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Slurry Phase Fischer-Tropsch Synthesis: Cobalt Plus a Water-Gas Shift Catalyst

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Summary

Experiments to study cobalt-catalyzed reactions of light 1-alkenes added to synthesis gas feed have been performed. Data have been collected at 220°C, 0.45 to 1.48 MPa and a synthesis gas flow rate between 0.015 and 0.030 Nl/(gcat·min) with H_2/CO of 1.45 to 2.25. C_2H_4, C_3H_6, and C_4H_8 were added to the synthesis gas feed in concentrations ranging from 0.5 to 1.2 mole% of total feed. For each material balance in which 1-alkenes were added, a material balance was performed at similar process conditions without 1-alkenes added. This use of "base case" process conditions should make data analysis and interpretation easier. Material balances without added 1-alkenes were also repeated to allow verification of catalyst selectivity stability. A total of 49 material balances were performed during a single run which lasted over 2,500 hours-on-stream. The hydrocarbon data have not yet been completely analyzed.

Scope and purpose of study

We have reported previously on the activity and selectivity of a Co/MgO/kieselguhr catalyst. The selectivity to desired high molecular weight products increased with decreasing H_2/CO ratio and increased with decreasing space velocity. The sensitivity of the hydrocarbon distribution to process variables seems to be greater than that encountered with iron catalysts. This implies that secondary reactions, such as chain incorporation, as well as 1-alkene hydrogenation and isomerization, may be important in determining the final product distribution. The objective of this part of our work is to develop a more fundamental understanding of the role of 1-alkenes in the hydrocarbon chain growth process on cobalt-based catalysts. In particular, we are concerned with the effects of process variables on the hydrocarbon product distribution and the secondary reactions of 1-alkenes.

The published literature contains very little information on reactions of added 1-alkenes during the Fischer-Tropsch synthesis on cobalt. Most alkene addition studies on cobalt were performed in conjunction with a more extensive study of feed additions to iron catalysts; as a result, cobalt catalysts were studied at only a few different process conditions. Although the consensus appears to be that 1-alkenes are incorporated into growing chains on the cobalt catalyst surface, there is little agreement as to the extent to which incorporation affects the product distribution. Further, no studies exist which cover a wide range of process conditions. Our study will attempt to quantify the effect of 1-alkene incorporation and correlate the effect of 1-alkene incorporation on the hydrocarbon product distribution with process variables.

Results and experiment design

The catalyst composition and reduction procedure have been reported by us previously. After reduction, the catalyst was allowed to achieve stable activity and selectivity and then process variables were manipulated to provide data over a broad range. Table 1 shows the process conditions for the material balances performed during 1-alkene additions. Data were obtained at 220°C, 0.45 to 1.48 MPa and a synthesis gas flow rate between 0.015 and 0.030 Nl/(gcat·min) with a H_2/CO ratio of 1.45 to 2.25.

Three light 1-alkenes were added to the synthesis gas feed separately; they were C_2H_4, C_3H_6, and C_4H_8 which were added in quantities to comprise from 0.5 to 1.2 mole% of total feed. At these feed rates, the added 1-alkenes are present in concentrations ranging from 2 to 10 times the normal. 15 material balances were performed adding C_2H_4, 6 adding C_3H_6, and 8 adding C_4H_8. These light 1-alkenes were chosen because they are not condensed to any significant extent in either the hot or cold traps. Thus, analysis of these light 1-alkenes is very accurate, and will allow us to close material balances on the added component or at the added component carbon number.

For each material balance in which 1-alkenes were added a material balance was performed at similar process conditions without 1-alkenes added. This use of "base case" process conditions should make data analysis and interpretation easier, as it facilitates simple comparison of hydrocarbon selectivity with and without alkene addition.

Material balances without added 1-alkenes were also repeated to allow verification of catalyst selectivity stability. A total of 49 material balances were performed during a single run which lasted over 2,500 hours-on-stream. The large number of organic liquid samples that were collected during the run have not been analyzed and, as a result, the hydrocarbon data have not yet been completely studied.

TABLE 1

MB [#]	T [C]	P [MPa]	H2/COin [molar]	H2+CO FLOW [l/min]	ADDED COMPONENT	ADDED FLOW [l/min]	BASE MB [#]
3	240	0.79	2.02	1.143	-------	-------	-------
4	240	0.79	1.85	0.256	C2H4	0.00181	-------
5	240	0.79	2.05	0.253	C2H4	0.00168	-------
6	240	0.79	1.25	0.253	C2H4	0.00227	-------
7	240	0.79	1.33	0.262	C2H4	0.00227	-------
8	220	0.79	1.74	0.278	-------	-------	-------
9	220	0.79	1.76	0.283	C2H4	0.00207	8
10	220	0.79	2.21	0.506	-------	-------	-------
11	220	0.79	2.21	0.518	C2H4	0.00326	10
12	220	0.79	1.45	0.492	-------	-------	-------
13	220	0.79	1.45	0.490	C2H4	0.00404	12
14	220	0.79	1.73	0.505	-------	-------	-------
15	220	0.79	1.73	0.509	C2H4	0.00377	14
16	220	0.79	1.58	0.297	-------	-------	-------
17	220	0.79	1.58	0.299	C2H4	0.00234	16
18	220	0.79	1.76	0.310	-------	-------	-------
19	220	0.79	1.76	0.297	C4H8	0.00217	18 or 8
20	220	1.48	1.85	0.305	-------	-------	-------
21	220	1.48	1.85	0.305	C4H8	0.00216	20
22	220	1.48	1.61	0.491	-------	-------	-------
23	220	1.48	1.61	0.486	C4H8	0.00376	22
24	220	1.48	1.61	0.482	C2H4	0.00373	22
25	220	1.48	1.92	0.481	-------	-------	-------
26	220	1.48	1.92	0.480	C2H4	0.00332	25
27	220	1.48	1.91	0.496	C4H8	0.00344	25
28	220	1.48	2.15	0.501	-------	-------	-------
29	220	1.48	2.15	0.504	C2H4	0.00323	28
30	220	1.48	2.15	0.517	C4H8	0.00332	28
31	220	1.48	2.15	0.494	C3H6	0.00317	28
32	220	1.48	1.92	0.480	C3H6	0.00332	25
33	220	1.48	1.63	0.472	C3H6	0.00353	22
34	220	0.45	1.61	0.486	-------	-------	-------
35	220	0.45	1.63	0.501	C2H4	0.00385	34
36	220	0.45	1.65	0.494	C3H6	0.00377	34
37	220	0.45	1.91	0.491	-------	-------	-------
38	220	0.45	1.70	0.495	C2H4	0.00370	37
39	220	0.45	1.73	0.498	C3H6	0.00368	37
40	220	0.45	2.25	0.500	-------	-------	-------
41	220	0.45	2.25	0.500	C2H4	0.00311	40
42	220	0.45	2.25	0.493	C3H6	0.00306	40
43	220	0.45	2.30	0.514	C4H8	0.00315	40
44	220	0.45	1.77	0.492	C4H8	0.00359	37
45	220	0.45	1.63	0.486	C4H8	0.00373	34
46	220	0.79	1.61	0.292	-------	-------	16 or 47
47	220	0.79	1.62	0.292	-------	-------	16 or 46
48	220	0.79	2.21	0.522	-------	-------	10 or 49
49	220	0.79	2.21	0.522	-------	-------	10 or 48

END

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