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TiO_2-SUPPORTED Fe-Co, Co-Ni, AND Ni-Fe ALLOY CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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The activities of TiO_2-supported bimetallic catalysts of Fe-Co, Co-Ni and Ni-Fe for CO conversion were greater than those of pure metal catalysts. The selectivities of alloy catalysts relative to pure metal catalysts were shifted to higher molecular hydrocarbons.

A great number of literatures related to F-T synthesis which have appeared in the past several years are connected with the catalytic production of hydrocarbon suitable for use as fuels. It is well-known about the characteristic of SiO_2-supported metal catalysts for F-T synthesis as following.$^{1)}$ Fe tends to form more olefins and oxigenated products compared to Co. Co shows the highest CO conversion. Ni is more methane selective than Fe and Co. Fe forms carbides during reaction. However, little information has been reported on F-T synthesis using the supported alloy catalysts of Fe, Co, and Ni. Delgass et al.$^{2)}$ have reported that the addition of Co to Fe supported on SiO_2 enhanced the reducibility of the iron and retarded the carburization rate. Butt et al.$^{3)}$ investigated the formation of carbides on SiO_2 supported Fe, Fe-Ni, and Fe-Co bimetallic catalysts, and concluded that the alloying agents of Ni and Co to Fe make the iron carbide less stable and enhance the activity for F-T synthesis. Moreover, supported bimetallic alloys of Fe, Co, and Ni are expected to possess unique catalytic properties for hydrocarbon synthesis compared to pure metal catalysts, particularly high activity and high selectivity for olefins and higher hydrocarbons. In this work we have investigated TiO_2-supported alloy catalysts of bimetallics (Fe-Co, Co-Ni, Ni-Fe) and an optimum range in the composition ratio is found to exist in which methane formation is minimized and C_2-C_5 olefins or C_{6+} hydrocarbons production is maximized.

The TiO_2-supported alloy catalysts used in this study were prepared by conventional incipient wetness techniques. An aqueous solution of the proper ratio of iron, cobalt, and nickel nitrate salts was added to TiO_2 soaked in water with constant mixing. The TiO_2 was obtained by hydration of $TiCl_4$ at 239 K and calcination at 673 K for 4 h. Simultaneous impregnation was used for the bimetallic samples as indicated in Table 1, in which compositions of the catalysts studied are exhibited. Impregnated samples were dried in air at 383 K for 4 h and the catalyst powder was then pressed at 200 kg/cm^2. The samples were crushed and screened to obtain particles of which size were between 20 and 10 mesh. The catalysts were calcined at 573 K for 4 h to decompose the nitrate salts and reduced at 673 K for 2 h under hydrogen stream. All catalyst compositions are reported as xFe yCo/TiO_2

Table 1. Product distribution in oxygenated compounds

Catalyst	CO conv. %	Oxygenated compounds selectivity %	Product distribution in oxygenated compounds (carbon atom-percentage) CH_3OH	C_2H_5OH	$n\text{-}C_3H_7OH$	$n\text{-}C_4H_9OH$	$i\text{-}C_4H_9OH$	$2\text{-}C_4H_9OH$	CH_3CHO
Fe	2.2	0	0	0	0	0	0	0	0
Co	20.3	1.7	60.2	20.5	7.6	6.1	2.1	0	3.4
Ni	15.5	2.0	36.9	38.1	21.7	0	3.3	0	0
7.5Fe2.5Co	5.9	4.6	54.9	37.3	0	0	0	0	7.8
5.0Fe5.0Co	28.5	5.3	37.4	37.3	11.2	0	0	0	14.1
2.5Fe7.5Co	14.5	5.4	40.8	34.5	13.9	7.0	3.7	0	0
7.5Co2.5Ni	24.5	4.5	66.0	31.0	3.0	0	0	0	0
5.0Co5.0Ni	46.0	6.0	39.5	25.0	33.9	1.5	0	0	0.8
2.5Co7.5Ni	28.5	5.3	48.6	28.8	22.6	0	0	0	0
7.5Ni2.5Fe	43.2	3.1	35.0	21.0	35.7	0	4.2	0	1.1
5.0Ni5.0Fe	20.5	2.3	24.3	23.1	49.2	0	1.6	0	0
2.5Ni7.5Fe	7.1	0.7	49.9	23.8	16.5	6.1	3.6	0	6.1

yCo zNi/TiO_2, or zNi xFe/TiO_2, where x, y, and z are the weight percentages of the Fe, Co, and Ni, respectively. All catalysts studied, including pure metal catalysts, had a total metel loading (x+y, y+z, x+z) of 10wt%. X-Ray diffraction of the Fe-TiO_2 catalyst showed the peaks due to unreduced phase, Fe_3O_4, and anatase form of TiO_2. No unreduced iron was detectable in the Fe-Co and Ni-Fe alloy catalysts. This enhancement of reducibility appears to be the result of the presenc of Co and Ni which have been known to be reduced more easily than Fe.

