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Supporting Information

Integration of metal organic framework with zeolite: A highly sustainable composite catalyst for the synthesis of γ-valerolactone and coumarins

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Pages S1-S17; Table S1; Figure S1-S10; Scheme S1

Catalyst preparation

Synthesis of Beta@Zr-BDC-MOF

In a typical synthesis of Beta@Zr-BDC-MOF, $ZrOCl_2.8H_2O$ (1.6 g, 5.0 mmol) was dissolved in 25 ml of DMF. Then, 1, 4-benzene dicarboxylic acid (H_2BDC) (1.0 g, 5.0 mmol) was added to the above reaction mixture and the resultant solution was stirred at ambient condition for 10 min. Subsequently, 1.66 g of unmodified H-Beta was added to the resultant solution and the reaction mixture was dispersed for 15 min using an ultrasonic bath. HCl (0.8 ml, 9.6 mmol) was added drop-wise to the above reaction mixture with vigorous stirring. The resulting mixture was kept in an oil bath at 423 K for 24 h. The resultant white product was filtered, washed with DMF and dried in an oven at 373 K for 12 h. To remove the un-reacted organic linker, the dried product was taken in 50 mL of DMF and stirred overnight at ambient condition. The solvent exchange was carried out similar to Beta-Zr-BDC-MOF.

Procedure for the catalytic reactions

Synthesis of γ-valerolactone

In a typical catalytic procedure, ethyl levulinate (1 mmol), alcohol (100 mmol), and catalyst (pre-activated at 423K, 200 mg) were charged into a Teflon-lined steel autoclave and the reaction mixture was thoroughly flushed with N_2 for 10 min. Then, the reaction mixture was magnetically stirred in a temperature-controlled oil bath at the desired temperature for the stipulated time period. After the reaction, the autoclave was cooled to ambient temperature and the catalyst was separated using centrifuge machine. The organic portion was collected and analyzed by gas-chromatograph (GC, Younglin YL6100; column BP-1 (SGE), 30 m × 0.25 mm × 0.25μm; FID detector) and products were identified by GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rxi-5Sil MS; 30 m × 0.25 mm × 0.25μm). All products investigated in this study are commercially available. They were procured from Sigma-Aldrich, India. Standard mixtures were prepared and analyzed by GC. Calibration curves were constructed by plotting the concentration and area under the peak obtained from the GC analysis (Standard addition method). The conversion was determined based on the results obtained from the GC analysis and these calibration curves. Each sample was measured three times and the standard deviation was calculated. Standard deviation was in the range of 0 to ±2.5 (more precisely in the range of ±0.3 to ±2.4). The average values (to the nearest integer) are provided in Table 2 and 3.

Synthesis of coumarin

In a typical catalytic procedure, phenol derivative (5 mmol), ethylacetoactetate (7.5 mmol), and catalyst (pre-activated at 423K, 100 mg) were charged into a Teflon-lined steel autoclave and the reaction was conducted at 423K for 4 h. After the reaction, the autoclave was cooled to ambient temperature and the catalyst was separated using a centrifuge machine. Organic portion was collected and analyzed by GC and products were identified by GC-MS.

Details of recycling and leaching studies

Catalyst was successfully reused multiple times. Catalyst was separated from the reaction mixture using centrifuge machine (rpm 8000). Catalyst was washed with ethyl acetate and ethanol and dried in an oven at 373 K for the next cycle. Recycling study shows that no significant decrease in the activity was observed even after five cycles (Fig. 8). XRD (Fig. S7a and Fig. S10a (ESI)), FT-IR (Fig. S7b and Fig. S10b (ESI)), TGA (Fig. S7c and Fig. S10c (ESI)) and textural properties (Table 1) of the recycled catalyst shows that the catalyst was stable after the recycling experiments. Leaching experiment was also performed to test the leaching of Zr, Al, and Si species during the γ-valerolactone synthesis. Reaction was performed for 2 h under the optimum reaction condition. After 2 h, catalyst was removed from the reaction mixture and the progress of the reaction was monitored. No further increase in the reactant conversion was obtained after the removal of catalyst (Fig S8), which demonstrated that no active species was leached during the reaction that could catalyze the reaction in the homogenous phase. Elemental analysis was performed of the reaction mixture after the reaction. Zr, Al, and Si species were not detected which confirmed that Zr/Al was not leached into the solution and those Zr/Al sites which were present in the catalyst are catalyzed the reaction as heterogeneous catalyst to produce the desired product.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer, using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA). Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at 150 °C for 3 h in the degas port of the adsorption apparatus. The specific surface area was calculated from the adsorption branch using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using non-local density functional theory (NLDFT) and Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy measurements (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out on a JEOL JSM-6610LV to investigate the morphology and chemical composition of the MOF. Structural analysis of the as prepared samples were carried out by TEM using FEI, Tecnai G^2 F30, S-Twin microscope operating at 300 kV equipped with a GATAN Orius CCD camera. The sample was dispersed in hexane using ultrasonic bath, drop cost on a carbon coated Cu grid, dried, and used for TEM measurements. Fourier transform infrared (FTIR) spectra were recorded on a Bruker spectrophotometer in the region 400–2000 cm^{-1} (spectral resolution = 4 cm^{-1}; number of scans = 100). Thermo gravimetric analysis (TGA) was performed in the range of 298-1173 K on a TGA/DSC 1 $STAR^e$ SYSTEM from Mettler Toledo, Switzerland, with temperature increments of 5 K/min in N_2 atmosphere.

