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Aqueous-phase selective oxidation of methane with oxygen over iron salts and Pd/C in the presence of hydrogen**

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Abstract: Direct conversion of methane into value-added chemicals is a challenging but worthwhile subject. In this communication, the direct conversion of methane into methane oxygenates was achieved in an aqueous solution at room temperature using iron salts and Pd/C as catalysts and hydrogen peroxide as an oxidant. The hydrogen peroxide can be directly added or generated *in situ* from hydrogen and oxygen. The Pd/C catalyst greatly enhanced the reaction rate together with the iron salts. The effect of some parameters such as reaction temperature, reaction time, pH, acid type, and catalyst amount on the yields of the methane oxygenates was also investigated. When hydrogen peroxide was directly added, the turnover frequency (TOF), defined as the moles of methane oxygenates per moles of Fe per unit time, at 293 K was 29 h⁻¹ at pH = 2.3. The TOF at 293 K was 42 h⁻¹ at pH = 1.3 with *in situ* generated hydrogen peroxide from hydrogen and oxygen.

Methane is considered as a clean energy source because it emits the smallest amount of CO2 owing to the fact that it has the highest H/C ratio among hydrocarbons. A recent upsurge in shale gas production has spurred research and development in the utilization of methane as a chemical feedstock.^[1] Currently methane is converted into various chemicals indirectly via syngas, a mixture of CO and H₂, which can be synthesized typically through an energy intensive steam reforming reaction $(CH_4 + H_2O \leftrightarrow CO + 3H_2, \Delta H^{o}_{298K} = 206 \text{ kJ/mol})$ at high temperatures. To circumvent this energy-consuming process, the direct conversion of methane has been sought in different ways but these effects have so far failed to be cost-competitive with an indirect pathway.^[2] In particular, the direct oxidation of methane into methane oxygenates such as methanol, formaldehyde, and formic acid under mild conditions is still challenging.[3,4]

The gas-phase partial oxidation of methane has been reported over Fe- or Cu-zeolites^[5,6] using N₂O,^[7] O₂,^[8] and H₂O^[9,10] as oxidants. However, most reactions can only proceed at relatively high temperatures (> 200 °C) resulting in low product yields.^[11] On the other hand, much higher yields of methane oxygenates have been reported in a liquid-phase system.^[3,4] Various homogeneous metal catalysts such as Hg,^[12] Pt,^[13-15] Pd,^[16,17] Eu,^[18] Rh,^[19] Co,^[20] Os,^[21] Cu,^[22,23] V,^[23,24] and Fe^[25,26] have been reported to be active in a protic solvent such as H₂SO₄^[12-15] and

trifluoroacetic acid (TFA)^[16-26] using SO₃,^[12-15] K₂S₂O₈,^[22] H₂O₂,^{[24-} $^{25]}$ and $O_2{}^{[20]}$ as an oxidant. CH_3OSO_3H and CF_3COOCH_3 have mostly been used as methanol precursors, which can be transformed into methanol via hydrolysis, in either H₂SO₄ or TFA. Although high yields to obtain the methanol precursors can be achieved in protic solvent systems, the requirements of strong acids, expensive oxidants, and excessive amounts of water in the hydrolysis step are still critical problems. To replace the expensive oxidants with dioxygen, some homogeneous catalysts were evaluated but failed to achieve high turnover frequencies (TOFs).^[20] The in situ generation of H₂O₂ was also tried in an effect to utilize dioxygen in methane functionalization.[23,25] However, all of these reactions were performed in strong acid solvent systems causing the dissolution of Pd metal which is responsible for the in situ generation of H₂O₂. Recently, selective formation of methanol and formic acid was reported over Au-Pd colloids,^[26] AuPd/TiO₂,^[27] ZSM-5,^[28] Fe/ZSM-5,^[29] Cu-Fe/ZSM- $5_{1}^{[30]}$ and Pd/ZSM- $5^{[31]}$ in an aqueous solution with H₂O₂. However, the selective oxidation of methane with dioxygen as an oxidant with high TOFs has not been reported in an aqueous solution. In this study, we report that formic acid can be produced from methane in the presence of an iron salt and Pd/C with H_2O_2 or a mixture of H₂ and O₂. The TOF is dependent on the pH of the aqueous solution but the reaction conditions are much milder than the previous protic solvent systems.

