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Photocoupling of Methane in Water Vapor to Saturated Hydrocarbons

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Abstract Methane can be converted into alkanes (from C_2 to C_6) continuously by ultraviolet (185 nm) irradiation in the presence of water vapor. The products from this reaction are alkanes, which is different from the comparable heterogeneous catalytic reactions, where alkene formation is also observed. The mechanism involves the coupling of alkyl radicals formed by hydrogen abstraction with OH radicals produced following the UV irradiation of water.

Keywords Methane coupling · UV irradiation · Natural gas · Alkane

1 Introduction

Methane is a major component of natural gas and is regarded as a promising resource in the development of new natural gas reserves, such as methane hydrate and biomass. The direct conversion of methane into hydrocarbons is an attractive technique for transporting and storaging liquid fuels. The formation of other hydrocarbons, all of which are less stable than methane at 1273 K, have unfavorable free energies of reaction and are strongly limited by equilibrium. These reactions typically need considerable energy input. Indeed, temperatures higher than 1273 K are required to transform methane into benzene, acetylene, ethylene, and ethane by the oxidative coupling of methane (OCM) with oxide catalysts [1, 2], while the combination of reforming with H_2O or CO_2 over Ni catalysts [1, 3, 4] and the Fischer–Tropsch (FT) synthesis, are all energy-intensive methods. Unlike most OCM reactions, such as the carbocationic OCM reaction with super-acids at low temperature [5, 6], the OCM involving photoreactions typically save hydrogen or wasted heating energy [7–14]. As a unique photoreaction, Crabtree et al. have reported the mercury photosensitized dehydrodimerization using low-pressure mercury lamp [12–14]. They showed that the excited state of mercury by a 254 nm photon homolyzes a C–H bond of alkanes (cyclopentane, methyl butane, pentane, and so on) or alcohols (methanol, ethanol, propanol, and so on) to give a carbon radical and a hydrogen atom. These carbon radicals recombine to give dimer.

We report here that water catalyzes the formation of C_2–C_6 or higher saturated hydrocarbons in the photocoupling of methane with a low-pressure mercury lamp in a flow reactor at 1 atm. Water is a convenient and harmless molecule, so that the photoreaction is attractive in practical use. Furthermore, this method is free from catalyst preparation [7–10] and light with high energy for the direct excitation of methane [10].

2 Method

The photochemical reactions using methane (10% methane diluted with Ar and 99.9% purity) and water were carried out in a quartz tubular reactor (inner diameter of 16 mm, length of 20 cm, volume of 40 cm^3) placed horizontally at 343 K. Using a flow controller at ambient pressure, the flow rate was maintained between 0.33 and 4.0 cm^3/min, to give an apparent residence time of 10–120 min. The temperature of the reactor was measured using a thermocouple located in a small tube in the reactor. Before each experiment, the reactor was calcined to 1073 K for 1 h and flushed with the

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reaction gas to remove all water vapor. This is because methane photocoupling may proceed without water either on the reactor wall or in the gas phase. However, it was confirmed that methane coupling did not take place in the absence of water vapor. A drop of water (0.2 mL) was injected into the reactor with a micro syringe. A 200 W low-pressure mercury lamp (intensity ratio of 185 nm/254 nm is 0.25, UVE-200J, Sen lights Co.) was used as the ultraviolet (UV) light source. The hydrocarbon products and hydrogen were analyzed using an online gas chromatograph (GC), equipped with a flame ionization detector (G180, Yanaco) and a GC with a thermal conductivity detector (GC-8A, Shimadzu), respectively. Here, the reacted gas in the sampling loop was switched between the GC and the exhaust vent by a 6-way valve. The intensity of radiation was measured using a UV power meter (C8026 and H8025-185, Hamamatsu Photonics, K.K.).

3 Results and Discussion

Figure 1 shows the yield of ethane and propane produced by the photoreaction of 10% methane with water vapor at 343 K and a residence time of 80 min. It is clearly shown that ethane and propane are continuously produced from CH_4 at high yields of 2.2 and 0.45 mol%, respectively, over 700 min. It is observed that the reaction stopped upon turning off the UV light (450 min) meaning that ethane and propane were formed by photoreaction. It is interesting that the production is only alkanes. This is in contrast to the heterogeneous catalytic reactions of hydrocarbon formation by CH_4 coupling [2, 7] or FT-synthesis, where both alkanes and alkenes are formed.

