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Advances in Fischer–Tropsch Chemistry

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Gasoline production in synthesis gas conversion can be increased to over 60% of total hydrocarbon and essentially 100% of the liquid product by combining a Fischer–Tropsch catalyst with an excess volume of a ZSM-5 class zeolite.

INTRODUCTION

Chang, Lang, and Silvestri (*1*) have reported in a parallel paper their discovery of a new class of synthesis gas conversion catalysts, comprising a carbon monoxide reduction function combined with a zeolite of the ZSM-5 class (*2*) that gives high yields of aromatics. These zeolites are members of the group of Mobil shape-selective zeolites that are characterized by pore openings intermediate between small pore zeolites, such as zeolite A and erionite, and large pore zeolites, such as the faujasities (*2*). The ZSM-5 class of zeolites is active for the conversion of methanol and other oxygenates to hydrocarbons (*3*).

Dry (*4*) has shown that in both theory and practice the selectivity for gasoline production peaks at 40% with conventional Fischer–Tropsch iron catalysts. This paper will demonstrate that the selectivity for gasoline production can be increased to over 60% of the total hydrocarbon product and essentially 100% of the liquid product by mixing the iron Fischer–Tropsch catalyst with an excess volume of zeolite. In addition to improved selectivity for gasoline production, the iron/ZSM-5 class composite catalyst improves the octane quality of that gasoline and enhances the activity of the iron under fixed-bed conditions. Experimental evidence will be offered to explain the synergistic function of the zeolite.

METHODS

Materials. The zeolite component of the composite catalyst used in this study was previously characterized (*2*). The Fischer–Tropsch component was a commercial, potassium promoted, ammonia synthesis catalyst obtained from Girdler under the code name G-82. Unless otherwise stated the composite catalyst was comprised of an intimate mixture of 12 to 25 mesh (700 to 1500 μm) particles of iron and of zeolite in a volume ratio of $\frac{1}{4}$. The premixed synthesis gas components were obtained from Matheson.

Apparatus and procedure. Fixed-bed continuous flow micro-reactors containing up to 10 ml of catalyst were used in this study. The preheater and reaction zones were made of 12.2-mm-i.d. stainless-steel enclosed in a three-zone electrical resistance, block heater. A representative tem-

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perature profile of the reaction zone measured from an axially centered thermocouple well, was: bed inlet, 320°C; immediate exotherm, 335°C maximum; bed outlet, 320°C. Gas flow rates were regulated by a Nupro metering valve, pressure by an Annin pressure release valve.

Liquid product was collected directly in a pressured Jerguson sight glass. The gas collection train included two dry ice–acetone traps and a wet testmeter. Hydrocarbon liquids from the weathered Jerguson and traps were combined, weighed, and analyzed by gas chromatography. Weathered and dry gases were analyzed by mass spectroscopy. The aqueous layer was measured separately and on occasion analyzed for soluble oxygen-containing compounds.

RESULTS AND DISCUSSION

Arrhenius plots of space–time yields from the potassium-promoted fused iron/zeolite composite catalyst are compared in Fig. 1 with the fixed-bed performance of typical fused and precipitated iron Fischer–Tropsch catalysts (*5*, *6*). Yields are calculated in terms of ml $H_2 + CO$ converted/hr/ml catalyst (*5*) and ml $H_2O + CO_2$ produced/hr/ml catalyst (*6*), with the fused iron and zeolite both included as catalyst volume. The activation energy of the reaction over the composite catalyst is about 5 kcal/mole, which is remarkably close to the 6 kcal/mole reported by Dry (*4*) for fluid bed operation within the same temperature range. Values of 15 to 21 kcal/mole have been reported for iron Fischer–Tropsch catalyst under fixed bed conditions (*5*, *6*).

In Table 1 typical liquid hydrocarbon products from the iron/zeolite fixed-bed process are compared with that of an iron-catalyzed fluid bed run (*7*). Both products were obtained at about the same reaction temperature. A further comparison is made in Table 2 between compositions of the C_5-fraction from the iron-catalyzed Hydrocol (*8*) process and from the iron/zeolite composite catalyst. The low α-olefin and high methylbutene contents obtained with the composite catalyst persist at higher carbon numbers and account for the high octane quality of the C_5 to 200°C fraction. The olefin content of the C_5 to 200°C fraction has been found to vary inversely with aromatics content, and ranges from 0 to 85 wt%.

