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Communication (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Cu nanoclusters supported on Co nanosheets for selective hydrogenation of CO

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ABSTRACT

Cu nanoclusters supported on Co nanosheets (denoted Cu/Co) were prepared using lysine as a surfactant template. The shape of the Cu/Co catalyst promotes selective hydrogenation of CO, enhancing CO conversion and the selectivity for higher alcohols, and decreasing methane selectivity, which is in marked contrast to current Cu–Co bimetallic nanoparticle catalysts. The distinct functional interface of the Cu(111) surface with face-centered cubic structure with the Co(100) surface with hexagonal closed-packed structure in the Cu/Co catalyst provides a breakthrough in understanding the catalytic nature of metal-metal interactions. The design of this bimetallic catalyst bridges the gap between model catalysts and realistic catalytic applications, and will ultimately allow us to gain a fundamental understanding of the mechanism of syngas conversion to higher alcohols.

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1. Introduction

The combination of limited oil supply with its increased demand has spurred the search for alternative fuels. Unconventional fuels like shale oil, oil sands, biofuels, coal-to-liquids, and gas-to-liquids are currently being examined [1]. Important fuel additives such as ethanol or higher alcohols are of interest because they can be used to transport hydrogen chemically as a liquid and can be added to gasoline to increase octane rating and decrease unburned hydrocarbons [2,3]. Although production of alcohols from syngas conversion has been studied for decades, a high-efficiency catalytic process to convert syngas to valuable ethanol and higher alcohols remains a major challenge in the field of energy chemistry [4,5]. The current syntheses of ethanol and higher alcohols are unable to meet the huge demand for fuels and fuel additives because of the low yield and poor selectivity for higher alcohols of this catalytic process.

Development of new catalysts may allow a breakthrough in the production of alcohols from syngas conversion.

Among the different types of catalysts being explored for producing alcohols from syngas, Cu–Co-based catalysts are some of the most promising [6–8]. Cu-based catalysts are commonly used for methanol synthesis from syngas, and Co-based catalysts are widely used in the formation of long-chain paraffins in the Fischer-Tropsch (F-T) reaction [9]. Cu–Co bimetallic nanoparticles have been used to catalyze synthesis of mixed alcohols from syngas since they were first designed in the 1970s [10]. Unsupported Cu–Co nanoparticles are realistic models to study the active sites and mechanism of CO hydrogenation, whereas supported Cu–Co-based catalysts with efficient dispersion and stability are used in pilot plants. In general, the factors determining the type of catalyst used for production of mixed alcohols from syngas conversion are the Cu–Co bimetallic sites and the synergy between metallic Cu and

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Co species [11–14]. Some researchers have investigated the effects of promoters, supports, and operating conditions on the performance of Cu–Co catalysts for conversion of syngas to ethanol and higher alcohols, aiming to suppress undesired products and to maximize the yields of higher alcohols. However, the yields of alcohols other than methanol are generally low, and the mechanism of the catalytic process remains controversial, which is partially ascribed to the catalyst preparation technique not controlling the shape of the metal particles with atomic-level precision [15–18]. To date, Cu–Co catalysts have predominantly been particles, and few Cu–Co bimetallic catalysts with novel structures have been reported. Therefore, considering the huge demand for higher alcohols, we attempted to produce novel model catalysts to shed new light on the synthesis of shape-controlled bimetallic catalysts as well as to further understand the mechanism of syngas conversion to higher alcohols over bimetallic catalysts.

In this work, a Cu–Co bimetallic catalyst with a novel structure of Cu nanoclusters supported on Co nanosheets (denoted Cu/Co) was designed and prepared using lysine as a surfactant template. The structure of the Cu/Co bimetallic catalyst set it apart from previous Cu–Co bimetallic nanoparticles. The packing of our Cu/Co catalyst overcomes the problem of conventional Cu–Co bimetallic nanoparticles like alloys or mixtures of bimetals, in which the packing structure of Cu and Co atoms is random in each nanoparticle and there is no clear metal-metal interface [19–21]. The cooperative sites of Cu/Co are at the metal-metal interface, that is, the interfacial sites of Cu particles and Co sheets determine the catalytic properties of Cu/Co. This finding provides a deep insight into the mechanism of structure-dependent heterogeneous catalysis. In particular, the catalytic performance of the Cu/Co bimetallic catalyst and conventional Cu–Co nanoparticles for CO hydrogenation differs considerably, which is attributed to the cooperative effect of Cu nanoclusters and Co nanosheets tuning the geometric and electronic structure of active sites. This in turn affects the sorption behavior of molecules on the surface of Cu/Co and affects its catalytic behavior.

