Supplementary Information (SI) for Green Chemistry.
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Supplementary Information

1. Experimental section

Calculation Methods

$$Glucose\ conversion\ (\%) = \frac{\text{mole of initial glucose - mole of glucose in product}}{\text{mole of initial glucose}} \times 100\ \%\ \ (S1)$$

$$Product\ yield\ (\%) = \frac{\text{mole of formed product}}{\text{mole of theoretical product}} \times 100\ \%\ (S2)$$

$$FA\ selectivity\ (\%) = \frac{\text{FA yield (\%)}}{\text{Glucose conversion (\%)}} \times 100\ \%\ (S3)$$

According to the equation of glucose oxidation to FA with H_2O_2:

$C_6H_{12}O_6 + 6H_2O_2 \rightarrow 6HCOOH + 6H_2O$.

6 mol of H_2O_2 are required to fully oxidize 1mol of glucose. Consequently, the theoretical FA amount was calculated by Eq.(S4):

$$Theoretical\ FA\ (mmol) = \frac{Initial\ glucose\ \ (mmol) \times FA\ stoichiometric\ number\ (6)}{\text{Glucose}\ stoichiometric\ number\ (1)} \times 100\ \%$$

(S4)

Similarly, the production of 1 mol arabinose, 1 mol glycolic acid (GA) and 1 mol acetic acid (AA) requires the consumption of 1 mol, 3 mol and 3 mol glucoses, respectively. Thus, theoretical by-product amount was also determined based on the relevant chemical equation S5, S6 and S7.

$$Theoretical\ arabinose\ (mmol) = \frac{Initial\ glucose\ \ (mmol)\ \times\ \text{arabinose}\ stoichiometric\ number\ (5)}{\text{Glucose}\ stoichiometric\ number\ (1)} \times 100\ \% \quad (S5)$$

$$Theoretical\ GA\ (mmol) = \frac{Initial\ glucose\ \ (mmol) \times\ GA\ stoichiometric\ number\ (3)}{\text{Glucose}\ stoichiometric\ number\ (1)} \times 100\ \%$$

(S6)

$$Theoretical\ AA\ (mmol) = \frac{Initial\ glucose\ \ (mmol) \times\ GA\ stoichiometric\ number\ (3)}{\text{Glucose}\ stoichiometric\ number\ (1)} \times 100\ \%$$

(S7)