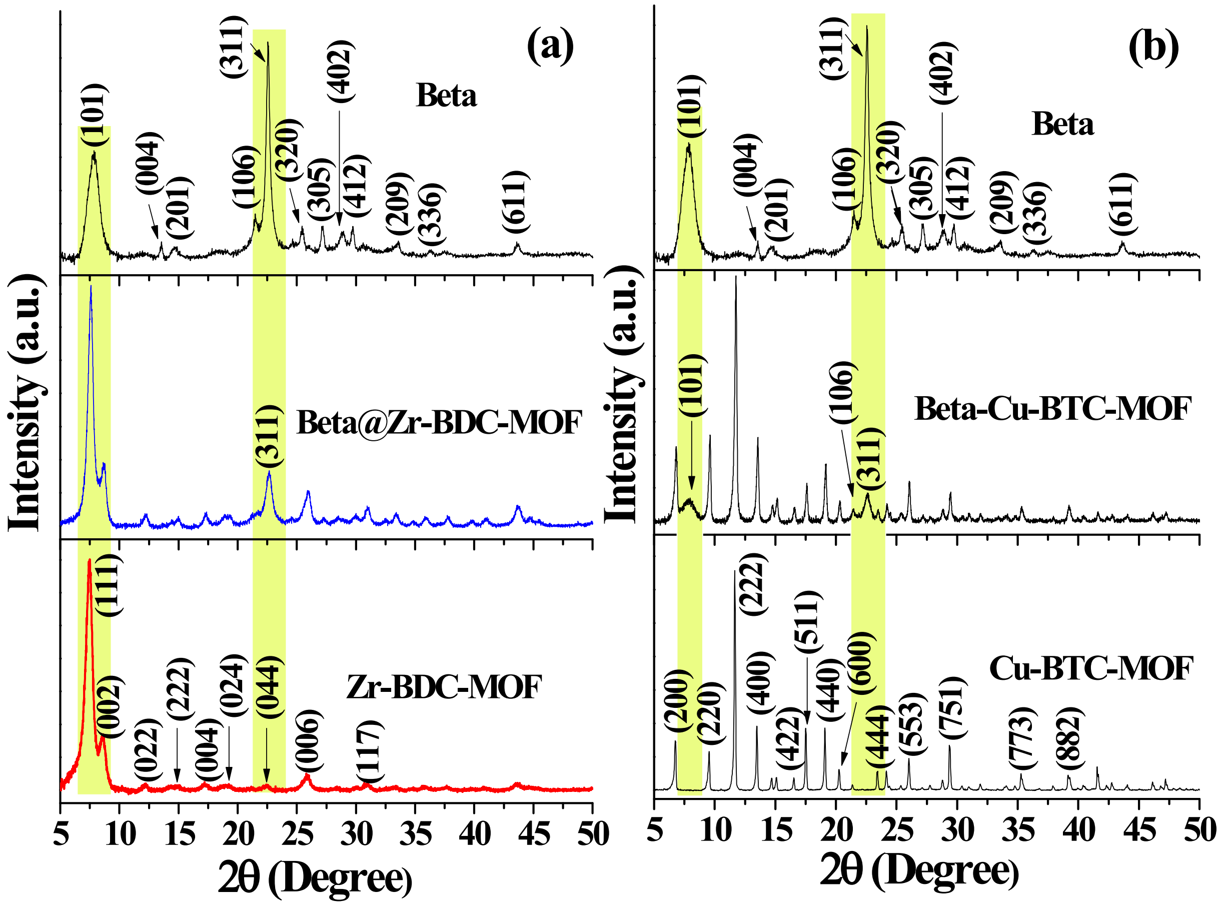


Fig. S1. Powder X-ray diffraction patterns of the parent and composite materials prepared in this study.

