

Preparation and characterization of ultrafine Fe-Cu-based catalysts for CO hydrogenation

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[Manuscript received May 23, 2008; revised September 4, 2008]

Abstract: The ultrafine particles of a new style Fe-Cu-based catalysts for CO hydrogenation were prepared by impregnating the organic sol of Fe(OH)₃ and Cu(OH)₂ onto the activated Al₂O₃, in which the organic sol of Fe(OH)₃ and Cu(OH)₂ were prepared in the microemulsion of dodecylbenzenesulfonic acid sodium(S)/*n*-butanol(A)/toluene(O)/water with $V(A)/V(O) = 0.25$ and $W(A)/W(S) = 1.50$. This catalyst was characterized by particle size analysis, XRD and TG. The results of particle size analysis showed that Fe(OH)₃ particles with a mean size of 17.1 nm and Cu(OH)₂ particles with an average size of 6.65 μm were obtained. TG analysis and XRD patterns suggested that 673 K is the optimal calcination temperature. CO hydrogenation produced C₂⁺OH with a high selectivity above 58 wt% by using the ultrafine particles as catalyst, and the total alcohol yield of 0.250 g·ml⁻¹·h⁻¹ was obtained when the contents of Al₂O₃ and K were 88.61 wt% and 1.60 wt%, respectively.

Key words: microemulsion; conductivity; ultrafine Fe-Cu-based catalyst; CO hydrogenation

1. Introduction

C₂⁺OH provides many advantages as a fuel alternative and an additive of gasoline. Yoshikazu Ito and his colleagues [1] have developed a new kind of gating membranes which would be applicable in the biofermentation process to produce ethanol, however membranes of this kind are sensitive to the concentration of ethanol and only 8 wt% of ethanol can be obtained. At present, most of C₂⁺OH are produced by the hydration of ethylene and propylene derived from naphtha. However, the world's petroleum supply will be exhausted in the near future, the other carbon resources, such as natural gas, coal, oil shale and tar sand are relatively abundant in view of the reserves, and these carbon resources can be easily converted into syngas by steam reforming. Therefore, to synthesize C₂⁺OH from syngas will be a promising alternative path.

Rh-based complexes are well known catalysts for the synthesis of C₂⁺OH from syngas [2,3] with high activity. However, it would be preferable to find some other active catalysts composed of inexpensive metals considering the high cost and limited availability of Rh. In recent years, great progress has been made in improving the activity of the catalysts composed of inexpensive metals, such as Fe [4], Co [5–7] and Cu [8,9] for the synthesis of C₂⁺OH from syngas. Among them, IFP Cu-Co catalysts are the most promising one for the synthesis

of alcohols from syngas with higher yield under mild reaction conditions. Although no catalyst has been claimed to be better than those developed by IFP, there still remain some drawbacks for the latter, such as the low selectivity to C₂⁺OH.

It was reported that the interaction between the metal-support molecules became stronger when the metal particle size decreased. There are several methods for the preparation of ultrafine particles. One way is to synthesize ultrafine particles in water-in-oil (w/o) microemulsion, which is transparent, isotropic, thermodynamically stable liquid media with nano-sized water droplets dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface. The surfactant-stabilized water droplets provide a microenvironment for the preparation of the ultrafine particles by exchanging their contents and preventing the excess aggregation of particles. Manuel Ojeda *et al.* [10] have successfully used microemulsions to prepare the nano-particles of Rh/Al₂O₃ catalysts for the CO hydrogenation reaction. The selectivity for oxygenation is increased with the decreasing of the Rh particle size. The microemulsion technology has been used to prepare Fe₂O₃ [11] also, but the microemulsion composition is still difficult to determine.

In this paper, we prepared the organic sol of Fe(OH)₃ and Cu(OH)₂ in w/o microemulsion of dodecylbenzenesulfonic acid sodium/*n*-butanol/toluene/water, and determined the w/o microemulsion composition *via* conductivity measurement.

