The Effect of Neodymia on the Activity of Hydrocarbon Synthesis Catalysts from Carbon Dioxide

Xin Ying LIU, Guo Cai DENG*, Yun Ti CHEN

Department of Chemistry, Nankai University, Tianjin 300071

Abstract: In this paper, neodymia was added into hydrocarbon synthesis catalysts by solid-mixing method to improve the activity of hydrocarbon synthesis catalyst from carbon dioxide. 0.1% Nd_2O_3 can improve the carbon dioxide conversion and light olefin selectivity at 523 and 573K, but decrease the activity at 623K.

Keyword: Neodymia, hydrocarbon synthesis, carbon dioxide hydrogenation

In recent years, iron base catalysts were used for carbon dioxide hydrogenation to light olefin at high pressure[1-4] and at normal pressure, Fe-Co bimetallic catalyst shows good carbon dioxide hydrogenation activity to light olefin[5,6]. Although hydrocarbon is thermodynamic favored than that of carbon monoxide at lower temperature, the catalysis activity of Fe-Co bimetallic catalyst is not high enough for hydrocarbon synthesis. In this paper, neodymia was added into the catalyst to improve its activity and light olefin selectivity.

The Fe-Co bimetallic catalysts were prepared by co-precipitation method with the molar ratio of Fe to Co as 2. A mixed aqueous solution of metal nitrates and an aqueous solution of NaOH were added dropwise to distilled water under string. The resulted precipitate was aged 24 hours and filtered out, washed with distilled water and dried in air at 393K for 12 hours and then calcined in air at 673K for 6h. The catalysts modified with neodymia were prepared by mixing the neodymia with this catalyst precursor. The modified catalysts were calcined again in air at 673K for 6 h and then meshed into 100~120 mesh. Before reaction, the catalyst was reduced in a pure hydrogen flow at 623K.

The hydrogenation of carbon dioxide was conducted at 523, 573 and 623K in a fixed bed reactor by feeding a gas mixture of H_2 and CO_2 with the H_2/CO_2 malor ratio of 3. The products were analyzed by a Gas Chromatograph (SP 2305) with two column system, a TDX-01 column to separate the carbon oxides and methane, a squalane/γ-Al_2O_3 column to separate hydrocarbon, the detector was TCD. Results were listed in **Table 1**.

With the addition of neodymia, the carbon dioxide conversion increased slightly, although the selectivity to hydrocarbon changed differently on different neodymia content and reaction temperature. When only 0.1% neodymia was added, light olefin appeared in the carbon dioxide hydrogenation products at 523K although carbon monoxide was the only product when neodymia was not used, that is to say, the addition of small amount of neodymia increased the selectivity to light olefin at this temperature. At 573K, the selectivity to light olefin and the paraffin on the 0.1% neodymia modified catalyst was also higher than that on the unmodified catalyst, but at 623K, the yields of olefin dropped to 0.7%, although it was 2.3% on the unmodified catalyst. With the increase of the amount of neodymia, the carbon dioxide conversion and the selectivity to light olefin all decreased. The characterization of these catalysts is in progress.

Table 1. Effect of neodymia as additives on catalyst performance

Nd_2O_3 wt%	Reaction Tempera-ture(K)	Conver-sion of CO_2(%)	Selectivity(%)						Yield of light olefin(%)	Ratio of olefin to paraffin
			CO	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8		
0	523	8.1	100	0	0	0	0	0	0	-
	573	16.2	87.9	4.9	2.9	0.6	3.6	0.2	1.0	8
	623	24.1	77.0	11.5	4.6	1.5	4.7	0.7	2.3	5
0.1	523	12.9	89.2	8.1	1.7	0.2	0.8	0.0	0.3	17
	573	25.6	84.4	8.0	3.7	0.5	3.4	0.0	1.8	14
	623	32.8	89.7	7.8	1.6	0.3	0.6	0.1	0.7	6
0.5	523	10.3	98.6	3.2	0	0	0	0	0	-
	573	24.5	91.2	12.0	3.5	0.5	2.8	0.1	1.5	11
	623	32.1	88.3	8.6	2.0	0.3	0.9	0	0.9	10
1.0	523	7.9	100	0	0	0	0	0	0	-
	573	21.6	88.9	5.9	3.3	0.4	1.2	0.2	1.0	7
	623	30.0	93.6	4.4	1.6	0.3	0	0	0.5	6

The Base catalyst component: Fe-Co with molar ratio of 2:1
Reaction condition: 0.1MPa, H_2/CO_2 =3 (vol), SV=5000 ml g^{-1} h

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