Development of basicity in mesoporous silicas and metallosilicates

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SUPPLEMENTARY INFORMATIONS

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S1. Synthesis of MCF and SBA-15 supports [1]

The synthesis of MCF was performed as follows. At the beginning, Pluronic P123 (16 g) (Aldrich) was dissolved in 600 cm^3 of 0.7 M HCl (POCH) solution at 35 – 40 ^oC in a polypropylene bottle. Next 1,3,5-trimethylbenzene – TMB (8 g) (Aldrich) and ammonium fluoride (0.1868 g) (Aldrich) were added together under vigorous stirring. After 1 h of gel mixing, TEOS (34.108 g) (Aldrich) was added. The obtained solution was then stirred at 35 – 40 ^oC for 20 h and heated in an oven at 100 ^oC under static conditions for 24 h. The obtained powder was filtered, washed with distilled water (1200 cm^3) and dried at room temperature (RT). The template was removed by calcination at 500 ^oC K for 8 h under static conditions.

The synthesis procedure of SBA-15 was almost the same as for MCF sample. The only difference was no addition of 1,3,5-trimethylbenzene and ammonium fluoride to the synthesis gel of silica. TEOS was added immediately after Pluronic P123 dissolution in HCl solution.

S2. Functionalization of supports with imidazole [1]

The modification of silicas SBA-15 and MCF and metallosilicates with (3-chloropropyl)trimethoxysilane (ClPTMS) was made according to [2]. The 5.5 g of solid, first dried overnight at 100 ^oC, was put into the flask. Then the silica was covered by 70 - 80 cm^3 of toluene and 5.5 cm^3 of ClPTMS was added. The obtained solution was stirred slowly for 15 min at room temperature and then heated at 110 ^oC for 24 h. Next, the obtained product was filtered, washed by 70 cm^3 of toluene and dried at 100 ^oC.

The anchoring of imidazole on MCF-Cl, SBA-15-Cl, Nb/MCF-Cl, Nb/SBA-15-Cl, Ce/MCF-Cl and Ce/SBA-15-Cl was made according to [3]. The 1.5 g of imidazole and 3 cm^3 of triethylamine were immersed to the solution containing 2 g of ClPTMS modified sample and 30 cm^3 of toluene. The mixture was then heated at 110 ^oC for 48 h. The solid sample was then

filtered, washed with 50 cm^3 of dichloromethane and 50 cm^3 of methanol and dried at 100 ^oC for 24 h.

S3. Characterization of catalysts [1,4]

N_2 adsorption/desorption isotherms were obtained using Quantachrome Instruments Autosorb IQ2. At the beginning materials were outgassed under vacuum at 150 ^oC (organosilanes modified samples) or 350 ^oC (MCF, SBA-15, Nb/MCF, Nb/SBA-15, Ce/MCF and Ce/SBA-15). The surface area was calculated using the BET method while the pore volume and diameter according to the Broekhoff-de Boer method with the Frenkel-Halsey-Hills approximation.[5]

XRD patterns were recorded at RT on a Bruker AXS D8 Advance apparatus using CuKα radiation (γ = 0.154 nm), with a step of 0.02 ^{o} in the small-angle and 0.05^o in the wide-angle range.

The elemental analysis of samples modified with imidazole, triazole and 1,2,3-triazol-4-ylmethanamine were carried out with Elemental Analyser Vario EL III by detection the wt. % of nitrogen content.

Infrared spectra were recorded using a Bruker Vector 22 FTIR spectrometer with an *in situ* vacuum cell (homemade). Before the measurement, the MCF, Ce/MCF or Nb/MCF were pressed under low pressure into a thin wafer of ca. 5-10 mg cm^{-2} and placed inside the cell. Solids were then activated before pyridine adsorption at 350 ^oC for 2 h. After this step the pyridine was admitted at 150 ^oC. After saturation with pyridine, the samples were degassed at 150 ^oC, 200 ^oC, 250 ^oC and 300 ^oC in vacuum for 30 min at each temperature. The spectrum without adsorbed probe molecule ("background spectrum" - after samples activation) was subtracted from all recorded spectra. The number of Lewis acidic sites was calculated assuming the extinction coefficient ε for a band at ca.1440 cm^{-1} = 2.22 μmol^{-1} cm.[7]

The DTA/TG analysis were performed using SETARAM SETSYS-12 equipment in air atmosphere with the temperature ramp 5 ^{o}C/min from 20 ^{o}C to 1000 ^{o}C.

