

## Supporting information

### Double metal cyanides as heterogeneous Lewis acid catalysts for nitrile synthesis via acid-nitrile exchange reactions

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## Experimental

### *Synthesis of DMCs*

The M'-Co DMCs were synthesized following previously reported procedures [1,2]. In short, 15 ml of a 0.1 M aqueous solution of  $K_3[Co(CN)_6]$  was added dropwise, under continuous stirring, to 150 ml of a 0.1 M aqueous solution of a  $M'Cl_2 \cdot xH_2O$  salt ( $FeCl_2 \cdot 4H_2O$ ,  $CoCl_2$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CuCl_2$  or  $ZnCl_2$ ) containing 1.5 mmol of poly(tetramethylene ether) glycol (PTMEG,  $M_n \sim 1000$ ). After both solutions were mixed, 37.5 ml of *tert*-butanol were added and the mixture was stirred for 3 h at room temperature. The precipitate was recovered by centrifugation, washed three times with 50 ml of a 1:1 mixture of water : *tert*-butanol and dried at 60 °C overnight. The solids Fe-Co, Co-Co, Ni-Co, Cu-Co and Zn-Co DMC were obtained using the respective M' sources.

### *Preparation of Zr-BEA*

Lewis acidic Zr-zeolite  $\beta$  was prepared following a procedure reported by Wolf et al. [3]. In short, a commercial  $\beta$  zeolite (CP811BL25, Si/Al = 12.5) was first dealuminated with a  $HNO_3$  solution (13 M, 100 °C, 20 h, 20 mL/g of zeolite) before being ion-exchanged (solid state) by grinding it with the appropriate amount of zirconium(IV)ethoxide. Finally, the solid was heated in an oven to 550 °C for 3 h (20 °C/min) to obtain the sample Zr-BEA (Zr wt.% = 10.1).

### *Characterization*

Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) analyses were used to determine the metal content of the catalysts using a Varian 720-ES equipped with a double-pass glass cyclonic spray chamber, a Sea Spray concentric glass nebulizer and a high solids torch. The digestion of the samples was

done following a previously reported procedure [4]. Powder X-ray diffraction (PXRD) patterns were collected over a 5-60° 2 $\theta$  range on a STOE Stadi MP diffractometer (in transmission mode) using an image plate detector and focusing Ge(111) monochromator (Cu $K_{\alpha 1}$  radiation,  $\lambda = 1.54060 \text{ \AA}$ ). Additional PXRD data for the sample Co-Co DMC were acquired on a Bruker-AXS D2 Phaser powder X-ray diffractometer (in Bragg–Brentano geometry), using  $\text{Co}_{K_{\alpha 1,2}} = 1.79026 \text{ \AA}$  and operated at 30 kV. The patterns were collected between 10 and 80° 2 $\theta$  using a step size of 0.051 and a scan speed of 1 s. The thermal stability of the DMCs was studied by high temperature PXRD and Thermogravimetric analysis (TGA). Variable temperature PXRD patterns were collected in an Anton Paar TTK 600 chamber on a Malvern PANalytical Empyrean diffractometer in reflection mode over a 10-50° 2 $\theta$  range, using a PIXcel3D solid state detector and Cu anode (Cu  $K_{\alpha 1}$ : 1.5406  $\text{\AA}$ ; Cu  $K_{\alpha 2}$ : 1.5444  $\text{\AA}$ ). A constant temperature was maintained during the PXRD measurements and a 5°C/min heating rate was applied between the different measurements. TGA measurements were carried out on a TGA Q500 of TA Instruments (10°C/min heating rate, compressed air atmosphere). N<sub>2</sub> physisorption isotherms were collected at -196°C on a Micromeritics 3Flex Surface Analyzer. The specific surface area ( $S_{\text{BET}}$ ) was determined using the BET method (0.05 – 0.3 p/p<sub>0</sub> range) and the specific external surface area ( $S_{\text{ext}}$ ) and micropore volume ( $V_{\text{micro}}$ ) were obtained using t-plot analysis. Before analyses the samples were after evacuated at 150°C for 16 h. FTIR spectra of KBr wafers (1 wt.% of sample) were collected on a Bruker IFS 66 v/S Vacuum FTIR spectrometer. The acid nature and acid site density were determined by pyridine adsorption followed by FTIR spectroscopy (Py-FTIR) using a Nicolet 6700 FTIR spectrometer. To this end, a self-supporting wafer (~10 mg/cm<sup>2</sup>) was placed in a cell under vacuum and activated at 250°C for 1 h. The cell was then cooled down and the probe molecule was adsorbed onto the wafer at 50°C until saturation (25 mbar). The physisorbed and excess pyridine were removed by evacuation for 30 min before reheating to 150°C to record the IR spectrum. The acid site density was calculated from the areas of the absorption bands around 1450 cm<sup>-1</sup>, which correspond to pyridine coordinated to Lewis acid sites and using the integrated molar extinction coefficient from Emeis [5].

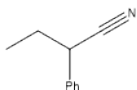
#### *Acid nitrile exchange*

In a glass tube, the nitrile (6 mmol) was added to a mixture of the carboxylic acid (0.375 mmol) and the catalyst (10 mol%). The tube was then sealed (with a screw cap) and the mixture was allowed to stir at 165°C or 215°C. After completion of the reaction (2.5, 5 or 16h), the products were analyzed by <sup>1</sup>H NMR or GC (and GC-MS) after derivatization.

## Product analyses

**<sup>1</sup>H NMR:** The crude product mixture (20 mg aliquot) was diluted with CDCl<sub>3</sub> (1 g) and analyzed by <sup>1</sup>H NMR and <sup>13</sup>C NMR. NMR spectra were recorded on a Bruker Advance 400 spectrometer.

