

*Article*

# Esterification of Levulinic Acid to Methyl Levulinate over Zr-MOFs Catalysts

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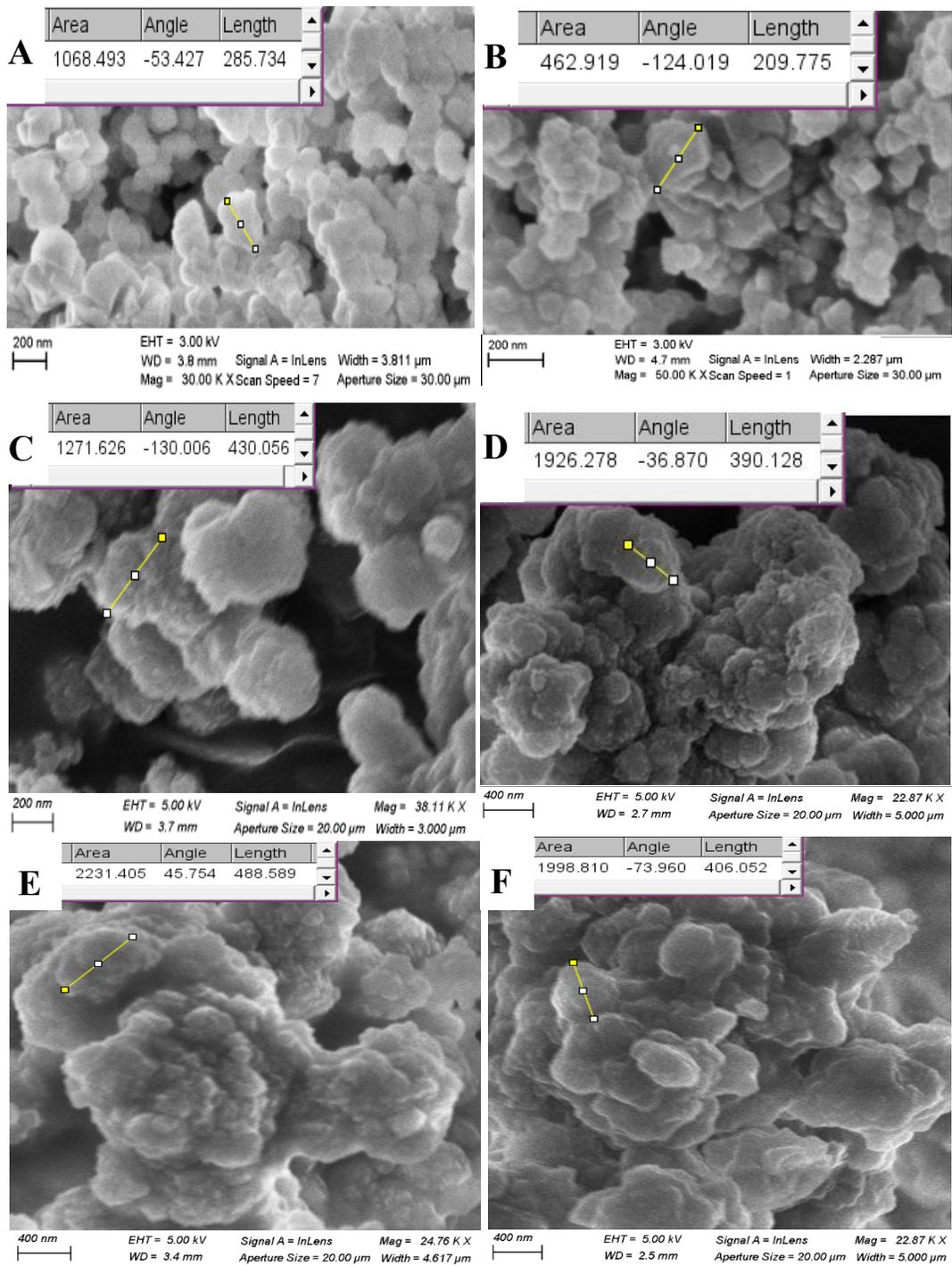
