH₃-TPD profile of 10Cu@SiO₂ has only one peak at approx. 82 °C, which indicates the desorption of NH_3 from the weak acid sites $^{[43]}$. The amounts of acid sites are compiled in Table 2, it can be seen that 9Ni1Cuphy@SiO₂ has the highest acid amount amongst the bimetallic catalysts, which reaches 0.75 mmol/g, and the total acid amounts of bimetallic catalysts are also decreased with the decrease of Ni/Cu ratio. For the Ni-Cu bimetallic catalyst, the weak acid desorption peak shifted slightly toward a higher temperature with the increase of Ni content, indicating that the synergy of Ni-Cu can cause an increase in the acid strength with the increase of Ni/Cu ratio. In our hydrogenation system, these functional acid sites (e.g. surface electron-defect Lewis acid sites which can be proved by Py-IR as reflected in Figure S6) from the surrounding of active Ni-Cu nanoparticles may act as association sites to attract the electron-rich C-OH group at the terminal of adsorbed BED intermediate^[27, 44-45], thus stabilizing the allyl alcohol existing form over the active Ni-Cu sites and further promoting the selectivity to BDO.

However, we should note here that another important synergistic effect of the coordination of Ni-Cu is that it can decrease the medium acid sites greatly as shown in Figure 6d. As frequently reported, the medium acid site is particularly efficient for assistant the C=O hydrogenolysis reactions^[27, 46], such as the negative formation of HTHF etc. in our catalytic system. With the existence of this medium acid site, the strong affinity of C=O groups will no doubt induce the isomerization of BED intermediate to γ -HALD. Combining with our long-term hydrogenation tests which will be detailed later, we deduced that the suppression of this type of acid site is vital for avoiding the negative conversion of HTHF, thus giving rise to a high BDO selectivity.

Kinetic curves of BYD hydrogenation over the Ni-Cu@SiO $_2$ coreshell catalysts

In order to get the intrinsic bimetallic synergy effect of the



Figure 7. Product evolution kinetic curves of BYD hydrogenation over NiCu@SiO₂ catalysts versus reaction time. a) Ni/SiO₂-im, b) 10Ni@SiO₂, c) 9Ni1Cu@SiO₂, d) 7Ni3Cu@SiO₂, e) 5Ni5Cu@SiO₂ and f) is the recycling test of 9Ni1Cu@SiO₂ catalyst in sequences of 3h reaction. (Reaction conditions: catalyst 0.2 g, BYD 10 wt.% in 40 mL methanol, reaction temperature 50 °C, reaction pressure 1 MPa).

FULL PAPER



 $\label{eq:scheme 2} \textbf{Scheme 2.} Proposed BYD hydrogenation mechanism over phyllosilicate derived NiCu@SiO_2 catalysts.$

NiCu@SiO₂ catalysts for BYD hydrogenation, a series of product generation/evolution kinetic curves of BYD hydrogenation over these catalysts were further explored versus a long-term reaction time (Figure 7). Comparative data show that BYD can be almost completely converted in 3h over NiCu@SiO₂ catalysts, which indicates again that the phyllosilicate structure and bimetal interaction are helpful for the hydrogenation.

In addition, for all the NiCu@SiO₂ catalysts, the BED yield was increased firstly and then reached a maximum at reaction time of 1~2 h, extending the reaction time resulted in the further hydrogenation of BED to BDO, and finally obtained a stable BDO yield higher than 90% after reaction time of 4h. Amongst them, 9Ni1Cu@SiO₂ showed the highest hydrogenation activity and the highest BDO yield (> 94.4%). As the reaction duration prolonged, the yields of by-products were first slightly increasing and then decreasing since some of the byproducts may also be reversibly hydrogenated to BDO ^[8, 47]. In order to prove this deduction, we also made an investigation on the product distribution by changing the H₂ pressures for 3h batch reaction. Data listed in Table S5 proved that HTHF can be suppressed or re-hydrogenated to BDO under a more intense hydrogenation condition.

It is worth noting that the BDO yields on catalysts of 7Ni3Cu@SiO₂ and 5Ni5Cu@SiO₂ are growing continually in the initial 4h but less than that of 10Ni@SiO₂ due to their lower active Ni sites. However, when the hydrogenation process reached the steady state on these catalysts, the obtained BDO yields on catalysts of 7Ni3Cu@SiO₂ and 5Ni5Cu@SiO₂ are much higher than that of 10Ni@SiO₂ with lower HTHF yields (<8.7%).