UV–Vis spectra were recorded using a Varian-Cary 300 Scan UV–Visible Spectrophotometer. Catalysts dried overnight at 100 ^{o}C, were put into the cell equipped with a quartz window. The spectra were recorded in the range between 800 - 190 nm. Spectralon was used as a reference material.

S4. Knoevenagel condensations [6]

In a typical experiment, an equimolecular solution of benzaldehyde and the corresponding methylenic compound (ethyl cyanoacetate, ethyl acetoacetate and diethyl malonate) were introduced together in a quartz reactor under helium atmosphere and without any solvent. When the reactants mixture had reached the desired temperature (90, 120 and 150 ^{o}C, respectively, depending on the methylene compound used) 1, 2 or 10 wt.% of the catalyst (preliminary dried overnight at 373 K) was put into the mixture under continuous stirring. The samples for GC analysis (Agilent 6890 GC-FID) were assembled at a definite time interval to follow the reaction progress.

References

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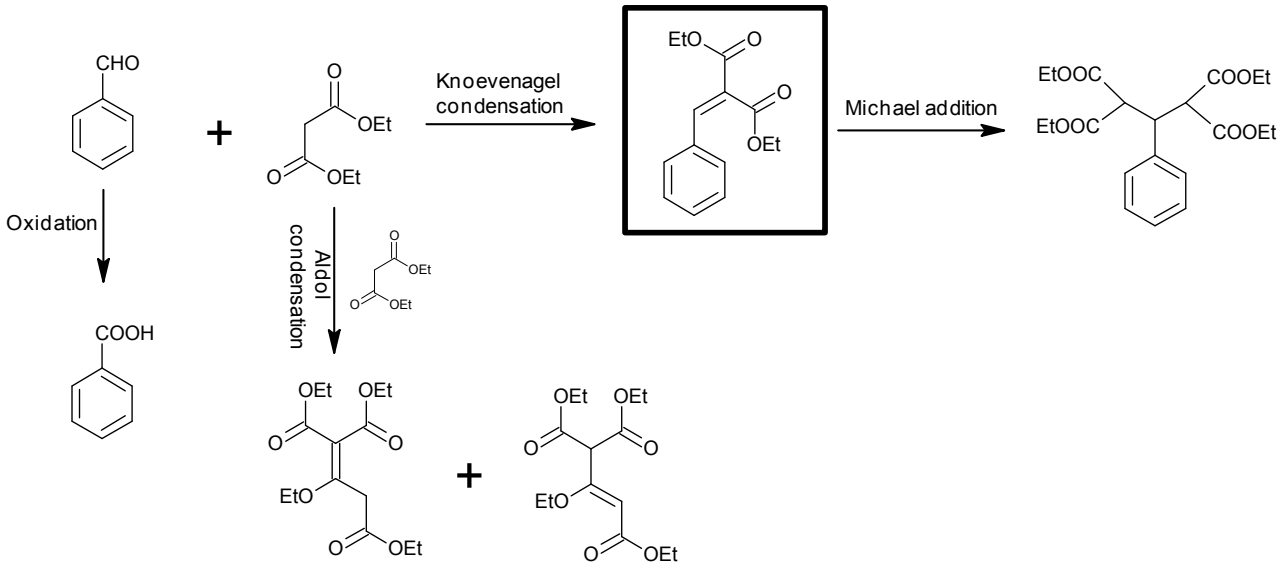
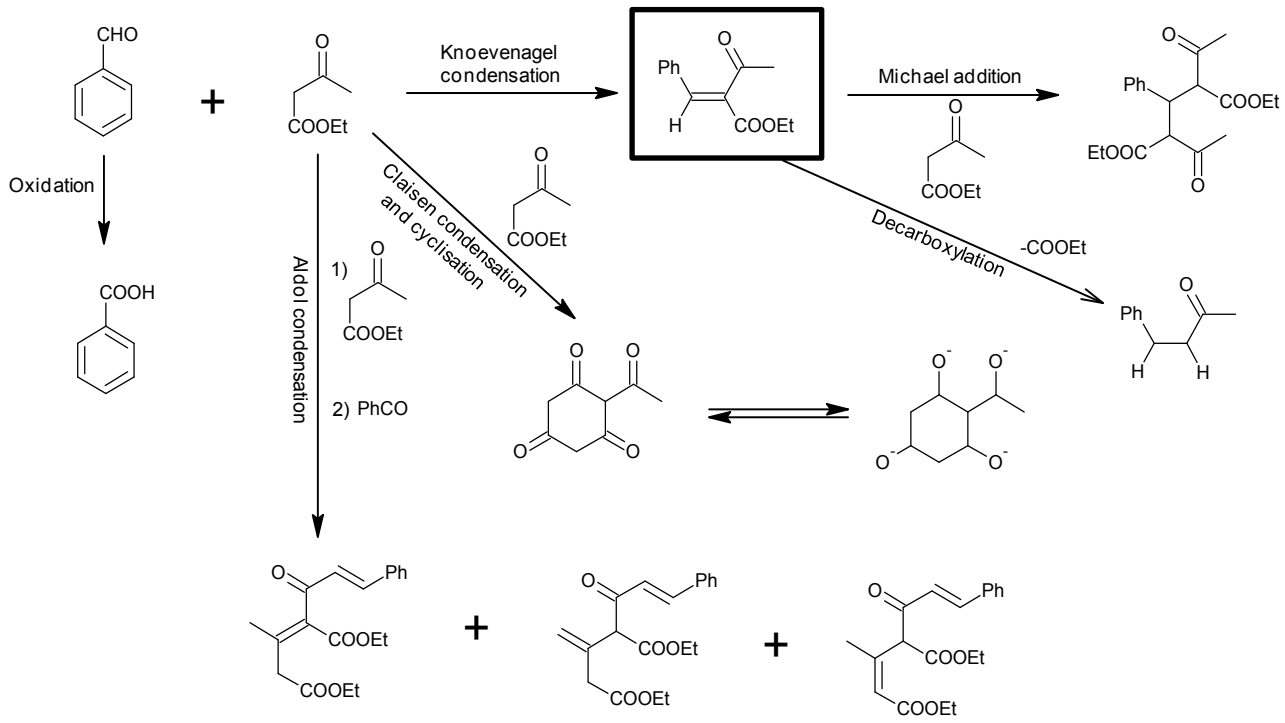