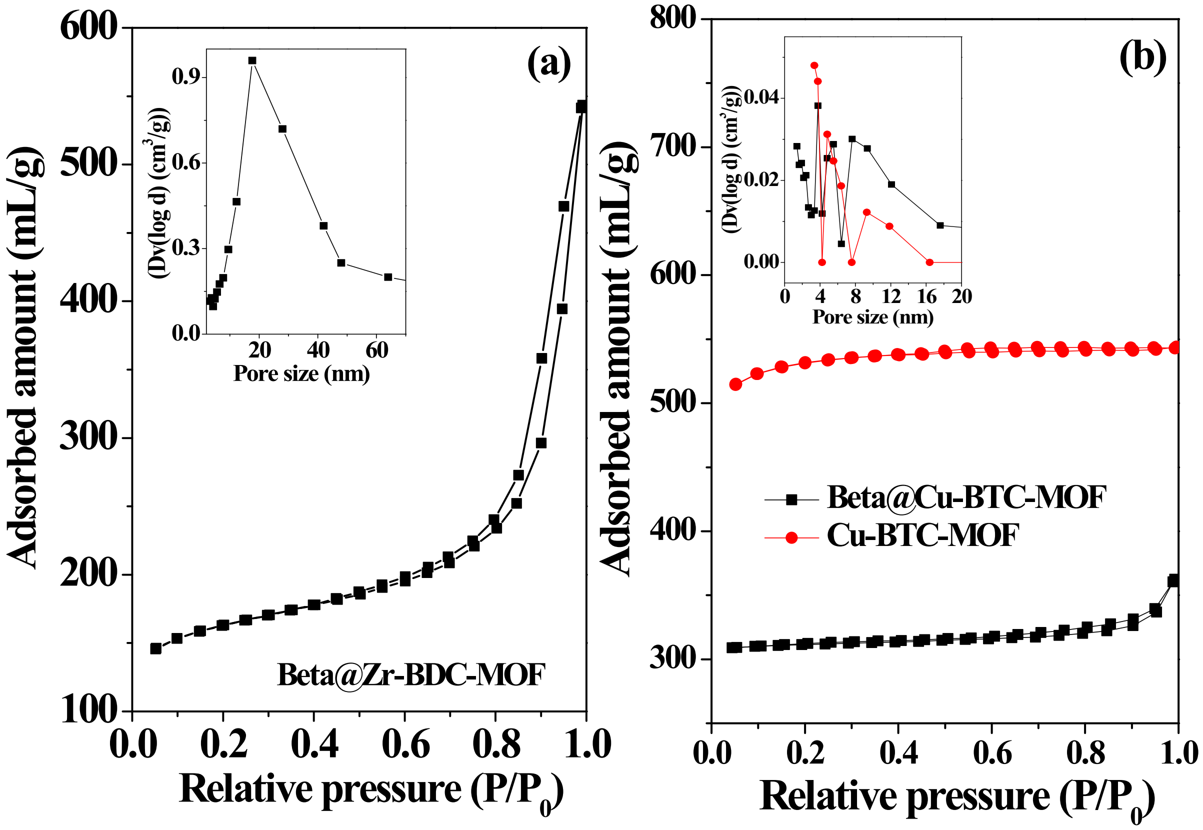


Fig. S2. N_2-adsorption isotherms of (a) Beta@Zr-BDC-MOF and (b) Cu-BTC-MOF and Beta-Cu-BTC-MOF. Inset shows