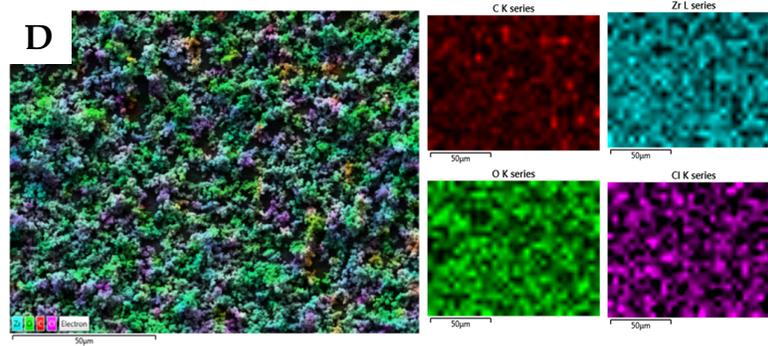
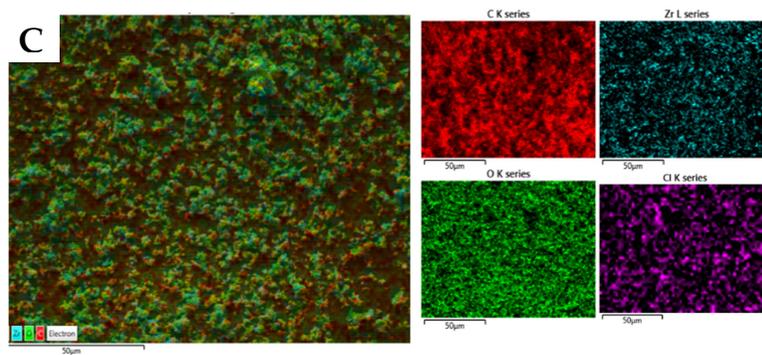
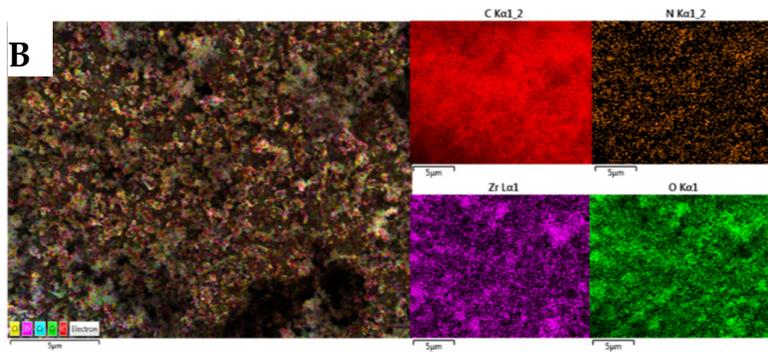
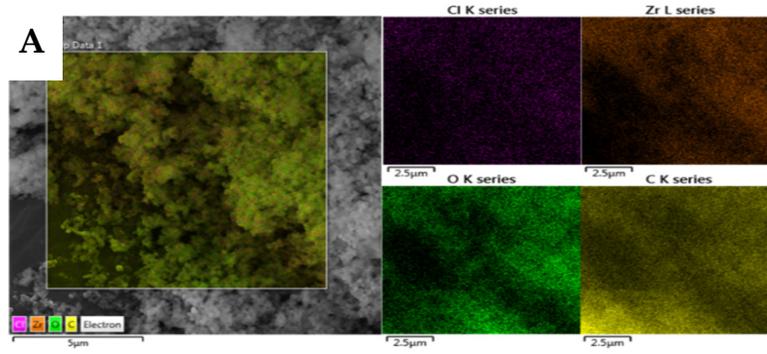


