

Supporting Information

Improving the hydrodeoxygenation activity of vanillin and its homologous compounds by employing MoO₃-incorporated Co-BTC MOF derived MoCoO_x@C

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Characterization

Powder X-ray diffraction (XRD) patterns were recorded on the Rigaku Miniflex III diffractometer (30 kV and 10 mA). The surface area of the catalyst was determined by Nitrogen sorption measurements performed at -200 °C by Quantachrome Instruments. The sample was degassed at 200 °C for 3 h in the degassing port of the adsorption apparatus. The surface area of the catalyst was calculated from the adsorption data points obtained for P/P_0 between 0.05-0.3 using the Branauer-Emmette-Teller (BET) equation. The Field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6610LV) was used for the morphological investigation. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 transmission electron microscope operating at 200 kV. The metal content of Mo and Co in present in all the carbonized material was determined by Agilent's microwave-plasma atomic emission spectrometer (MP-AES). The surface composition of the catalyst was investigated by X-ray photoelectron spectroscopy (XPS) analysis by an XPS system PHI 5000 VersaProbeII (ULVAC-PHI, INC, Japan) with a microfocus (100 μ m, 25 W, 15 kV) monochromatic Al-K α source ($h\nu = 1486.6$ eV), a hemispherical analyzer and a multichannel detector. The ammonia temperature-programmed desorption (NH₃-TPD), hydrogen temperature-programmed reduction (H₂-TPR), hydrogen temperature-Programmed Desorption (H₂-TPD) were carried out on a Quantachrome, CHEMBETTM TPR/TPD instrument using diluted NH₃ (10 % in He), H₂ (5 % in He) as the probe gases. The sample was preheated at 150 °C at a heating rate of 10 °C /min under a continuous He gas flow for 30 min. Then, after cooling to 50 °C, H₂ gas or NH₃ gas was allowed to adsorb on the sample for 1 h. After adsorption, the temperature was ramped, and the desorption of H₂ or NH₃ was recorded by a TCD detector as a function of temperature. For TPR measurement, after sample degassing, the H₂ consumption was recorded under the continuous gas flow (10 ml/min) as a function of temperature on a TCD detector.

Experimental section

Catalyst preparation: At first, MoO₃ was synthesized by a reported method with few modifications.¹ 20 mL aqueous solution of 0.2 M ammonium heptamolybdate tetrahydrate was taken and continuously stirred for 10 min. Afterward, 5 mL concentrated nitric acid was added dropwise and the resultant solution was subjected to a probe sonication for 1 h. Finally, the white precipitate was washed with water and ethanol several times and then dried under a vacuum oven at 70 °C.

Co-BTC MOF was prepared using a solvothermal method.² Co(NO₃)₂·6H₂O (1.2 g) was dissolved in 5 mL H₂O, and H₃BTC (0.5 g) was dissolved in 35 mL of ethanol. After 30 min, these solutions were mixed together and sonicated for 1 h. The resultant solution was transferred to a Teflon-lined autoclave and heated at 150 °C for 24 h. The resulting precipitate was washed several times with water and finally with ethanol three times and dried under a vacuum at 80 °C for 12 h. For the synthesis of MoO₃@Co-BTC MOF, first, a desired amount of MoO₃ was dispersed in ethanol, Co(NO₃)₂·6H₂O was added to this solution, followed by the addition of H₃BTC according to the above procedure. Various loading of MoO₃ (100 mg, 200 mg, and 300 mg) containing Co-BTC was prepared and designated as MoO₃@Co-BTC-1, MoO₃@Co-BTC-2, and MoO₃@Co-BTC-3 respectively. Finally, the synthesized precursors were subjected to pyrolysis under a static nitrogen atmosphere at 550 °C for 30 min to obtain MoCoO_x@C-x (x = 1, 2 and 3). Similarly, when the bare Co-BTC MOF was carbonized under a similar condition, CoO_x@C was obtained, and for Co@C, it was carbonized under 10 % H₂ in Ar atmosphere. The metallic contents present in all the carbonized catalysts were determined using MP-AES analysis, and the values are given below in Table S1.

Hydrodeoxygenation of vanillin

Vanillin (1 mmol), catalyst (40 mg), and H₂O (10 mL) were charged into a high-pressure Parr reactor. The reactor was purged with H₂ gas three times. Finally, the reactor was pressurized to 7 bar and heated to 150 °C for 1.5 h. After the reaction, the reaction mixture was extracted with ethyl acetate and analyzed using GC (GC, Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 mm). The product was confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra Rtx - 5 Sil Ms; 30 m × 0.25 mm × 0.25 mm). The recovered catalyst was washed with water and ethanol for subsequent use in the recycling study.

Quantification of products

The reactant conversion and product selectivity were determined by calculating the response factor obtained from the GC calibration using a standard addition method. For example, GC calibration curves for vanillin, vanillyl alcohol, and MMP are given below in order to find out the vanillin conversion and product (vanillyl alcohol and MMP) selectivity.