mesopore size distribution.

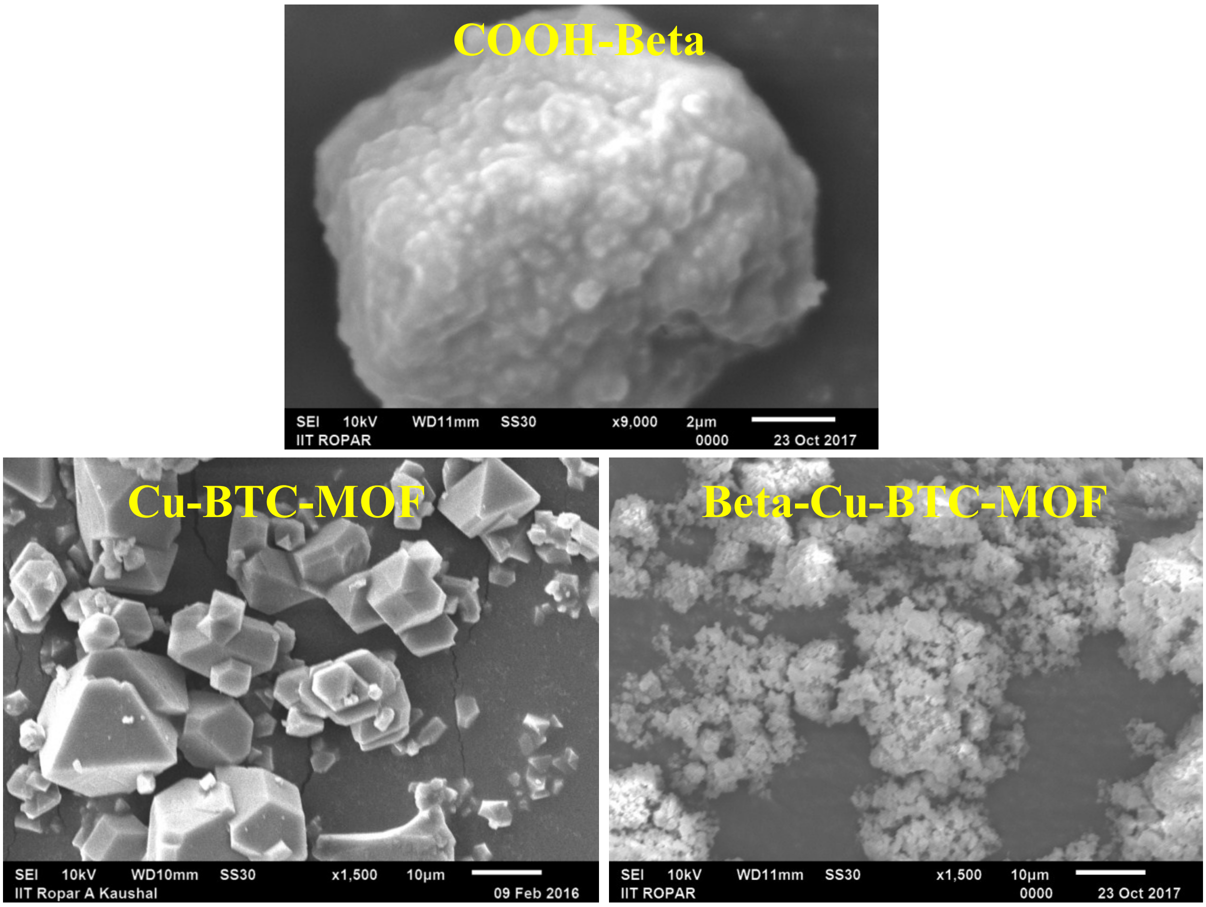
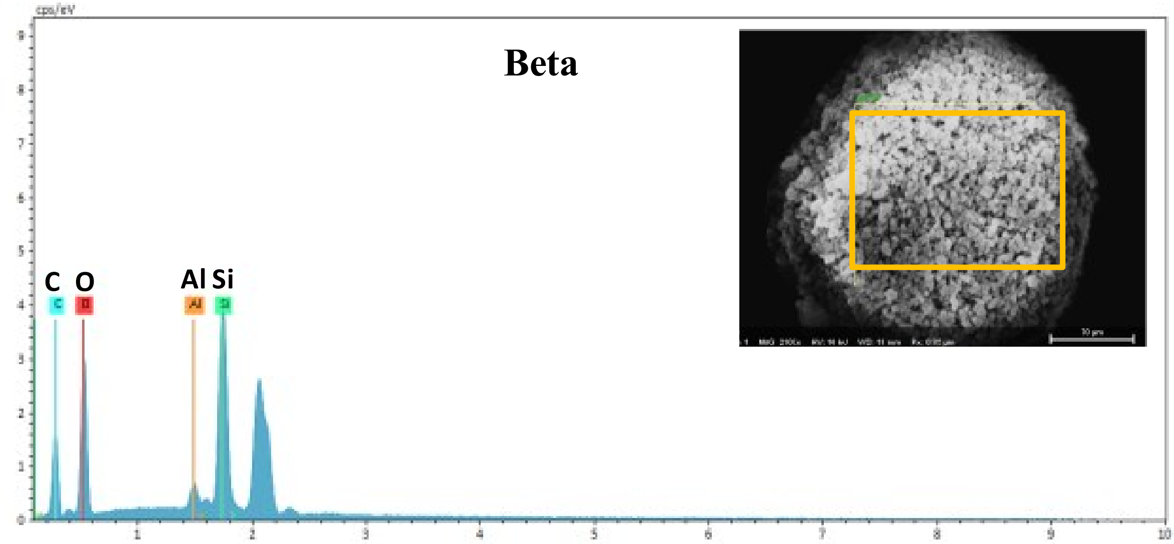
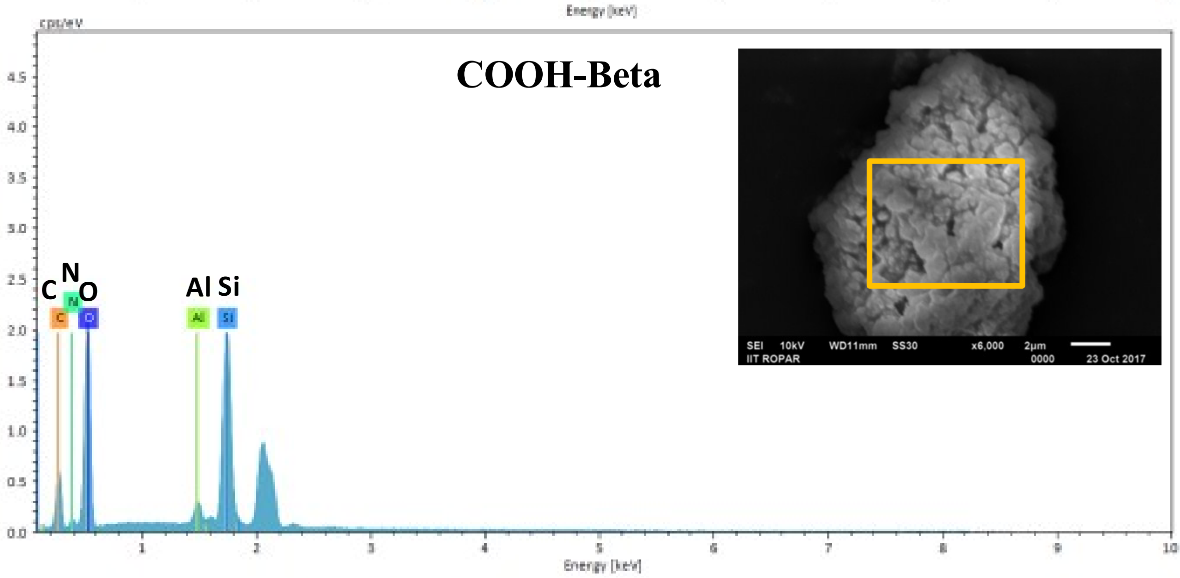