Proposed reaction mechanism of BYD hydrogenation over NiCu@SiO₂ catalysts

Based on the hydrogenation behaviors of the different Ni-Cu catalysts as well as their various synergy effects illustrated above, we may summarize a proposed BYD hydrogenation mechanism over our phyllosilicate derived NiCu@SiO₂ catalysts. As listed in the Scheme 2 and Figure S7, BYD was first adsorbed on the metal sites with the C≡C bond and semi-hydrogenated to cis-BED (namely, 2-butene-1,4-diol) intermediate, however, the electronegative electron clouds have fluidity over the whole activated carbon chains of cis-BED, thus the adsorbed cis-BED

can transform to enol formed 1-butene-1,4-diol and then the isomerization product $\gamma\text{-HALD}^{[21]}.$

We assume the key point in the facilitating of the direct hydrogenation to BDO is how to stabilize the cis-BED hydrogenation configuration before the second semihydrogenation process. While for phyllosilicate derived NiCu@SiO₂ catalysts, we deem that a "three-center-synergy" effect was exist for the persistence of cis-BED adsorption configuration and direct hydrogenation to BDO. Firstly, due to the strong H₂ adsorption/activation ability of Ni site, it is the prerequisite for the high hydrogenation activity. Secondly, the addition of Cu metal could induce the formation of newly easyreducible Ni-Cu alloy active sites, which, on one hand, manifest an obvious electropositive property benefiting for the fixation of electron clouds above the C-C bonds; and on the other hand, can effectively elevate the H₂ spillover intensity to promise the fast H₂ delivery over the adsorption interface. Finally, the nearby functional acid sites from the surrounding of active Ni-Cu nanoparticles may act as association sites to distract the electron clouds density at the terminal C-OH group of adsorbed BED intermediate. With the synergy of these three cooperative sites, the NiCu@SiO₂ catalysts could stabilize the activated C=C-C-OH bond (cis-BED species) adsorbing on the neighboring bimetallic sites to avoid their isomerization to C-C-C=O bond (y-HALD species). Consequently, it can undoubtedly enhance the selectivity to the diol product BDO.

Combined with their different Ni-Cu contents, we assume that a large amount of active Ni sites content can prompt the fast hydrogenation of BYD/BED, but appropriate amount of bimetallic Cu sites are beneficial for the inhibition of BED isomerization process and thus lifting the equilibrium/final BDO yield in our hydrogenation system. i.e. the bimetallic NiCu@SiO₂ hydrogenation catalyst could enable the effective direct C=C/C=C bonds hydrogenation with little influence of the C-O bonds. Due to the best match of fast hydrogenation and isomerization inhibition effects originating from the "three-center-synergy" effect (active metal dispersion, intensified H₂ delivery/activation, strong electronic interaction, property acidity sites etc.), 9Ni1Cu@SiO₂ shows the optimum BYD direct hydrogenation performance.

Recyclability of 9Ni1Cu@SiO2 catalyst

FULL PAPER

The structural stability of phyllosilicate derived core-shell catalyst was verified by repeating the hydrogenation cycles of 9Ni1Cu@SiO₂ catalyst, and a referential commercial Raney Ni catalyst was also tested for the recyclability under the same reaction condition. As shown in Figure 7f and Figure S8, after being reused for four times under the batch reaction for 3h, neither obvious deactivation nor selectivity decline was observed over 9Ni1Cu@SiO₂ catalyst. In contrast, the Raney Ni catalyst showed a rather low BYD hydrogenation conversion (< 54.1 %) under the same reaction conditions, and serious catalytic deactivation was observed for the commercial Raney Ni catalyst. What's more, further XRD and ICP characterization results of the fresh and 4time-usage 9Ni1Cu@SiO₂ catalyst (Figure S9 and Table S6) also confirmed the structural stability of the phyllosilicate derived 9Ni1Cu@SiO₂ catalyst, which is prerequisite for the highintensive industrial application.

