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Effect of support and promoter on the catalytic performance and structural properties of the Fe–Co–Ni catalysts for CO hydrogenation

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ABSTRACT

Co-precipitated Fe–Co–Ni catalysts were tested for production of light olefins via Fischer–Tropsch synthesis. The effects of different supports such as Al_2O_3, SiO_2, TiO_2 and MgO and subsequently the effect of optimum support loading and also the effect of different promoters including Li, Cs, K, Rb and Ru on the catalytic performance and structure of Fe–Co–Ni catalyst were investigated. It was found that the Fe–Co–Ni catalyst containing 10 wt% MgO has shown the better catalytic performance for FTS. The yield of methane, ethylene, propylene and C_4^+ olefins were calculated and reported. Characterization of the catalyst precursors and calcined samples was carried out using XRD, SEM, EDS and BET.

1. Introduction

Fischer–Tropsch synthesis (FTS) is an important technology in the production of liquid fuels and chemichals from syngas (Anderson and Firth ed, 1984). Most group VIII metals such as Fe, Co, Ni and Ru have measurable activity in CO hydrogenation but yield different products, including hydrocarbons, alcohols, acids and esters. Iron-based catalysts are useful for the production of olefins and branched hydrocarbons, depending upon process conditions employed, and have been successfully applied in the industrial process when the H_2/CO ratio is low (due to the water-gas-shift reaction activity of Fe) (Nakhaei Pure et al., 2010; Atashi et al., 2010). Cobalt-based catalysts are preferred in synthesis of straight-chain hydrocarbons or waxes from natural gas due to their high activity and selectivity to these products (Schweitzer and Viguie, 2009; Van Steen and Schulz, 1999). Nickel shows different catalytic behavior, since the molecular weight of the resulting hydrocarbons is much lower for Ni than Fe and Co catalysts (Mollavali et al., 2008). Thus, addition of Ni to Fe or Co catalysts could lead to increase in light hydrocarbons formation.

A key element to improving the economics of FTS is increasing the selectivity toward desired products such as light olefins, high-octan gasoline and paraffinic waxes or long-chain hydrocarbons (Duvenhage and Coville, 2005; Soled et al., 2003). Many inorganic oxides such as Al_2O_3, SiO_2, TiO_2, MgO and ZrO_2 have been used as supports for improving the structural stability, activity and selectivity of FTS catalysts (Schanke et al, 2004; Martinez and Lopez, 2005; Morales et al., 2005; Jacobs et al., 2007; Mirzaei et al., 2011). It has been reported that the addition of support to Fe catalysts, would be useful since it could reduce catalyst density and encourage catalyst application, especially in fluidized or slurry reactor (Zhao et al., 2001; Sudsakorn et al., 2001). Supported Co catalysts are preferred in FTS, due to resistance toward deactivation and great influence of support on the dispersion and reducibility of cobalt (Bessell, 1993; Spadaro et al., 2005).

The addition of chemical promoters is believed to be important in improving the chemical behavior of iron catalyst, for example, facilitating the reduction of the catalyst and the adsorption and dissociation of H_2 and CO on the catalyst surface (Yang et al., 2005). It is known that the addition of some promoters to cobalt catalyst could modify the support's texture and increase cobalt dispersion and reducibility (Schanke et al, 1995).

It has been reported in the literature that the mixing of metal components has a great effect on the activity and selectivity because of the possible electronic interaction between metal species (Wang et al., 2003; Cooper and Frost, 1990; Jothimurugesan and Gangwal, 1998). Many studies have been done over bimetallic catalysts. However, studies that report on the

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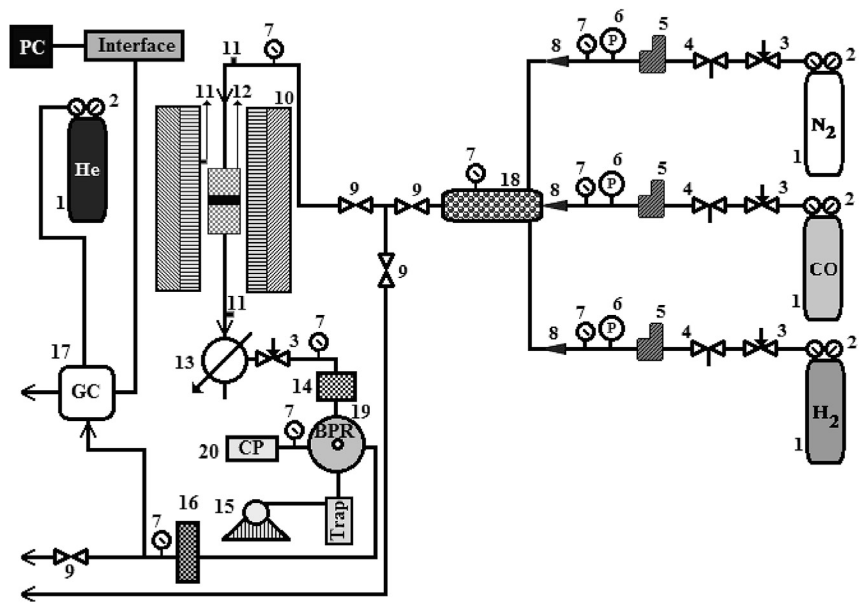

