

## Improvement of the selectivity to aniline from benzene amination over Cu/TS-1 by potassium

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Table S1 Example of parallel tests for activity measurement

	Yield(mol%)		Conversion of benzene(%)	Selectivity of aniline (%)
	Aniline	Phenol		
0	2.12	0.01	2.13	99.5
1	2.15	0.01	2.16	99.5
2	2.12	0.02	2.14	99.5
3	2.08	0.01	2.09	99.5
4	2.13	0.02	2.15	99.1
5	2.12	0.01	2.13	99.5

Reaction conditions: 0.5 g Cu/TS-1, 40.0 mL H<sub>2</sub>O, 0.25 mL benzene, 1 g KNO<sub>3</sub>, 10 mL NH<sub>3</sub>·H<sub>2</sub>O and 2.5 mL H<sub>2</sub>O<sub>2</sub>, reaction temperature 60 °C, reaction time 4 h

Table S2 The effect of benzene loading on the amination reaction

The amount of benzene (mL)	The amount of aniline (umol)	Yield (mol%)		Conversion of benzene (%)	Selectivity to aniline (%)
		Aniline	Phenol		
0.25	59.36	2.12	0.01	2.13	99.5
0.5	117.04	2.09	0.01	2.10	99.5
1.0	239.68	2.14	0.02	2.16	99.1
2.0	472.64	2.11	0.01	2.12	99.5

Reaction conditions: a: 0.5 g 1.0K-Cu/TS-1, 40 mL H<sub>2</sub>O, 10 mL NH<sub>3</sub>·H<sub>2</sub>O and 2.5 mL H<sub>2</sub>O<sub>2</sub>, reaction temperature 60 °C, reaction time 4 h.

Table S3 The effect of  $\text{KNO}_3$  on the amination reaction over TS-1 catalyst

$\text{KNO}_3$ additive amount (g)	Yield(mol%)		Conversion of benzene (%)	Selectivity of aniline (%)
	Aniline	Phenol		
0	0.038	0.47	0.51	7.5
1	0.22	0	0.22	100

Reaction conditions: 0.5 g TS-1, 40.0 mL  $\text{H}_2\text{O}$ , 0.25 mL benzene, 10 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and 2.5 mL  $\text{H}_2\text{O}_2$ , reaction temperature 60 °C, reaction time 4 h

Table S4 The XPS peak area ratio of Ti species for several typical catalysts

Catalyst	$S_{\text{Ti-O-Si}} : S_{\text{Ti-O-Cu}} : S_{\text{Ti-O-K}}$
Cu/TS-1	1 : 1.36 : 0
1.0K-Cu/TS-1	1 : 1.29 : 0
Cu/TS-1-1.0K	1 : 1.52 : 1.17
Catalyst 1	1 : 1.23 : 0
Catalyst 2	1 : 1.06 : 1.35

