CONVERSION OF METHANE TO GASOLINE-RANGE HYDROCARBONS

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Existing processes have been assembled in a novel combination capable of producing higher hydrocarbons from methane with high yield and selectivity. Methane, oxygen, and hydrogen chloride react over an oxyhydrochlorination (OHC) catalyst in the first stage to produce predominantly chloromethane and water. In the second stage, the chloromethane is catalytically converted to higher hydrocarbons, namely, paraffins, cycloparaffins, olefins, and aromatics, by an alumino-silicate zeolite. In the process described, the final hydrocarbon mixture is largely in the gasoline (C_4-C_{10}) boiling range.

The first stage of the process has been carried out under varying conditions of temperature and residence times. The conversion of reactants, the yields, and the product selectivities are tabulated over the operating range of the catalyst.

The second-stage reaction has been carried out utilizing feeds of chloromethane and various mixtures of chloromethane, dichloromethane, and trichloromethane. A long-term study on a commercial zeolite has shown no significant changes in conversions or product distribution after multiple regeneration cycles.

INTRODUCTION

Current technology for the conversion of methane to more useful compounds includes steam reforming reactions;[1] halogenation;[2] oxychlorination;[3] oxidation, including oxidative coupling and metal oxide reactions;[4] reaction with superacids;[5] and various other methods.[6] At present, these conversion schemes are unattractive because they are marked by low overall carbon conversions or poor selectivities.

In 1975, Mobil Oil Corporation patented a process for the conversion of methanol to higher hydrocarbons by reaction over a zeolite catalyst, such as ZSM-5.[7] Although later Mobil patents claimed that ZSM-5 would convert any monofunctionalized methane to higher hydrocarbons,[8] methanol was the feedstock of interest. In 1982, Ione et al.[9] reported that the conversion products of monofunctionalized methanes over zeolites were independent of the substituent and, for a given catalyst, depended only on the reaction conditions.

In work done at Allied Chemical Corporation, Pieters et al.[10,11] and Conner et al.[12,13] reported the selective functionalization of methane by reaction with oxygen and hydrogen chloride over a supported copper chloride catalyst to give tetrachloromethane as the major product. The advantages of the Allied process are significant. Reaction conditions are mild, and conversion and product distribution are stated to be functions of feed stoichiometry and temperature.

If a modification of the OHC reaction conditions produced predominantly chloromethane, a two-step process (Figure 1), in which the chloromethane oligomerization step provides the hydrogen chloride needed for methane chlorination, would be possible. Chlorine, as

hydrogen chloride, is essentially a placeholder in the methylene synthon. This is the basis of the PETC process.

The work described below demonstrates that an effective method for selective functionalization in combination with oligomerization over a zeolite catalyst provides a facile route for conversion of methane to higher hydrocarbons.

EXPERIMENTAL

The details of the two-stage laboratory reactor system are shown in Figure 2. All the reactants were introduced at slightly above atmospheric pressure from gas cylinders. Flow rates were controlled by a Brooks four-channel mass-flow controller. The feed stream for the first-stage reactor was sampled before and after the experimental run, while the product stream was continuously sampled on line during the run to obtain a mass balance around the OHC reaction. A quadrupole mass spectrometer was used to analyze the feed and product streams. Oligomerization reaction products were collected at dry ice temperatures and analyzed on a Hewlett-Packard 5880 capillary column gas chromatograph equipped with a Hewlett-Packard 5970 mass selective detector (GC/MSD).

Thermogravimetric (TG) measurements were conducted using a Perkin-Elmer TGS-2 system. Differential Scanning Calorimetry (DSC) measurements were conducted using a Perkin-Elmer DSC-2C calorimeter. Both the TG and the DSC were connected to a TADS data station. Heating rates of $10^{o}C\ min^{-1}$ were employed for 3-6 mg of activated OHC catalyst contained in a gold pan under an inert atmosphere.

The catalysts were contained between quartz wool plugs within horizontal 1- X 35- centimeter quartz tubes enclosed in split tube furnaces. Temperatures were controlled by a feedback controller.

