

*Supporting Information for*

**Catalytic oxidation of light alkanes  
mediated at room temperature by a  
tricopper cluster complex immobilized in  
mesoporous silica nanoparticles<sup>1</sup>**

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<sup>1</sup>This article is dedicated to Professor Istvan Horvath on the occasion of his 65<sup>th</sup> birthday.

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References

## Materials and Methods

All solvents and chemicals used were of commercially available analytical grade, if not mentioned otherwise. Solvents for air-sensitive reactions were distilled under argon.

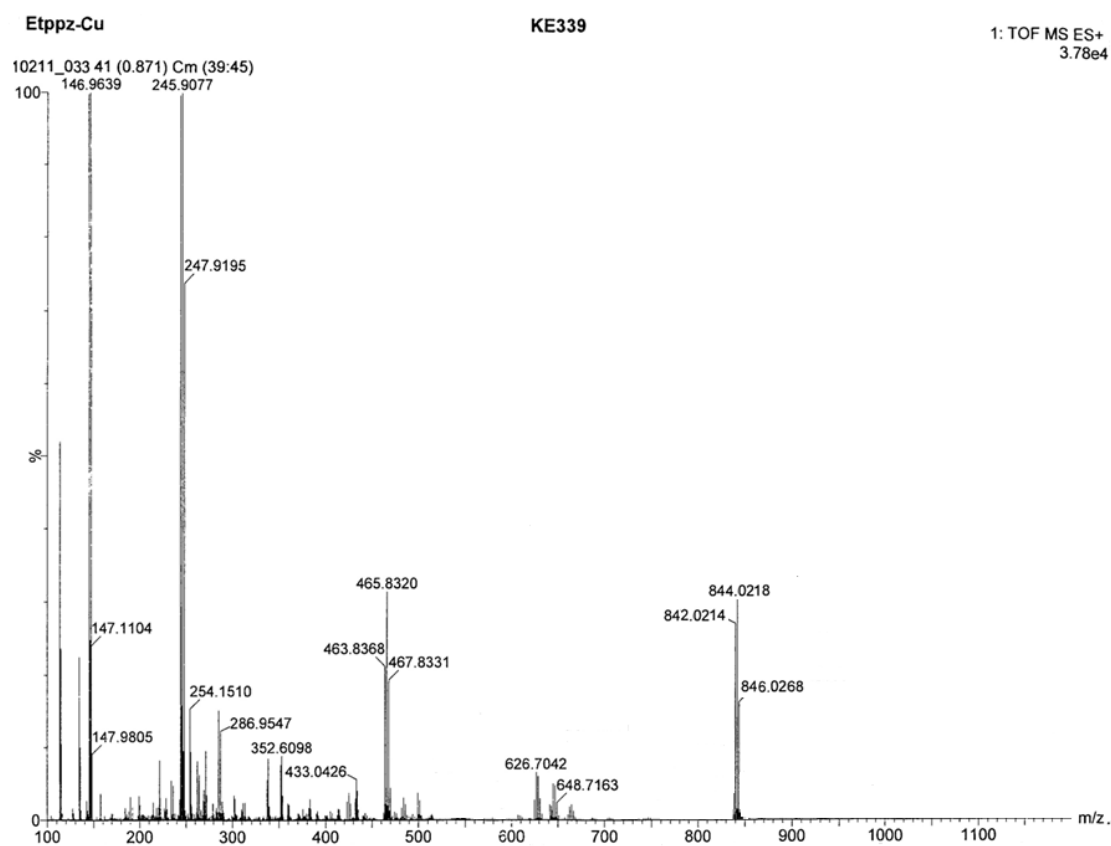
### Synthesis of ligands and preparation of the tricopper complex

**Preparation of 3,3'-[1,4-diazepane-1,4-diyl]bis(1-chloropropan-2-ol) (1).** A solution of epichlorohydrin (1.85 g, 20 mmol) dissolved in methanol (15.0 ml) was added drop-wise to a solution of homopiperazine (1.02 g, 10 mmol) dissolved in methanol (30.0 ml) and stirred at 5 °C. After stirring for 72 h at 5 °C, the resulting mixture was purified by column chromatography on silica gel using a mixed solvent (8% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>) as the eluent. Compound **1** was obtained in 88% yield (2.50 g).

