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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Synthesis of Co–Sn Intermetallic Nanocatalysts toward Selective Hydrogenation of Citral †

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In this work, three supported Co–Sn intermetallic compounds (IMCs) catalysts (Co_{2.9}Sn₂, CoSn and CoSn₂) with particle size of ~20 nm were prepared *via* a facile hydrotalcite approach, and their catalytic performances were evaluated in selective hydrogenation of citral to unsaturated alcohol (geraniol and nerol). EXAFS, *in situ* CO-FTIR and DFT calculations results reveal that the introduction of Sn in Co–Sn IMCs dramatically optimizes the geometric and electronic structure of active Co, in which Sn isolates the Co active-site and electron transfer occurs from Sn to Co atom. H₂-TPD measurements indicate the presence of four different Co sites (labeled as α , β , γ and σ) on the surface of these IMCs; the sample of CoSn IMC shows the largest $\beta/(\gamma+\sigma)$ ratio, which results in the highest selectivity toward unsaturated alcohol (S_{UA}: 67.6%). DFT studies prove that the geometric and electronic effect of CoSn IMC weaken the hydrogenation of C=C group, accounting for the largely enhanced hydrogenation selectivity of citral to unsaturated alcohol.

1. Introduction

Selective hydrogenation of α, β -unsaturated aldehydes to corresponding unsaturated alcohols is an important reaction in the production of fine chemicals and pharmaceuticals.^{1,2} Conventional hydrogenation catalysts based on noble or transition metals (e.g., Ru, Pt, Rh, Ni or Co) are highly active, but saturated aldehydes are normally the dominating products since hydrogenation of the alkene bond (C=C) is more thermodynamically and kinetically favorable than the C=O bond.³⁻⁷ To resolve this issue, great efforts have been made for the design of new catalysts with improved selectivity. For instance, the modification of active metal by the second metal (e.g., Sn, Ge, or Fe) is a promising approach, and the resulting bimetallic catalysts show enhanced selectivity toward unsaturated alcohols.⁸⁻¹² However, how to rationally design and prepare efficient bimetallic catalysts for selective hydrogenation of α, β -unsaturated aldehydes and uncover the structure-property correlation still remains a huge challenge.

Intermetallic compounds (IMCs) with specific electronic and geometric structure have attracted extensive research interest for their unique catalytic properties.¹³⁻¹⁷ Most notably, IMCs



In this work, we further extend this synthesis to Co-Sn IMCs via a modified LDHs approach (impregnation-coreduction method). Na₂SnO₄ was homogeneously impregnated with CoZnAl-LDHs, followed by a coreduction process to obtain the supported Co-Sn IMCs with uniform particle size (~20 nm) but various chemical compositions (Co2.9Sn2, CoSn and CoSn2). Both experimental and computatinal study verify the activesite isolation of Co by Sn and electron transfer from Sn to Co. Compared with pristine Co, the Co-Sn IMCs exhibit largely enhanced selectivity toward unsaturated alcohols, and the best selectivity is obtained over the CoSn IMC with an unsaturated alcohol yield of 67.6%. The remarkably increased hydrogenation selectivity can be attributed to the observed Co-Sn synergistic effect. This work provides a facile method for the preparation of Co-based IMCs catalysts, which can be potentially used in selective hydrogenation of α , β -unsaturated aldehydes.

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⁺Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x ‡ Contributed equally to this work.

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2. Experimental

2.1. Materials

All the inorganic and organic reagent was purchased from J&K^{*}, Amethyst^{*}, or Sigma aldrich. The following analytical grade inorganic chemicals were used without further purification: urea, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Na_2SnO_3 \cdot 3H_2O$. Deionized water was used in all the experimental processes.

2.2. Fabrication of the Co-Sn IMCs catalysts

Synthesis of CoZnAl-LDHs precursor. The CoZnAl-LDHs with a certain molar ratio were synthesized by a urea decomposition method. In brief, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and urea were dissolved in 250 mL of deionized water to give a transparent solution with the concentration of 0.048 M, 0.112 M, 0.08 M and 2 M, respectively. The resulting solution was stirred in a flask at 100 °C for 24 h. The obtained precipitation was washed thoroughly with water and dried in an oven at 60 °C overnight.