The standards containing a fixed concentration of n-decane with different concentrations of vanillin, vanillyl alcohol, and MMP were prepared in ethyl acetate. Solutions were injected in GC (triplicate injection), and the area was recorded. After the analysis, the calibration curve was plotted with concentration (g/L) vs peak area (Figure S1), and the vanillin

conversion and its corresponding product selectivity (vanillyl alcohol and MMP) were determined using the following expression.

$$\text{Vanillin conversion} = \frac{C_0 - C_t}{C_0} \times 100\%$$

$$\text{Product selectivity} = \frac{C_p}{C_0 - C_t} \times 100\%$$

where C_0 is the initial concentration of vanillin, C_t is the vanillin concentration after time t , and C_p is the concentration of product (vanillyl alcohol/MMP) at time t .

The response factors for reactant and product were calculated using the following equation. For the calculation of the response factor, n-decane was used as an internal standard in the reaction mixture. The calculated response factors (RFs) were 0.23 for vanillin, 0.216 for vanillyl alcohol, and 0.564 for MMP.

$$\frac{\text{Area}(x)}{[x]} = F \frac{\text{Area}(s)}{[s]}$$

Where F is the response factor, $\text{Area}(x)$ and $\text{Area}(s)$ are areas under the peaks for analyte and n-decane, respectively. $[x]$ and $[s]$ are the concentrations of Analyte and n-decane, respectively.

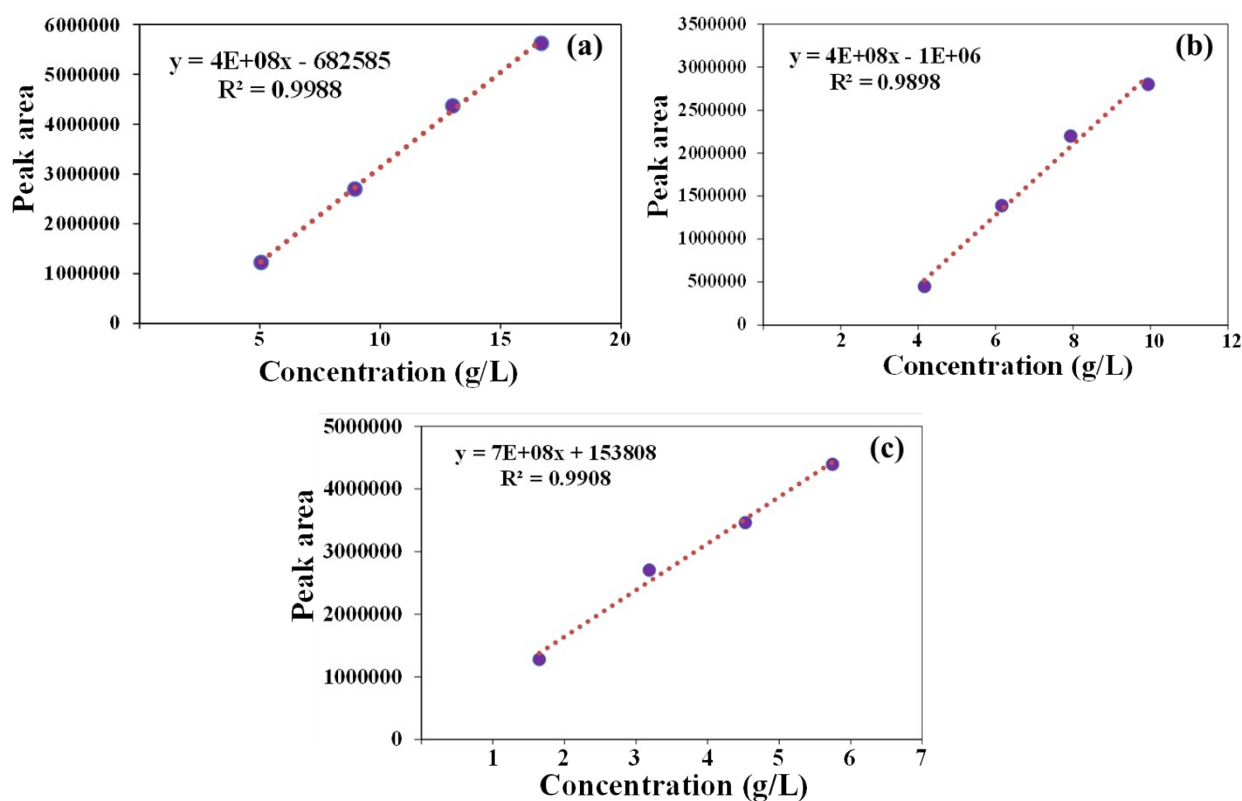


Fig. S1 Calibration curves for (a) vanillin, (b) vanillyl alcohol, and (c) MMP.

Table S1 Wt% of metals present in CoO_x@C, Co@C, MoCoO_x@C-1, MoCoO_x@C-2, and MoCoO_x@C-3 estimated using MP-AES analysis.

Catalyst	Co content (wt%)	Mo content (wt%)	Mo/Co (Wt ratio)
CoO _x @C	35.6	NA	NA
Co@C	34.9	NA	NA
MoCoO _x @C-1	29.6	11.4	0.38
MoCoO _x @C-2	25.8	19.2	0.74
MoCoO _x @C-3	22.3	24.9	1.11
MoCoO _x @C-2 (spent)	25.1	18.8	0.75

Table S2 Textural properties of various synthesized materials.