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The ultrafine Fe-Cu-based catalysts were produced by impregnating the activated Al_2O_3 into the organic sol of $\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$. The catalytic performances in CO hydrogenation were reported and the influence of Al_2O_3 and K loading for the C_2^+OH synthesis were also discussed.

2. Experimental

2.1. General

The anion surfactant DBS, toluene, *n*-butanol, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaOH were all AR grade and used without further purification. The conductivity was measured using Shanghai Leici DDS11A conductivity meter (associating with DJS1 platinum black electrode). The particle sizes were determined on Malvern-3000 HS Model particle size analyser. X-ray diffraction (XRD) measurements were performed on a Bruker PW3040/60 Model X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). Thermal stability was measured with a Dupont TG-990 Model

thermogravimeter, and the adsorption amount was obtained from the weight loss at a constant heating rate of $20 \text{ K}\cdot\text{min}^{-1}$ in air flow.

2.2. Composition studies

The microemulsion system used in this study consisted of dodecylbenzenesulfonic acid sodium as a surfactant (S), *n*-butanol as an assisting-surfactant (A), toluene as the continuous oil phase (O), and either Fe^{3+} or Cu^{2+} precursor solution as the dispersed aqueous phase. In order to determine the maximum solubilizing power of the microemulsion, a series of solutions were made with a constant volume of O ($V(\text{O})$) and different weight ratios of A to S ($W(\text{A})/W(\text{S})$), or with a constant weight of S ($W(\text{S})$) and different volume ratios of A to O ($V(\text{A})/V(\text{O})$), and then the solutions were titrated by water at 313 K. The conductivity of the solutions was determined during the titrating and the results were correspondingly given in Table 1 and Table 2 respectively.

Table 1. Conductivity values of microemulsion with different $W(\text{A})/W(\text{S})$ ratios

$W(\text{A})/W(\text{S})$	Electrolytic conductivity for different volume of H_2O^* ($k \times 10^3/\text{S}\cdot\text{cm}^{-1}$)												
	0.0	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0	6.5	7.0	7.5	8.0
16.10	0.3	2.7	15.5	18.0	—	—	—	—	—	—	—	—	—
8.05	3.0	6.4	9.1	13.9	14.4	33.8	—	—	—	—	—	—	—
4.03	4.3	6.3	12.5	17.2	19.4	27.5	27.0	76.0	—	—	—	—	—
1.61	2.7	4.1	12.7	11.5	14.7	19.1	17.6	22.6	22.1	19.4	22.5	20.6	49.0
1.15	4.8	5.2	7.2	11.0	14.9	14.0	14.0	16.5	16.8	17.4	19.2	19.6	50.0
1.00	4.4	2.5	2.6	5.0	5.1	6.3	5.7	10.3	29.0	—	—	—	—

*Unit of H_2O volume is ml

Table 2. Conductivity values of microemulsion with different $V(\text{A})/V(\text{O})$ ratios

$V(\text{A})/V(\text{O})$	Electrolytic conductivity for different volume of H_2O^* ($k \times 10^3/\text{S}\cdot\text{cm}^{-1}$)												
	0.0	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0.50	2.7	4.1	12.7	11.5	14.7	13.1	12.6	12.7	14.4	42.5	—	—	—
0.33	1.8	1.7	2.8	4.1	4.2	4.5	4.7	7.5	8.7	8.7	94.0	—	—
0.25	1.6	1.8	1.5	1.9	1.6	2.4	2.6	2.7	4.2	4.8	6.8	9.7	141.0
0.20	0.3	0.2	0.8	2.3	2.5	1.6	4.1	3.9	6.7	7.4	69.0	—	—

