

GENERAL PAPERS - POSTER SESSION
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. MEETING, AUGUST 28 - SEPTEMBER 2, 1983

RADIOACTIVE (^{14}C) TRACER STUDIES OF METHANOL CONVERSION
OVER A Ni-ZSM-5 ZEOLITE

By

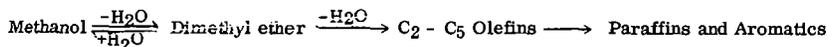
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INTRODUCTION

Within the last few years, researchers at the Mobil Research and Development Corporation (1) have synthesized a novel zeolite catalyst, ZSM-5, which is capable of converting oxygenates, e.g., methanol, into aliphatics and aromatic hydrocarbons in the gasoline boiling range. Since technology exists for making methanol from coal-derived synthesis gas (2), this new process provides an additional source of chemical feedstocks and transportation fuels.

In the conversion of methanol to hydrocarbons over such catalysts, more than 100 different compounds have been identified (3,4). The major hydrocarbon products can be classified into three categories: olefins, paraffins, and aromatics. There is a strong possibility that some of these products, once formed, react further to produce other products. The objective of this research was to investigate this possibility by labeling some of the products and following the transfer of the label to other products.

The reaction is thought to follow the sequence



The interconversion of methanol and dimethyl ether over such catalysts has been confirmed in several studies (5,6). At very low conversion of methanol, dimethyl ether is the major product, and the transformation of methanol into dimethyl ether is 20 to 30 times faster than hydrocarbon formation (6). On the other hand, when dimethyl ether is the starting material, both methanol and hydrocarbons are formed readily (5,6). The intermediate role of dimethyl ether was also confirmed by using a $^{13}\text{CH}_3\text{-O-}^{13}\text{CH}_3$ tracer technique (6).

The roles played by the lightweight olefins were investigated by Dejaifve et al. (7). They carried out reactions of C_2 , C_3 , and C_4 olefins over ZSM-5 catalysts and observed similar aromatic product distributions from both methanol and all the olefins. Therefore, they concluded that light olefins were intermediates of methanol conversion to gasoline boiling range products.

This research was aimed at identifying some of the major reactions involved in the overall methanol reaction. A ^{14}C -labeled tracer technique was developed to explore the roles played by the various species, including olefins, paraffins, and aromatics. The results are described herein.

EXPERIMENTAL

Catalyst

The original ZSM-5 catalyst was prepared at the Exxon Research and Development Laboratories. This material was in the sodium form and was calcined for 2 hours at 600°C . It was then soaked in a solution of ammonium nitrate (9 wt%) for another 2 hours with constant agitation. After the resulting $\text{NH}_4\text{-ZSM-5}$ had been washed and filtered, it was impregnated with a solution of 0.0439 g nickel acetate/g of dry zeolite and then heated until dry at 120°C . This impregnated Ni-ZSM-5 catalyst was subsequently blended with alumina, which served as a binder, in the proportion 0.3 g alumina/g ZSM-5. All catalysts used for these reaction studies were pelletized, crushed, and screened to 30/40 mesh.

Chemicals

Methanol (99.99% purity) was obtained from Fisher Scientific Company. The radioactive compounds, along with their suppliers, are shown in Table I. Both chemical and radiochemical purities of each were checked by the radio-gas chromatograph described later. Since the methanol,

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propylene, 1-butene, n-hexane, n-heptane, and benzene were satisfactory in both chemical and radiochemical purities, they were used as received. However, radioactive impurities were found in the original ethylene and iso-butane, which necessitated purification with a preparative GLC column (30 ft. long 5/16 in. O. D. Porapak Q at 100-150°C).

Reactor System

Figure 1 shows the experimental set-up. Liquid methanol was admitted into a stream of helium carrier gas by a syringe pump. To facilitate rapid vaporization of the liquid reactant, the glass sections immediately before and after the syringe injection port were packed with glass beads and heated by nichrome wire. A 250 ml mixing volume was installed before the reactor to moderate any pulsations in the reactant concentration.