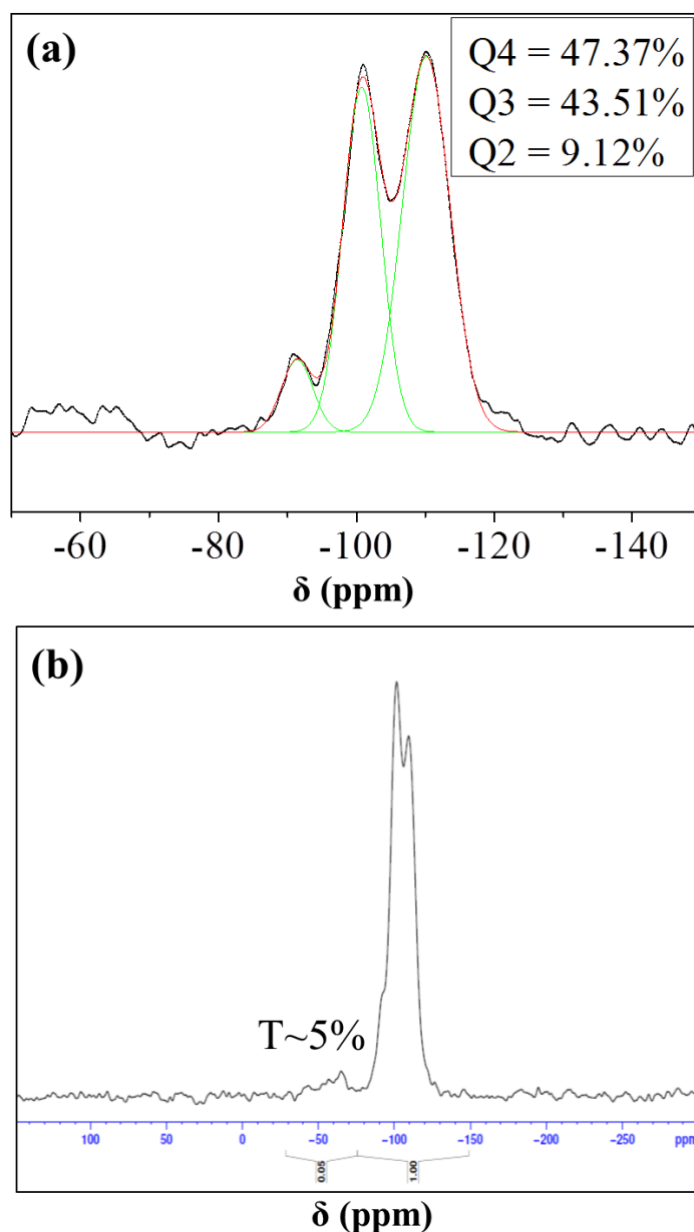
**Synthesis of the ligand (3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylpiperazine-1-yl)propan-2-ol]) (7-N-Etppz).** K<sub>2</sub>CO<sub>3</sub> (4.15 g, 30 mmol) was added to a CH<sub>3</sub>CN (15.0 ml) solution containing compound **1** (4.28 g, 15 mmol), and 1-ethylpiperazine (3.46 g, 30 mmol). The mixture was then heated to 70-80 °C for 48 h under a N<sub>2</sub> atmosphere. After cooling to room temperature, the solution was filtered, and upon evaporation of the filtrate to dryness, the ligand **7-N-Etppz** was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 1.8 (t, 2H, CH<sub>3</sub>); 2.05-2.93 (m, CH<sub>2</sub>); 3.6 (s, 2H, CH), 4.4 (s 2H, CH). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): the major peaks appeared at 11.74, 11.82, 27.10, 52.0, 52.5, 53.2, 54.4, 55.3, 62.2, 62.4, and 64.7. ESI-MS (positive ion): m/z 441.

**Preparation of the tricopper complex Cu<sup>II</sup>Cu<sup>II</sup>Cu<sup>II</sup>(7-N-Etppz).** A anhydrous CH<sub>3</sub>CN solution (25 ml) containing **7-N-Etppz** (2.205 g, 5.0 mmol) and three equivalents of Cu<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (5.49 g, 15.1 mmol) were mixed and stirred for 1 h to give a deep