Scheme S1. Possible products (main and others) obtained during the Knoevenagel condensation between benzaldehyde and diethyl malonate (pKa = 13.3).



Scheme S2. Possible products (main and others) in the Knoevenagel condensation between benzaldehyde and ethyl acetoacetate (pKa = 10.7).

Table S1. Texture/structure parameters (from nitrogen adsorption/desorption isotherms).

Catalyst	S $[m^2g^{-1}]$	S_{micro} $[m^2g^{-1}]$	V_{cell} $[cm^3g^{-1}]$	$V_{mesop.}$ $[cm^3g^{-1}]$	$V_{microp.}$ $[cm^3g^{-1}]$	d_{cell} [nm]	d_{window} [nm]	$D_{mesop.}$ [nm]
SBA-15	900	200	-	1.09	0.08	-	-	7.8
SBA-15-Im	500	traces	-	0.71	-	-	-	6.6
MCF	760	-	3.12	-	-	37.3	17.9	-
MCF-Im	480	-	1.63	-	-	24.3	8.8	-
MCF-Tr	500	-	1.74	-	-	26.5	9.8	
Ce/SBA-15-103	720	140	-	0.91	0.05	-	-	7.5
Ce/SBA-15-19	650	130	-	0.82	0.05	-	-	6.6
Ce/SBA-15-103-Im	400	0	-	0.60	0	-	-	6.8
Ce/SBA-15-19-Im	370	-	-	0.56	-	-	-	6.5
Ce/SBA-15-103-Tr	460	-	-	0.66	-	-	-	6.5
Ce/MCF-103	710		2.85	-	-	36.5	26.9	-
Ce/MCF-19	550	-	2.19	-	-	36.0	12.9	-
Ce/MCF-103-Im	330	-	1.58	-	-	35.9	11.9	-
Ce/MCF-19-Im	370	-	1.34	-	-	33.0	11.4	-
Ce/MCF-103-Tr	350	-	1.61	-	-	35.2	11.8	-
Nb/SBA-15-103	770	160	-	0.86	0.06	-	-	7.5
Nb/SBA-15-19	760	140	-	0.86	0.05	-	-	7.3
Nb/SBA-15-103-Im	350	0	-	0.50	0	-	-	6.7
Nb/SBA-15-19-Im	337	0	-	0.47	0	-	-	6.7
Nb/MCF-103	590	-	2.40	-	-	34.9	18.1	-
Nb/MCF-19	530	-	2.29	-	-	36.0	15.4	-
Nb/MCF-103-Im	330	-	1.56	-	-	34.5	15.1	-
Nb/MCF-19-Im	290	-	1.44	-	-	32.8	16.0	-
Nb/MCF-103-Tr	350	-	1.61	-	-	34.7	15.0	-
SBA-15-Tr-NH_2	300	-	-	0.6	-	-	-	6.6
NbSBA-15-Tr-NH_2	250	-	-	0.5	-	-	-	6.5
MCF-Tr-NH_2	290	-	1.6	-	-	32.1	19.5	-
NbMCF-Tr-NH_2	270	-	1.5	-	-	33.1	20.3	-

