第二金属对 Co/SiO₂ 加氢催化剂结构和性能的影响

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摘要: 通过考察 Co/SiO₂ 催化剂中活性组分的结构变化及其催化乳酸酯液相氢化反应结果, 来研究第二金属添加物对催化剂结构及其催化性能的影响。结果表明, 随着金属添加物的加入双金属催化剂中金属 Co 的表面电子性质以及分散度不断变化, 而 Co 物种颗粒粒径不断减小, 因此 Co 物种和载体 SiO₂ 间相互作用不断增强, 从而降低 Co 还原度。乳酸酯氢化反应结果表明, 催化剂中活性组分的颗粒大小及其比表面积以及 Co 物种的还原度和分散度均影响其氢化反应的活性。

关键词: 钴; 金属添加物; 结构; 乳酸酯; 氢化

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Effect of Metal Additives on Structure and Properties of a Co/SiO₂ Hydrogenation Catalyst

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Abstract: The effects of metal additives (Zn, Fe, Cu, and Sn) on the properties and catalytic performance of a Co/SiO₂ catalyst (prepared by a co-precipitation method) in the liquid-phase hydrogenation of ethyl lactate were investigated. The electronic properties and surface distribution of Co in the catalyst were significantly changed by incorporation of the additives. The particle size of the cobalt species was reduced, which strengthened the interaction between the cobalt particles and the silica support and decreased the reducibility of the catalyst. As a consequence, both ethyl lactate conversion and 1,2-propanediol selectivity decreased upon incorporation of the additives. Ethyl lactate conversion was related less to the size and surface area of the catalyst particles than to the distribution of the cobalt species and the reducibility of the catalyst.

Key words: cobalt; metal additive; structure; ethyl lactate; hydrogenation

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Lactic acid, an important biomass-derived platform molecule, has been commercially produced by fermentation of renewable resources, such as sugars, starches, and xylose

[1]. Much effort has been directed toward transforming lactic acid into high-value chemicals [1–9]. In particular, the selective hydrogenolysis of lactic acid to 1,2-propanediol

(1,2-PDO), an important feedstock for the manufacture of polymers and pharmaceuticals, is a promising and environmentally benign alternative to the traditional petroleum-based process for the production of 1,2-PDO [2–7]. Previous reports on the hydrogenation of lactic acid have indicated that Ru- and Cu-based catalysts are significantly more active, however, severe reaction conditions (e.g., high temperature and pressure) are generally required with these catalysts [2,6]. Pd-based catalysts have also been evaluated for this important reaction, but they require a relatively high temperature (>300 °C) for reasonable activity [10].

In view of the severe reaction conditions required for the direct hydrogenolysis of lactic acid, as well as the lower reactivity of lactic acid relative to that of lactate, producing 1,2-PDO by hydrogenolysis of lactate is advisable. From the standpoint of molecular structure with a reactive hydroxyl group, high reaction temperature is undesirable for the hydrogenolysis of lactate because of the potential for side reactions such as polymerization, dehydration, and transesterification, which decrease the 1,2-PDO selectivity [2,6]. Therefore, it is of great importance to develop active catalysts with the research of the influence of the support, the preparation methods, the nature of the active phases, and the use of metal additives.

Bimetallic catalysts are of particular interest because they exhibit better selectivity, higher stability, fewer side reactions, and greater potential for reactivation than monometallic catalysts. Luo et al. [4,5,11] have extensively studied Ru-based catalysts with various metal additives prepared by a chemical reduction method for the hydrogenation of lactate. These investigators found that various RuM/B (M = metal) bimetallic catalysts exhibit different activities and selectivities owing to differences in electron transfer between B and metallic Ru and differences in H₂ adsorption behavior resulting from incorporation of the additives. Luo et al. proposed a catalytic mechanism based on the synergy between metallic Ru and oxidic additives during the hydrogenolysis.