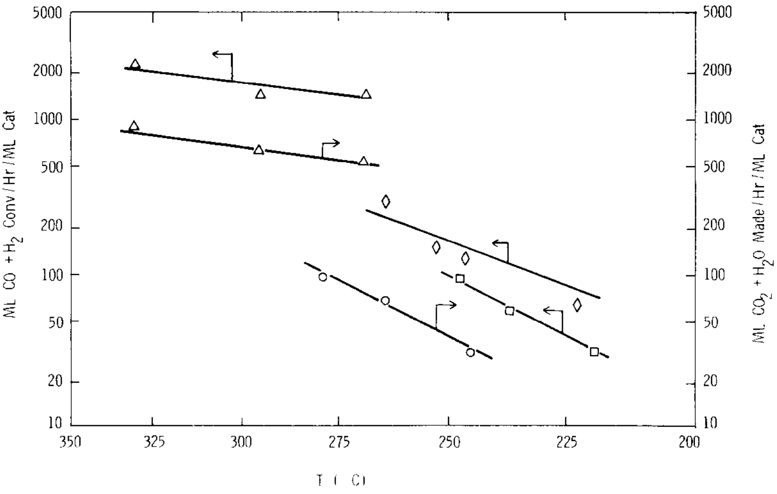


FIG. 1. Arrhenius plots of space–time yields vs reciprocal of absolute temperature in °C: △, fused iron/zeolite; ◇, fused iron (*5*); □, precipitated iron (*5*); ○, fused iron (*6*).

TABLE 1

Carbon Number Distribution in Weight Percent of Liquid Product

C-Number	Fluid-bed fused iron catalyst (*5*) (320°C)	Fixed-bed fused iron/zeolite composite catalyst (330°C)	
		Experiment A	Experiment B
4	5.3	15	14
5	12.7	14	14
6	16.6	17	18
7	16.0	15	11
8	14.1	14	16
9	10.9	20	15
10	6.9	4	9
11	4.3	1	3
12	3.3	~1	~2
13	2.4	—	—
14	1.9	—	—
15	1.5	—	—
16	1.1	—	—
17	0.9	—	—
>17	2.1	—	—

Table 3 shows the effect of geometric arrangement of the two components of the iron/zeolite composite catalyst on activity, selectivity, and rate of deactivation of the Fischer–Tropsch component. A typical formulation of composite catalyst used in most of this study is represented by Ex-

TABLE 2

Composition of C_5 Fraction from Potassium-Promoted Fused Iron Catalyst Systems at 325°C and 12 Bars

Component	Hydrocol (*6*)	Fe/Zeolite
Isopentane	3.5	32
n-Pentane	7.9	11
1-Pentene	67.2	3
2-Pentene	5.8	18
2-Methyl-1-butene	3.5	19
3-Methyl-1-butene	11.1	2
2-Methyl-2-butene	0.7	58
Unsaturates (wt% total)	88.5	57
Research octane number (C_5—200°C)	68.5	92

TABLE 3

Effect of Formulation of Catalyst Components on Performance[a]

Experiment	1		2		3		4		5	
Fe/zeolite/quartz (vol)	1/4/0		1/4/20		1/0/4		2.5/2.5/0		1/0/4//0/0/4//0/4/0	
Time on-stream (days)	2	5	2	5	1	2	2	4	1	3
CO conv. (wt%)	95	94	98	90	76	18	97	Wax plug	25	14
H_2 conv. (wt%)	54	49	56	40	47	Wax plug	58	—	16	Wax plug
Product (C_5—200°C)										
Wt% of total HC	53	61	56	58	40	40	52	—	61	—
Aromatics (wt%)	40	20	30	24	Trace	Trace	30	—	30	—
Olefins (wt%)	3	36	14	38	84	82	Trace	—	Nil	Nil
Oxygen (wt%)	0.1	—	—	—	—	1.4	—	—	—	—