Table. S2 Conversion (%) of benzaldehyde in the condensation with ethyl cyanoacetate (pKa = 9) after different reaction time.

Catalyst	5 min	15 min	30min	60 min	120 min	180 min	240 min
SBA-15-Im	6.5	18.6	30.9	61.4	66.9	77.7	81.9
MCF-Im	10.2	22.7	35.8	49.6	63.7	74.6	79.0
Ce/SBA-15-Im-103	4.4	12.2	22.5	36.8	55.4	63.6	70.3
Ce/SBA-15-Im19	4.8	13.0	25.1	39.0	53.8	64.2	68.2
Ce/MCF-Im-103	9.5	18.2	30.1	47.4	62.6	72.8	77.2
Ce/MCF-Im-19	6.0	14.1	25.6	40.6	56.5	66.4	72.7
Nb/SBA-15-Im-103	6.0	14.4	25.3	40.0	57.3	67.4	73.9
Nb/SBA-15-Im-19	10.8	26.9	41.2	63.6	79.7	84.7	86.7
Nb/MCF-Im-103	4.9	12.2	23.9	39.7	58.7	68.3	75.2
Nb/MCF-Im-19	8.8	19.1	32.6	50.2	68.2	77.2	82.8
MCF-Tr	1.9	2.1	6.5	9.6	15.9	19.8	24.6
Ce/MCF-Tr-103	1.7	3.1	6.1	10.9	17.0	24.3	30.3
Ce/SBA-15-Tr-103	2.7	4.5	7.3	16.2	24.0	33.0	33.3
Nb/MCF-Tr-103	2.8	5.0	8.5	13.9	22.3	29.5	34.4
SBA-15-Tr-NH_2	0.3	4.8	8.1	25.5	45.4	51.1	56.0
NbSBA-15-Tr-NH_2	0.1	2.9	4.3	13.7	25.7	33.0	34.9
MCF-Tr-NH_2	7.9	13.1	21.7	29.0	37.4	44.7	49.0
NbMCF-Tr-NH_2	6.9	6.1	15.7	22.4	32.9	40.8	41.7

Reaction conditions: benzaldehyde (14 mmol, 1.48 g); ethyl cyanoacetate (14 mmol, 1.58 g) pKa = 9; 1 wt.% of catalyst (0.031 g), temp. 90^{o}C

Table S3. Conversion (%) of benzaldehyde in the condensation with ethyl acetoacetate (pKa = 10.7) and selectivity after different reaction time.