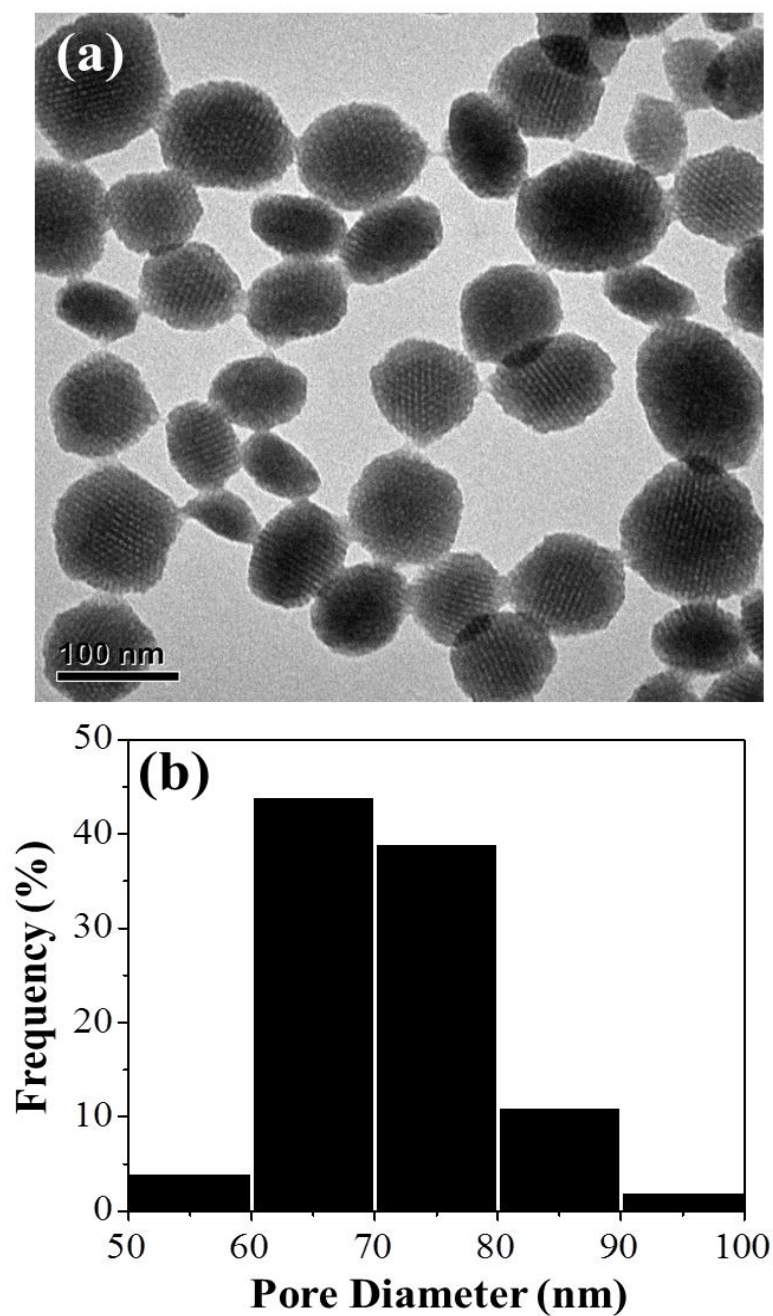
green solution, which was filtered, washed with  $\text{CH}_2\text{Cl}_2$ , and dried in vacuum to give a green powder. The calculated yield was 4.00 g (95%). The elemental analysis of  $\text{C}_{23}\text{H}_{46}\text{O}_{11}\text{N}_6\text{Cl}_2\text{Cu}_3$  gave C, 32.77; H, 5.50; N, 9.94%, which were the same as the calculated values within experimental uncertainty: C, 32.72; H, 5.49; N, 9.96%. ESI-MS (positive ion):  $m/z$  844.02.