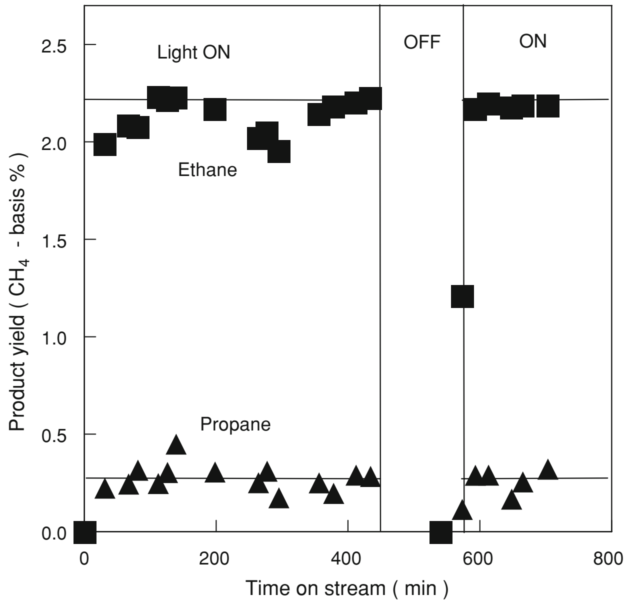

Fig. 1 UV response of the yield of ethane and propane produced by the photoreaction of 10% methane with water vapor at 343 K and a residence time of 80 min

We performed the photoreaction using pure methane to examine the product distribution at atmospheric pressure. As shown in Table 1, the photochemical reaction of pure methane and water vapor produced higher alkanes of butane, pentane and hexane, compared to the reaction with 10% methane.

It is known that water vapor absorbs UV light at 143 and 186 nm, causing it to decompose to form $^{\cdot}OH$ and $^{\cdot}H$ radicals [9, 15, 16]. On the other hand, methane does not absorb UV light generated from a low-pressure mercury lamp ($\lambda = 185, 254$ nm), because the UV light absorption spectra of methane lies below 154 nm [17, 18]. Accordingly, the coupling of methane is initiated by water vapor absorbing UV light of 185 nm generated by the low-pressure mercury lamp. In fact, the photocoupling reaction does not take place in the absence of water. This means that the water-catalyzed photocoupling of methane occurs in the gas phase. The photolysis of water vapor by UV light of 185 nm occurs as follows [9, 15, 16]:

$$H_2O + h\nu \rightarrow H^{\cdot} + {}^{\cdot}OH \qquad (1)$$

The resultant OH radicals are highly reactive such that they are able to abstract hydrogen from methane [19]. The methyl radicals thus formed are then able to couple to form ethane. The reaction mechanism for the methane coupling is thus considered as follows:

$$CH_4 + {}^{\cdot}OH \rightarrow CH_3^{\cdot} + H_2O \qquad (2)$$

$$2CH_3^{\cdot} \rightarrow C_2H_6 \qquad (3)$$

$$2H^{\cdot} \rightarrow H_2 \qquad (4)$$

Simultaneously, hydrogen is produced according to Eq. 4. Alkanes are not considered to decompose with UV light of 185 nm or below due to a lack of absorbance [17, 18]. It is considered that higher alkanes are formed in the same way by hydrogen abstraction from alkanes. To prove the reaction mechanism, we carried out ethane coupling by irradiating UV light onto flowing 99.8% ethane (0.5 cm^3/min, methane being included 0.2%) in the presence of 0.2 mL water. Table 2 shows the products and the yields of the 99.8% ethane coupling reactions. Alkanes with an even number of carbons (i.e. *n*-butane and 3-methylpentane) were mainly produced. The total product yield of alkane was 9.05% with respect to ethane, in which the yields of *n*-butane (C_4) and 3-methylpentane (C_6) were 6.57% and 1.36%, respectively. As in the methane case, the products were composed of alkanes. These results reveal C_4 and C_6 to be the main products, implying that the same mechanism was evident in this reaction as was in the methane coupling reaction. That is, the OH radicals generated by the