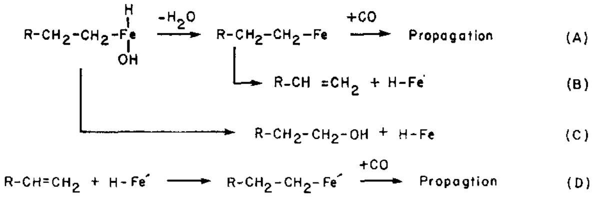
[a] 330°C hot spot: 3300 GHSV: $H_2/CO = 2:12$ bars.

periment 1. On a statistical basis each iron particle is surrounded by one or more zeolite particles. Experiment 2 preserves that configuration but provides a highly diluted bed with a long mean path between catalyst particles. This demonstrates that the observed chemistry cannot result from some hypothetical iron–zeolite surface interaction but must involve stable intermediate molecules. There was no evidence of wax in the unit after these two runs. Experiment 3 is a replica of Experiment 1 with particles of quartz substituted for the zeolite. The unit plugged with wax after 2 days. In Experiment 4 the volumes of iron and zeolite components are equivalent. Thus, there are statistically too few zeolite particles to separate the bulk of the iron particles. Wax formation terminated the run in 4 days. Experiment 5 illustrates the effects of two separate beds; iron catalyst diluted with quartz above and zeolite below a separate layer of quartz. In addition to low conversion of synthesis gas, wax formed rapidly and plugged the reactor in 3 days.[1]

Reaction Mechanism

The similarity in activation energies of the potassium-promoted fused-iron catalyst in conventional fluid-bed and iron/zeolite composite fixed-bed operations suggests that there is a similarity in the synthesis gas conversion mechanism involved in these two systems. The liquid products, however, differ vastly. In fact, those from the composite catalyst are reminiscent of the reaction products of alcohols (*3*) and olefins (*9*) over these same shape-selective zeolites. Moreover, carbon number distribution in weight percent of liquid product is essentially constant for the iron/zeolite reaction over the C_4 to C_9 range and abruptly terminates around C_{11} (Table 1). As a consequence of this selectivity the C_5 to 200°C fraction comprises 55 to 65% of the overall hydrocarbon product (Table 3). These results differ from conventional Fischer–Tropsch technology in two respects. Henrici-Olivé and Olivé (*10*) have shown that Fischer–Tropsch liquid products peak in molecular weight distribution, then decline over a broad carbon number range. They liken this phenomenon to the Schulz/Flory distribution of molecular weights frequently found in oligomerization and polymerization processes. And, Dry (*4*) has demonstrated that the theoretical yield of C_5 to 200°C material reaches a maximum at about 40%.

The observations above could be explained by the obvious two-step reaction were it not for the evidence of Experiments 1 and 2, Table 3, in which waxy products are eliminated by surrounding each iron particle with zeolite particles. This phenomenon suggests a "non-trivial polystep" reaction, the principles of which have been elucidated by Weisz (*11*). For example, it appears that the zeolite function is to intercept molecular intermediates in the chain propagation sequence and convert them to forms that are inert to further chain growth. The requisite molecular intermediates can be realized with one modification of the following chain propagation mechanism of Henrici-Olivé and Olivé (*10*).



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[1] It was subsequently found that the cycle life of the iron is affected by the solid diluent. Alumina is superior to quartz by a factor of ten in prolonging cycle life.

We propose that chain propagation by coordination of α-olefins (reaction D) becomes the major route in iron Fischer–Tropsch chemistry as the reaction temperature is raised from 250 to 350°C. If zeolite sites are then placed between Fischer–Tropsch sites, H–Fe and H–Fé, the α-olefins are converted to aromatics, branched and internal olefins, etc.

$$R\text{–}CH_2\text{–}CH{=}CH_2 + \text{zeolite} \rightarrow R\text{–}CH{=}CH\text{–}CH_3, \text{ etc.} \qquad (E)$$

These molecules complex slowly or not at all with fresh iron sites and propagation is terminated.

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