2. Experimental

In a typical synthesis of Cu nanoclusters supported on Co nanosheets, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) and $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2 mmol) were dissolved in an aqueous solution of lysine (4 mmol, 300 mL). The mixture was heated to 60 °C, and then NaBH_4 (20 mmol) was added. The mixture was heated at 60 °C for 20 h under an N_2 . The product was washed with distilled water and stored in ethanol.

For the synthesis of Cu–Co bimetallic nanoparticles, $\text{Co}(\text{acac})_2$ (2 mmol) and $\text{Cu}(\text{acac})_2$ (2 mmol) were dissolved in a mixture of oleylamine (30 mL) and 1-octadecene (30 mL) heated at 85 °C in an oil bath. The dissolved metal precursors were transferred to a 100-mL autoclave. The autoclave was flushed with Ar gas for 20 min to remove air. The hermetical autoclave was kept at 230 °C for 12 h. When the reaction was complete, an excess of absolute ethanol was added to form a cloudy black suspension. This suspension was separated by

centrifugation, allowing the Cu–Co bimetallic nanoparticles to be collected.

CO hydrogenation was carried out in a fixed-bed stainless steel tubular microreactor (internal diameter = 11.3 mm). Catalyst (2 mL, equivalent to approximately 2 g of catalyst) was used in each test. The average catalyst grain diameter was 60–80 mesh. Prior to the reaction, the catalyst samples were reduced under a flow of H_2 (67 mL/min, gas hourly space velocity (GHSV) = 2000 mL/(h·g)). The reduction temperature was programmed to rise from room temperature to 300 °C, to maintain that temperature for 8 h, and then to decrease to the desired temperature for the catalyst test. The premixed syngas with a molar ratio of $\text{H}_2/\text{CO}/\text{N}_2 = 65/32/3$ was gradually introduced to the catalyst. The pressure was gradually raised to 6 MPa. Then, the temperature was slowly increased to the desired value. The gaseous products were analyzed by three online gas chromatographs (GC). Analysis of N_2 , CO, CO_2 , and CH_4 was performed using a packed TDX-01 carbon molecular sieves column and a thermal conductivity detector (TCD) using He as the carrier gas (Haixin GC-950, Shanghai). H_2 and CO were analyzed through a TDX-1 carbon molecular sieves column with a TCD using Ar as the carrier gas (Shimadzu GC 2014, Japan). Gaseous hydrocarbons (C_1 – C_8) were separated in a capillary PoraPLOT Q column and analyzed by a flame ionization detector (FID) (GC 2014, Shimadzu, Japan). The aqueous products were analyzed offline by a GC (Shimadzu GC-2014) that was equipped with dual detectors (TCD for H_2O and CH_3OH detection, FID for C_1 – C_5 oxygenates detection) and dual Porapak Q columns (USA). CH_3OH was used as a reference to calibrate the results. The oil products were separated in a HP-1 column and analyzed by an FID (Shimadzu GC 2014). Analysis of the wax products, which were dissolved in carbon disulfide, was performed using an MXT-1 column and an FID detector (Shimadzu GC 2014).

Powder X-ray diffraction (XRD) measurements were performed with a Rigaku D/Max-RB X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were recorded with a transmission electron microscope (JEM-2100, JEOL, Japan). BET surface areas were determined by N_2 adsorption-desorption isotherm measurements at –196 °C (Auto-sorb-ZQ-MP, Quantachrome, USA). The catalytic products were analyzed by a GC (Shimadzu GC 2014).

3. Results and discussion

The morphology and composition of the Cu nanoclusters supported on Co nanosheets were detected by TEM. Figure 1(a) shows that the Cu nanoclusters were around 15 nm in diameter and each Co nanosheet was a hexagonal plate with sides of 150 nm. Energy-dispersive spectroscopy (EDS) of the nanosheet domain revealed that they were composed of Co rather than Cu (Fig. 1(e)). The results from SAED measurements of the nanosheets indicated the single-crystalline nature of the Co nanosheets (inset of Fig. 1(a)). High-resolution transmission electron microscopy (HRTEM) analysis of the nanosheets showed that the lattice fringes were separated by 0.45, 0.27,

Fig. 1. (a) TEM image of Cu nanoclusters supported on Co nanosheets, inset is the corresponding SAED pattern of Co nanosheets; (b) HRTEM image of a nanosheet, inset is a fast Fourier transform (FFT) analysis; (c) HRTEM image of a nanocluster, inset is a FFT analysis; (d) EDS of an entire domain of Cu nanoclusters supported on Co nanosheets; (e) EDS of an isolated nanosheet.

