

# Supplementary materials: Liquid-phase selective oxidation of methane to methane oxygenates

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\* **Correspondence:** Correspondence: edpark@ajou.ac.kr1. Catalyst preparation

## 1. Catalyst preparation

0.38 wt.% Fe-ZSM-5 was prepared from FeCl<sub>2</sub>·4H<sub>2</sub>O (Sigma Aldrich, St. Louis, MO, USA) and NH<sub>4</sub>-ZSM-5 (Zeolyst, CBV3024E, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30, S<sub>BET</sub> = 405 m<sup>2</sup>/g) using an adsorption method. More specifically, 0.99 kg of NH<sub>4</sub>-ZSM-5 was added to 1.40 L of a 129 mM aqueous solution of FeCl<sub>2</sub>·4H<sub>2</sub>O at 30 °C for 12 h in a static container. The water was removed through a filter. The recovered cake was dried at 110 °C overnight and then calcined in air at 550 °C for 3 h.

## 2. Activity test

The prepared catalyst was evaluated for the selective oxidation of methane with H<sub>2</sub>O<sub>2</sub> in liquid water. This reaction experiment was performed in an autoclave with a total working volume of 125 mL. The glass liner was placed in an autoclave. Different concentrations of hydrogen peroxide were added to the liquid water. A certain amount of the catalyst was added to the liquid water. In the gas phase, the methane was charged to the target pressure after five purges at a specific pressure. Subsequently, the temperature of the reactor was increased to different temperatures. Then, the reaction was performed for various reaction times while stirring with a magnetic stirrer at a speed of 1200 rpm. After the reaction, the autoclave was rapidly cooled to below 10 °C with liquid nitrogen. Methane dissolved in water is oxidized with hydrogen peroxide in the presence of Fe/ZSM-5 catalyst into various methane oxygenates (methanol, methyl hydroperoxide, and formic acid) and carbon dioxide. The product gas was separated with a Carbosphere-packed column (Agilent) in an online gas chromatograph (Younglin) and passed through a methanizer. Then, methane from CO<sub>2</sub> was measured using a flame ionization detector. The product CO<sub>2</sub> was quantified using a standard gas containing 1000 ppm CO<sub>2</sub>. The liquid mixture was filtered with a microfilter (Millex) for nuclear magnetic resonance (NMR) analysis and hydrogen peroxide quantification. <sup>1</sup>H-NMR was measured at room temperature with a Jeol Resonance ECZ600R (<sup>1</sup>H 600 MHz) using 0.1% trimethylsilylpropanoic acid sodium salt (TMSP)/D<sub>2</sub>O (Euriso-top) as the standard and a solvent suppression program to minimize the H<sub>2</sub>O peak. The concentration of H<sub>2</sub>O<sub>2</sub> was determined with the titration method using Ce(SO<sub>4</sub>) [1,2].

The methane conversion ( $X_{CH_4}$ ), H<sub>2</sub>O<sub>2</sub> conversion ( $X_{H_2O_2}$ ), and selectivity for methane oxygenates ( $S_{MO}$ ) were calculated as follows:

$$X_{CH_4} = \left( \frac{[CH_3OH] + [CH_3OOH] + [HCOOH] + [CO_2]}{[CH_4]_i} \right) \times 100 \quad (1)$$

$$X_{H_2O_2} = \left( 1 - \frac{[H_2O_2]_f}{[H_2O_2]_i} \right) \times 100 \quad (2)$$

$$S_{MO} = \left( \frac{[CH_3OH] + [CH_3OOH] + [HCOOH]}{[CH_3OH] + [CH_3OOH] + [HCOOH] + [CO_2]} \right) \times 100 \quad (3)$$

where  $[CH_3OH]$ ,  $[CH_3OOH]$ ,  $[HCOOH]$ ,  $[CO_2]$ ,  $[CH_4]_i$ ,  $[H_2O_2]_i$ , and  $[H_2O_2]_f$  are the final moles of CH<sub>3</sub>OH, final moles of CH<sub>3</sub>COOH, final moles of HCOOH, final moles

of CO<sub>2</sub>, initial moles of methane, initial concentration of H<sub>2</sub>O<sub>2</sub>, and final concentration of H<sub>2</sub>O<sub>2</sub>, respectively.