*Unit of H_2O volume is ml

2.3. Preparation and characterization of ultrafine particles

Ultrafine particles of $\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$ were prepared using w/o microemulsions. The composition of the microemulsion system used in this work was determined as described in section 2.2. The surfactant concentration in toluene was 0.26 and the concentrations of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ in water were both $0.10 \text{ mol}/\text{dm}^3$. All the microemulsion systems were prepared by adding 40 ml precursor aqueous solution to 50 ml surfactant solution at 313 K. Then the temperature of the mixture was decreased to room temperature, and a NaOH solution was added dropwise into the mixture with stirring. The organic sol of $\text{Fe}(\text{OH})_3$ or $\text{Cu}(\text{OH})_2$ would appear on the top when the pH of the mixture was adjusted to 2.0–2.8 using HNO_3 . Then the mixture was delaminated, and the or-

ganic layer was collected. The solvent was removed under reduced pressure, then the ultrafine particles of $\text{Fe}(\text{OH})_3$ or $\text{Cu}(\text{OH})_2$ were obtained.

2.4. Preparation of ultrafine Fe-Cu-based catalysts and CO hydrogenation studies

The ultrafine Fe-Cu-based catalysts were prepared by impregnating quantitatively activated Al_2O_3 (200–300 mesh) into the corresponding volume of the organic sol of $\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$ with $W(\text{Fe})/W(\text{Cu}) = 10$ during 12 h, and then dried at 353 K overnight, and calcined at 673 K for 2 h. The calcined samples were pressed into disks and crashed through 20–40 mesh.

The CO hydrogenations were performed in a continuous flow system with a fixed-bed stainless steel reactor (6 mm *i.d.*,

operating a reaction with a blank reactor before the catalytic run) using 0.25 ml of catalyst. The air in the system was removed by a syngas flow prior to the reaction, the detailed program is as follows: the temperature was raised from room temperature to 423 K within 60 min and kept for 30 min, then raised to 523 K within another 60 min and maintained for 30 min, after that, the temperature was raised to 653 K within 60 min and held for 180 min. During the process, the total pressure in the system was kept at 4.0 MPa, the ratio of $n(\text{H}_2)/n(\text{CO})$ was 2.68 and the space velocity was 10000 h^{-1} . The gaseous products were passed through a heated line and then determined by gas chromatographs (MR-GC-80) (the influence of the wall of the reactor must be deducted from the data analysis).

3. Results and discussion

3.1. Composition

The stability of the microemulsion is very important in order to control the size of the metal particle, so the composition of the microemulsion with the largest solubilizing power must be established at first. According to JF Fang's percolation and effective medium theories [12], the conductivity of a w/o microemulsion system should increase rapidly to a much higher level when the system reached the largest solubilizing power. As shown in Table 1 and Table 2, the microemulsion system reached the largest solubilizing power when $W(\text{A})/W(\text{S}) = 1.61 - 1.15$ and $V(\text{A})/V(\text{O}) = 0.25$. The microemulsion properties were investigated when $W(\text{A})/W(\text{S}) = 1.50$ and $V(\text{A})/V(\text{O}) = 0.25$, the results showed that the microemulsion system was stable under the given conditions, the microemulsion droplets were too fine to be observed by the microscope. The results suggested that the microemulsion system is suitable for the preparation of ultrafine particles when $W(\text{A})/W(\text{S}) = 1.50$, $V(\text{A})/V(\text{O}) = 0.25$.

3.2. Characterization of ultrafine particles

As seen in Figure 1, the particle-size distribution of the organic sol of $\text{Fe}(\text{OH})_3$ was narrow in all runs with a mean size of 17.1 nm. Whereas the particle-size distribution of the organic sol of $\text{Cu}(\text{OH})_2$ was wider with an average size of $6.65 \mu\text{m}$.