Catalyst	5 min			15 min			30 min			60 min			120 min			180 min			240 min		
	Conv., %	Select., %		Conv., %	Select., %		Conv., %	Select., %		Conv., %	Select., %		Conv., %	Select., %		Conv., %	Select., %		Conv., %	Select., %	
		main	others		main	others		main	others		main	others		main	others		main	others		main	others
Nb/MCF-Im-103	2.9	74.5	25.5	5.1	75.5	24.5	8.5	79.2	20.8	15.2	88.3	11.7	27.8	88.0	12.0	46.0	84.4	15.6	54.0	82.1	17.9
Nb/MCF-Im-19	0	0	0	0	0	0	5.0	84.7	15.3	8.7	91.0	9	15.8	93.4	6.6	22.9	93.1	6.9	30.2	92.1	7.9
Nb/SBA-15-Im-103	2.0	57.1	42.9	2.9	68.1	31.9	5.4	81.8	11.2	9.9	88.3	11.7	16.6	91.2	8.8	23.4	92.0	8.0	30.0	90.1	9.9
Nb/SBA-15-Im-19	3.1	57.5	42.5	4.1	76.5	23.5	6.8	82.7	17.3	11.5	88.8	11.2	18.3	90.1	9.9	27.9	90.0	10.0	34.4	89.3	10.7
Ce/MCF-Im-103	9.0	69.1	30.9	7.7	89.8	10.2	12.4	91.2	8.8	20.8	91.2	8.8	33.3	81.4	18.6	47.9	78.0	22.0	60.2	75.2	24.8
Ce/MCF-Im-19	2.3	77.8	22.2	5.0	88.0	12.0	8.7	89.4	10.6	13.8	90.0	10.0	24.6	92.5	7.5	32.8	93.1	6.9	40.0	92.2	7.8
Ce/SBA-15-Im-103	4.0	64.5	35.5	5.7	73.9	26.1	6.8	77.4	22.6	10.5	86.3	16.7	18.9	88.5	11.5	27.0	90.4	9.6	33.6	86.2	13.8
Ce/SBA-15-Im-19	2.6	100	0	5.5	80.2	29.8	7.3	83.4	16.6	12.4	82.9	13.1	19.7	81.1	18.9	27.4	80.2	19.8	35.3	82.1	17.9
MCF-Im	0	0	0	4.5	50.9	49.1	6.2	64.2	35.8	7.9	72.5	27.5	15.4	83.4	16.6	23.4	82.9	17.1	30.8	84.4	15.6
SBA-15-Im	2.3	17.0	83.0	5.4	38.7	61.3	7.9	56.7	43.3	12.6	71.4	28.6	20.9	77.4	22.6	29.2	79.5	20.5	37.0	80.8	19.2
Nb/MCF-103	1.6	25.5	74.5	2.5	30.0	70.0	4.2	57.7	42.3	5.8	58.1	41.9	9.4	69.0	31.0	14.2	75.5	24.5	21.6	74.7	25.3
Nb/MCF-19	1.9	36.0	64.0	3.0	47.4	52.6	4.8	61.8	38.2	6.9	61.7	38.3	13.3	66.7	33.3	18.4	67.7	32.3	28.7	71.0	29.0
Ce/MCF-103	3.8	49.6	50.4	6.8	67.0	33.0	11.7	73.2	26.8	17.7	79.1	20.9	28.6	78.1	21.9	40.7	76.0	24.0	53.1	73.3	26.7
Ce/MCF-19	3.4	54.1	45.9	3.5	46.4	53.6	8.4	74.9	25.1	9.1	78.0	22.0	17.5	76.4	23.6	27.4	77.0	23.0	35.1	78.1	21.9

Reaction conditions: Benzaldehyde (9 mmol, 0.954 g); ethyl acetoacetate (9 mmol, 1.17 g) pKa = 10.7; 2 wt% of catalyst (0.043 g), temp. 120^{o}C

Table S4. Conversion (%) of benzaldehyde in the condensation with diethyl malonate (pKa = 13.3) and selectivity after different reaction time.

Catalyst	Reaction time: 3h			Reaction time: 5h		
	Conv., %	Select., %		Conv., %	Select., %	
		main	others		main	others
Ce/MCF-Im-103	24.7	56.1	43.9	35.7	57.1	42.9
Ce/MCF-Im-19	32.4	64.2	35.8	51.7	64.7	35.3
Nb/MCF-Im-103	36.6	57.7	42.3	38.7	53.0	47.0
Nb/MCF-Im-19	27.1	61.7	38.3	41.6	61.2	38.8
Ce/SBA-15-Im-103	22.7	43.8	56.2	36.9	47.4	52.6
Ce/SBA-15-Im-19	33.3	50.3	49.7	52.9	51.0	49.0
Nb/SBA-15-Im-103	25.4	67.4	32.6	40.8	65.9	34.1
Nb/SBA-15-Im-19	24.9	54.7	45.3	38.5	55.7	44.3

Reaction conditions: Benzaldehyde (7 mmol, 0.742 g); diethyl malonate (7 mmol, 1.13 g) pKa = 13.3; 10 wt% of catalyst (0.187 g), temp. 150^{o}C