2. Supplementary Figures

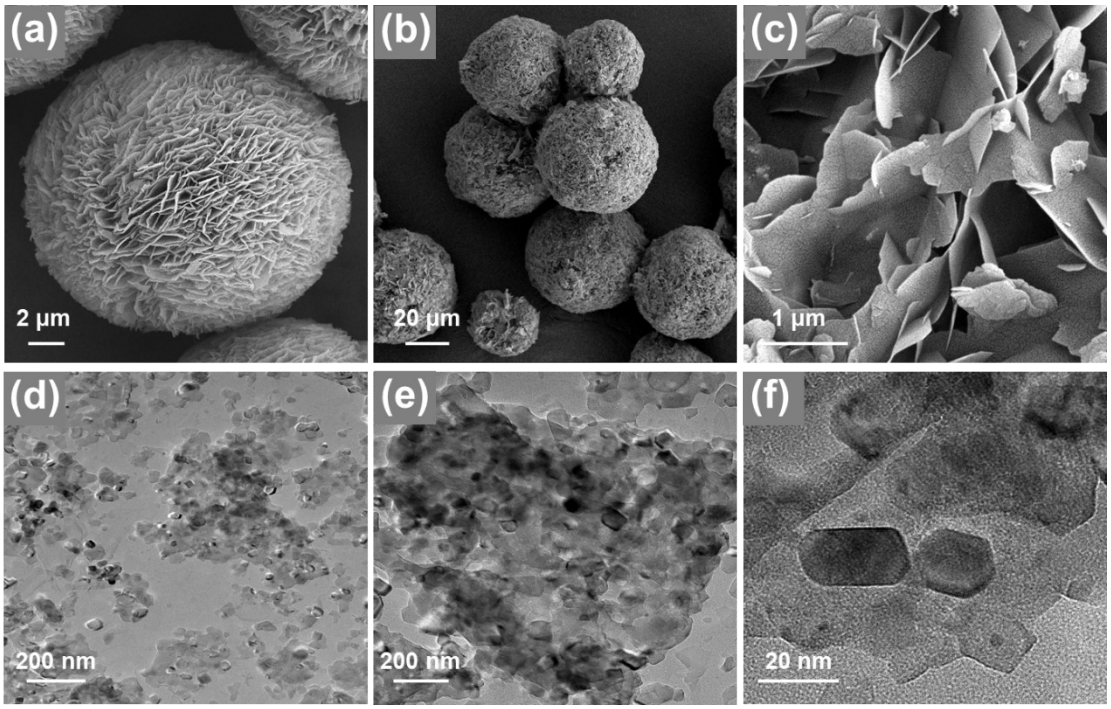

Figure S1. SEM image of (a) pristine MgO, (b) (c) $Ce_{1.0\%}$-MgO, (d) (e) and (f) TEM image of $Ce_{1.0\%}$-MgO.

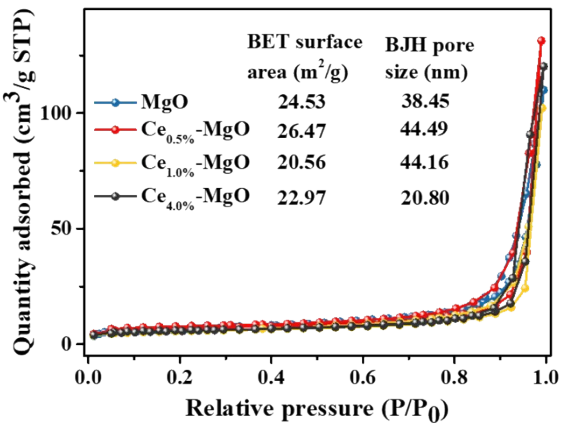

Figure S2. Nitrogen adsorption/desorption isotherm of MgO and Ce-MgO catalysts.

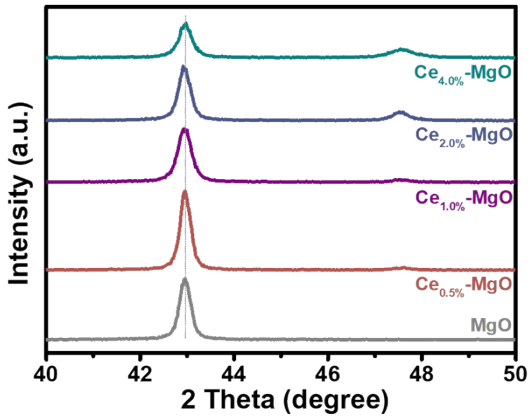

Figure S3. Partially enlarged XRD patterns of MgO and Ce-MgO catalysts.

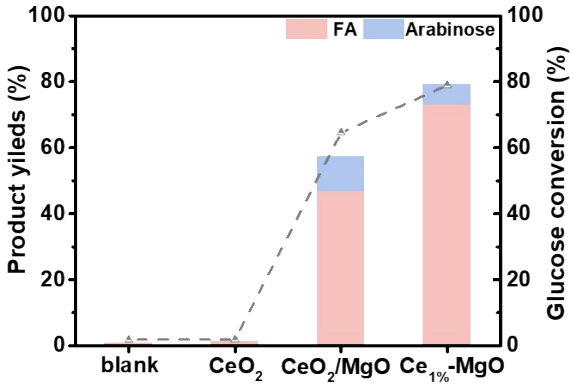

Figure S4. Product yields and glucose conversion of different catalysts (reaction conditions: 10 g·L^{-1} glucose, 120 mg catalysts, 100% H_2O_2, 30 °C , 4 h).

Notes:

CeO_2 preparation method: a calculated amount of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) were dissolved into 60 mL deionized water. Then, the mixed solution was slowly added dropwise to 0.7 mol/L (35 mL) potassium carbonate (K_2CO_3) solution. After stirring and precipitation, the separated precipitate was hydrothermally heated in an oven at 180°C for 2 h. The solid was washed several times and then calcined in a muffle furnace at 800°C for 5 h.

CeO_2/MgO preparation method: The pure MgO prepared in the study was used as a carrier and

impregnated with a calculated amount of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) solution. The resulting solid was then calcined at 800 °C in air for 5 hours.