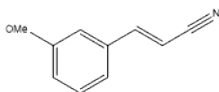
- 2-Phenylbutyronitrile:



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.41-7.29 (m, 5 H), 3.74 (t,  $J$  = 7.2 Hz, 1 H), 1.95 (quint,  $J$  = 7.2 Hz, 2 H), 1.08 (t,  $J$  = 7.2 Hz, 3 H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.9, 129.1, 128.1, 127.4, 120.9, 39.0, 29.4, 11.6.

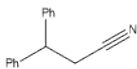
- (*E*)-3-(3-Methoxyphenyl)acrylonitrile:



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38-7.30 (m, 2 H), 7.05-6.95 (m, 3H), 5.87 (d,  $J$  = 16.8 Hz, 1 H), 3.83 (s, 3 H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.0, 150.7, 134.9, 130.3, 120.1, 118.2, 116.9, 112.6, 96.8, 55.6.

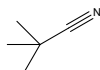
- Diphenylpropanenitrile:



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34-7.20 (m, 10 H), 4.36 (t,  $J$  = 7.6 Hz, 1 H), 3.02 (d,  $J$  = 7.6 Hz, 2 H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.5, 129.0, 127.7, 127.6, 118.6, 47.3, 24.4.

- Pivalonitrile:

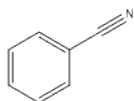


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.36 (s, 9 H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 126.0, 28.6, 28.2.

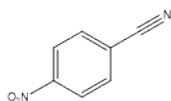
GC (and GC-MS) after derivatization: the product mixture (20 mg aliquot) was silylated with BSTFA-TMCS 99:1 (TCI Europe N.V) for 90 min at 60°C to ensure full derivatization. Then the mixture was analyzed by GC on a Shimadzu 2014 GC equipped with a FID detector and a CP-Sil 5 CB column and GC-MS on a Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer.

- Benzonitrile: (MW = 103.04)



GC/MS (EI, 70 eV): m/z (rel. int., %): 104 (8), 103 (100), 77 (6), 76 (35), 75 (9), 74 (5), 52 (5), 51 (9), 50 (16), 39 (4).

- 4-Nitro benzonitrile: (MW = 148.12)



GC/MS (EI, 70 eV): m/z (rel. int., %): 148 (44), 118 (8), 103 (8), 102 (100), 90 (23), 76 (18), 75 (30), 51 (20), 50 (15), 30 (31).

## Results

Table S1. Elemental composition determined by ICP

Sample	M' (wt.%)	Co (wt.%)
Zn-Co DMC	32.0	18.7
Co-Co DMC	-	49.1
Fe-Co DMC	31.8	18.7
Cu-Co DMC	35.8	17.6
Co-Co DMC <sup>a</sup>	-	49.0

<sup>a</sup> Sample taken after one reaction cycle (16 h run)

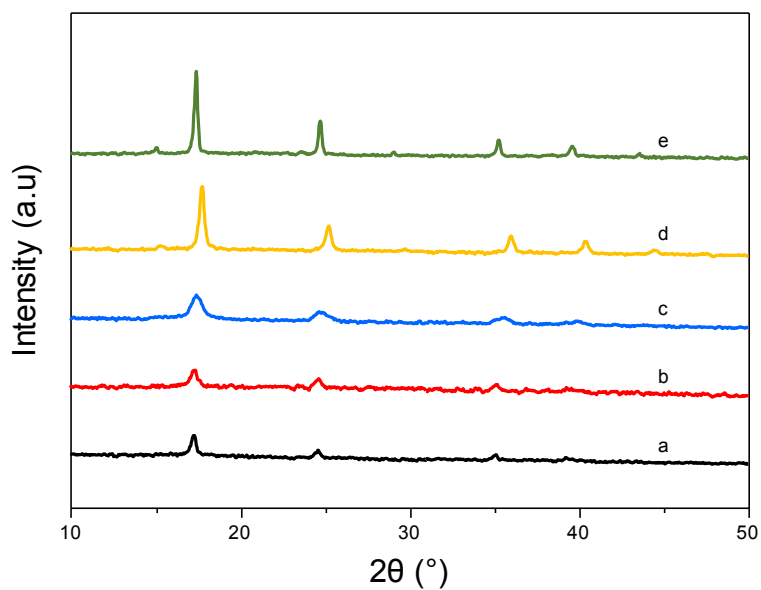


Fig. S1. PXRD patterns collected on a STOE Stadi MP diffractometer for DMC samples: a) Fe-Co, b) Co-Co, c) Ni-Co, d) Cu-Co and e) Zn-Co.

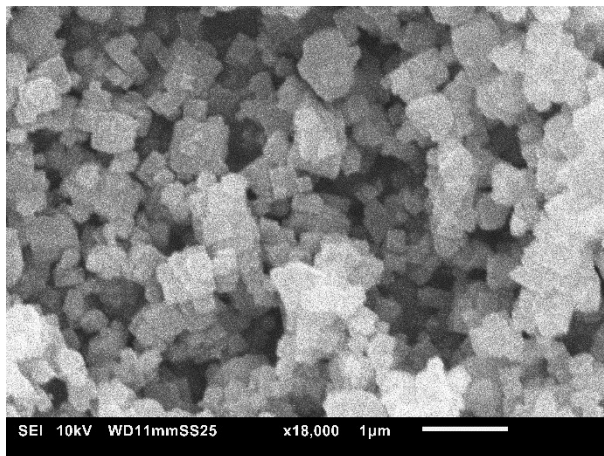
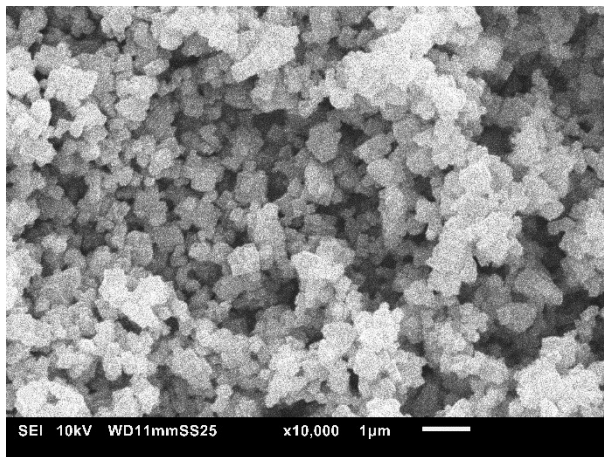
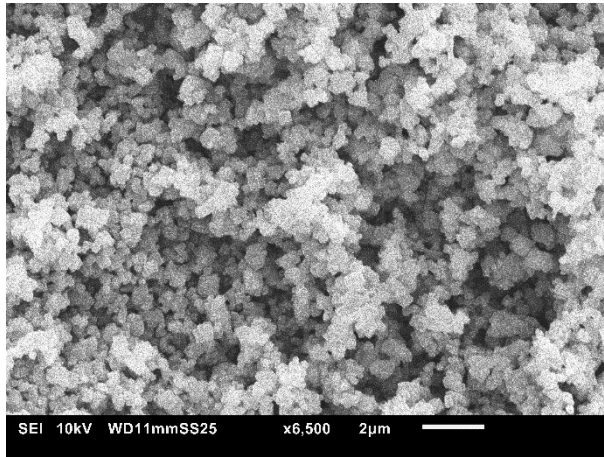


