Supporting information

High yield production of C_2-C_3 olefins and *para*-xylene from methanol using a SiO_2-coated FeOx/ZSM-5 catalyst

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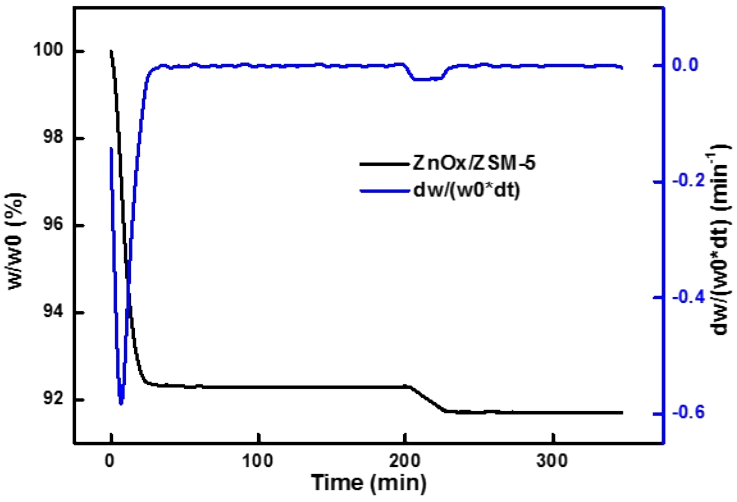
SI-1 Characterization of the external surface

2,6-di-tert-butylpyridine(DTBP) was used as probe molecules, which only adsorbed on external surface of the catalyst, but was unable to enter pores of zeolite. Firstly, certain sample of catalyst(Ws) was put into the instrument of thermogravimetric analysis (TGA, TG2050A) and was elevated from ambient temperature to 500 °C in N_2. The step was to remove water and gases impurities physically adsorbed on the zeolite. Secondly, the temperature was decreased to 150 °C and allowed the adsorption of 2,6-di-tert-butylpyridine for 30 min. Mass after this step was denoted as W0. Thirdly, temperature was elevated to 250 °C for purging with N_2 for 3 hrs. Molecules physically adsorbed were deadsorped and the mass was denoted as W1。 Fourth, the temperature was elevated to 500 °C to remove all molecules chemically adsorped. The mass was denoted as W2. Density of external acids can be calculated as:

