Supplementary materials: Selective oxidation of methane over Fe-zeolites by *in situ* generated H_2O_2

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Table S1. Metal contents and BET surface area of Fe-zeolites.

Name	Fe (wt.%)	Al (wt.%)	SiO_2/Al_2O_3	Surface area (m^2/g)
Fe-ZSM-5	0.919	2.12	30	355
Fe-mordenite	1.48	3.27	20	493
Fe-β	1.16	2.65	25	553
Fe-Y	0.705	5.05	12	703
Fe-ferrierite	0.218	3.25	20	299

Table S2. Metal contents in Fe-zeolites before the reaction and in the liquid after the reaction.[a]

Fe-zeolites	Metal content (μmol)		Fe/Al	Metal content in the liquid (μmol)		Fraction of leached metal[b] (%)	
	Fe	Al		Fe	Al	Fe	Al
Fe-ZSM-5	8.2	39	0.21	0.41	0.93	5.0	2.4
Fe-mordenite	13	61	0.22	0.57	2.1	4.3	3.4
Fe-β	10	49	0.21	5.2	21	50	43
Fe-Y	6.3	94	6.7×10^{-2}	4.3	71	69	76
Fe-ferrierite	1.9	60	3.2×10^{-2}	0.0	1.0	0	1.7

[a]Reaction conditions: 50 mg of each catalysts was used; reaction temperature = 30 °C, reaction time = 30 min. V_{liquid} = 30 mL, [H_2SO_4] = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

[b]The fraction of leached metal is the ratio of the amount of metal in the liquid after a reaction to the amount of metal introduced initially.

Table S3. Catalytic performance of 1.07 wt.% Fe-ZSM-5 and 1 wt.% Pd/AC at different reaction temperatures in the partial oxidation of methane.[a]

Reaction temperature (°C)	$[H_2O_2]_{fin}$ (mM)	Product (μmol)					Selectivity to methane oxygenates [b] (%)
		CH_3OH	HCOOH	CH_3OOH	CO_2	Total product	
0	31	12	30	2	1	45	98
10	24	7	42	2	3	54	94
20	18	9	55	2	9	75	88
30	8	17	84	2	28	131	79
40	11	6	117	5	54	182	70
50	7	8	124	4	56	192	71

[a]Reaction conditions: 50 mg of each catalysts was used; reaction time = 30 min, V_{liquid} = 30 mL, $[H_2SO_4]$ = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

[b]The selectivity to methane oxygenates was calculated as [moles of products excluding CO_2]/[moles of total products] * 100(%).

Table S4. Effect of pH on the performance of 0.766 wt.% Fe-ZSM-5 and 1 wt.% Pd/AC catalysts in the partial oxidation of methane.[a]

$[H_2SO_4]$ (mM)	pH	$[H_2O_2]_{fin}$ (mM)	Product (μmol)					Selectivity to methane oxygenates[b] (%)
			CH_3OH	HCOOH	CH_3OOH	CO_2	Total product	
0.15	3.3	0	2	0	0	0	2	100
1.5	2.3	1	11	5	1	5	22	77
15	1.3	10	13	60	3	11	87	87
150	0.7	17	21	89	2	22	134	84

[a]Reaction conditions: 50 mg of each catalysts was used; reaction temperature = 30 °C, reaction time = 30 min, V_{liquid} = 30 mL, V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar. H_2SO_4 was used to adjust pH.

[b]The selectivity to methane oxygenates were calculated as [moles of products excluding CO_2]/[moles of total products] * 100(%).

Table S5. Effect of 1 wt.% Pd/AC on the catalytic performance of 0.766 wt.% Fe-ZSM-5 and 1 wt.% Pd/AC in the partial oxidation of methane.[a]

Pd (μmol)	$[H_2O_2]_{fin}$ (mM)	Product (μmol)					Selectivity to methane oxygenates [b] (%)
		CH_3OH	HCOOH	CH_3OOH	CO_2	Total product	
0.94	30	11	24	3	2	40	95
2.82	14	9	37	3	8	57	85
4.70	10	13	60	3	11	87	87

[a]Reaction conditions: 50 mg of 0.766 wt.% Fe-ZSM-5 and different amounts of 1 wt.% Pd/AC catalysts were used; reaction temperature = 30 °C, reaction time = 30 min; V_{liquid} = 30 mL, $[H_2SO_4]$ = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

[b]The selectivity to methane oxygenates was calculated as [moles of products excluding CO_2]/[moles of total products] * 100(%). Metal content in 50 mg of catalyst was 6.85 μmol for Fe.

