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Highly Dispersed Cu-Base Catalyst Derived from Layered Double Hydroxides for CO Hydrogenation

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Abstract

Highly dispersed Cu-base catalyst has been prepared via thermal decomposition of layered double hydroxides precursors. The XRD pattern and the HRTEM images of the as prepared catalyst confirmed the high dispersion of Cu and Fe ions. Results show that the catalyst has a relatively high selectivity of alkanes at low temperature.

Keywords

Highly Dispersed, LDHs, CO Hydrogenation, Cu Base

1. Introduction

Cu-based catalysts containing active metal toward Fischer-Tropsch synthesis such as Cu-Fe based catalyst, is considered as one of the most promising catalysts for higher alcohols synthesis from syngas [1-3]. Most researchers considered the synergistic effect between Cu and Fe played a key role in the higher alcohol synthesis (HAS) [4]. However, the copper sintering at higher temperature has a negative influence on the synergistic effect. In the layer structure of the layered double hydroxides (LDHs), metal ions mixed with each other homogeneously [5], which might facilitate the synergetic effect of the active metal particles and inhibit the sintering of the metals. Thus, in this paper catalyst derived from layered double hydroxides containing highly dispersed Cu has been prepared by hydrothermal method and its application in the CO hydration has been examined.

2. Experiments

Highly dispersed Cu-base catalyst was prepared according to the reference [5] with some modification. In a typical process, 1.21 g $Cu(NO_3)_2 \cdot 3H_2O$, 2.02 g $Fe(NO_3)_3 \cdot 9H_2O$, 5 g $Al(NO_3)_3 \cdot 9H_2O$ and 12.8 g $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved together in 400 mL deionized water (molar ratio, MII/MIII = 3), which was referred as solution A. Solution B was the mixture of K_2CO_3 and KOH with concentration of 0.25 and 0.8 mol/L. Solutions A and B

were simultaneously added into a glass reactor under vigorous stirring at room temperature and a pH value of 9.5.

The slurry was aged at 393 K for 20 h, filtered off, and washed thoroughly with distilled water. The precipitate was then dried at 353 K for 12 h and identified as CuFe-LDH. The layered structure of prepared CuFe-LDH sample was confirmed by XRD (see **Figure 1**).

These Cu-containing layered double hydroxides were calcined at 573 K in a stationary air for 4 h and the product catalysts were identified as CuFeMgAl. The catalytic performance was tested in a fixed-bed reactor.

3. Results and Discussions

The XRD patterns of the precursor before and after calcination are shown in **Figure 1**. The XRD patterns before calcination illustrate the typical peaks for LDHs. Peaks at 11.6, 23.3, 34.7, 39.3, 46.7, 60.5, and 61.8 are observed in the precursor, which are assigned to the (003), (006), (012), (015), (018), (110), and (113) diffractions of LDHs.

Further more, from the XRD pattern no clear peaks of Cu , Fe or CuFe oxide species are found which mean that the Cu and Fe ions are highly dispersed in the precursor. After calcination, peak at 13 was assigned as the remain layered structure and peaks at 60.5 and 61.8 are the remain structure of LDHs within the layers which we can also see at **Figure 2(b)**.

Figure 2(a) shows the cross-section of layered platelet in CuFeMgAl, from which it can be found that the layered structure of hydrotalcite. Agreed with the result of XRD pattern, no Cu or Fe oxide particles can be found in the plates which indicate the highly dispersion of metal ions in the LDHs.

The catalytic performance of the catalyst towards CO hydrogenation was examined under the following reaction conditions: 4.0 MPa, GHSV of 5000 h^{-1}, $n(H_2)/n(CO) = 2.0$ and the results are shown in **Table 1**. It could be seen that the main products at low temperature was alkanes with selectivity of 93.8 wt.%. Along with the rise of temperature, the selectivity of alkanes fall down and the selectivity of alcohols changed from 1.09 wt.% at
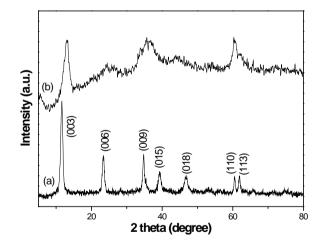

Figure 1. XRD patterns of the precursor before (a) and after (b) calcinations.
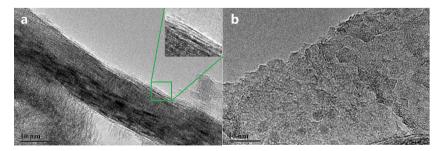

Figure 2. Layered structure of the calcinlated sample, stand up (a) and lie down (b).

Table 1. Catalytic results of layered double hydroxides (LDHs) supported catalyst.

Catalyst	T(K)	CO conversion (%)	STY$_{ROH}$	Selectivity (wt.%)			Alcohol distribution (wt.%)	
			(g/g/h)	ROH	CHn	CO$_2$	C1OH	C2 + OH
CuFeMgAl	493	8.05	0.00	1.09	93.80	5.11	59.61	40.39
	513	19.39	0.01	3.28	83.86	12.86	61.47	38.53
	533	32.28	0.06	9.91	67.79	22.30	58.86	41.14
	553	54.99	0.11	9.04	54.03	36.93	53.63	46.37

Reaction conditions: H$_2$/CO = 2.0, GHSV = 5000 h^{-1}, P = 4.0 MPa.

493 K to 9.91 wt.% at 533 K. And at 553 K the selectivity of alcohols slightly fell may be due to the sintering of Cu.

4. Conclusion

In summary, this work confirmed that bimetallic highly dispersed Cu-base catalysts could be prepared via thermal decomposition of layered double hydroxides precursors. This is attributed to the layered structure of hydrotalcite which could efficiently inhibit the sintering of the Cu and Fe ions. Furthermore, at low temperature the main products of the catalyst were alkanes and as temperature grows the selectivity of alcohols becomes higher.

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