Synthesis of supported Co–Sn IMCs. Three CoSn(OH)₆/CoZnAl-LDHs samples with total Sn/Co molar ratio of 2/2.9, 1/1, 2/1, respectively, were obtained by adding CoZnAl-LDHs into Na₂SnO₃·3H₂O solution. The resulting slurry was washed thoroughly with deionized water and dried at 100 °C for 12 h in an oven. Subsequently, 1.0 g of the above mixture was reduced in a H₂/N₂ (10/90, v/v) stream at different reduction temperatures (from 500 to 700 °C) for 4 h, with an initial heating rate of 2 °C/min. The reduction process results in the generation of supported Co-Sn IMCs. The resulting product was slowly cooled to the room temperature in a N₂ stream for the following catalytic evaluation.

2.3. Catalytic evaluation toward selective hydrogenation of citral

Catalyst (0.05 g: 0.1 mmol of Co), citral (1 mL), and iso-PrOH (30 mL) as solvent were placed into a stainless steel reaction reactor, which was fitted inside a Teflon tank. The air in the vessel was replaced by 4.5 MPa hydrogen five times, vented and sealed. After the reactor temperature was increased to 160 °C, H₂ was introduced into the reactor with an initial pressure of 4.0 MPa. At a given reaction time, the reaction product was analyzed off-line *via* GC-MS analysis.

2.4. Characterization

Hydrogen temperature programmed reduction (H₂-TPR) and the hydrogen temperature programmed desorption (H₂-TPD) were conducted in a quartz tube reactor on a Micromeritics ChemiSorb 2720 with a thermal conductivity detector (TCD). In a typical H₂-TPR process, 100 mg of a sample was sealed in the reactor, and then a gaseous mixture of H₂ and Ar (1:9, v/v) was fed to the reactor at 40 mL/min. The temperature was raised to 1000 °C at a heating rate of 10 °C/min. For the H₂-TPD process, 150 mg of a sample was first sealed and reduced in the reactor in the gaseous mixture of H₂ and Ar (1:9, v/v) at 400 °C. Subsequently, the reduced sample was purged in Ar at 450 °C for 30 min, then cooled down to 25 °C for readsorption of H₂; after flushing with Ar until the baseline was stable, the temperature was raised to 800 °C at a heating rate of 10 °C/min in Ar atmosphere.

Powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation 3/C=0.95418 nm) at 40 kV, 40 mA, with a scanning rate of 5°/min, and a 2 θ angle ranging from 10° to 90°. Transmission electron microscopy (TEM) images were recorded with JEOL JEM-2010 high resolution transmission electron microscopes. The accelerating voltage was 200 kV. The metal loading content in these supported catalysts was determined by ICP-AES (Shimadzu ICPS-7500). The specific surface area measurements were performed based on Brunauer-Emmett-Teller (BET) method by using a Quantachrome Autosorb-1C-VP analyzer. The Co XAFS measurements were performed at the beam line 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The infrared spectroscopy was recorded using a Vector22 (Bruker) spectrophotometer with 4 cm⁻¹ of resolution.

2.5. Computational method

All calculations were performed with the periodic density functional theory (DFT) method using CASTEP module in Material Studio 6.1 software package (Accelrys Inc.: San, Diego, CA). The models for Co_{2.9}Sn₂, CoSn, and CoSn₂ were built on the basis of the XRD standard cards, in which the crystal structures are in accordance with experimental results: Co_{2.9}Sn₂, Pnma (62); CoSn, P6/mmm (191); CoSn₂, I4/mcm (140) (see details in Fig. S6). The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional with the generalized gradient approximation (GGA). The electron-ion interactions were described by ultrasoft pseudopotentials (USPP). The convergence criteria for structure optimization and energy calculation were set to MEDIUM quality with the tolerance for SCF, energy, maximum force, and maximum displacement of 2.0×10^{-6} eV/atom, $2.0 \times$ 10^{-5} eV/atom, 0.05 eV/Å, and 2.0 × 10^{-3} Å, respectively.

Surface adsorption takes place on the surface layer of the slab. All adsorbate atoms were allowed to relax to their optimized positions. The adsorption energy, E_{ads} , is defined as $E_{ads}=E_t-E_{slab}-E_{gas}$ (1) where E_t is the total energy of the slab with adsorbate; E_{slab} is

the energy of the slab, and E_{gas} is the energy of adsorbate; E_{slab} is gas state. For H, E_{gas} is half energy of H₂.