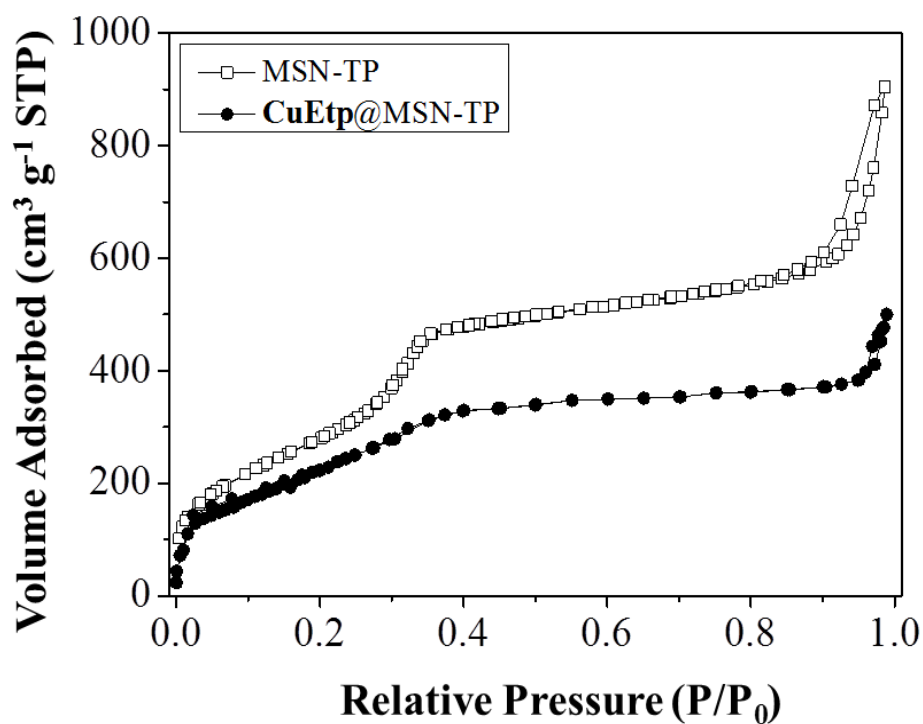
## Supporting Figures



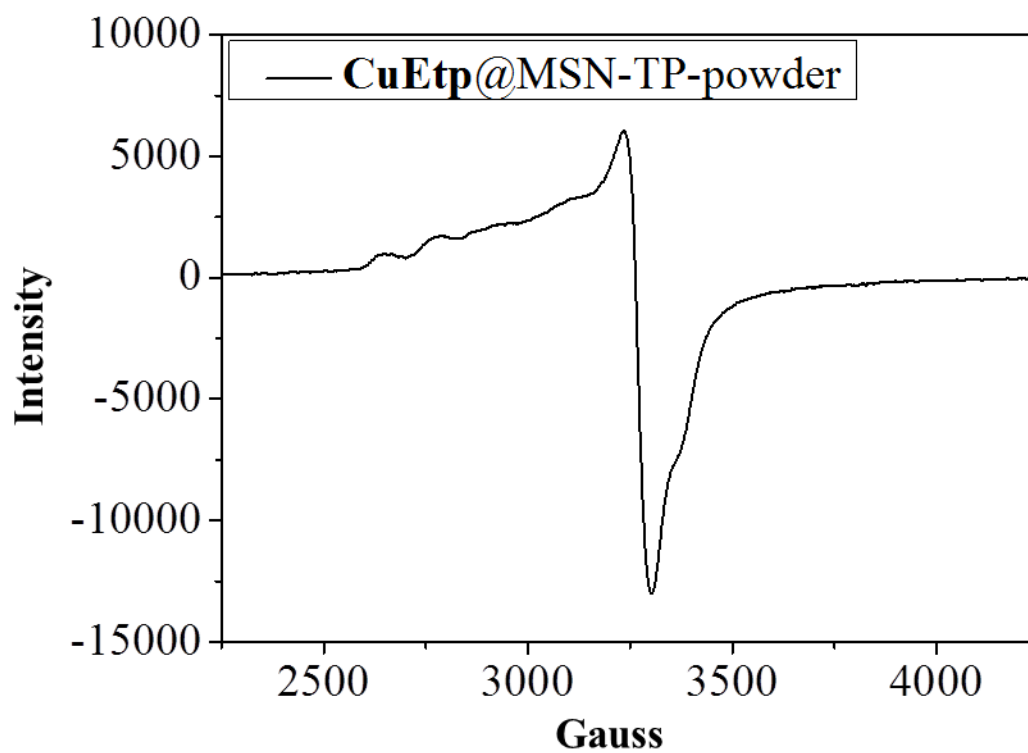
**Figure S1.** (a)  $^{29}\text{Si}$  solid-state NMR spectra of the MSN-TP sample. The Q2, Q3, and Q4 signals are attributed to the  $\text{Si}(\text{OH})_2(\text{OSi})_2$ ,  $\text{Si}(\text{OH})(\text{OSi})_3$ , and  $\text{Si}(\text{OSi})_4$  substructures, respectively. The peak percentages are obtained by de-convoluting each spectrum into their components and fitting the full-width at half-maximum of each component spectrum. (b)  $^{29}\text{Si}$  NMR spectrum of the MSN-TP sample, comparing the T signals ( $[\text{C}-\text{Si}(\text{OH})(\text{OSi})_2]$  or  $[\text{C}-\text{Si}(\text{OSi})_3]$ ) to the Q signals. The ratio of the areas of the T and Q signals indicates that 5% of the silica surface is conjugated to the functionalizing TP group. [Taken from reference 1. Reproduced with permission of The Royal Society of Chemistry.]



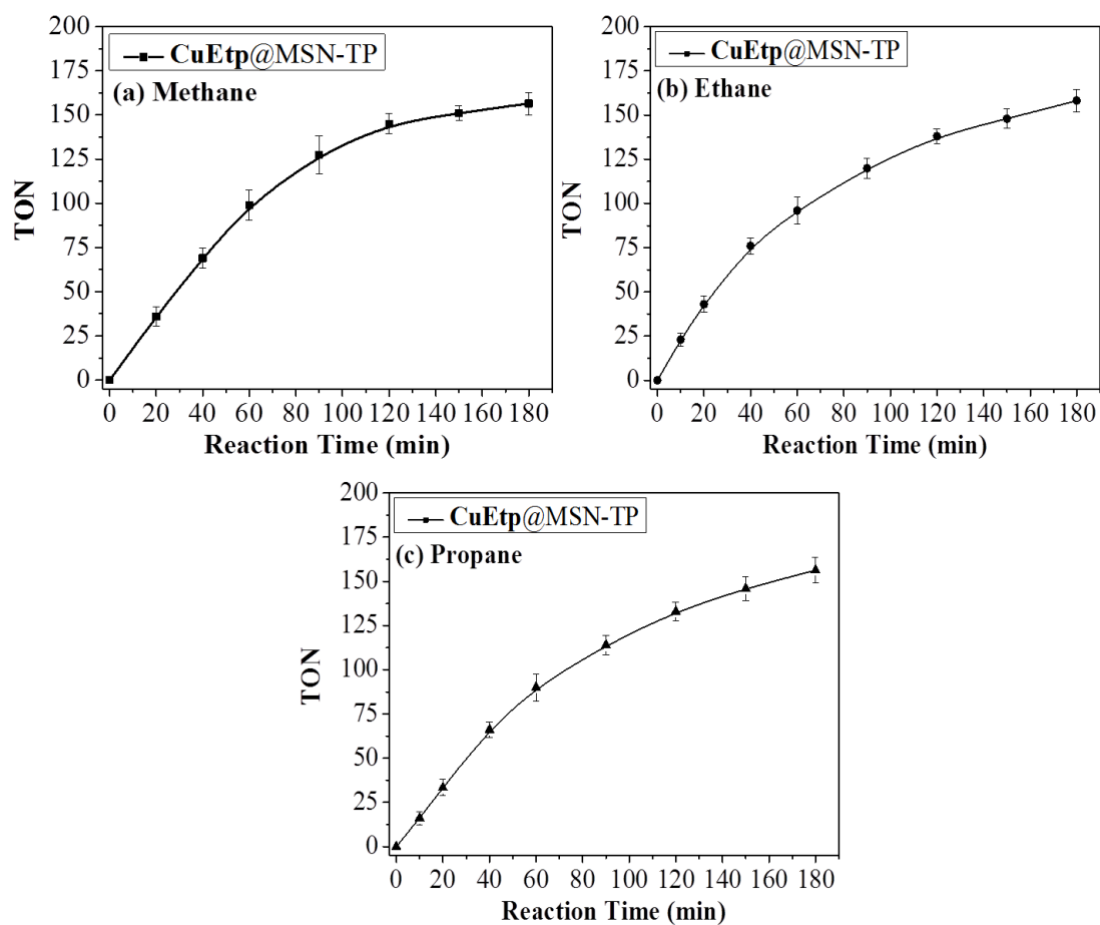
**Figure S2.** (a) Transmission electron microscopy (TEM) images of the functionalized MSN-TP nanoparticles with 100 nm scale bar. (b) The statistical analysis of the TEM image gives a particle size distribution of  $71.4 \pm 7.8$  nm for the MSN-TP nanoparticles (based on a patch size of 100 particles). [Data taken from reference 2. Reproduced with permission of The Royal Society of Chemistry.]