Fig. S2. SEM images of Co-Co DMC.

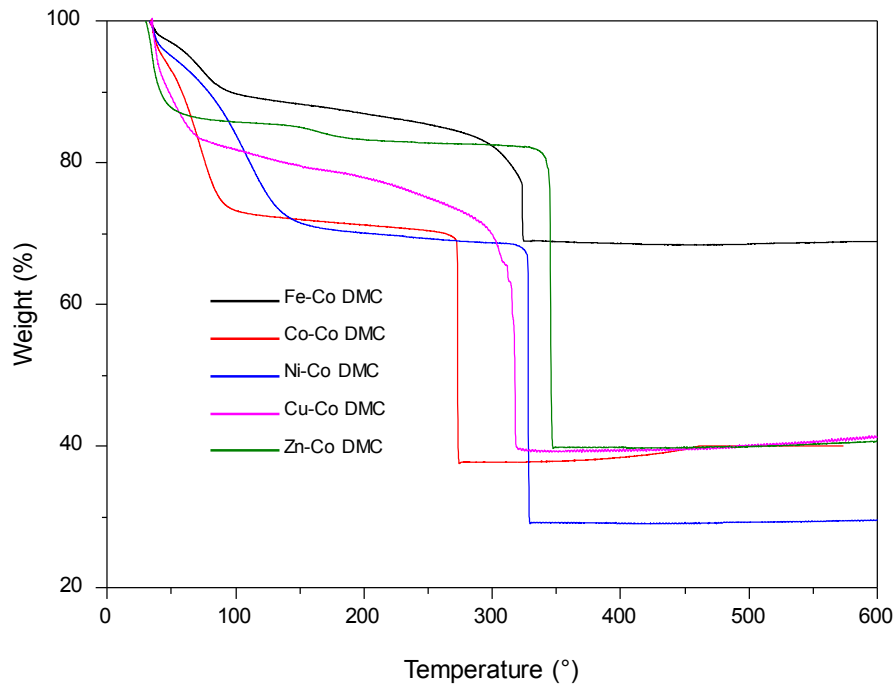


Fig. S3. TGA profiles of DMC samples.

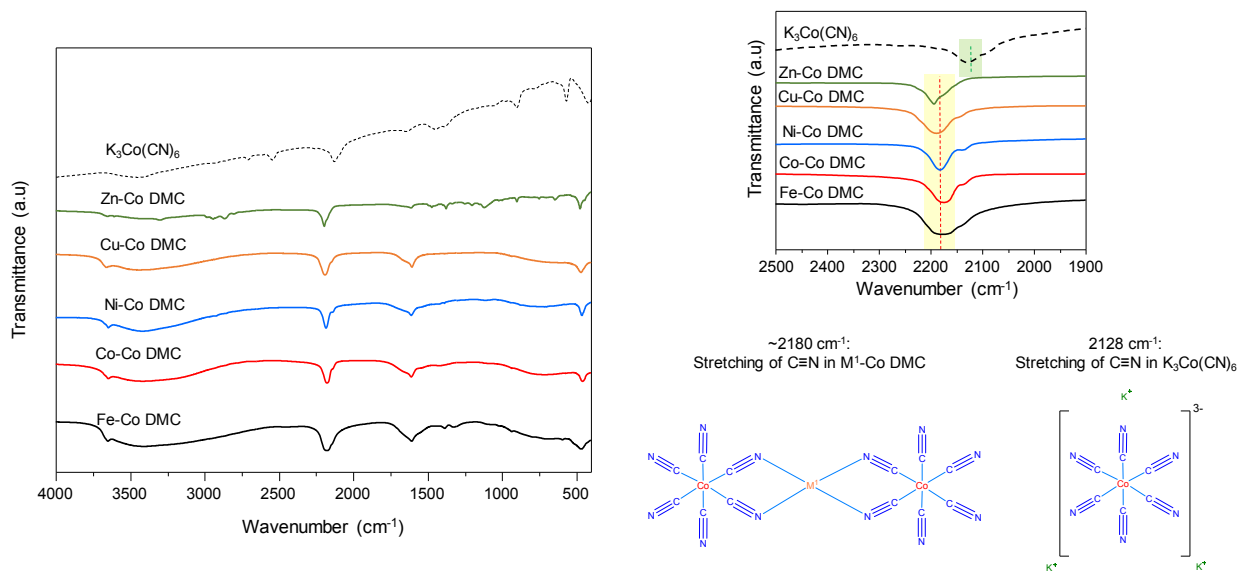


Fig. S4. FTIR spectra (left) and C≡N stretching region of the FTIR spectra (right) of DMC samples

