

SUPPORTING INFORMATION

Metal doping of porous materials via post-synthetic mechano-chemical approach: a general route to design low-loaded versatile catalytic systems

M. Dolores Marquez-Medina,^a Rafael Luque^{*a,b} Alina M. Balu^a, Francisco Ivars-Barceló^{c,d} and Carolina Carrillo-Carrión^{*a}

^a Department of Organic Chemistry, University of Córdoba, Campus de Rabanales, Edificio Marie Curie, Ctra Nnal IV-A Km. 396, E-14014, Cordoba, (Spain).

^b Peoples Friendship University of Russia (RUDN University), 6 Miklukho Maklaya str., 117198, Moscow, Russia

^c Dept. Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Paseo Senda del Rey, 9, 28040 Madrid, Spain

^d Instituto de Catálisis y Petroleoquímica (ICP-CSIC), C/Marie Curie, 2, Cantoblanco, 28049 Madrid, Spain

*Correspondence: Rafael Luque (q62alsor@uco.es); Carolina Carrillo-Carrión (carrillocarrion.carolina@gmail.com)

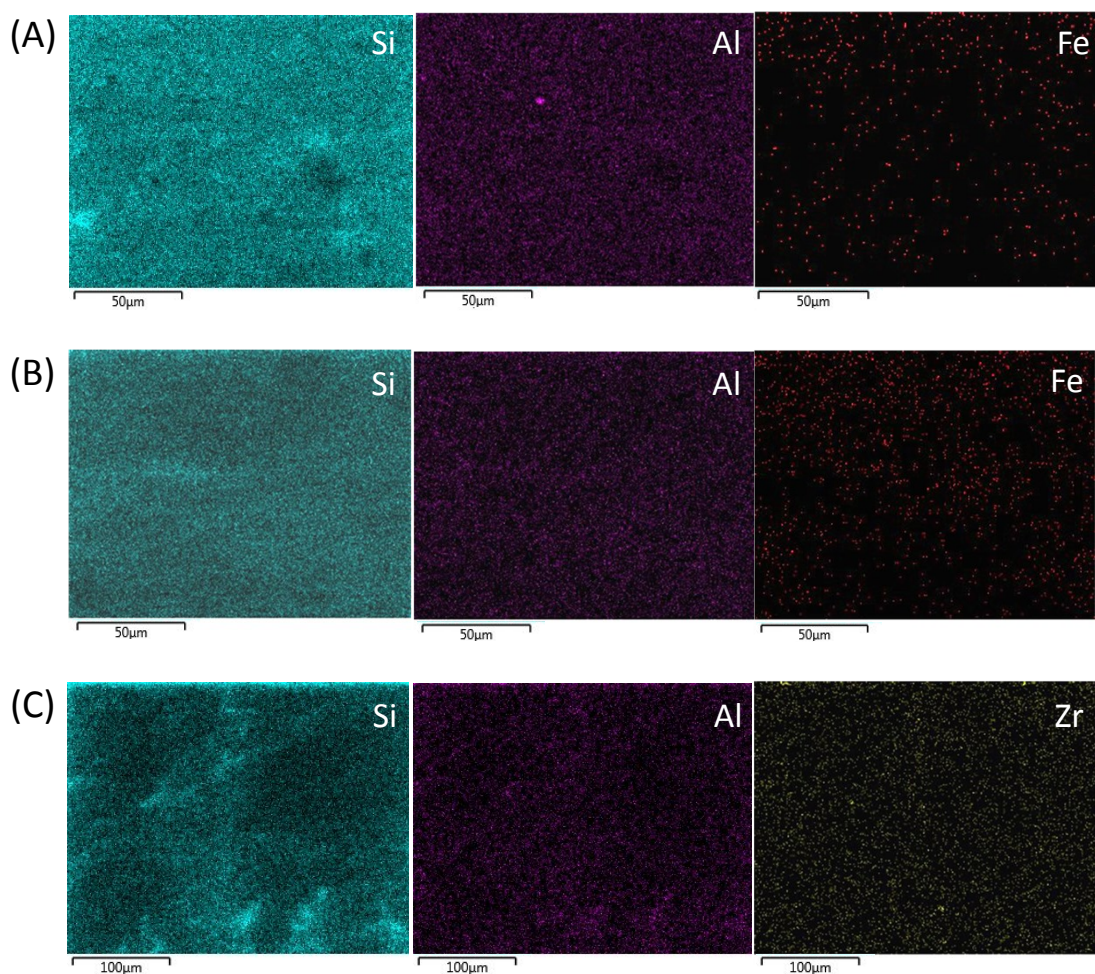


Figure S1. EDX elemental mapping profiles of (A) SBA15-Fe, (B) SBA15-FeMOF53, and (C) SBA-ZrMOF. Color code: Si (blue), Al (purple), Fe (red), Zr (yellow).

