Electronic Supporting Information

Green synthesis of furfural acetone by solvent free aldol condensation of furfural with acetone over La_2O_3-MgO mixed oxide catalyst

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1. Catalyst preparation

Hydrothermal synthesis method

The typical process for the synthesis of La_1Mg_3MO-H follows: 2.1 g $La(NO_3)_3 \cdot 9H_2O$, 3.86 g $Mg(NO_3)_2 \cdot 6H_2O$ and 6 g urea were dissolved in 150 mL distilled water and stirred for 1 h until the solution became homogeneous. Then it was transferred into a Teflon lined bomb reactor and heated to 160 °C for 12 h in temperature controlled oven. The solid material obtained was then washed with distilled water. After filtration, it was dried at 120 °C. The same procedure was followed for preparation of MgO-H and La_2O_3-H and then calcined at 650 °C for 4 h.

2. GC and GC-MS analysis

Figure S1 shows the GC spectra of reaction mixture with retention time at 4.19, 5.12, 10.92 and 15.37 corresponds to the mesityl oxide, furfural, n-dacane and furfural acetone (FAc) respectively. And the identification of product (FAc) of the reaction using GCMS spectra in Figure S2.

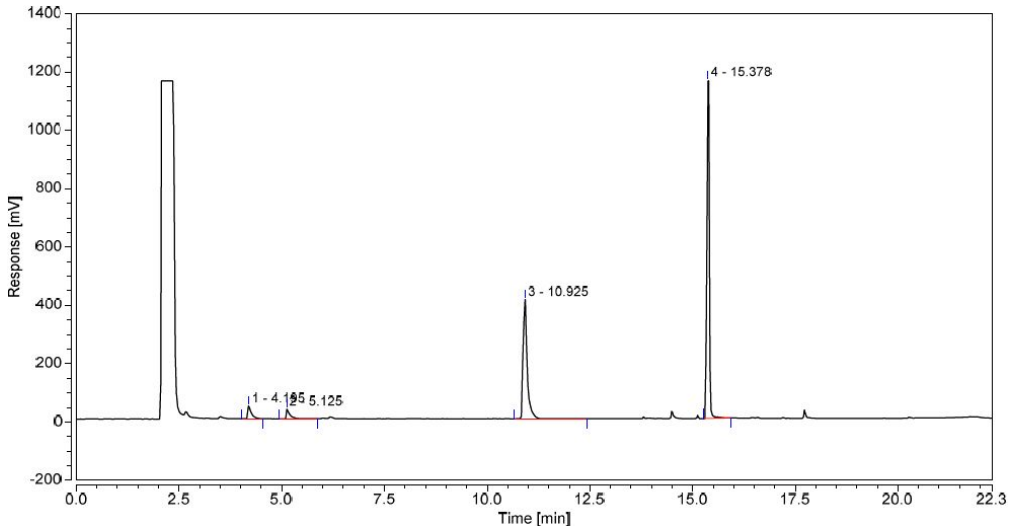

Figure S1. GC spectra of reaction mixture

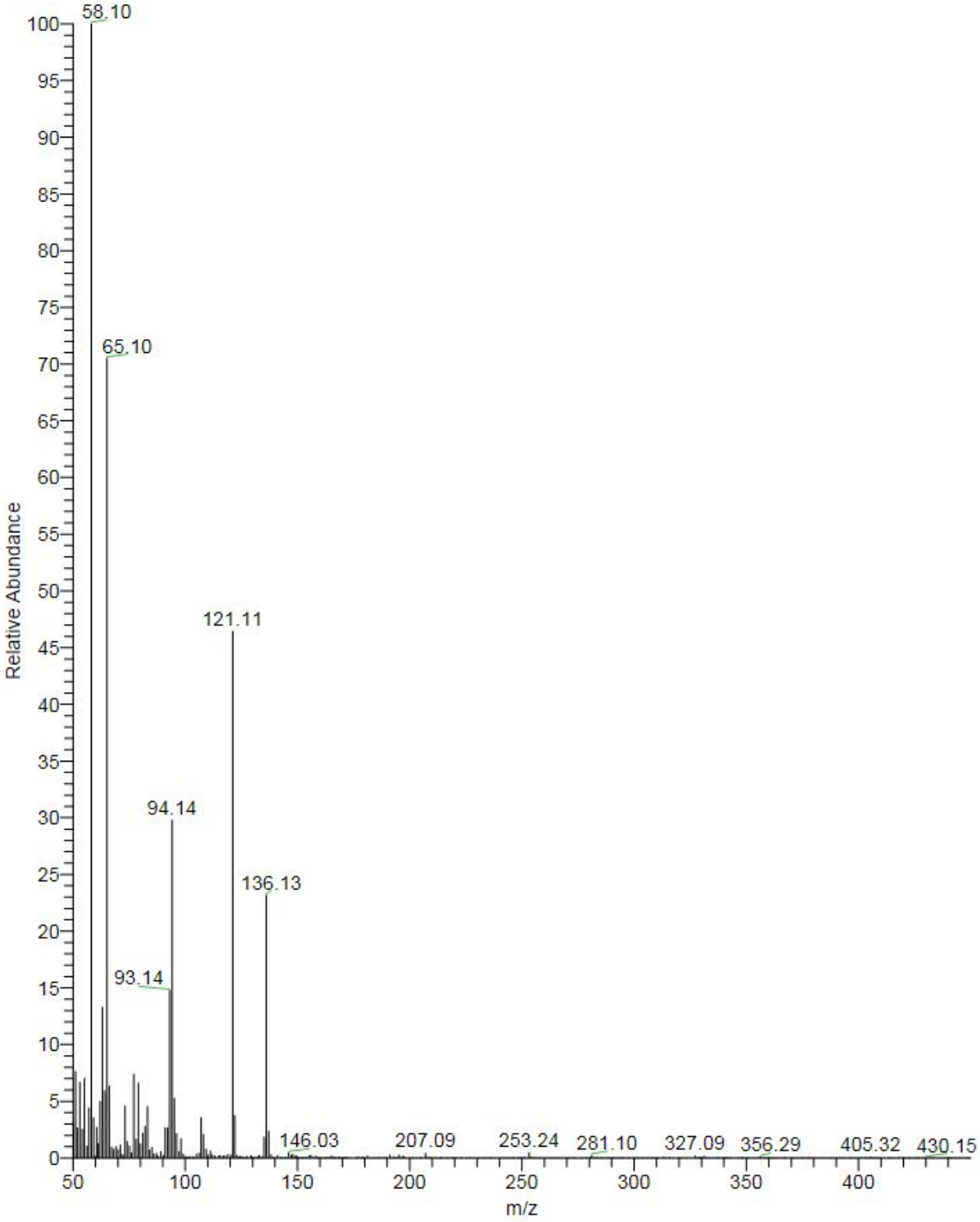

Figure S2. GCMS spectra of FAc

3. XRD

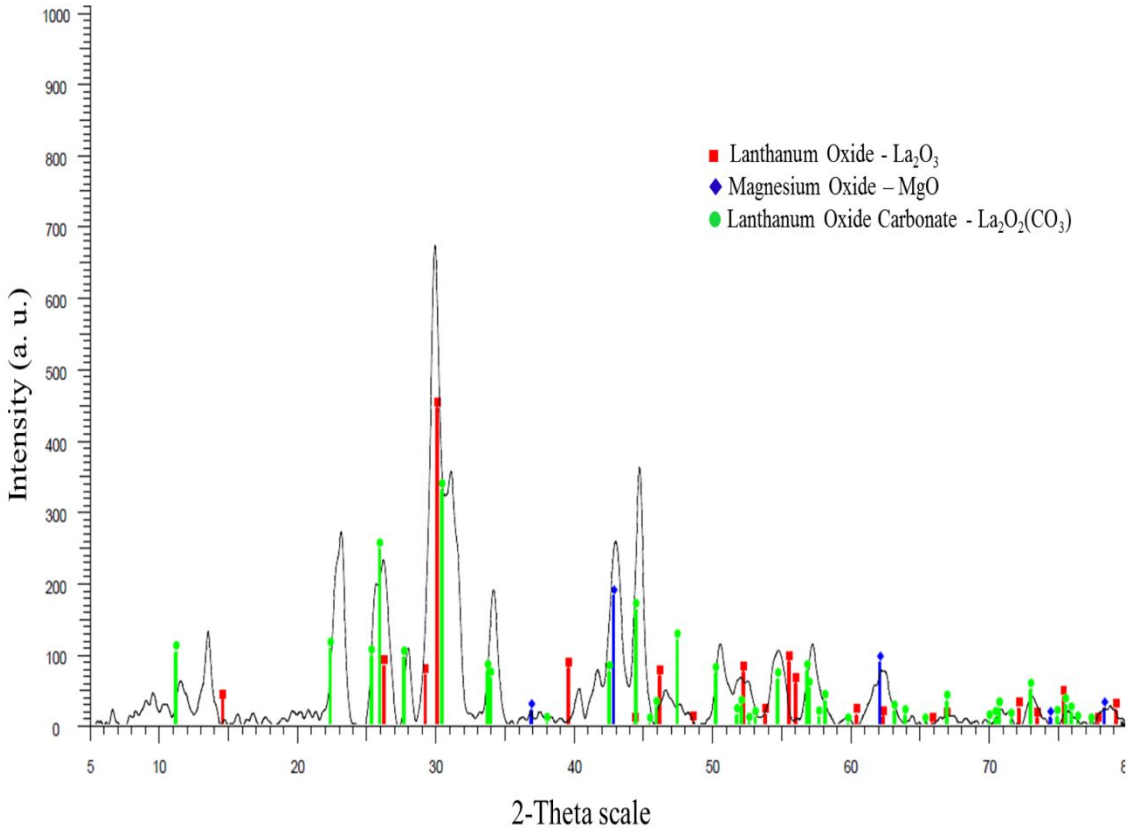

Figure S3. XRD of pattern of La_1Mg_3MO-H catalyst

4. Rietveld refinement of La_1Mg_3MO-H catalyst

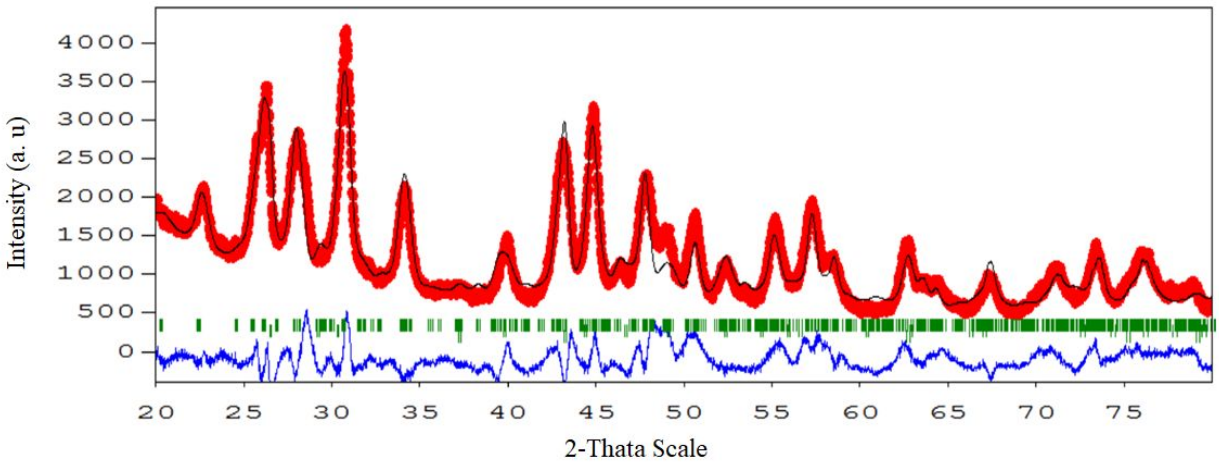

Figure S4. Rietveld refined XRD pattern of La_1Mg_3MO-H catalyst

5. Individual FTIR of the catalysts

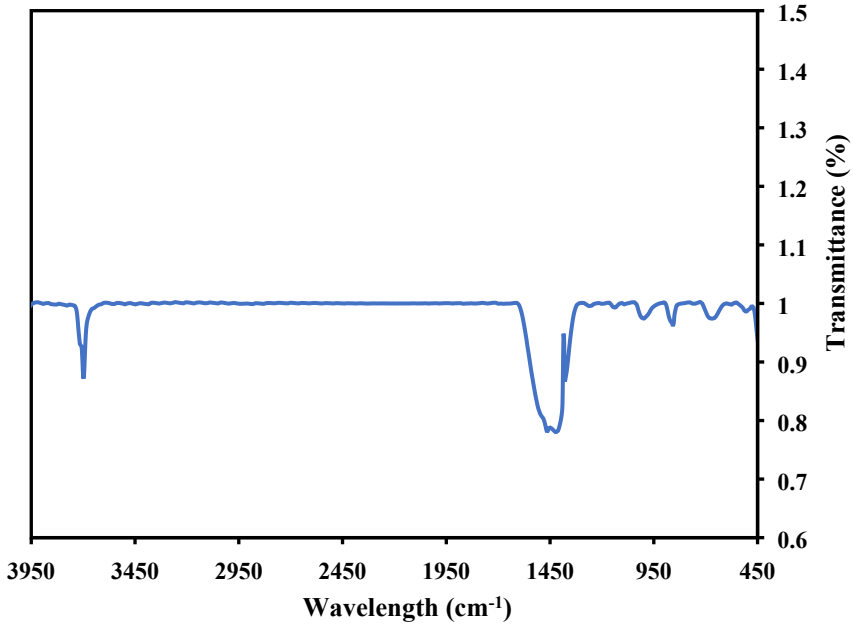

Figure S5 (a). FTIR spectra of MgO-H

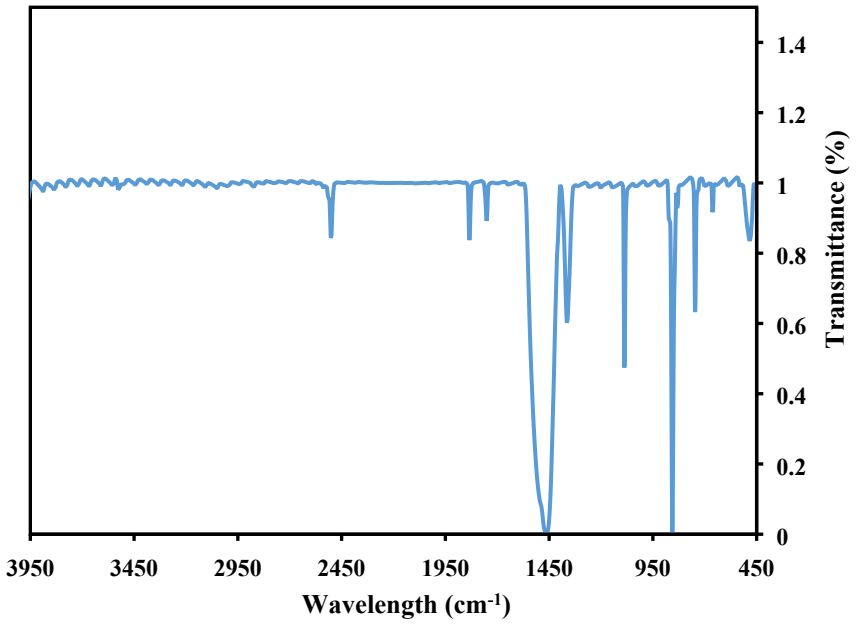