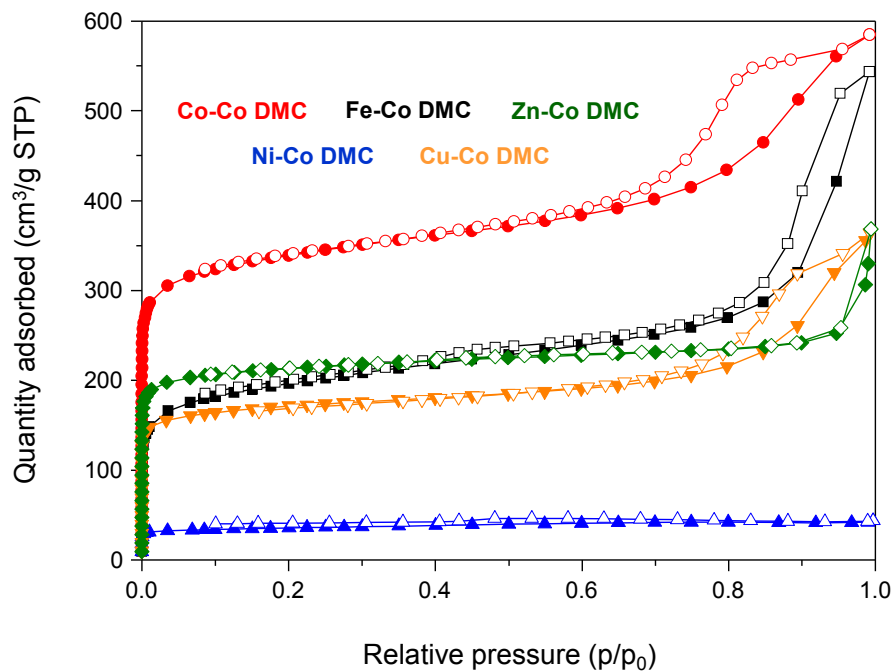


Fig. S5. Nitrogen physisorption isotherms (77 K) of DMC samples. Filled symbols denote adsorption and open symbols denote desorption

Table S2. Textural properties of DMCs determined from N<sub>2</sub> physisorption at -196°C and Lewis acid properties determined by pyridine adsorption followed by FTIR spectroscopy.

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{ext}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	LAS (mmol/g)
Fe-Co DMC	641	311	0.168	0.0877
Co-Co DMC	1076	327	0.382	0.0889
Cu-Co DMC	540	147	0.201	0.0439
Zn-Co DMC	666	138	0.270	0.1049
Ni-Co DMC	114	39	0.038	0.0136



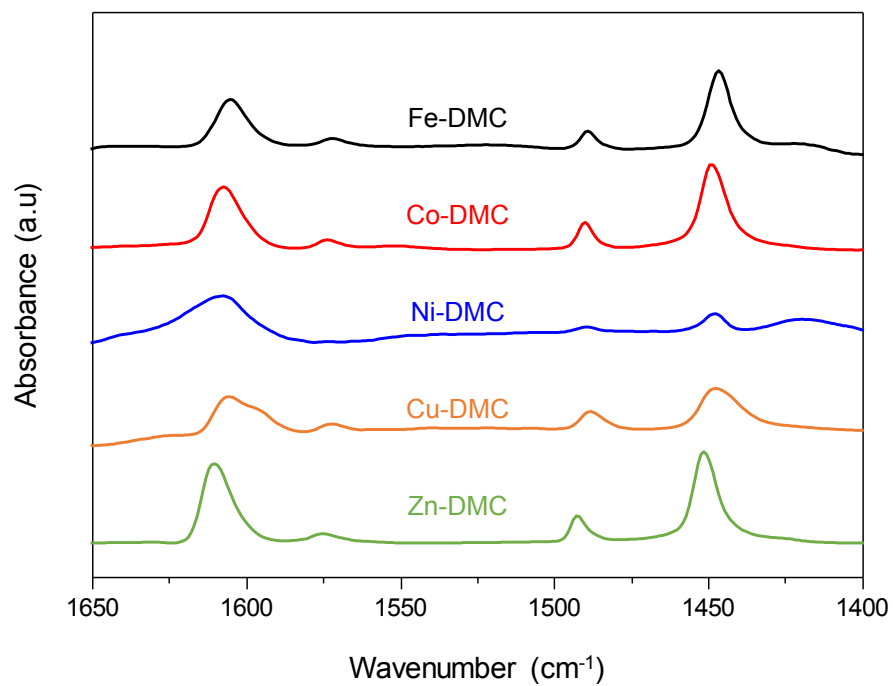


Fig. S6. Difference IR spectra of adsorbed pyridine (normalized to 10 mg of sample/ $\text{cm}^2$ ) for the DMCs.

