

Electronic Supplementary Material

Fabrication and catalytic performance of meso-ZSM-5 zeolite encapsulated ferric oxide nanoparticles for phenol hydroxylation

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Synthesis of ferric oleate

Ferric oleate was prepared according to the literature method [1]. In a typical procedure, 10.8 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 36.5 g sodium oleate were dissolved in a solvent mixture of 80 mL ethanol, 60 mL distilled water and 140 mL hexane. The solution was refluxed at 65 °C for 4 h. When the reaction was completed, the upper organic layer was collected and washed twice with distilled water. Then, the product was heated in a vacuum oven at 70 °C for 4 h and ferric oleate was obtained in a waxy solid form.

Characterization

The ferric oleate sample was characterized by FTIR. To prepare the sample for analysis, ferric oleate was dissolved in CCl_4 and then spread evenly on KBr pellets to form a thin film after solvent evaporation. The FTIR spectrum was collected on a FTIR Bruker Equinox spectrometer (Vertex 70, Billerica, MA, USA).

Hydroxyl radical quantitation

The quantitative determination of $\bullet\text{OH}$ was carried out using benzoic acid (BA) as a probe molecule according to literature reports [2, 3]. In a typical procedure, 30 mL of a mixture of

catalyst, BA and H₂O₂ with pH value, catalyst dosage, BA and H₂O₂ concentrations of x (3, 5, 6.8 or 9), 3.33 mg/mL, 0.33 mol/L and y (0.33, 0.66 or 0.99) mol/L, respectively, was stirred and heated to 70 °C in a water bath. After reaction for 90 min, a certain amount of *n*-propanol was added into the solution and then the products were detected by Shimadzu Kyoto HPLC with an ODS-2 column (4.6 × 250 mm, 5 μm) and a UV detector (254 nm). Hydroxyl radical was quantified indirectly and approximately by the conversion of benzoic acid.

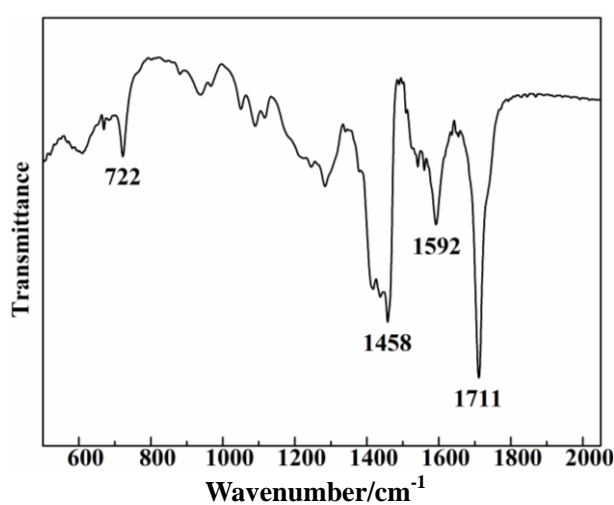


Fig. S1 FT-IR spectrum of ferric oleate. The peaks at 722, 1458, 1592, and 1711 cm⁻¹ correspond to long-alkyl side chain of the catalyst, symmetric stretching vibration of metal carboxylates, antisymmetric stretching vibration of metal carboxylates, and asymmetrical stretching vibration of unidentate carboxylate [4].

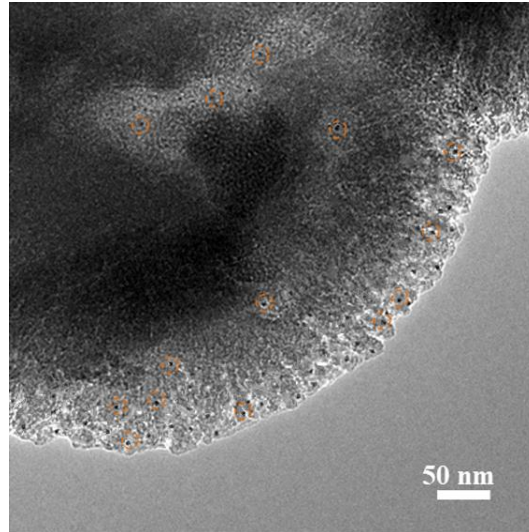


Fig. S2 TEM image of Fe@MZ5.