The reactants were preheated to $175^{o}C$ before entering the catalyst zone. The effluent stream was maintained at $150^{o}C$ to prevent product condensation before the cold trap or in the capillary inlet to the mass spectrometer.

The oxyhydrochlorination catalyst was prepared according to the literature[10,11] by sequential layering of CuCl, KCl, and $LaCl_3$ onto a fumed silica support in nonaqueous solvents. The OHC catalyst was activated in a stream of hydrogen chloride at $300^{o}C$ for ten minutes prior to use. The ZSM-5 was obtained from Mobil Oil Corporation in the ammonium form with a silica-to-alumina ratio of 70:1. The ammonium form was converted to the acid form by calcining in air at $538^{o}C$ for 16 hours. The iron-promoted ZSM-5, prepared according to the method of Rao and Gormley,[14] contained 14.5% iron by weight and had a silica-to-alumina ratio of 27:1.

The reaction conditions for the oligomerization of chloromethane were similar to those reported for methanol,[15] i.e., reaction temperature of $350^{o}C$ and WHSV = 1, using 1 gram of catalyst.

The zeolite catalyst was regenerated by exposure to oxygen at temperatures between 350° and $550^{o}C$ until the presence of carbon dioxide in the effluent stream was no longer detected by the mass spectrometer. Removal of carbon restored the catalyst to its initial activity even after 14 cycles.

RESULTS

Conversion of methane to chloromethane

The conversion of methane to chloromethane has been observed under various reaction conditions. The data (Table I and Figure 3) show a material balance around 100% and display several trends. Note that methane conversion and polychlorination both increase as residence time and temperature increase.

The highest level of methane conversion occurred around 345°C, which is in the neighborhood of reported eutectic melting points for several $CuCl-KCl-LaCl_3$ mixtures.[11] When the temperature exceeded 350°C, conversion decreased. The DSC measurements showed an endotherm with an onset at 385°C and a maximum at 406°C. The maximum corresponds to the reported melting point of the supported $CuCl-KCl-LaCl_3$ layers.[13] The loss of activity occurs well below the experimentally determined melting point and may be explained as the result of a surface area decrease because of phase transitions in the supported phase or a loss of stratification due to diffusion.

Production of carbon dioxide and formic acid, undesirable by-products, also varied with residence time and temperature. As either the residence time or temperature increased, the amount of carbon dioxide increased while the amount of formic acid decreased. Carbon monoxide was not detected in the product stream.

The OHC catalyst is also susceptible to deactivation by exposure to oxygen in the absence of methane at temperatures greater than 100°C. Reactivation requires exposure of the catalyst to hydrogen gas at temperatures between 280° and 300°C. The catalyst is stable in air at ambient temperatures but is hygroscopic. Surface moisture is indicated by a color change from brown to green. Removal of water from hydrated catalyst by heating above 100°C in an inert gas stream gave a catalyst with less OHC activity than freshly prepared and activated catalyst.

Conversion of chloromethane to gasoline

Conversion of chloromethane over ZSM-5 to gasoline-range hydrocarbons has been observed to occur under conditions similar to those for the conversion of methanol. Two forms of the oligomerization catalyst were used in this study. One was a sample of iron-promoted ZSM-5 synthesized in our laboratory; the other was a sample of H-ZSM-5 obtained from Mobil Oil Corporation. Both catalysts produced similar products under the same reaction conditions. The gas chromatograms of the products collected from methanol or chloromethane oligomerization over ZSM-5 are shown in Figures 4 and 5, respectively. The mass selective detector allowed identification of most of the components in the samples, which are listed in Table II. Generally, the products contain ten carbons or less, and a large fraction of the product is aromatic. The presence of chlorinated aromatics was not observed for any of the oligomerization reactions conducted.

Trace amounts of 2-chloropropane and 2-chlorobutane were also found in one of the chloromethane oligomerization products. We hypothesized that these compounds had been formed by vapor phase addition of hydrogen chloride to propene and butene, products of chloromethane oligomerization. This type of addition has been reported to occur under similar conditions.[16] It was further proposed that if these

chlorinated alkanes came in contact with the zeolite catalyst, they would be oligomerized. To test the latter theory, several primary, secondary, and tertiary chlorocompounds of propane, butane, and pentane were allowed to react over ZSM-5 at the conditions for chloromethane oligomerization. In each case, the halocarbon was converted to aromatic hydrocarbons and hydrogen chloride, confirming our hypothesis.