**Figure S3.** The nitrogen adsorption–desorption isotherms before and after the immobilization of the  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(7\text{-}N\text{-Etppz})^{4+}$  tricopper complex. [Taken from reference 2. Reproduced with permission of The Royal Society of Chemistry.]

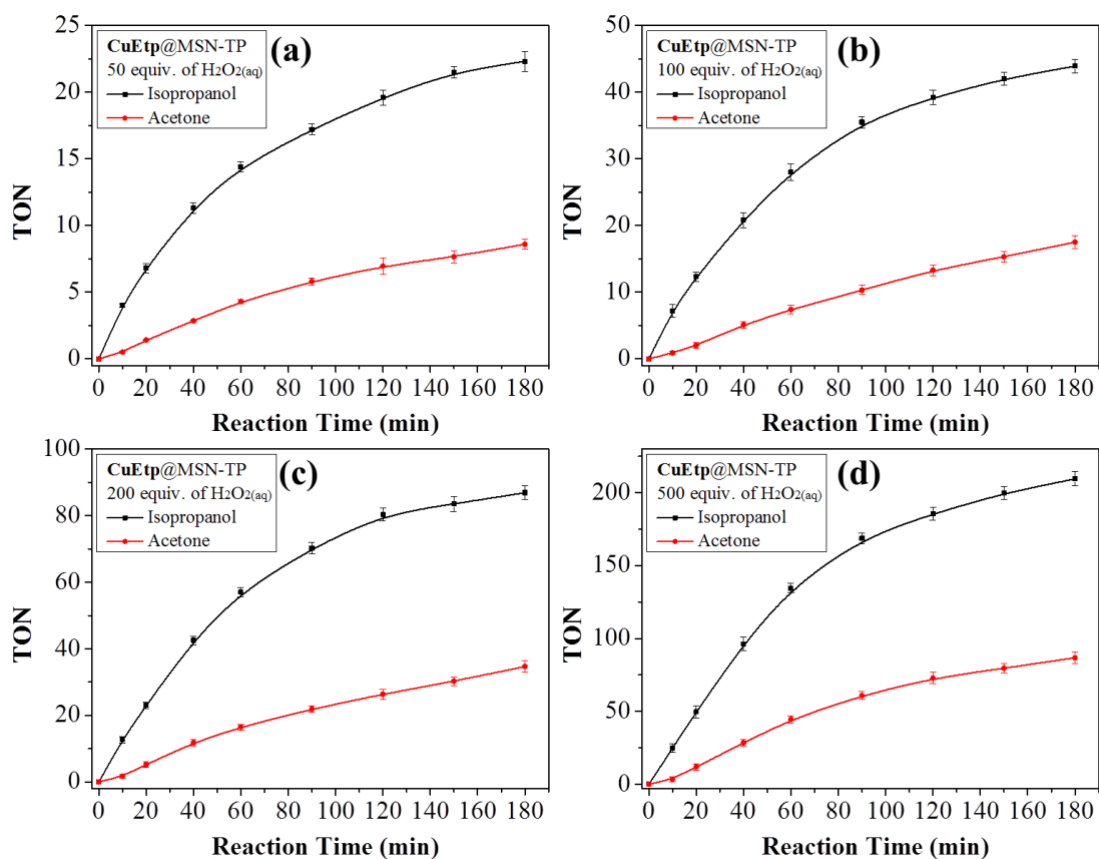


**Figure S4.** X-band EPR spectrum of **CuEtp@MSN-TP** powder sample at 77 K. Conditions: Microwave frequency: 9.45 GHz; microwave power: 10 mW; and modulation amplitude: 4G.

