Short Communication

Direct synthesis of formic acid by partial oxidation of methane on H-ZSM-5 solid acid catalyst

Abul Kalam Md. Lutfor Rahman [1,*], Masako Kumashiro, Tatsumi Ishihara *

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

A B S T R A C T

The direct synthesis of formic acid by partial oxidation of methane was studied using hydrogen peroxide (H_2O_2) as oxidant with keeping reaction temperature of 373 K and a pressure of 2.6 MPa. High yield (13.0%) and selectivity (66.8%) of formic acid (HCOOH) an important oxygenated compound in chemical industry were achieved using protonated pentasil-type zeolite (H-ZSM-5) as a solid acid catalyst. Tryphenylphosphene (Ph_3P) was used as a promoter in reaction system. A fairly large amount of CO_2 was also observed as deep oxidation product.

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1. Introduction

Direct conversion of methane (CH_4) to oxygenated compounds such as acetic acid (CH_3COOH), formic acid (HCOOH) and methanol (CH_3OH) under mild reaction conditions is of interest in both organic and bioinorganic chemistry with the special interest in catalysis. Many researchers have investigated metal-catalyzed oxidation systems for direct conversion of methane into useful oxygenates. Most active catalysts that operate at low temperature require the presence of strong oxidants such as SO_3 [1, 2], $K_2S_2O_8$ [3-6] or $NaIO_4$ [7]. However, environmental and economic concerns favor the use of oxidants such as H_2O_2 (the only by-product being H_2O) or O_2 that are both harmless to the environment and atom efficient. A number of studies of the partial oxidation of alkane using H_2O_2 oxidant have been reported [8-12]. The present work extends these studies by focusing on the partial oxidation of methane into oxygenated compound using H_2O_2 oxidant.

Several reports exist on the selective oxidation of methane into formic acid, but yields are still poor ($\leq 5\%$) [13-16]. Galina et al. [13] reported the oxidation of methane in the presence of air and obtained HCOOH of 5.2%. Kuzmin et al. [14] found that 0.08×10^{-3} M of HCOOH by oxidation of methane using H_2O_2 in the presence of copper(II) peroxocomplexes. Min et al. [15] reported the selective oxygenation

of methane into formic acid with $8.7 \times 10^{-2}\%$ conversion of methane. Seki et al. [16] used H_2O_2 oxidant and $H_4PV_1Mo_{11}O_{40}$ catalyst; reaction gave a total yield of 4.4% including HCOOH. In summary, all the studies published to date on formic acid synthesis from methane report yields of just a few percent. Clearly, a strong need exists for a new catalyst for partial oxidation of methane that gives higher yields and greater selectivity.

ZSM-5, a pentasil-type zeolite, is known to be an active catalyst [17, 18]. Han et al. [17] reported the production of C_5^+ liquid hydrocarbons in the presence of C_3^+ additive by direct partial oxidation of methane with O_2 over H-ZSM-5 catalyst. CH_3OH was the primary oxygenated product in partial oxidation of methane under pressurized conditions [17, 18]. We therefore chose to investigate the activity of pentasil-type zeolite catalyst for the liquid-phase oxidation of methane using H_2O_2 oxidant, a reaction that has not heretofore been studied in detail.

2. Experimental

High silica zeolite of NaZSM-5 supplied by Tosoh Corporation, Japan was used as catalyst. The elemental composition of zeolite catalyst is listed in the Supporting information (SI). Protonated zeolites were obtained via ion exchange of Na-type zeolite. Na-zeolite was first ion-exchanged into its ammonium form by NH_4NO_3 aqueous solution at about 368 K for 2 h. The sample was then dried at 333 K overnight and calcined at 773 K for 3 h. Catalyst was fed into a 200-ml reactor with H_2O_2 and H_2O. The reactor was flushed with N_2 several times to remove air inside it. Pure CH_4 was fed into the reactor vessel at the designated pressure. The temperature of the reaction was kept

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* Corresponding authors. Tel.: +81 92 802 2869; fax: +81 92 802 2871.
 E-mail addresses: lrahman1973@gmail.com (A.K.M.L. Rahman),
ishihara@cstf.kyushu-u.ac.jp (T. Ishihara).
[1] Present Address: Department of Chemistry, Jagannath University, Dhaka 1100, Bangladesh. Tel.: +880 1732108451; +880 27176191; fax: +880 7113752.

Table 1
Product yields for the partial oxidation of methane using H_2O_2 oxidant and various catalysts.