Table 1

Catalytic performance of Cu/Co catalyst for selective hydrogenation of CO.

$T/^{\circ}\text{C}$	$X(\text{CO})/\%$	Selectivity (C mol%)				ROH distribution (wt%)					HC distribution (wt%)				
		ROH	RCHO	CH_x	CO_2	MeOH	EtOH	PrOH	BuOH	C_5+OH	C_1	C_2	C_3	C_4	C_5+
240	3.5	3.4	0.1	54.6	41.9	72.9	19.6	5.5	1.6	0.4	36.7	17.1	17.9	9.6	18.7
260	7.5	6.6	0.8	42.9	49.7	69.2	20.0	7.5	3.0	0.3	32.6	16.7	19.1	10.7	20.9
280	17.7	13.1	1.7	35.7	49.5	55.2	27.8	8.2	5.1	3.7	32.1	16.0	19.4	11.2	21.3
300	35.6	14.1	1.1	40.4	44.4	43.8	30.7	9.0	5.3	11.2	28.3	12.9	15.6	8.8	34.4

Reaction conditions: 6.0 MPa, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 65/32/3$, GHSV = 10000 mL/(h·g).

and 0.23 nm, corresponding to the (001), (100), and (101) planes of hexagonal closed-packed (hcp) cobalt hydroxide (Fig. 1(b)), respectively, indicating the (100)-dominated surface structure of the nanosheets [22]. During reduction, the cobalt hydroxide nanosheets transform into Co nanosheets enclosed by the (100) plane. The interplanar spacing detected from the legible lattice fringes in an HRTEM image of the nanoclusters (Fig. 1(c)) was 0.21 nm, implying that they were face centered cubic (fcc) Cu nanoclusters enclosed by {111} planes [23,24]. The overall atomic ratio of Co to Cu in the Cu/Co sample was about 1.3:1, which was determined by EDS analysis (Fig. 1(d)). The structure of Cu nanoclusters supported on Co nanosheets was further verified by performing control experiments. Using only $\text{Co}(\text{NO}_3)_3$ without $\text{Cu}(\text{NO}_3)_2$ as a starting material, Co nanosheets were obtained, whereas using $\text{Cu}(\text{NO}_3)_2$ as a starting reagent gave Cu nanoclusters. These results indicate the existence of Cu in nanoclusters and Co in nanosheets.

To elucidate the shape specificity of the novel structure of Cu nanoclusters supported on Co nanosheets, the ability of Cu/Co to catalyze the selective hydrogenation of CO was investigated (Table 1). Prior to the catalytic test, the Cu/CO was reduced in a H_2 flow. The reduction temperature was programmed to rise from room temperature to 300 °C, to maintain that temperature for 8 h, and then to lower to the desired temperature for the catalyst reaction. The reduction treatment is important to transform cobalt hydroxide to metallic cobalt and convert remaining hcp crystalline packing enclosed by (100)

planes [22]. Interestingly, the structure of nanoclusters supported on nanosheets changed little after hydrogenation, clearly revealing excellent stability, as shown in Fig. 2. The Cu/Co catalyst achieved CO conversion of up to 35.6% with a selectivity for alcohols of 14.1% at 300 °C. The Cu/Co catalyst exhibited low conversion of CO and low selectivity towards alcohols at 300 °C. Importantly, with increasing temperature, methanol selectivity decreased, ethanol selectivity increased, and the selectivity for higher alcohols increased. With regard to the hydrocarbon distribution, the selectivity for methane decreased and the selectivity for C_5+ hydrocarbons increased with temperature; the selectivity for all hydrocarbons was hardly affected by temperature. Notably, at temperatures as high as

Fig. 2. TEM image of Cu/Co catalyst after hydrogenation.

300 °C, the formation of C₅₊ hydrocarbons dominated over that of methane. Temperature hardly affected the selectivity for CO₂. This is different from the reported observation that the selectivity for all alcohols goes through a maximum with temperature because at higher temperatures CO₂ formation dominates [25].

