Appendix A. Supplementary data:

Effects of support on bifunctional one-step synthesis of methylal via methanol oxidation catalyzsed by Fe-Mo-based catalyst

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Content:

Table S1. Specific surface areas and pore structure data of the catalysts.

Catalyst	Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Mo:Fe(2) /HY zeolite	225.31	3.34	0.146
Mo:Fe(2) / Al_2O_3	313.52	2.13	0.109
Mo:Fe(2) /HZSM-5 (40)	325.32	2.15	0.110
Mo:Fe(2) /HZSM-5 (80)	316.47	2.28	0.099
Mo:Fe(2) / SiO_2	309.88	2.23	0.089

Table S2. The NH_3-TPD results of the catalysts

Catalyst	Weak acid		Stronger acid	
	T(°C)	NO.(μmol·g^{-1})	T(°C)	NO.(μmol·g^{-1})
Mo:Fe(2) /HY zeolite	200	651.93	500	220.59
Mo:Fe(2) / Al_2O_3	200	158.89	375	90.22
Mo:Fe(2) /HZSM-5 (40)	225	814.74	475	407.14
Mo:Fe(2) /HZSM-5 (80)	200	659.83	450	244.09
Mo:Fe(2) / SiO_2	--	--	--	--

Table S3. Acidic Properties of catalysts with different carriers.

catalyst	Lewis[a]	Brönsted[b]	B/L[c]	total
Mo-Fe (2) /HY zeolite	1.12	4.81	4.29	5.93
Mo-Fe (2)/ Al_2O_3	1.10	3.44	3.13	4.54
Mo-Fe (2) /HZSM-5 (40)	1.87	4.46	2.39	6.33
Mo-Fe (2)/HZSM-5 (80)	0.91	4.11	4.52	5.02
Mo-Fe (2) / SiO_2	1.14	0	0	1.14
HZSM-5 (40)	0.99	4.67	4.72	5.66

[a]Lewis' range: 1432~1460 cm^{-1}.[b]Bands' range: 1510~1560 cm^{-1}. [c]Brönsted/Lewis bands ratio.

Table S4. Specific surface areas and pore structure data of the catalysts.

Catalyst	Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Mo:Fe(2) /HY zeolite	225.31	3.34	0.146
Mo:Fe(2) /HZSM-5 (40)	325.32	2.15	0.110
Mo:Fe(2) /HZSM-5 (80)	316.47	2.28	0.099
Mo:Fe(2)/HY zeolite+HZSM-5(80)	231.88	3.49	0.160
Mo:Fe(2) / HZSM-5 (40+80)	321.37	2.13	0.099
Mo:Fe(2) / HZSM-5 (80+80)	305.32	2.18	0.094

Table S5. The NH_3-TPD results of the catalysts

Catalyst	Weak acid		Middle stronger acid		Total	Stronger acid	
	T/°C	NO.(μmol·g^{-1})	T/°C	NO.(μmol·g^{-1})		T/°C	NO.(μmol·g^{-1})
Mo:Fe(2)/HY zeolite+HZSM-5(80)	225	1136.4	--	--	1136.4	490	464.4
Mo:Fe(2) /HZSM-5 (40+80)	175	515.2	275	932.6	1447.8	475	616.8
Mo:Fe(2) /HZSM-5 (80+80)	175	639.3	275	821.5	1460.8	450	570.6

Table S6. Acidic Properties of catalysts with Mo/Fe different ratio.

catalyst	Lewis[a]	Brönsted[b]	B/L[c]	total
Mo:Fe(2)/HY zeolite+HZSM-5(80)	1.21	4.22	3.49	5.43
Mo:Fe(2) /HZSM-5 (40+80)	1.62	4.19	2.59	5.81
Mo:Fe(2) /HZSM-5 (80+80)	1.23	4.71	3.82	5.94

[a]Bands' range: 1432~1460 cm^{-1}.[b]Bands' range: 1510~1560 cm^{-1}. [c]Brönsted/Lewis bands ratio.

Table S7. Catalytic activity of Fe-Mo-based catalysts with different Si/Al ratios.

