Coprecipitation preparation of copper -cobalt based catalysts for higher alcohol production

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Abstract: A series of K modified copper-cobalt based catalysts were prepared using step by step continuous coprecipitation method, and the catalytic performance of the catalysts was investigated. The experimental results showed that the catalyst exhibited the best activity, CO conversion, the yield of C_2+OH in liquid products and the mass fraction of C_2+OH was 65.74%,0.062 g·(mL·h)-I and 18.95%, respectively, under the condition as follows: mass ratio of cobalt to copper 1:1, K_2CO_3 loading mass fraction 1%, pH=7.2 and reaction temperature 310 ℃.

Keywords: catalyst engineering; higher alcohol; coprecipitation; copper-cobalt based catalyst

1. Introduction

Since the beginning of the 20th century, oil resources have been exhausted, and the future energy structure will be dominated by coal and natural gas. From natural gas or coal to syngas (CO+H_2) selective catalytic synthesis of low carbon mixed alcohol (C_2OH) is one of the important ways of clean utilization of coal resources. C_2+OH can be used as an additive and gasoline, instead of methyl tert-butyl ether to improve the gasoline octane value, methanol, ethanol, propanol, butanol and pentamol, used as solvent and esterification solvent, can also be used as raw material for chemical products. Making C_2+OH from syngas has become a research hotspot in the field of energy and chemical industry at home and abroad, and a variety of synthetic C_2+OH catalysts [1,2] have been developed. The concentrated catalysts mainly include modified methanol synthesis catalyst, copper-cobalt-based catalyst and MoS_2 -based catalyst. Among them, copper / cobalt-based catalyst is regarded as a promising synthetic C_2+OH catalyst [3-5] due to its mild operating conditions and high catalytic activity.

In this paper, a series of K-modified copper-cobalt-based catalysts were prepared to investigate the influence of cobalt-copper mass ratio, K_2CO_3 mass fraction, pH value and reaction temperature on the catalyst activity.

2. Experimental section

2.1. Reagents and instruments

$Cu(NO_3)_2\cdot 3H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, anhydrous K_2CO_3, $Al(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2\cdot 6H\ _2O$.HPMR-1822 high pressure microreverse device, BLS-J15 stirring reactor, ZK270N centrifuge, Agilent 6820 gas chromatograph, DB205 electric blast drying box, maver furnace.

2.2. Chromatographic conditions

Capillary column, HP-INNOWAX,30m×0.32mm 0.5μm, detector for hydrogen flame ion detector, carrier gas for helium, purity 99.999%, sample volume 0.2μL, inlet temperature 250℃, column box temperature, 40℃ for 2min, rise to 230℃ at 10℃·min^{-1}, hold for 2min, 5℃·min^{-1}Up to 250℃ and maintain for 5min.

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2.3. Catalyst preparation

Step 1, fixed proportion of aluminum nitrate, zinc nitrate and potassium carbonate solution, fully stir dissolved, preheat, add the reaction kettle, fully reaction to the production of no obvious bubbles, stand for 45min; step 2 continue to prepare a certain proportion of copper nitrate, cobalt nitrate, zinc nitrate, aluminum nitrate, stirring rate, 45min, remove the slurry. Was washed with 75℃ deionized water until the K * mass fraction in the slurry was less than 0.02%.

To load quantitative K * on the catalyst, the corresponding content of K_2CO_3 solution was prepared as slurry. After the centrifuge, the material was dried in a 120℃ oven for 12h, roasted in a 400℃ mav furnace for 4h, mixed and pressed.

2.4. Evaluation of the catalytic activity of the catalyst

Using HPMR-1822, place 4mL (20-20) catalyst in the reaction tube and adjust the reaction gas with CO and H_2 through a flow meter. The temperature of catalyst bed is controlled by intelligent program heating instrument, and K-type thermocouple temperature measurement.1%H_2 was raised through the reaction tube to 300℃ at 1.0℃ · min^{-1}heating rate, stabilized for 4h, cooled to 200℃, and increased the pressure to be detected. The liquid phase products were detected by a hydrogen flame ion detector.

3. Results and Discussion

3.1. Cobalt-copper mass ratio

Mahdavi V et al. [6,7] showed that the copper-cobalt oxide in the catalyst consists of CuO, Co_3O_4 and Cu-Co spinel. In the syngas reaction medium, Cu-Co spinel is consumed to produce highly separated Cu-Co clusters, which is the active site formed by alcohol, and Cu-Co interaction promotes oxide reduction. Copper-cobalt-based catalysts have properties such as small particle size, large specific surface area and highly dispersed active components. When the mass of cobalt-copper is relatively low, a single spinel structure can be formed. With the increase of cobalt-copper mass ratio, the thermal stability of Cu-Co spinel structure decreases, and CuO is easy to precipitate. The deposition-precipitation catalyst was prepared without loading K*, and the catalytic performance were investigated. After the reduction of the catalyst, the system was boosted to 5MPa and switched to reaction gas with an air speed of 5000h-1. The effects of the cobalt-copper mass ratio in the catalyst on the C_2 + OH yield and its mass fraction in the liquid phase products are shown in Table 1.