TABLE I
RADIOACTIVE CHEMICALS

<u>Compound</u>	<u>Specific Activity (mC/mmole)</u>	<u>Chemical Purity</u>	<u>Manufacturer*</u>
Methanol	6.7	98+%	PLI
Ethylene (1,2- ¹⁴ C)	3.5	98%	CBC
Propylene (1- ¹⁴ C)	1.0	98%	CBC
1-Butene (4- ¹⁴ C)	5.0	---	ICN
1-Butane (2- ¹⁴ C)	1.02	98%	CBC
n-Hexane (1- ¹⁴ C)	1.0	---	ARC
n-Heptane (1- ¹⁴ C)	1.0	---	ARC
Benzene	1.0	---	ARC

*PLC - Pathfinder Laboratories, Inc.

CBC - California Bionuclear Corp.

ARC - American Radiochemical Corp.

Pulses of radioactive tracers were introduced into the pre-evacuated doser through the standard taper ST1. The pressure in the doser was monitored with a mercury manometer.

The catalyst bed and a bed of vycor chips, located just upstream from and having the same mesh size as the catalyst, were sandwiched in the reactor between two glass wool plugs. The vycor chips served as a preheater and helped develop plug flow in the catalyst bed.

Radio-Gas Chromatograph System

A radio-gas chromatograph (RGC) system, shown schematically in Figure 1, was integrated with the reaction system to facilitate periodic sampling and on-line analysis of the products from the reactor. This system consisted of a modified Varian model 3700 gas chromatograph, three different types of detectors (TCD, FIC, ICD), a separation column, and a changeable sample loop connected to a 6-port valve V3.

The temperature programmed chromatographic column was a 7-ft. by 1/8-in. O. D. stainless steel tube packed with 15% squalane on 80/100 mesh chromosorb P. Connected to the column exit was a stream splitter which divided the effluent stream into two parts in the approximate ratio 1:10. The smaller stream went to the FID (flame ionization detector) and the larger stream was directed into the ICD (ionization chamber). The argon quench gas was used to sweep the radioactive gases out of the 4.5 ml ionization chamber quickly for improved peak resolution (10).

Experimental Procedure

The reaction was carried out in a finite-tracer but continuous-reactant flow manner. This arrangement was used to minimize the consumption of expensive radioactive chemicals and yet to conduct the experiment in the "steady state" so that meaningful kinetic data could be extracted.

With methanol and helium flowing through the reactor, the reaction was brought to the steady state at a fixed set of conditions with the effluent bypassing the sample loop. A very small amount of tracer was introduced into the large pre-evacuated doser (50 ml). The tracer was then diluted with a portion of the reactant stream to make the pressure in the doser the same as that in the reaction system. This made the composition of material in the doser identical to that in the reactant stream except for the small amount of tracer in the doser.

Each radio-tracer experiment was begun by diverting the reactant stream to flow through the doser, and a liquid nitrogen trap collected all the hydrocarbons (except methane) in the product stream. After all the radioactive materials were trapped in the sample loop (usually about 8 minutes),

the sampling valve was returned to its original position, the liquid nitrogen dewar flask was removed, and the products were flashed into the GLC column. The amount of each product was monitored on the FID, and the radioactivity in each peak was measured by the ICD.

The specific activity A_i in each of the analyzed peaks was calculated by the following equation:

$$A_i = \frac{\frac{\text{(Radioactivity in product } i, \text{ mC)}}{\text{(Total radioactivity in all hydrocarbon products, mC)}}}{\frac{\text{Moles of product } i}{\text{Total moles of hydrocarbon products}}}$$

RESULTS

Different types of ^{14}C -labeled tracers -- olefins (ethylene, propylene, l-butene, paraffins (iso-butane, n -hexane, n -heptane), and aromatics (benzene) -- were used to investigate the roles that these several species play in the overall methanol-to-hydrocarbon reaction.

