

Synthesis Gas Conversion to Aromatic Hydrocarbons

CLARENCE D. CHANG, WILLIAM H. LANG, AND ANTHONY J. SILVESTRI

Mobil Research and Development Corporation, P.O. Box 1025, Princeton New Jersey 08540

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The conversion of synthesis gas to aromatic hydrocarbons over a new class of catalysts comprising a CO reduction function combined with a ZSM-5 class zeolite is reported. The polystep nature of the catalysis is analyzed.

INTRODUCTION

Depending on choice of catalysts, synthesis gas can be converted to methane (1), methanol (2), or higher hydrocarbons. In the latter category are the Isosynthesis process (3) and Fischer-Tropsch synthesis (4). In the Isosynthesis process, synthesis gas is converted primarily to isobutane. The Fischer-Tropsch synthesis yields a broad spectrum of products, ranging from methane to heavy oils and waxes. Significant amounts of oxygenates are also produced. The gasoline cut (C_5 - C_{11}) consists mainly of normal paraffins and linear α -olefins with little or no aromatics.

We wish to report a new class of synthesis gas conversion catalysts comprising a CO reduction function combined with a new family of zeolites. Due to both the polyfunctional and shape-selective characteristics of the composite catalysts, two features are observed:

(a) Aromatics production is substantially increased over that observed with the same CO reduction catalyst in the absence of zeolite.

(b) Formation of hydrocarbons boiling above the gasoline range is eliminated or substantially reduced relative to that obtained in the absence of zeolite.

Synthesis gas reactions over metal-zeolites such as Group VIII metal-exchanged faujasites (5) and mixed Co- or Co-MgO-faujasite (6) have been reported. The exchanged faujasites yielded only light gases, while the mixed cobalt catalysts gave products with MW distributions similar to the conventional F-T.

The zeolites of the present work are members of the ZSM-5 class of zeolites which are characterized by pore openings intermediate between small pore zeolites, such as zeolite A and erionite, and large pore zeolites, such as the faujasites (7). Such zeolites are active for the conversion of methanol and other oxygenates to hydrocarbons (8).

METHODS

The catalysts were prepared either by vacuum impregnation with metal nitrate solutions, drying at 100°C and calcining in air at 1000°F, or the metal components were prepared separately from hydroxide gels before combining with the zeolite. In the latter case, the precalcined components were then milled together (-60 mesh) and pelleted. In general, exposure to flowing synthesis gas overnight at reaction conditions was sufficient for activation.

Fixed-bed microreactors used in the study were made from 9-mm-i.d. 304 stainless-steel tubing. The reaction zone contained 4-6 cc catalyst. The microreactors were heated with electrical resistance heaters. Pressure was maintained using a Grove back-pressure regulator at the exit of an air-cooled high pressure receiver downstream from the reactor. Gas flow was controlled using a Brooks Instrument (Emerson Electric Co.) flow controller. Low boiling components were condensed at atmospheric pressure in traps cooled by liquid N₂ while noncondensables were metered through a wet test meter.

Product analyses were carried out by gas chromatography.

RESULTS

Results with a composite catalyst consisting of Fe and a ZSM-5 class zeolite are given in Table 1 (Ex. 1B). As indicated, the C₅⁺ fraction is 25.2% aromatic and the aromatics are essentially low boiling (A₆-A₁₀). The effect of the zeolite can be seen by comparing Ex. 1B with Ex. 1A (3% Fe on Al₂O₃). In addition to promoting aromatics formation, incorporation of the zeolite in the catalyst reduces product olefinicity, suppresses oxygenate formation, and shifts the hydrocarbon distribution toward C₄⁺. The C₄ fraction contains 64% isobutane. The zeolite itself has no activity for synthesis gas conversion.