The combination of FeSO₄ and Pd/C, with an average Pd particle size of 3.5 nm (Fig. S1), was effective for the selective methane oxidation with H_2O_2 (Table 1, entry 1) to produce HCOOH and CH₃OOH. Only trace amounts of methane oxygenates were detected using FeSO₄ with H_2O_2 (Table S1, entry 1). However, no methane oxygenates were obtained using Pd/C with H_2O_2 (Table S1, entry 2) indicating that there is a synergistic effect between FeSO₄ and Pd/C. The decomposition of H_2O_2 was accelerated in the presence of Pd/C (Table S1). The decomposition of the carbon support in Pd/C during reaction can be excluded because there was no oxygenated carbon species in the liquid and gas phase without methane (Table S1, entry 3). In order to find out the effect of iron salts, various iron salts were active in this reaction in the presence of H_2O_2 (Table 1).

Instead of H_2O_2 , a gas mixture of H_2 and O_2 was used to generate H_2O_2 *in situ* to oxidize methane into methane oxygenates. The gas composition was fixed to produce theoretically the same amount of H_2O_2 added directly in Table 1, which can be obtained only when hydrogen was converted into H_2O_2 with a 100% yield. Interestingly, much higher yields of methane oxygenates were achieved with *in situ* generated H_2O_2 (Table 2) than with directly added H_2O_2 (Table 1). To investigate the reason for the increased yield in *'in situ* conditions', controlled experiments were conducted by changing the gas composition in the case of the direct H_2O_2 injection system (Table S1, entries 4, 5, 6 and 7). The positive effect of H_2 on the methane oxygenate yield was observed only in the copresence of FeSO₄ and Pd/C (Table S1, entry 6). It should be noted that the product yields of

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Table 1: Catalytic performance for the selective oxidation of methane over iron salts and Pd/C with H2O2.[a]

Entry	Iron salt	Product [µmol]				Methane	[Tota]	H ₂ O ₂
		CH ₃ OH ^[b]	HCOOH ^[b]	CH ₃ OOH ^[b]	$\mathrm{CO}_2^{[c]}$	oxygenates selectivity [%] ^[d]	products]/[Fe] ^[e]	conversion [%]
1	FeSO ₄	5 ± 0	36 ± 4	19 ± 3	11 ± 4	85 ± 6	6.3 ± 0.2	40 ± 7
2	$Fe_2(SO_4)_3$	7 ± 1	67 ± 2	17 ± 2	12 ± 5	89 ± 4	9.1 ± 0.8	51 ± 2
3	FeCl ₂	6 ± 0	38 ± 3	22 ± 5	7 ± 1	90 ± 2	6.5 ± 0.6	32 ± 4
4	FeCl ₃	6 ± 1	23 ± 3	22 ± 0	3 ± 0	95 ± 1	4.7 ± 0.3	25 ± 1
5	Fe(NO ₃) ₃	5 ± 1	70 ± 3	18 ± 5	10 ± 0	90 ± 1	9.1 ± 0.7	39 ± 1
6	Fe(CH ₃ COO) ₂	5 ± 2	69 ± 4	22 ± 2	12 ± 2	90 ± 2	9.5 ± 0.2	46 ± 6

[a] Standard reaction conditions: $V_{liquid} = 30 \text{ mL}$, $V_{gas} = 95 \text{ mL}$, $[H_2O_2] = 0.28 \text{ M}$, $[H_2SO_4] = 15 \text{ mM}$, [Fe] = 0.37 mM, 1% Pd/C 50 mg, $P_{CH4} = 15 \text{ bar}$, $P_{N2} = 13 \text{ bar}$, $T = 20 \degree$ C, reaction time = 30 min. [b] Analyzed by ¹H-NMR, TMSP was used as a reference. [c] Analyzed by GC-FID. [d] (moles of methane oxygenates except for CO₂)/(moles of total methane oxygenates including CO₂)× 100. [e] (moles of total methane oxygenates including CO₂)/(moles of Fe added). The numbers in the table are mean values after two iteration, and the numbers in parentheses indicate the error range.