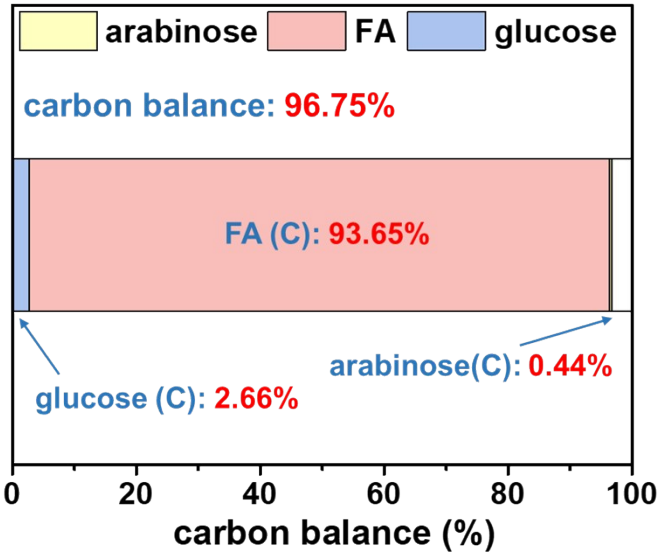

Figure S5. Carbon balance obtained after oxidation reaction with $Ce_{1.0\%}$-MgO catalyst (reaction conditions: 5 g·L^{-1} glucose, 120 mg catalysts, 100% H_2O_2, 30°C, 4 h).

Notes:

The total C input was 1.5 mmol. The detailed calculations are as follows:

From HPLC data, it was determined that the C-containing substances present in the liquid phase at the end of the reaction were glucose, arabinose and formic acid. The carbon concentrations of these were calculated separately as:

glucose (C): 0.0067 × 6 = 0.0402 mmol, 2.66% of the total C

formic acid (C): 1.405 × 1 = 1.405 mmol, 93.65% of the total C

arabinose (C): 0.0013 × 5 = 0.0066 mmol, 0.44% of the total C

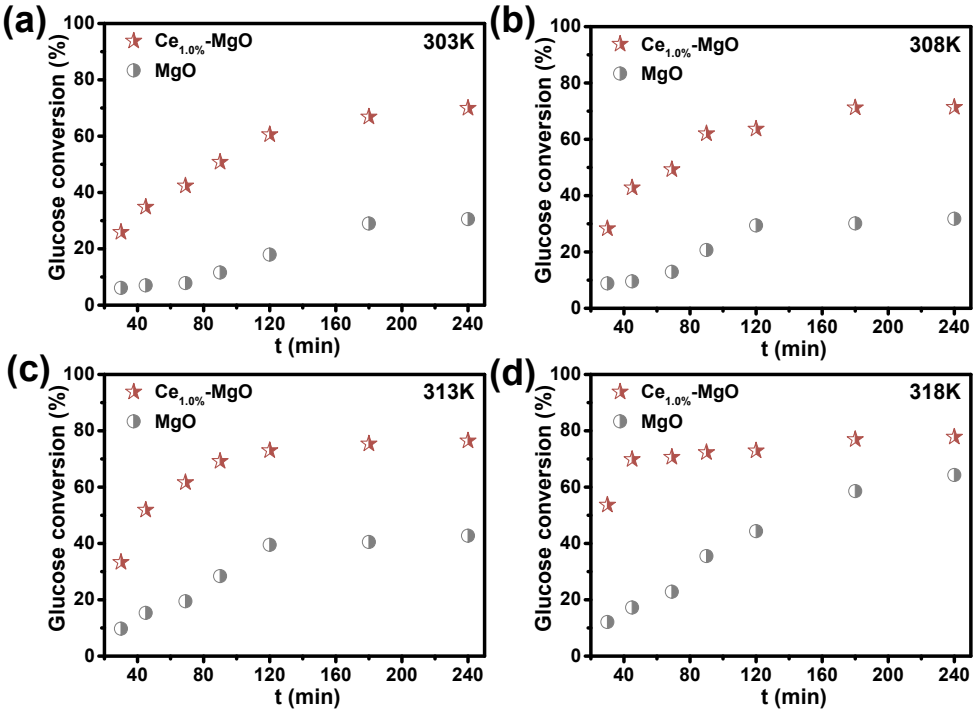

Figure S6. Variation of glucose conversion with time over $Ce_{1.0\%}$-MgO and MgO at (a) 303K, (b) 308K, (c) 323K and (d) 318K (reaction conditions: 10 g·L^{-1} glucose, 120 mg catalysts, 100% H_2O_2 , 4 h).