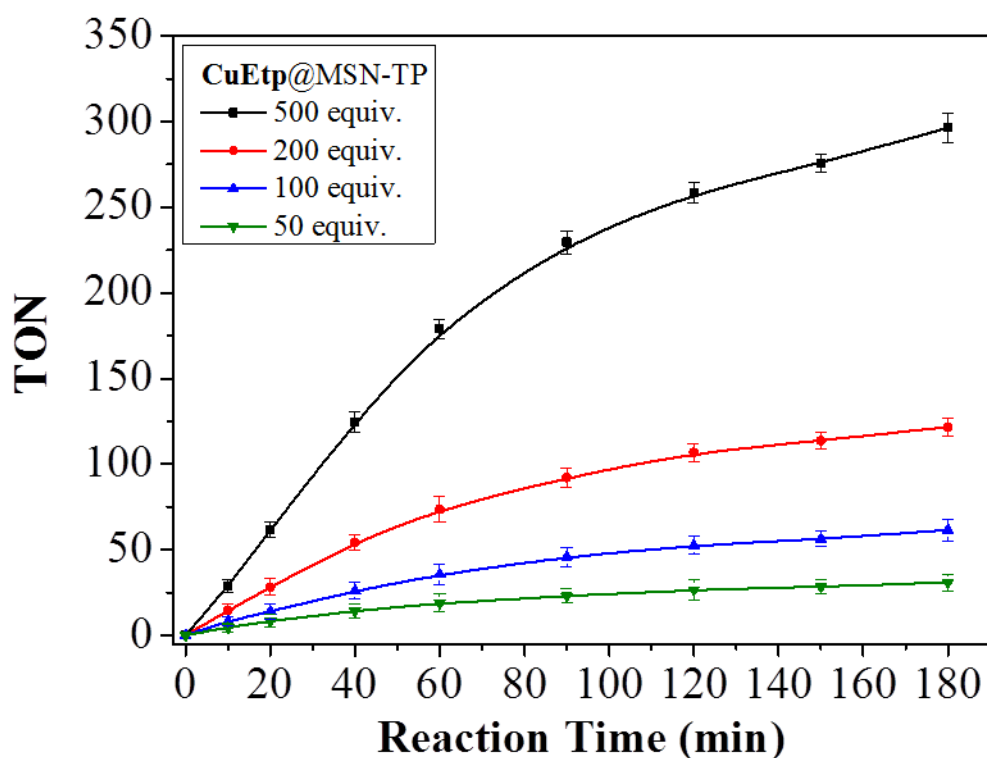


**Figure S5.** Time course of (a) the product turnover numbers (TON) of methanol in methane oxidation, (b) the product turnover numbers (TON) of ethanol in ethane oxidation, and (c) the product turnover numbers of isopropanol and acetone (TON-ol + 2 TON-one) obtained in propane oxidation, catalyzed by the **CuEtp@MSN-TP** catalyst at room temperature using 200 equiv. of  $\text{H}_2\text{O}_2$  to initiate the catalytic turnover. *Panel (a)* is taken from reference 1. Reproduced with permission of The Royal Society of Chemistry.] The starting amount of alkane gas ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , or  $\text{C}_3\text{H}_8$ ) in each of the experiments is 4.1 mmol; and the quantity of the tricopper complex immobilized in the MSN-TP is 2.28  $\mu\text{mole}$ .

