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Syngas Conversion to Ethane over Metal–Zeolite Catalysts

CLARENCE D. CHANG, JOSEPH N. MIALE, AND RICHARD F. SOCHA

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

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Synthesis gas is selectively converted to ethane over a dual-functional catalyst comprised of HZSM-5 zeolite ($SiO_2/Al_2O_3 = 70$) containing Cr, Zn, and Al in the atomic ratios 1 : 1 : 1 (zeolitic Al) at 343–482°C, 100 atm, and 500 hr^{-1} GHSV. Ethane selectivities as high as 83 wt% were obtained. The roles of metal and zeolite are defined and the reaction path is elucidated.

INTRODUCTION

Methanation and methanol synthesis are the only known CO hydrogenation reactions where perfect selectivity is approached. The higher hydrocarbons and alcohols are believed to be formed by a chain-growth mechanism involving stepwise addition of C_1 units. It has been recognized (*1, 2*) that such a process should obey Schulz–Flory (SF) polymerization kinetics (*3*). According to the SF model

$$W_n = n\alpha^{n-1}(1 - \alpha)^2, \qquad (1)$$

where n = chain length; α = probability of chain propagation, assumed constant; W_n = weight fraction of nth chain. It follows from Eq. (1) that

$$W_{n,\max} = 4n(n - 1)^{n-1}/(n + 1)^{n+1} \qquad (2)$$

from which $W_n < 1$ for $n > 1$. Despite its simplicity, the SF model has enjoyed remarkable success in predicting a wide spectrum of Fischer–Tropsch product distributions (*4, 5*), although a few exceptions have been reported (*6, 7, 15*).

Circumvention of the SF distribution in CO hydrogenations has proven to be a fascinating challenge to many researchers. One approach is to intercept the growing chain and divert it into a new reaction pathway. This was first demonstrated by Chang *et al.* (*8*) and Caesar *et al.* (*9*), who designed catalysts that contained both metal CO hydrogenation and acid (zeolite) functions. The zeolite served to interrupt chain growth through cracking, isomerization, and aromatization reactions. Other examples are now known (*10–12, 22*).

We report a new example of "non-SF" CO hydrogenation. Syngas is converted to ethane in high selectivity utilizing the dual-functional catalytic approach.

Ethane is the preferred feed for ethylene synthesis by steam cracking (*15*). The conversion of syngas to light olefins for use in petrochemical feedstocks has been the goal of much research. Direct syngas conversion to ethylene (*16–18*) has been marked by low reactivity or poor selectivity. Indirect conversion routes, which are generally based on the Mobil methanol-to-hydrocarbon technology (*14*), yield mixtures of olefins (*19*). In one variant (*20*), ethylene selectivities ~30% of hydrocarbon product were achieved by operation with steam dilution, at partial conversion and recycle of unconverted feed. This process has been successfully tested in pilot plant. The present finding offers a potential new high-selectivity route to ethylene from coal via syngas.

EXPERIMENTAL

Zeolites used in this study were ZSM-5 with $SiO_2/Al_2O_3 = 70$ and 26,000 prepared

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TABLE 1

Syngas Conversion to Ethane: Effect of Temperature

$H_2/CO = 2$, 100 atm, 500 hr^{-1} GHSV

Run number	1	2	3	4	5	6
Temperature, °C	343	371	399	427	454	482
Conversion, %						
H_2	4	10	12	22	33	51
CO	11	15	27	39	61	75
Selectivity, wt%						
CH_4	5.2	12.1	10.1	17.7	32.9	55.6
C_2H_6	82.8	81.4	82.7	73.6	58.2	38.8
C_3H_8	7.2	3.1	4.1	6.3	6.8	4.7
C_4H_{10}	4.8	3.4	3.1	3.0	2.1	1.0

according to the method of Argauer and Landolt (*13*).

Metals were impregnated into the zeolite from solutions of their nitrates. The impregnated catalysts were calcined in air at 538°C and then reduced in dilute H_2 (8.5% H_2 in He) at 204°C prior to use.

Syngas was obtained premixed and analyzed from Matheson.

Dimethyl ether was Research Purity Grade from Matheson.

Reactions were carried out in stainless-steel microreactors previously described (*8*).

Analyses were performed by gas chromatography. For separation of H_2, CO, CH_4, and N_2, molecular sieve 13× columns were used; for CO_2, C_2H_4, and C_2H_6, Porapak QS; and for higher hydrocarbons, OV-17 and OV-101.

RESULTS AND DISCUSSION

Syngas ($H_2/CO = 2$) was passed over a catalyst comprising HZSM-5 zeolite ($SiO_2/Al_2O_3 = 70$) containing Cr, Zn, and Al in the atomic ratios 1 : 1 : 1 (zeolitic Al), at 343–482°C, 100 atm, and 500 hr^{-1} GHSV. Table 1 shows the effect of increasing temperature on conversion and selectivity. The non-SF character of the product distribution is immediately evident. As seen, ethane selectivities are as high as ~83% at the lower temperatures and decrease to ~39% at 482°C. The maximum ethane consistent with the SF model is 29.6% (Eq. (2)). With increasing temperature, ethane selectivity loss is accountable almost completely by the increase in methane.