Sample	BET surface area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Pore size (nm)
Co-BTC MOF	129	0.39	3.8
MoO ₃ @Co-BTC-2	33	0.13	4.0
MoCoO _x @C-1	112	0.30	4.5
MoCoO _x @C-2	104	0.26	4.1
MoCoO _x @C-3	98	0.21	4.2

Table S3 Surface atomic concentration of elements presents in MoCoO_x@C-2 and MoCoO_x@C-3, obtained from XPS analysis.

Elements	Atomic % in MoCoO _x @C-2	Atomic % in MoCoO _x @C-3
Co	7.3	5.4
Mo	4.1	6.1
C	67.5	66.1
O	21.1	22.4

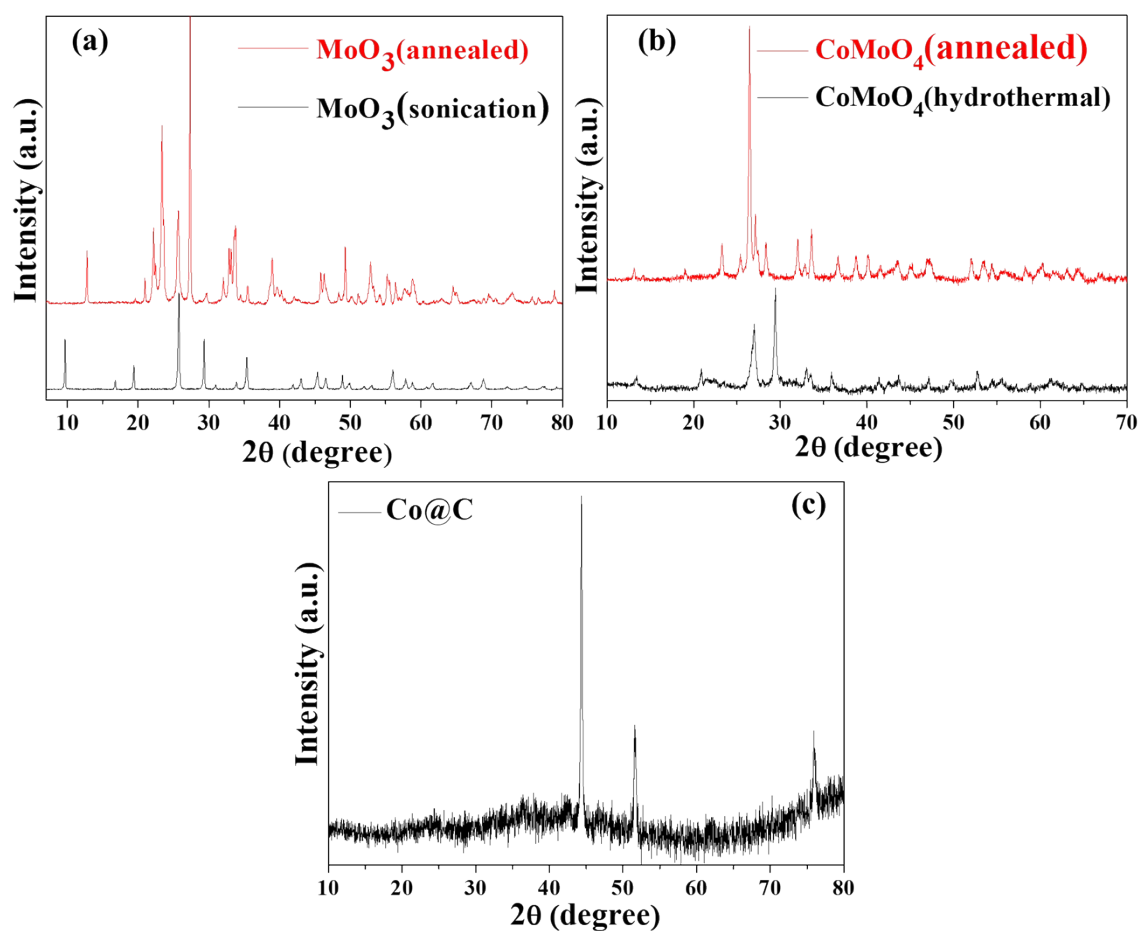


Fig. S2 Powder XRD patterns of (a) MoO_3 prepared in both the sonication method and annealed at 550°C under N_2 , (b) CoMoO_4 prepared under hydrothermal method and annealed at 550°C under N_2 and (c) Co@C .