The XRD results (partially shown in Figure 2a) showed the composition change of Fe, Cu samples with the increasing calcination temperature. The $\text{Fe}(\text{OH})_3$ aggregated after being calcined for 2 h at 523 K with amorphous structure (Figure 2a(1)). The crystallinity was detected after calcining for 2 h at 623 K, the characteristic peaks of the Fe_3O_4 structure at 32.94° , 43.32° , 63.74° (2θ) had been marked (Figure 2a(2)). With the calcination temperature up to 673 K, the peaks became stronger, and the typical XRD pattern corresponding to the pure Fe_2O_3 structure was observed (Figure 2a(3)). The XRD patterns of ultrafine Cu samples were given in Figure 2b. The diffraction peak at 21.34° emerged after 2 h of calcina-

tion at 523 K, which corresponded to the characteristic peak of CuOOH structure (Figure 2b(1)). After calcining for 2 h at 623 K (Figure 2b(2)), the characteristic peaks of the CuO structure at 32.52° , 35.50° and peaks of Cu_2O structure at 36.62° , 61.54° dramatically increased except the characteristic peak 21.34° of CuOOH . Finally the peaks of CuO structure became stronger and the peaks of Cu_2O structure disappeared after the calcination temperature rose to 673 K (Figure 2b(3)). This suggested that the Cu samples were completely dehydrated and oxidized to CuO after being calcined for 2 h at 673 K.

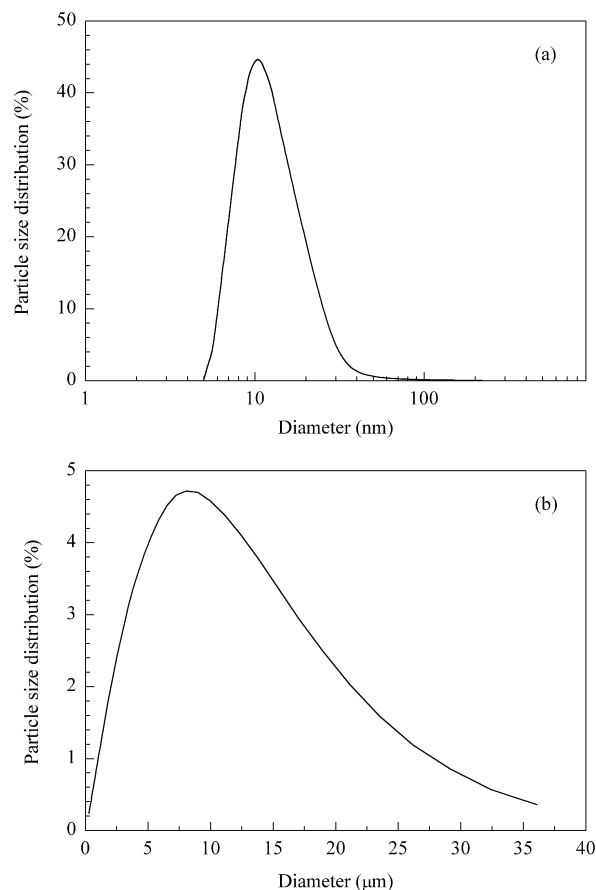


Figure 1. Particle size distribution of ultrafine $\text{Fe}(\text{OH})_3$ (a) and $\text{Cu}(\text{OH})_2$ (b) prepared by w/o microemulsion technique

TG results indicated that the thermal stability of both species were similar. As shown in Figure 3, there was a slow decline of weight with the increasing of temperature from room temperature to 508 K, which corresponded to the volatilization of the water remaining in the powders. The sharp weight loss occurred from 508 to 525 K indicated the decomposition of the surfactant. Above 525 K, the weight loss should stand for a series of dehydration and chemical reaction process of the precursor. The reaction process of Fe sample is complicated as Fe can provide several valences. As shown in Figure 3(1), several turning points appeared on the weight loss curve, and all the reactions were completed at 647 K. The reaction process of Cu sample was simple, so the weight loss

was continuous and nearly linear until 715 K (Figure 3(2)). As illustrated in XRD results, the Cu species have already existed in the reacting valence to the CO hydrogenation at 673 K. The difference between TG and XRD for the Cu species was due to too much surfactant remained in the Cu sample. In view of the effect of the calcination temperature on the aggregation of the ultrafine particles, 673 K was chosen to be the optimum calcination temperature for Fe-Cu-based catalysts.