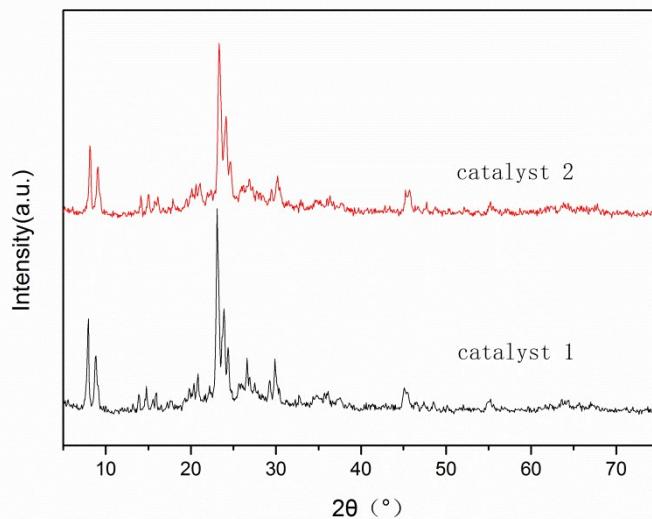


Fig. S1. XRD patterns of the catalysts 1 and 2

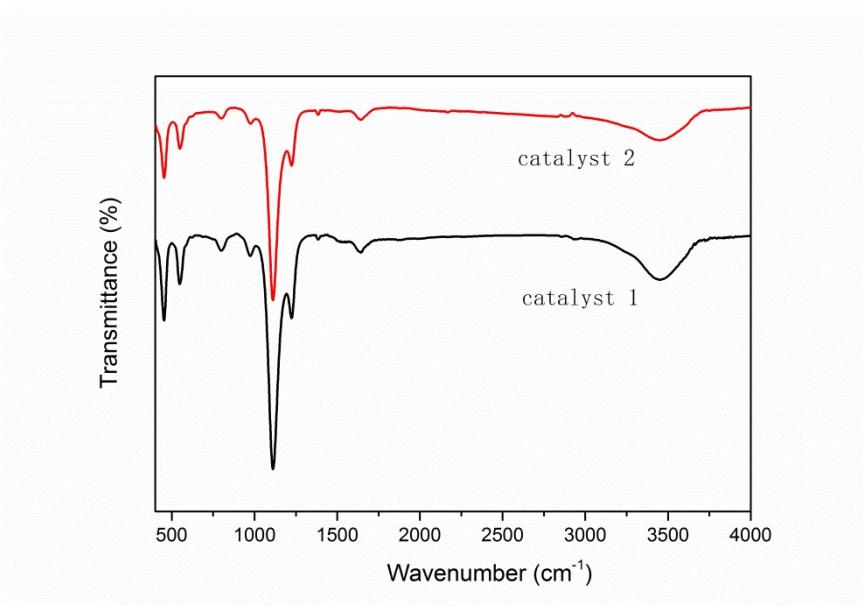


Fig.S2 FT-IR spectra of the catalysts 1 and 2

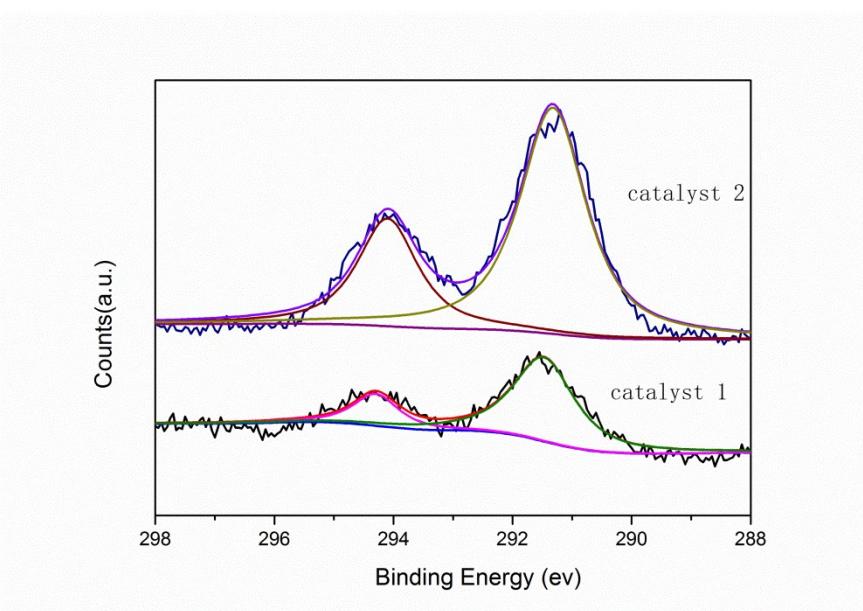


Fig.S3 K<sub>2p</sub> spectra of the catalysts 1 and 2