Key to the PETC process is the ability of the ZSM-5 to convert mixtures of chloromethanes, especially those with compositions similar to the OHC product stream, without excessive deactivation due to coking. To determine the effect of feed composition on catalyst coking, mixtures of chloromethane, dichloromethane, and trichloromethane, including one with molar ratios identical to the OHC product stream (Table I, 5.14 seconds), were reacted over ZSM-5. Conversions and coke formation on the zeolite were comparable to those experienced for straight chloromethane (Figure 6) when the molar ratio of chloromethane to dichloromethane was at least 2.75 to 1 and the trichloromethane was 2.3 mole percent or less.

The effects of catalyst aging, caused by prolonged contact of the ZSM-5 with the products of reaction, mainly hydrogen chloride, have been addressed. Conversion studies were undertaken on a single 1-gram ZSM-5 sample exposed to various mixtures of chloromethane, dichloromethane, and trichloromethane under reaction conditions. When conversions dropped below 50%, the zeolite was regenerated by removal of the coke as described above. After regeneration, the initial conversion of chloromethane returned to ~100%. Product distribution exhibited no noticeable change during 800 hours of operation and 14 regeneration cycles.

Conclusion

Methane has been converted to higher hydrocarbons boiling in the gasoline range by the two-stage process described. In the first stage, mixtures of chloromethane, dichloromethane, and trichloromethane were produced by the OHC catalyst in ratios dependent on reaction temperature, residence time, and large changes in feed stoichiometry. Under the conditions described, the ratio of chloromethane to dichloromethane varied from 3.82 to 1.70 as residence time increased from 4.20 to 9.58 seconds. These experiments were conducted at a reaction temperature producing maximum methane conversion. Chloroform production also increased with increasing residence time. Tetrachloromethane formation was at or below detectability limits during all experiments.

The oligomerization of chloromethane to gasoline-boiling-range hydrocarbons occurred under conditions identical to those for methanol. Hydrogen chloride, the by-product of oligomerization, is recoverable from the product stream and may be recycled for use in the OHC step. Mixtures of chloromethane and dichloromethane in ratios of greater than 2.75 to 1, respectively, along with mixtures of chloromethane, dichloromethane, and trichloromethane in the same molar ratios as produced in the oxyhydrochlorination stage, are also oligomerized by ZSM-5. The oligomerization of the mixtures containing the polychlorinated methanes occurs without observable difference in conversion or coke deposition from that experienced for chloromethane or methanol. Long-term exposure of the zeolite to hydrogen chloride and multiple regenerations do not appear to affect either conversions or product distribution.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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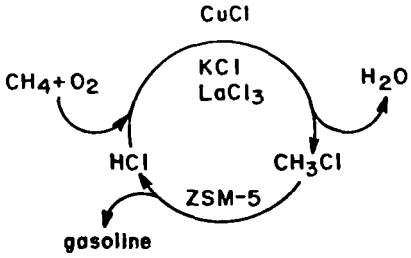