methane oxygenates in the direct H_2O_2 injection system (Table S1, entry 6) are comparable to those in the in situ H₂O₂ generation system (Table 2, entry 1). There was a slight increase in the product yield in the presence of oxygen in the direct H₂O₂ injection system (Table S1, entry 7). In the case of the in situ H_2O_2 generation system, the possibility of oxidation of the carbon support to oxygenates can be excluded because no product was obtained in the absence of methane, (Table S2, entry 1). Additionally, if any of the two reactant gases (H₂ and air) was substituted by N₂, no product was obtained (Table S2). In order to find out the effect of iron salts, various iron salts were also evaluated in the presence of Pd/C with H₂ and O₂. All of the iron salts were active in this reaction in the presence of a gas mixture of H_2 and O_2 (Table 2). In any case, the *in situ* generated H_2O_2 was better at achieving a higher yield of methane oxygenates (Table 2) than directly added H₂O₂ (Table 1). This is a remarkable result because all of the H₂ and O₂ cannot be transformed into H_2O_2 with a 100% yield under these reaction conditions.^[32] This implies that the presence of hydrogen exerts a positive effect on the catalytic activity in both systems as revealed in the direct H₂O₂ injection system (Table S1, entry 6). The residual concentrations of H₂O₂ in the in situ system (Table 2) were low because the hydrogen peroxide formed from H_2 and O_2 is consumed simultaneously to convert methane. The lower methane oxygenates selectivity was obtained in in situ H₂O₂ generation system (Table 2) than in the direct H_2O_2 injection system (Table 1).

Other transition metal salts were examined under the same reaction conditions. Among the tested catalysts, no transition metal salt showed a comparable catalytic activity with the iron salts in the direct H_2O_2 injection or *in situ* H_2O_2 generation system (Tables S3 and S4) indicating that this reaction is uniquely performed over iron salts in the presence of Pd/C. Other noble metal catalysts such as Pt/C with an average Pt particle size of 2.1 nm and Rh/C with an average Rh particle size of 2.8 nm (Fig. Table 2: Catalytic performance for the selective oxidation of methane over iron salts in the selective oxidation of methane

S1) were also examined for this reaction with FeSO₄. The formation of methane oxygenates was observed for the catalyst system composed of FeSO₄ and either Pt/C or Rh/C irrespective of the presence of H₂O₂ or a gas mixture of H₂ and O₂ (Tables S5 and S6). In the case of direct H_2O_2 injection system, Pt/C and Rh/C showed comparable methane oxygenate yields. However, Pt/C provided a much higher yield of methane oxygenates than Rh/C in the in situ H₂O₂ generation system. This might be closely related to the different production rates of H₂O₂ from H₂ and O₂ over these two metal catalysts. It is worth mentioning that Pt/C gave a higher methane oxygenate yields in the in situ H2O2 generation system than in the direct H₂O₂ injection system. On the other hand, Rh/C provided a higher methane oxygenate yields in the direct H_2O_2 injection system than in the in situ H_2O_2 generation system. In any case, the yields of methane oxygenates over Pt/C + FeSO₄ or Rh/C + FeSO₄ were much lower than those over Pd/C + FeSO₄. The other supported Pd catalysts such as Pd/SiO₂ and Pd/ZSM-5 were also active for selective methane oxidation with $FeSO_4$ in the presence of H_2 and O_2 (Table S7). However, the yields of methane oxygenates were much lower than those of Pd/C. The yield of methane oxygenates appears to increase with decreasing Pd particle size (Fig. S1) which is reported to be closely related to the H_2O_2 formation rate.^[33, 34]

The effect of the metal content of the iron salts and Pd/C on the catalytic activity was evaluated in the direct H_2O_2 injection or *in situ* H_2O_2 generation system. The yield of methane oxygenates increased with the amount of FeSO₄ and Pd/C in both cases (Tables S8, S9, S10, and S11). In the direct H_2O_2 injection system, the H_2O_2 conversion generally increased with the amount of FeSO₄ and Pd/C (Tables S8 and S9). The turnover number (TON) based on the moles of Fe increased with the amount of Pd/C and reached a maximum value (Table S9). In the case of the *in situ* H_2O_2 generation system, the selectivity for methane oxygenates decreased with an increasing amount of Pd/C or FeSO₄ (Tables S10 and S11).