Table 2 contains a detailed breakdown of the products from Run 3 (Table 1). From the data the following reaction stoichiometry is deduced

$$4.4\ CO + 2.58\ H_2 \rightarrow C_2H_6 + 2.13\ CO_2 + 0.26\ \text{other} \quad (3)$$

This shows completion of the water–gas shift reaction and approaches the ideal reaction

$$4CO + 3H_2 \rightarrow C_2H_6 + 2CO_2 \quad (4)$$

Mechanistically, two likely reaction pathways may be considered

Scheme A:

$$4H_2 + 2CO \xrightarrow{M} C_2H_5OH + H_2O$$

$$C_2H_5OH \overset{Z}{\rightleftharpoons} C_2H_4 + H_2O$$

$$H_2O + CO \overset{M}{\rightleftharpoons} H_2 + CO_2$$

$$C_2H_4 + H_2 \overset{M}{\rightleftharpoons} C_2H_6$$

Scheme B:

$$2H_2 + CO \overset{M}{\rightleftharpoons} CH_3OH$$

$$2CH_3OH \overset{Z}{\rightleftharpoons} CH_3OCH_3 + H_2O$$

$$CH_3OCH_3 \overset{Z}{\rightleftharpoons} C_2H_4 + H_2O$$

$$H_2O + CO \overset{M}{\rightleftharpoons} H_2 + CO_2$$

$$C_2H_4 + H_2 \overset{M}{\rightleftharpoons} C_2H_6$$

M = metal function; Z = zeolite function.

In Scheme A, it is postulated that the metal component, or metal–zeolite combination, had unique ethanol synthesis activity. Ethanol dehydration would give ethene as the key ethane precursor.

In Scheme B, methanol is the initial product, which is converted to olefin by the

TABLE 2

Syngas Conversion to Ethane: Reactor Effluent Composition[a]

Product	mole%
H_2	66.3
CO	26.2
CO_2	4.7
CH_4	0.5
C_2H_6	2.18
C_3H_8	0.07
C_4H_{10}	0.05
	100.00

[a] Run 3, Table 1.

TABLE 3

Syngas Conversion to Ethane: Role of Metal/Zeolite Functions

Catalyst: CrZnAl/ZSM-5 Reaction conditions: $H_2/CO = 2$, 100 atm, 399°C, 500 hr^{-1} GHSV

Zeolite SiO_2/Al_2O_3	70	26,000
Conversion, %		
H_2	12	5
CO	27	15
Selectivity, wt%		
CH_4	10.1	8.7
C_2H_6	82.7	2.9
C_3H_8	4.1	0.8
C_4H_{10}	3.1	0.0
CH_3OH	0.0	8.2
CH_3OCH_3	0.0	79.4

well-known reaction over ZSM-5 zeolite (*14*), and thence to ethane by hydrogenation.

To discriminate between these two possibilities, experiments were carried out where the metal loading was held constant and the zeolite acidity decreased by increasing SiO_2/Al_2O_3. Data shown in Table 3 compare the Run 1 (Table 1) results with an experiment where an ultrahigh silica ZSM-5 (SiO_2/Al_2O_3 = 26,000) was used as the support for the metal. It is seen that the latter catalyst afforded mostly dimethyl ether. It may be inferred therefore that Scheme A is inapplicable and Scheme B is the more likely pathway. It will also be noted that the conversion is significantly lower in the case of the high-silica catalyst. This may be taken as evidence of lower efficiency of equilibrium displacement due to the extremely low acidity of the zeolite component.

Additional support for this interpretation

TABLE 4

Syngas Conversion to Ethane: Effect of Function Intimacy

	CrZnAl/ZSM-5, $H_2/CO = 2$, 343°C, 100 atm, 500 hr^{-1} GHSV		CH_3OCH_3 Feed, 343°C, 1 atm
	Impregnated catalyst	Physically mixed catalyst	HZSM-5 (SiO_2/Al_2O_3 = 70)
Conversion, %			
H_2	4	5	2.2 (%CH_2)
CO	11	14	
Selectivity, wt%			
C_1	5.2	7.5	0.6
C_2	82.8	28.8	17.9
C_3	7.2	46.2	49.7
C_4	4.8	15.6	27.4
C_5	0.0	2.0	4.4

was obtained in an experiment where the metal component was placed outside the zeolite crystal, i.e., physically mixed, rather than impregnated into the zeolite. As shown in Table 3, the physically mixed catalyst system afforded a mixture of light paraffins with propane as the major product. Finally, the carbon number distribution of this mixture is compared in Table 4 with data from the reaction of dimethyl ether over HZSM-5 ($SiO_2/Al_2O_3 = 70$) at 343°C, at low conversion (2.2%). The distributions are quite comparable though not identical. It may be concluded that the olefins formed from methanol/dimethyl ether in the zeolite interior rapidly undergo homologation and emerge from the zeolite pore as a mixture, which is hydrogenated on the external metal catalyst particles. When the metal catalyst is placed inside zeolite pore, its proximity to the acid sites allows interception of the olefin intermediate before substantial homologation has occurred.

It may be of interest to note that these results provide strong evidence that ethene is the "first" olefin produced in methanol/dimethyl ether conversion to hydrocarbons over ZSM-5 zeolite, a question which has generated some controversy (*12, 23*).

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