In all experiments, the reaction was carried out over 100 mg of the Ni-ZSM-5 catalyst at 368°C and 1 atm total pressure. The partial pressure of methanol in the inlet stream was 0.05 atm, and the space time τ was 218 mg cat·sec/cm³-STP. Other reaction conditions for each experiment are given in Table II.

TABLE II
REACTION CONDITIONS FOR TRACERS

	<u>Ethylene</u>	<u>Propylene</u>	<u>l-Butene</u>	<u>i-Butane</u>	<u>n-Hexane</u>	<u>n-Heptane</u>	<u>Benzene</u>
Amount Added (μmole)	0.51	0.76	0.76	1.14	2.53	2.53	1.03
Radioactivity (μC)	1.79	0.76	0.10	1.16	0.10	0.10	0.30
Partial pressure of methanol - 0.05 atm							
τ (Space time) - 218 mg cat·sec/cm ³ -STP							
Reactor temperature - 368°C							

Table III lists the specific activity A_i for all the products (or groups of products) when the olefins, ethylene, propylene, and l-butene, were used as tracers. For propylene and l-butene, the radioactivity was almost uniformly spread among all the products, even including the compound initially labeled. However, for ethylene less than 50% of the radioactivity was incorporated into other products with the majority remaining in the ethylene. For this reason, the radioactivity in the ethylene was excluded from the normalization of the radioactivity in each of the products. In other words, the distribution of radioactivity among the various products was based only on the ethylene that reacted, and not on the total radioactive ethylene admitted.

TABLE III
RADIOACTIVITY DISTRIBUTION AMONG HYDROCARBON PRODUCTS

<u>Tracer</u>	<u>Specific Activity in Products</u>						
	<u>C₂</u>	<u>C₃</u>	<u>C₄</u>	<u>C₅</u>	<u>C₆⁺</u>	<u>Toluene</u>	<u>Xylenes</u>
C ₂ H ₄	----*	1.29	1.03	1.43	1.00	2.18	1.62
C ₃ H ₆	0.39	1.15	1.00	1.38	0.95	2.27	1.81
1-C ₄ H ₈	0.35	0.91	1.35	1.52	1.18	2.06	1.64

*Since more than 50% of the added radioactivity remained in the ethylene, its radioactivity was not included in calculating the specific activity of the other products. Thus, the specific activities given are based only on the ethylene that reacted, not the amount added.

The paraffins were much less reactive than the olefins. For example, in the runs with iso-butane as the tracer, essentially no radioactivity was found in any reaction products other than in the iso-butane. When n -hexane and n -heptane were used as tracers, most (ca. 80%) of the radioactivity

remained in the starting labeled tracer compound. There was a small amount of radioactivity in the C₂ to C₄ aliphatics. Significantly, no radioactivity was detected in the aromatic products.

When labeled benzene was used as a tracer, no radioactivity was found in any of the products except certain aromatics, i. e. there was no measurable radioactivity in the aliphatics. The majority (52%) of the radioactivity remained in the benzene. Considerable radioactivity was in the toluene (26%), followed by (o+m)-xylene (18%), o-xylene (3%), and trimethylbenzene (1%). Since the products contained about 6 times as much (o+p)-xylene as m-xylene, the "specific activity" for these dimethyl aromatics must be the same. Toluene had a higher specific activity (approximately by a factor of 3.4) than the xylenes, while trimethylbenzene had less (about 0.2) relative to the xylenes.

In all cases the conversion of methanol was 100%.

DISCUSSION

Olefin Tracers

The observation of radioactivity in all the hydrocarbons from methanol conversion when labeled ethylene, propylene, or 1-butene were used as tracers clearly indicates that these three light olefins play very important roles in the overall methanol-to-hydrocarbon reaction. Especially, the results have verified that even ethylene is involved in the reactions (as postulated by Dejaifve et al. (7) and suspected by Anderson et al. (8)), although ethylene is much less active than are the larger olefins.