Table 2: Catalytic performance for the selective oxidation of methane over iron salts and Pd/C with H_2 and O_2 .^[a]

Entry	Iron salt	Product [µmol]				Methane oxygenates	Residual concentration	[Total
		CH ₃ OH ^[b]	HCOOH ^[b]	CH ₃ OOH ^[b]	CO ₂ ^[c]	selectivity [%] ^[d]	of H ₂ O ₂ [mM]	products]/[Fe][e]
1	FeSO ₄	11 ± 1	218 ± 0	7 ± 1	124 ± 8	66 ± 1	12	32.1 ± 0.6
2	$Fe_2(SO_4)_3$	10 ± 1	216 ± 2	8 ± 1	132 ± 18	64 ± 4	16	32.7 ± 1.4
3	FeCl ₂	9 ± 0	198 ± 2	9 ± 0	137 ± 3	61 ± 0	18	31.5 ± 0.4
4	FeCl ₃	10 ± 0	205 ± 29	10 ± 1	83 ± 10	73 ± 0	16	27.5 ± 3.5
5	Fe(NO ₃) ₃	8 ± 0	218 ± 5	9 ± 1	139 ± 19	63 ± 3	18	33.4 ± 2.2
6	Fe(CH ₃ COO) ₂	10 ± 0	218 ± 10	10 ± 2	131 ± 3	64 ± 1	13	33.0 ± 1.4

[a] Standard reaction conditions: $V_{iiquid} = 30 \text{ mL}$, $V_{gas} = 95 \text{ mL}$, $[H_2SO_4] = 15 \text{ mM}$, [Fe] = 0.37 mM, 1% Pd/C 50 mg, $P_{CH4} = 15 \text{ bar}$, $P_{H2} = 3 \text{ bar}$, $P_{air} = 10 \text{ bar}$, $T = 20 \degree$ C, reaction time = 30 min. [b] Analyzed by ¹H-NMR, TMSP was used as a reference. [c] Analyzed by GC-FID. [d] (moles of methane oxygenates except for CO₂)/(moles of total methane oxygenates including CO₂)× 100. [e] (moles of total methane oxygenates including CO₂)/(moles of Fe added). The numbers in the table are mean values after two iteration, and the numbers in parentheses indicate the error range.

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Figure 1. Effects of pH on the selective oxidation of methane over FeSO₄ and Pd/C with $[H_2 + O_2]$ (green) and $[H_2O_2]$ (blue).^[a]. *Standard reaction conditions: $V_{IIquid} = 30 \text{ mL}, V_{gas} = 95 \text{ mL}, [H_2SO_4] = 0.015 \text{ mM} - 150 \text{ mM}, [Fe] = 0.37 \text{ mM}, 1% Pd/C 50 \text{ mg}, T = 20 °C, reaction time = 30 min. Reaction with <math>[H_2 + O_2]$: $P_{CH4} = 15 \text{ bar}, P_{H2} = 3 \text{ bar}, P_{air} = 10 \text{ bar}.$ Reaction with H_2O_2 : $[H_2O_2]=0.28 \text{ M}, P_{CH4} = 15 \text{ bar}, P_{N2} = 13 \text{ bar}$

The effect of pH on the catalytic performance was also examined (Tables S12 and S13). In the case of direct H₂O₂ injection system the total product yield to methane oxygenates increased with decreasing pH from 4.3 to 2.3 and showed a maximum value at pH of 2.3. This then decreased with further decreasing pH (Fig. 1 blue, Table S12). A similar trend was also observed in the case of the in situ H₂O₂ generation system (Fig. 1 green, Table S13). However, the maximum yield was obtained at a lower pH of 1.4 than in the case of the direct H₂O₂ injection system. This is clearly related to the stability of H₂O₂ which is strongly affected by pH. In Fenton chemistry, it is generally accepted that iron hydroxide can be formed at a pH above 4, which is not favorable for the generation of hydroxyl radical species.[35-37] A lower pH is favorable for stabilizing H_2O_2 but the formation of $H_3O_2^+$, which occurs at a pH below 2, is not desirable for the formation of reactive hydroxyl radical species.[35-37] A close correlation can be found between the total product yield and H₂O₂ conversion in the direct H₂O₂ injection system. It should be noted that the selectivity for methane oxygenates increased with decreasing pH in both systems. The preferential formation of CO2 with increasing pH above 2 is in line with the previous report by Duesterberg et al.,[38] in which the reaction rate between formic acid and hydroxyl radical to form CO₂ increased with increasing pH from 2.5 to 4.0. It is worth mentioning that the fraction of leached Pd from Pd/C was determined to be less than 2% of the total Pd in the in situ H_2O_2 generation system even at the lowest pH of 0.7, which indicates that the Pd/C system is relatively stable under these reaction conditions. The effect of acid to control the pH was also examined. The pH was fixed at 1.3 and various protic acids were compared for this reaction. Both H₂SO₄, HNO₃ and TFA resulted in high yields of methane oxygenates among the tested acids (Table S14). On the other hand, HCI was inferior to the above mentioned acids indicating that the anion can affect the catalytic activity for this reaction (Table S14). HCl was reported to scavenge hydroxyl radical in Fenton chemistry.^[39] The product distribution was monitored as a function of reaction time. The yields of HCOOH and CO₂ increased with reaction time. On the other hand, the yields of CH₃OH and CH₃OOH appeared to be maintained (Tables S15 and S16). It should be noted that the turnover frequency based on a Fe atom (TOF) is higher in the in