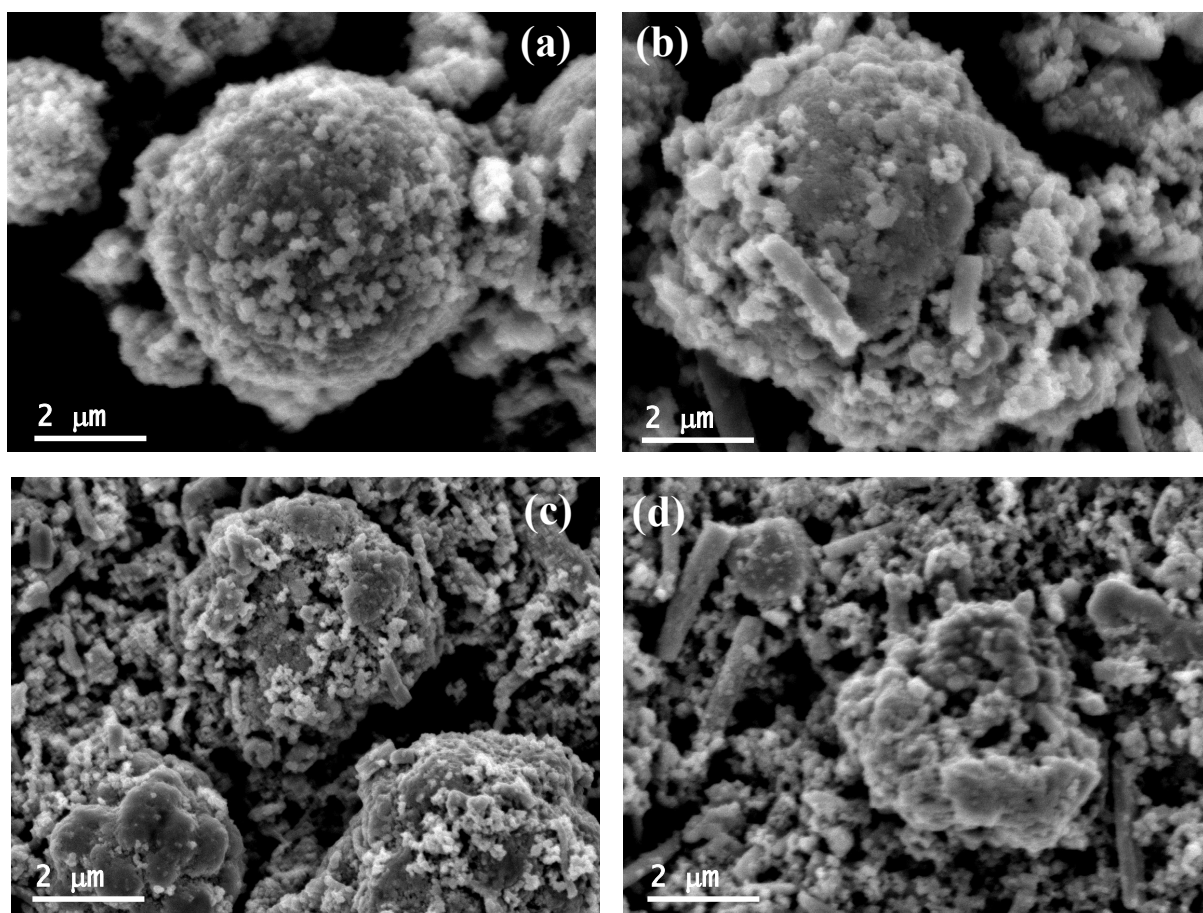


Fig. S3 SEM images of (a) CoO_x@C, (b) MoCoO_x@C-1, (c) MoCoO_x@C-2, and (d) MoCoO_x@C-3.

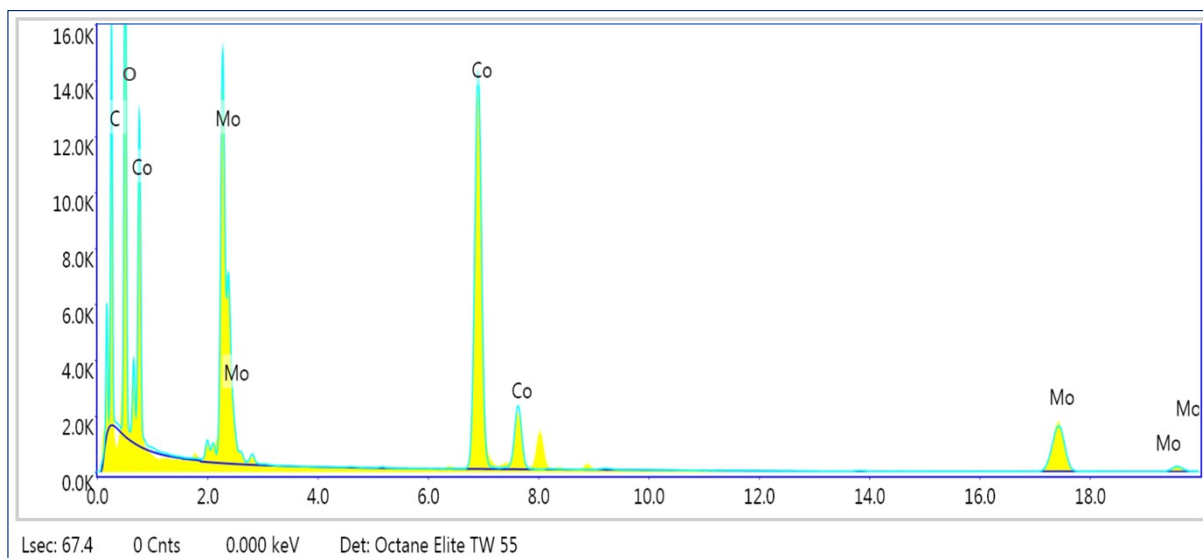


Fig. S4 EDS spectrum of MoCoO_x@C-2.