Notes:

The rate constant is calculated by the following equation:

$$lnC_{A_t} = -kt \quad (S8)$$

Where C_{At} is the concentration of glucose at different times.

The activation energy is calculated according to Arrhenius equation:

$$\ln k = \frac{-E_a}{\mathrm{RT}} + \ln \mathrm{A} \quad (S9)$$

Where k is the reaction rate constant at different temperatures, R is the ideal gas constant, T is temperature, and A is the frequency factor.

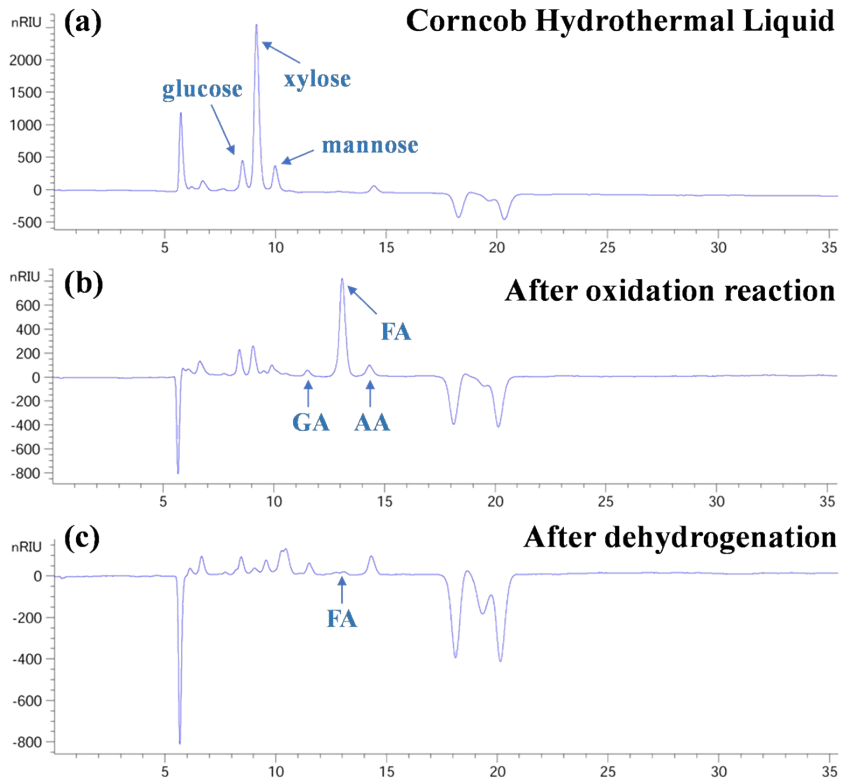

Figure S7. HPLC spectrum of corncob hydrothermal liquid, solution after oxidation reaction and after dehydrogenation.

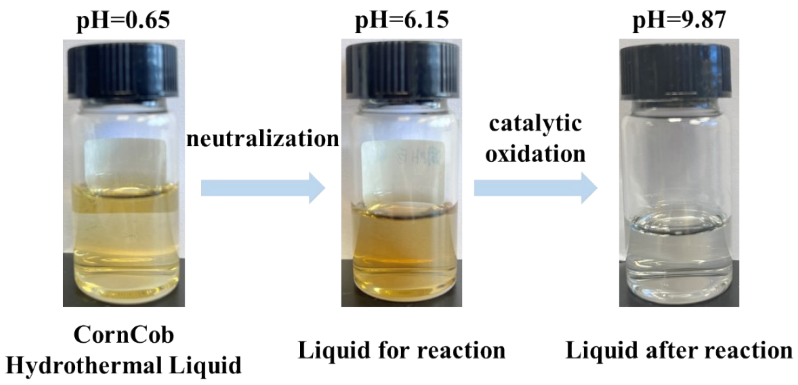

Figure S8. Schematic diagram from corncob hydrothermal liquid to FA.