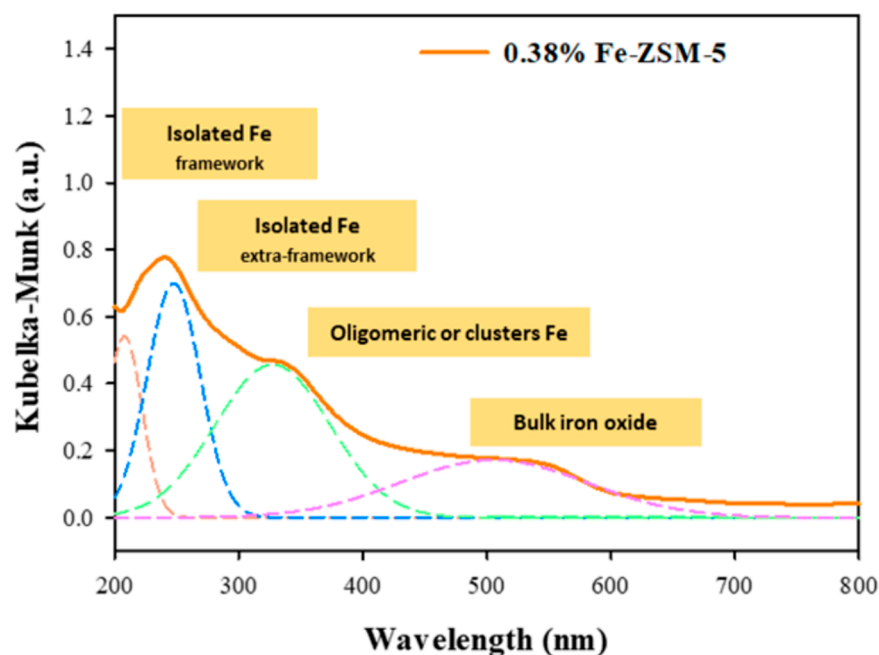
### 3. Catalyst characterization

ICP-AES was performed using a Thermo Scientific iCAP 6500 instrument to determine the Fe content of each catalyst. UV–Vis spectra were obtained using a Jasco V-650 spectrophotometer. **Table S1**. The catalytic performance for selective oxidation of methane with H<sub>2</sub>O<sub>2</sub> over 0.38 wt.% Fe-ZSM-5 under different conditions.

**Table S1.** The catalytic performance for selective oxidation of methane with H<sub>2</sub>O<sub>2</sub> over 0.38 wt.% Fe-ZSM-5 under different conditions.

Entry	Amount of Catalyst (g)	Volume of water (mL)	Concentration of H <sub>2</sub> O <sub>2</sub> (mM)	CH <sub>4</sub> Pressure (bar)	Reaction temperature (°C)	Reaction time (h)	Yield of CH <sub>3</sub> OH (mmol)	Yield of CH <sub>3</sub> COOH (mmol)	Yield of HCOOH (mmol)	Yield of CO <sub>2</sub> (mmol)	X <sub>C</sub> <sub>H4</sub> (%)	X <sub>H2</sub> <sub>O2</sub> (%)	S <sub>M</sub> <sub>O</sub> (%)
1	0.050	30	295	11	25	4	0.023	0.030	0.204	0.016	1.8	23	95
2	0.50	90	295	11	25	4	0.056	0.018	1.370	0.083	10	42	95
3	1.0	90	295	11	25	4	0.067	0.020	3.029	0.189	21	71	95
4	1.5	90	295	11	25	4	0.062	0.009	3.275	0.288	23	86	92
5	1.0	30	295	11	25	4	0.041	0.0	1.243	0.069	9.0	92	95
6	1.0	60	295	11	25	4	0.065	0.004	2.332	0.125	16	85	95
7	1.0	90	100	11	25	4	0.060	0.005	1.370	0.066	10	95	96
8	1.0	90	600	11	25	4	0.035	0.009	3.943	0.618	30	68	87
9	1.0	90	295	4	25	4	0.012	0.011	1.475	0.148	29	53	91
10	1.0	90	295	7	25	4	0.027	0.006	1.978	0.178	22	65	92
11	1.0	90	295	16	25	4	0.089	0.012	3.379	0.230	16	73	94
12	1.0	90	295	21	25	4	0.107	0.012	3.588	0.282	14	75	93
13	1.0	90	295	26	25	4	0.110	0.004	3.692	0.313	11	76	92
14	1.0	90	295	11	20	4	0.060	0.0	2.508	0.153	19	64	95
15	1.0	90	295	11	30	4	0.072	0.008	3.667	0.228	26	83	94
16	1.0	90	295	11	25	3	0.040	0.004	2.680	0.181	19	64	94
17	1.0	90	295	11	25	5	0.071	0.004	3.270	0.204	23	75	94