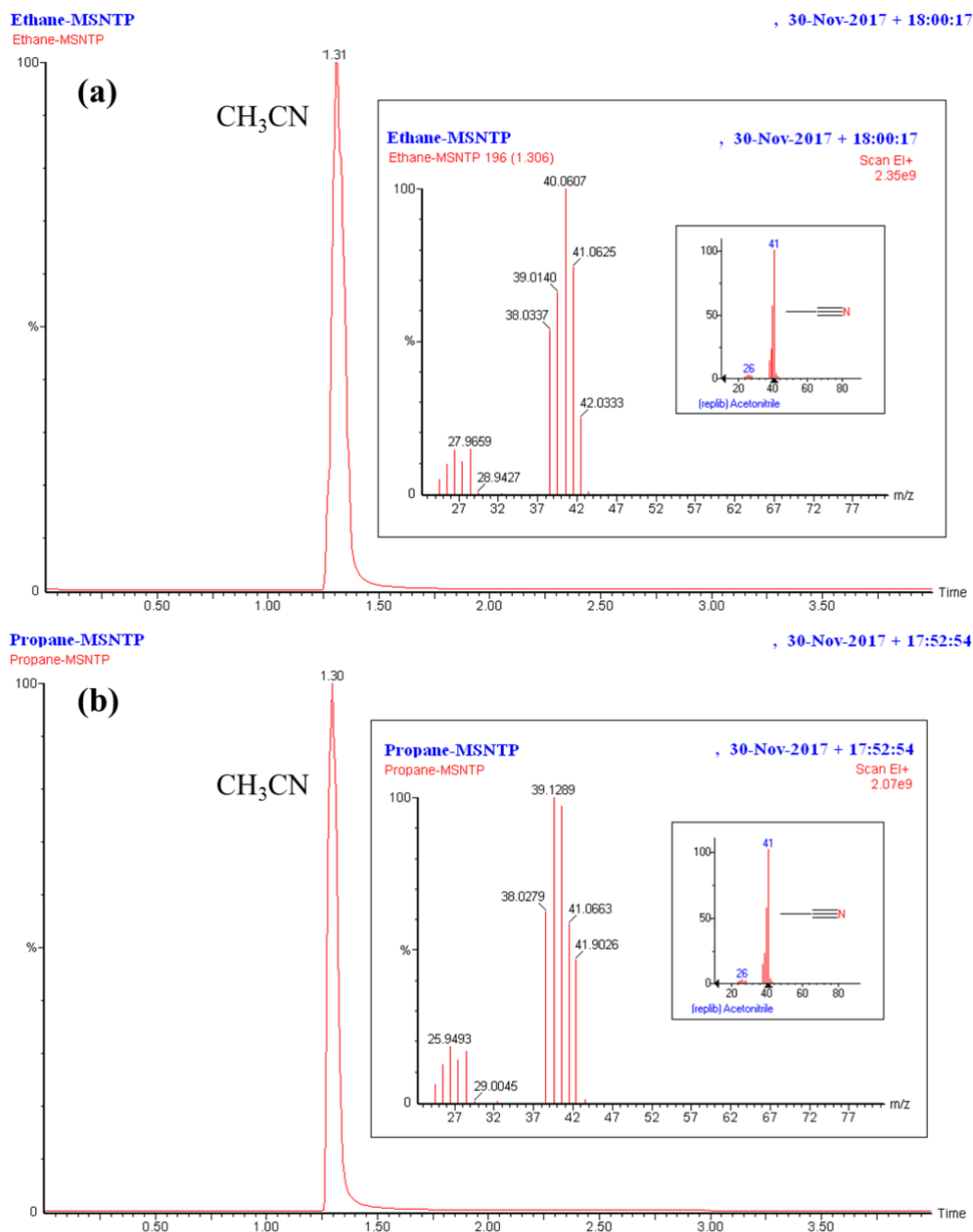




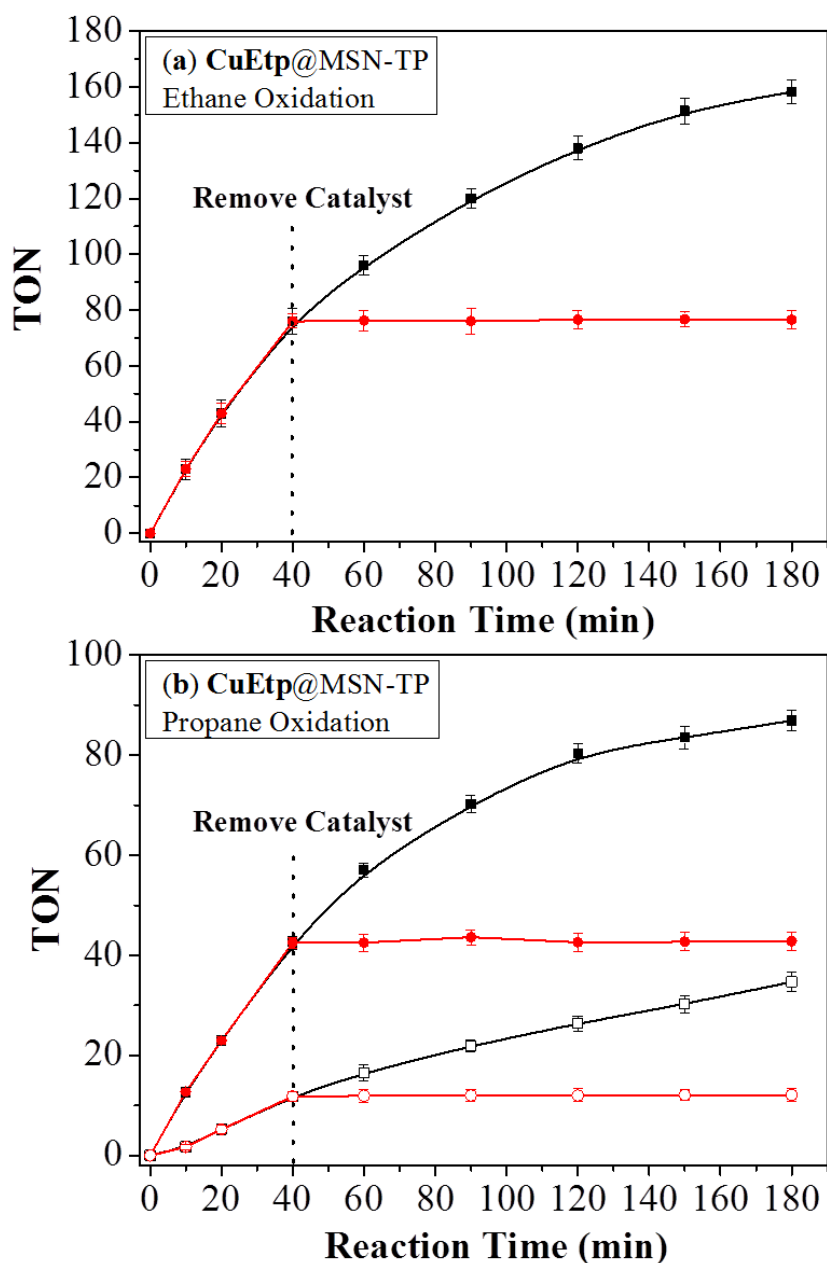
**Figure S6.** Time course of the individual product TONs (isopropanol and acetone) in the propane oxidation catalyzed by the **CuEtp@MSN-TP** catalyst with (a) 50 equiv., (b) 100 equiv., (c) 200 equiv., and (d) 500 equiv. of  $\text{H}_2\text{O}_2$  (35%, aqueous), the quantity of  $[\text{H}_2\text{O}_2]_0$  used to initiate the catalytic turnover. The starting amount of propane gas in each of the experiments is 4.1 mmol; and the quantity of the tricopper complex immobilized in the MSN-TP is 2.28  $\mu\text{mole}$ .