Table 1 Hydrocarbon products formed during the photocoupling of pure methane with water vapor

	C_2H_6	C_3H_8	C_4H_{10}		C_5H_{12}			C_6H_{14}	Total	H_2
			iso	n	neo	iso	n			
Amount (10^{-10} mol)	499	69.3	21.6	9.02	32.3	4.12	–	14	649.34	4540
Yield (%)	2.81	0.59	0.24	0.1	0.45	0.06	–	0.24	4.48	–
Selectivity (%)	62.59	13.05	5.43	2.26	10.12	1.29	–	5.26	100	–

Water volume: 0.2 mL. Methane flow rate: 0.50 cm^3/min. Reaction temperature: 343 K. Residence time: 80 min. The amount of methane sampling: 3.57×10^{-6} mol

photolysis of water abstract hydrogen atoms from ethane [17], which then leads to the coupling of ethyl radicals, and the ultimate formation of butane and higher alkanes with an even number of carbons. The UV absorption spectrum of ethane shows that this alkane absorbs light with $\lambda < 155$ nm [18], confirming that there is thus no possibility that ethane absorbs the UV light emitted from a low-pressure mercury lamp directly. It is thus concluded that the chain growth of alkanes is due to the coupling reactions of alkyl radicals. As for the C_4–C_6 alkanes, more branched-chain rather than straight-chain alkanes were produced, which is probably due to the hydrogen-abstraction step, in which hydrogen is more easily abstracted in the order of the following [20].

$$CH_3{-}H < RCH_2{-}H < R_2CH{-}H < R_3C{-}H$$
$$(R: \text{ alkylgroup})$$

Table 1 shows distribution of hydrocarbon products formed by the photocoupling of methane with water. As shown here, more branched-alkane tends to form. That is the yield of neopentane (0.45%) was greater than those of other C_4–C_6 compounds (0.06–0.24%). In general, the rate coefficients for the reactions of hydroxyl radicals with alkanes increase with the number of carbons in the alkane. Moreover, for alkanes with the same number of carbons, those with a branched-chain are more reactive than those with a straight-chain [21, 22]. However, it is also known that the rate coefficient of neopentane is smaller than the coefficients of other C_5-alkanes, which is comparable with those of ethane and propane [21, 22]. This is due to the molecular structure of neopentane, which consists of four lesser reactive CH_3 groups and an inactive quaternary carbon. Indeed, this is one of the reasons why larger amounts of neopentane are detected compared to the other C_5 alkanes in this study.

In the ethane coupling reaction, alkanes with an odd number of carbons were produced as shown in Table 2. Even in the absence of water, small amounts of methane and propane are detected. Although the mechanism is not clear, ethane may be decomposed into two methyl radicals on the reactor wall or in gas phase by the UV light. The methyl radicals probably react with hydrogen radical or ethyl radical, leading to methane and propane, respectively.

Figure 2 shows the dependence of residence time on the product yield in the photoreaction of methane with water. Methane gas was allowed to flow into a reactor containing 0.2 mL of water under UV light illumination at 343 K. Note that the concentration of methane is different between the experiments of Fig. 1 (10%) and Fig. 2 (100%). Here, the total product yield of alkanes is observed to increase with residence time until 20 min. After such time, the total product yield of alkanes decreases gradually and becomes constant, which is attributed to the change in the concentration of OH radicals. For short residence times, the concentration of OH radicals generated by decomposition of water vapor is low. Most of the generated OH radicals are used to abstract hydrogen from methane, leading to the formation of methyl radicals. The coupling of alkyl radicals then takes place to produce alkanes. However, the OH radical concentration is expected to increase at longer residence times. So that OH radicals react with methyl radicals to produce methanol. However, we were not able to detect methanol in this work because as we have confirmed, UV irradiation ($\lambda = 185$ nm) decomposes methanol through photodecomposition [23]. At high OH radical concentration,

Table 2 Product of the hydrocarbons in photocoupling of 99.8% ethane with water vapor