Cobalt-based catalysts with various supports and metal additives are the most used catalysts for hydrogenation reactions in a variety of systems. Copper, zinc, tin, iron, and noble metals have already been studied as promoters for cobalt-based catalysts [12,13,17,28,35]. The addition of relatively small amounts of noble metals greatly enhances the performance of cobalt-based catalysts by increasing their reducibility [12,13]. Recently, vapor-phase hydrogenolysis of a lactate ester to 1,2-PDO over a Co/SiO₂ catalyst prepared by impregnation was systematically investigated [14], and a linear relationship between hydrogenolysis activity and the percentage of the bulk-like Co₃O₄ in the catalyst was observed. In our previous work, we found that the method used to prepare the Co/SiO₂ catalyst signifi-

cantly affects the liquid-phase hydrogenolysis of lactate to 1,2-PDO, owing to variations in the cobalt species formed [15]. The significant catalytic activities were in correlation with different cobalt species based on the inherent different chemical phenomena during contrary preparation procedures from the Co–OH–Co ololation and Si–O–Co oxolation molecular mechanisms.

In the present work, we investigated the effect of metal additives on Co-based catalysts for the hydrogenation of ethyl lactate. A series of CoM/SiO₂ bimetallic catalysts were prepared by a co-precipitation method. The catalyst structures were characterized by means of various chemical and physical techniques, including N₂ adsorption, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and transmission electron microscopy (TEM), and the resulting information was used to correlate the microstructures of the solid catalysts with their performance in the catalytic hydrogenolysis of ethyl lactate.

1 Experimental

1.1 Catalyst preparation

The monometallic Co/SiO₂ catalyst was prepared by a precipitation-gel method as follows. An aqueous solution of NaOH (4 mol/L) was added dropwise to a solution of Co(NO₃)₂ (0.55 mol/L) at a constant rate under vigorous stirring. A calculated amount of colloidal aqueous silica solution (SiO₂, 40.0 wt%, pH = 9.0–9.5, Guangzhou Renmin Chemical Plant, Guangzhou, China) was added dropwise to the resulting precipitate to form a gel, which was allowed to age at 80 °C for 4 h. The resulting slurry of the gel was filtered, and the gel was thoroughly washed with hot distilled water, dried at 120 °C overnight, and calcined at 450 °C under air for 3 h.

The bimetallic catalysts CoM/SiO₂ (M = Zn, Fe, Cu, or Sn) were prepared in a manner similar to that described for the monometallic catalyst except that solutions containing the desired concentrations of Co(NO₃)₂ and the corresponding metal salt of the metal additive used. The precursors for the Zn, Fe, Cu, and Sn metal additives were Zn(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, and SnCl₂·2H₂O (analytical purity), respectively.

The metallic cobalt loadings, determined by X-ray fluorescence spectroscopy (XFS, PANalytical Magix PW 2403), were 19.6 wt%, 17.6 wt%, 18.0 wt%, 18.5 wt%, and 16.9 wt% for Co/SiO₂, CoZn/SiO₂, CoFe/SiO₂, CoCu/SiO₂, and CoSn/SiO₂, respectively. The metal additive content was determined to be 3 wt% for all the CoM/SiO₂ catalysts.

1.2 Catalyst characterization

The XRD patterns of the catalysts were obtained on a PANalytical X'pert Pro diffractometer using Ni-filtered Cu K_{α} radiation with a scanning angle (2θ) of 15° – 80° , a scanning speed of $2^{\circ}/\text{min}$, and a voltage and current of 40 kV and 30 mA, respectively. The average Co_3O_4 particle sizes were calculated from the most intense Co_3O_4 line ($2\theta = 36.8^{\circ}$), using the Scherrer formula.

XPS spectra were obtained with a VG ESCALAB 210 spectrometer equipped with a Mg K_{α} X-ray radiation source ($h\nu = 1253.6$ eV) and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 20 eV, and all binding energies (BEs) were calibrated using the Si 2p peak at 103.4 eV as the reference.