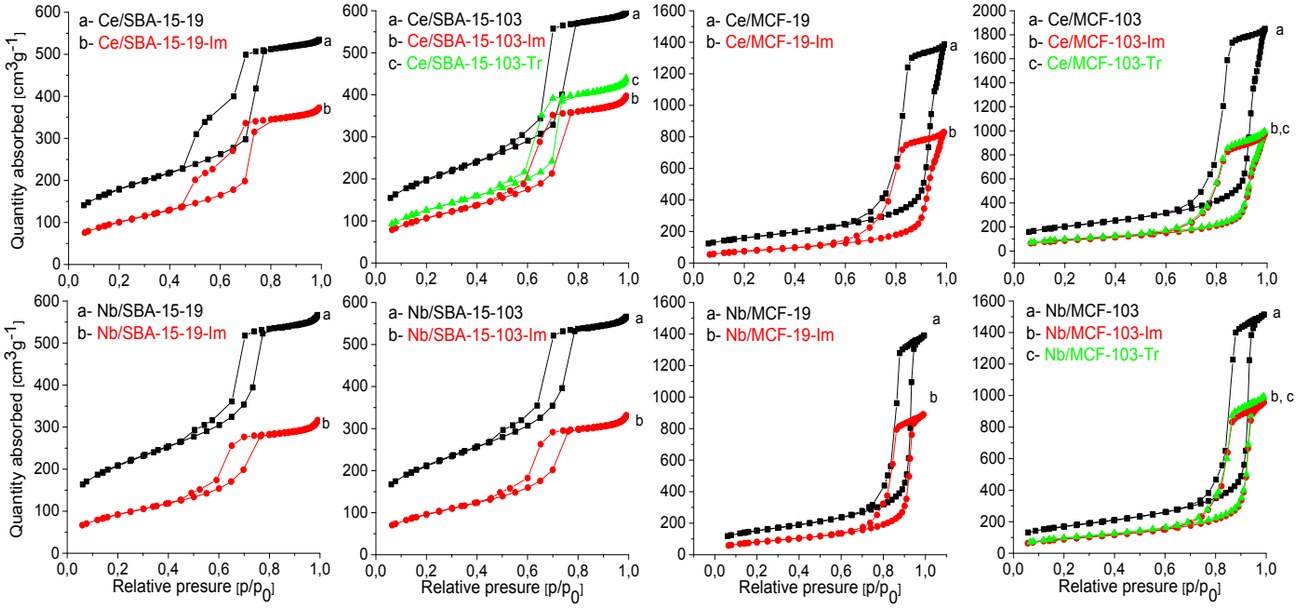


Figure S1. Nitrogen adsorption isotherms of metal doped catalysts before and after modification with imidazole and triazole.