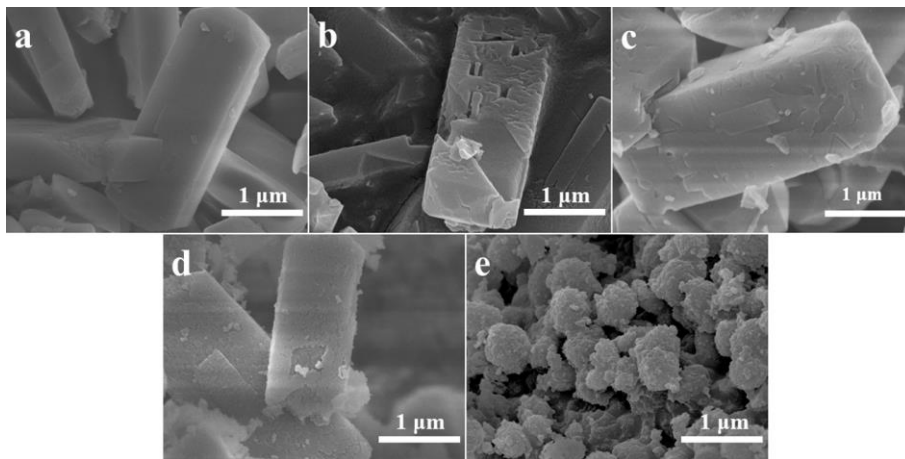


Fig. S3 SEM images of Fe/Z5 (a), MFe/Z5 (b), MFe/Z5@Z5 (c), MFe/Z5@M41 (d) and Fe@MZ5 (e).

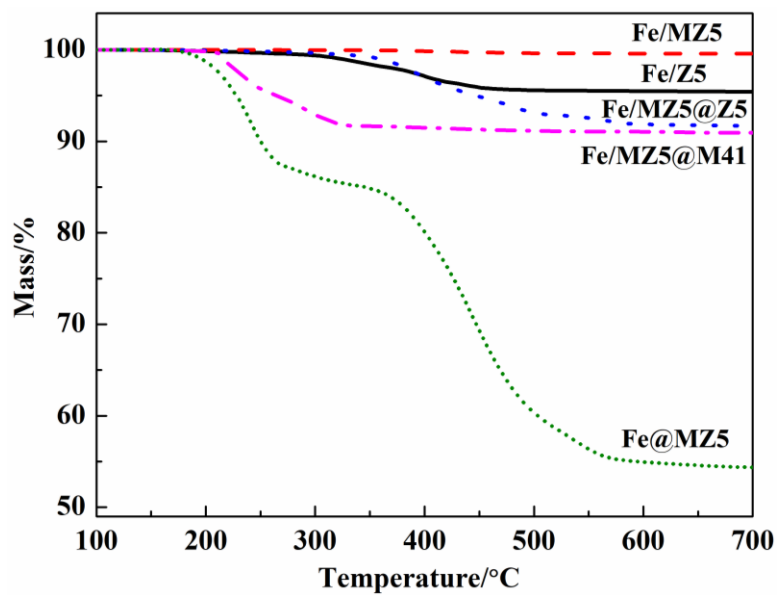


Fig. S4 TG curves of the as-prepared catalysts.

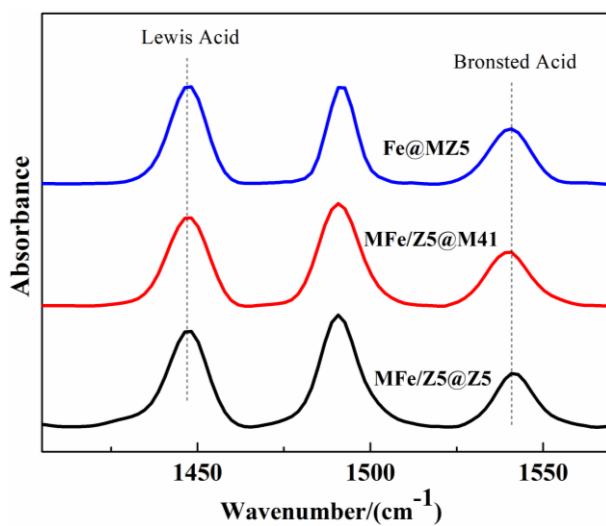


Fig. S5 Py-IR spectra of catalysts at 150 °C.