Conclusions

Phyllosilicate-derived NiCu@SiO₂ bimetallic catalysts with different Ni/Cu ratios were successfully prepared using a simple hydrothermal method and their catalytic performances were investigated for liquid phase BYD direct hydrogenation to BDO. The rigid phyllosilicate shell structure can remarkably improve the active metal dispersion and the shell porosity, thus can well confine the nano Ni particles on the core-shell interface or inside the phyllosilicate matrix after reduction and reaction, resulting in an enhanced hydrogenation activity and structure stability which are beneficial for the sustainable liquid hydrogenation process.

The introduction of second metal Cu can form a strong bimetallic synergy effect for NiCu@SiO₂ catalysts, which induces a new highly dispersed/active Ni-Cu alloy species that differentiated from the Niphy matrix responsible for the high BYD activation and BDO selectivity. Meanwhile, With a proposed "three-center-synergy" effect, the NiCu@SiO₂ catalysts could stabilize the activated C=C-C-OH bond (cis-BED species) adsorbing on the neighboring bimetallic sites to avoid their isomerization to C-C-C=O bond (γ -HALD species). Consequently, it can undoubtedly enhance the selectivity to the diol product BDO. Due to the best match of fast hydrogenation and isomerization inhibition effects originating from the bimetallic synergy, phyllosilicate-derived core-shell 9Ni1Cu@SiO₂ displays the optimum BYD direct hydrogenation performance to obtain a high BDO yield larger than 90.5% in 3h batch reaction.

Experimental Section

Catalyst preparation

Preparation of SiO₂ nanospheres. Silica nanospheres were prepared using a classical Stöber method as reported by Guan et al.^[48]. In brief, the solvent was prepared by mixing 47 mL water, 127 mL isopropanol and 26 mL ammonia. Afterwards, 1.2 mL tetraethyl orthosilicate (TEOS) was first added dropwise into this mixture for 1h to obtain SiO₂ seeds. Then, another 10 mL TEOS was added and the final mixture was stirred at 35 °C

for 2 h. The obtained slurry was centrifuged, washed, and dried overnight in an oven at 80 $^{\circ}C$ to obtain SiO_2 nanospheres.

Preparation of NiCu@SiO2 catalyst. 1.0 g SiO2 nanospheres were dispersed in 40mL ethanol solvent; meanwhile, a certain amount of Ni(NO₃)₂ and Cu(NO₃)₂ water solution were adjusted to a pH of 11-12 by ammonia. The above two solutions were uniformly mixed and transferred to an autoclave for hydrothermal treatment at 140 °C overnight. During this hydrothermal procedure, the outer surface of SiO₂ core can be ionized and dissolved by hydroxide anions, and then gave the chance to form phyllosilicate shell by metal species inserting or depositing on the ionized silica surface. Thereafter, the resulting slurry was recovered by centrifugation and drying, followed by calcination at 450 °C for 4 h to remove the residuals. The obtained core-shell type samples were designed to possess 18 wt% active metal content with the Ni/Cu molar ratios of x:y (10:0, 9:1, 7:3, 5:5 and 0:10, respectively) and the resulted core-shell phyllosilicate samples were denoted as xNiyCuphy@SiO2. In order to be used for the hydrogenation reaction, these samples were reduced at 500°C for 3 h under 25% H₂/N₂ gas flow, and the reduced catalysts were thus denoted as phyllosilicate derived xNiyCu@SiO2.

Preparation of Ni/SiO₂-im catalyst. For comparison, a referential Ni/SiO₂ was prepared by incipient impregnation of Ni(NO₃)₂ aqueous solution over SiO₂ nanospheres without hydrothermal treatment, the rest post-handling method is the same to Ni@SiO₂, and the resultant sample was denoted as Ni/SiO₂-im.