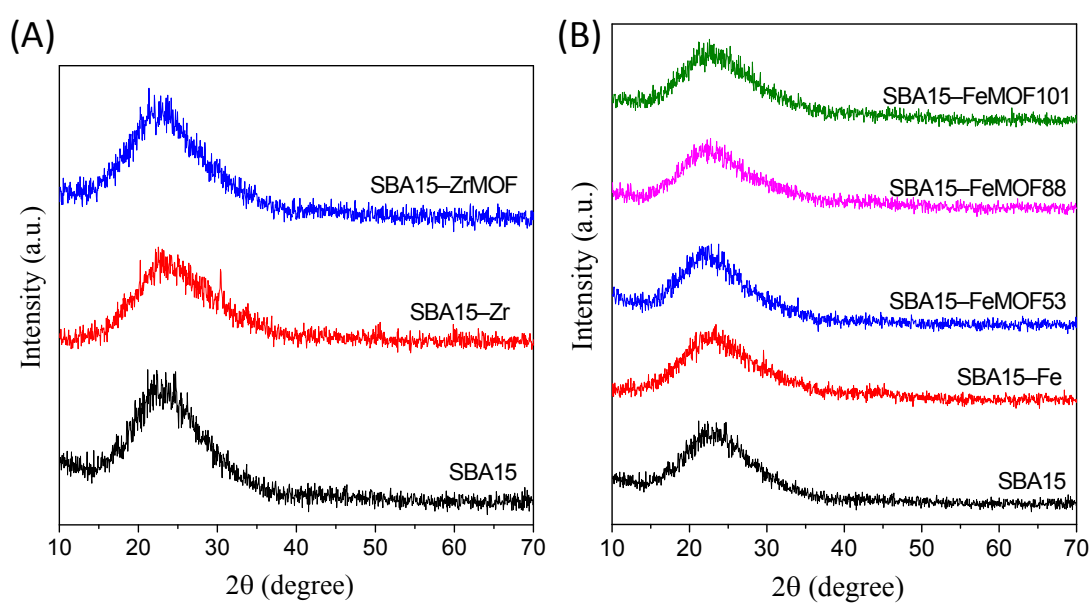


Figure S2. XDR spectra of the different (A) Zr-doped and (B) Fe-doped materials.