For comparison, conventional Cu–Co bimetallic nanoparticles were also prepared and evaluated for selective hydrogenation of CO. The as-prepared Cu–Co nanoparticles were uniform with a diameter of around 15 nm, as determined by TEM observation (Fig. 3(a)). The crystalline nature of the Cu–Co bimetallic nanoparticles was revealed by their SAED pattern (inset of Fig. 3(a)). The XRD pattern of the Cu–Co nanoparticles also indicated the formation of crystalline Cu and Co because all reflections could be indexed to fcc Cu and hcp Co (Fig. 3(b)), which is basically consistent with equivalent reported compounds [26,27]. Elemental analysis by inductively coupled plasma spectroscopy indicated that the Cu:Co atomic ratio in the as-synthesized Cu–Co bimetallic nanoparticles was about 1:1.3, which is similar to the composition of the Cu/Co sample. The BET surface areas of the Cu/Co and Cu–Co catalysts were determined from N₂ sorption measurements, which are shown in Fig. 4. The surface area of the Cu/Co catalyst was 33.9 m²/g, which is much larger than that of the Cu–Co nanoparticle catalyst of 2.8 m²/g. This difference is mostly ascribed to the shape of the nanosheets; they spread out so that a large surface is exposed.

Cu–Co bimetallic nanoparticles were also used as a catalyst for CO hydrogenation and exhibited different catalytic performance compared to the Cu/Co catalyst (Table 2). Although higher temperatures were needed to enhance the selectivity for all alcohols, the CO conversion was much lower even at 300 °C using the Cu–Co nanoparticle catalyst, and hydrocarbons were the predominant products. In particular, the selectivities for methanol, ethanol, and higher alcohols did not increase with

Fig. 4. N₂ adsorption isotherms measured at –196 °C for Cu/Co (a) and Cu–Co nanoparticle catalysts (b).

temperature as they did for the Cu/Co catalyst. An increase of selectivity for CO₂ with temperature was found for the Cu–Co nanoparticles, which is consistent with reported results [25]. It is worthwhile to note that over the Cu–Co nanoparticle catalyst, no obvious change of the distribution of hydrocarbons occurred with temperature, and methane was always the major hydrocarbon product, which was not observed for the Cu/Co case. Overall, the Cu/Co catalyst exhibits better catalytic activity and higher selectivity for higher alcohols from syngas conversion than the corresponding Cu–Co bimetallic nanoparticles.

The superior performance of the Cu/Co catalyst versus the Cu–Co nanoparticle catalyst prompted us to explore their structure-dependent catalytic properties. Cu nanoclusters have

Fig. 3. TEM image (a) and XRD pattern (b) of Cu–Co bimetallic nanoparticles. The inset of (a) is the SAED pattern.

Table 2

Catalytic performance of Cu–Co bimetallic nanoparticles as a catalyst for selective hydrogenation of CO.

T/°C	X(CO)/%	Selectivity (C mol%)				ROH distribution (wt%)					HC distribution (wt%)				
		ROH	RCHO	CH _x	CO ₂	MeOH	EtOH	PrOH	BuOH	C ₅₊ OH	C ₁	C ₂	C ₃	C ₄	C ₅₊
260	3.8	1.8	trace	93.5	4.7	69.1	20.5	7.2	2.7	0.5	52.9	15.3	15.9	6.8	9.1
280	6.0	4.7	trace	87.3	8.0	75.6	19.3	4.2	0.9	0.0	54.1	14.9	15.0	6.9	9.1
300	9.4	15.2	0.2	66.0	18.6	70.4	20.9	6.0	1.9	0.8	55.9	14.2	14.0	7.1	8.8

Reaction conditions: 6.0 MPa, V(H₂)/V(CO)/V(N₂) = 65/32/3, GHSV = 10000 mL/(h·g).

Table 3

Catalytic performance of Co nanosheets as a catalyst for selective hydrogenation of CO.