Brunauer-Emmett-Teller (BET) surface areas of the catalysts were measured on a Micromeritics Tristar II 3020 instrument at liquid nitrogen temperature. Both the nitrogen adsorption-desorption isotherms and pore size distributions of the samples were measured.

TPR experiments were conducted with an instrument constructed in our laboratory. A sample of catalyst precursor (20 mg) was pretreated in a He flow (50 ml/min) at 200°C for 1 h and then cooled to room temperature. Then a reducing gas composed of 5% H_2/Ar was introduced at a flow rate of 50 ml/min, with a heating rate of $10^{\circ}\text{C}/\text{min}$ from ambient temperature to 850°C . H_2 consumption was continuously monitored with a thermal conductivity detector.

TEM images were obtained with a JEM2010 electron microscope at 200 kV. Catalyst powders were suspended in alcohol with ultrasonic dispersion for 30 min, and then the resulting solution was dropped on a carbon film on a copper grid.

1.3 Catalytic hydrogenolysis

Discontinuous hydrogenolysis of ethyl lactate was carried out in a 100 ml stainless steel autoclave at a stirring speed of 400 r/min. Unless otherwise stated, Co/SiO_2 and CoM/SiO_2 prereduced in a H_2 stream at 350°C for 3 h were used. The hydrogenolysis reaction was carried out under the following standard conditions: 160°C , 6.0 MPa of initial H_2 pressure, 2 g of ethyl lactate, 18 g of ethanol solvent, 1 g of reduced catalyst, reaction time 10 h. After the reactor was purged, it was heated to the reaction temperature, and the H_2 pressure was increased to about 8.0 MPa and maintained at that pressure during the reaction. The liquid-phase products were analyzed with a gas chromatograph equipped with a SE-54 capillary column ($50\text{ m} \times 0.32\text{ mm}$) and a flame ionization detector. The major liquid products included 1,2-PDO, 1-propanol, methanol, and ethyl propionate. Conversions and selectivities were calculated on the basis of a carbon described by Miyazawa et al. [16].

2 Results and discussion

2.1 XRD analysis

In the diffraction patterns of all the catalysts (Fig. 1), the broad and diffuse pattern clearly observed at around $2\theta = 21.7^{\circ}$ was attributed to amorphous silica. In all the diffractograms, the catalyst precursor showed diffraction lines at 36.8 , 44.8 , 59.3 , and 65.2° , indicating that cobalt was present mainly in the form of Co_3O_4 spinel structure after calcination at 450°C . However, these diffraction lines broadened and decreased in intensity upon incorporation of the additives, suggesting that the Co_3O_4 particle size was smaller in the bimetallic catalysts than in the monometallic catalyst (Table 1). The Co_3O_4 particles in the CoCu/SiO_2 and CoSn/SiO_2 catalysts were much smaller than those in CoZn/SiO_2 and CoFe/SiO_2 . Interestingly, no diffraction lines pertaining to the Zn, Fe, Sn, and Cu in the bimetallic catalysts were observed, probably due to small particle sizes near or below the limitation for the XRD detectability [17,18] or the formation of oxide solid solution between cobalt and additive species [19,20,21].

2.2 XPS analysis

We used XPS spectra to investigate the surface composition and chemical states of the catalyst precursors (Fig. 2,

Fig. 1. XRD patterns of Co/SiO_2 (1), CoSn/SiO_2 (2), CoCu/SiO_2 (3), CoFe/SiO_2 (4), and CoZn/SiO_2 (5).

Table 1 Textural Properties of the Co/SiO_2 and CoM/SiO_2 catalysts

Sample	$A_{\text{BET}}^a/(\text{m}^2/\text{g})$	$V_p^b/(\text{ml}/\text{g})$	d_p^b/nm	Particle size ^c (nm)
CoZn	156	0.6616	38.3	9.0
CoFe	169	0.7433	35.0	9.5
CoCu	170	0.6550	34.5	7.0
CoSn	171	0.7753	34.3	6.0
Co	125	0.6533	10.4	12.1

^aBET method.