In view of the lower reactivity of gaseous ethylene as evidenced by the retention of much more radioactivity in itself than occurred with the labeled propylene and 1-butene, we suggest that the desorption of ethylene is faster than its reactive chemisorption. Moreover, the appearance of radioactive propylene from the initial ethylene tracer supports the claim that the surface reaction of chemisorbed ethylene with methanol is relatively fast. Such a facile reaction of surface ethylene with methanol and/or dimethyl ether, viewed as an autocatalytic step, has been described by Chen and Reagan (9).

The data in Table III show that specific radioactivities of C₂, C₃, C₄, and C₅ aliphatics are of the same order of magnitude. This strongly suggests that the formation of aliphatics proceeds mainly via a C₁ step addition, or more specifically through alkylation with methanol or dimethyl ether.

The detection of much less specific radioactivity in the C₂ aliphatics from the propylene tracer and in the C₂ - C₃ aliphatics when 1-butene was the tracer implies that these small olefins are not cracked substantially but are rather incorporated into higher molecular weight products. These larger hydrocarbons may then be cracked into lower molecular weight compounds.

Similar specific radioactivities were found in both toluene and in the xylenes, regardless of which olefinic tracer was used. This observation illustrates the common role played by these light olefins in the formation of aromatics during methanol conversion of the Ni-ZSM-5 catalyst. Furthermore, since the specific radioactivities in the aromatics are 1.5 to 2.0 times greater than those in the C₃ and C₄ products, it is reasonable to infer that a major pathway of toluene and xylene formation is the reaction between one C₃ and one C₄ or two C₄ species. This conclusion was also drawn by Derouane and co-workers (7).

Paraffin Tracers

Paraffins are relatively stable final products in the methanol conversion system. The fact that ¹⁴C-tagged iso-butane retains essentially all its radioactivity within itself among the hydrocarbon products shows that neither isomerization of butanes nor alkylation of iso-butane with prevailing olefins is occurring at 368°C.

In methanol conversion over ZSM-5-type zeolites, monomethyl paraffins and olefins predominate over their straight-chain counterparts (5,8). The same was observed with our Ni-ZSM-5 catalyst. In general, this is consistent with thermodynamic equilibrium (the methyl paraffins are more stable than the corresponding straight chain molecules), except for the butanes. At 368°C thermodynamics predicts that n-butane is more stable than iso-butane (57% vs. 43%). Since these two paraffins are not interconverted under reaction conditions, they are probably formed mainly by hydrogen transfer to the respective n-butenes or iso-butene.

Aromatic Tracers

Benzene is a very thermodynamically stable compound. However, its low concentration among the reaction products causes one to question its function in the overall methanol conversion reactions. The radioactivity distribution among the aromatic products when benzene was used as a tracer reveals that alkylation of benzene to form toluene, the xylenes, and trimethylbenzene is a major route for their formation.

Benzene may be alkylated with methanol or with dimethyl ether to produce toluene, which in turn reacts with more methanol or ether molecules to form first the xylenes and then the trimethylbenzenes. This is consistent with the specific activity ratio following the order toluene > xylenes >

