## **Supplementary Information**

## A green route for methanol carbonylation<sup>†</sup>

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Fig. S1 X-ray diffraction patterns of Py-MOR and H-MOR. Black curve: H-MOR,

Red curve: Py-MOR.





Fig. S2 Field-emission scanning electron microscopy images of Py-MOR and H-MOR.



Fig. S3 Fourier transform infrared spectra. Black curve: H-MOR, Red curve: Py-MOR, Blue curve: The differential spectrum.

Fig. S3 compares the fourier transform infrared spectra of H-MOR and Py-MOR. A sharp band, which is assigned to the total Brønsted acid sites, is observed at 3600 cm<sup>-1</sup> for H-MOR. However for Py-MOR, the band is obviously weakened and a small band, which is attributed to Brønsted acid sites in 8-MR, is observed at about 3585 cm<sup>-1</sup>, indicating that Brønsted acid sites in 8-MR are unchanged after pyridine absorption. Two bands at 1541 and 1450 cm<sup>-1</sup> are attributed to the vibration of pyridine absorbed on Brønsted and Lewis acid sites, respectively, whereas the band at 1489 cm<sup>-1</sup> is classified to the sum of them. These findings prove that pyridine selectively reacts with Brønsted acid sites in 12-MR pores rather than 8-MR of H-MOR. The observation of a band at 1631 cm<sup>-1</sup>, which is assigned to pyridinium H-bonded with pyridine, discloses that the adsorption of pyridine on the as-prepared Py-MOR catalyst is saturated

![](_page_4_Figure_0.jpeg)

Fig. S4 Effect of reaction temperature on methanol conversion and products selectivity of the optimized pyridine modified mordenite catalyst. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 18/1, WHSV (methanol) = 0.222 g(g catalyst)<sup>-1</sup>h<sup>-1</sup>. • Methanol conversion,  $\infty$ HAc selectivity,  $\Box$  MAc selectivity,  $\propto$  STY of HAc.

![](_page_5_Figure_0.jpeg)

Fig. S5 Effect of reaction temperature on methanol conversion and products selectivity of Py-MOR catalyst. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 20/1, WHSV (methanol) = 0.15 g(g catalyst)<sup>-1</sup>h<sup>-1</sup>. • Methanol conversion,  $\infty$ HAc selectivity,  $\Box$  MAc selectivity,  $\Box$ DME selectivity,  $\propto$  STY of HAc.

![](_page_6_Figure_0.jpeg)

Fig. S6 Reaction performances. (a) H-MOR; (b) Py-MOR; (c) Cu-MOR. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 80/1, reaction temperature = 543 K, WHSV (methanol) = 0.32 g(g catalyst)<sup>-1</sup>h<sup>-1</sup>. • Methanol conversion, 50HAc selectivity,  $\Box$  MAc selectivity,  $\Box$ DME selectivity.

![](_page_7_Figure_0.jpeg)

**Fig. S7 (a) Thermo gravimetric (TG) analysis curves. (b) Derivative thermo gravimetric (DTG) curves.** Black curve: Fresh Py-MOR, Red curve: Py-MOR after reaction for 145 h, Blue curve: H-MOR after reaction for 45 h.