3. Results and discussion

3.1. Structural and morphological characterization of Co-Sn IMCs

XRD, SEM and H₂-TPR were performed to study the precursor structure of Na₂SnO₃ and CoZnAl-LDHs. XRD pattern (Fig. S1A) confirms the high purity of CoZnAl-LDHs phase with characteristic (003) and (006) peak at 2θ 11.50° and 23.14°, respectively; SEM image (Fig. S1B) displays a platelet-like morphology with a diameter of ~2 µm. After the impregnation of Na₂SnO₃, the hybrid material shows the existence of both a CoSn(OH)₆ phase (PDF#13-0356) and the original LDHs one (Fig. S2A: denoted as CoSn(OH)₆/CoZnAl-LDHs), which is further confirmed by the H₂-TPR measurements (Fig. S3). It is observed that the CoZnAl-LDHs (Fig. S3a) shows two peaks of H₂

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consumption: one peak centred at 300 °C and another broad peak from 450 to 780 °C. The first one corresponds to the reduction of Co_3O_4 to CoO whereas the second broad one could be ascribed to a complicated interaction between CoO and the support. $^{\rm 27,28}\,$ The main reduction peak of CoSn(OH)_6 is observed at ~560 °C (Fig. S3e). For the CoSn(OH)₆/CoZnAl-LDHs samples (Fig. S3b-d), besides the reduction peak of CoO, a reduction peak due to $CoSn(OH)_6$ phase is also found at ~550 °C. The results indicate a co-reduction process in CoSn(OH)₆/CoZnAl-LDHs samples via this impregnationreduction approach. After the subsequent reduction process in H₂ atmosphere, Co and Sn species transform to corresponding metal state, whose XRD patterns are shown in Fig. 1. The pristine CoZnAl-LDHs sample transfers to supported metal Co phase (2θ 44.21°, 51.52°) on a Al₂ZnO₄ spinel phase (PDF#65-3104; Fig. 1a). Upon the introduction of Sn with increasing Sn/Co ratio, the pristine Co phase disappears; and three new Co-Sn IMC phases are observed, which can be indexed to Co2.9Sn2, CoSn and CoSn2, respectively (Fig. 1b-1d: Co2.9Sn2-PDF#65-8982, CoSn-PDF#65-5600, CoSn₂-PDF#65-5843). The XRD results confirm the successful synthesis of Co-Sn IMCs by the impregnation-coreduction method via LDHs approach.



Fig. 1 XRD patterns of the as-synthesized Co and Co–Sn IMCs: (a) Co, (b) $Co_{2.9}Sn_2$, (c) CoSn, and (d) $CoSn_2$. XRD standard cards for Al_2ZnO_4 , Co and Co–Sn IMCs are shown in the lower part of the panels: Al2ZnO4–PDF#65-3104, Co–PDF#15-0806, Co2.9Sn2-PDF#65-8882, CoSn–PDF#65-5600 and CoSn2–PDF#65-5843.

SEM images (Fig. S4) of all the reduced products (Co and Co– Sn IMCs) show that they inherit the morphology of original CoZnAl–LDHs precursor, with uniform nanoparticles distributed on each platelet. TEM was used to further study the structure of these reduced products (Fig. 2). The supported Co nanoparticles show a mean size of 15.3 nm, in accordance with the result calculated by Scherrer formula according to XRD pattern (15.1 nm). The introduction of Sn element results in the formation of Co–Sn IMCs, with a high dispersion ARTICLE



Fig. 2 TEM images of the as-synthesized Co and Co–Sn IMCs: (A1) Co, (B1) $Co_{2.9}Sn_2$, (C1) CoSn, (D1) $CoSn_2$. The corresponding HRTEM lattice fringe images are shown in A2, B2, C2, and D2, respectively. The inset shows their size distribution for these Co–Sn IMCs.