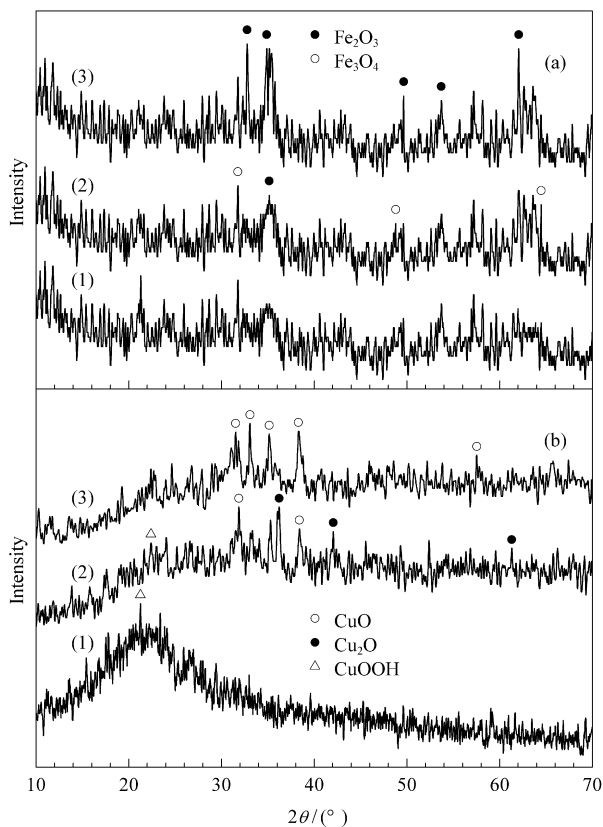


Figure 2. X-ray diffraction patterns of Fe samples (a) and Cu samples (b) calcined at different temperature: (1) 523 K; (2) 623 K; (3) 673 K

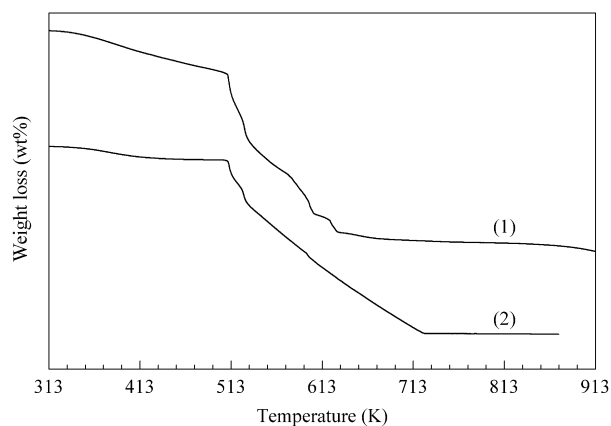


Figure 3. TG analysis of Fe(OH)₃ (1) and Cu(OH)₂ (2) ultrafine particles

3.3. Effect of Al₂O₃ amount and K loading on catalytic behavior

In order to investigate the effect of Al₂O₃ amount on the catalytic behavior, the Al₂O₃ amount was changed within the range of 80 wt%–90 wt% according to the reference [13]. The selectivity and the yield of C₂⁺OH in total alcohols of the catalysts with different Al₂O₃ amount were shown in Table 3. The C₂⁺OH selectivity was improved with the increase of Al₂O₃ amount. The yield of total alcohols almost kept invariably with the increase of Al₂O₃ amount when the Al₂O₃ amount was lower than 88.61%, but it decreased quickly with the Al₂O₃ loading further increased. That is to say, when Al₂O₃ amount was about 88.61%, the catalyst exhibited the maximum C₂⁺OH yield in total alcohols and a preferable selectivity.

