Supplementary Information

A green route for methanol carbonylation†

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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\(^{-1}\) 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\(^{-1}\), indicating that Brønsted acid sites in 8-MR are unchanged after pyridine absorption. Two bands at 1541 and 1450 cm\(^{-1}\) are attributed to the vibration of pyridine absorbed on Brønsted and Lewis acid sites, respectively, whereas the band at 1489 cm\(^{-1}\) 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\(^{-1}\), which is assigned to pyridinium H-bonded with pyridine, discloses that the adsorption of pyridine on the as-prepared Py-MOR catalyst is saturated.
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)^{-1}h^{-1}. ○ Methanol conversion, □ HAc selectivity, ▲ MAc selectivity, ◆ STY of HAc.
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)$^{-1}$h$^{-1}$. ○ Methanol conversion, □ HAc selectivity, ▲ MAc selectivity, ▲ DME selectivity, ◊ STY of HAc.
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)⁻¹h⁻¹. ○ Methanol conversion, ▲ HAc selectivity, ◻ MAc selectivity, ▼ DME selectivity.
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.