The mean particle size of the supported $Co_{2.9}Sn_2$, CoSn and $CoSn_2$ is 17.9 nm, 19.3 nm and 20.1 nm, respectively, close to the XRD results (Table S3). Generally, IMCs with relatively large particle size from hundred nanometers to several micrometers have been reported by conventional solid phase reactions, but

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the Co-Sn IMCs prepared in this work show greatly decreased particle size in spite of high reaction temperature (500 °C-700 °C), which is due to the anchoring effect of the LDHs matrix.^{24,29-31} Thus, by means of changing Sn/Co ratio in the CoSn(OH)₆/CoZnAl-LDHs precursor via the impregnationreduction method, three types of Co-Sn IMCs nanocrystalline (Co_{2.9}Sn₂, CoSn and CoSn₂) with small particle size (~20 nm) are obtained.



Fig. 3 (A) The normalized intensity of Co K-edge XANES spectra for the Co-Sn IMCs and Co foil; (B) corresponding Fourier transform k^3 -weighted EXAFS spectra in R space compared with Co foil.

Table 1 Curve-fitting and DFT-calculation results of Co K-edge EXAFS spectra of Co_{2.9}Sn₂, CoSn and CoSn₂ IMC

Sample	Shell	<i>R</i> (Å)– CF ^ª	R(Å)− DFT ^b	CN– CF ^c	CN– DFT ^d	Δσ²(Å) ^e
Co foil	Co–Co	2.494	2.465	12	12	-0.0157
Co _{2.9} Sn ₂	Co1–Co ^f	2.600	2.588	4	4	-0.1283
	Co–Sn	2.594	2.605	3	3	-0.1163
	Co2–Co ^f	2.456	2.563	2	2	0.0353
	Co–Sn	2.594	2.605	3	3	-0.1163
CoSn	Co–Co	2.649	2.635	4	4	0.0096
	Co–Sn	2.609	2.623	6	6	-0.0101
CoSn ₂	Co–Co	2.671	2.704	2	2	0.0714
	Co–Sn	2.682	2.668	7	7	-0.0694

^a Distance between absorber and backscatter atom, determined by curve fitting

^b Distance between absorber and backscatter atom, determined by DFT calculation.

Coordination number, determined by curve fitting.

¹ Coordination number, determined by DFT calculation Change in the Debye-Waller factor value relative to the reference sample.

^f Two kinds of Co in Co_{2.9}Sn₂ (Co1 and Co2).

The X-ray absorption near-edge structure (XANES) spectra can provide crucial electronic structural information, and Fig. 3A shows the normalized XANES spectra of these Co-Sn IMCs nanocrystalline as well as the reference sample (Co foil). A shoulder peak appears at 7711 eV for Co foil and at 7708 eV for IMCs. The first inflection point of these Co-Sn IMCs is observed at 7705 eV, rather close to that of Co foil, indicating the metallic state of Co⁰ in Co–Sn IMCs.¹⁰ In the cases of IMCs, both the peaks at ~7716 eV and 7725 eV with different intensity exhibit their characteristic Co K-edge XANES. The introduction of Sn notably affects the metallic state of Co atoms. With the increase of Sn/Co ratio from Co to $CoSn_2$, the absorption edge shifts to low photon energy with a decrease of the white line intensity, which confirms the enhanced

electronegativity of Co atom (denoted as $Co^{\delta-}$)³²/_{lew} This may result from the electron transfer from SP atom 36 Co atom. The Fourier transform of Co K-edge EXAFS oscillations in R space (Fig. 3B) was used to study the detailed atomic configuration for these Co-Sn IMCs. Compared with the Co foil, the intensity of the first nearest-neighbor distance for these IMCs decreases significantly, indicating the reduced Co-Co coordination by the introduction of Sn element. For Co_{2.9}Sn₂ IMC, a shoulder peak appears at high R value. Two main peaks at the first nearest-neighbor distance are even observed in the cases of the CoSn and CoSn₂ IMC. The results qualitatively indicate the strong Co-Sn interaction as well as the variation in the chemical bonding or coordination environment. Curvefitting data of these samples are listed in Table 1, from which the coordination number (CN) of Co-Co bond decreases from 12 in Co foil to 2 in $CoSn_2$; while the CN of Co-Sn bond increases from 3 in Co_{2.9}Sn₂ to 7 in CoSn₂. The results indicate Co atoms are gradually dispersed by Sn atoms through the Co-Sn coordination along with the increase of Sn/Co ratio.