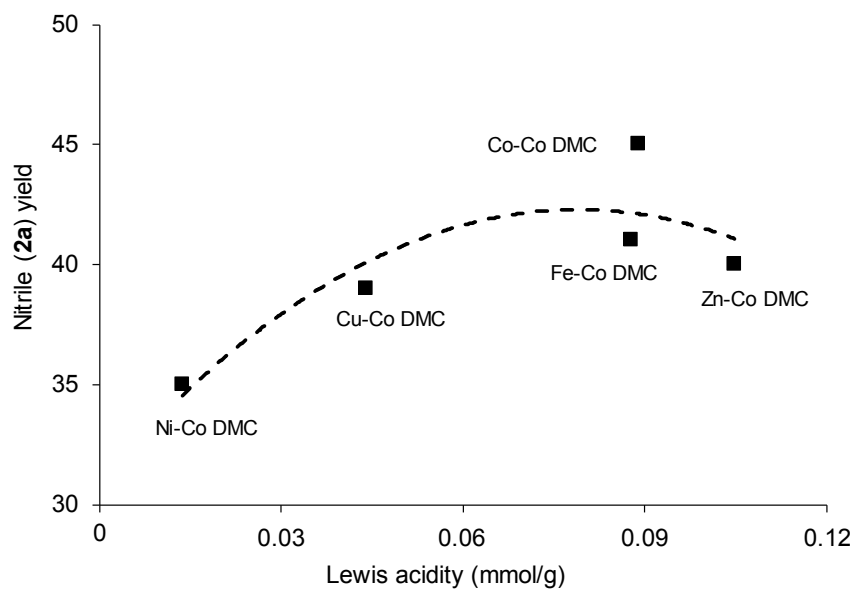
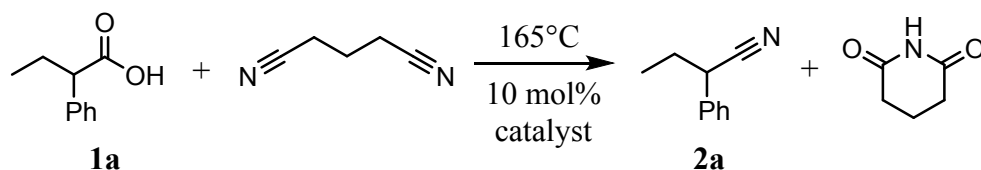


Fig. S7. Plot of the yield of nitrile (**2a**) after 2.5 h reaction time vs. the number of Lewis sites (mmol/g).

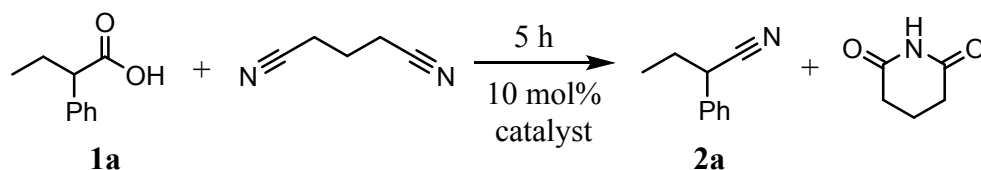
Table S3. Yield (%) of 2-phenylbutyronitrile (**2a**) obtained with different catalysts in the acid-nitrile exchange reaction between 2-phenylbutyric acid (**1a**) and glutaronitrile<sup>a</sup>



Entry	Catalyst	2a Yield (%) <sup>b</sup>		
		5 h	16 h	24 h
1	-	3	12	18
2	Fe-Co DMC	28	44	50
3	Co-Co DMC	40	63	72
4	Zn-Co DMC	23	35	41
5	AlCl <sub>3</sub>	42	71	80
6	Zr BEA	15	30	37

<sup>a</sup> Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of glutaronitrile, 10 mol% of catalyst at 165°C. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

Table S4. Effect of temperature on the yield (%) of 2-phenylbutyronitrile (**2a**) obtained with different catalysts in the acid-nitrile exchange reaction between 2-phenylbutyric acid (**1a**) and glutaronitrile<sup>a</sup>



Entry	Catalyst	2a Yield (%) <sup>b</sup>	
		165°C	215°C
1	-	3	31
2	Fe-Co DMC	28	51
3	Co-Co DMC	40	58
4	Zn-Co DMC	23	49
5	AlCl <sub>3</sub>	42	66
6	Zr BEA	15	53

<sup>a</sup> Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of glutaronitrile, 10 mol% of catalyst for 5 h. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

Table S5. Nitrile yields obtained with different carboxylic acids<sup>a</sup>

Entry	Acid	Product	Nitrile yield after 5 h (%)	Nitrile yield after 16 h (%)
1			58 (30) <sup>b</sup>	86 (52) <sup>b</sup>
2			42 (25) <sup>b</sup>	80 (39) <sup>b</sup>
3			20 (5) <sup>b</sup>	67 (29) <sup>b</sup>
4			42 (21) <sup>c</sup>	88 (37) <sup>c</sup>
5			74 (27) <sup>c</sup>	96 (42) <sup>c</sup>
6			38 (8) <sup>b,d</sup>	54 (12) <sup>b,e</sup>

<sup>a</sup> Reaction conditions: 0.375 mmol of carboxylic acid, 6 mmol of glutaronitrile, 10 mol% of catalyst at 215°C. Values between parentheses correspond to the yield obtain in the absence of catalysts. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Determined by GC after derivatization. <sup>d</sup> Under microwave radiation at 200°C for 0.5 h reaction time. <sup>e</sup> Under microwave radiation at 200°C for 1.5 h reaction time.