Fig. S3. SEM images of COOH-Beta, Cu-BTC-MOF, and Beta-Cu-BTC-MOF.



Beta
cps/eV
9
8
7
6
5
4
3
2
1
0
C
O
Al
Si
C
O
Al
Si
1
2
3
4
5
6
7
8
9
10
Energy [keV]
10 µm



COOH-Beta
cps/eV
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
C
N
O
Al
Si
C
N
O
Al
Si
1
2
3
4
5
6
7
8
9
10
Energy [keV]
SEI 10kV WD11mm SS30 x6,000 2µm
IIT ROPAR 0000 23 Oct 2017

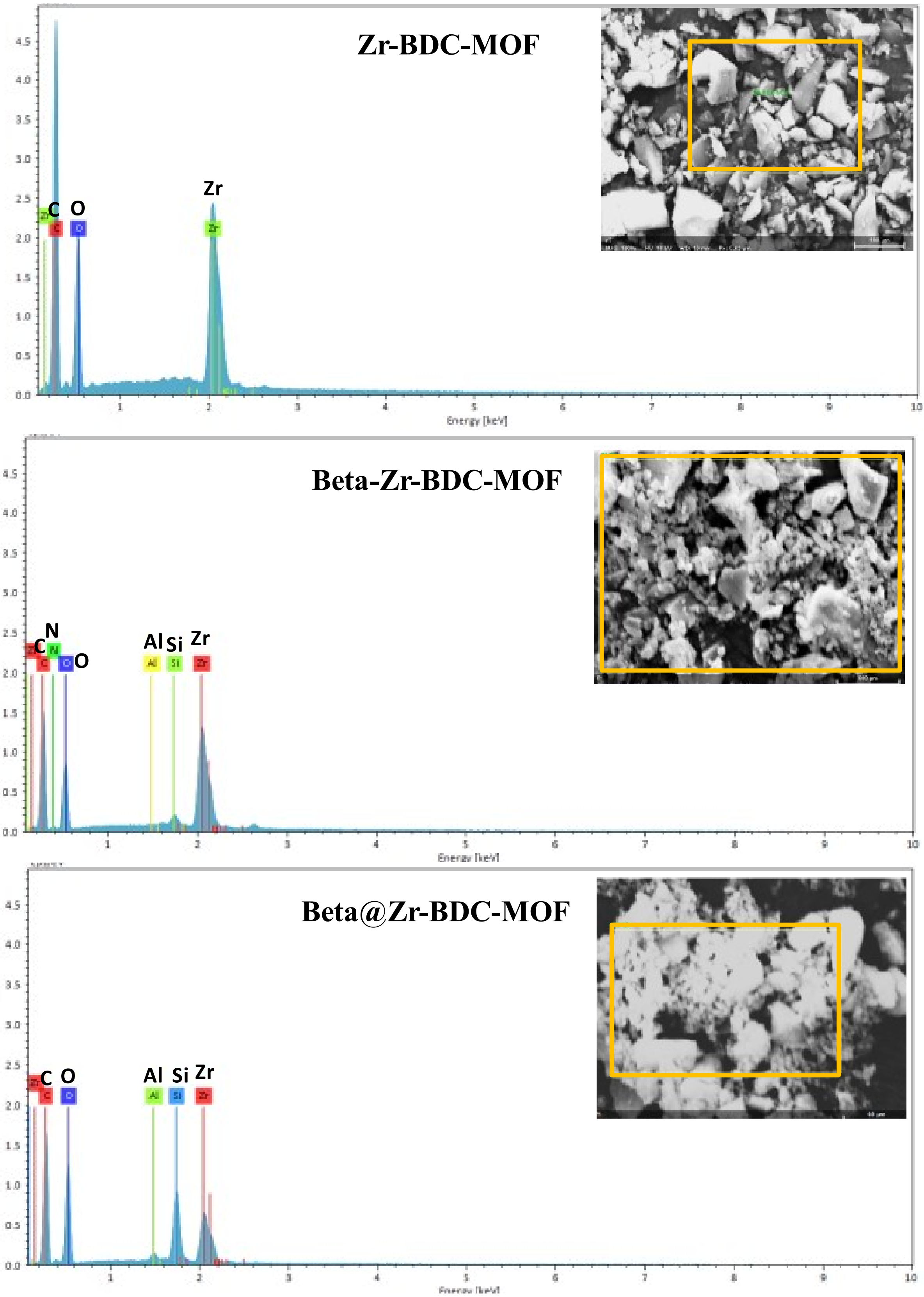


Fig. S4. EDS spectra of parent and composite materials prepared in this study.

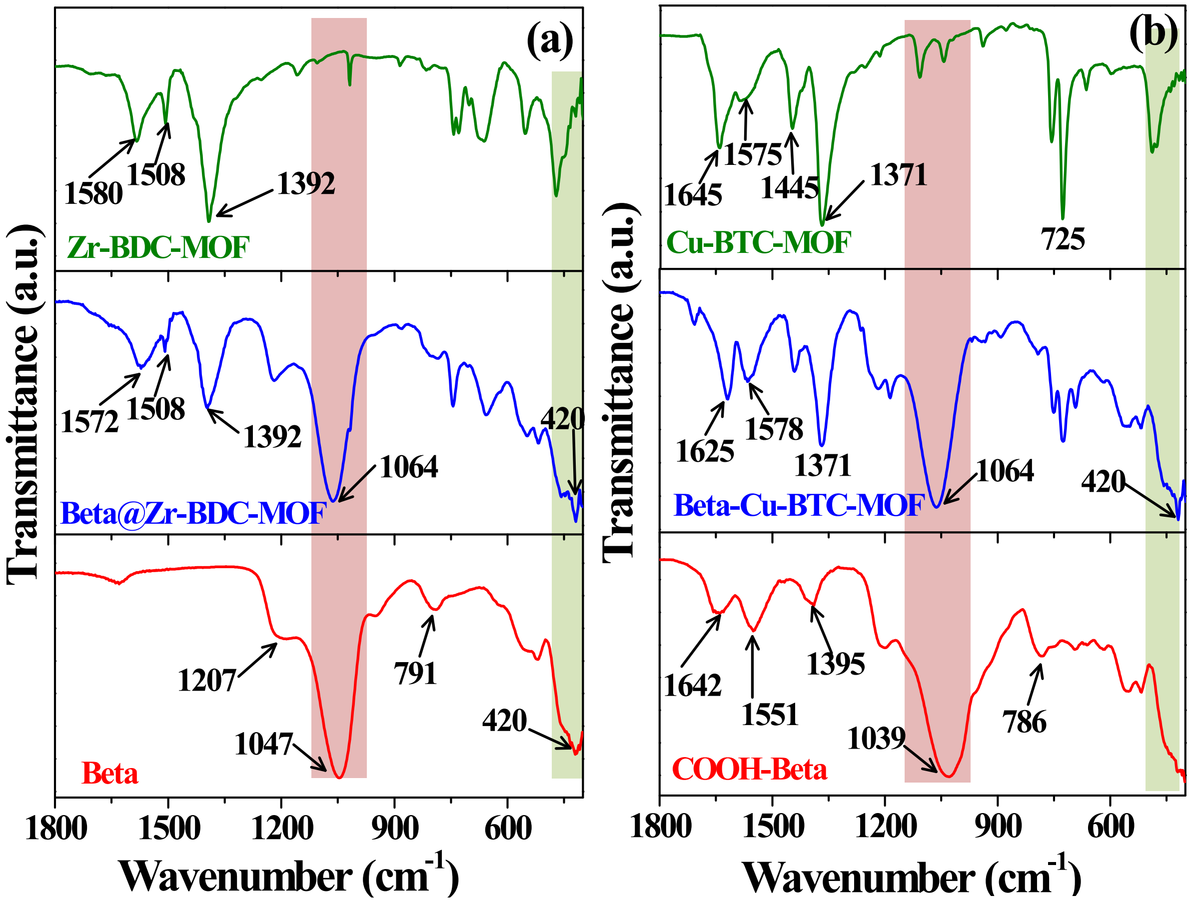


Fig. S5. FT-IR spectra of various materials prepared in this study.