Table S6. Effect of Fe content in Fe-ZSM-5 on the performance of Fe-ZSM-5 and 1 wt.% Pd/AC catalysts in the partial oxidation of methane. [a]

Fe (μmol)	$[H_2O_2]_{fin}$ (mM)	Product (μmol)					Selectivity to methane oxygenates [b] (%)
		CH_3OH	HCOOH	CH_3OOH	CO_2	Total product	
0.13	7	5	4	0	0	9	100
0.95	5	10	4	0	0	14	100
3.87	8	12	22	3	4	41	90
6.85	10	13	60	3	11	87	87
9.57	8	17	84	2	28	131	79

[a]Reaction conditions: 50 mg of each catalysts was used; reaction temperature = 30 °C, reaction time = 30 min, V_{liquid} = 30 mL, $[H_2SO_4]$ = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

[b]The selectivity to methane oxygenates was calculated as [moles of products excluding CO_2]/[moles of total products] * 100(%).

Table S7. Metal content in the liquid and the fraction of leached metal after the reaction with 1.07 wt.% Fe-ZSM-5 and 1 wt.% Pd/AC at different temperatures.[a]

Temperature (°C)	Metal content in liquid (μmol)		Fraction of metal leached[b] (%)	
	Fe	Al	Fe	Al
0	0.417	1.389	4.3	3.6
10	0.454	1.490	4.7	3.8
20	0.540	1.470	5.6	3.8
30	0.700	1.650	7.3	4.2
40	0.935	1.741	9.8	4.5
50	1.02	1.89	10.7	4.9

[a]Reaction conditions are same as those in Table S3.

[b]The fraction of leached metal is the ratio of the amount of metal in the liquid after a reaction to the amount of metal introduced initially.

Table S8. Metal content in the liquid and the fraction of leached metal after a reaction with 0.766 wt.% Fe-ZSM-5 and 1 wt.% Pd/AC at different pH.[a]

$[H_2SO_4]$ (mM)	pH	Metal content in liquid (μmol)			Fraction of metal leached[b] (%)		
		Fe	Al	Pd	Fe	Al	Pd
0.15	3.3	0	0	0	0	0	0
1.5	2.3	0.26	1.19	0	3.8	3.0	0
15	1.3	0.53	1.62	0	7.8	4.1	0
150	0.7	0.64	1.62	0.09	9.4	4.1	1.9

[a]Reaction conditions are same as those in Table S4. Metal content in 50 mg of catalyst was 6.8 μmol for Fe, 39.7 μmol for Al, and 4.7 μmol for Pd.

[b]The fraction of metal leached is the percentage of the amount of metal in liquid after reaction to the amount of metal introduced.

Table S9. Metal content in the liquid and the fraction of leached metal after a reaction with Fe-ZSM-5 containing different Fe contents and 1 wt.% Pd/AC catalysts.[a]

Catalyst	Initial Fe content (μmol)	Initial molar ratio of Fe/Al	Metal content in the liquid (μmol)		Fraction of metal leached (%)	
			Fe	Al	Fe	Al
H-ZSM-5	0.13	0.003	0	1.48	0	3.8
0.106% Fe-ZSM-5	0.9	0.024	0.06	1.58	6.4	4.0
0.433% Fe-ZSM-5	3.9	0.097	0.20	1.75	5.0	4.4
0.766% Fe-ZSM-5	6.8	0.173	0.53	1.62	7.8	4.1
1.07% Fe-ZSM-5	9.6	0.246	0.70	1.65	7.3	4.2

[a]Reaction conditions are same as Table S7.

[b]The fraction of metal leached is the percentage of the amount of metal in liquid after reaction to the amount of metal introduced.

Table S10. Catalytic performance of different concentrations of 1 wt.% Pd/AC and $FeSO_4$ in the partial oxidation of methane.[a]

Fe (μmol)	$[H_2O_2]_{fin}$ (mM)	Product (μmol)				Total product	Selectivity to methane oxygenates[b] (%)
		CH_3OH	HCOOH	CH_3OOH	CO_2		
0.015	1	5	2	0	0	7	100
0.15	10	7	20	0	9	36	76
0.96	13	11	84	0	31	126	75
4.78	7	19	171	5	140	335	58
11.2	5	13	218	6	303	540	44

[a]Reaction conditions: 50 mg of 1 wt.% Pd/AC were used; reaction temperature = 30 °C, reaction time = 30 min, V_{liquid} = 30 mL, $[H_2SO_4]$ = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

[b]The selectivity to methane oxygenates was calculated as [moles of products excluding CO_2]/[moles of total products] * 100(%).