^bBJH desorption average pore diameter.

^cCalculated from the Scherrer equation.

Fig. 2. Co 2*p* XPS spectra of Co/SiO₂ (1), CoZn/SiO₂ (2), CoFe/SiO₂ (3), CoCu/SiO₂ (4), and CoSn/SiO₂ (5).

Table 2 XPS-determined compositions and BEs of the Co/SiO₂ and CoM/SiO₂ catalysts

Sample	BE (eV)		Δ BE (eV)	Co/Si	M/Si	M/Co
	Co 2 <i>p</i> _{3/2}	Co 2 <i>p</i> _{1/2}				
CoZn	780.8	796.5	15.7	0.51	0.08	0.15
CoFe	780.7	796.2	15.5	0.52	0.06	0.12
CoCu	780.7	796.5	15.8	0.55	0.27	0.49
CoSn	781.1	797.4	16.3	0.45	0.05	0.12
Co	780.3	795.4	15.1	0.61	0	—

Table 2). Considering the Co 2*p* photoelectron spectra for the catalyst precursors, the Co₃O₄ spinel structure has already been proved to present on the catalyst surface from the typical Co 2*p* spectrum [15,22]. The electronic properties of cobalt were changed by the incorporation of the additives: the Co 2*p*_{3/2} peaks for all the bimetallic catalysts appeared at higher BE than the peaks for the monometallic catalyst (Fig. 2). The curve-fitting results for the Co peaks showed that the BE of the Co 2*p*_{3/2} peak was shifted slightly positively by 0.4–0.5 eV upon addition of Zn, Fe, or Cu and shifted sharply by 0.8 eV upon the addition of Sn. These observations are contrary to previously reported results showing a decrease in the BEs of the Co 2*p*_{3/2} peaks of doped catalysts, a decrease that was attributed to the formation of mixed spinel Co_{1-x}²⁺M_x²⁺[Co³⁺]₂O₄ [23]. The increase that we observed in the BE of the Co 2*p*_{3/2} main peak in the bimetallic catalysts may have been related to a decrease in the electron density of Co; to an increase in the Co²⁺ content at the expense of Co³⁺ ions in the spinel lattice after doping with Zn, Fe, Cu, or Sn; or to both factors. The relative intensity of the shake-up satellite structures centered at around 787 and 804 eV was also observed for all the bimetallic catalysts. All these XPS features were derived from Co²⁺ ions interacting with the support as cobalt(II) silicate [15,24,25] and were responsible for the H₂-TPR profiles at high temperature, as will be described later. This revealed

that Zn, Fe, Cu, and Sn in Co-containing catalysts accelerated the formation of cobalt(II) silicate. On the basis of our results and previously reported results for similar cobalt-based catalysts [15,17,26], we propose that both Co₃O₄ and cobalt phyllosilicate were present on the surface of the bimetallic catalysts. The absence of cobalt phyllosilicate diffraction peaks from the XRD patterns may have been due to the amorphous structure of this species.

BE values obtained from curve-fitting of the XPS peaks of Zn, Fe, Cu, and Sn indicated that all the additives were in an oxidized state in the bimetallic catalysts (Table 3).