FIGURE 1. REACTION, RADIO-GAS CHROMATOGRAPHIC SYSTEMS

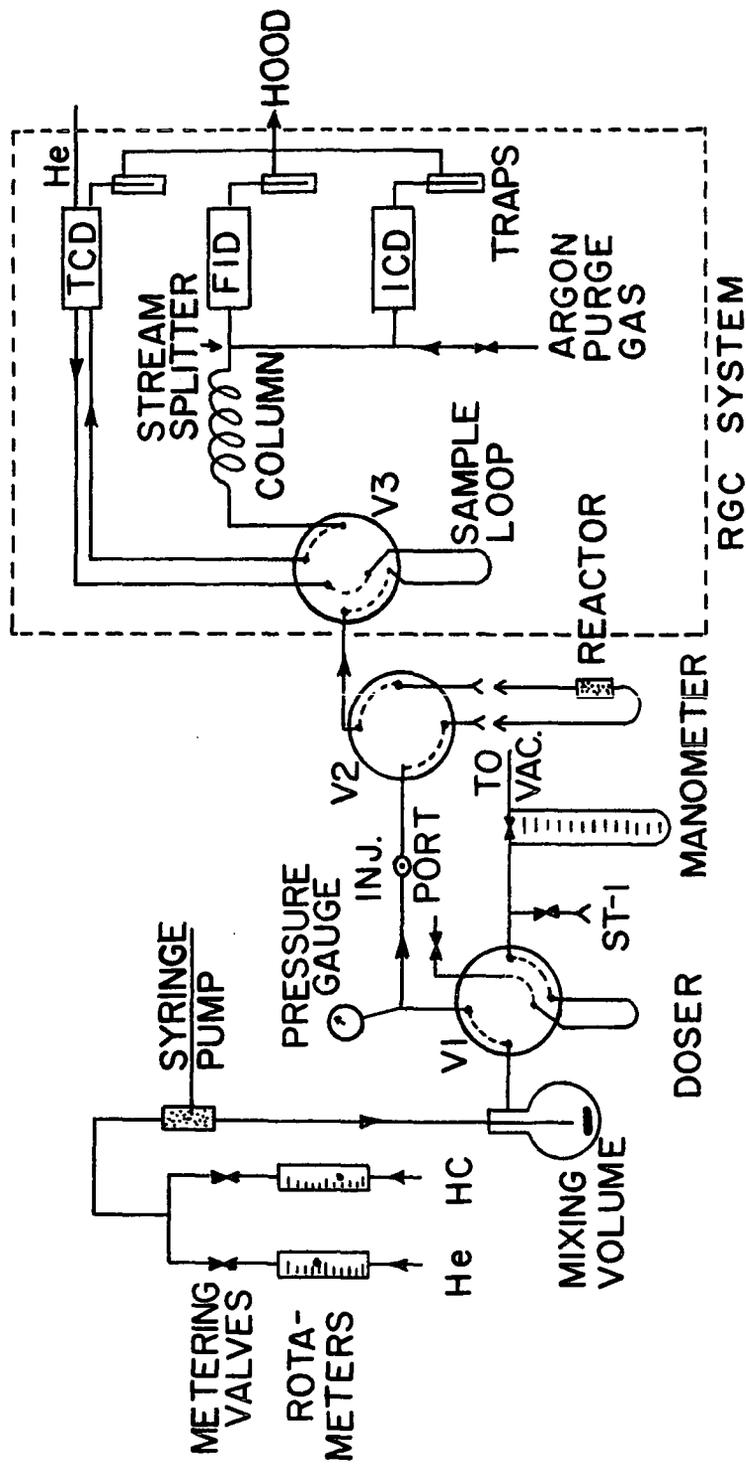
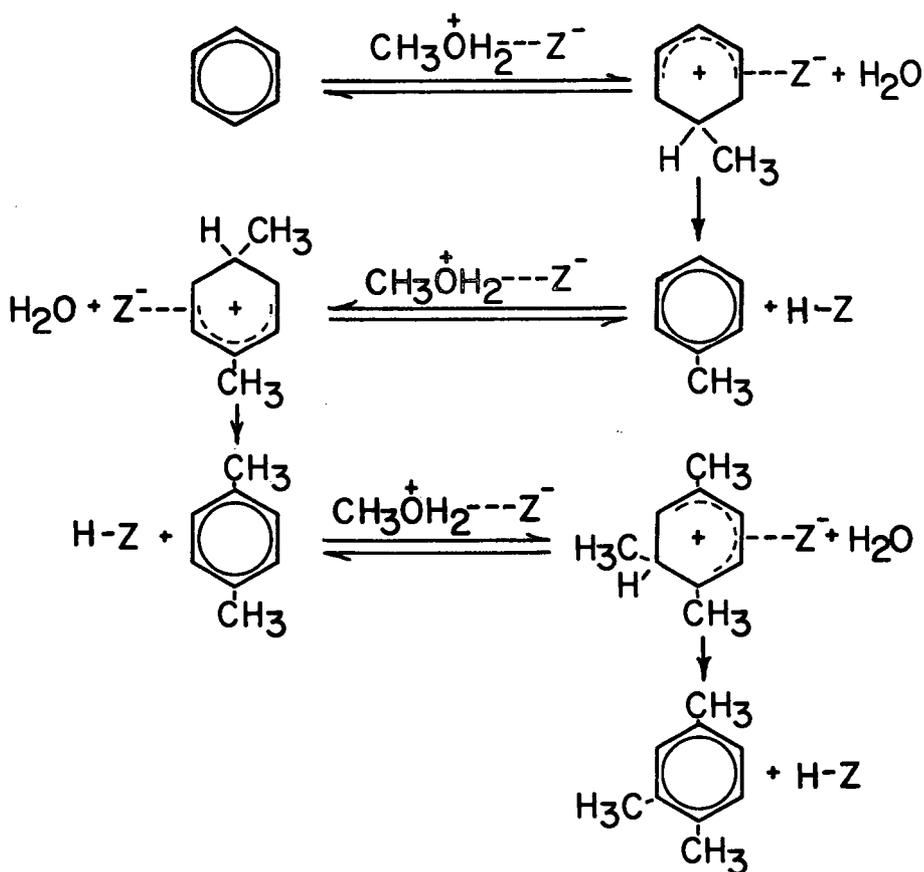


