Time-on Stream Performance of Co-Ni/TiO_2 and HZSM-5 Catalyst Systems for Fischer-Tropsch Synthesis

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Time-on-stream Fischer-Tropsch (FT) product distributions using a 5% Co-5% Ni/TiO_2 catalyst and a catalyst prepared by mixing this catalyst with HZSM-5 underwent dramatic variations during the first 20 h of operation. Deactivation of the FT catalyst over 100 h was significantly lower in the presence of HZSM-5.

It has been reported that a catalyst prepared by alloying two or more Group VIII metals over a conventional support, e.g., SiO_2 and TiO_2, exhibits reduced methane selectivity and increased activity and C_5^+ hydrocarbon selectivity for FT synthesis over the corresponding monometallic catalysts.[1-2] Also, bifunctional catalysts composed of a single FT active metal and zeolite (e.g., HZSM-5) have been the focus of attention for several years in order to overcome the nonselective Anderson-Schultz-Flory distribution to produce high octane gasoline.[3-4] We have recently reported the steady-state FT results of monometallic-bifunctional and bimetallic-bifunctional catalysts.[5] In the present study, we investigated the time-on-stream FT performance of a 5% Co-5% Ni/TiO_2 catalyst both as is and when mixed with HZSM-5 zeolite at realistic FT conditions.

The bimetallic 5% Co-5% Ni/TiO_2 catalyst was prepared by aqueous incipient wetness impregnation using P-25 TiO_2 from Degussa having a BET surface area of 48 m^2/g. The HZSM-5 catalyst (BET surface area = 290 m^2/g) was prepared using a ZSM-5 zeolite from PQ Corporation (CBV 3062E) with a SiO_2/Al_2O_3 ratio of 30 as starting material. The alloy formation between Co and Ni in the bimetallic FT catalyst was confirmed by lattice constant measurement using X-ray diffraction (XRD). Complete details of the catalyst preparation and characterization are available.[5]

FT reaction studies comparing the FT catalyst alone with that mixed with HZSM-5 were carried out in a 1-cm i.d. high-pressure fixed-bed reactor system.[5] The catalyst bed size for the time-on-stream run with Co-Ni/TiO_2 catalyst alone was 1 g. On the other hand, the mixed-bed run was carried out with 1 g Co-Ni/TiO_2 catalyst mixed with 4 g of HZSM-5. Other conditions for the two runs were identical (temperature = 250 ∞C; pressure = 1.0 MPa; weight hourly space velocity [WHSV] = 0.77 h^{-1}; feed gas volumetric composition-CO = 47.5%, H_2 = 47.5%, and Ar internal standard = 5%). The WHSV value corresponds to only the FT catalyst. Thus, linear velocity was the same in both runs. Each run was conducted for 100 h with on-line gas chromatograph (GC) measurements throughout the duration.

The CO conversion began at around 50% and dropped to 40% over the first 22 h of operation for both catalyst runs. However, after 22 h, the deactivation was much more rapid for the FT catalyst run as opposed to FT+HZSM-5 run. At the end of 100 h, the conversion with FT catalyst was 10%, whereas with the FT+HZSM-5 catalyst it was 26%. FT catalyst deactivation is caused by a carbonaceous surface layer that forms from CO dissociation or coke deposition from FT products, e.g., long-chain olefins that are coke precursors. For the first 22 h, the former appears to be the predominant deactivation mechanism for both catalysts. Beyond 22 h, however, catalyst deactivation also appears to be caused due to formation of FT products that are coke precursors. Reduced deactivation in the presence of HZSM-5 may be due to conversion of these potential coke precursors to products that do not deposit coke, e.g., by secondary reactions such as hydrogenation, aromatization, cyclization, and/or isomerization. The selectivities to both oxygenates and CO_2 were found to be negligible in both runs.