Table 3 Curve-fitting results for XPS peaks of M in CoM/SiO₂ catalysts

Catalyst	M	BE (eV)	Species
CoZn	Zn LMM	988.6	ZnO
CoFe	Fe 2 <i>p</i> _{3/2}	710.4	Fe ₂ O ₃
CoCu	Cu 2 <i>p</i> _{3/2}	934.3	CuO
CoSn	Sn 3 <i>d</i> _{5/2}	487.2	SnO

XPS intensity ratios of the metal cations in the supported metal oxide to those in the oxide support can provide important information about the dispersion and crystallite size of supported particles [27]. The Co/Si ratios in the bimetallic catalysts were lower than those in the monometallic catalyst, indicating that some of the cobalt particles may have been superficially coated by the additives. Both the strong interaction between cobalt and silica and the lower Co/Si ratio may have been responsible for the poor lactate hydrogenation activity of the bimetallic catalysts, as will be discussed below.

2.3 BET surface area and N₂ adsorption

Incorporation of additives substantially affected the textural properties of the supported catalysts (Table 1). The specific surface areas, pore volumes, and average pore diameters of the bimetallic catalysts were clearly higher than those of the monometallic catalyst. The addition of Sn, Cu, and Fe significantly increased the specific surface area of the catalysts by ~30% and all the values were approximately 170 m²/g. It has been reported that increases in the specific surface area of bimetallic catalysts relative to that of monometallic catalysts may be due to the formation of cobalt phyllosilicate [28], as indicated by XPS. The pore volumes of the catalysts were increased by the addition of Sn and Fe, and the incorporation of Cu greatly increased the average pore diameter from 10.4 to 38.3 nm.

2.4 H₂-TPR analysis

TPR is widely used to study the reducibility of supported

cobalt catalysts. Many variables, including Co particle size, support interaction, and reduction gas composition, are known to influence the reduction behavior and thus the locations of the TPR peaks of cobalt catalysts [29]. Knowing the species formed in the catalyst precursors makes the TPR profiles of such samples easier to interpret. The reduction profile of the monometallic catalyst exhibited two peaks close to each other, a low peak at 296 °C and a more intense prominent peak at 335 °C, indicating that two consecutive steps were involved in the reduction of Co_3O_4 spinel (Fig. 3) [15,30]. The TPR profiles of the bimetallic samples were completely distinct from the profile of the monometallic sample. The presence of more than two reduction peaks in the former profiles indicated the existence of more than one cobalt oxide species in the bimetallic systems. These peaks could be attributed to cobalt in various oxidation states and to various interactions of cobalt with the support surface. Taken together with the XRD results, the TPR profiles suggest that cobalt with low dispersion and large particle sizes was reduced at low temperature. These reduction peaks in the TPR profiles were attributed to the reduction of Co^{3+} to Co^{2+} and the reduction of Co^{2+} to Co, respectively. From the TPR profiles, we can see that the onset reduction temperatures of Co_3O_4 spinel for all the bimetallic catalysts were higher than the temperature for the monometallic catalyst. This result is consistent with previous reports indicating that the onset reduction temperatures of cobalt catalysts shift to lower temperatures with the incorporation of Cu and Zn [17, 28]. In contrast, the peak reduction temperatures of Co_3O_4 spinel increased from 296 °C for the monometallic catalyst to 335, 339, 304, and 328 °C upon the addition of Zn, Fe, Cu, and Sn, respectively. The higher onset reduction temperature here could be ascribed to the decreased particle size of Co_3O_4 , which is consistent with the report that small particles that interact strongly with the support are much more difficult to reduce than weakly interacting large particles [29]. Also of consequence is the appearance of several

Fig. 3. H_2 -TPR profiles of the Co/SiO_2 and CoM/SiO_2 catalysts.

maxima of Co_3O_4 spinel, which were attributed to several reduction steps. Bimetallic catalysts showed multiple reduction peaks, but only one peak was observed after Cu and Sn were incorporated. This change may be due to reduction in the particle sizes of the CoCu/SiO_2 and CoSn/SiO_2 catalysts (Table 3), which is consistent with previous results indicating that the reduction of a supported Co_3O_4 phase with small particle sizes occurs in a single step [31–34]. This possibility is also consistent with the XRD results, which indicated that the particle sizes of CoCu/SiO_2 and CoSn/SiO_2 were only 7.0 and 6.0 nm, respectively. The TPR profiles of the CoZn/SiO_2 and CoFe/SiO_2 catalysts were characterized by an intense peak at around 337 °C with a small shoulder peak at around 382 °C and two additional small shoulders at 379 and 384 °C; the latter two shoulders were likely due to the reduction of small particles of CoO (arising from the first reduction of Co_3O_4) and/or cobalt species strongly interacting with the silica support.