Fig. 4 Atomic arrangement and chemical bonding of the preferential crystal facet of Co and Co-Sn IMCs (based on XRD diffraction): (A) Co (111) face, (B) Co_{2.9}Sn₂ (004) face, (C) CoSn (201) face, (D) CoSn₂ (211) face.

DFT calculations were further performed to give a better understanding on the electron and geometry features of these Co-Sn IMCs. The structure models of Co and Co-Sn IMCs are shown in Fig. S5, which are built according to their XRD patterns. The uniform interspersion between Co and Sn element is clearly observed in Fig. 4. For the pristine Co nanoparticles, each Co atom is coordinated by other 12 Co atoms, and the Co(111) surface is flat (Fig. 4A). With the increase of Sn/Co ratio, the Co-Co coordination number decreases gradually while the Co-Sn coordination number increases, and the crystal facet becomes corrugated. Moreover, the Hirshfield charge analysis shows that the atomic charge of Co changes from -0.13e (Co_{2.9}Sn₂) to -0.21e (CoSn₂) with the increase of Sn/Co ratio. This suggests electron transfer occurs from neighboring Sn to Co atom, which may affect the adsorption of reactants.³³⁻³⁶ The results demonstrate that the interspersion between Co and Sn leads to particular electronic interaction and geometric reconstruction. The details of Co-Co

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and Co–Sn bond length and coordination number obtained from the DFT calculations are listed in Table 1, which are in agreement with those of the curve-fitting of Co K-edge EXAFS spectra.

We perform the in situ Fourier-transformed infrared absorption of CO molecule over monometallic Co sample and Co-Sn IMCs (Fig. 5), so as to give a deep insight into the surface structure. Normally, CO adsorbs on Co⁰ with two different modes, namely linear adsorption (above 2000 cm⁻¹) and multi-coordinated adsorption (below 2000 cm^{-1});³⁷ while CO adsorption on Sn⁰ surface is too weak to be detected at room temperature. For the monometallic Co sample (Fig. 5a), only the linear adsorption peak at 2058 cm⁻¹ is observed. In the cases of Co-Sn IMCs, the linear peak reduces gradually with broadened full-width half-maximum as the Sn/Co ratio increases from $Co_{2.9}Sn_2$ to $CoSn_2$. Moreover, a gradual red-shift $(\sim 13 \text{ cm}^{-1})$ of linear adsorption is observed from Co to CoSn₂ IMC. This agrees well with the electron transfer from neighboring Sn to Co atom as confirmed by XANES and DFT, which enhances the electron back-donation from the dmetallic orbitals to the π^* anti-bonding molecular orbital of CO and thus weakens the bond order of C≡O triple bond.



Fig. 5 In situ Fourier-transformed infrared spectra of CO adsorption over (a) Co, (b) $Co_{2,9}Sn_{2}$, (c) CoSn, (d) $CoSn_{2}$.





Fig. 6 Structures of citral and its main hydrogenation products: (a) citronellal; (b) geraniol (E-b), nerol (Z-b); (c) citronellol; (d) 3,7-dimethyloctan-1-ol.

For this study the citral hydrogenation was selected to evaluate the catalytic performances of the as-prepared Co–Sn

IMCs. Citral is an interesting molecule with three different unsaturated bonds: a carbonyl group, a @=C1B6h2P/conjugated with the carbonyl group and an isolated C=C bond.³⁸ The structures of citral and its main hydrogenation products are shown in Fig. 6. Fig. 7 demonstrates the catalytic conversion and corresponding selectivity over these catalysts vs. reaction time, and the catalytic selectivity at the end of reaction is shown in Fig. 8B. It is observed that the conversion of all these samples is close to 100%. The monometallic Co catalyst shows the worst selectivity (5.2%) for unsaturated alcohol (geraniol and nerol, denoted as UA). The selectivity toward UA (Sua) of the three Co-Sn IMCs displays a large enhancement with the following order: Co_{2.9}Sn₂< CoSn₂< CoSn. The best selectivity is present in the CoSn sample (67.6%). Moreover, it's worth mention that Co catalyst prefers to hydrogenate the C=C bond and leads to the formation of saturated aldehyde (citronellal) and saturated alcohol (citronellol and 3,7-dimethyloctan-1-ol); while these Co-Sn IMCs show a low selectivity toward byproducts. Therefore, the incorporation of Sn inhibits the hydrogenation of C=C bond, accounting for the enhanced selectivity and productivity toward unsaturated alcohol.