Characterization of catalysts

The chemical compositions of NiCu@SiO2 catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, AtomScan 16, Thermo Scientific). The samples were acid digested with HNO3 and HCl at 120 °C for 3 hs before analysis. The pyllosilicate and core-shell structure of resulted catalysts as well as their metal particle size distributions after reduction were observed by a JEM 2010 high-resolution transmission electron microscope (TEM) operating at 200.0 kV. The surface area and pore size distributions of the NiCuphy@SiO2 were measured by the N₂ adsorption using a Micromeritics ASAP 2020 instrument. X-ray diffraction (XRD) experiments of the calcined and reduced catalysts were carried out on a Bruker D8 Advance X-ray diffractometer with monochromatized Cu K α radiation (λ = 1.542 Å) at a setting of 40 kV and 40 mA, a scan range of 10° to 80°, and a scan rate of 4°/min. The FT-IR spectra were operated on a German Bruck Tensor 27 instrument in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. Hydrogen temperature programmed reduction (H₂-TPR) experiments were carried out using Xianquan chemical adsorption instrument. 80 mg test sample was heated to 750 °C in a 5% H_2/N_2 mixture (30 ml/min) with a ramp rate of 10 °C/min. The H₂ consumption was monitored by a thermal conductivity detector (TCD). H₂-temperature programmed desorption (H₂-TPD) experiments were performed by using Builder PCA-1200 chemisorption instrument with a TCD. 100 mg of catalyst was reduced at 500 °C for 1 h and then purged with pure Ar at 500 °C for 1 h. Next, adsorption was carried out with pure H_2 at 50 $^\circ C$ for 1 h, and then heated to 600 °C with a ramping rate of 10 °C/min. The H_2 desorption was also monitored by a TCD. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250 Xi photoelectron spectrometer with a monochromatic AI Ka X-ray source. All binding energies were adjusted to the line position of C1s. For the analysis of the reduced samples, the catalysts were pre-reduced at 500 °C for 3 h and cooled down to room temperature, then they were sealed into ethanol under flowing N2 and stored in a reagent bottle before test. Temperature

FULL PAPER

programmed desorption of NH₃ (NH₃-TPD) experiments were conducted on the AutoChem II 2920 instrument equipped with a TCD. The catalysts (100 mg) were in situ reduced in H₂ at 500 °C for 1 h and then purged with pure Ar at 500 °C for 1 h. After that, they were exposed to NH3 for 1 h at 50 °C to reach saturated adsorption. Subsequently, the catalysts were heated to 700 °C with a ramp rate of 10 °C /min and the desorption signal was collected by TCD.

Catalytic performance

The catalyst activity tests for BYD hydrogenation were performed in a 100 mL stainless steel autoclave inbuilt with a pressure gauge setup. In a typical experiment, 10 wt% BYD, 0.2 g catalyst and 40 mL methanol containing 1, 2-propylene glycol as the internal standard were charged into a high-pressure reactor. After sealed, the reaction system was first flushed with N_2 and H_2 for 5 times, and then pressurized with pure H_2 to the desired pressure. The reaction temperature and pressure were set at 50 °C and 1 MPa with a stirring rate of 800 r/min for 3 h. After reaction, the reaction mixture was separated by filtration to analyze the product contents by an Agilent 7890A GC with a HP-INNOWAX column. The BYD conversion and products selectivity/yields were calculated in the following methods, and their carbon balance were maintained above 95%.

$$BYD conversion = \frac{moles of BYD (initial) - moles of BYD (initial)}{moles of BYD (initial)} \times 100\%$$

$$Products selectivity = \frac{moles of BYD (initial)}{moles of BYD (initial)} \times 100\%$$

$$Products value of the transformation of the transformatio$$

Products yield = BYD conversion x products selectivity x 100%

The product generation kinetics of BYD hydrogenation versus longterm reaction was investigated under the similar reaction condition, while keeping the H₂ pressure constant at 1 MPa. For the recycling experiment, the same catalyst was repeatedly used for 4 times under the reaction condition of 50 °C and 1 MPa for 3 h.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (21603127, 21673132, U1710221), the Natural Science Foundation of Shanxi Province (201601D202020). Also thanks are due to Shanxi University Future Development Foundation for the supporting Dr Tiancun Xiao.

