

Effects of the addition of ethylene on cobalt catalysts in carbon monoxide hydrogenation

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Abstract

The synthesis of hydrocarbons from catalytic hydrogenation of ethylene and carbon monoxide was investigated over Co/ alumina, Co/NaY and Co/NaX catalysts . These catalysts were characterized by hydrogen chemisorption, X-ray diffraction (XRD), and temperature-programmed reduction. The type of support had pronounced effects on the activity and selectivity of cobalt. Carbon monoxide hydrogenation and ethylene hydroformylation share some mechanistic features, CO insertion and metal-carbon bond hydrogenation. The addition of ethylene increased the the selectivity for the hydroformylation over hydrogenation under different support, the catalytic activity was reduced. It was found that the acidity of the zeolites could modify the catalytic properties by increasing CO conversion and increasing the selectivities for olefins formation.

Keywords: carbon monoxide hydrogenation

1 Introduction

The major disadvantage of classical Fischer-Tropsch (FT) synthesis is that it produces a broad range of hydrocarbons from methane to waxes. The development of cobalt catalysts for the FT reaction has been studied extensively. Evidence has shown that molecular sieve zeolites can influence the cobalt metal particle size and also its activity and selectivity. Hydroformylation of alkenes is an important chemical process. We proposed the addition of ethylene on cobalt catalysts in carbon monoxide

hydrogenation to form oxygenated compounds. [1-3].

2 Experimental

All catalysts were prepared by an impregnation method of 4 wt% of cobalt on alumina, NaY, and NaX different support with an aqueous solution. After impregnation, The samples were dried in air at 675K for 12 h. These catalysts were characterized by hydrogen chemisorption and X-ray diffraction measurement (XRD) were applied to determine the dispersion of cobalt particle. The temperature-programmed reduction (TPR) was also used. A study of the catalyst activity and selectivity was conducted under typical FT reaction conditions. Ethylene hydroformylation was carried out in a conventional fixed-bed flow reactor. After reduction of catalyst in hydrogen stream, a mixed gas (ethylene+ syngas) was introduced and then the reaction was started.

3 Results and discussion

Table1: Reaction rate and activation energy

Catalyst	r_{HC}	r_{HC}^* (umole/g.cat.sec)	Eact	Eact*(Kcal/mole)
Co/alumina	4.94	6.22	20.36	11.13
Co/NaX	0.42	4.02	30.80	8.41
Co/NaY	0.14	3.94	21.90	7.76

*: Feed=H₂/CO/C₂H₄

Table2: Product distribution

Catalyst	C1	C2	C3	C4	C5+	MEOH	HCHO
Co/Alumina	70.2	9.19	13.1	5.16	0.60	0.20	1.55
Co/Alumina*	36.5	40.2	11.6	5.99	3.99	1.67	0.05
Co/NaX	41.2	10.7	16.6	11.4	4.72	0.26	15.12
Co/NaX *	4.23	87.2	3.70	2.96	1.84	0.02	0.05
Co/NaY	40.0	8.54	9.91	6.03	15.7	1.71	18.11
Co/NaY*	19.4	68.9	4.91	2.71	2.18	1.59	0.31

*: Feed=H₂/CO/C₂H₄

The temperature-programmed reduction spectra indicated that there is some interaction between cobalt particle and support. The particle sizes were calculated from cobalt dispersion measured by hydrogen chemisorption, and it corresponded to the values observed by XRD line broadening method. As shown in Table1, CO hydrogenation was examined using several modified catalysts which could be compared to the ethylene hydroformylation. The addition of ethylene in CO hydrogenation increased the reaction rate. And decreased the methane selectivity in CO hydrogenation product distribution.

4 Conclusion

The type of support had pronounced effects on the activity and selectivity of cobalt. Carbon monoxide hydrogenation and ethylene hydroformylation share some mechanistic features, CO insertion and metal-carbon bond hydrogenation. The addition of ethylene increased the selectivity for the hydroformylation over hydrogenation

under different support, the catalytic activity was reduced. It was found that the acidity of the zeolites could modify the catalytic properties by increasing CO conversion and increasing the selectivities for olefins formation.

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