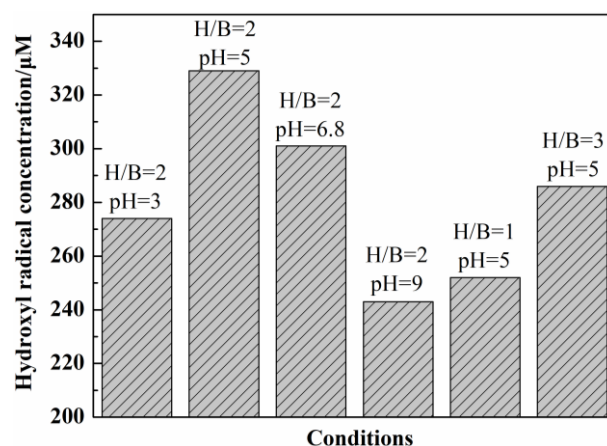


Fig. S6 The concentration of generated $\bullet\text{OH}$ with different pH values and H_2O_2 /benzoic acid molar ratios (H/B). Conditions: reaction mixture 30 mL, catalyst amount 3.33 mg/mL, benzoic acid 0.33 mol/L, reaction temperature 70 °C, and reaction time 90 min.

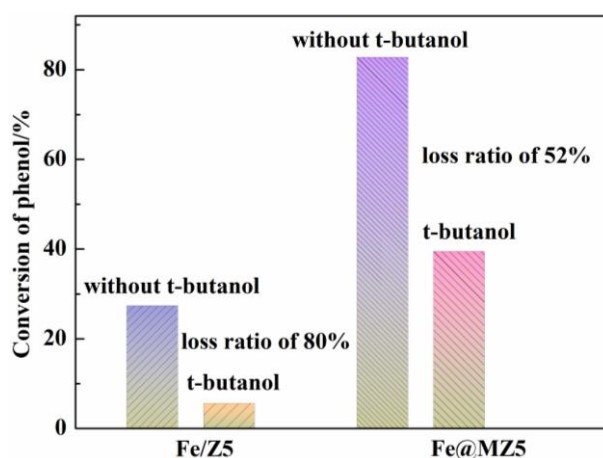


Fig. S7 Effect of radical scavenger on phenol hydroxylation. Conditions: reaction mixture 30 mL, pH = 5, catalyst amount 100 mg, H_2O_2 /phenol molar ratio 2:1, reaction temperature 70 °C, reaction time 90 min, and t-butanol/ H_2O_2 molar ratio 10:1.

Table S1 Catalytic performance of phenol hydroxylation over Fe-based catalysts

Samples	Tem. /°C	Time /min	Catalyst ^a /mg	H/P ^b	pH	x(Ph) /%	Selectivities/%				Ref.
							CAT	HQ	Others	Y _{HQ} ^c	
Fe@MZ5	70	90	100	2:1	5	82.8	45.6	49.2	5.2	40.7	/
Fe@MZ5-3 ^d	70	90	100	2:1	5	80.9	45.7	48.8	5.5	39.5	/
Fe@MZ5-5 ^e	70	90	100	2:1	5	80.6	46.8	47.9	5.3	38.6	/
3Fe/Al-AMS	30	240	660	2:1	7	46.6	49.9	33.3	16.8	15.5	5
Fe-MCM-41/ZSM-5	70	120	150	1:1	7	46.2	52.7	37.4	0	17.3	6
Fe(phon) ₃ ²⁺	55	360	94	1:1	7	20.0	70.0	29.0	1.00	5.8	7
Fe-MCM-41(NPS)	60	180	150	3:1	/	24.0	55.0	45.0	/	10.8	8
Fe-MCM-41	70	10	60	1:1	/	60.0	68.0	32.0	/	19.2	9
Fe ²⁺ /Fe ³⁺ -ZSM-5	70	90	16.1	2:1	/	80.0	71.0	29.0	/	23.2	10
Complex 1	20	30	3.75	1:3	/	20.5	60.0	23.1	/	4.7	11
5Fe-Si	25	90	45	1:1	/	47.3	48.3	48.3	1.60	22.8	12
Fe-ZSM-5	50	240	100	1:1	/	40.1	53.4	33.4	/	13.4	13
20/CuMgFe	50	30	15	1:1	/	69.7	49.6	21.6	/	15.0	14
5Fe-MA	25	120	220	2:1	/	23.4	60.1	33.1	6.8	7.75	15
FAM-MS	25	120	50	1:3	/	25.3	58.6	36.7	4.7	9.28	16
0.03Fe/ γ -Al ₂ O ₃ -1	80	240	50	1:1.5	/	58.7	/	/	3.8	/	17
Fe-BTC	25	75	50	1:1	/	52.2	44.3	35.0	/	18.3	18

^a Catalyst mass in 30 mL reaction mixture. ^b H₂O₂/phenol molar ratio. ^c HQ yield. ^d Catalyst reused for three times. ^e Catalyst reused for five times.

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