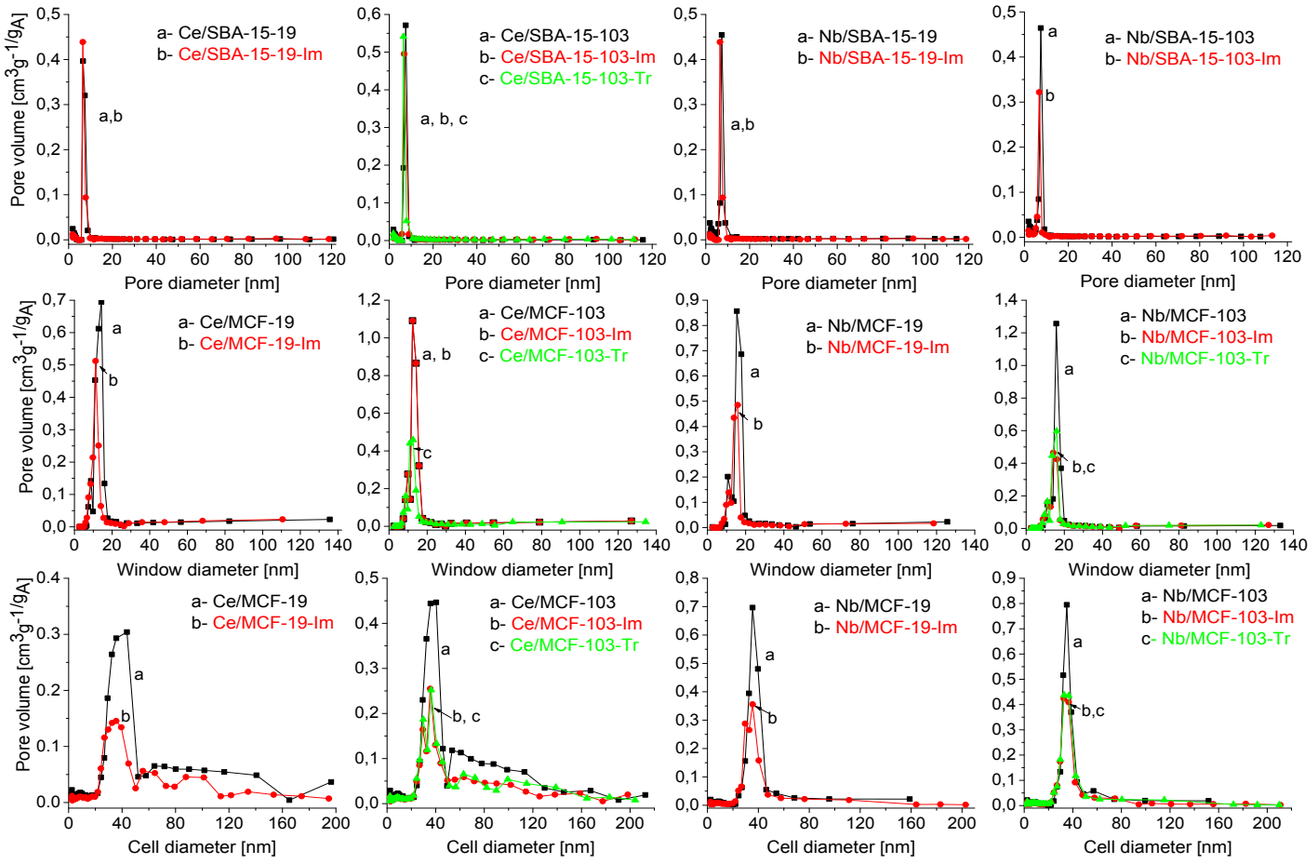


Figure S2. Pore size distribution (PSD) in metal doped catalysts before and after modification with imidazole and triazole.

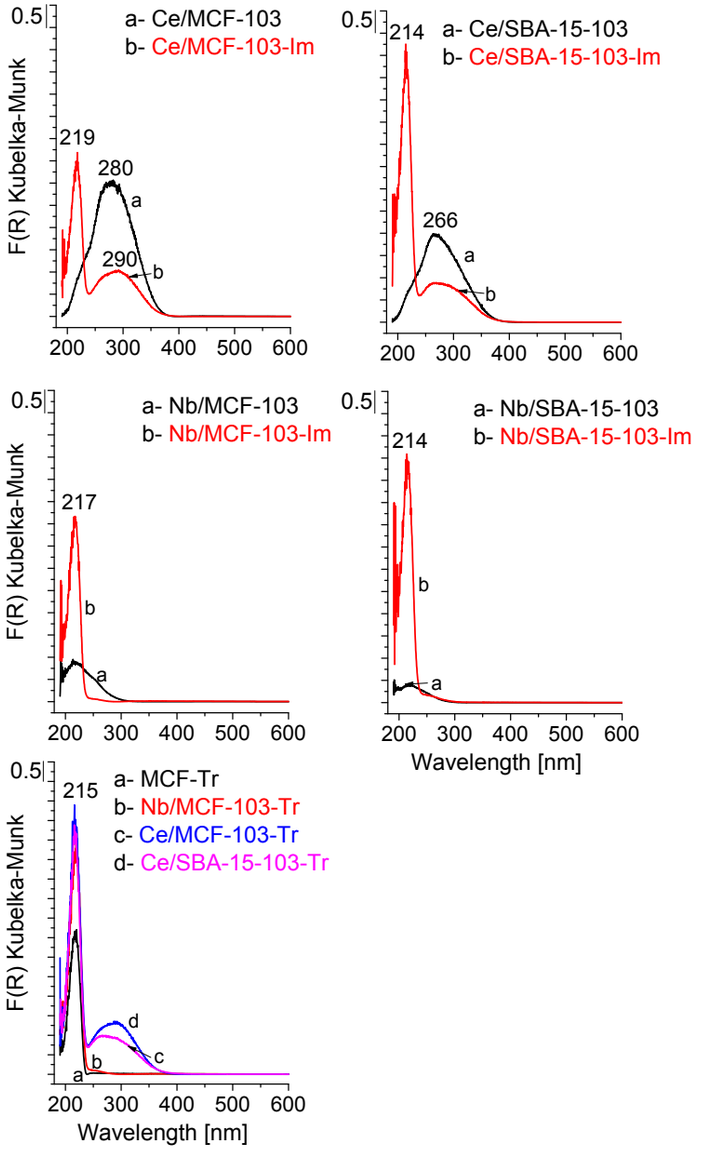


Figure S3. UV-Vis DR spectra of the samples modified with imidazole and triazole.