Results with zirconia catalysts are presented in Table 2. Pure ZrO₂ (Ex. 2A) produces largely methane, methanol-dimethyl ether, and higher boiling (C₁₁⁺) hydrocarbons, including aromatics. The presence of a large pore zeolite, H-mordenite (Ex. 2B), alters the product distribution by increasing methane and aromatics, and reducing oxygenates. The aromatics distribution is not significantly changed, with 45.5% A₁₁⁺ produced. The presence of the ZSM-5 class zeolite (Ex. 2C) induces profound changes in product distribution. Methane is nearly eliminated

TABLE I
Synthesis Gas (H₂/CO = 1) Conversion over
Metal-Zeolites

	Fe catalysts	
	1A	1B
Example number	1A	1B
Catalyst ^a		
Metal component	Fe	Fe
Zeolite	None	ZSM-5 class
Reaction conditions		
T (°C)	371	371
P (atm)	35	35
GHSV (hr ⁻¹)	3180	3000
Total effluent (wt%)		
H ₂	6.23	5.87
CO	84.18	81.66
CO ₂	7.35	4.33
H ₂ O	Trace	Trace
Oxygenates	0.32	—
Hydrocarbons	1.92	8.14
[H ₂ + CO] conversion (mole%)	8.0	12.0
Product distribution (wt%)		
C ₁	30.7	33.4
C ₂	17.5	10.8
C ₃	17.1	17.3
C ₄	6.7 ^b	19.3 ^c
C ₅ ⁺	14.3	19.2
Oxygenates	13.7	0
Percentage olefins in product	35.6	5.1
Percentage aromatics in C ₅ ⁺	0	25.2
Aromatics distribution (wt%)		
A ₆ -A ₁₀	—	100.0
A ₁₁	—	Trace

^a Ex. 1A, 3% Fe on Al₂O₃; Ex. 1B, 3% Fe on a ZSM-5 class zeolite in Al₂O₃.

^b 0.4% *n*-butane, 0.2% *i*-butane, 6.1% butenes.

^c 5.8% *n*-butane, 12.4% *i*-butane, 1.1% butenes.

as are olefins, and oxygenates are completely eliminated. The C₅⁺ fraction is seen to comprise 84.8% of the organic product and consists mainly of A₆-A₁₀ aromatics.

Finally, results with a Zn-Cr catalyst are presented in Table 3. The Zn-Cr component, in the absence of zeolite (Ex. 3A), converts synthesis gas to a mixture consisting largely of methane, methanol, and dimethyl ether. The effect of added zeolite is shown in Ex. 3B and C. In Ex. 3B, the catalyst bed consisted of a physical mixture of 60/80 mesh particles of Zn-Cr and zeolite. In the presence of zeolite the conversion is more than doubled, methane is drastically reduced, olefins and oxygenates are virtually eliminated, and gasoline boiling range aromatics are formed. The effect of reduced particle size is demonstrated in Ex. 3C. In this experiment the

TABLE 2
 Synthesis Gas ($H_2/CO = 1$) Conversion over Metal-Zeolites

Example number	Zr catalysts		
	2A	2B	2C
Catalyst ^a			
Metal component	Zr	Zr	Zr
Zeolite	None	H-Mordenite	ZSM-5 class
Reaction conditions			
T (°C)	427	427	427
P (atm)	83	83	83
GHSV (hr ⁻¹)	720	720	720
Total effluent (wt%)			
H ₂	6.17	6.39	5.74
CO	85.99	90.08	80.38
CO ₂	5.80	1.04	4.30
H ₂ O	0.42	1.24	3.55
Oxygenates	0.56	0.06	—
Hydrocarbons	1.06	1.19	6.03
[H ₂ + CO] conversion (mole%)	7.5	3.6	13.8
Product distribution (wt%)			
C ₁	24.8	44.9	1.6
C ₂	4.7	9.1	6.8
C ₃	2.5	2.5	6.0
C ₄	9.5	4.6	0.8
C ₅ ⁺	24.0	34.8	84.8
Oxygenates	34.5 ^b	4.1 ^b	0
Percentage olefins in product	11.0	7.8	0.5
Percentage aromatics in C ₅ ⁺	53.1	94.5	99.8
Aromatics distribution (wt%)			
A ₆ -A ₁₀	46.0	54.5	97.3
A ₁₁ ⁺	54.0	45.5	2.7

^a Ex. 2A, 50% ZrO₂, 50% SiO₂; Ex. 2B, 50% ZrO₂, 50% H-mordenite (Norton Zeolon); Ex. 2C, 50% ZrO₂, 50% ZSM-5 class zeolite.