The reusability of CoSn IMC catalyst was investigated by five recycling tests under the same reaction conditions (Fig. S6). The conversion still remains above 95% and a slight decrease in selectivity is found (from 67.6% to 63.9%) after 5 recycles. The results show a satisfactory stability and reusability of the CoSn IMC catalyst.



Fig. 7 Catalytic conversion and corresponding selectivity vs. reaction time for the hydrogenation of citral over various catalysts: (A) Co, (B) Co_{2.9}Sn₂, (C) CoSn, (D) CoSn₂. Reaction conditions: citral/Co ratio = 58; citral: 1.0 mL; iso-PrOH: 30 mL; temperature: 160 °C; H₂ pressure: 4 MPa. (a) citronellal; (b) geraniol (E) and nerol (Z); (c) citronellol; (d) 3,7-dimethyloctan-1-ol.

H₂-TPD was performed to understand the adsorption properties of hydrogen on Co and Co–Sn IMCs (Fig. 8A). The TPD curve can be deconvoluted into four doublets by Gaussian function for all these four samples, which are labeled as α , β , γ and σ . For the monometallic Co sample, the H₂-TPD profile shows peaks at 65, 113, 167 and 242 °C, which are assigned to different modes of hydrogen chemisorption and/or hydrogen chemisorbed on different metal surface structures.³⁹ In the cases of the three Co–Sn IMCs, four peaks are observed at lower temperatures relative to Co catalyst (63, 106, 144 and

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209 °C for Co_{2.9}Sn₂; 59, 93, 130 and 158 °C for CoSn; 48, 69, 117 and 146 °C for CoSn₂). This is related to the weak binding of H₂ adsorption over Co resulting from the electron transfer from Sn to Co. For Co-Sn IMCs, it is interesting that a good linear correlation is found between S_{UA} and the ratio of $\beta/(\gamma + \gamma)$ σ) (Fig. 8B). For the supported monometallic Co catalyst, although the ratio of $\theta/(\gamma + \sigma)$ is close to $Co_{2.9}Sn_2$ IMCs (0.99 for Co and 1.06 for $Co_{2.9}Sn_2$), its selectivity is much lower (5.2% for Co and 61.3% for $Co_{2.9}Sn_2$). The results indicate that the formation of intermetallic compound is beneficial for the selectivity toward unsaturated alcohol. Bueno et al. suggested that for supported monometallic Co catalysts, the four adsorption H-Co sites originate from different precursor species of CoO_x interacting with the support.^{40,41} In this work, in order to understand the structure-property correlation between Co–Sn IMCs and $S_{\text{UA}}\text{,}$ DFT calculations on hydrogen adsorption were performed to figure out the four adsorption sites in CoSn, Co_{2.9}Sn₂ and CoSn₂, respectively (shown in Fig. 9, Fig. S7 and Fig. S8). Four kinds of stable hydrogen adsorption states over the CoSn (201) facet are shown in Fig. 9 (A-D), with the adsorption energy (E_{ads}) sequence of A < B < C < D, which correspond to α , β , γ , σ adsorption state in H₂-TPD, respectively. DFT results reveal that the α adsorption site is located at Co inside the crystal below the second layer, where the hydrogenation of citral can hardly take place. The θ adsorption site is located at the Co with Co-Sn coordination; while both the γ and σ site relate with Co sites of Co–Co coordination. The DFT calculation results indicate the hetaadsorption site (Co-Sn coordination) serves as the active center for the hydrogenation of C=O bond, in accordance with the H₂-TPD observations.



Fig. 8 (A) H₂-TPD profiles of the as-synthesized Co and Co–Sn IMCs. (B) Selectivity toward unsaturated alcohol as a function of $\beta/(\gamma+\sigma)$: (a) Co, (b) Co_{2.9}Sn₂, (c) CoSn, (d) CoSn₂.