situ H_2O_2 generation system than in the direct H_2O_2 injection system. This implies that the catalytic cycle can be facilitated in the in situ H₂O₂ generation system compared to the direct H₂O₂ injection system. Under the same reaction conditions, CH₃OH was converted into HCOOH and CO₂ (Table S17). HCOOH was easily transformed into CO₂ (Table S17). This implies that the consecutive reactions from methane to CO₂ through CH₃OOH, CH₃OH, and HCOOH are prevalent under these reaction conditions. The product yields were also dependent on the reaction temperature. The higher yields of methane oxygenates were achieved with an increasing reaction temperature from 10 to 30 °C in both cases (Tables S18 and S19). However, the selectivity for methane oxygenates decreased with increasing temperature because the further oxidation reactions of the methane oxygenates are accelerated more with increasing reaction temperature.

When ethane was used as a reactant, ethane oxygenates due to C-H activation (C₂H₅OH and CH₃COOH) as well as methane oxygenates owing to C-C scission and C-H activation (CH₃OH, HCOOH, CH₃OOH) were obtained (Table S20). This implies that radical species as nonselective intermediates must be involved in this reaction system. In Fenton chemistry, the hydroxyl radical is reported to be formed via the reaction between Fe²⁺ and H₂O₂, which is as follows:^[40]

 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_{\bullet} + OH^-$ (1)

This formed hydroxyl radical (HO \cdot) is active enough to break down the C-H bond in methane to form the methyl radical as follows:

(2)

$CH_4 + HO_{\bullet} \rightarrow CH_{3^{\bullet}} + H_2O$

A further radical-initiated reaction can be carried out to form CH₃OOH, CH₃OH, HCOOH, and CO₂.^[26] However, the reduction of Fe³⁺ into Fe²⁺ should occur easily under reaction conditions to increase the turnover number. Very low methane oxygenate yields obtained in the presence of FeSO₄ and H₂O₂ indicate that this reduction of Fe³⁺ into Fe²⁺ does not occur spontaneously under the given reaction conditions. The aqueous FeSO₄ solution in 15 mM sulfuric acid has a low absorption band in the wavelength range of 300 - 400 nm in UV-Vis spectra (Fig. S2). On the other hand, a strong absorption band can be observed for the aqueous $Fe_2(SO_4)_3$ solution in 15 mM sulfuric acid (Fig. S2). There was no change in the absorption band due to Fe³⁺ even after injection of H₂O₂ into the Fe₂(SO₄)₃ solution (Fig. S2A). On the other hand, once H_2O_2 is added to the aqueous FeSO₄ solution, the absorption band appears indicating the oxidation of Fe^{2+} into Fe^{3+} (Fig. S2B). In the presence of H₂ and Pd/C, dihydrogen can be easily dissociated into atomic hydrogen over Pd/C and the reduction of Fe³⁺ into Fe²⁺ can be facilitated (Fig. S3), which results in the production of reactive hydroxyl radicals to activate methane (eqn. (2)).

$$\begin{array}{l} H_2 + 2^* \leftrightarrow 2H^* \qquad (3) \\ H^* + Fe^{3+} \rightarrow {}^* + Fe^{2+} + H^+ \quad (4) \end{array}$$