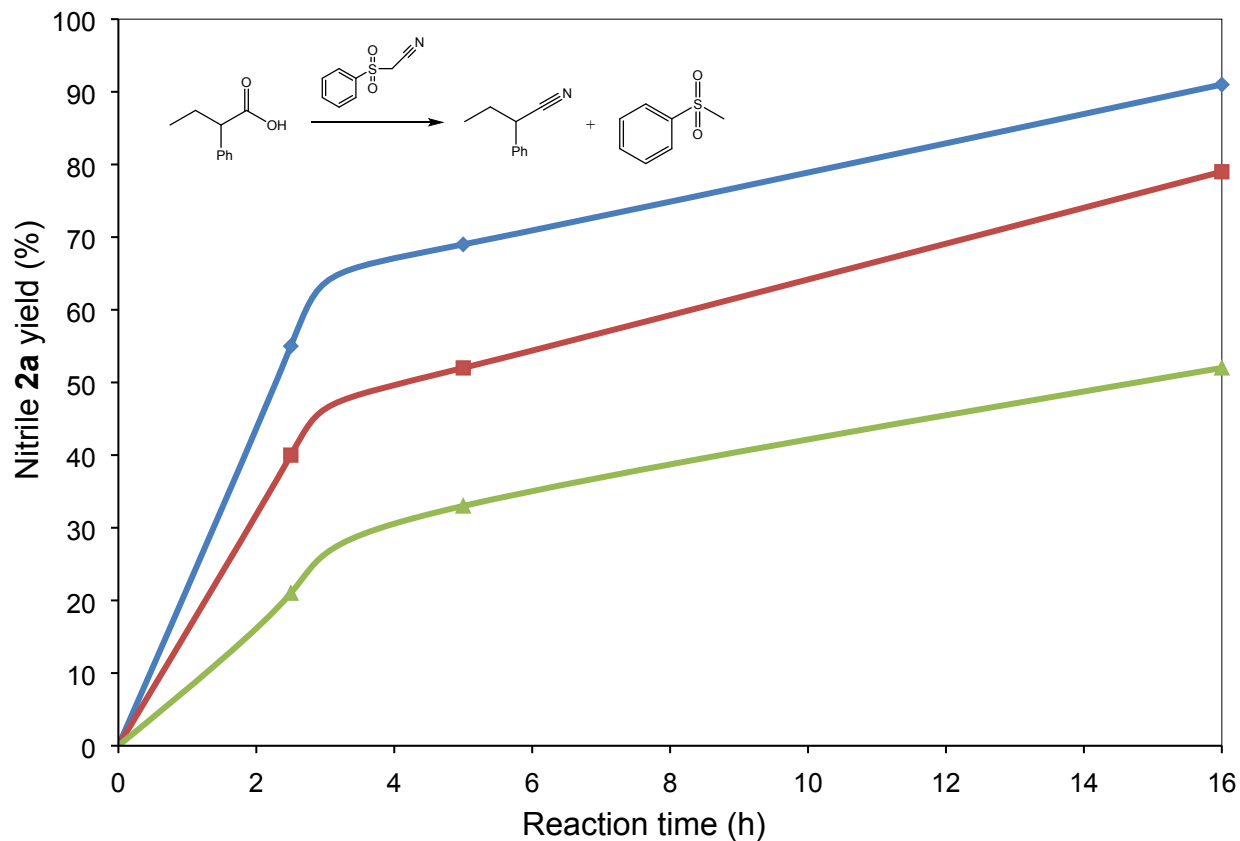


Fig. S8. Yield (%) of 2-phenylbutyronitrile (**2a**) vs time plot obtained with AlCl<sub>3</sub> (blue line), Co-Co DMC (red line) and without catalyst (green line). Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of (phenylsulfonyl)acetonitrile, 10 mol% of catalyst, 215°C. Yields determined by <sup>1</sup>H NMR spectroscopy.

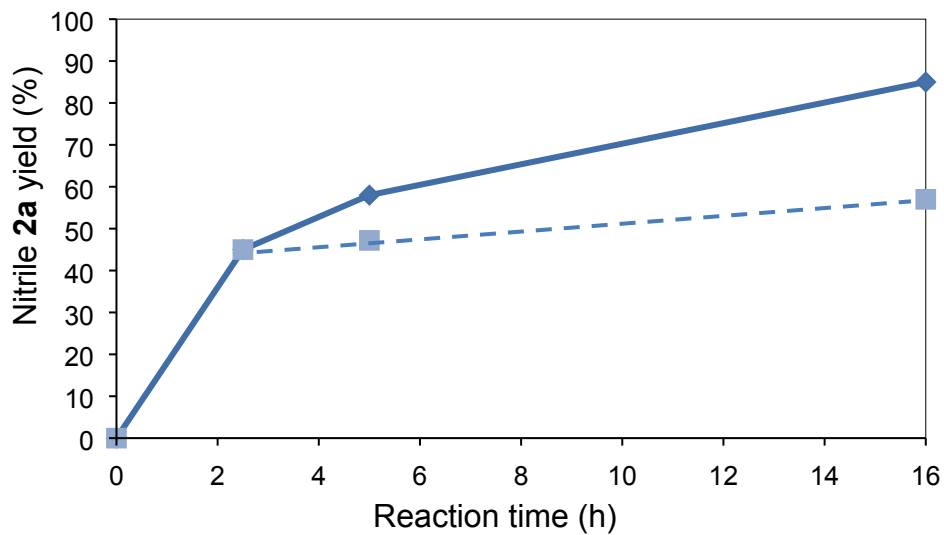


Fig. S9. Co-Co DMC hot filtration test. Dashed line represents the nitrile (**2a**) yield after removal of the catalysts. Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of glutaronitrile, 10 mol% of catalyst, 215°C.

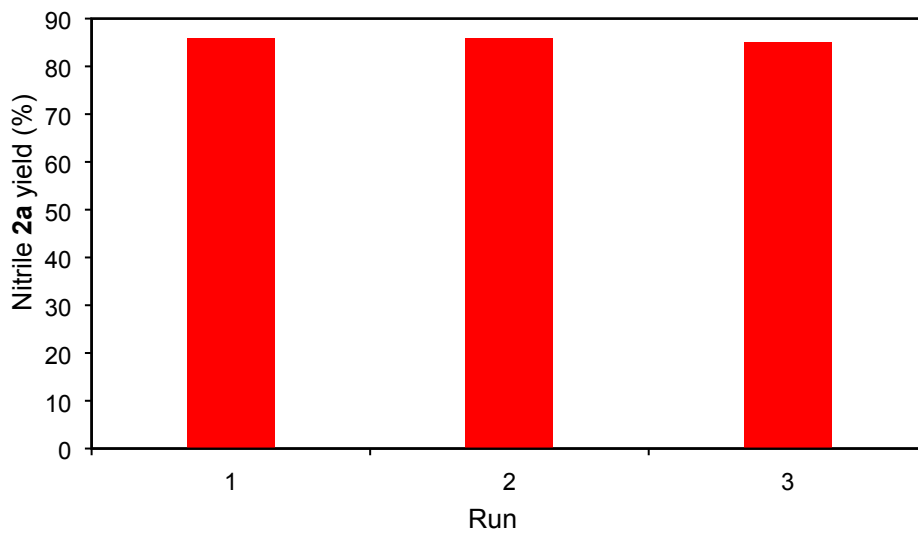


Fig. S10. Co-Co DMC recycling test. Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of glutaronitrile, 10 mol% of catalyst, 215°C, 16 h.