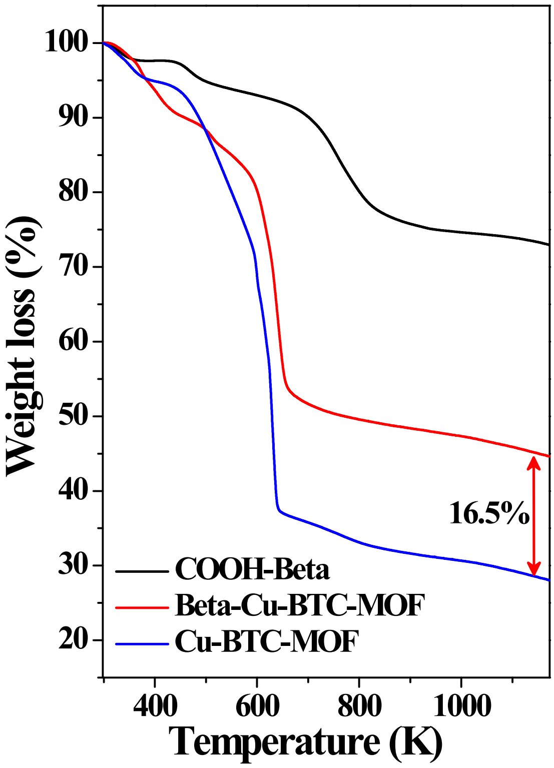


Fig. S6. Thermograms of Cu-BTC-MOF, COOH-Beta, and Beta-Cu-BTC-MOF.

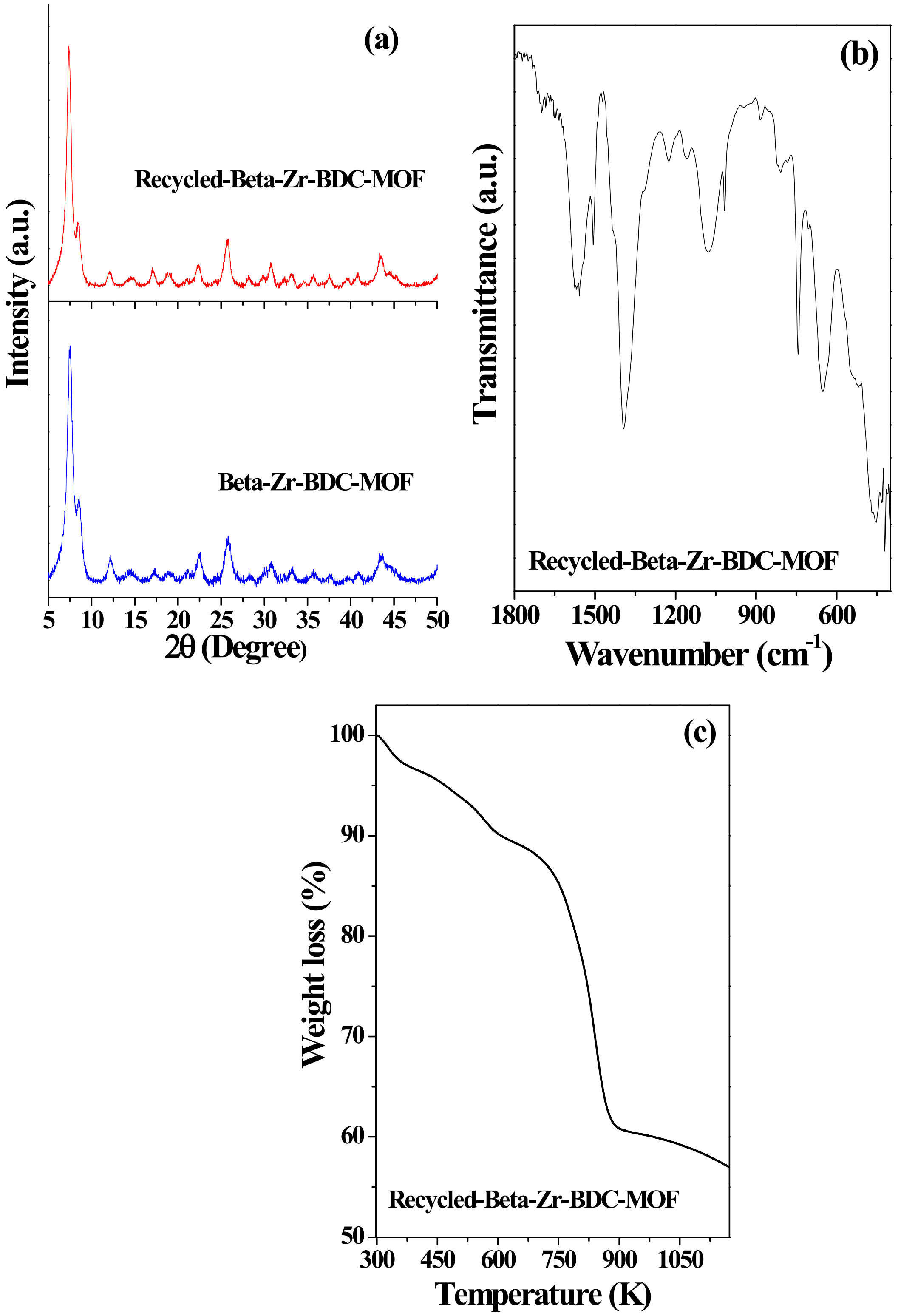


Fig. S7. (a) Powder X-ray diffraction patterns, (b) FT-IR spectrum, and (c) thermogram of the catalyst obtained after fifth recycle in the γ-valerolactone synthesis.