FIGURE 1. CYCLIC PATHWAY FOR THE CONVERSION OF METHANE TO GASOLINE BY THE TWO-STAGE PETC PROCESS

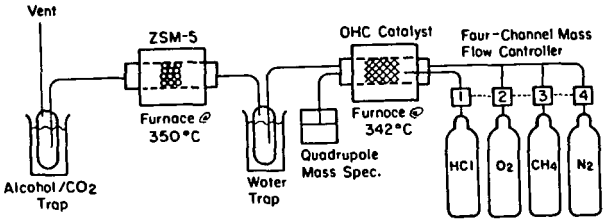

FIGURE 2. LABORATORY-SCALE UNIT FOR THE CONVERSION OF METHANE TO GASOLINE

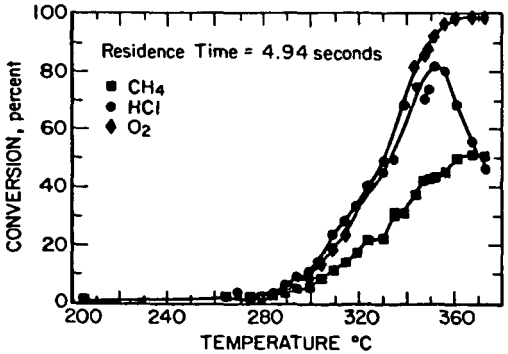

FIGURE 3. CONVERSION OF OXYHYDROCHLORINATION REACTANTS AS A FUNCTION OF TEMPERATURE

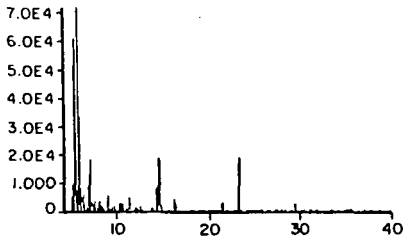

FIGURE 4. GAS CHROMATOGRAM OF METHANOL OLIGOMERIZATION PRODUCTS

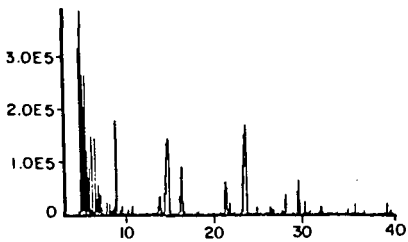

FIGURE 5. GAS CHROMATOGRAM OF CHLOROMETHANE OLIGOMERIZATION PRODUCTS

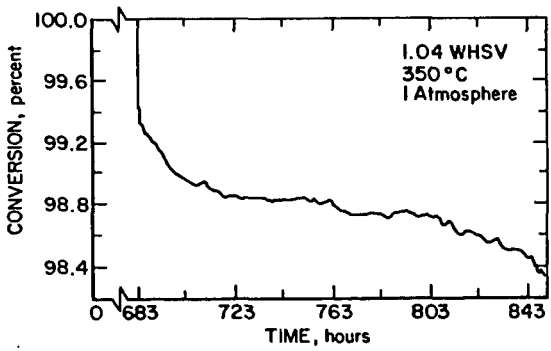

FIGURE 6. CHLOROMETHANE CONVERSION AS A FUNCTION OF TIME AFTER THE 14TH REGENERATION

TABLE I

Selectivity of the OHC Reaction at 342°C

Calculated Residence Time (Sec)[a]	% Conversion[b]			% Product							CH_2Cl/CH_2Cl_2
	CH_4	HCl	O_2	CH_3Cl	CH_2Cl_2	$CHCL_3$	CCl_4	CO	CO_2	HCOOH	
4.17	25.20	30.17	34.01	75.32	19.72	1.58	0.00	0.00	0.81	2.57	3.82
5.14	28.36	39.28	38.89	73.96	21.24	1.96	0.00	0.00	0.93	1.90	3.48
8.06	38.36	50.71	55.21	68.42	25.83	2.92	0.01	0.00	1.43	1.39	2.65
6.26	36.36	57.72	57.95	67.90	26.16	2.70	0.00	0.00	1.60	1.64	2.60
6.37	45.25	62.41	62.89	66.70	27.15	3.32	0.01	0.00	1.62	1.19	2.46
7.71	42.12	96.36	97.36	64.90	27.47	3.82	0.01	0.00	2.16	1.62	2.36
9.12	53.48	98.00	92.89	57.34	32.31	5.95	0.02	0.00	3.45	0.93	1.77

[a]Residence Time = (catalyst void space)/(total inlet gas flow rate).

[b]% Conversion = 100*([IN] - [OUT])/[IN].

TABLE II

Oligomerization Product Identification

Retention Time (Min.)	Compound
5.088	Pentane
5.259	Butane
5.356	Benzene
6.255	Cyclohexane
6.638	Hexane
8.980	Toluene
13.763	Xylene
14.645	Xylene
16.352	Xylene
21.716	1,3,5-Trimethylbenzene
23.276	1,2,3 + 1,2,4-Trimethylbenzene
26.020	Tetramethylbenzene
29.506	Durene
32.078	Pentamethylbenzene