Furthermore, high-temperature reduction peaks (>650 °C) characteristic of cobalt species interacting strongly with silica were also observed for all the bimetallic catalysts. These peaks may have been related to the reduction of the cobalt phyllosilicate phase, as indicated by XPS. The incorporation of additives seems to have accelerated the formation of this phase, with this plot becoming much more obvious. Zn has been found to weaken the interaction between cobalt and titania as a result of the formation a “sandwich layer” between the cobalt and the support [28,35]. Cu-containing bimetallic systems are reported to show markedly increased reducibility by suppressing of the formation of the CoAl_2O_4 phase [17]. The main cobalt species formed in the calcination of the CoZn/SiO_2 , CoFe/SiO_2 , and CoSn/SiO_2 catalysts was the cobalt phyllosilicate phase (Fig. 3). In contrast, Co_3O_4 spinel was the main constituent of the CoCu sample, together with a small amount of cobalt phyllosilicate. On the whole, the TPR results were in good agreement with the XRD and XPS results. Undoubtedly, the presence of additives strongly affected the nature of the cobalt species in the catalysts by modifying their interaction with the material support as well as their reduction degree, leading to different TPR profiles. More importantly, the data also suggest that the catalyst surface was more similar to cobalt than to the additives.

2.5 TEM analysis

Structural information about the cobalt catalysts was obtained by means of TEM analysis, which complimented the results obtained from the analytical methods described above. The TEM features of the monometallic and bimetallic catalysts were substantially different (Fig. 4). The monometallic catalyst exhibited small spherical particles

(5–20 nm) that were evenly distributed on the surface of the support and showed good crystallinity [15]. In contrast, we observed two kinds of microstructures in the bimetallic catalysts, spherical particles and a lamellar structure consisting of claylike lines, which probably indicates that both Co₃O₄ and cobalt phyllosilicate were present [36–38]. Thus, the TEM observations supported the results obtained by means of XRD, XPS, and TPR.

2.6 Catalytic hydrogenation

We evaluated the activity of the Co/SiO₂ and CoM/SiO₂ catalysts for liquid-phase hydrogenation of ethyl lactate (Table 4). When the reaction was carried out over the monometallic catalyst, lactate conversion and 1,2-PDO selectivity were high (90.4% and 95.8%, respectively). Incorporation of Zn, Fe, Cu, or Sn deactivated the catalyst, especially in the cases of Fe and Sn. The ethyl lactate conversions with CoFe/SiO₂ and CoSn/SiO₂ decreased sharply relative to the conversion with the monometallic catalyst (from 90.4% to 9.0% and 0.6%, respectively). In contrast, the conversions with CoCu/SiO₂ and CoZn/SiO₂ decreased only to 71.6% and 50.9%, respectively. As is well known, the activity of a metal catalyst is directly related to the reducibility of the catalyst, as well as to the number of active surface atoms, which is affected by the degree of metal dispersion and the strength of the metal-support interaction.

Table 4 Effect of additives on the performance of Co/SiO₂ in the liquid-phase hydrogenation of ethyl lactate

Catalyst	X/%	Selectivity (%)			
		1,2-PDO	Ethyl propionate	1-Propanal	Methanol
CoZn	50.9	73.6	13.7	12.3	0.3
CoFe	9.0	30.3	65.6	2.4	1.7
CoCu	71.6	86.5	3.0	9.9	0.7
CoSn	0.6	69.3	11.0	5.9	13.8
Co	90.4	95.8	0.4	3.1	0.7

Reaction conditions: catalyst 1 g, ethyl lactate 2 g, ethanol 18 g, temperature 160 °C, H₂ pressure 8.0 MPa, reaction time 10 h.