	CH_4	C_3H_8	C_4H_{10}		C_5H_{12}		C_6H_{14}		Total
			iso	n	iso	n	3- CH_3	n	
Amount (10^{-10} mol)	29.7	90.4	–	1050	22.7	9.13	198	22	1420
Yield (%)	0.17	0.52	–	6.07	0.13	0.05	1.14	0.13	8.21
Selectivity (%)	2.09	6.35	–	73.85	1.60	0.64	13.92	1.55	100

Water volume: 0.2 mL. Ethane flow rate: 0.50 cm^3/min. Reaction temperature: 343 K. Residence time: 80 min. The amount of sampling of ethane: 1.8×10^{-6} mol

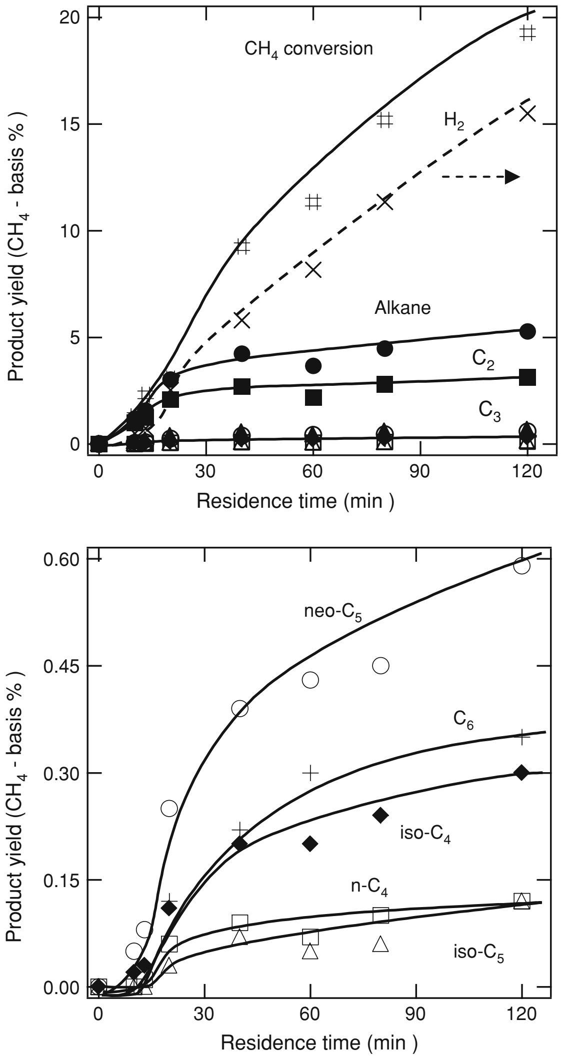

Fig. 2 Residence time dependence of the product yield in the photoreaction of pure methane with water vapor at 343 K

the methanol formed in the initial stage, undergoes further reaction with OH radicals to form oxygenated compounds such as formaldehyde (CH_2O) and acetic acid ($C_2H_4O_2$), as reported by Ogura et al. [9]. In the reactor the oxygenated products became dissolved in the water, which in the present experiments, is observed to be cloudy after the reaction and found to have an irritating odor. The UV irradiation of this cloudy liquid in helium led to the production of CO_2 and CH_4. That is, the oxygenated compounds generated from methane are solved in water. This may be the reason for the difference between the methane conversion and the total amount of alkane products in Fig. 2.

4 Conclusion

In summary, we succeeded in producing higher hydrocarbons continuously from methane and water in a flow reactor irradiated with low-pressure mercury lamps at room temperature. In contrast to the Fischer–Tropsch synthesis or the OCM reaction, this process can be regarded as a convenient synthesis method for the homologation of methane without high temperature and high pressure. The products of hydrocarbons were composed of only alkane such as ethane, propane, iso-butane, *n*-butane, neopentane, iso-pentane, and C_6. The alkane yields were 4.5% with an ethane selectivity of 62.6%. The reaction mechanism is ascribed to a radical coupling reaction involving methane or alkyl radicals in the gas phase, where a hydrogen atom is abstracted from an alkane by an OH radical formed by the UV irradiation of water.

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