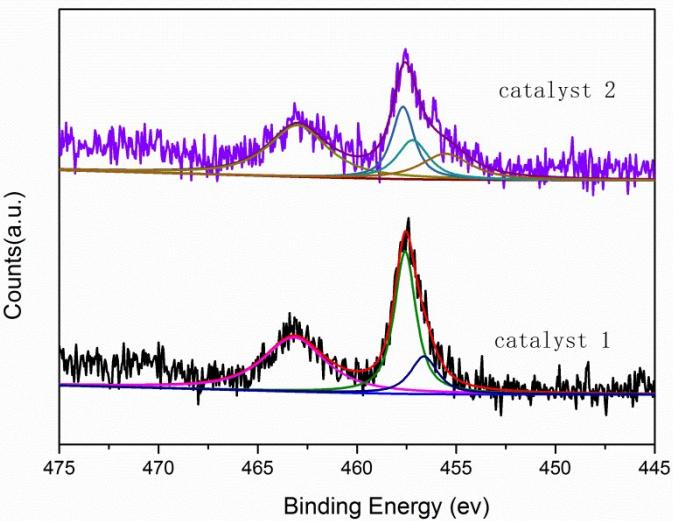


Fig.S4 Ti<sub>2p</sub> spectra of the catalysts 1 and 2

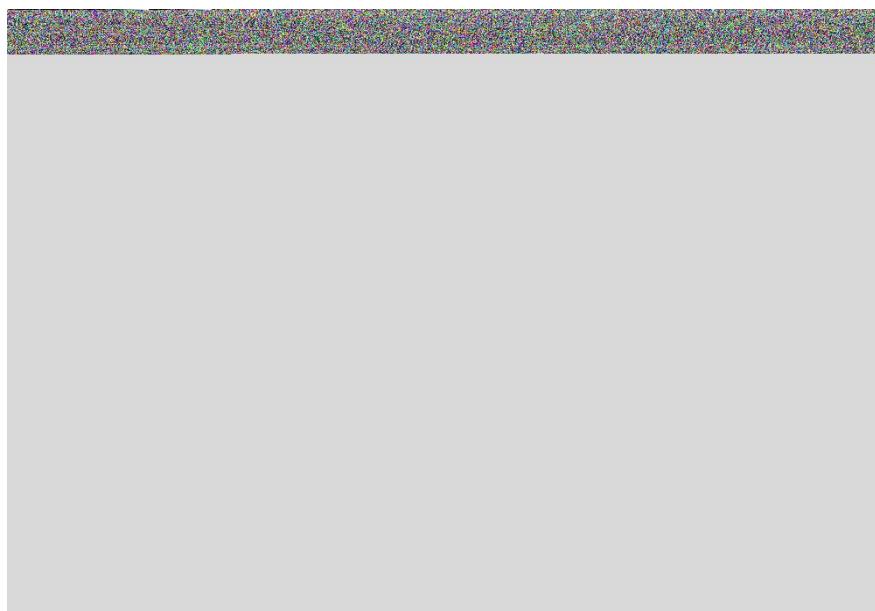


Fig. S5. UV-Vis spectra of the catalysts 1 and 2

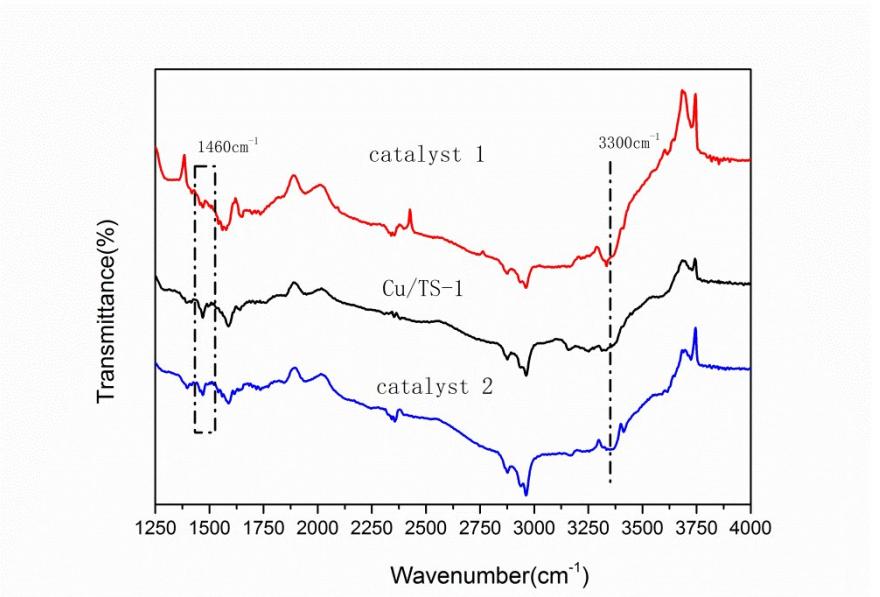


Fig. S6 NH<sub>3</sub>-IR analysis of Cu/TS-1, the catalysts 1 and 2