Catalyst	Methanol conversion (%)	Product selectivity (%)					
		DMM	FA	MF	DME	CO_x	Yeild
Mo-Fe (2) /HZSM-5 (20)	30.81	48.28	8.9	40.03	2.02	0.77	14.05
Mo-Fe (2) /HZSM-5 (60)	25.71	62.77	9.11	24.67	2.91	0.54	16.14
Mo-Fe (2) /HZSM-5 (100)	21.89	70.01	10.1	14.34	5.14	0.41	16.73
Mo-Fe (2) /HZSM-5 (80+20)	60.77	60.1	6.10	26.83	6.66	0.31	36.52
Mo-Fe (2) /HZSM-5 (80+60)	80.17	79.44	5.61	11.6	3.01	0.34	63.69
Mo-Fe (2) /HZSM-5 (80+100)	84.41	85.77	2.60	8.12	3.51	0.29	72.39

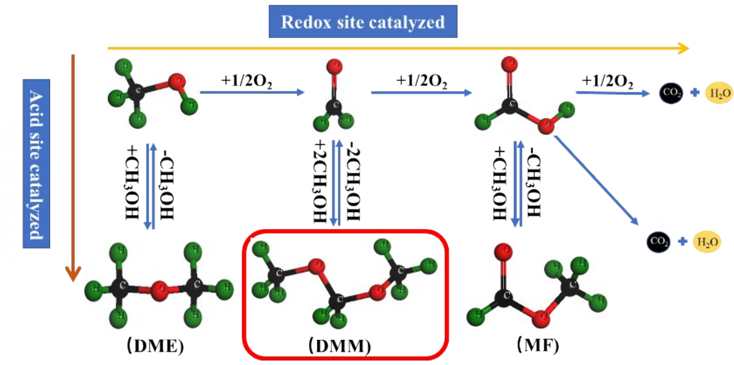

Fig. S1. Scheme of oxidation/dehydration of methanol

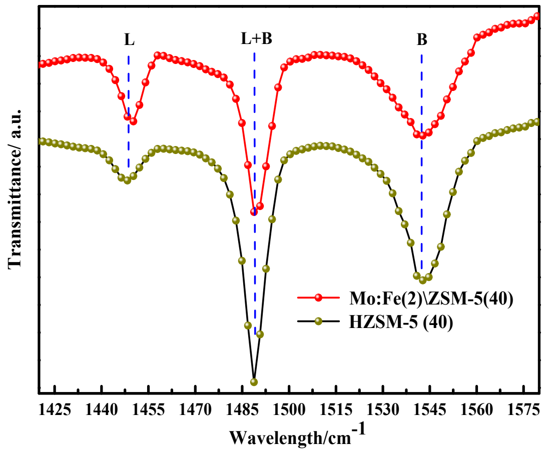

Fig.S2. FTIR spectra of pyridine adsorbed on the ZSM-5 (40) and Mo: Fe (2) / HZSM-5 (40) catalysts.

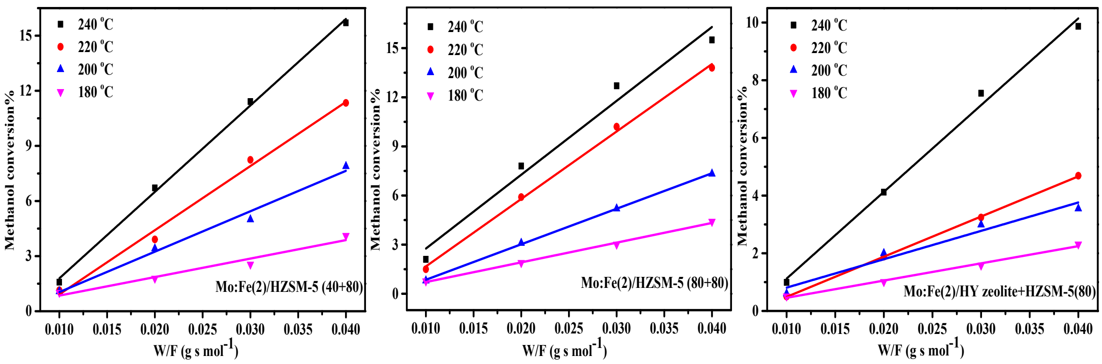

Fig. S3. Variation of methanol conversion with W/F for different catalysts.