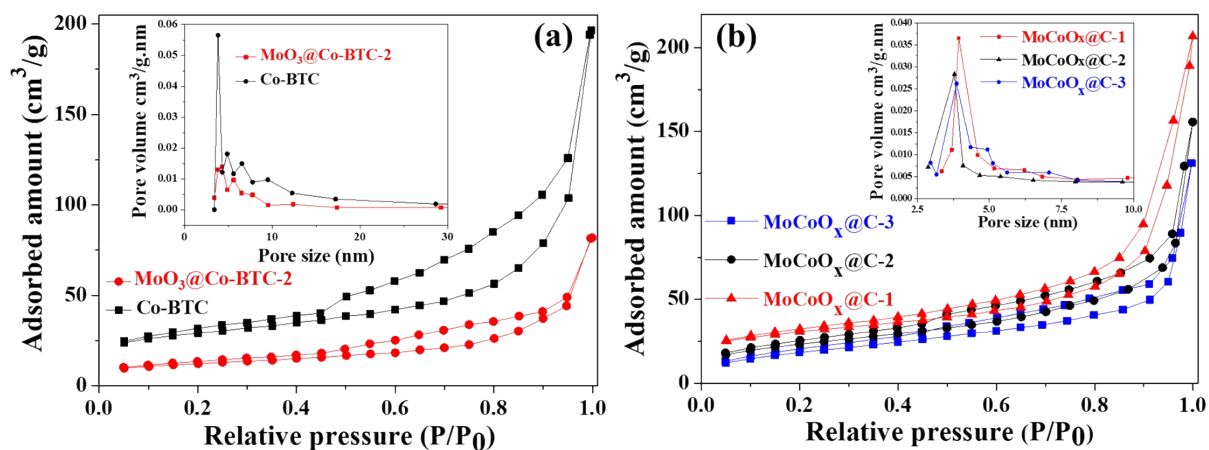


Fig. S5 N₂ adsorption-desorption isotherms and BJH pore size distribution of (a) Co-BTC and MoO₃@Co-BTC-2, (b) MoCoO_x@C-1, MoCoO_x@C-2 and MoCoO_x@C-3.

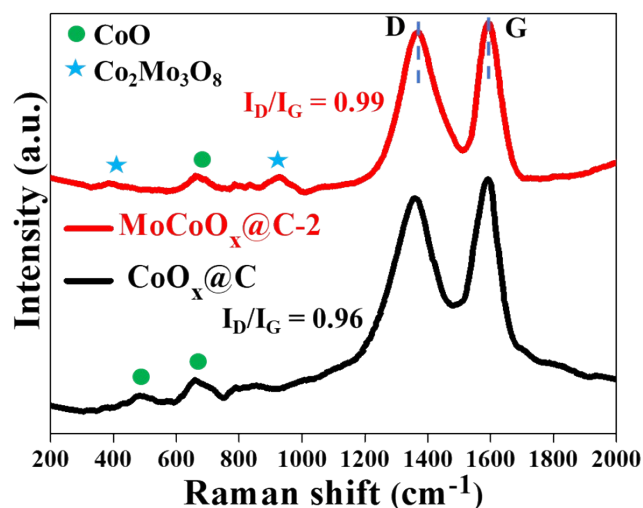


Fig. S6 Raman spectra of CoO_x@C and MoCoO_x@C-2.

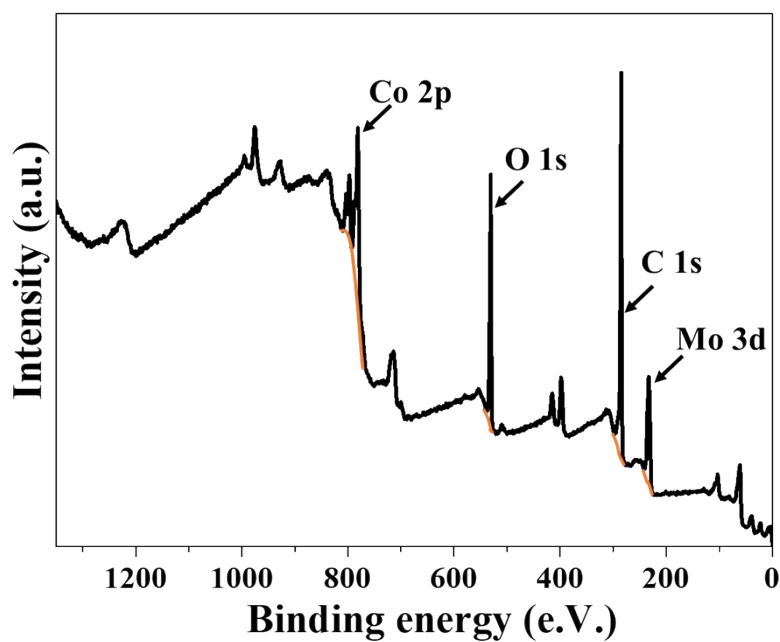


Fig. S7 XPS surface survey analysis of MoCoO_x@C-2.