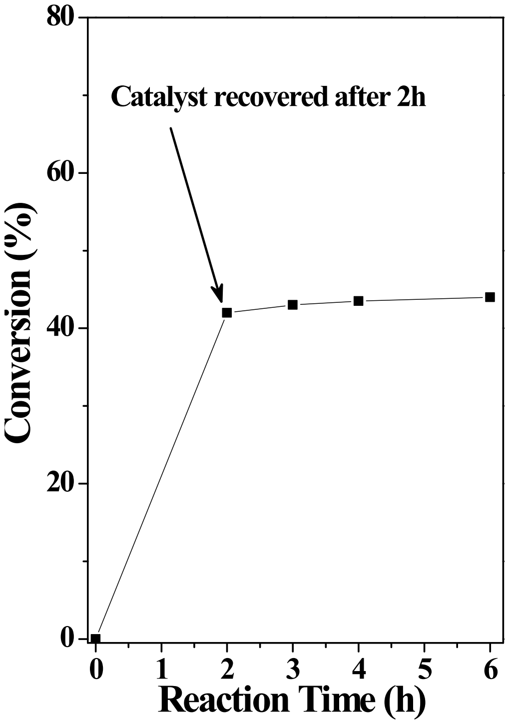


Fig. S8. Leaching test for the catalyst removed after 2 h after the start of the reaction from the reaction mixture in the γ-valerolactone synthesis.

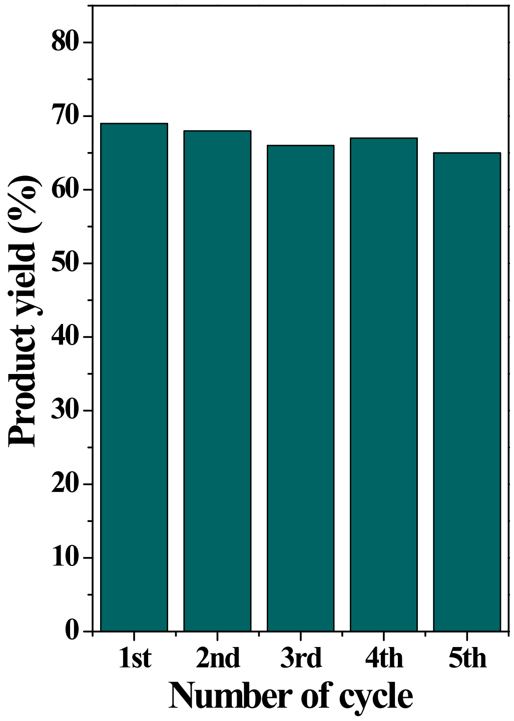


Fig. S9. Reusability of the catalyst in the coumarin synthesis.