Figure S1. SEM image with average particle size included. (A) M<sub>A</sub>, (B) M<sub>B</sub>, (C) M<sub>A-U</sub>, (D) M<sub>B-U</sub>, (E) M<sub>A-UT</sub> and (F) M<sub>B-UT</sub>.



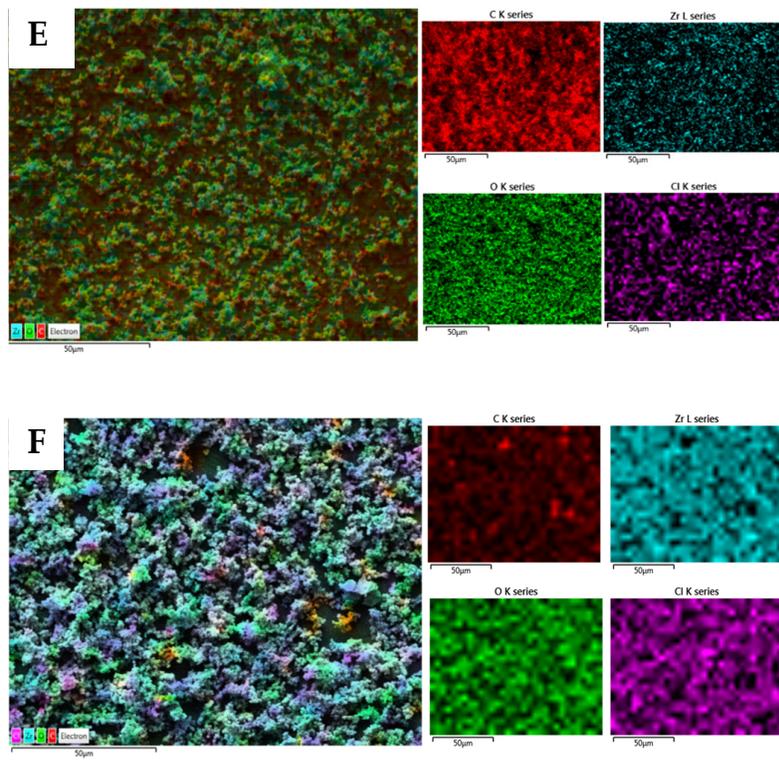
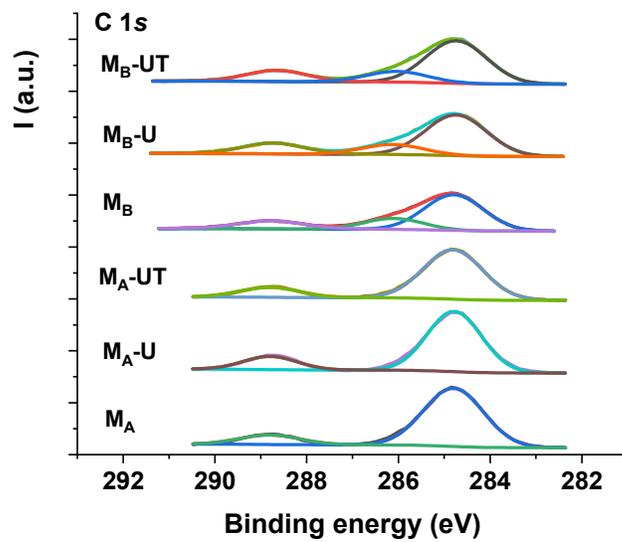


Figure S2. SEM elemental mapping of the (A)  $M_A$ , (B)  $M_B$ , (C)  $M_{A-U}$ , (D)  $M_{B-U}$ , (E)  $M_{A-UT}$  and (F)  $M_{B-UT}$ .



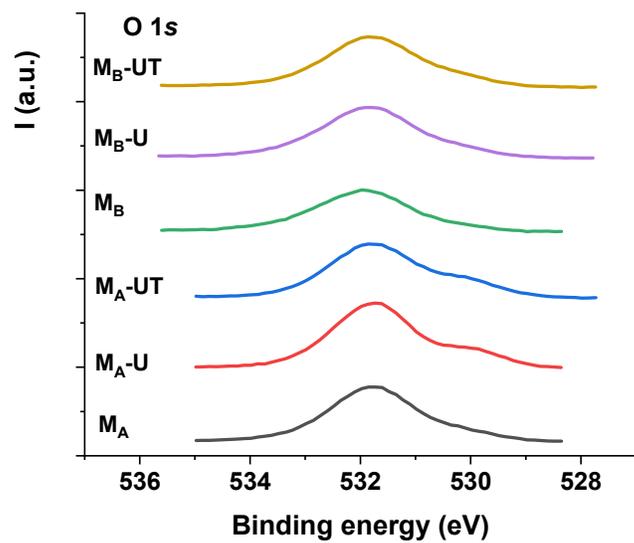


Figure S3. C 1s and O 1s core level spectra for samples MOF.