Generally, for citral hydrogenation, the dissociation adsorption of H₂ is not the rate determining step but the addition of the second H atom.⁴²⁻⁴⁴ Moreover, selective hydrogenation of α , β -unsaturated aldehydes to corresponding unsaturated alcohols is mainly determined by the activation/adsorption of C=O group and inhibition of C=C group adsorption.^{4,38,44-46} For the purpose of understanding the adsorption state of C=O bond and C=C bond over Co–Sn IMCs, the adsorption of HCHO and C₂H₄ on the CoSn(201) facet were studied as model systems. The adsorption modes of HCHO and C₂H₄ are shown in Fig. S9, and the detailed



parameters are listed in Table S1 and Table S2, respectively tink is found that the C=C bond is not prone to adsorb Con A 4564

structure containing Sn atom, which indicates the Co-Sn

coordination reduces the adsorption and activation of C=C

bond. The most stable mode for HCHO adsorption over Co-Co

coordination is di- σ_{col} with the adsorption energy (E_{ads}) of

-1.75 eV. Only one adsorption mode of C₂H₄ adsorbed on the

Co–Co coordination (di- $\sigma_{\rm CC}$ l; $E_{\rm ads}$ is –1.85 eV) is observed.

Therefore, C_2H_4 is more stably adsorbed on the Co–Co

coordination than HCHO. Moreover, the elongation of the C=C

bond length (1.44 Å vs. 1.33 Å in free C_2H_4) and the change in bond angle (\angle HCH: 113° vs. 120° in free C_2H_4) demonstrate

the activation of C_2H_4 molecule,^{19,47} accounting for the facile

hydrogenation of C=C bond over Co-Co coordination. In

contrast, HCHO prefers to adsorb on the Co–Sn coordination (di- $\sigma_{\rm co}$ Sn). The elongated C=O bond length (from 1.22 Å to

1.29 Å) and the decreased bond angle (\angle HCO: from 120° to

107°) leads to the activation and hydrogenation of C=O bond.

The activation of C_2H_4 and HCHO molecule in di- $\sigma_{cc}l$ and di- $\sigma_{co}Sn$ adsorption mode is further confirmed by partial

densities of states (PDOS) results (Fig. S10), in which both the

highest-occupied molecular orbital (HOMO) and the lowest-

unoccupied molecule orbital (LUMO) of the adsorbed C₂H₄ and

HCHO shift downward and significantly broadened. Therefore,

the γ and σ site (Co–Co coordination) favor the hydrogenation

of C=C bond to saturated aldehyde and saturated alcohol;

while the β site (Co–Sn coordination) favors the hydrogenation

of C=O bond to unsaturated alcohol. This coincides with the

correlation between the selectivity toward unsaturated

alcohol and the $\beta/(\gamma + \sigma)$ ratio.

Fig. 9 Adsorption states of hydrogen on the CoSn(201) facet. A, B, C and D correspond to α , β , γ and σ adsorption peak in H₂-TPD, respectively.

4. Conclusions

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Three Co-Sn IMCs (Co_{2.9}Sn₂, CoSn and CoSn₂) were prepared by a modified impregnation-reduction method based on an LDHs approach. The resulting catalysts exhibit largelyenhanced catalytic selectivity for hydrogenation of citral to unsaturated alcohol (5.2% for Co and more than 60% for Co-Sn IMCs). H₂-TPD measurements suggest the presence of four different H–Co adsorption sites (α , β , γ and σ) on surface of Co-Sn IMCs, and a good linear correlation is obtained between the selectivity toward unsaturated alcohol and the ratio of β / $(\gamma + \sigma)$. The charge transfer from Sn to Co as well as the isolation effect of Co active sites by Sn, as confirmed by the in situ CO-IR, EXAFS and DFT calculations, lead to the formation of Co-Sn coordination. This weakens the hydrogenation of C=C bond, resulting in the enhanced selectivity. Our approach holds significant promise for Co-Sn IMCs as efficient catalysts toward selective hydrogenation of citral, and gives a deep insight into the intrinsic structure-property relationship.

Acknowledgements

This work was supported by the 973 Program (Grant No. 2014CB932104), the National Natural Science Foundation of China, and the Specialized Research Fund for the Doctoral Program of Higher Education (20130010110013). Author thanks the support of BSRF (Bejing Synchrotron Radiation Facility) during the XAFS measurements.

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Synthesis of Co–Sn Intermetallic Nanocatalysts toward Selective

Hydrogenation of Citral

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Three Co–Sn intermetallic compound catalysts are prepared *via* hydrotalcite approach, which show satisfactory catalytic performance toward selective hydrogenation of citral.