Keywords: bimetallic synergy • NiCu phyllosilicate • threecenter-synergy • 1,4-butynediol hydrogenation• antiisomerization

- [1] S. K. Tanielyan, S. R. More, R. L. Augustine, S. R. Schmidt, Org. Process Res. Dev., 2017, 21, 327-335.
- I.-T. Trotuş, T. Zimmermann, F. Schüth, Chem. Rev., 2014, 114, [2] 1761-1782
- M. M. Telkar, C. V. Rode, V. H. Rane, R. Jaganathan, R. V. Chaudhari, Appl. Catal. A., 2001, 216, 13-22. [3]
- C. Li, M. Zhang, X. Di, D. Yin, W. Li, C. Liang, Chin. J. Catal., 2016, [4] 37, 1555-1561
- [5] D. Francova, N. Tanchoux, C. Gerardin, P. Trens, F. Prinetto, G. Ghiotti, D. Tichit, B. Coq, Micropor. Mesopor. Mater., 2007, 99, 118-125
- [6] M. Telkar, C. Rode, V. Rane, R. Chaudhari, Catal. Commun., 2005, 6, 725-730.
- Zhao, Y. Ikushima, M. Arai, Catal. Today, 2004, 93-95, 439-443. [7] F S. Tanielyan, S. Schmidt, N. Marin, G. Alvez, R. Augustine, Top. [8] Catal., 2010, 53, 1145-1149.

