Electronic Supplementary Information

Elucidating the nature and role of copper species in catalytic carbonylation of methanol to methyl acetate over copper/Titania-silica mixed oxides

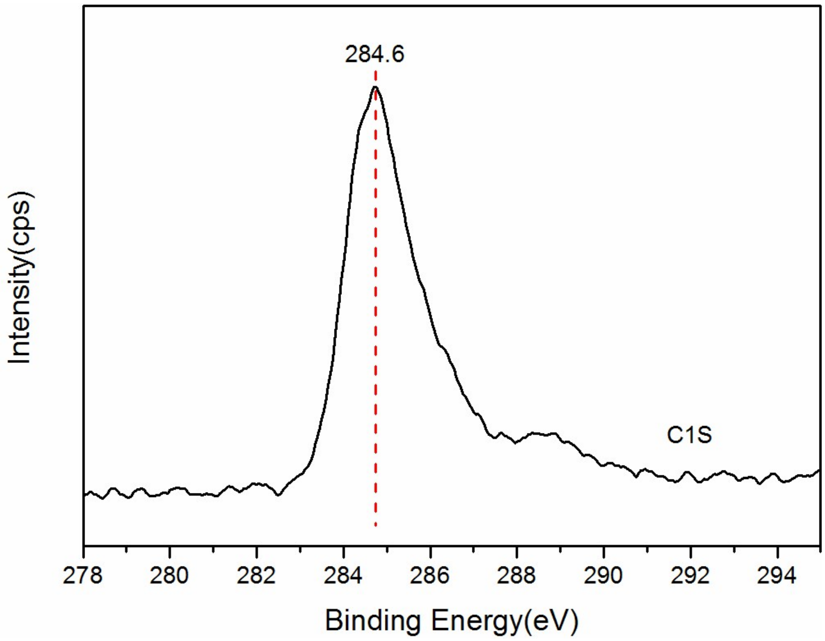

Fig.S1 XPS spectrum of the adventitious carbon

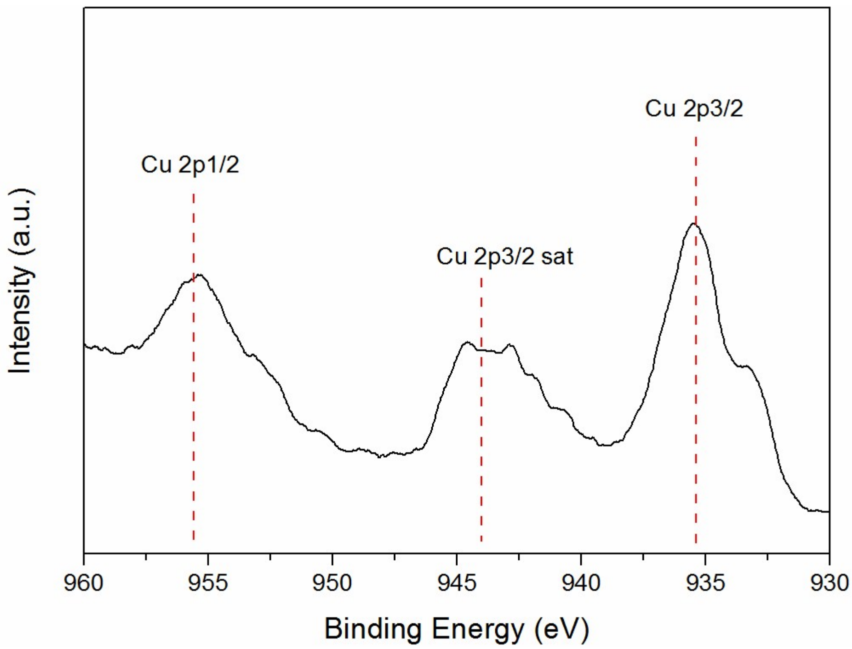

Fig.S2 Cu2p XPS spectrum of the 10.24 Cu/TS catalyst before reduction

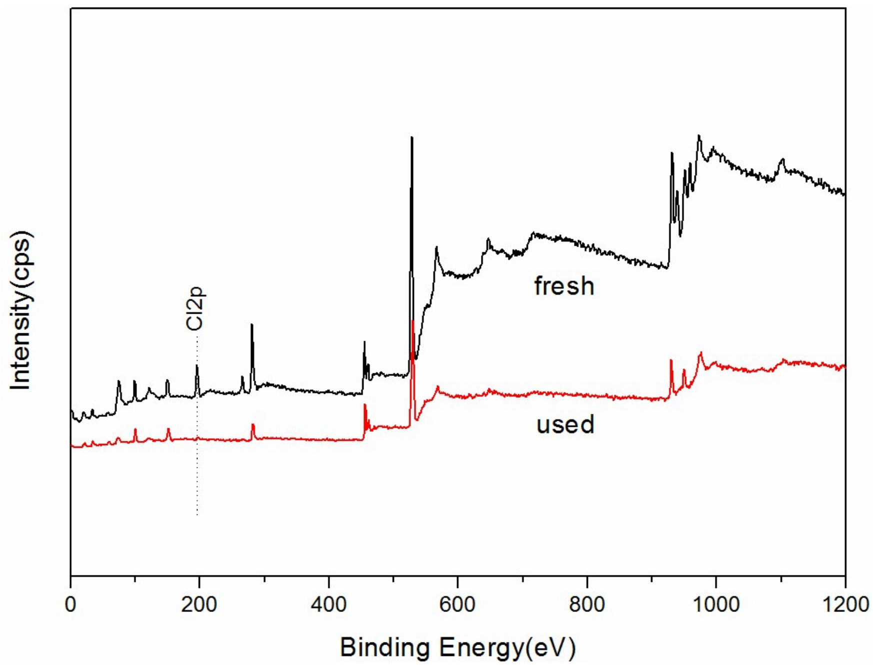

Fig.S3 The loss of the Cl in the reaction (Reaction condition: same as above; Fresh: the catalyst before carbonylation reaction and after 4 h of pretreatment in the CO under 503 K; Used: the catalyst after 24 h of carbonylation reaction)

Table S1 Average chloride content of 10.24 Cu/TS catalyst during the carbonylation of methanol by means of EDXRF elemental analysis

	Fresh[a]	Reaction time (h)			
		6	12	18	24
Chloride content (wt%)	2.080	1.156	0.757	0.532	0.264
Atomic ratio Cl/Cu	0.378	0.210	0.136	0.099	0.050
