Elucidating the nature and role of Cu species in enhanced catalytic carbonylation of dimethyl ether over Cu/H-MOR

Supporting Information

Fig. S1 FTIR spectra in the O–H stretching region of H-M sample (-) and deconvoluted bands corresponding to H\(^+\) in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).
Fig. S2 FTIR spectra in the O–H stretching region of unreduced Cu/H-M(3.35) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).

Fig. S3 FTIR spectra in the O–H stretching region of reduced Cu/H-M(3.35) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).
**Fig. S4** FTIR spectra in the O–H stretching region of unreduced Cu/H-M(4.55) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).

**Fig. S5** FTIR spectra in the O–H stretching region of reduced Cu/H-M(4.55) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).
**Fig. S6** FTIR spectra in the O–H stretching region of unreduced Cu/H-M(6.16) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).

**Fig. S7** FTIR spectra in the O–H stretching region of reduced Cu/H-M(6.16) sample (-) and deconvoluted bands corresponding to H⁺ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).
**Fig. S8** FTIR spectra in the O–H stretching region of unreduced Cu/H-M(10.28) sample (-) and deconvoluted bands corresponding to H$^+$ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).

**Fig. S9** FTIR spectra in the O–H stretching region of reduced Cu/H-M(10.28) sample (-) and deconvoluted bands corresponding to H$^+$ in 8-MR (-) and 12-MR (-), extra-framework Al–OH (-) and Si–OH (-).
Fig. S10 FTIR spectra in the O–H stretching region of H-MOR and SSIE Cu/H-M(x) samples

Fig. S11 FTIR spectra of pyridine adsorbed on H-MOR and SSIE Cu/H-M(x) samples
XRD patterns of the unreduced Cu/H-M(x) samples reveal that no bulk Cu species can be detected at low Cu loading. With the increase of Cu loading, a slight characteristic peak at 38.9° attributed to CuO can be distinguished, indicating the presence of CuO aggregates.
Fig. S13 TEM images of the unreduced Cu/H-M(x) samples. (-u: unreduced)

TEM images of the unreduced Cu/H-M(x) samples present that few Cu oxides particles can be found for Cu/H-M(3.35) sample, while the number and size of Cu oxides particles increase with the increase of Cu loading.
The satellite peaks in Cu 2p XPS spectrum at about 942.7 (Cu 2p 3/2) and 962.5 eV (Cu 2p 1/2 for CuO) proves the existence of divalent Cu, and the broad peak in Cu LMM XAES spectrum demonstrates the coexistence of multiple valence state of Cu species.
**Fig. S15** FTIR spectra of CO adsorption for reduced Cu/H-M(x) samples (-) and deconvoluted bands corresponding to Cu$^+$ in 8-MR (-) and 12-MR (-) channels.
All of the as-prepared Cu/H-M(x) samples are reduced and re-evaluated under the conditions as mentioned in the text, and then cooled down to room temperature in N₂ flow after 8 h reaction. The spent catalysts are transferred and sealed in a glove box and characterized by XRD, TEM as well as CO-adsorption IR.

As shown in Fig. S16, zeolitic framework of the spent Cu/H-M(x) catalysts is well maintained. The characteristic peaks at 43.3° and 50.5° assigned to Cu⁰ exhibit few differences compared with the reduced Cu/H-M(x) samples.

**Fig. S16** XRD patterns of the reduced and spent Cu/H-M(x) samples. (-s: spent)
The distribution and particle size of Cu$^0$ particles for the spent Cu/H-M(x) samples are similar to that for the reduced Cu/H-M(x) samples (shown in Fig. 3 of the paper).
The *in situ* DRIFTS of CO adsorption is used to provide detailed information of Cu$^+$ species in spent Cu/H-M(x) samples. As the presence of adsorbed methyl groups leads to a consumption of CO on the spent catalysts, we extend the adsorption time of samples to 4 h in CO flow. And the spectra are collected after He purging for 2 h until the intensities of bands are not changed. The similarity of the IR bands in the range of 2100 ~ 2200 cm$^{-1}$ between the fresh catalysts (shown in Fig. 8 of the paper) and used ones indicates that the location and amount of Cu$^+$ remain almost unchanged. Hence, we suggest that Cu species are relatively stable during reaction.

**Fig. S18** FTIR spectra of CO adsorption for spent Cu/H-M(x) samples. (-s: spent)
In order to testify the acceleration effect of Cu$^0$, the influence of different reduction temperature for Cu/H-M(3.35) sample are investigated. With increase of reduction temperature from 473 K to 673 K, the activity is apparently improved with the similar selectivity. It also supports our conclusion strongly.