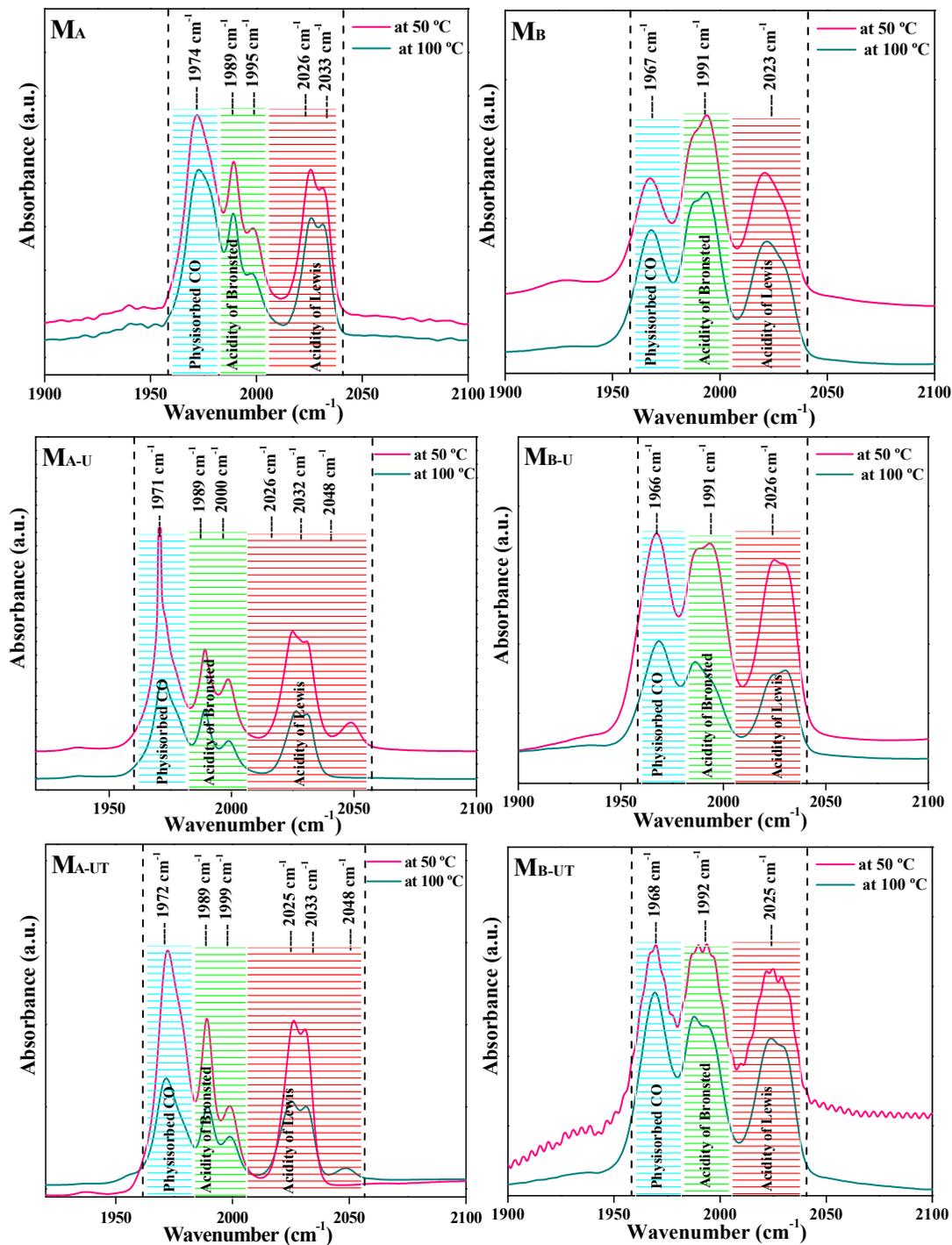


Figure S4. CO-FTIR absorption spectra. Contributions of 50 and 100 °C.

The experimental data were fitted in a pseudo-first order kinetic equation to find the constant of reaction  $k$  (Eq. 1).

$$\ln[\text{LA}_t] = -k t + \ln[\text{LA}_0] \quad (\text{S1})$$

Where  $[\text{LA}_0]$  is the initial concentration of LA ( $\text{mol.L}^{-1}$ ) and  $[\text{LA}_t]$  is the concentration at any time  $t$ . On the other hand,  $k$  is the slope and  $\ln[\text{LA}_0]$  is the intercept in a plot of  $\ln[\text{LA}_t]$  versus  $t$  (Fig. S5).