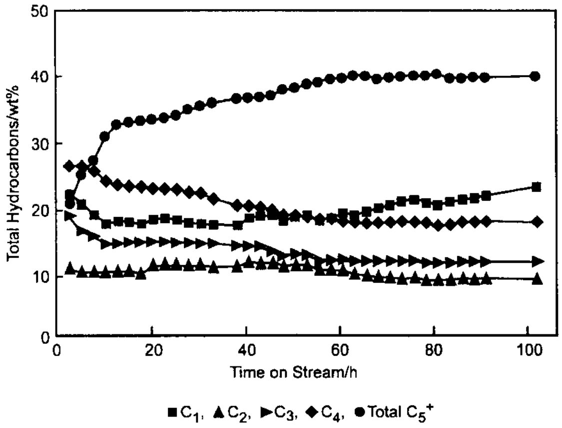

Figure 1. Hydrocarbon selectivities for Co-Ni/TiO_2 catalyst.

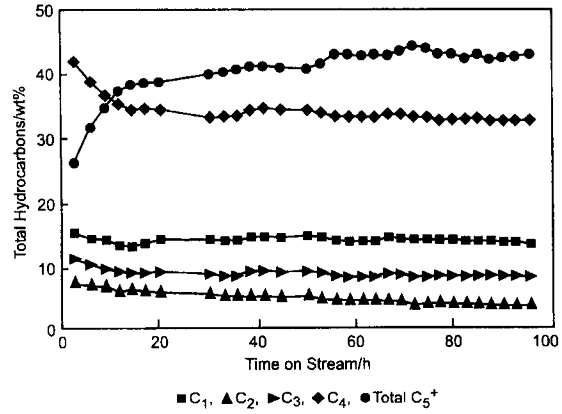

Figure 2. Hydrocarbon selectivities for Co-Ni/TiO_2+HZSM-5 catalyst.

The 100-h time-on-stream selectivities to C_1 to C_5^+ hydrocarbons for the FT run and FT+HZSM-5 run are shown in Figures 1 and 2, respectively. The C_5+ selectivity in both runs increases rapidly over the first 20 h and then continues to increase slowly and stabilize after about 60 h of operation. This appears to be primarily at the expense of C_4 selectivity for the FT+HZSM-5 run and at the expense of C_1, C_3, and C_4 selectivity with the FT run. The total C_1 to C_3 selectivity for the FT+HZSM-5 run is much lower than for the FT run. Correspondingly, the total C_4 and C_5^+ selectivity for the FT+HZSM-5 run is much higher than that for the FT run. An induction period thus exists for both catalysts, in conjunction with their deactivation. For the FT+HZSM-5 catalyst, the induction period is accompanied with increased yield (conversion × selectivity) of C_5^+ at the expense of significantly reduced yield of C_4 fraction. On the other hand, even though the weight fraction (selectivity) of the C_5^+ fraction increases for the FT only catalyst, the yield of C_5^+ (conversion × selectivity) remains about constant. This primary difference in the two induction periods is attributed to the catalytic functionality of the HZSM-5. Of the C_5^+ fraction, the percentage of aromatics (not shown in the figure) in the FT catalyst run was less than 4%, whereas in the FT+HZSM-5 run it was close to 23% after 20 h. The aromatic to aliphatic C_5^+ ratio in the FT+HZSM-5 run increases rapidly from about 0.08 at the start to about 0.23 after 20 h of operation. This induction period is again attributed to the autocatalytic nature of the aromatization reactions[6] over the zeolite. The aromatics produced over the FT+HZSM-5 catalyst are mostly methyl- and ethyl-substituted benzenes terminating at around C_{12}, whereas the aliphatic compounds terminate at C_9. The sharp cutoff of aliphatics at C_9 and the formation of aromatic products up to C_{12} are essentially due to the shape selective nature of HZSM-5.

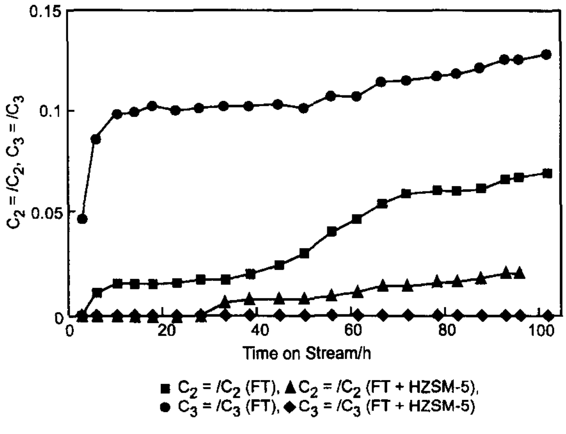

Figure 3. Olefin to alkane ratios as a function of on-stream time.