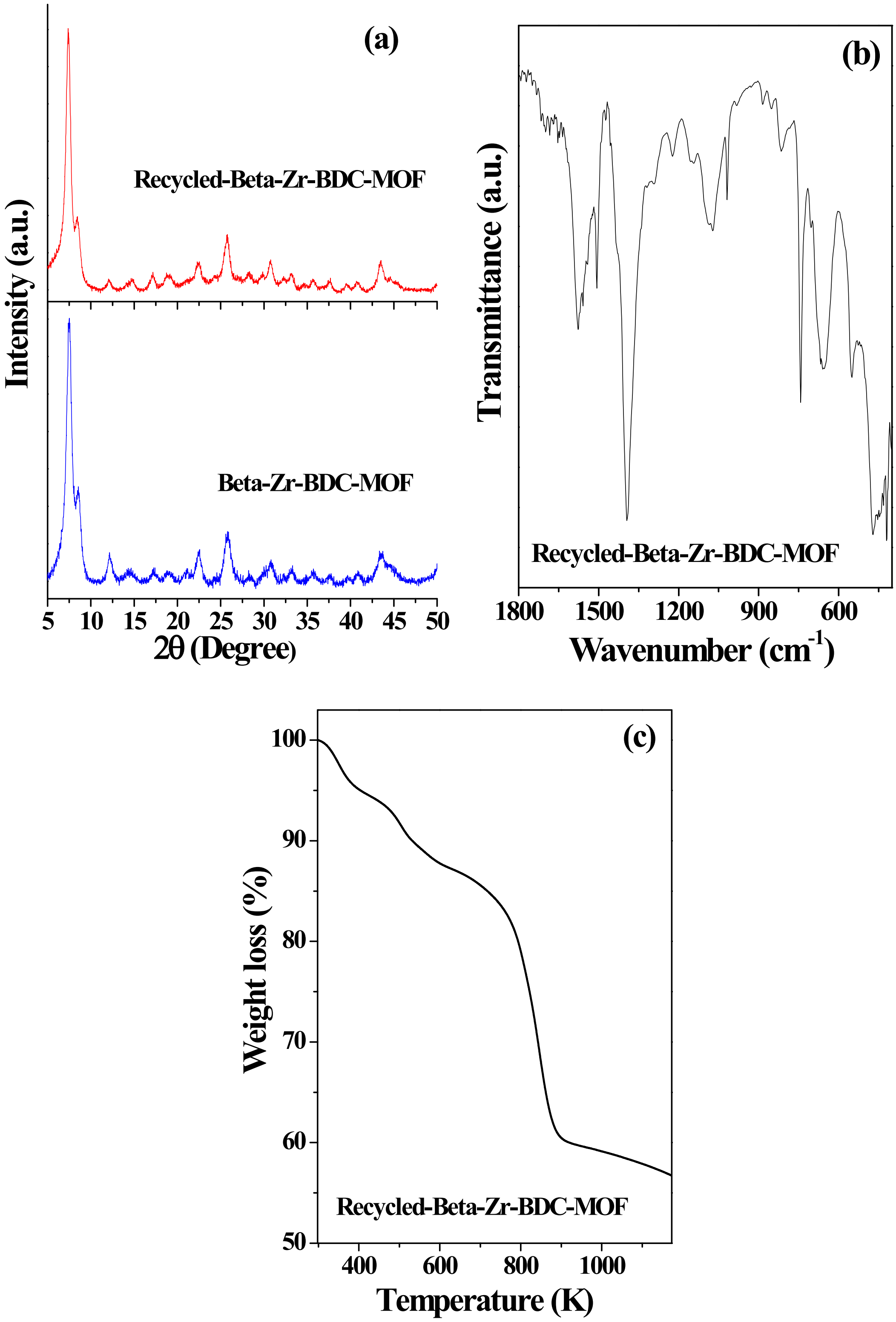
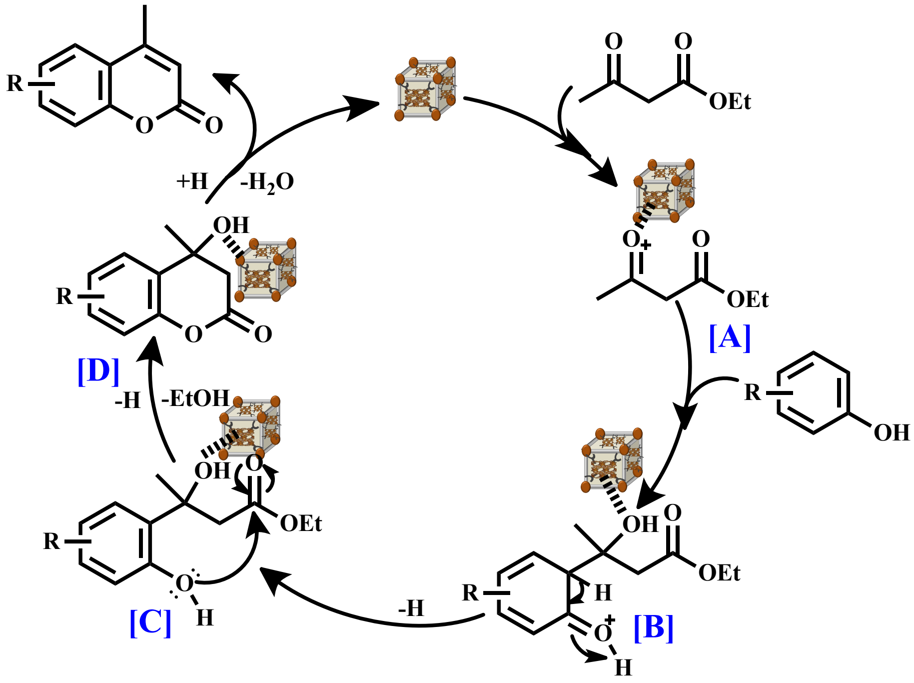


Fig. S10. (a) Powder X-ray diffraction patterns, (b) FT-IR spectrum, and (c) thermogram of the catalyst obtained after fifth recycle in the coumarin synthesis.



Scheme S1. A plausible mechanism for the synthesis of coumarins.

Table S1. Comparative catalytic activity of various catalysts reported in literature with respect to the catalyst reported in this study.

Catalyst	H-donor	Reaction parameter	Conv. (%)	GVL Sel. (%)	Ref.
Beta-Zr-BDC-MOF	2-Propanol	Ethyl levulinate (1.0 mmol), 2-propanol (6 mL), catalyst (200 mg), temp. (413 K), time (6 h).	100	75	This work
UiO-66	2-Butanol	Methyl levulinate (1.0 mmol), 2-butanol (5 mL), catalyst (100 mg), temp. (403 K), time (9 h).	70	51	43
UiO-66-S_{60}	2-Butanol	Methyl levulinate (1.0 mmol), 2-butanol (5 mL), catalyst (100 mg), temp. (403 K), time (9 h).	98	82	43
UiO-66-COOH	2-Propanol	Ethyl levulinate (1.0 mmol), 2-propanol (6 mL), catalyst (200 mg), temp. (403 K), time (3 h).	28.5	13.9	36
MOF-808	2-Propanol	Ethyl levulinate (1.0 mmol), 2-propanol (6 mL), catalyst (200 mg), temp. (403 K), time (3 h).	100	85	36
MOF-808	2-Propanol	Ethyl levulinate (1.0 mmol), 2-propanol (6 mL), catalyst (200 mg), temp. (403 K), time (3 h).	28.1	12.2	36
ZrFeO(1:1)-110	2-Propanol	Ethyl levulinate (4.5 mmol), 2-propanol (15 mL), catalyst (200 mg), temp. (503 K), time (0.5 h).	97.5	85.7	44
$Zr(OH)_4$	2-Propanol	Ethyl levulinate (13.8 mmol), 2-propanol (48.3 mL), catalyst	93.6	94.5	34

		(1 g), temp. (473 K), time (1 h).			
Zr-PhyA	2-Propanol	Ethyl levulinate (1 mmol), 2-propanol (4 mL), catalyst (200 mg), temp. (403 K), time (8 h).	98.9	95.4	45
ZrO_2	2-Propanol	Ethyl levulinate (1 mmol), 2-propanol (4 mL), catalyst (200 mg), temp. (403 K), time (8 h).	10.5	7.8	45