Catalyst	Yield (%)					Selectivity to HCOOH (%)	Conv. Of H_2O_2(%)	Efficiency of H_2O_2(%)
	HCOOH	CO_2	CH_3CHO	CH_3OH	CH_3COOH			
$VOSO_4$	0.4	–	–	–	0.03	87.4	100	0.4
$H_4PVMo_{11}O_{40}$	1.3	3.2	–	–	0.18	26.4	100	1.9
TS-1	0.6	–	0.1	–	0.09	59.6	79.8	0.9
H-Ferrierite	0.2	1.1	0.1	0.02	0.07	11.9	12.7	0.2
H-Y	0.2	1.0	0.1	–	0.03	13.4	25.5	0.4
H-ZSM-5	13.0	5.6	0.3	0.02	0.14	66.8	98.0	14.0
H-ZSM-5[*]	7.9	6.4	–	0.01	–	55.0	100	9.0

Catalyst 1.5 g; Ph3P 0.3 g; H_2O_2 121.88 mmol; H_2O 70 ml; CH_4 pressure 26 atm (118 mmol); temperature 373 K and reaction time−5 h.
[*] Reaction without Ph3P. Selectivity was calculated based on the total amount of detected carbon containing products.

at 373 K. Reaction was run for 5 h. Gas sampling was monitored by Gas chromatographs (TCD) with column containing molecular sieve (4 mm×5 m) and active carbon (4 mm×2 m). Yield of formic acid was measured by DIONEX Ion Chromatograph of DX-120 enclosed with the IonPacAS9-HC Analytical, 4×250 mm column. CH_3CHO and CH_3OH were detected by a Gas chromatography–mass spectroscopy (GC–MS, Shimadzu, GC–MS-QP2010 Plus) containing the column of Stabilwax 0.32 mm×60 m. Acetic acid obtained as by-product was detected by DIONEX Ion Chromatography of ICS 1000 fabricated with IonPacICE-AS6 Ion exclusion column (9×250 mm). The amount of H_2O_2 before and after the reaction was estimated through automatic redox titration. Details in the experiment and analysis were given in the Supporting information (SI).

3. Results and discussion

A screening test was performed in the present study with different catalyst systems. The product yields from partial oxidation of methane using H_2O_2 oxidant and various catalysts are listed in Table 1.

We carried out partial oxidations of methane using different types of protonated zeolite catalysts. Since TS-1- and vanadium-based catalysts such as $VOSO_4$ and $H_4PVMo_{11}O_{40}$ are active catalysts for the reaction of methane partial oxidation, we also investigated their use under similar reaction conditions.

For all catalysts examined, the reaction gave HCOOH, CH_3CHO, a small amount of CH_3COOH by-product and the deep oxidation product CO_2. H-ZSM-5 catalyst ($SiO_2/Al_2O_3 = 23.8$) gave the highest yield of HCOOH, indicating that H-ZSM-5 shows higher activity to the partial oxidation of methane using H_2O_2 oxidant than does the conventional catalyst, even under similar reaction conditions. We thus conclude that for this catalyst the acid site seems to be the active site for the partial oxidation of methane.

Triphenylphosphine (Ph3P) is known to be an efficient promoter of methane oxidation [19, 20]. We therefore investigated the effects of adding Ph3P to the reaction mixture. Table 1 shows that the addition

of Ph3P greatly improves the yields of both HCOOH and CH_3COOH. With added Ph3P, H-ZSM-5 catalyst gives HCOOH in a yield of 13.0% and with a selectivity of 66.8%.

Acidity has been suggested to be an important parameter for the partial oxidation of methane. We therefore investigated the effects of the H-ZSM-5 catalyst's SiO_2/Al_2O_3 ratio, which determines its acidity. Fig. 1 shows plots of HCOOH yield and selectivity as a function of SiO_2/Al_2O_3 ratio. Yield is strongly affected and selectivity is clearly affected by the ratio: yield is highest at the lowest ratio (23.8) and decreases with increasing ratio.

The ratio is supposedly related to the number of acid sites that are responsible for the activation of methane and is thus more important than the actual acid strength. Han et al. [17] reported that for reaction using higher alumina-content (lower ratio, more acid sites) H-ZSM-5 catalyst, the yields of C_2^+ and C_5^+ liquid hydrocarbons from the partial oxidation of methane are higher than those for reaction using lower alumina-content H-ZSM-5 catalyst. Farizul et al. [21] also reported that higher conversions of palm oil were achieved using H-ZSM-5 with lower SiO_2/Al_2O_3 ratio.

We investigated the effect of reaction temperature on HCOOH yield and H_2O_2 conversion. Fig. 2 shows plots of HCOOH yield and selectivity and H_2O_2 conversion as a function of reaction temperature. Both yield and conversion increase with increasing temperature and reach the highest at 373 K. Since simple decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$) increases with increasing temperature and H_2O_2 conversion reaches nearly 100% at 373 K. Although, production of molecular O_2 which is a by-product of H_2O_2 increases with temperature and remain in the gas phase but no effect observed for molecular oxygen in the yield of HCOOH. It suggests that active oxygen species which is responsible for the partial oxidation come not from the O_2 in gas phase but rather from H_2O_2. Anyway, based on the simple decomposition of H_2O_2, the optimum reaction temperature seems to be 373 K.