Table 1 Effect of mass ratio of cobaltto copper in the cataly stson they ield and the mass fraction of C_2, OH in liquid products

Cobalt-copper mass ratio	C_2 + OH yield / g · (mL·h) -l	o(C $_2$.OH)/%
0	0.004	0.01
1:9	0.018	5.64
1:3	0.029	14.22
1:1	0.048	16.85
3:1	0.031	13.17

As shown in Table 1, the Cu-Co interaction has a significant effect on the catalyst performance, with zero cobalt content, C_2, and extremely low OH content. With the increase of cobalt-copper mass ratio, the OH mass fraction in the liquid phase product increases significantly; when the cobalt-copper mass ratio exceeds 1:1, the OH mass fraction in the liquid phase product decreases, and the appropriate cobalt-copper mass ratio is 1:1.

3.2. Potassium salt load amount

Boz It is believed that alkali metal is the promoter of low carbon mixed alcohol, and the addition of appropriate alkali metal can form the catalytic active center, improve the physical structure and properties of the catalyst, improve the activation performance of CO, and increase the selectivity of C_2+OH. Liu

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Jinyao et al. [8] found that the surface structure of the catalyst was severely damaged, the Cu distribution was uneven, the specific surface area decreased, and the catalytic performance was reduced.

After the reduction of the catalyst, the system was boosted to 5MPa and switched to reaction gas, with an air speed of 5000h^{-1}. Under the condition of 1:1 cobalt-copper mass ratio, the influence of K_2CO_3 mass fraction on the yield of C_2+OH and its mass fraction in the liquid phase products was investigated. The results are shown in Table 2.

Table 2 Effects of K_2CO_3 mass fractionon they ieldand the mass fraction of C_2,OH in liquid products

w(K_2CO_3)/ %	C_2 + OH yield / g·(mL·h)-	w(C_2+OH)/ %
0	0.021	10.44
0.2	0.043	14.68
1	0.062	18.95
10	0.034	13.38
32	0.014	10.45

As can be seen from Table 2, the addition of K_2CO_3 has a significant effect on the C_2 + OH yield and its mass fraction in the liquid products. With the increase of K_2CO_3 mass fraction, the C_2 and OH production and its mass fraction increase; when the K_2CO_3 mass fraction exceeds 1%, the yield and C_2 and OH mass fraction decrease, and the best K_2CO_3 mass fraction occurs for 1%.

3.3. PH value

Under the condition of cobalt-copper mass ratio of 1:1 and K_2CO_3 mass fraction of 1%, the influence of pH value on the mass fraction of C_{24}OH in the liquid phase product was investigated, and the results are shown in Figure 1.

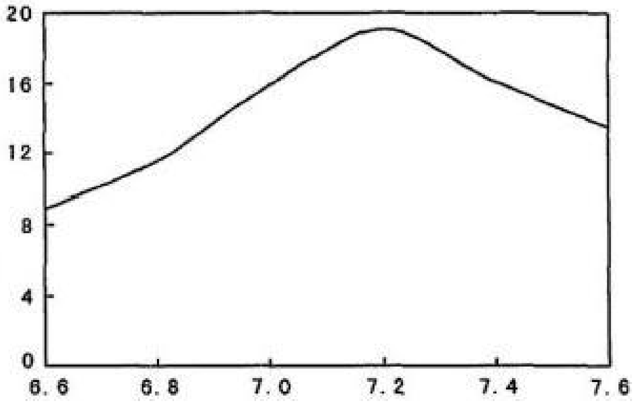

Figure1 Effects of pH values on C_2.OH mass fraction in liquid products

As can be seen from Figure 1, the catalyst prepared under acidic conditions, C_2, low OH mass fraction in the liquid phase product, at pH=7.2, the C_2 + OH mass fraction reached the maximum, the best catalyst performance.

3.4. Reaction temperature

Under the condition of cobalt-copper mass ratio 1:1 and K_2CO_3 mass fraction 1%, the influence of reaction temperature on CO conversion was investigated, and the results are shown in Figure 2.

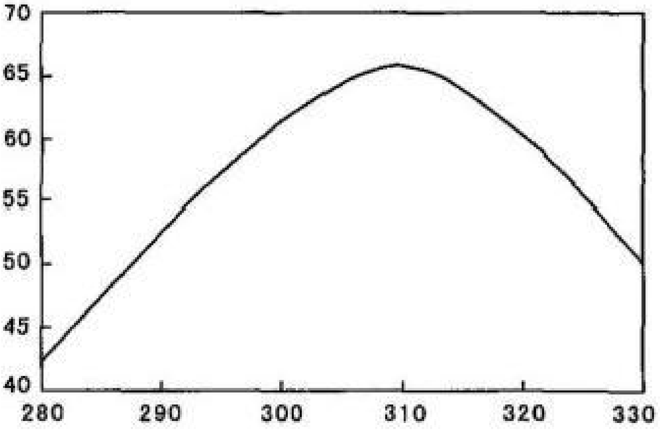

Figure2 Effect of reaction temperatures on syngas conversion

As can be seen from Figure 2, as the reaction temperature increases, the CO conversion rate increases, the reaction temperature rises to 310 °C, and the CO conversion rate reaches 65.74%; if the reaction temperature increases, the CO conversion rate decreases. The reaction was performed at 310°C.

4. Conclusion

Under the cobalt-copper mass ratio of 1:1, K_2CO_3 mass fraction 1%, pH=7.2 and reaction temperature 310°C, the catalyst performance was the best, the CO conversion was 65.74%, the C_2 + OH mass fraction in the liquid product was 18.95%, and the C_{24}OH yield was 0.062g·(mL· h).

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