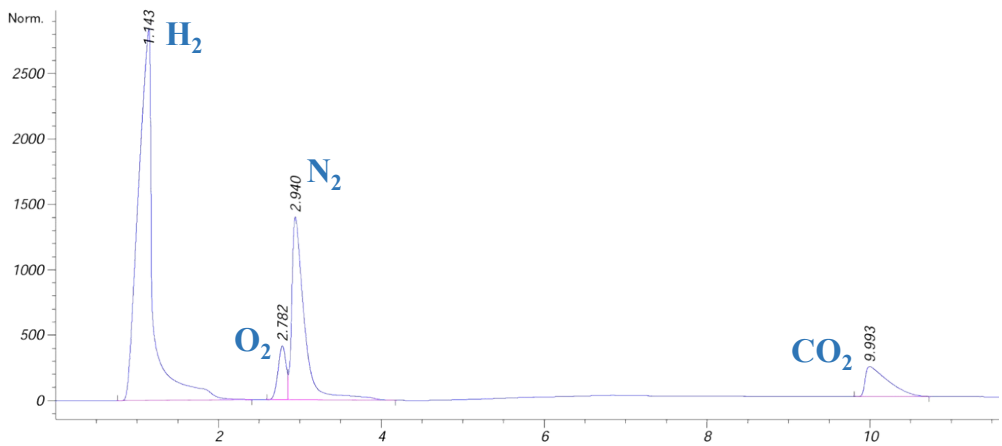

Figure S9. GC spectra of the product gas from the dehydrogenation reaction.

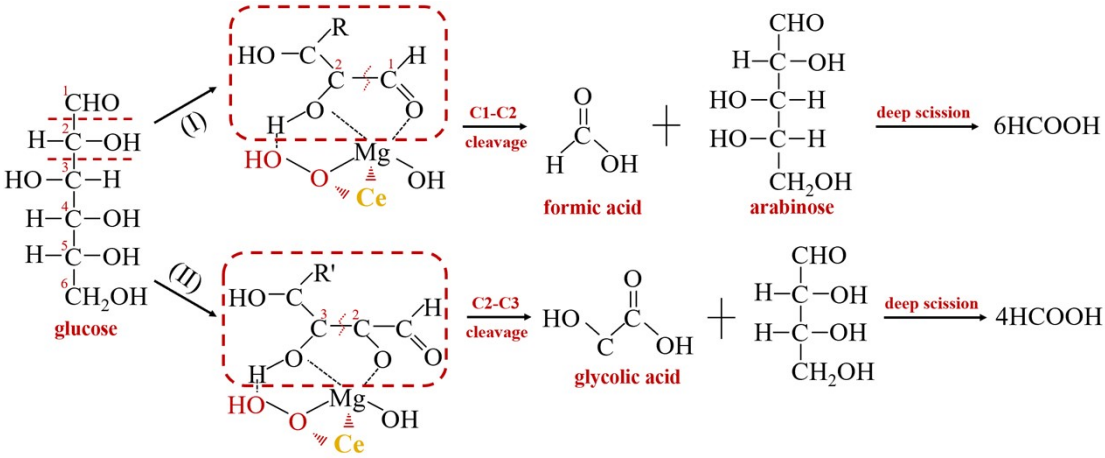

Figure S10. Proposed reaction pathway of glucose oxidation to FA over Ce-MgO catalyst (R = −(CHOH)$_2$CH$_2$OH, R' = −(CHOH)CH$_2$OH).

3. Supplementary Tables

Table S1. Binding energies and surface relative contents of Mn and O species over MnO_x catalysts before and after reaction

Catalyst	Mg 1s (eV)	O_{latt} (eV)	Ce^{4+} $3d_{3/2}$ (eV)
MgO	1303.96	529.71	-
$Ce_{0.5\%}$-MgO	1303.45	529.51	915.98
$Ce_{1.0\%}$-MgO	1303.35	529.00	915.60
$Ce_{2.0\%}$-MgO	1303.57	529.53	916.20
$Ce_{4.0\%}$-MgO	1303.70	529.50	916.20

Table S2. Quantitative analysis of NH_3-TPD and CO_2-TPD

Catalyst	CO_2-TPD total consumption ($mmol \cdot g^{-1}$)	NH_3-TPD total consumption ($mmol \cdot g^{-1}$)
MgO	0.183	0.780
$Ce_{1.0\%}$-MgO	1.393	1.959
$Ce_{4.0\%}$-MgO	1.069	3.667

Table S3. Composition of corncob hydrolyzed solution

Components	Concentration (mol/L)
Glucose	0.003
Xylose	0.021
Mannose	0.003