We examined the effect of the amount of H_2O_2 on HCOOH yield. Fig. 3 shows plots of HCOOH yield as a function of the amount of H_2O_2.
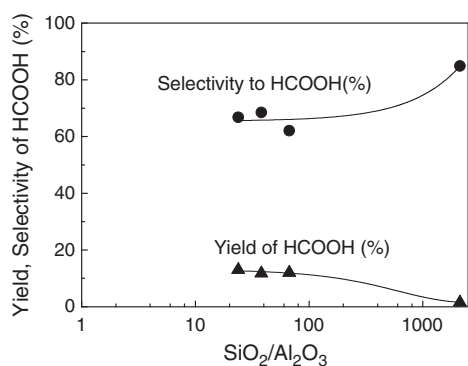

Fig. 1. Yield and selectivity of HCOOH as a function of SiO_2/Al_2O_3 ratio of H-ZSM-5 catalyst.
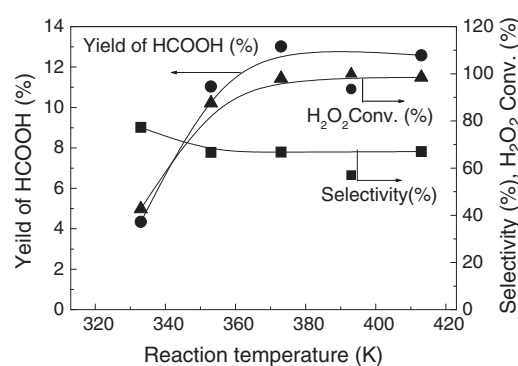

Fig. 2. Yield and, selectivity of HCOOH and H_2O_2 conversion as a function of reaction temperature.
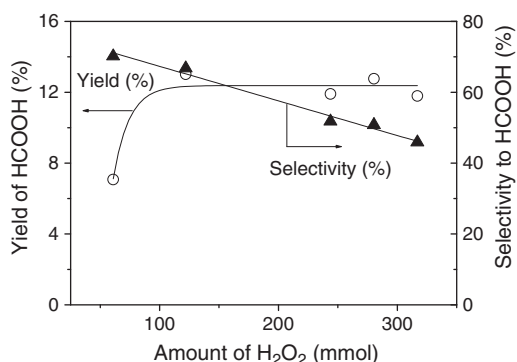
**Fig. 3.** Yield and selectivity of HCOOH as a function of the amount of H_2O_2.

Yield increases with increasing amounts of H_2O_2, reaches a maximum of 13.0% with a selectivity of 66.8% at 121.88 mmol of H_2O_2, and decreases slightly at higher amounts of H_2O_2 because of oxidation of HCOOH with H_2O_2 or gaseous O_2. Under the reaction conditions used, the decomposition of H_2O_2 is 98% with the efficiency to produce HCOOH of 14.0%, estimated by mole of HCOOH per mole of H_2O_2 with subtraction of the O_2 produced from initial amount of H_2O_2. On the other hand, selectivity decreases gradually with increasing H_2O_2 amounts.

Acetaldehyde (CH_3CHO) and CH_3OH were observed by GC–MS in the reaction product. Larger amounts of CH_3CHO were associated with larger amounts of HCOOH product obtained. HCOOH has been speculated to form by the oxidation of CH_3CHO [22]. Bar-Nahun et al. [23] reported that CH_4 can be transformed to CH_3CHO via CH_3OH. Therefore, the CH_3COOH obtained in our experiments might be from further oxidation of CH_3CHO. CH_3OH is considered to be the intermediate product in direct methane oxidation [16, 17]. Although reaction mechanism on H-ZSM-5 is not clear in details, however, CH_3OH might be a possible intermediate in synthesis of HCOOH. Considering the fairly large amount of CO_2 formed, we tentatively propose Scheme 1 for reaction pathways on H-ZSM-5 catalyst.

Anyway it could be proposed that the strong solid acid of H-ZSM-5 is highly active in synthesis of HCOOH by direct partial oxidation of CH_4 using H_2O_2 as oxidant.

Acknowledgements

$$CH_4 + [O] \dashrightarrow \left[\text{Oxygenated compound , } CH_3OH \right]$$
$$+ [O] \longrightarrow HCOOH + CO_2 + H_2O$$
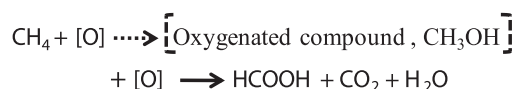
Scheme 1. Proposed pathway for synthesis of formic acid from partial oxidation of methane.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.04.001.

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