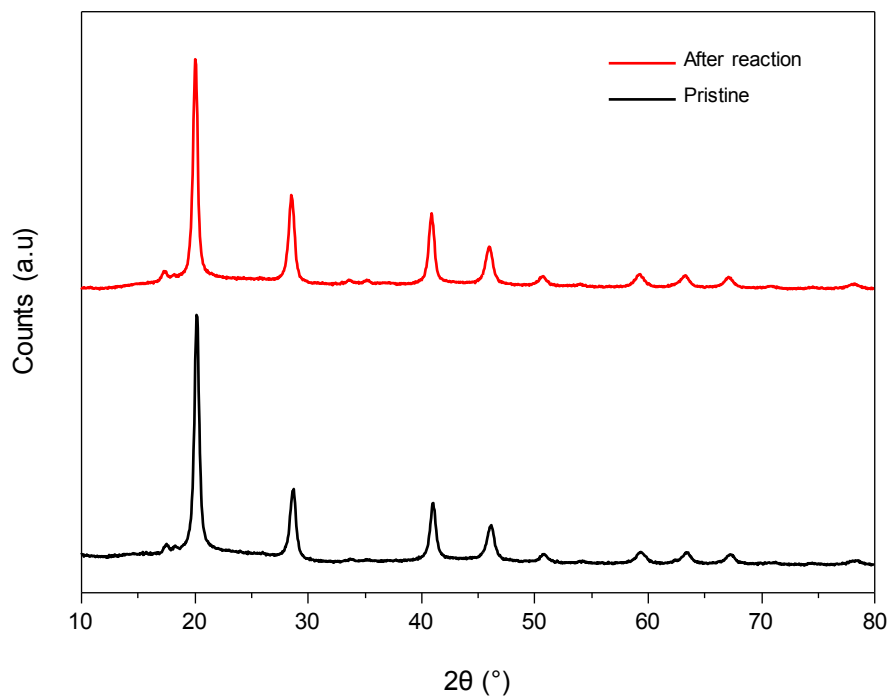
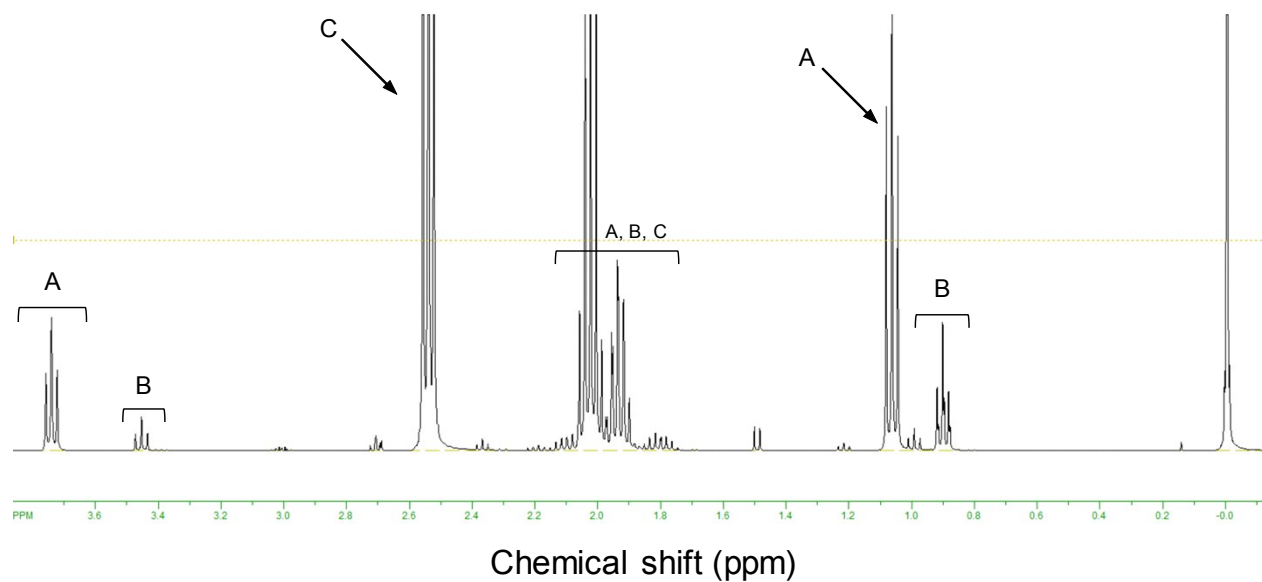
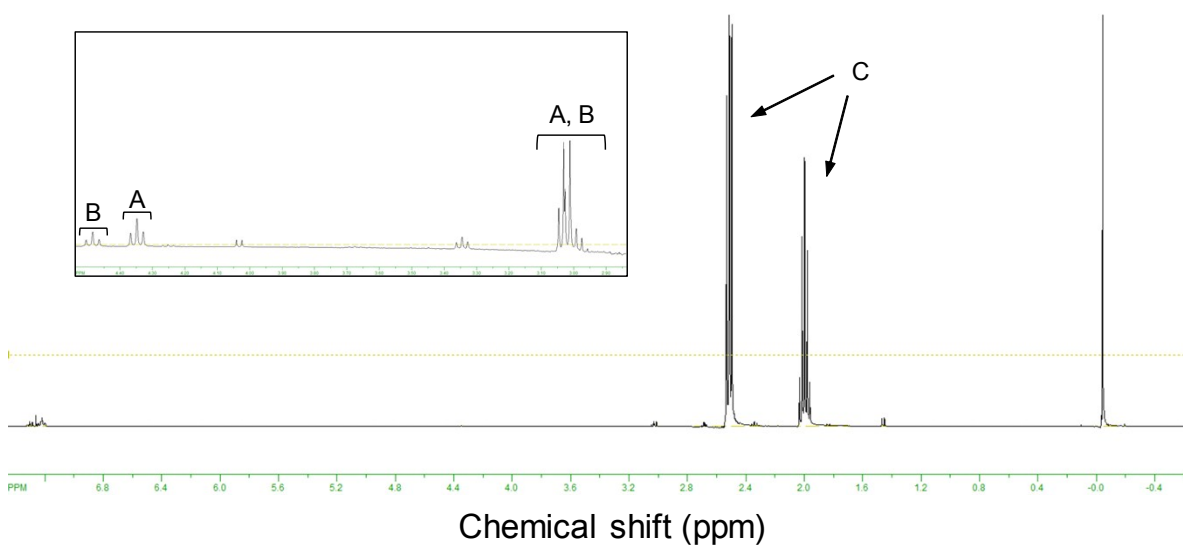