WILEY-VCH

- K. Hadjiivanov, M. Mihaylov, D. Klissurski, P. Stefanov, N. Abadjieva, [9]
- E. Vassileva, L. Mintchev, *J. Catal.*, **1999**, *185*, 314-323. H. Li, Y. Zhao, C. Gao, Y. Wang, Z. Sun, X. Liang, *Chem. Eng. J.* [10]
- 2012, 181-182, 501-507 [11] X. Chen, M. Zhang, K. Yang, C. T. Williams, C. Liang, Catal. Lett.,
- 2014, 144, 1118-1126. [12] J. M. Campelo, R. Guardeno, D. Luna, J. M. Marinas, J. Morales, J.
- L. Tirado, J. Mol. Catal., 1993, 85, 305-325. [13] D. Chen, Z. Guo, T. Sun, F. Du, Mate. Res. Bull., 2012, 47, 2344-2348.
 - Z. Li, S. Kawi, Catal. Sci. Technol., 2018, 8, 1915-1922.
- [14] [15] Y. Liu, J. Zhao, J. Feng, Y. He, Y. Du, D. Li, J. Catal., 2018, 359, 251-260
- [16] X. Wang, S. Zhu, S. Wang, J. Wang, W. Fan, Y. Lv, Appl. Catal. A, 2018, 568, 231-241.
- X. Z. Sun, F.-L. Du, Chemistryselect, 2016, 1, 6972-6978. [17] J. Wood, L. Bodenes, J. Bennett, K. Deplanche, L. E. Macaskie, Ind. [18]
- Eng. Chem. Res., 2010, 49, 980-988. J. A. Bennett, G. A. Attard, K. Deplanche, M. Casadesus, S. E. [19]
- Huxter, L. E. Macaskie, J. Wood, ACS Catal., 2012, 2, 504-511. [20] C. Berguerand, I. Yuranov, F. Cardenas-Lizana, T. Yuranova, L.
- Kiwi-Minsker, J. Phys. Chem. C, 2014, 118, 12250-12259. [21] M. G. Musolino, C. M. S. Cutrupi, A. Donato, D. Pietropaolo, R. Pietropaolo, *Appl. Catal. A*, **2003**, *243*, 333-346.
- [22] J. Ashok, Y. Kathiraser, M. L. Ang, S. Kawi, Catal. Sci. Technol., 2015, 5, 4398-4409.
- A. Egeberg, C. Dietrich, C. Kind, R. Popescu, D. Gerthsen, S. [23] Behrens, C. Feldmann, ChemCatChem, 2017, 9, 3534-3543.
- [24] F. Zhang, Z. Li, C. Ma, X. Han, X. Dong, Z. Dong, X.-M. Zhang, ChemCatChem, 2019
- [25] T. Sasaki, N. Ichikuni, T. Hara, S. Shimazu, Catal. Today, 2018, 307, 29-34.
- [26] M. Yang, P. Jin, Y. Fan, C. Huang, N. Zhang, W. Weng, M. Chen, H. Wan, Catal. Sci. Technol., 2015, 5, 5095-5099. X. Kong, Y. Zhu, H. Zheng, X. Li, Y. Zhu, Y.-W. Li, ACS Catal., 2015,
- [27] 5. 5914-5920.
- M. M. Telkar, C. V. Rode, R. Jaganathan, V. H. Rane, R. V. Chaudhari, J. Mol. Catal., 2002, 187, 81-93. [28]
- M. G. Musolino, C. M. S. Cutrupi, A. Donato, D. Pietropaolo, R. Pietropaolo, J. Mol. Catal., 2003, 195, 147-157. [29]
- C. V. Rode, P. R. Tayade, J. M. Nadgeri, R. Jaganathan, R. V. [30] Chaudhari, Org. Process Res. Dev., 2006, 10, 278-284
- [31] H. Yue, Y. Zhao, S. Zhao, B. Wang, X. Ma, J. Gong, Nat. commun., 2013, 4, 2339.
- [32] S. Pendem, I. Mondal, A. Shrotri, B. S. Rao, N. Lingaiah, J. Mondal, Sustain. Energ. Fuels, 2018, 2, 1516-1529
- X. Huang, C. Ji, C. Wang, F. Xiao, N. Zhao, N. Sun, W. Wei, Y. Sun, Catal. Today, 2017, 281, Part 2, 241-249. [33]
- [34] C. Wang, N. Sun, N. Zhao, W. Wei, Y. Zhao, Catal. Today, 2017, 281, 268-275
- [35] C. Wang, Y. Zhang, Y. Wang, Y. Zhao, Chinese J Che., 2017, 35, 113-120
- W. Gao, Y. F. Zhao, H. R. Chen, H. Chen, Y. W. Li, S. He, Y. K. Zhang, M. Wei, D. G. Evans, X. Duan, *Green Chem.*, **2015**, *17*, 1525-1534. [36]
- Y. Zhao, B. Zhao, J. Liu, G. Chen, R. Gao, S. Yao, M. Li, Q. Zhang, [37] L. Gu, J. Xie, X. Wen, L.-Z. Wu, C.-H. Tung, D. Ma, T. Zhang, Angew. Chemie, 2016, 55, 4215-4219.
- M. L. Ang, J. T. Miller, Y. Cui, L. Mo, S. Kawi, Catal. Sci. Technol., [38] 2016. 6. 3394-3409.
- [39] P. Maki-Arvela, J. Hajek, T. Salmi, D. Y. Murzin, Appl. Catal. A., 2005, 292. 1-49.
- C. I. Meyer, A. J. Marchi, A. Monzon, T. F. Garetto, Appl. Catal. A., [40] 2009, 367, 122-129.
- Y. Chen, C. Li, J. Zhou, S. Zhang, D. Rao, S. He, M. Wei, D. G. [41] Evans, X. Duan, ACS Catal., 2015, 5, 5756-5765.
- [42] J. Ashok, Z. Bian, Z. Wang, S. Kawi, Catal. Sci. Technol., 2018, 8, 1730-1742. [43]
 - X. Li, M. Xiang, D. Wu, Catal. Commun., 2019, 119, 170-175.
- M. G. Musolino, G. Apa, A. Donato, R. Pietropaolo, F. Frusteri, *Appl. Catal. A*, **2007**, 325, 112-120. [44] [45] K. N. T. Tseng, J. W. Kampf, N. K. Szymczak, J. ACS, 2016, 138,
- 10378-10381. X. Kong, Y. Zhu, H. Zheng, Y. Zhu, Z. Fang, ACS Sustain. Chem. [46]
- Eng., 2017, 5, 11280-11289 Z. Huang, K. J. Barnett, J. P. Chada, Z. J. Brentzel, Z. Xu, J. A. [47]
 - Dumesic, G. W. Huber, ACS Catal., **2017**, *7*, 8429-8440. B. Guan, X. Wang, Y. Xiao, Y. Liu, Q. Huo, *Nanoscale* **2013**, *5*, 2469-
- [48] 2475.

FULL PAPER

Entry for the Table of Contents

FULL PAPER



With the synergy of three cooperative sites, the NiCu@SiO₂ catalysts can stabilize the activated C=C-C-OH bond (cis-BED species) adsorbing on the neighboring bimetallic sites to avoid their isomerization to C-C-C=O bond.

Changzhen Wang^[a], Yani Tian^[a], Ruifang Wu^[a], Haitao Li^[a], Benzhen Yao^[b], Yongxiang Zhao^{*[a]} and Tiancun Xiao^{*[b]}

Page No. – Page No.

Bimetallic synergy effects of phyllosilicate-derived NiCu@SiO₂ catalysts for 1,4-butynediol direct hydrogenation to 1,4-butanediol