The dissociation of molecular hydrogen into atomic hydrogen can occur over noble metals such as Pt, Pd, and Rh. In the presence of hydrogen and oxygen, H_2O_2 can be produced from molecular oxygen and dissociated hydrogen atoms as follows.

$$2H^* + O_2 \leftrightarrow H_2O_2 + 2^*$$
 (5)

This reaction is reported to be strongly dependent on the metal and the activity of the metals generally decreased in the following order: Pd > Pt >> Rh.^[34, 41] This can explain why the methane oxygenate yields depended on the noble metal catalysts in the *in situ* H₂O₂ generation system. Based on them, the reaction scheme for the synthesis of methane oxygenates from methane,

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 $\begin{array}{l} \mathsf{H}_2 + 2^* \leftrightarrow 2\mathsf{H}^* \\ 2\mathsf{H}^* + \mathsf{O}_2 \leftrightarrow \mathsf{H}_2\mathsf{O}_2 + 2^* \\ \mathsf{F}e^{2+} + \mathsf{H}_2\mathsf{O}_2 \rightarrow \mathsf{F}e^{3+} + \mathsf{HO}^{\scriptscriptstyle +} + \mathsf{OH}^{\scriptscriptstyle -} \\ \mathsf{CH}_4 + \mathsf{HO}^{\scriptscriptstyle -} \rightarrow \mathsf{CH}_3^{\scriptscriptstyle -} + \mathsf{H}_2\mathsf{O} \\ \mathsf{CH}_3^{\scriptscriptstyle +} + \mathsf{O}_2 \rightarrow \mathsf{CH}_3\mathsf{OO}^{\scriptscriptstyle +} \\ \mathsf{CH}_3\mathsf{OO}^{\scriptscriptstyle +} \overset{--+}{\longrightarrow} [\mathsf{CH}_3\mathsf{OOH}, \mathsf{CH}_3\mathsf{OH}, \mathsf{HCOOH}] \xrightarrow{--+} \mathsf{CO}_2 \\ \mathsf{F}e^{3+} + \mathsf{H}^* \rightarrow \mathsf{F}e^{2+} + \mathsf{H}^+ \\ \mathsf{H}^+ + \mathsf{OH}^{\scriptscriptstyle -} \rightarrow \mathsf{H}_2\mathsf{O} \end{array}$

H_{2} + O_{2} + CH_{4} \rightarrow methane oxygenates + water

Scheme 1. Reaction scheme for the synthesis of methane oxygenates from methane, oxygen, and hydrogen.

oxygen, and hydrogen can be proposed (scheme 1).

Previously Pd or Pt was incorporated into heteropoly acids to enhance the catalytic activity for gas-phase methane oxidation in the presence of H₂ and O₂, resulting in very low yields of methane oxygenates.^[42, 43] Liu *et al.*^[44] reported that Pd and Pt ions in the presence of a Fenton system could augment the production of OH-. Li *et al.*^[45] also found that Pd and PdO in a Pd/PdO/Fe₂O₃/SBA-15 catalyst played important roles in the Fenton reaction for dye degradation. However, the promotional effect of hydrogen on the Fenton system have not been elucidated. The catalytic activity of the present catalyst system is compared with those of the previous systems (Table S21). It can be said that the present system has an excellent catalytic performance considering the reaction temperature and solvent system.

In conclusion, in the presence of hydrogen and a Pd/C catalyst, the reduction of Fe³⁺ into Fe²⁺ can be accelerated by atomic hydrogen dissociated from molecular hydrogen on Pd. This Fe²⁺ can produce hydroxyl radicals via a reaction with directly added H₂O₂ or *in situ* generated H₂O₂ from H₂ and O₂ over Pd/C. This formed hydroxyl radical can oxidize methane into methane oxygenates including CH₃OOH, CH₃OH, and HCOOH. This is one example in which the *in situ* H₂O₂ injection system.

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Methane-to-Oxygenates: Aqueousphase selective oxidation of methane with molecular oxygen under mild conditions was successfully demonstrated using iron salts and Pd/C in the presence of molecular hydrogen



Jongkyu Kang and Eun Duck Park*

Page No. – Page No. Aqueous-phase selective oxidation of methane with oxygen over iron salts and Pd/C in the presence of hydrogen