FIGURE 2. ALKYLATION OF AROMATICS



trimethylbenzenes when benzene was used as the tracer.

It is worth noting that the role played by benzene in the formation of alkylated benzenes is quite similar to that of ethylene in the production of higher aliphatics. As observed for the ethylene tracer, ^{14}C -labeled benzene retains most of its radioactivity intact, again indicating that reactive chemisorption is relatively slow. However, the formation of radioactive toluene suggests that the surface reaction of the chemisorbed benzene with methanol or dimethyl ether occurs readily. These results also seem to point out that the nature of this reaction is autocatalytic, as proposed by Chen and Reagan (9) for ethylene reaction with methanol or dimethyl ether to account for the low concentration of ethylene in the product.

In light of the acidic properties of the ZSM-5 catalyst, a carbenium ion mechanism can be proposed for the formation of alkylated benzenes from benzene as indicated in Figure 2.

CONCLUSIONS

Through the use of ^{14}C -labeled tracer compounds, some important secondary reactions have been identified in the overall conversion of methanol to hydrocarbons over a Ni-ZSM-5 catalyst. The major findings are:

1. The alkylation of light olefins with methanol or dimethyl ether is a major pathway for the formation of larger olefins with one more carbon atom.
2. Paraffins are mainly produced by hydrogen transfer reactions to their corresponding olefins, i.e., ones having the same carbon skeleton.
3. Except for minor cracking reactions, paraffins with up to at least 7 C atoms are final stable products; isomerization among paraffin isomers does not take place at 368°C.
4. Light olefins, e.g., ethylene, propylene, and butenes, are reactive intermediates for aromatics formation.
5. Aromatic compounds can also be produced by methanol- or di-methyl ether-alkylation of benzene and subsequent alkylated benzenes.

ACKNOWLEDGMENTS

The authors are grateful to Dr. H. E. Robson at the Exxon Research and Development Labs for providing a sample of the ZSM-5 zeolite and to the Robert A. Welch Foundation and Haldor Topsøe A/S (Denmark) for financial support.

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