Clean synthesis of acetaldehyde oxime through ammoximation on titanosilicate

catalysts

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Fig. S1. The ^{1}H NMR (a) and ^{13}C NMR (b) for AAO. For *trans*-AAO, ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.18 (s, 1H), 7.45 (q, J = 6 Hz, 1H), 1.85 (d, J = 6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl^3): 148.01, 14.92. For *cis*-AAO, ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.59 (s, 1H), 6.83 (q, J = 5.6 Hz, 1H), 1.87 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl^3): 147.68, 11.00.
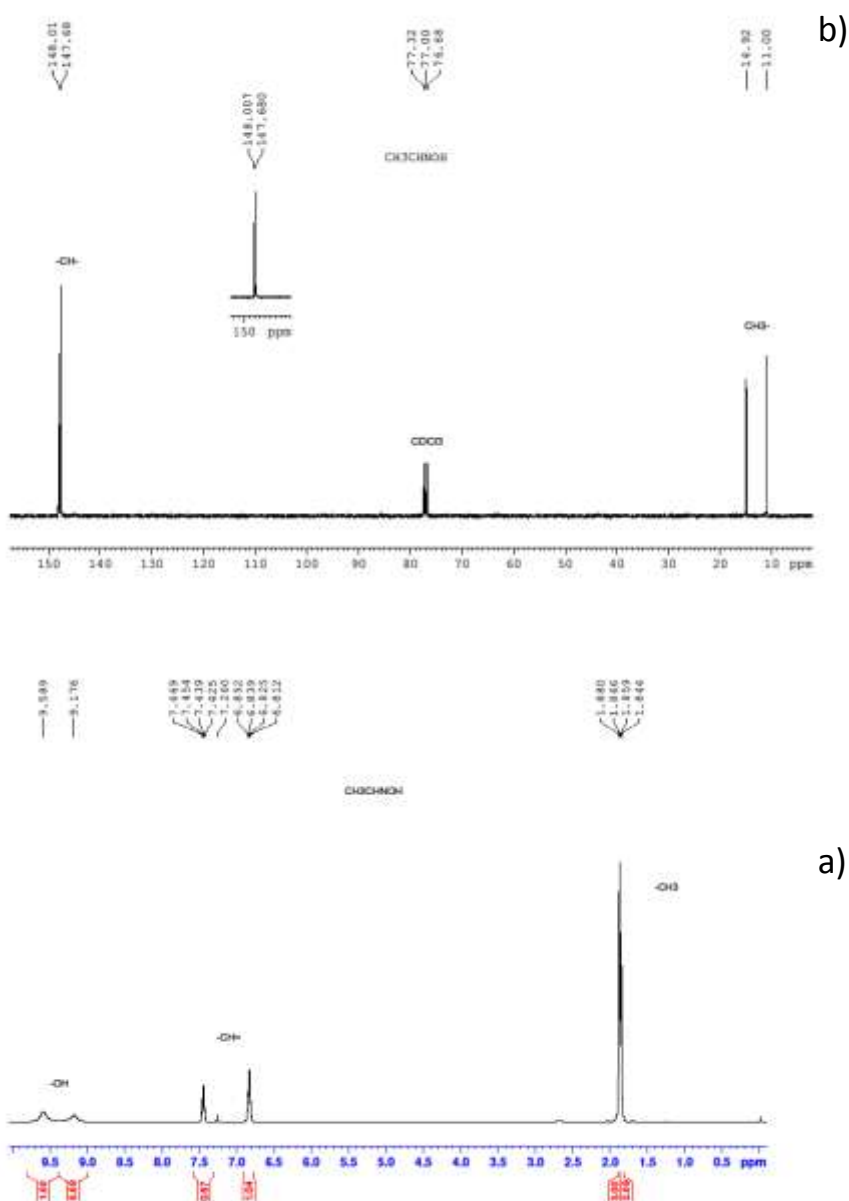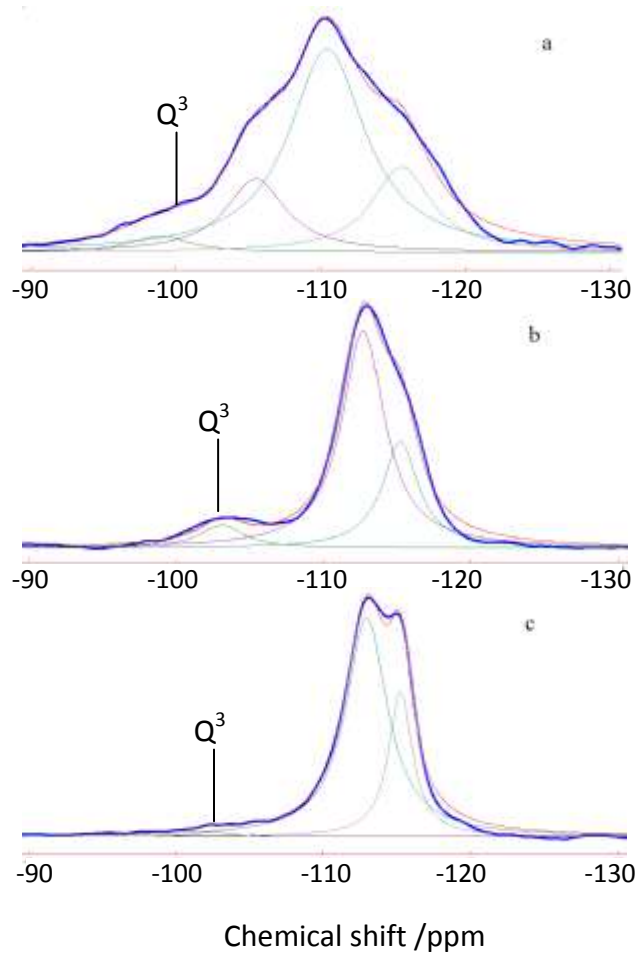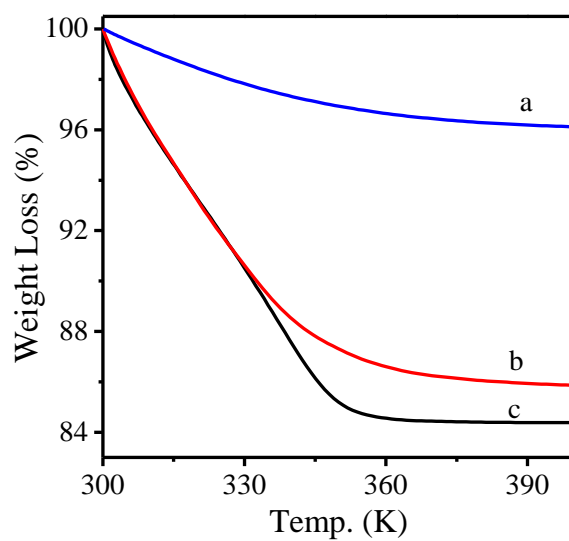
Fig. S2. ^{29}Si MAS NMR spectra (red) and fitting results (blue) of Ti-MWW (a), TS-1 (b) and Ti-MOR (c).