$$(w_1\text{-}w_2)/w_s/M_{DTBP}$$



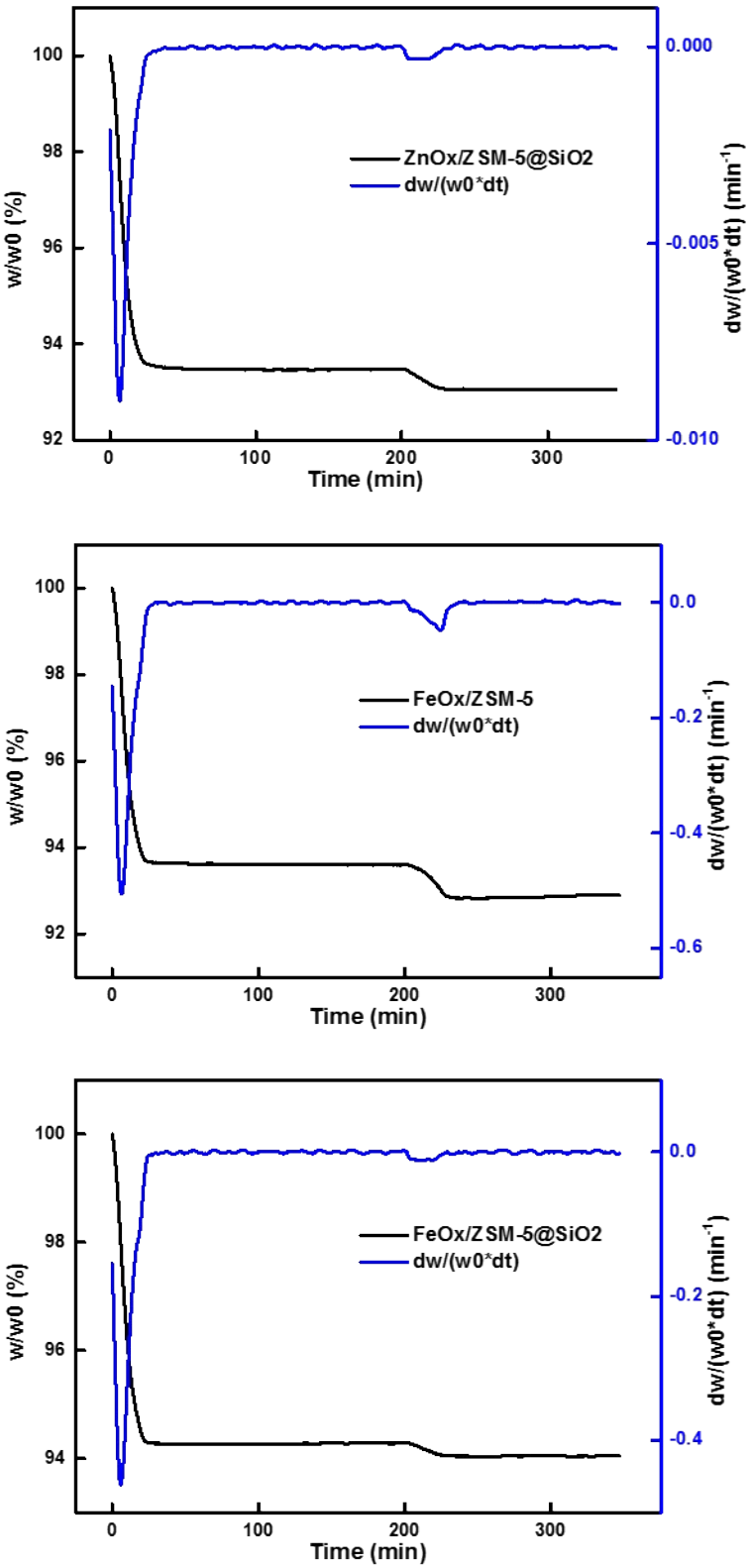


Fig.S1 TG curve to determine the acidic amount inside pores and on the external surface with different catalysts.