Fig. S11. XRD pattern of Co-Co DMC before and after reaction (16 h) collected on a Bruker-AXS D2 Phaser powder X-ray diffractometer. Reaction conditions: 0.375 mmol of 2-phenylbutyric acid (**1a**), 6 mmol of glutaronitrile, 10 mol% of catalyst, 215°C.

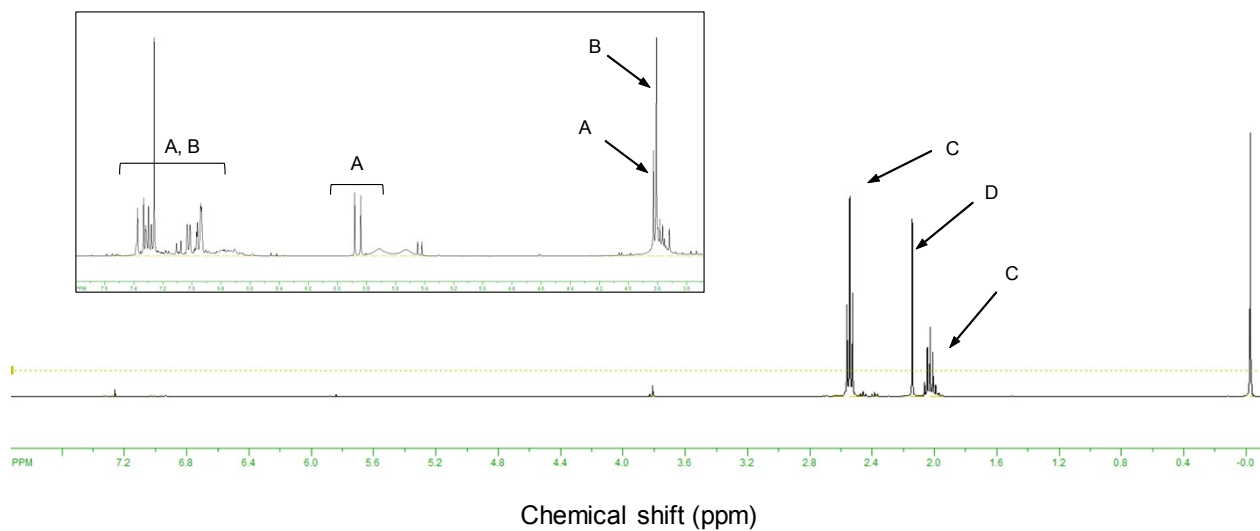
## <sup>1</sup>H NMR spectra of the product mixtures



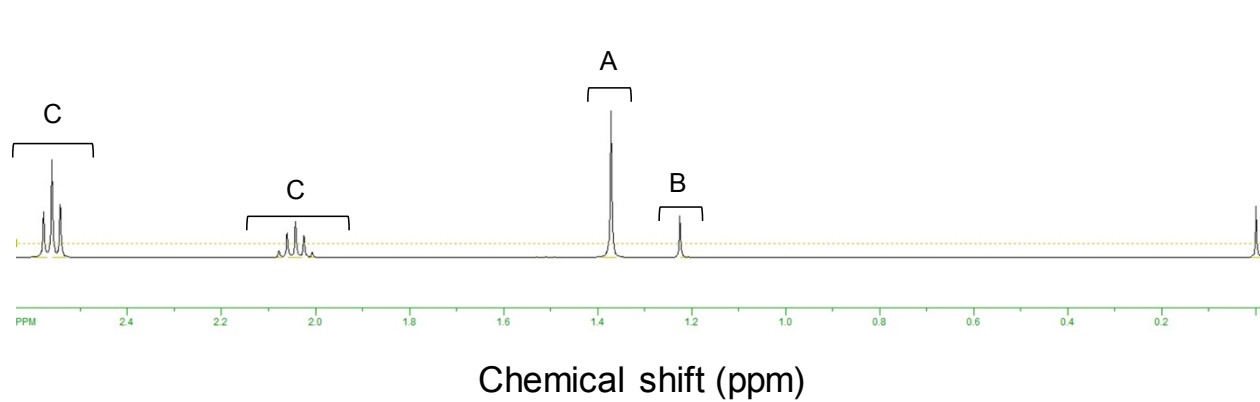
A: 2-Phenylbutyronitrile, B: 2-phenylbutyric acid and C: glutaronitrile.



A: Diphenylpropanenitrile, B: diphenylpropionic acid and C: glutaronitrile.



A: (*E*)-3-(3-Methoxyphenyl)acrylonitrile, B: 3-methoxycinnamic acid, C: glutaronitrile, D: acetone (contamination).



A: Pivalonitrile, B: pivalic acid and C: glutaronitrile.



## References

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- [4] Lee, Y.; Kim, S.; Kang, J. K.; Cohen, S. M. *Chem. Commun.* 2015, 51, 5735-5738.
- [5] Emeis, C. A. *J Catal.* 1993, 141, 347-354.