Table S11. Catalytic performance for partial oxidation of methane under different conditions.

Entry	Catalyst	H_2O_2 conv. (%)	Product (μmol)				Selectivity to methane oxygenate (%)
			CH_3OH	HCOOH	CH_3OOH	CO_2	
1[a]	0.919% Fe-ZSM-5	11	17	102	13	10	93
2[b]	0.919% Fe-ZSM-5	7	18	104	12	3	98
3[c]	Leaching solution [d]	0	0	0	0	0	n.d.
4[e]	0.919%Fe-ZSM-5+1%Pd/AC	In situ	22	52	0	16	82

[a]Reaction conditions: 50 mg of catalyst was used. Reaction temperature = 30 °C, reaction time = 30 min; V_{liquid} = 30 mL, [H_2O_2]=0.28 M in H_2O; V_{gas} = 95 mL, P_{CH4} =15 bar, P_{N2} = 13 bar.

[b]Reaction conditions: 50 mg of catalyst was used. Reaction temperature = 30 °C, reaction time = 30 min; V_{liquid} = 30 mL, [H_2O_2]=0.28 M in H_2O, [H_2SO_4] = 15 mM; V_{gas} = 95 mL, P_{CH4} =15 bar, P_{N2} = 13 bar.

[c]Reaction conditions: Reaction temperature = 30 °C, reaction time = 30 min; V_{liquid} = 30 mL, [H_2O_2]=0.28 M in H_2O; V_{gas} = 95 mL, P_{CH4} =15 bar, P_{N2} = 13 bar.

[d]Leaction solution was obtained by contacting 50 mg of Fe-ZSM-5 with 30 mL of aqueous 15 mM of H_2SO_4 at 30 °C for 30 min.

[e]Reaction conditions: 50 mg of Fe-ZSM-5 and 50 mg of Pd/AC catalyst was used. Reaction temperature = 30 °C, reaction time = 30 min; V_{liquid} = 30 mL, [H_2SO_4] = 15 mM. V_{gas} = 90 mL, P_{CH4} =15 bar, P_{H2} = 3 bar, P_{Air} = 10 bar.