Figure S5 (b). FTIR spectra of La_2O_3-H

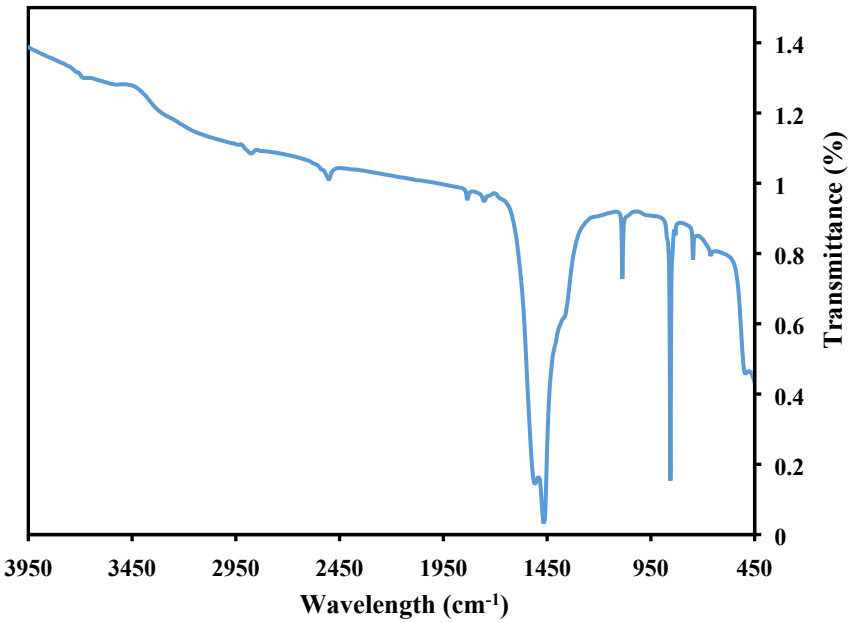

Figure S5 (c). FTIR spectra of La_1Mg_1MO-H

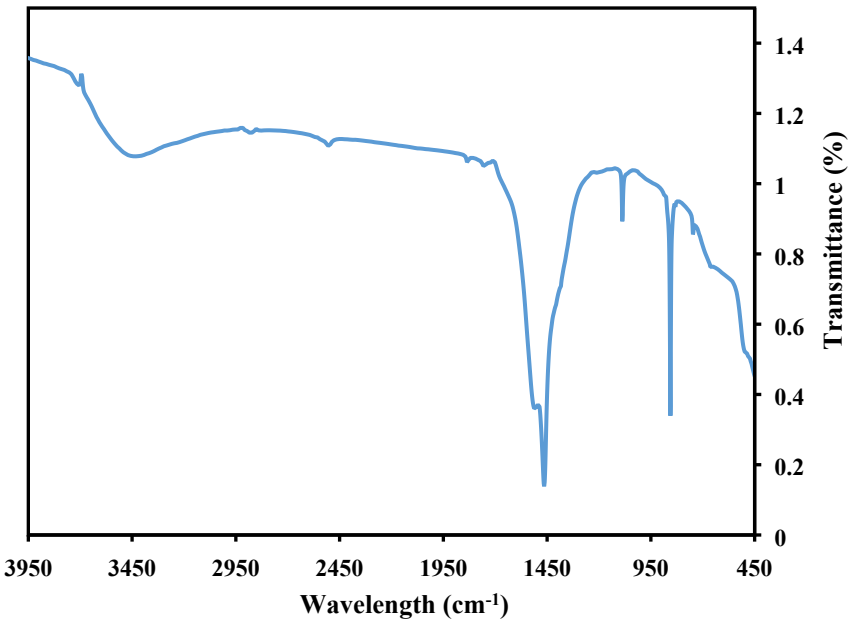

Figure S5 (d). FTIR spectra of La_1Mg_2MO-H

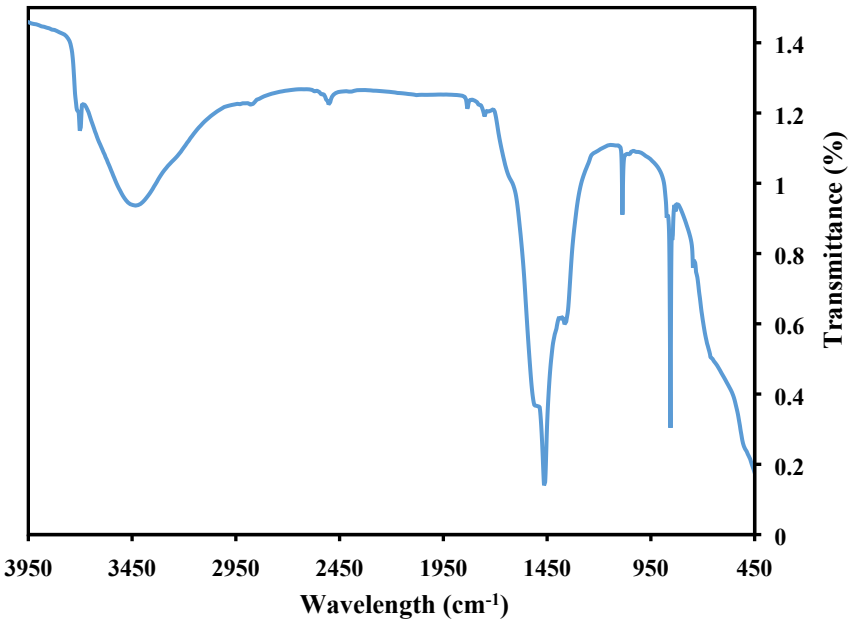

Figure S5 (e). FTIR spectra of La_1Mg_3MO-H

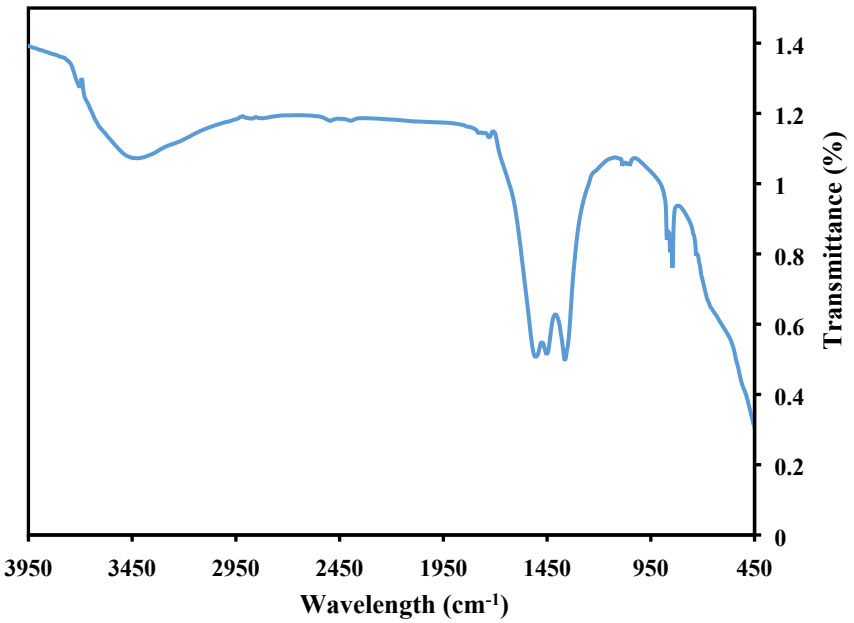

Figure S5 (f). FTIR spectra of La_1Mg_4MO-H

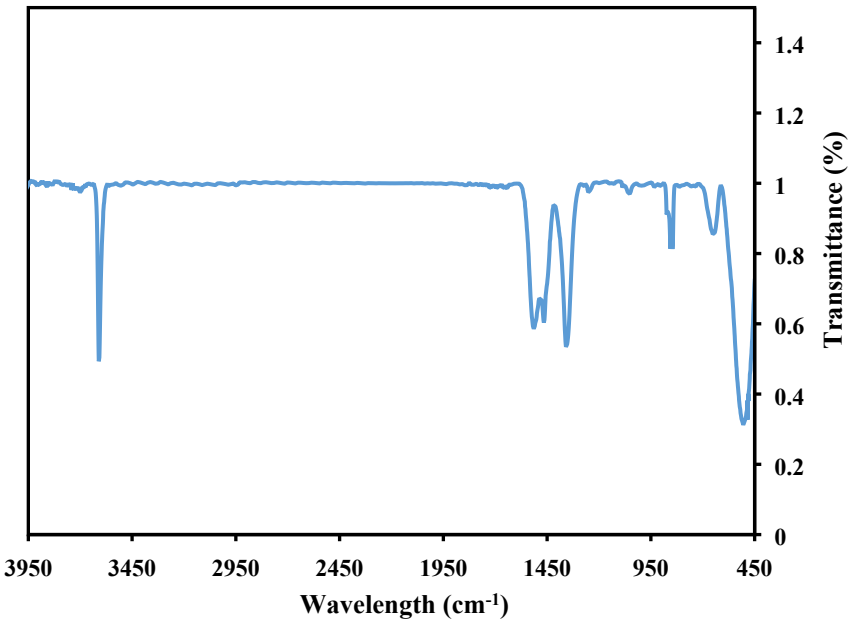

Figure S5 (g). FTIR spectra of La_1Mg_3MO-C

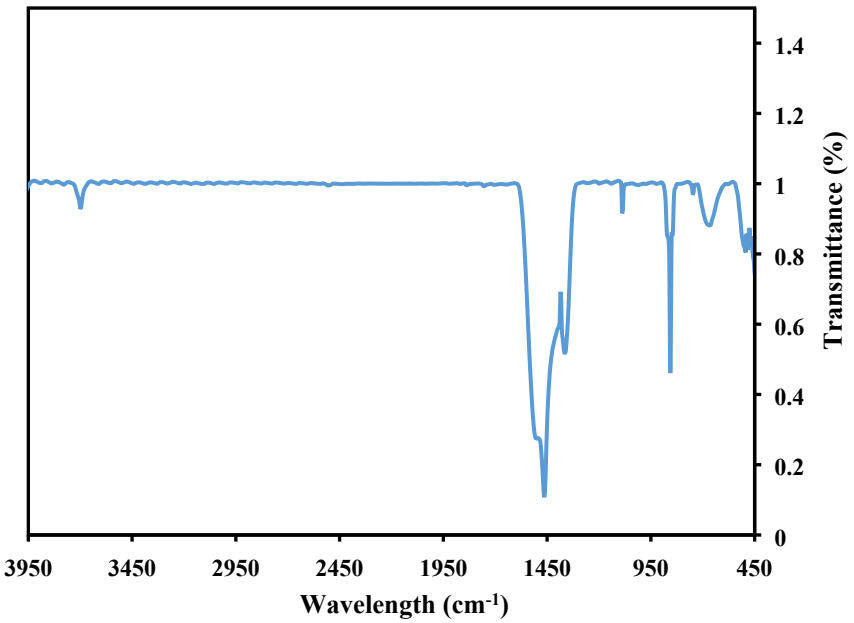

Figure S5 (h). FTIR spectra of La_1Mg_3MO-H

6. Elemental Dispersive X-ray Analysis