$T/^{\circ}\text{C}$	$X(\text{CO})/\%$	Selectivity (C mol%)				ROH distribution (wt%)					HC distribution (wt%)				
		ROH	RCHO	CH_x	CO_2	MeOH	EtOH	PrOH	BuOH	C_{5+}OH	C_1	C_2	C_3	C_4	C_{5+}
260	12.8	7.0	trace	92.4	0.6	42.6	20.0	2.6	1.3	33.5	29.3	4.4	8.3	7.9	50.1
280	23.1	6.7	trace	90.6	2.7	40.5	41.1	2.3	0.4	15.7	34.9	5.1	8.2	7.4	44.4
300	25.8	4.5	trace	92.6	2.9	67.5	16.2	2.3	0.2	13.8	36.6	8.3	10.9	9.0	35.2

Reaction conditions: 6.0 MPa, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 65/32/3$, GHSV = 10000 mL/(h·g).

negligible catalytic ability for syngas conversion, whereas fresh Co nanosheets are a typical F-T catalyst, as shown in Table 3.

The higher catalytic activity of the Cu/Co catalyst can be partially ascribed to its larger surface area; however, this cannot account for the distributions of alcohols and hydrocarbons. In particular, the suppression of undesired products such as methane and methanol as well as the improved selectivity for higher alcohols over the Cu/Co catalyst compared with the Cu–Co nanoparticles led us to believe that the structure of the (111) facets of Cu nanoclusters supported on the (100) planes of Co nanosheets plays an important role in syngas conversion to higher alcohols. The cooperative contact at the interfaces of hcp Co(100) and fcc Cu(111) surfaces is believed to be responsible for the selectivity for higher alcohols. Somorjai et al. [28] proposed that catalytic selectivity is determined by the relative energy difference between the activation energy barriers in a multipath reaction. CO dissociation and hydrocarbon chain growth are favored on Co(100) nanosheets [7]. Longer chain alcohols and hydrocarbons are prevalent as products on Co because it is more metallic than Cu. Therefore, the role of the Cu(111) surface is to moderate the hydrogenation activity of the Co(100) surface to suppress formation of methanol and methane [29,30]. The close contact of the Cu(111) surfaces in fcc Cu nanoclusters with the Co(100) surfaces of hcp Co nanosheets here might enhance the interaction between Cu and Co atoms. Stable CH_x species are present at the interfaces between Co nanosheets and Cu nanoclusters. These species can undergo kinetically facile C–C chain growth or coupling reactions with CO or CH_x species to form higher alcohols and oxygenated hydrocarbons, respectively [31]. The synergy and packing configuration of Cu and Co atoms could change the electronic structure of the bimetal. We speculate that electron transfer might occur at the interface of Cu(111) and Co(100) facets, similar to electron transfer between a metal and oxide support [32]. Therefore, to further investigate this mechanism and prove CO and H_2 activation, we plan to perform density functional theory calculations of Cu/Co with CO and H_2 in the future.

4. Conclusions

A novel structure of Cu nanoclusters supported on Co nanosheets was fabricated using lysine as a surfactant template. The shape of the Cu/Co catalyst improves its activity for hydrogenation of CO, enhancing selectivity for higher alcohols and decreasing that for methane, which is in marked contrast to current Cu–Co bimetallic nanoparticle catalysts. This report demonstrates our ability to produce bimetallic nanocatalysts

with complex nanostructures with high surface area and stability, and defined morphology. The model Cu/Co catalyst synthesized here might not be practical as an industrial catalyst; however, the functional interface of Cu(111) surfaces with fcc structure and Co(100) surfaces with hcp structure in the Cu/Co catalyst makes a breakthrough in understanding the role of metal-metal interactions in catalysis. The novel design of this bimetallic catalyst bridges the gap between model catalyst and realistic catalytic applications, and should ultimately achieve a fundamental understanding of the mechanism of syngas conversion to higher alcohols.