^b MeOH + Me₂O.

catalyst components were separately milled to -200 mesh and then mixed together and pelleted. The somewhat lower resultant conversion is attributed to the lower bulk density of the Ex. 3C catalyst. The reduction in particle size from 60/80 mesh to -200 mesh causes a major shift in product distribution toward increased aromatics yield and decreased C₅⁻ paraffins, indicating the importance of diffusional considerations (*vide infra*).

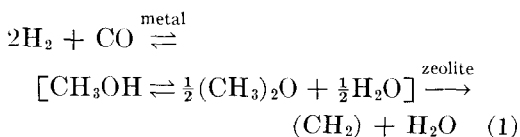
DISCUSSION

The nontrivial polystep (10) nature of the Fe/ZSM-5 class zeolite catalyst system

was first identified by Caesar *et al.* and is presented in a parallel paper (9).

In this paper, we will describe both the polyfunctional and shape selective characteristics of the Zr- and Zn-Cr/ZSM-5 class zeolite catalyst systems. As shown in Tables 2 and 3, the zeolite component significantly enhances conversions in these catalysts. The presence of methanol and dimethyl ether in the nonzeolite experiments suggests that these are intermediates, and that the zeolite provides a drain-off mechanism to overcome an equilibrium limitation. This is a condition for the occurrence of Weisz's "nontrivial polystep"

reaction (10). The overall reaction scheme may be written as follows:



Carbon dioxide may also be formed via the water gas shift, depending on the particular choice of metal component.

A second type of polyfunctional reaction, that of selectivity change by interception of a usual reaction path, is also exhibited by the data. The most striking example of

this is the effect of the ZSM-5 class zeolite on methane formation with the Zr and Zn-Cr catalysts. Since methane is a thermodynamically stable end product under the conditions, its suppression by the zeolite must be through interception of a precursor. This effect appears to be absent in the case of the Fe catalyst, suggesting either that the methane precursor is more strongly bound and immobile on the Fe surface, or the mechanism of methane formation on the Fe catalyst is different, e.g., via carbide intermediates from dissociative sorption of CO (11), as opposed to M(CH)OH species

TABLE 3
Synthesis Gas ($\text{H}_2/\text{CO} = 1$) Conversion over Metal-Zeolites

Example number Catalyst ^a	Zn-Cr catalysts		
	3A	3B	3C
Metal component	Zn-Cr	Zn-Cr	Zn-Cr
Zeolite	None	ZSM-5 class	ZSM-5 class
Component particle size (mesh)	-60	60/80 ^b	-200 ^b
Reaction conditions			
T (°C)	427	427	427
P (atm)	83	83	83
GHSV (hr)	1740	1780	1780
Total effluent (wt%)			
H ₂	5.51	4.35	4.80
CO	73.91	43.09	48.95
CO ₂	13.59	39.43	34.50
H ₂ O	0.40	1.53	1.67
Oxygenates	2.47	—	—
Hydrocarbons	4.12	11.60	10.08
[H ₂ + CO] conversion (mole%)	18.9	44.1	37.7
Product distribution (wt%)			
C ₁	42.2	3.9	2.5
C ₂	9.8	13.1	12.3
C ₃	3.8	22.9	9.9
C ₄	1.8	15.5	3.3
C ₅ ⁺	4.9	44.6	72.0
Oxygenates	37.5 ^c	<0.1	0
Percentage olefins in product	2.8	0.6	0.1
Percentage aromatics in C ₆ ⁺	0	75.6	97.3
Aromatics distribution (wt%)			
A ₆ -A ₁₀	—	89.3	83.6
A ₁₁	—	10.7	16.4

^a Ex. 3A, 16% ZnO, 44% Cr₂O₃, 40% SiO₂; Ex. 3B and C, 16% ZnO, 44% Cr₂O₃, 40% ZSM-5 class zeolite.