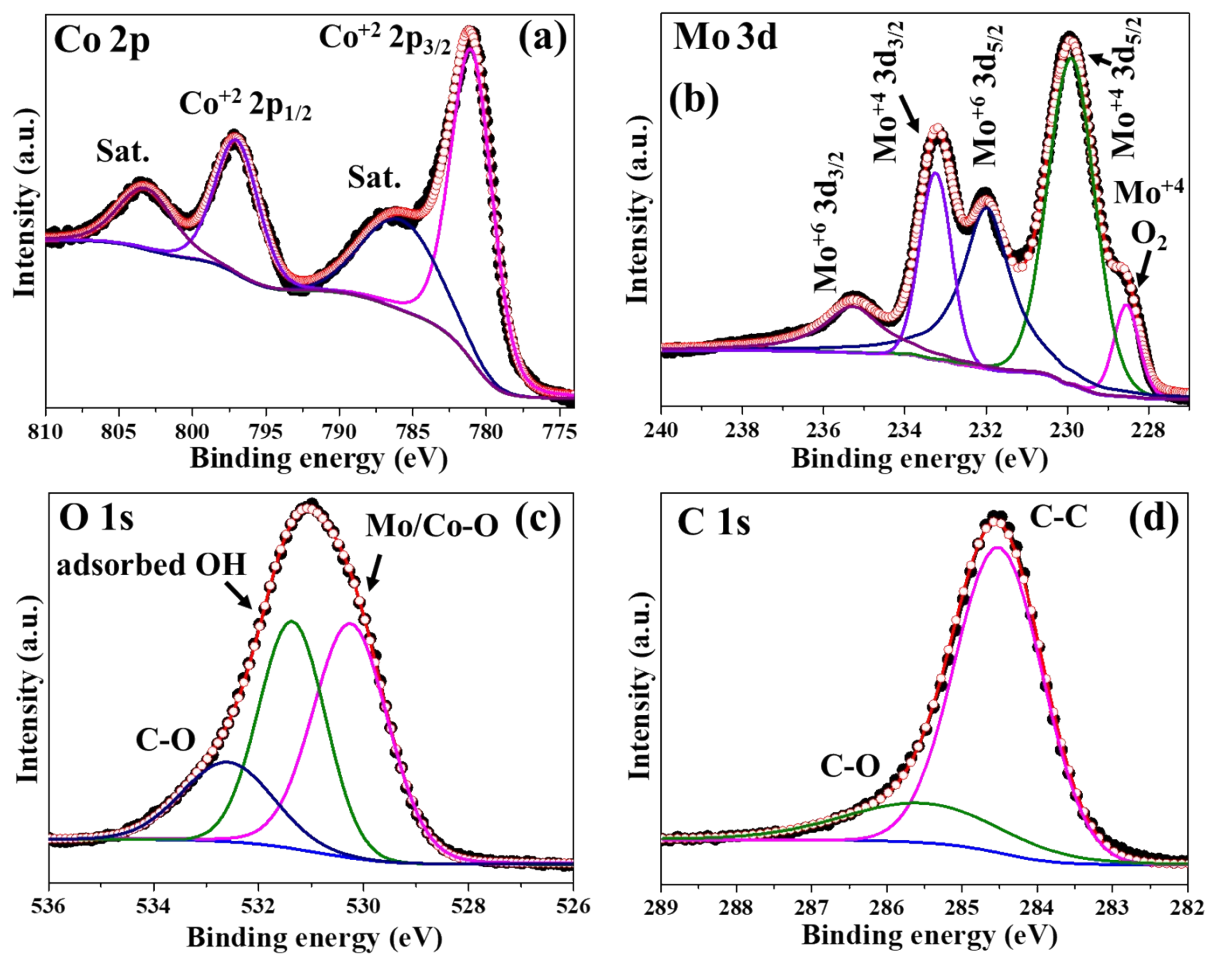


Fig. S8 High resolution XPS spectra of (a) Co 2p, (b) Mo 3d, (c) O 1s, and (d) C 1s of MoCoO_x@C-3.