References

- [1] Subramani V, Gangwal S K. *Energy Fuels*, 2008, 22: 814
- [2] Spivory J J, Egbeki A. *Chem Soc Rev*, 2007, 36: 1514
- [3] Herman R G. *Catal Today*, 2000, 55: 233
- [4] Kirubakaran V, Sivaramakrishnan V, Nalini R, Sekar T, Premalatha M, Subramanian P. *Renew Sustain Energy Rev*, 2009, 13: 179
- [5] Digman B, Joo H S, Kim D S. *Environ Prog Sustain Energy*, 2009, 28: 47
- [6] Dong X, Liang X L, Li H Y, Lin G D, Zhang P, Zhang H B. *Catal Today*, 2009, 147: 158
- [7] Gupta M, Smith M L, Spivory J. *ACS Catal*, 2011, 1: 641
- [8] Wang J J, Chernavskii P A, Khodakov A Y, Wang Y. *J Catal*, 2012, 286: 51
- [9] Fang K G, Li D B, Lin M G, Xiang M L, Wei W, Sun Y H. *Catal Today*, 2009, 147: 133
- [10] Courty P, Durand D, Freund E, Sugier A. *J Mol Catal*, 1982, 17: 241
- [11] Baker J E, Burch R, Hibble S J, Loader P K. *Appl Catal*, 1990, 65: 281
- [12] Shaheen W M, Ali A A. *Mater Res Bull*, 2001, 36: 1703
- [13] Subramanian N D, Balaji G, Kumar C S S R, Spivey J J. *Catal Today*, 2009, 147: 100
- [14] Zhang H B, Dong X, Lin G D, Liang X L, Li H Y. *Chem Commun*, 2005: 5094
- [15] Bailliard-Letournel R M, Gomez Cobo A J, Mirodatos C, Primet M, Dalmon J A. *Catal Lett*, 1989, 2: 149
- [16] Sheffer G R, Jacobson R A, King T S. *J Catal*, 1989, 116: 95
- [17] Baker J E, Bruch R, Niu Y Q. *Appl Catal*, 1991, 73: 135
- [18] Figueiredo R T, Granados M L, Fierro J L G, Vigas L, de la Pisona P R, Homs N. *Appl Catal A*, 1998, 170: 145
- [19] Mahdavi V, Peyrovi M H, Islami M, Mehr J Y. *Appl Catal A*, 2005, 281: 259
- [20] Tien-Zhao N, Zahedi-Niaki M H, Alamdari H, Kaliaguine S. *J Catal*, 2007, 245: 348
- [21] Shi L M, Chu W, Deng S Y, Xu H Y. *J Nat Gas Chem*, 2008, 17: 397
- [22] Xie X W, Li Y, Liu Z Q, Haruta M, Shen W J. *Nature*, 2009, 458: 746
- [23] Soumare Y, Garcia C, Maurer T, Chaboussant G, Ott F, Fievet F, Piquemal J Y, Viau G. *Adv Funct Mater*, 2009, 19: 1971
- [24] Jin M S, He G N, Zhang H, Zeng J, Xie Z X, Xia Y N. *Angew Chem Int Ed*, 2011, 50: 10560

Graphical Abstract

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Cu nanoclusters supported on Co nanosheets for selective hydrogenation of CO

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A catalyst consisting of Cu nanoclusters supported on Co nanosheets has a functional interface of Cu(111) surfaces and Co(100) surfaces and shows shape specificity in CO hydrogenation, enhancing selectivity for higher alcohols and decreasing that for methane.

[25] Boz I. *Catal Lett*, 2003, 87: 187

[26] Miranda M G M, Estevez-Rams E, Martinez G, Baibich M N. *Phys Rev B*, 2003, 68: 014434

[27] Meneghini C, Garcia Prieto A, Fdez-Gubieda M L, Mobilio S. *J Magn Magn Mater*, 2003, 262: 92

[28] Somorjai G A, Park J Y. *Angew Chem Int Ed*, 2008, 47: 9212

[29] Tien-Thao N, Zahedi-Niaki M H, Alamdari H, Kaliaguine S. *Appl Catal A*, 2007, 326: 152

[30] Gucci L, Boskovic G, Kiss E. *Catal Rev-Sci Eng*, 2010, 52: 133

[31] Lebarbier V M, Mei D H, Kim D H, Andersen A, Male J L, Holladay J E, Rousseau R, Wang Y. *J Phys Chem C*, 2011, 115: 17440

[32] Corma A, Garcia H. *Chem Soc Rev*, 2008, 37: 2096

铜纳米粒子负载于钴纳米片的双金属催化剂催化CO选择性加氢

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摘要: 使用赖氨酸作为表面活性剂模板, 合成了Cu纳米粒子负载于Co纳米片的双金属催化剂Cu/Co。与常规的Cu-Co双金属纳米颗粒催化剂相比, Cu/Co催化剂对CO选择性加氢反应表现出特殊的结构效应, 提高了CO转化率和高级醇选择性, 降低了甲烷选择性。Cu/Co催化剂中, Cu(111)面与Co(100)面相互作用的功能化界面有利于深入研究金属-金属的相互作用。这种双金属催化剂可以将模型催化剂和现实催化应用联系起来, 将有助于获得对合成气转化制高级醇反应机理的本质认识。

关键词: 铜纳米粒子; 钴纳米片; 双金属催化剂; 功能化界面; 一氧化碳加氢

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