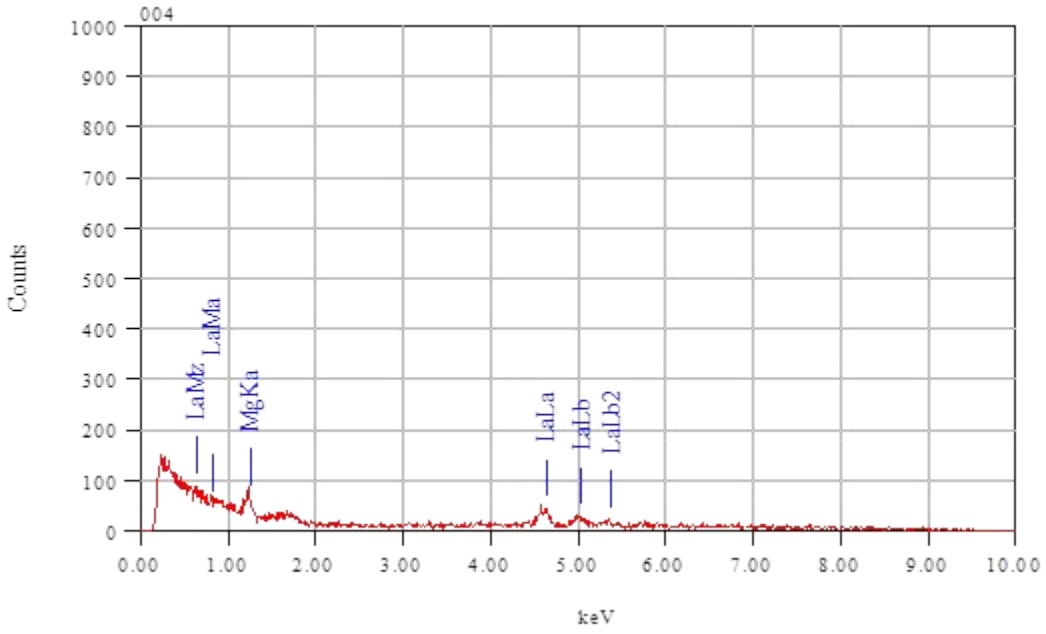

Figure S6 (a). EDX spectra of La_1Mg_1MO-H

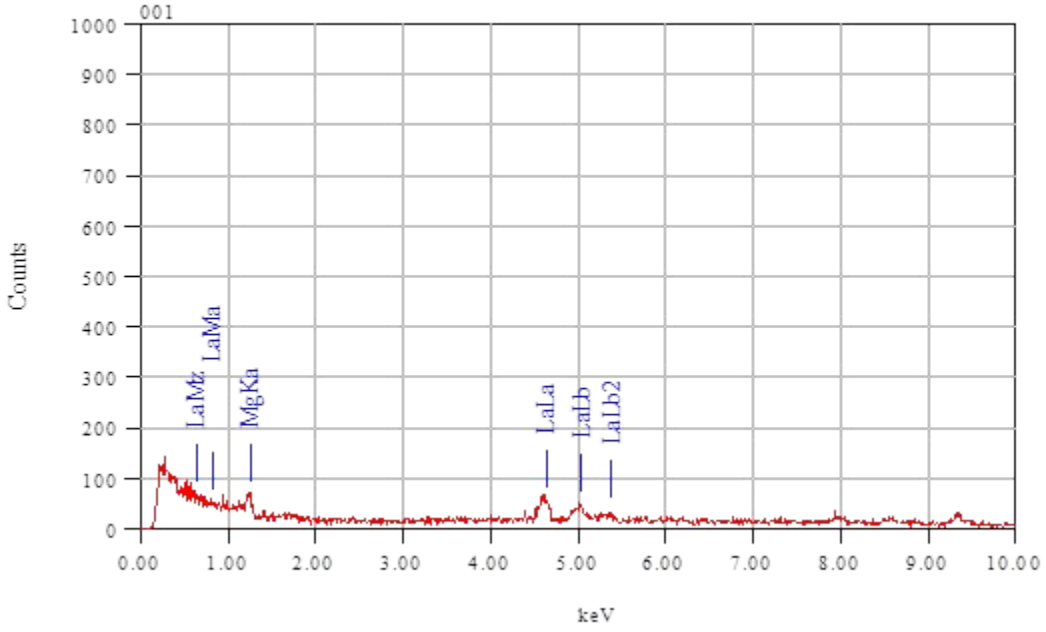

Figure S6 (b). EDX spectra of La_1Mg_2MO-H

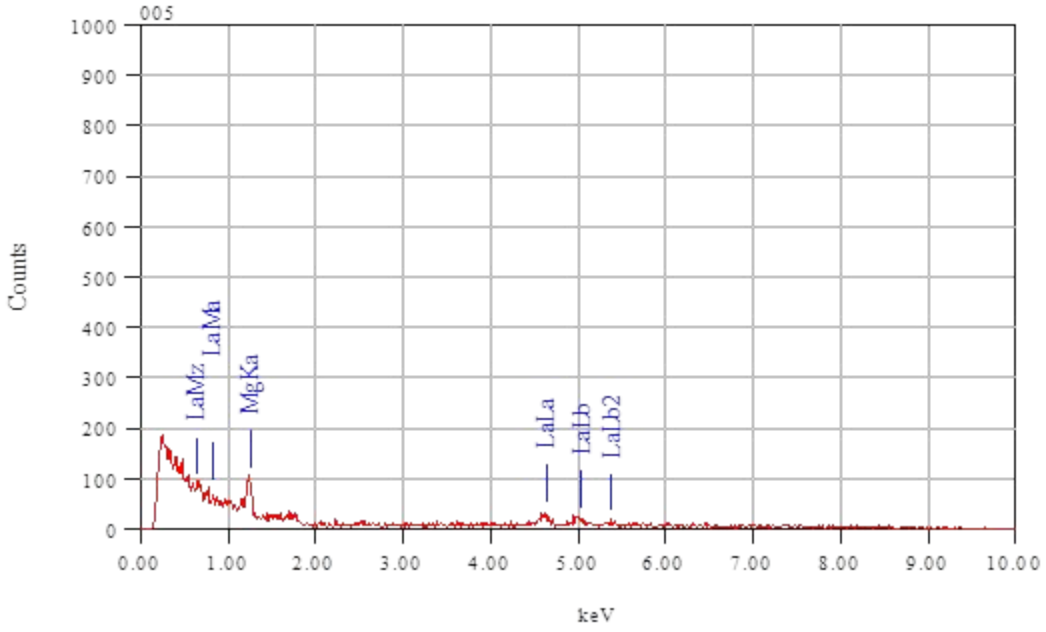

Figure S6 (c). EDX spectra of La_1Mg_3MO-H

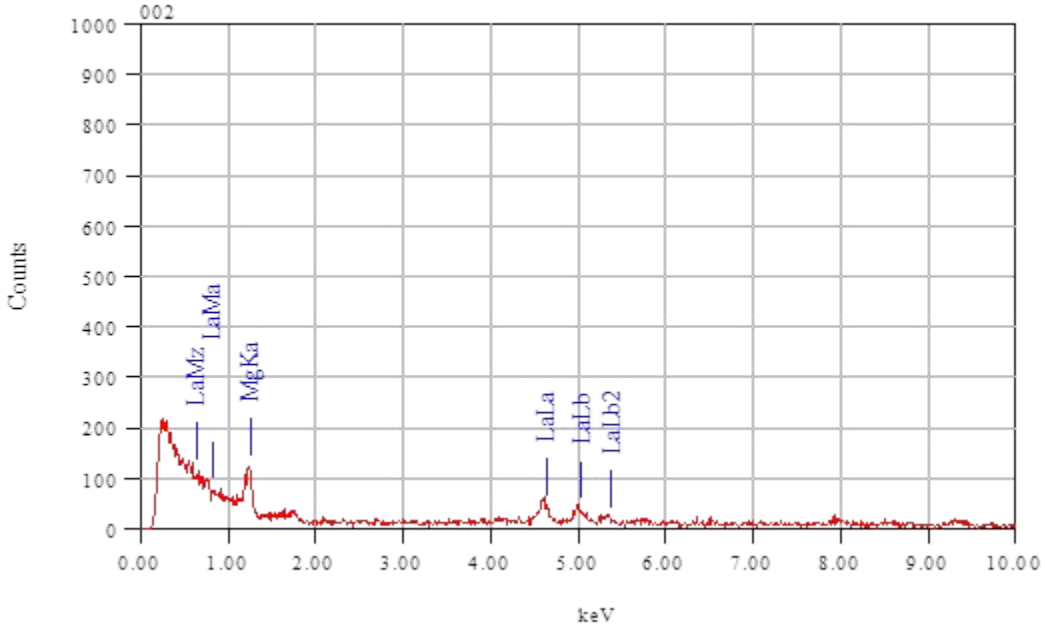

Figure S6 (d). EDX spectra of La_1Mg_4MO-H

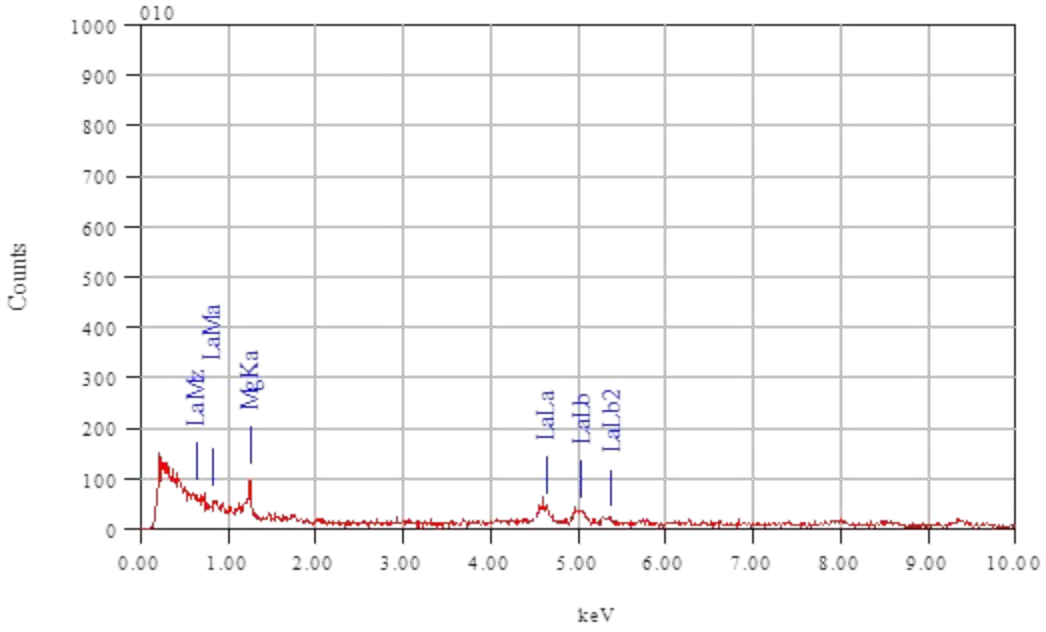

Figure S6 (e). EDX spectra of La_1Mg_3MO-C

7. Mathematical model for the aldol condensation of furfural with acetone