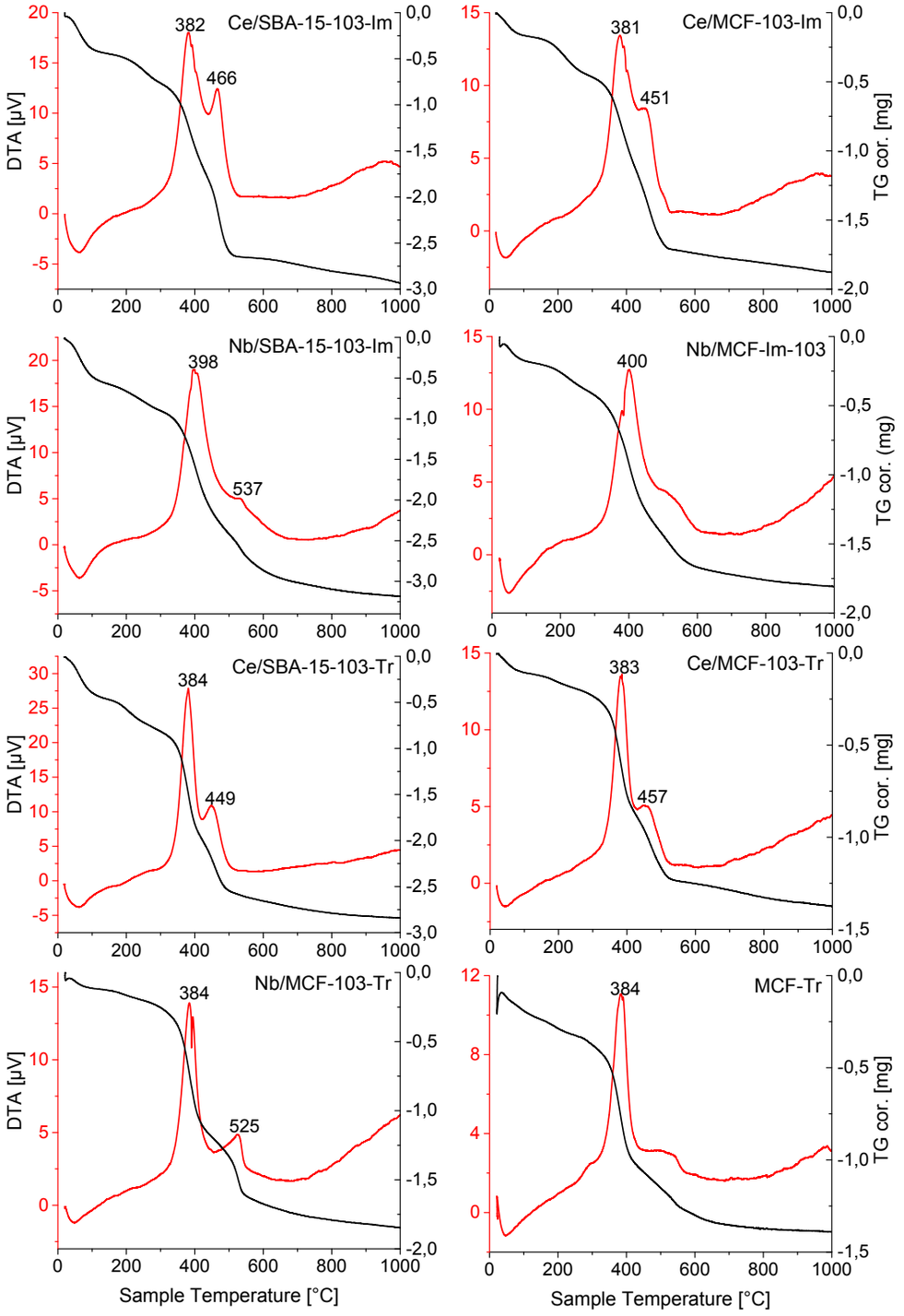


Figure S4. Thermogravimetric study of imidazole and triazole containing samples (modifiers loaded on the supports possessing lower amount of metal (Si/metal = 103).