The carbon monoxide hydrogenation was carried out in a stainless steel tubular reactor, in which a 400 mm pyrex glass tube, 15 mm in diameter, was located. The reactor was positioned vertically in an electric furnace and was usually loaded with 1.0 g of catalyst, and 2 mm pyrex glass beads were packed above and below the catalyst bed. In order to reduce the catalysts, a hydrogen stream was supplied at 523 K for 1 h before catalytic reactions were started. The feed stream consisted of a mixture of H_2, CO,and Ar (H_2 :CO :Ar =62 : 33 : 5). Feed gases were purified by passage over active carbon and/or Linde 13X molecular sieves to remove water and decompose any carbonyl impurities. Flow rate was controlled by an electromagnetic type flow controller. The reactions were normally performed at 523 K under 1.0 MPa. W / F was 10 g-cat·h /mol, where W is the catalyst weight (grams) and F is the total flow rate (moles per hour). The reactor exit stream passed through a back pressure regulator, for controlling the flow rate and pressure. All transfer lines were heated and led directly to a heated sampling valve of a gas chromatograph for periodic analysis of the effluent gas. The effluent gas was analyzed for CO and Ar on a molecular sieve column, CO_2 on a silica gel column, C_1-C_5 hydrocarbons on a sebaconitrile column, and C_6-C_{20} hydrocarbons on an SE-30 column. An active alumina column was used for the separation of ethane and ethylene. After exiting the gas sampling valve, the gases passed through a trap containing cold water to condense and dissolve oxygenated compounds. These compounds were analyzed by a gas chromatograph using a PEG column.

The product distribution is presented on a weight basis, which is a better representation of CO utilization and is more useful for practical consideration. No carbon dioxide was formed over all supported pure metal and alloy catalysts under the operated reaction conditions and a small amount of alcohols was produced except for Fe-TiO_2 catalyst. Therefore, hydrocarbons of main products are grouped into four categories, CH_4, C_2-C_5 olefins and paraffins, and C_{6+} hydrocarbons. We discuss the selectivity using three important categories except C_2-C_5 paraffins.

Activities of these catalysts decreased gradually until about 2 h after the reaction was started and reached constant. Large decrease in CO conversion was observed only for Fe-TiO_2 catalyst. We calculated the conversion and the product distribution from the results between 5 h and 7 h after the reaction was started. A comparison of the global rates of CO consumption per gram of catalyst shows that the activities of TiO_2-supported Ni-Co alloy catalysts were higher than pure Co and Ni catalysts, as shown in Fig. 1. Both Co/TiO_2 and Ni/TiO_2 catalysts produced more methane and are less C_2-C_5 olefins selective than alloy catalysts. Ni/TiO_2, Co/TiO_2 and Co-Ni alloy catalysts produced oxygenated compounds, mainly methanol, ethanol and propanol, as shown in Table 1. As content of Ni in alloy catalysts increased, both CO conversion and C_2-C_5 olefin selectivity increased and attained a maximum at 5.0Ni 5.0Co/TiO_2 catalyst and then decreased. In contrast, methane selectivity showed a contrary tendency. Therefore, 5.0Co 5.0Ni/TiO_2 catalyst has been found to have the highest activity and the lowest selectivity for methane. From these results it is to be noted that the most active catalyst for CO conversion was fortunately unselective towards methanation and hence is one of the best candidates for the desired catalyst of producing C_{6+} hydrocarbons. Both 7.5Co 2.5Ni/TiO_2 and 2.5Co 7.5Ni/TiO_2 catalysts showed nearly 40% selectivity for C_{6+} hydrocarbons. TiO_2-supported

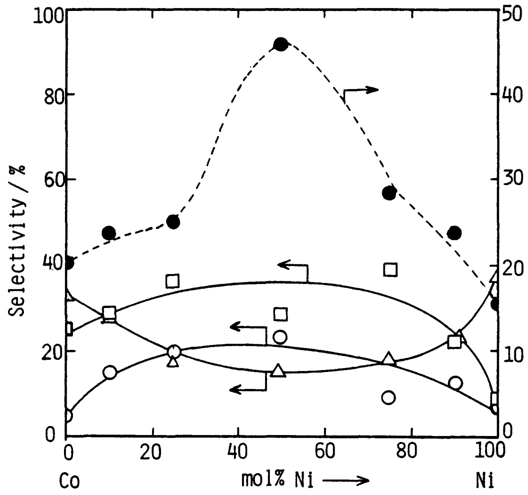

Fig. 1. Conversion and selectivity for CO hydrogenation over Co-Ni/TiO_2 catalysts as a function of bulk composition.
(523K , 1.0 MPa, H_2/CO=1.9 , W/F=10 g·cat·h/mol)
--●-- CO conv. —△— CH_4
—○— C_2-C_5 olefin —□— C_{6+}

