

Supporting Information

Active, selective and recyclable $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$ and $\text{Zr}(\text{SO}_4)_2/\text{AC}$ solid acid catalysts for esterification of malic acid to dimethyl malate

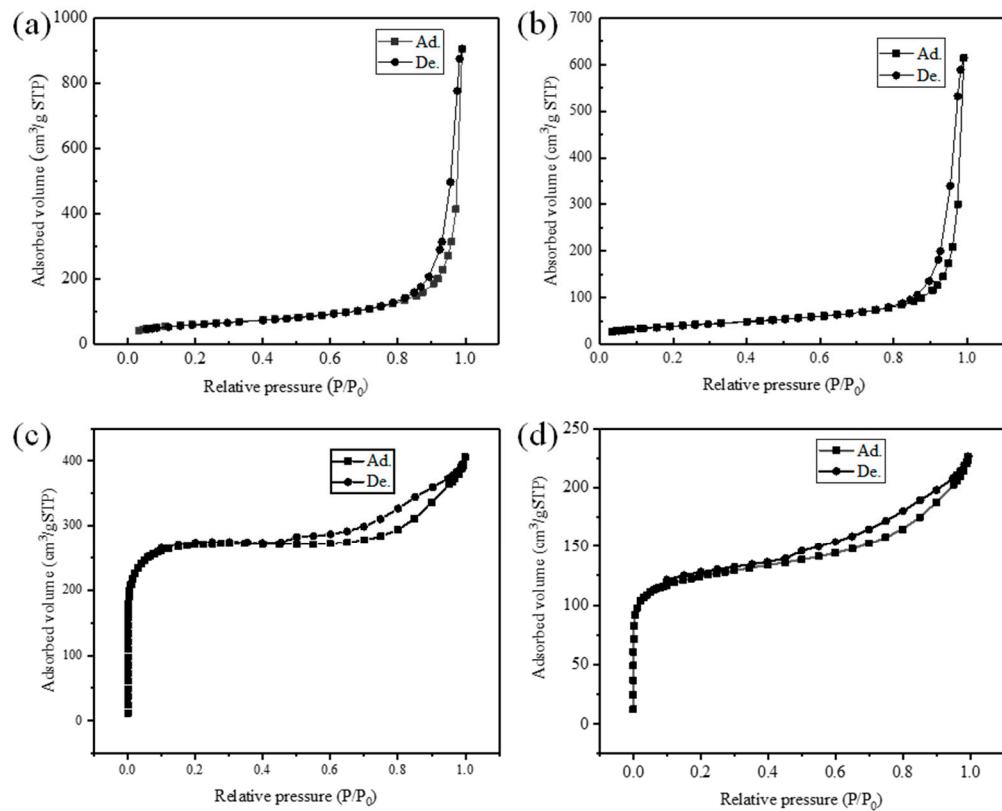


Figure S1. N₂ physical adsorption isotherms of (a) SiO_2 , (b) $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$, (c) AC and (d) $\text{Zr}(\text{SO}_4)_2/\text{AC}$ samples.

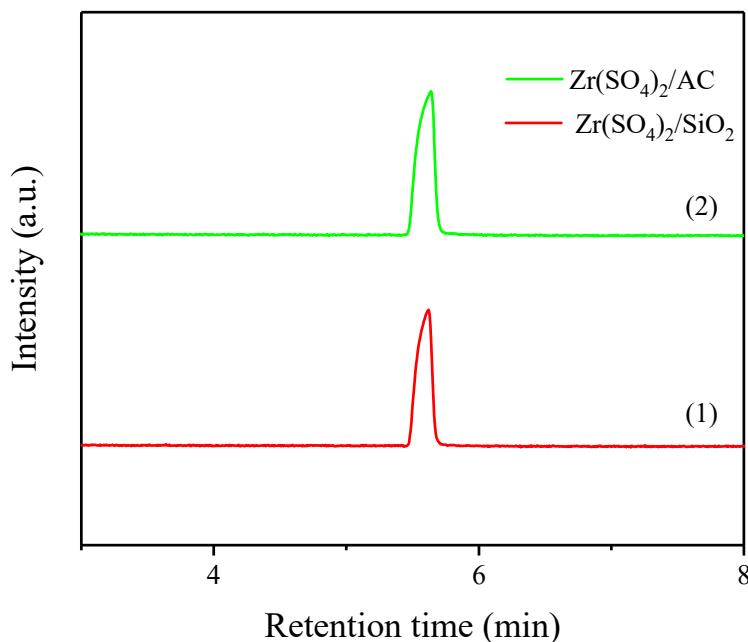


Figure S2. GC-MS spectra of post-reaction solution over (1) $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$ and (2) $\text{Zr}(\text{SO}_4)_2/\text{AC}$ catalysts.

Table 1. The concentration of Zr ion in the solution after the reaction.

Catalyst	Cycle 1 (ppm)	Cycle 2 (ppm)	Cycle 3 (ppm)	Cycle 4 (ppm)	Cycle 5 (ppm)
$\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$	15.2	12.4	10.5	11.1	6.12
$\text{Zr}(\text{SO}_4)_2/\text{AC}$	17.3	14.9	5.31	16.4	7.86

Table 2. The $\text{Zr}(\text{SO}_4)_2$ loadings of $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$ and $\text{Zr}(\text{SO}_4)_2/\text{AC}$ catalysts after the 5 cycles reaction.

Catalyst	$\text{Zr}(\text{SO}_4)_2$ loading (wt%)
$\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$	28.3
$\text{Zr}(\text{SO}_4)_2/\text{AC}$	27.4

Table 3. Scale-up experimental results over $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$ and $\text{Zr}(\text{SO}_4)_2/\text{AC}$ catalysts.

Catalyst	Malic acid conversion (%)	dimethyl malate selectivity (%)
$\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$	98	99
$\text{Zr}(\text{SO}_4)_2/\text{AC}$	97	99

Scale-up reaction conditions: malic acid amount (10 g), methanol amount (50 mL), catalyst amount (1 g), reaction temperature (65 °C), reaction time (2 h), stirring speed (600 rpm).

Table 4. Catalytic performance of $\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$ and $\text{Zr}(\text{SO}_4)_2/\text{AC}$ catalysts for malic acid esterification by ethanol.

Catalyst	Malic acid conversion (%)	Diethyl malate selectivity (%)
$\text{Zr}(\text{SO}_4)_2/\text{SiO}_2$	97	99
$\text{Zr}(\text{SO}_4)_2/\text{AC}$	98	99

Reaction conditions: malic acid amount (1 g), methanol amount (5 mL), catalyst amount (0.1 g), reaction temperature (65 °C), reaction time (2 h), stirring speed (600 rpm).