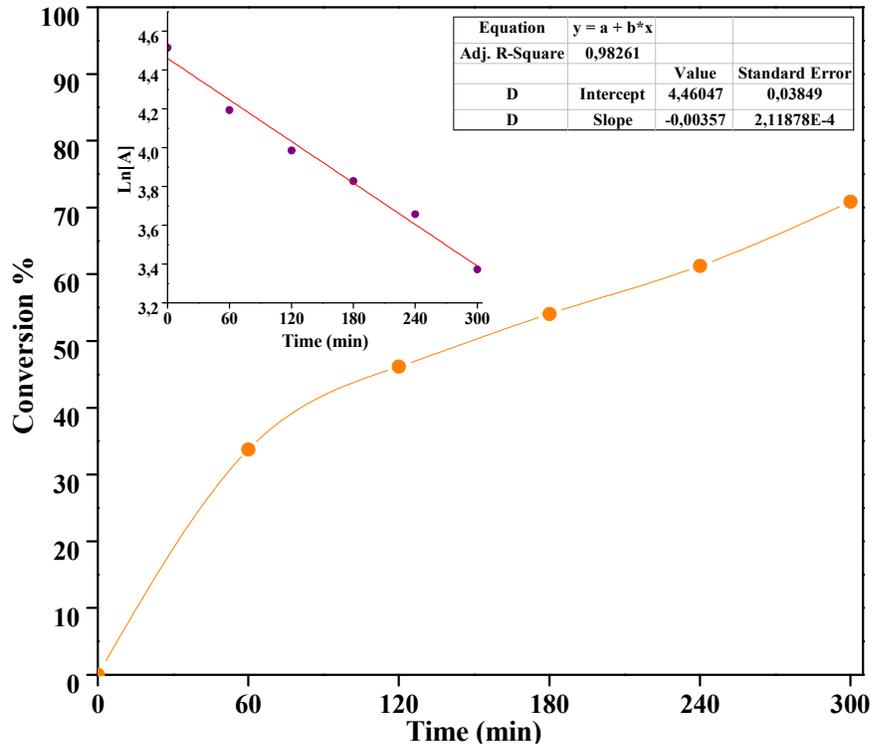
Therefore, the reaction rate can be expressed as:

$$r_A = - \frac{dC_{LA}}{dt} = k C_{LA} \quad (S2)$$

Table S1 shows experimental data used in the kinetic model.

**Table S1.** Estimation of kinetic parameters

Time (min)	% Conversion	[A]	Ln [A]
0	0	91.52802	4.51665
60	33.76	66.24109	4.1933
120	46.17	53.83173	3.98586
180	54.05	45.95343	3.82763
240	61.27	38.73362	3.65671
300	70.87	29.13334	3.37188



**Figure S5.** Kinetic constant adjustment (k)

**Table S2.** Data for equation of Arrhenius

Temperature [K]	1/T	K [s-1]	Ln (k)
328.15	0.00305	$0.0021 * 1/60 = 3.50 E^{-5}$	-10.26016
333.15	0.00300	$0.00285 * 1/60 = 4.75 E^{-5}$	-9.95478
338.15	0.00296	$0.00375 * 1/60 = 5.95 E^{-5}$	-9.72953

$$\frac{-E_a}{R_g} = -5892.0653 \rightarrow E_A = 5892.0653 \text{ K} * 8.3143 \frac{\text{J}}{\text{mol K}} \rightarrow E_A = 48988.40 \frac{\text{J}}{\text{mol}}$$