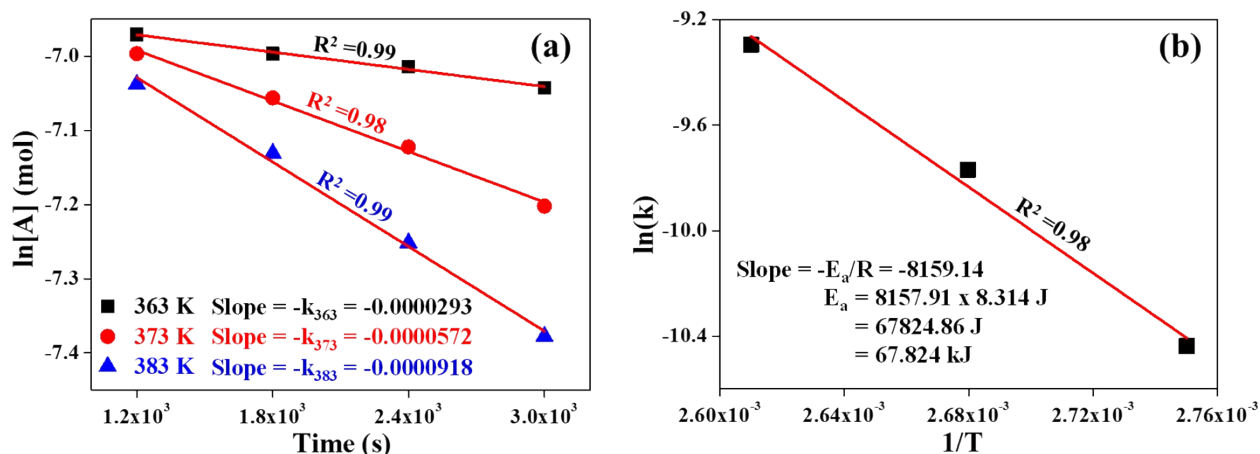


Fig. S9 (a) Temperature – time plot and (b) $\ln(k)$ vs. $1/T$ (Arrhenius plot) for the vanillin conversion using $\text{MoCoO}_x@\text{C-2}$ catalyst.

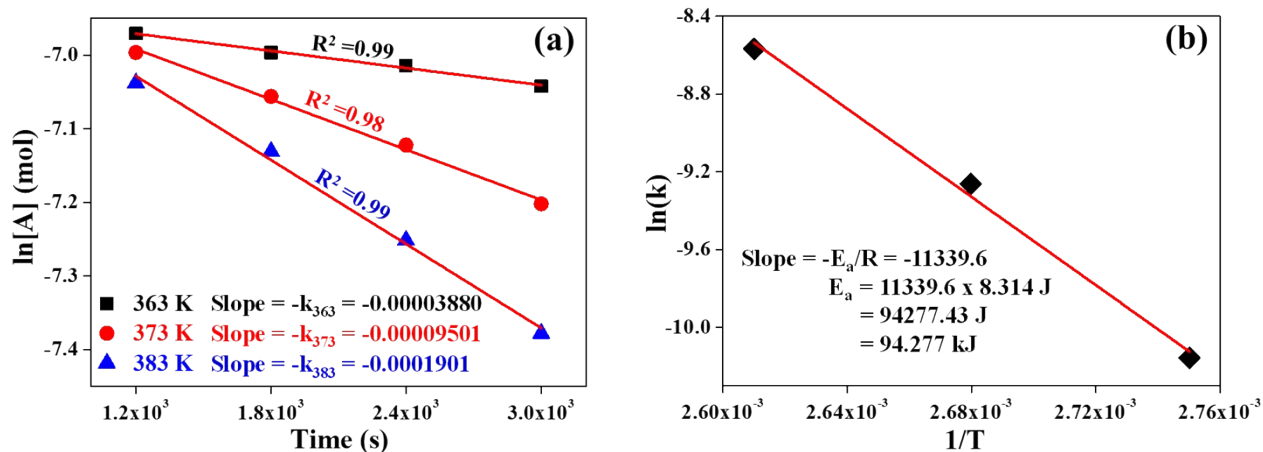


Fig. S10 (a) Temperature – time plot and (b) $\ln(k)$ vs. $1/T$ (Arrhenius plot) for the vanillyl alcohol conversion using $\text{MoCoO}_x@\text{C-2}$ catalyst.

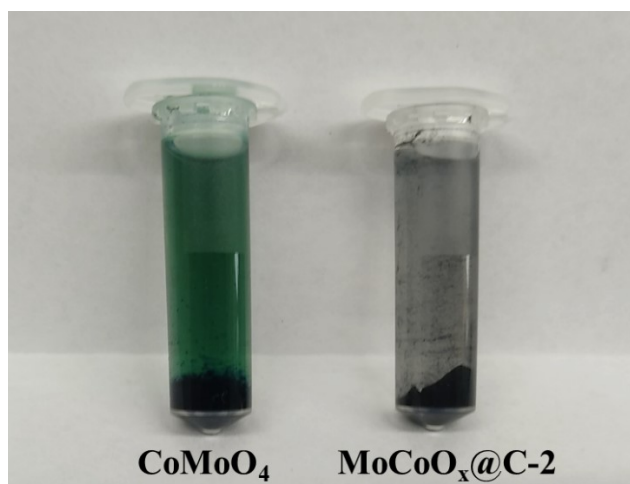


Fig. S11 Photograph of the reaction mixture carried out using CoMoO_4 and $\text{MoCoO}_x@\text{C-2}$ catalyst.