As shown in **Table S1**, the catalytic performance is strongly dependent on the reaction conditions. The methane conversion increases with increasing amounts of catalyst (**Entries 2, 3, and 4; Table S1**), volume of water (**Entries 3, 5, and 6; Table S1**), H<sub>2</sub>O<sub>2</sub> concentration (**Entries 3, 7, and 8; Table S1**), reaction temperature (**Entries 3, 14, and 15; Table S1**), and reaction time (**Entries 3, 16, and 17; Table S1**). The methane conversion also increases with decreasing total pressure of methane (**Entries 3, 9, 10, 11, 12, and 13; Table S1**). On the other hand, the selectivity to methane oxygenates generally decreases with methane conversion. There exist optimum conditions to achieve high selectivities to methane oxygenates while maintaining relatively high methane conversions (e.g., **entry 3, Table S1**).



**Figure S1.** UV–Vis spectra of 0.38 wt.% Fe-ZSM-5. The raw data and deconvoluted data were plotted as solid and dotted lines, respectively.

The UV–Vis spectra of the prepared Fe-ZSM-5 show a sharp peak at 250 nm with a shoulder at 320 nm and a rather broad peak in the range of 400–600 nm (Figure S1). It is generally accepted that Fe species in Fe-ZSM-5 show UV–Vis bands of (i) 200–250 nm (isolated  $\text{Fe}^{3+}$  in framework positions), (ii) 250–350 nm (isolated or oligonuclear extra-framework Fe species), (iii) 350–450 nm (iron oxide clusters), and (iv) above 450 nm (larger iron oxide aggregates on the external crystal surface) [3,4]. Therefore, it can be said that most Fe species in this catalyst are present as isolated or oligonuclear extra-framework Fe species.

## References

1. Hammond, C.; Forde, M.M.; Ab Rahim, M.H.; Thetford, A.; He, Q.; Jenkins, R.L.; Dimitratos, N.; Lopez-Sanchez, J.A.; Dummer, N.F.; Murphy, D.M.; et al. Direct Catalytic Conversion of Methane to Methanol in an Aqueous Medium by Using Copper-Promoted Fe-ZSM-5. *Angewandte Chemie - International Edition* **2012**, *51*, 5129–5133, doi:10.1002/anie.201108706.
2. Liang, C.; He, B. A Titration Method for Determining Individual Oxidant Concentration in the Dual Sodium Persulfate and Hydrogen Peroxide Oxidation System. *Chemosphere* **2018**, *198*, 297–302, doi:10.1016/j.chemosphere.2018.01.115.
3. Forde, M.M.; Armstrong, R.D.; McVicker, R.; Wells, P.P.; Dimitratos, N.; He, Q.; Lu, L.; Jenkins, R.L.; Hammond, C.; Lopez-Sanchez, J.A.; et al. Light Alkane Oxidation Using Catalysts Prepared by Chemical Vapour Impregnation: Tuning Alcohol Selectivity through Catalyst Pre-Treatment. *Chem Sci* **2014**, *5*, 3603–3616, doi:10.1039/c4sc00545g.
4. Forde, M.M.; Armstrong, R.D.; Hammond, C.; He, Q.; Jenkins, R.L.; Kondrat, S.A.; Dimitratos, N.; Lopez-Sanchez, J.A.; Taylor, S.H.; Willock, D.; et al. Partial Oxidation of Ethane to Oxygenates Using Fe- and Cu-Containing ZSM-5. *J Am Chem Soc* **2013**, *135*, 11087–11099, doi:10.1021/ja403060n.