^b Ex. 3B, $P_B = 1.1$; Ex. 3C, $P_B = 1.0$.

^c MeOH + Me₂O.

formed by reactions between H(ads) and CO(ads) (12).

The shape selective influence of the ZSM-5 class zeolite on aromatics distribution is also apparent from the data. This is due to its unique pore geometry, which provides constrained access (and egress) for certain sorbates, depending on size and shape. Molecules with critical dimensions larger than durene experience difficulty penetrating the zeolite pore system (8). This property is responsible for the narrow distribution of product molecular weights, terminating at about C₁₁, which corresponds to the end-point of conventional gasoline.

The role of mass transport in polyfunctional catalysis has been considered in detail by Weisz (10). Diffusional kinetics are likely to be particularly important in the present system. Interparticle diffusivity will be high relative to intracrystalline diffusivity. Assuming that the zeolite exterior has negligible catalytic activity, pore diffusion will be the rate-controlling process, especially where the catalyst is composed of separate particles of reducing component and zeolite.

Weisz has derived a general criterion, largely insensitive to particle shape and exact kinetics, which defines the physical conditions of intimacy between catalyst components for absence of mass-transport inhibition. In terms of the partial pressure of *B*, the diffusing intermediate, the requirement is

$$\Phi = (dN/dt)(RT/P_B)(r^2/D) < 1 \quad (2)$$

where

- T* = reaction temperature
R = gas constant (cc atm mol⁻¹ deg⁻¹)
dN/dt = reaction rate (moles sec⁻¹ cm⁻³)
r = particle radius (cm)
D = diffusivity (cm² sec⁻¹).

Applying Eq. (2) to the system under consideration, we gain an appreciation of

the order-of-magnitude of the effect of key parameters. Focusing attention on Ex. 3A, Table 3, the mean rate of *B* formation (in our case methanol and dimethyl ether) is 3.5×10^{-6} moles sec⁻¹ cm⁻³. As indicated, the catalyst particles were 60/80 mesh, or $0.09 \text{ mm} < r < 0.13 \text{ mm}$ (Ex. 3B).

The diffusivity of methanol in ZSM-5 class zeolite has not been determined for the reaction temperatures under consideration. A lower limit of $D = 10^{-7}$ cm² sec⁻¹ has been determined by Chen and Pelrine (13) at 67.5°C. The diffusivity of methanol in the large pore zeolite HY has been studied by Salvador and Garcia-Gonzalez (14), who report an activation energy of 25 ± 2.5 kJ mol⁻¹. The activation energy for methanol in ZSM-5 class zeolites is expected to be somewhat higher in view of the smaller pore size of ZSM-5. However, to obtain a conservative estimate, the value of 25 kJ mol⁻¹ may be used with the data of Chen and Pelrine, resulting in $D > 10^{-5}$ cm² sec⁻¹ at 427°C. Assuming that the water-gas shift goes to equilibrium, and utilizing published free energy data (15), the equilibrium partial pressure, calculated by an iterative procedure, is

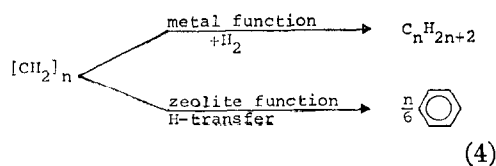
$$P_{B_{eq}} = 2.5 \text{ atm} [\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{O}] \quad (3)$$

Applying Eq. (2) we find

$$0.6 < \Phi < 1.4$$

indicating that the reaction is substantially free from diffusional limitation. In this example, therefore, the maximum polystep rate is closely approached.

The observed particle size effect on aromatics selectivity can be interpreted with the assumption of competing reactions as in the following idealized scheme.



Selectivity will be dependent on the relative effectiveness, which in turn is governed by diffusion criteria, of the two catalyst components.

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