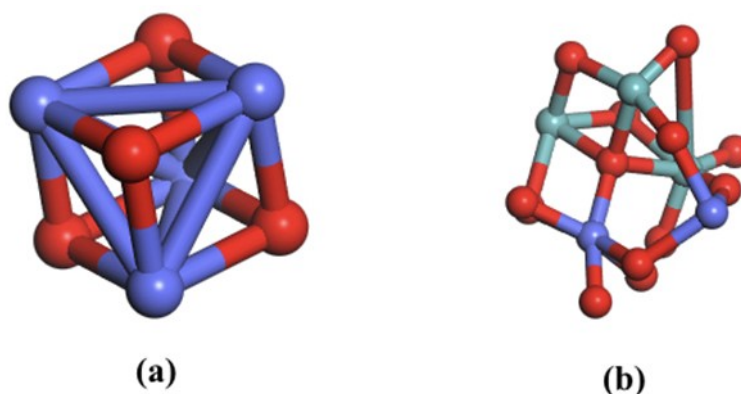


Fig. S12 The optimized geometries of CoO (a) and $\text{Co}_2\text{Mo}_3\text{O}_8$ (b) model systems obtained at the GGA-PBE/DND level of theory which resembles the $\text{CoO}_x@\text{C}$ and $\text{MoCoO}_x@\text{C-2}$ catalyst respectively. The red, blue, and green colors indicate oxygen, cobalt, and molybdenum atoms, respectively.

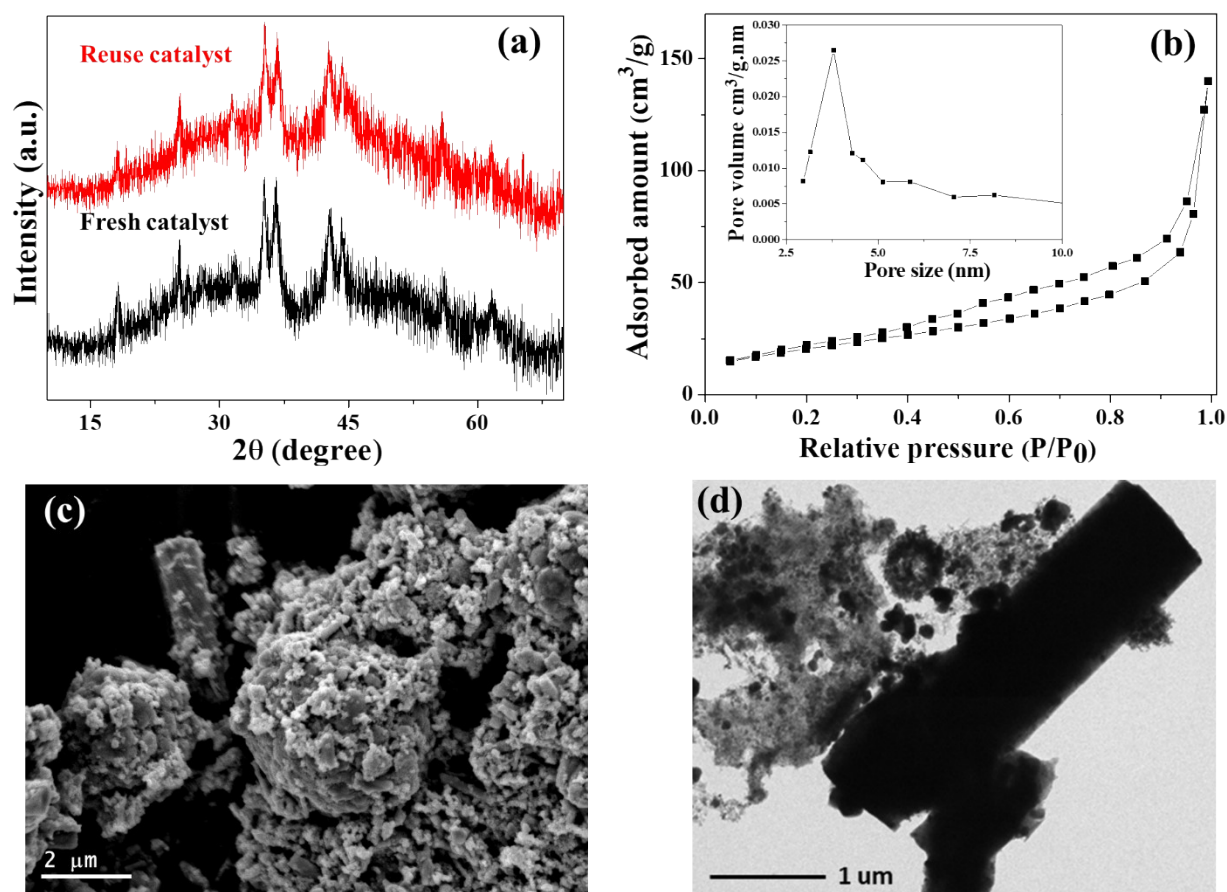


Fig. S13 (a) PXRD of fresh and spent catalysts, (b) N_2 adsorption-desorption isotherm and BJH pore size distribution of spent catalyst, (c) SEM image of spent catalyst and (d) TEM image of spent catalyst.

References

- [1] H. Hu, C. Deng, J. Xu, K. Zhang and M. Sun, *J. Exp. Nanosci.*, 2015, **10**, 1336–1346.
- [2] T. Li, C. Li, X. Hu, X. Lou, H. Hu, L. Pan, Q. Chen, M. Shen and B. Hu, *RSC Adv.*, 2016, **6**, 61319–61324.