Table 4 shows the effect of K (CH₃COOK as an additive: weighing the given amount of CH₃COOK, dissolving into the organic sol of Fe(OH)₃ and Cu(OH)₂, then impregnating the activated Al₂O₃ in the same way as the method of preparation in Experimental 2.3) loading on the catalytic performance

Table 3. Catalytic behavior of the ultrafine Fe-Cu/Al₂O₃ catalysts with different Al₂O₃ loading when time-on-stream is 60 min

Al ₂ O ₃ loading (wt%)	Yield (g·ml ⁻¹ ·h ⁻¹)	S _{C₂⁺OH} (wt%)	Distribution of alcohols (wt%)						
			Methanol	Ethanol	Isopropanol	Propanol	Isobutanol	Butanol	Pentanol
81.63	0.149	44.76	55.24	24.55	3.78	6.24	4.22	5.97	–
84.74	0.147	45.33	54.67	26.28	4.75	7.27	4.04	2.99	–
85.94	0.140	48.05	51.95	28.05	4.13	7.46	3.83	4.57	–
88.61	0.154	59.84	40.16	37.48	0.32	12.14	1.05	8.17	1.68
89.29	0.044	62.27	37.73	31.91	–	30.36	–	–	–

Reaction condition: 653 K, 4.0 MPa, n(H₂)/n(CO) = 2.68, SV = 10000 h⁻¹

of the ultrafine Fe-Cu-based catalysts with Al₂O₃ loading of 88.61wt%. It was shown that the yield of total alcohols increased obviously although C₂⁺OH selectivity almost kept constant when a small quantity of K was loaded into the catalyst. The catalyst exhibited a highest C₂⁺OH selectivity of 58.8 wt%, and a maximum total alcohol yield of 0.250 g·ml⁻¹·h⁻¹ when the K loading was 1.60 wt% (the percentage composition of CH₃COOK in the catalyst).

Hayashi *et al.* [14] suggested that the amount of metal oxide species remaining after reduction is in accordance with that of the activity and the C₂⁺OH selectivity. The sequence of the amount of metal oxide species is as follows: the catalysts with small metal particles are greater than the catalysts with large metal particles. Perhaps this is why the ultrafine catalysts show a high activity and C₂⁺OH selectivity, as described in Tables 3 and 4.

Table 4. Catalytic behavior of the ultrafine Fe-Cu/Al₂O₃ catalysts with different amount of CH₃COOK when time-on-stream is 60 min

K weight (wt%)	Yield (g·ml ⁻¹ ·h ⁻¹)	S _{C₂OH} ⁺ (wt%)	Distribution of alcohols (wt%)						
			Methanol	Ethanol	Isopropanol	Propanol	Isobutanol	Butanol	Pentanol
0.81	0.212	62.76	37.24	24.31	2.07	20.78	4.24	11.36	–
1.23	0.223	59.62	40.38	26.35	1.97	18.44	3.17	9.69	–
1.60	0.250	58.83	41.17	29.54	1.40	17.91	2.97	7.02	–
2.02	0.244	51.37	48.63	29.83	1.52	12.04	–	5.24	–

Reaction condition: 653 K, 4.0 MPa, $n(\text{H}_2)/n(\text{CO}) = 2.68$, $\text{SV} = 10000 \text{ h}^{-1}$

4. Conclusions

The Fe(OH)₃ and Cu(OH)₂ ultrafine particles have been synthesized in the microemulsion of DBS/*n*-butanol/toluene/water (w/o). When $V(\text{O})$ or $W(\text{S})$ was a constant, the composition of the given microemulsion system was conveniently determined by measuring the conductivity of samples with different amount of H₂O *via* adjusting the ratio of $W(\text{A})/W(\text{S})$ and $V(\text{A})/V(\text{O})$, respectively. The results of the particle size analysis showed that a narrow size distribution of Fe(OH)₃ particles with a mean size of 17.1 nm and Cu(OH)₂ particles with an average size of 6.65 μm were obtained.

The ultrafine Fe-Cu-based catalysts prepared by impregnating Al₂O₃ into the organic sol of Fe(OH)₃ and Cu(OH)₂ were highly active for the C₂OH synthesis in CO hydrogenation. The additive of Al₂O₃ and K influenced the catalytic behavior significantly.

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