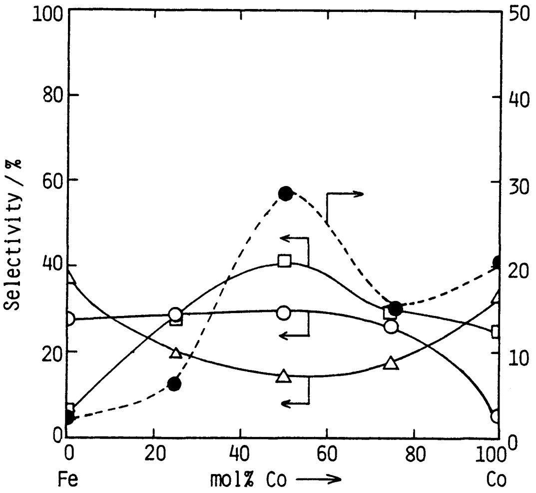

Fig. 2. Conversion and selectivity for CO hydrogenation over Fe-Co/TiO_2 catalysts as a function of bulk composition.
(523K, 1.0 MPa, H_2/CO=1.9, W/F=10 g·cat·h/mol)
--●-- CO conv. —△— CH_4
—○— C_2-C_5 olefin —□— C_{6+}

Co-Ni alloy catalysts promoted chain growth reaction with higher selectivity for heavier hydrocarbon production compared to a pure Co or Ni catalyst. The selectivity shift to higher carbon numbers which occurred concomitantly with an increase in the catalyst activity appears to be unique to these bimetallic catalysts. The shift in product distribution resulted from an increase in the activity of carbon-carbon bond making reactions rather than a suppression of methanation activity.

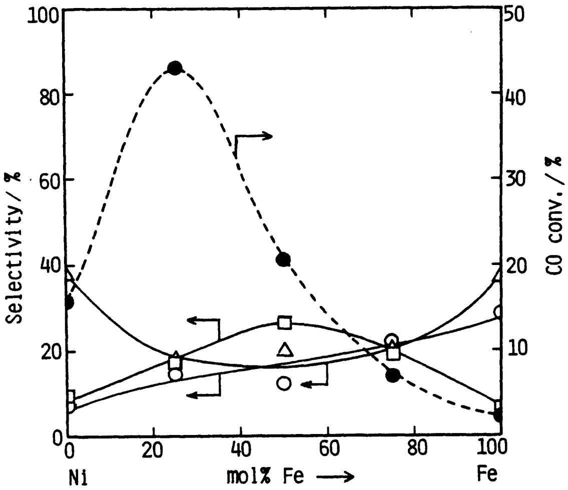

Fig. 3. Conversion and selectivity for CO hydrogenation over Ni-Fe/TiO_2 catalysts as a function of bulk composition.
(523K, 1.0 MPa, $H_2/CO=1.9$, W/F=10 g·cat·h/mol)
--●-- CO conv. —△— CH_4
—○— C_2-C_5 olefin —□— C_{6+}

Fe/TiO_2 catalyst showed a very low conversion and a high selectivity for methane and C_2-C_5 olefins and no C_{6+} hydrocarbons were produced. Co/TiO_2 was about an order of magnitude more active than Fe/TiO_2. In contrast, Co/TiO_2 produced C_1-C_{11} hydrocarbons and a small amount of oxygenated compounds and its selectivity for C_2-C_5 olefin formation was very small. 5.0Fe 5.0Co/TiO_2 catalyst showed the highest CO conversion, the highest yield of C_{6+} hydrocarbons, and the lowest methane selectivity in the Fe-Co alloy system. Fe catalyst formed carbides and oxides during F-T reaction and the surface carbides significantly lowered the activity. The addition of Co to Fe would probably suppress carbide formation on the catalyst surface, and the working 5.0Fe 5.0Ni/TiO_2 catalyst would then be drastically different from a pure Fe catalyst. Alloying of Fe and Co also resulted in high selectivity for C_2-C_5 olefins and C_{6+} hydrocarbons and low selectivity for methane.

In iron-nickel system, alloying also resulted in higher activity and higher selectivity to C_{6+} hydrocarbons and lower selectivity to methane as shown in Fig.3. 5.0Fe 5.0Co/TiO_2 had the highest selectivity to C_{6+} hydrocarbons. On the other hand, 7.5Ni 2.5Fe/TiO_2 catalyst was the most active and had the lowest methane selectivity. Fe/TiO_2 produced no oxygenated compounds, however Ni/TiO_2 and iron-nickel alloy catalysts produced a small amount of methanol, ethanol etc. With increasing iron content, the selectivity to C_2-C_5 olefins increased slightly.

The activities of TiO_2-supported alloy catalysts for CO conversion were greater than those of pure metal catalysts. The alloy catalysts have increased selectivity for C_2-C_5 olefins. Moreover, the selectivities of alloy catalysts relative to pure metal catalysts were shifted to higher molecular hydrocarbons. The shift in selectivity was not accompanied by a suppression of the methanation activity, but resulted from an increase in the rates of chain growth reactions producing an overall increase in catalyst activity.

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