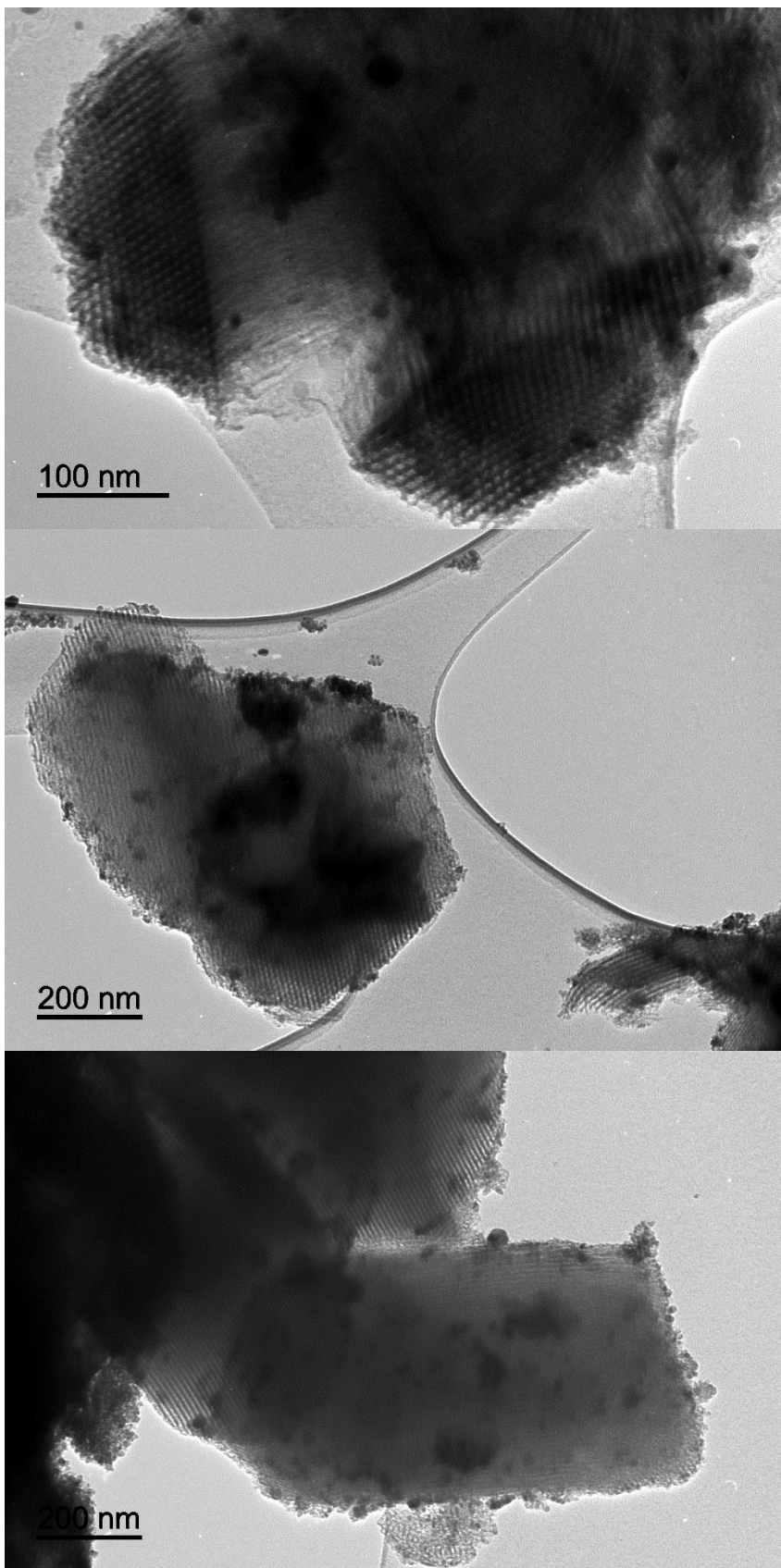


Figure S3. TEM images of SBA-MOF53 (top), SBA-MOF88 (middle), SBA-FeMOF101 (bottom)

Table S1. SEM/EDX and ICP-MS analyses of materials before and after their use for catalyzing the oxidation of isoeugenol to vanillin under optimized conditions. Elemental composition expressed in weight percentage (%).

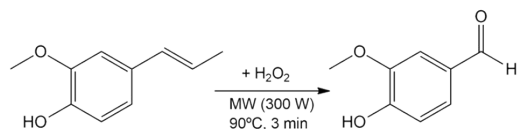
Catalyst	SEM/EDX (%)				ICP-MS (%)			
	Si	Al	Zr	Fe	Si	Al	Zr	Fe
SBA15-ZrMOF before	97.1	2.3	0.7	-	78.7	4.5	0.85	-
SBA15-ZrMOF after	96.9	2.6	0.6	-	72.6	4.3	0.82	-
SBA-FeMOF101 before	97.3	2.5	-	0.5	78.0	3.3	-	0.80
SBA-FeMOF101 after	97.3	2.4	-	0.5	76.7	3.5	-	0.82

Table S2. Catalytic performance of the different studied materials towards the oxidation of benzyl alcohol to benzaldehyde.^a

Catalyst	Conversion (% mol)	Selectivity (% mol)
Blank	9.8	100
SBA15	10.0	100
MCM41	9.4	100
SBA15-Zr	39.3	100
SBA15-ZrMOF	29.6	100
MCM41-ZrMOF	33.2	100
SBA15-Fe	39.8	100
SBA15-FeMOF53	25.1	100
SBA15-FeMOF88	24.9	100
SBA15-FeMOF101	45.8	100
MCM41-Fe	41.1	100
MCM41-FeMOF53	39.4	100
SBA15-Al	18.0	100
SBA15-AlMOF	20.0	100

^aReaction conditions: 1.9 mmol (0.2 mL) benzyl alcohol, 2.9 mmol (0.3 mL) of 30% (w/w) H₂O₂ in water, 0.175 mol % catalyst (25 mg catalyst), and 2 mL of acetonitrile microwaved at 300 W, 90 °C for 3 min.

Table S3. Catalytic performance of the different studied materials towards the oxidation of isoeugenol to vanillin.^a



Catalyst	Conversion (% mol)	Selectivity (% mol)
Blank	7.3	2.2
SBA15	8.2	2.6
MCM41	14.7	7.7
SBA15-Zr	59.7	42.6
SBA15-ZrMOF	38.0	21.6
MCM41-ZrMOF	24.7	20.9
SBA15-Fe	52.6	47.9
SBA15-FeMOF53	42.9	43.7
SBA15-FeMOF88	38.9	40.1
SBA15-FeMOF101	60.9	43.9
MCM41-Fe	31.9	22.8
MCM41-FeMOF53	28.7	20.9
SBA15-Al	25.0	16.0
SBA15-AlMOF	27.0	27.0

^aReaction conditions: 1.2 mmol (0.2 mL) isoeugenol, 2.9 mmol (0.3 mL) of 30% (w/w) H₂O₂ in water, 0.175 mol % catalyst (25 mg catalyst), and 2 mL of acetonitrile microwaved at 300 W, 90 °C for 3 min.