Figure 3 shows that the $C_2=/C_2$ ratios increase with time on stream for the FT catalyst and FT+HZSM-5 catalyst runs; however, ethylene selectivity is significantly lower for the FT+HZSM-5 run. The $C_3=/C_3$ ratio increases very rapidly for the FT catalyst run over the first 10 h, whereas essentially no $C_3=$ (less than 1% of total C_3) is produced with FT+HZSM-5 throughout the 100 h. Thus, it is seen that the reduction in the olefinicity of the C_3 fraction is much higher compared to that in the C_2 fraction. It is known that the olefins, which are the primary FT products, are essentially involved in reactions over HZSM-5 leading to the formation of aromatics. The decrease in $C_2=$ and $C_3=$ fractions as found in this work is indicative of the cyclization and aromatization reactions over HZSM-5. A large decrease in the olefinicity of C_3 fraction compared to C_2 fraction suggests that the propylene is more reactive compared to ethylene in the formation of aromatics. This is in agreement with the recent studies dealing with conversion of olefins over HZSM-5 indicating that, among olefins, ethylene is least reactive over HZSM-5.[4] The i-C_4/C_4 ratio (not shown in the figure) decreases slightly over the first 5 h and then stabilizes. This ratio is around 0.6 for the FT+HZSM-5 run, whereas it is only 0.02 for the FT run. Thus, in addition to promoting C_5^+ and aromatic formation, the zeolite significantly reduces product olefinicity and shifts the C_4 hydrocarbon distribution toward isobutane. These changes are attributed to cracking and aromatization over HZSM-5.[7]

Table 1. Carbon content and BET surface area

	C (wt%)	BET surface area (m^2/g)
Fresh FT catalyst	0.0193	40
Fresh HZSM-5	0.023	290
FT run, FT catalyst	6.87	7.3
FT+HZSM-5 run		
FT catalyst	1.61	29.9
HZSM-5	1.22	273

The BET surface area and carbon content of the catalyst samples after 100 h of operation are shown in Table 1. For the FT+HZSM-5 run, the catalysts were separated physically for analysis. SEM micrographs (not shown) showed clear coke deposition on the metal surface. The BET surface area of the FT metal only catalyst reduced much more than that of the FT+HZSM-5 run FT catalyst, presumably due to much more coke deposition which caused blocking of the pores of the catalyst. This could explain the greater deactivation of the FT only catalyst. The decrease in methane followed by an increase for the FT run (Figure 1) may be due to the direct reaction of coke precursors with hydrogen after coke deposition.

Over the HZSM-5 catalyst, the coke deposition occurs due to the cracking reactions taking place on the catalyst. In the presence of HZSM-5, the selectivity of olefins is reduced while that of paraffins increases. The unsaturated compounds reacting over HZSM-5 either build up coke or get converted to aromatics. Because there is no significant decline in aromatic selectivity with increased aging of the catalyst up to the run period of 100 h, the rate of coke deposition over the zeolite component is low. This is in accordance with the deactivation characteristics of intermediate pore zeolites such as HZSM-5. The carbon formation in zeolites has been shown to be a shape-selective reaction.[8] Consequently, the coke formation is controlled by pore structure of the zeolite.

To summarize, a dramatic increase in the C_5^+ selectivity with a concomitant reduction in C_4 selectivity takes place on the bimetallic Co+Ni FT+HZSM-5 catalyst over the first 20 h of operation. The deactivation of the Co+Ni catalyst begins to promote the formation of CH_4. For the FT+HZSM-5 system, the presence of HZSM-5 results in significant reduction in the rate of deactivation of the FT catalyst. Olefinic content of the products is significantly lower, whereas isobutane make is significantly higher in the presence of HZSM-5.

References and Notes

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