$X_{Methanol}$ (%)	---	23.413	28.311	32.263	30.015
STY_{MA}(mol/h.Kg_{cat})	---	1.241	1.506	1.804	1.779

[a]the catalyst after drying

Reaction condition: same as above

Furthermore, to further rule out the effect of chlorine species, we also prepared another catalyst using $Cu(NO_3)_2$ as precursor (marked as 10Cu/TS-N). The catalytic performance showed that, through suitable pretreatment, the 10Cu/TS-N catalyst can exhibit similar catalytic activity to the 10.24Cu/TS ($CuCl_2$ precursor) catalyst in MA synthesis, which supports our above deduction (see Table S2).

Table S2 Catalytic performance for methanol carbonylation on the different catalysts

Catalyst	$X_{Methanol}$ (%)	S_i (mol %)			STY_{MA}(mol/h.Kg_{cat})
		MA	MF	DME	
10.24Cu/TS	29. 215	50.133	22.992	26.875	1.770
10Cu/TS-N	22.837	53.016	17.425	29.559	1.463

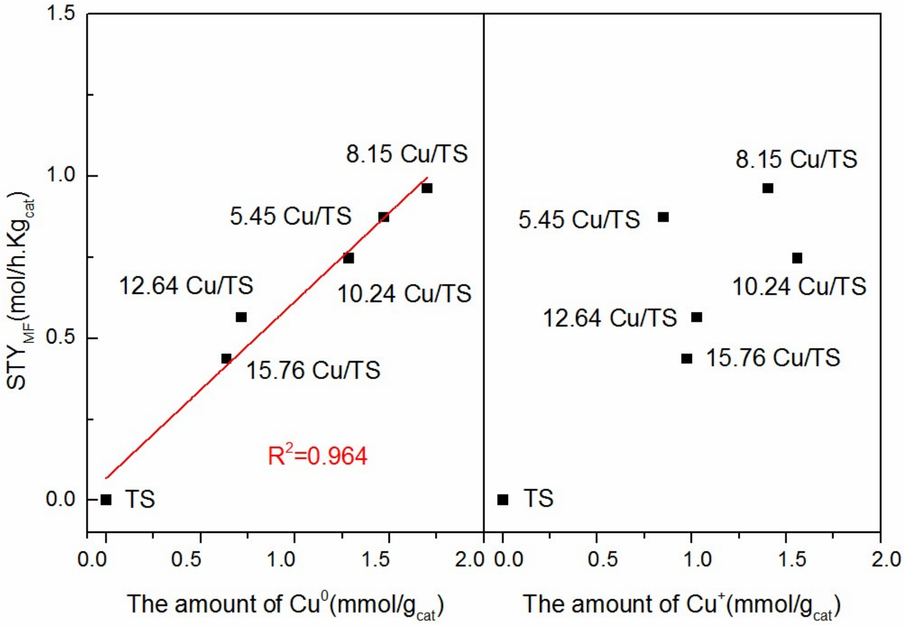

Fig.S4 The correlation of STY_{MF} with Cu^0 and Cu^+ for the reduced catalysts