Chemical shift /ppm

The Q^3 group accounts for 3.68 %, 6.98 % and 1.34 % of total silicon population for Ti-MWW, TS-1 and Ti-MOR, respectively. This indicates that Ti-MOR was the most hydrophobic.

Fig. S3. The TG profiles of Ti-MOR (a), Ti-MWW (b) and TS-1 (c).

The amount of adsorbed water determined by thermogravimetry was 4 % for Ti-MOR, 14 % for Ti-MWW and 16 % for TS-1 (c). The results were in agreement with ^{29}Si NMR investigation, verifying that Ti-MOR was more hydrophobic than TS-1 and Ti-MWW.

Fig. S4. IR spectra of Ti-MOR samples prepared by TiCl$_4$ treatment at 673 K for 0.5 h

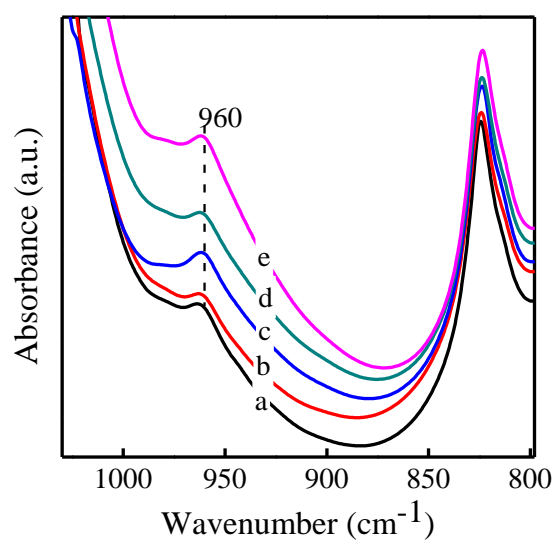(a), 1 h (b), 2 h (c), 3 h (d), and 4 h (e).

Fig. S5 The AA conversion and oxime selectivity of the ammoximation performed on regenerated Ti-MOR. Ammoximation conditions: all substrates were added at once; others, see Table 2 except for that the reaction scale was enlarged by twenty times. The used catalyst was regenerated by acetone washing, drying at 393 K for 5 h, and further calcination at 773 K for 5 h.