## **Supporting information**

## Formation of Copper Nanoparticles in LTL Nanosized Zeolite: Spectroscopic Characterization

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The areas of v(CO) bands associated with CO adsorption on various Cu<sup>n+</sup> species were obtained by spectral deconvolution with MagicPlot software using the Gaussian function. The same procedure was applied to all the spectra obtained on the series of non-reduced and reduced Cucontaining samples. As shown in Figure S 1 (A), the obtained IR spectrum of CO adsorbed on Cu<sup>2+</sup>-LTL sample activated under O<sub>2</sub> atmosphere at 673 K was fitted with six peaks, while that for Cu<sup>0</sup>-LTL activated at 723 K in vacuum was fitted with eight peaks (Figure S 1 (B)). For the decomposition of all spectra, the peak center was fixed and the full width at half maximum (FWHM) of the peaks was allowed to vary in a small range.





Figure S 1 Spectral deconvolution of the IR spectrum of CO adsorbed ( $n_{CO}=1600 \ \mu mol/g$ , T=100 K) on (A) Cu<sup>2+</sup>-LTL sample pretreated with O<sub>2</sub> at 673 K and (B) Cu<sup>0</sup>-LTL activated at 723 K in vacuum with MagicPlot software





Figure S 2. Evolution of the IR spectra of copper containing LTL sample (2300-2000 cm<sup>-1</sup>) upon evacuation at 100 K: sample activated at 673 K in  $O_2(A)$ , vacuum (B), and  $H_2(C)$ ; Cu<sup>0</sup>-LTL sample activated at 723 K in vacuum (D).

Table S 1 Evaluation of number of Cu<sup>+</sup> sites with respect to the total amount of copper in the samples.

Sample	m <sub>pellet</sub> , g	ε, cm/µmol	S, cm <sup>2</sup>	Area, cm <sup>-1</sup>	n <sub>CO</sub> , μmol/g	$n_{Cu^+}, \mu mol/g$	wt <sub>Cu</sub> , %	m <sub>Cu+</sub> , mg	m <sub>Cu</sub> , mg	$m_{Cu^+}/m_{Cu}$	%
(a)	0.02	13.5	2.01	2.59	80	19.7	1.24	0.025	0.243	0.10	10.1
(b)	0.02	13.5	2.01	10.98	194	83.5	1.24	0.104	0.243	0.43	42.8
(c)	0.02	13.5	2.01	5.69	225	43.2	1.24	0.054	0.243	0.22	22.2
(d)	0.02	13.5	2.01	5.08	197	38.9	1.24	0.048	0.241	0.20	20.0
Cu <sup>+</sup> -CO species evaluated based on the band at 2126 cm <sup>-1</sup>											
Sample	m <sub>pellet</sub> , g	ε, cm/µmol	S, cm <sup>2</sup>	Area, cm <sup>-1</sup>	n <sub>CO</sub> , μmol/g	n <sub>Cu+</sub> , μmol/g	wt <sub>Cu</sub> , %	m <sub>Cu+</sub> , mg	m <sub>Cu</sub> , mg	$m_{Cu+}/m_{Cu}$	%
(a)	0.02	10.0	2.01	2.13	80	21.8	1.24	0.027	0.243	0.11	11.2
(b)	0.02	10.0	2.01	7.97	194	81.8	1.24	0.102	0.243	0.42	41.9
(c)	0.02	10.0	2.01	3.85	225	39.5	1.24	0.049	0.243	0.20	20.2
(d)	0.02	10.0	2.01	4.47	197	46.3	1.24	0.057	0.241	0.24	23.7

Cu<sup>+</sup>-CO species evaluated based on the band at 2140 cm<sup>-1</sup>

(a)  $Cu^{2+}$ -LTL activated at 673 K in  $O_2$ , (b)  $Cu^{2+}$ -LTL activated at 673 K in vacuum, (c)  $Cu^{2+}$ -LTL activated at 673 K in  $H_2$  and (d)  $Cu^0$ -LTL activated at 723 K in vacuum

Where  $n_{Cu^+}$  is the concentration of  $Cu^+$  (µmol/g);

 $m_{Cu^+}$  is the mass of  $Cu^+$  species in the sample (g)

Area is obtained from the CO adsorption bands at 2140 and 2126 cm<sup>-1</sup> derived after the deconvolution (cm<sup>-1</sup>);

 $\epsilon$  is the molar absorption coefficient of CO on Cu<sup>+</sup> (cm/µmol); <sup>1</sup>

 $S_{pellet}$  is the surface of the pellet (2 cm<sup>2</sup>);

m<sub>pellet</sub> is the mass of the pellet (g);

 $n_{CO}$  is the amount of CO adsorbed on Cu<sup>+</sup> at "saturation" determined from the intersection of two trend lines built on the slope and plateau on the graph of integrated area of the v(CO) band at 2140 cm<sup>-1</sup> and at 2128 cm<sup>-1</sup> bound to copper as a function of the amount of introduced CO;

 $m_{Cu^+}$  is the mass of  $Cu^+$  species in the pellet (mg);

 $m_{Cu}$  is the total mass of Cu in the pellet (mg).

## References

1 K. I. Hadjiivanov, *Adv. Catal.*, 2002, **47**, 307–511.