SI-2 TEM of ZnOx/ZSM-5 and FeOx/ZSM-5

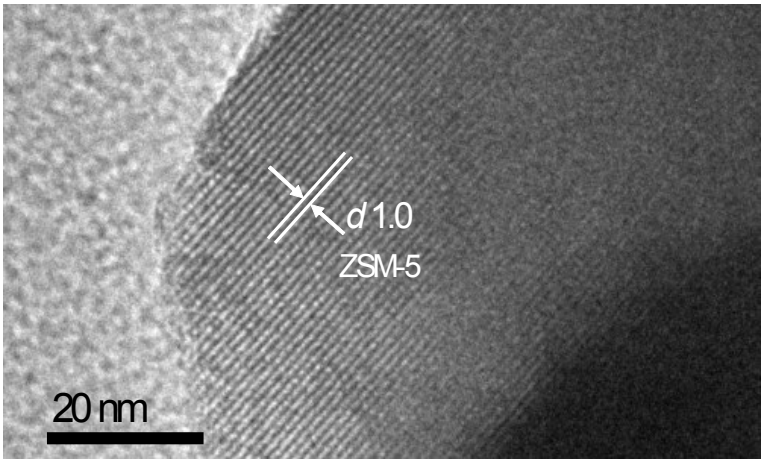


Fig S2 TEM of ZnOx/ZSM-5

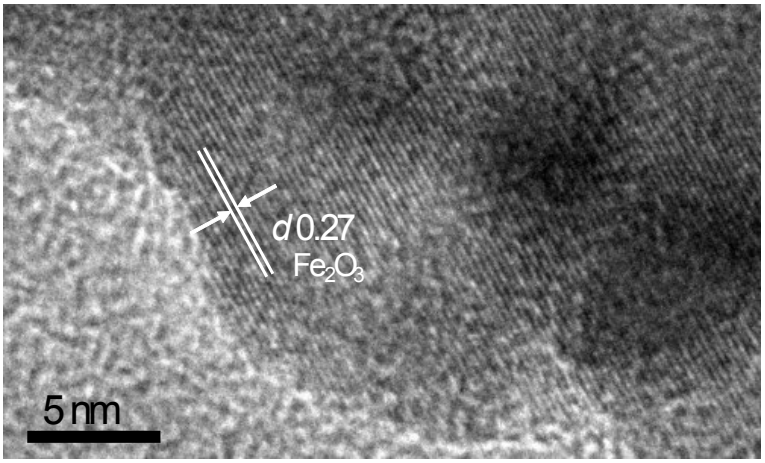


Fig S3 TEM of FeOx/ZSM-5

SI-3TPR of FeOx/ZSM-5

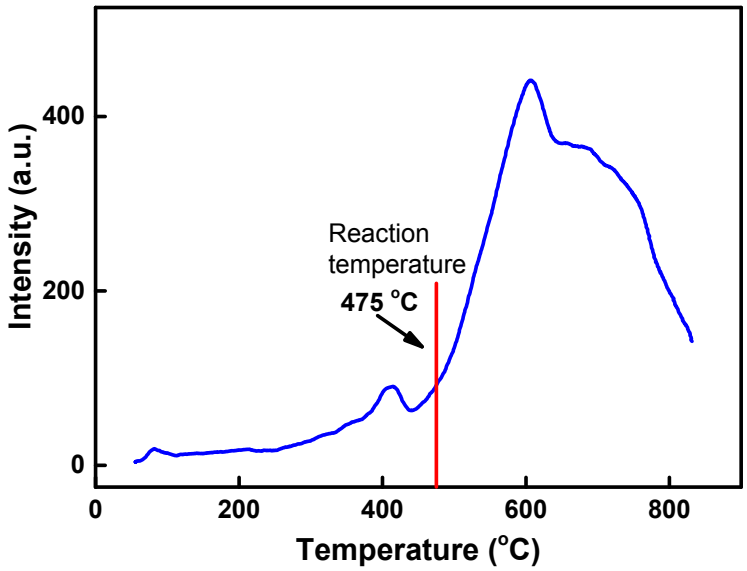


Fig S4 TPR of FeOx/ZSM-5

SI-4 NH3-TPD information of catalysts

Table S1. Peak fitting of NH3-TPD curve to determine the ratio of weak, strong, medium strong acids.

Catalyst	Total area	Parameter	Weak acids	Medium strong acids		Strong acids
HZSM-5	19568	Peak temperature, °C Area (a.u.) Percentage, %	227.3 4943 25.3		315.6 11864 60.6	542.9 2761 14.1
FeOx/ZSM-5	14519	Peak temperature, °C Area (a.u.) Percentage, %	224.7 1313 9.0	259.6 5336 36.8	328.9 7870 54.2	
ZnOx/ZSM-5	16161	Peak temperature, °C Area (a.u.) Percentage, %	221.4 1788 11.1	266.2 4289 26.5	342.7 10084 62.4	

SI-5 Comparison of the four modified ZSM-5 and H-ZSM-5

Table S2. Acidity, effect of SiO_2 on the external acidity, specific surface area and pore volume of different catalysts.

□	Acid density(mmol/g)			Effect of SiO_2 coat on external acidity	External acid/ Total acid	Specific surface area(m^2/g)	Acid density (umol/m^2)	Pore volume(mL/g)
	Total	External	Inner					
H-ZSM-5	1.246	0.272	0.974		21.83%	402	3.096	0.246
Zn/ZSM-5	1.029	0.034	0.995	-29%	3.27%	360	2.858	0.166
Zn/ZSM-5@SiO_2	0.983	0.024	0.959		2.44%	318	3.091	0.153
Fe/ZSM-5	0.752	0.044	0.708	-70%	5.85%	345	2.179	0.163
Fe/ZSM-5@SiO_2	0.737	0.013	0.724		1.81%	331	2.227	0.155