Our findings indicate that the hydrogenation activity of the tested cobalt catalysts depended strongly on their reducibility. Cobalt metal is reported to be the active phase for lactate hydrogenation [13]. From the TPR characterizations we know that although the onset reduction temperatures for the bimetallic catalysts are lower than that of the mono-cobalt catalyst, however, owing to the formation of cobalt species that interacted strongly with the support, probably cobalt phyllosilicate, a large proportion of the cobalt species in the bimetallic catalysts could not be reduced to metallic cobalt under the prereluction conditions (350 °C for 10 h). As a result, less of the cobalt species was converted to the catalytically active species after the pre-activation procedure. Thus, insufficient prereluction of the bimetallic catalysts was likely the main reason for their poor activity. In addi-

Fig. 4. TEM images of the monometallic and bimetallic catalysts.

tion, the surface coverage of the active cobalt species by the metal additives (inferred from XPS results) may have decreased the activity of the bimetallic catalysts somewhat.

The selectivity of the reaction for ethyl propionate increased at the expense of 1,2-PDO selectivity when the metal additives were incorporated into the catalysts. This was especially true for the Fe-doped catalyst, which showed an ethyl propionate selectivity that was twice the 1,2-PDO selectivity. The selectivity for 1-propanol was increased by the incorporation of Fe or Sn. Also of interest is the fact that even though the conversions of ethyl lactate obtained with the CoZn/SiO₂ and CoSn/SiO₂ catalysts differed substantially (Table 4), the 1,2-PDO and ethyl propionate selectivities of the two catalysts were similar. These observations suggest that although the catalyst activity was dominated by cobalt, the selectivity was influenced by the presence of the additives.

On the basis of the product distribution, we propose the following reaction pathway for the liquid-phase hydrogenolysis of ethyl lactate (Scheme 1). According to the literature, 1,2-PDO is formed mainly via direct hydrogenation of ethyl lactate over the catalysts rather than by a stepwise process (e.g., the hydrolysis of ethyl lactate followed by hydrogenation of lactic acid), as indicated by the lower amounts of lactic acid in the product distribution over a wide range of conversion percentages [4,5,11]. Because ethyl lactate has a reactive hydroxyl group, hydrogenation and dehydration reactions are competitive during the liquid-phase hydrogenation of ethyl lactate. The product distribution suggests that the dehydration of ethyl lactate to ethyl propionate was preferred when CoFe/SiO₂ was used as

the catalyst.

3 Conclusions

We studied the effect of Zn, Fe, Cu, and Sn additives on the structure and catalytic performance of a Co/SiO₂ catalyst. Analytical results showed that the bimetallic catalysts had higher dispersion and BET surface areas than the monometallic catalyst. Incorporation of additives decreased the size of the cobalt particles, which resulted in accelerated formation of cobalt species that interacted strongly with the support, that is, cobalt phyllosilicate. The results of catalytic hydrogenation of biomass-derived ethyl lactate to 1,2-PDO showed that incorporation of the metal additives profoundly inhibited the catalyst activity, especially when Fe or Sn was incorporated. In addition, the incorporation of the additives did not improve the selectivity for 1,2-PDO. The poorer activity of the bimetallic catalysts likely resulted from insufficient prereduction owing to the formation of a difficult-to-reduce cobalt phyllosilicate species. Our findings suggest that although metal and non-metal additives are widely used to improve the activity, selectivity, and stability of catalysts, the formation of difficult-to-reduce species needs to be considered.

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Scheme 1. Proposed reaction pathway for liquid-phase hydrogenolysis of ethyl lactate over Co/SiO₂ catalysts.

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