A catalyst having moderate to strong basic site (S_1) and weak to moderate acidic site (S_2) both sites were useful for the cross aldol condensation of furfural with acetone. On the surface of basic (S_1) site acetone adsorbed and acidic site (S_2) furfural adsorbed.

Acetone (A) and furfural (B) are adsorbed on vacant basic site S_1 and adjacent acidic site S_2 respectively:

$$A + S_1 \xleftrightarrow{K_A} AS_1 \qquad (1)$$

$$B + S_2 \xleftrightarrow{K_B} BS_2 \qquad (2)$$

Chemisorbed AS_1 and BS_2 react to produce DS_2 (H_2O) and ES_1 (FAc) on the respective catalytic sites S_1 and S_2:

$$AS_1 + BS_2 \xleftrightarrow{k_1} ES_1 + DS_2 \quad (3)$$

Desorption of ES_1 (FAc) and DS_2 (H_2O) is given by:

$$ES_1 \xleftrightarrow{1/K_E} E + S_1 \quad (4)$$

$$DS_2 \xleftrightarrow{1/K_D} D + S_2 \quad (5)$$

Total site balance for S_1 and S_2 can be written as:

$$C_{T_1} = C_{S_1} + C_{AS_1} + C_{ES_1} \quad (6)$$

$$C_{T_2} = C_{S_2} + C_{BS_2} + C_{DS_2} \quad (7)$$

Also, the following were derived:

$$C_{AS_1} = K_A C_A C_{S_1} \quad (8)$$

$$C_{BS_2} = K_B C_B C_{S_2} \quad (9)$$

$$C_{DS_2} = K_D C_D C_{S_2} \quad (10)$$

$$C_{ES_1} = K_E C_E C_{S_1} \quad (11)$$

Now equation (6) can be written as:

$$C_{T_1} = C_{S_1} + K_A C_A C_{S_1} + K_E C_E C_{S_1} \quad (12)$$

$$C_{S_1} = \frac{C_{T_1}}{(1 + K_A C_A + K_E C_E)} \quad (13)$$

Equation (7) can be written as:

$$C_{T_2} = C_{S_2} + K_B C_B C_{S_2} + K_D C_D C_{S_2} \quad (14)$$

$$C_{S_2} = \frac{C_{T_2}}{(1 + K_B C_B + K_D C_D)} \quad (15)$$

The rate of reaction of B is given by:

$$r_B = \frac{-dC_B}{dt} = k_1 C_{AS_1} C_{BS_2} - k_1' C_{ES_1} C_{DS_2} \quad (16)$$

$$\frac{-dC_B}{dt} = \frac{[k_1 K_A C_A K_B C_B - k_1' K_D C_D K_E C_E] C_{T_1} C_{T_2}}{[1 + K_A C_A + K_E C_E][1 + K_B C_B + K_D C_D]} \quad (17)$$

Where, W = catalyst loading = $C_{T_1} C_{T_2}$

$$\frac{-dC_B}{dt} = \frac{[k_1 K_A C_A K_B C_B - k_1' K_D C_D K_E C_E] \mathrm{w}}{[1 + K_A C_A + K_E C_E][1 + K_B C_B + K_D C_D]} \quad (18)$$

For initial rate data averages, we can assume that the $k_1' K_D, K_E$ constants are very small at t =0 and thus so equation (18) can be written as,

$$\frac{-dC_B}{dt} = \frac{k_1 K_A K_B C_A C_B \mathrm{w}}{[1 + K_A C_A][1 + K_B C_B]} \quad (19)$$

Table S1. Adsorption constants at different temperature.

Reaction temperature (°C)	Adsorption constants for reaction (L mol^{-1})	
	K_A	K_B

130	0.064809	0.008671
140	0.174321	0.02381
150	0.169374	0.010227
160	0.088865	0.049771

After solving the equation (19) in polymath 6, the values of K_A and K_B are obtained (table S1.).

The values of K_A and K_B are very small and thus, they are neglected thereafter.

$$\frac{-dC_B}{dt} = k_1 K_A K_B C_A C_B \text{ w} \qquad (20)$$

$$\frac{-dC_B}{dt} = k_2 K_A K_B \qquad (21)$$

Whereas $k_2 = k_1 K_A K_B w$

The ratio of concentration of acetone to furfural is equal to $M (= C_{A_0} / \mathrm{C}_{B_0})$ at time t = 0,

fractional conversion of equation (21) can be written as,

$$\frac{-dX_B}{dt} = k_2 K_{B_0} (1 - \mathrm{X}_B)(\mathrm{M} - \mathrm{X}_B) \qquad (22)$$

Which on integration gives:

$$\ln \frac{(\mathrm{M} - \mathrm{X}_B)}{\mathrm{M}(1 - \mathrm{X}_B)} = k_2 \, \mathrm{C}_{B_0} (\mathrm{M} - 1) \, \mathrm{t} \qquad (23)$$

When M>>1, then the equation (23) can be written as a pseudo-first order equation leading to:

$$-\ln(1 - \mathrm{X}_B) = kt \qquad (24)$$

8. **Validation of kinetic model**

The kinetic model has been validated with experimental data and the parity plot (Figure S6.) of experimental rate vs theoretical rate shows that there is a good agreement of similarity.

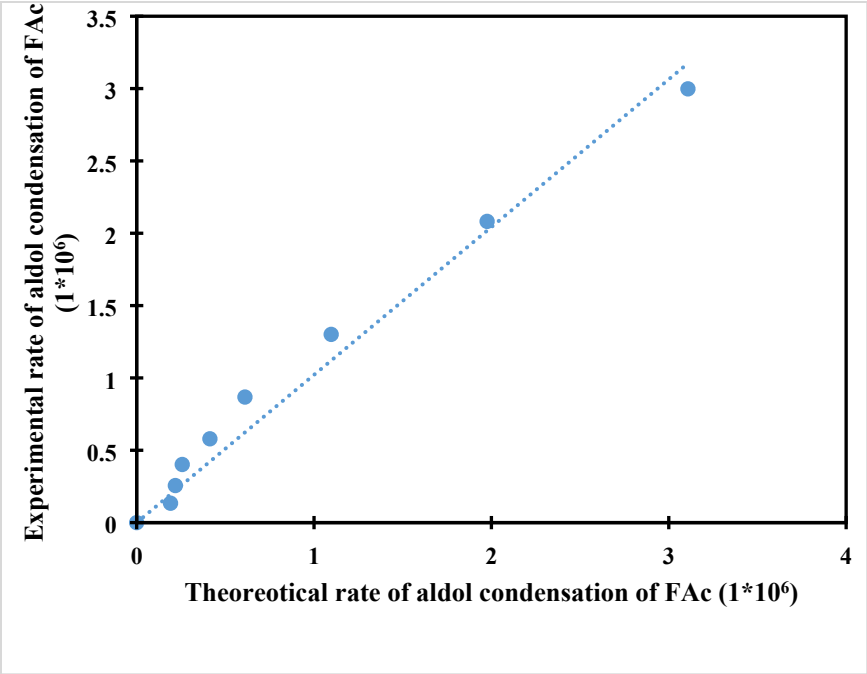

Figure S7. Parity plot for the theoretical and experimental rate of aldol condensation of furfural with acetone ($mol.cm^{-3}.min^{-1}$).