$$\text{Ln (A)} = 7.70709 \rightarrow A = e^{7.70709} \rightarrow A = 2224.06$$

$$E_a = 48.99 \text{ kJ/mol}$$

$$A = 2224.06$$

$$\text{con } R^2 = 0.988$$

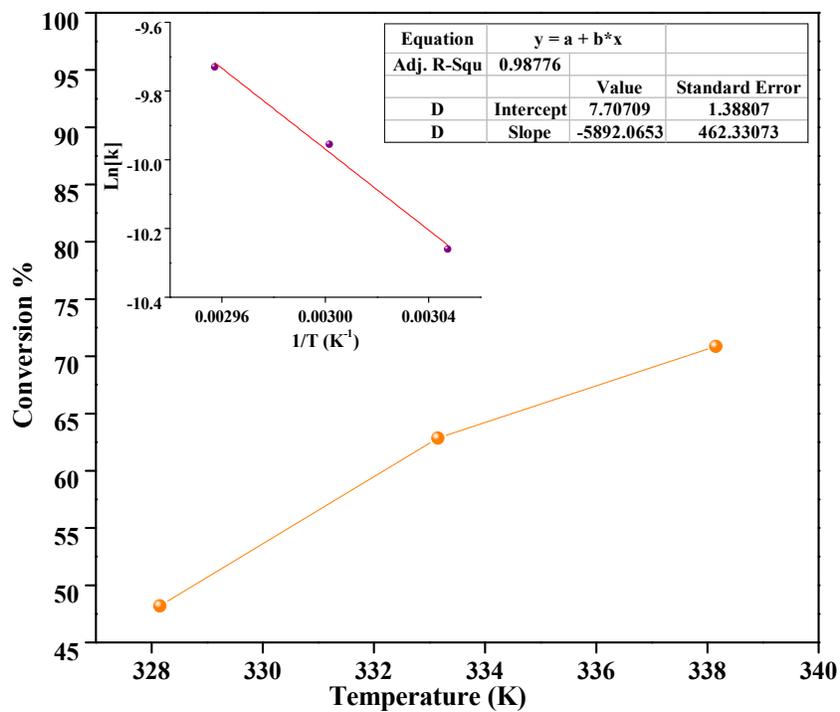


Figure S6. Adjust activation energy ( $E_a$ ) and pre-exponential factor ( $A$ )

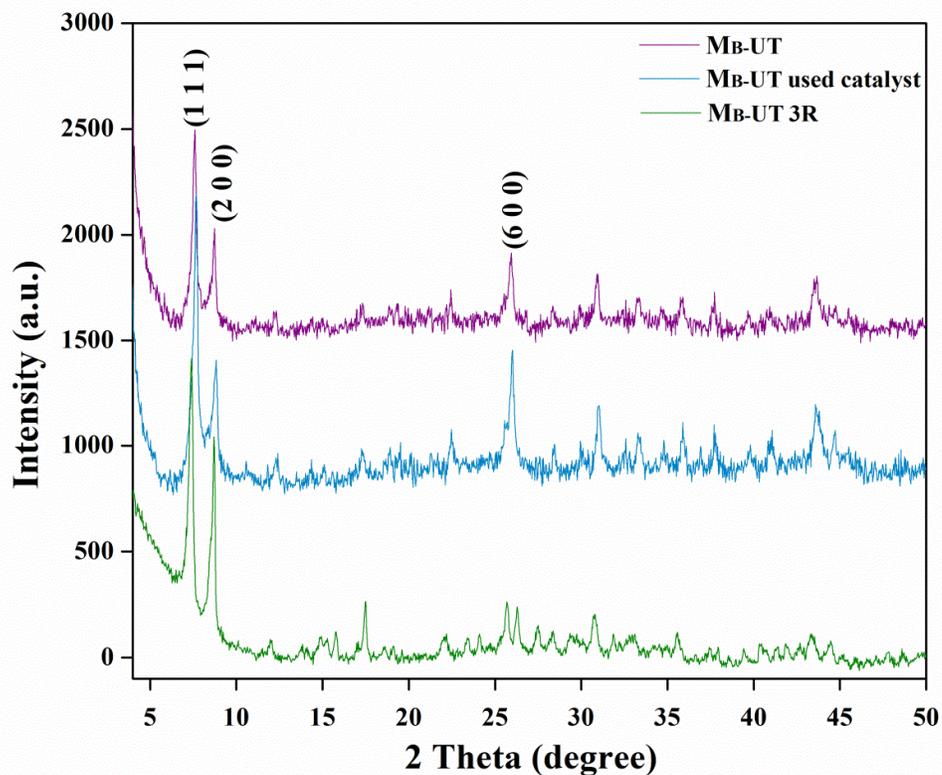


Figure S7. XRD patterns for MB-UT catalyst.