Fig. 1. Schematic representation of the reactor in a flow diagram used. 1-Gas cylinders, 2-Pressure regulators, 3-Needle valves, 4-Valves, 5-Mass Flow Controllers (MFC), 6-Digital pressure controllers, 7-Pressure Gauges, 8-Non return valves, 9-Ball valves, 10-Tubular Furnace, 11-Temperature indicators, 12-Tubular reactor and catalyst bed, 13-Condenser, 14-Trap, 15-Air pump, 16-Silica gel column, 17-Gas Chromatograph (GC), 18-Mixing chamber, 19-BPR: Back Pressure Regulator (Electronically type), 20- CP (Control panel).

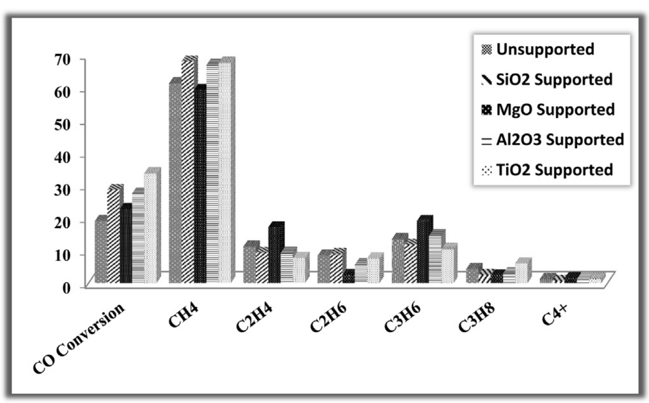

Fig. 2. Effect of different supports on the catalytic performance of Fe–Co–Ni catalyst.

ternary catalytic system are rare in the literature (Arsalanfar et al., 2013). This work was carried out to investigate the effect of different supports including Al_2O_3, SiO_2, TiO_2 and MgO and different promoters such as Li, K, Rb, Cs and Ru on the catalytic performance of co-precipitated Fe–Co–Ni ternary catalysts for FTS. We also characterized the precursors and calcined catalysts (before and after the test) using various the techniques such as XRD, SEM, EDS and BET.

Table 1
Effect of different supports on the catalytic performance.

Support	Yield (%)			
	CH_4	C_2H_4	C_3H_6	C_4^+ olefins
Unsupported	11.59	2.09	2.54	0.23
SiO_2	19.25	2.60	3.28	0.15
MgO	**13.04**	**4.01**	**4.29**	**0.33**
Al_2O_3	18.18	2.48	3.94	0.29
TiO_2	22.58	2.55	3.45	0.42

The bold rows in the table show the result of optimum support and optimum support loading on the catalytic performance, respectively.

2. Experimental

2.1. Catalyst preparation

In this study, the supported iron-cobalt-nickel catalyst was prepared using coprecipitation procedure as follows. Aqueous solutions of $Co(NO_3)_2.6H_2O$ (2M) (99% Merck), $Fe(NO_3)_3.9H_2O$ (2M) (99% Merck) and $Ni(NO_3)_2.6H_2O$ (2M) (99% Merck) with the optimum molar ratios (20%Fe–60%Co–20%Ni) were premixed and then the same amount (10wt%) of each support (SiO_2, TiO_2, Al_2O_3 and MgO) was added to separate mixed solutions of iron, cobalt and nickel nitrates. The resulting solution was heated to 70 °C in around bottomed flask fitted with a condenser. Aqueous Na_2CO_3 (2M) (99% Merck) was added dropwise to the mixed nitrate solution with stirring while the temperature was maintained at 70 °C

Table 2
EDS data of Fe–Co–Ni fresh calcined catalysts containing different supports.

Fresh calcined catalyst	Elements	Weight%	Atomic%
Unsupported	Fe	16.80	16.58
	Co	40.51	34.14
	Ni	13.40	14.28
	O	29.29	35.00
Al_2O_3 supported	Fe	11.99	15.01
	Co	42.25	25.22
	Ni	12.13	13.36
	O	29.62	40.61
	Al	4.01	5.80
MgO supported	Fe	14.89	13.92
	Co	41.96	36.75
	Ni	14.76	12.38
	O	23.99	31.61
	Mg	4.40	5.34
TiO_2 supported	Fe	12.01	11.22
	Co	39.53	22.01
	Ni	13.31	10.80
	O	30.62	53.36
	Ti	4.53	2.61
SiO_2 supported	Fe	13.86	12.39
	Co	40.90	37.57
	Ni	14.85	13.83
	O	26.95	30.20
	Si	3.44	6.01