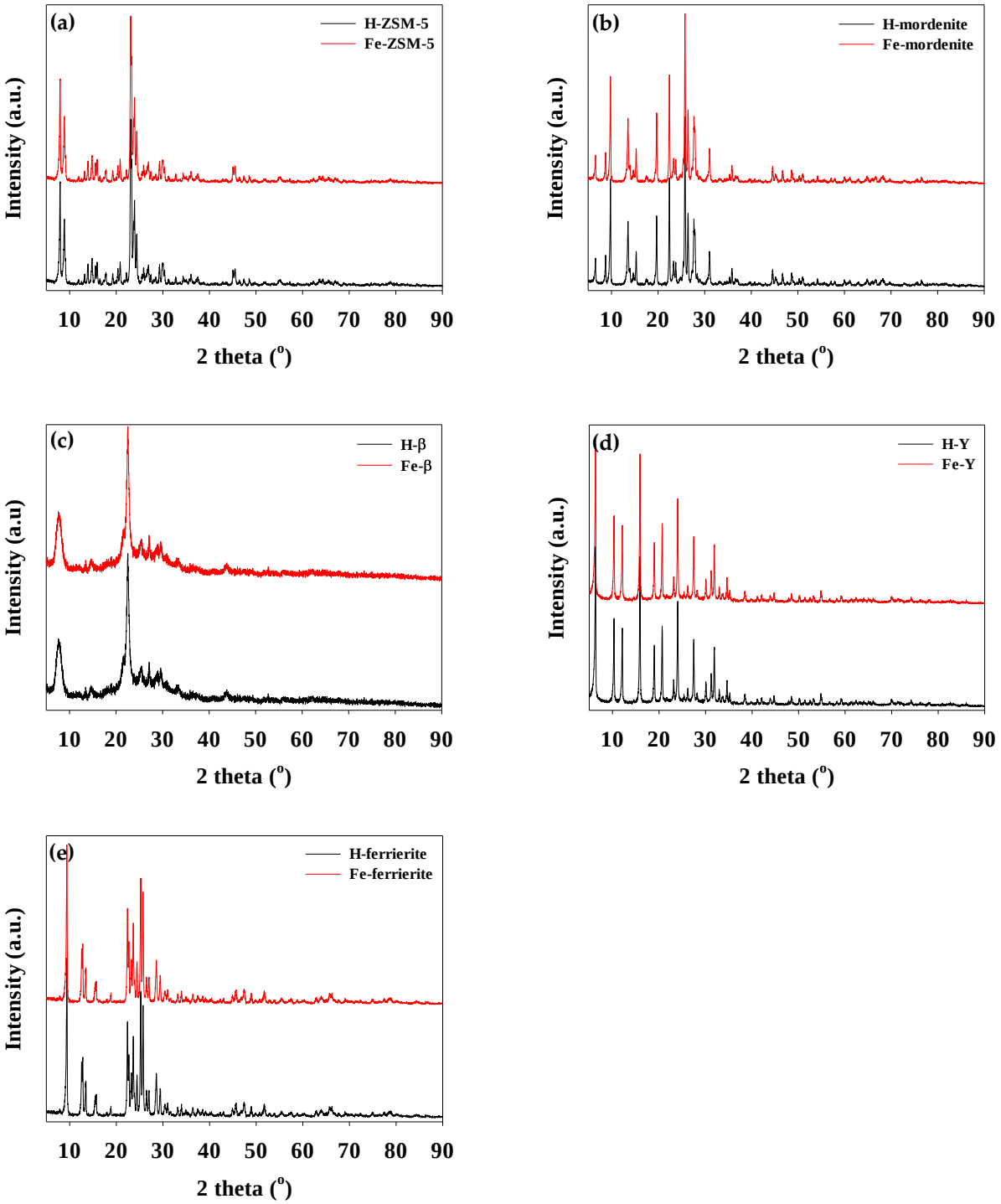

Figure S1. XRD patterns of (a) H-ZSM-5 and Fe-ZSM-5, (b) H-mordenite and Fe-mordenite, (c) H-β and Fe-β, (d) H-Y and Fe-Y, and (e) H-ferrierite and Fe-ferrierite.

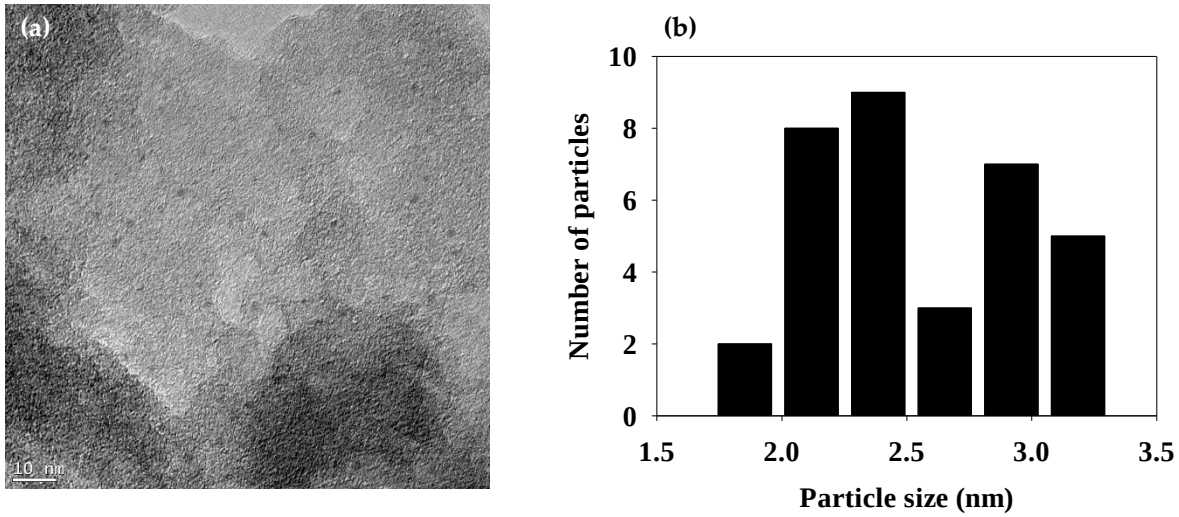

Fig. S2. TEM image (a) and particle size distribution of Pd metal (b) of 1 wt.% Pd/AC .