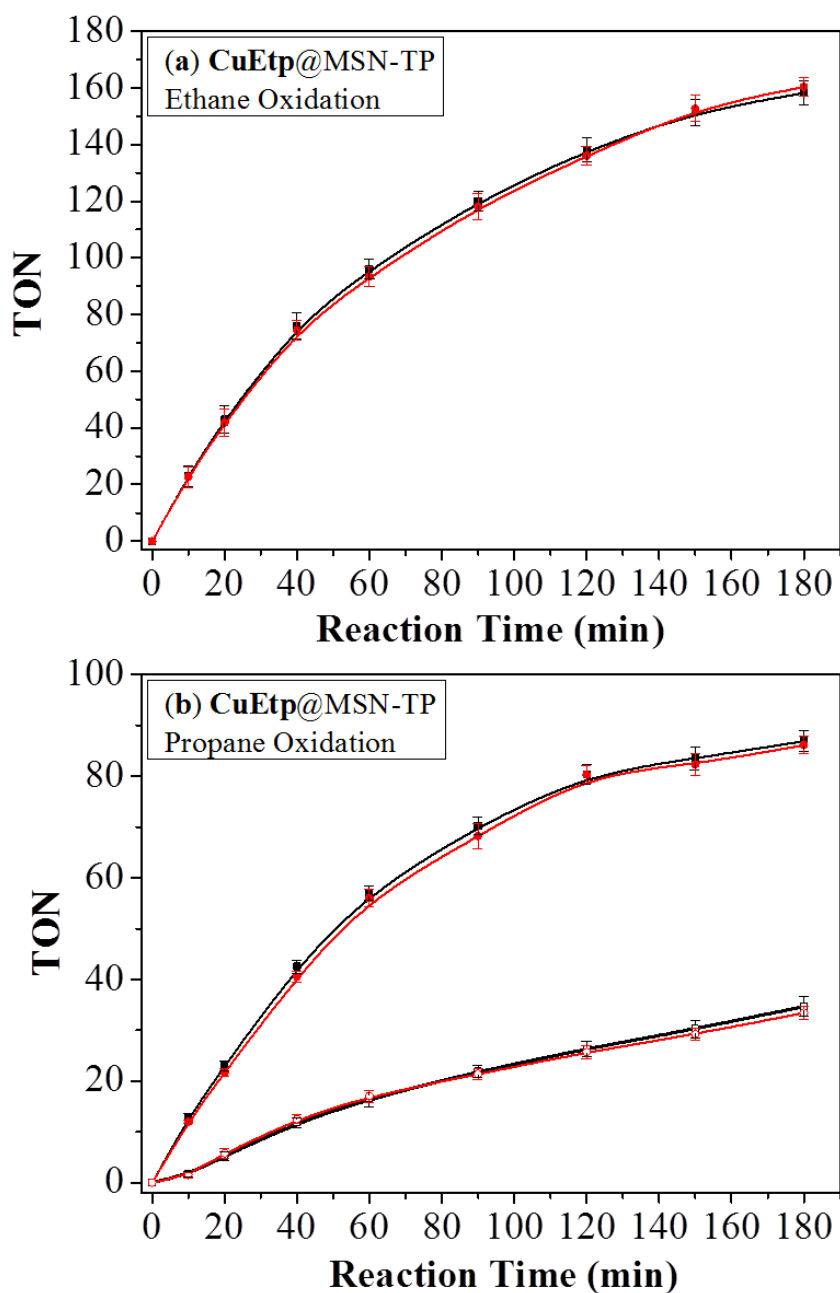
**Figure S7.** Time course of the total product TONs ( $\text{TON}_{\text{ol}} + \text{TON}_{\text{one}}$ ) in the propane oxidation catalyzed by the **CuEtp@MSN-TP** catalyst at room temperature using different starting amounts of  $\text{H}_2\text{O}_2$  ( $[\text{H}_2\text{O}_2]_0$ , in equiv.) to drive the catalytic turnover.  $\text{TON}_{\text{ol}}$  and  $\text{TON}_{\text{one}}$  denote the product TONs of isopropanol and acetone, respectively. The starting amount of propane gas in each of the experiments is 4.1 mmol; and the quantity of the tricopper complex immobilized in the MSN-TP is 2.28  $\mu\text{mole}$ .



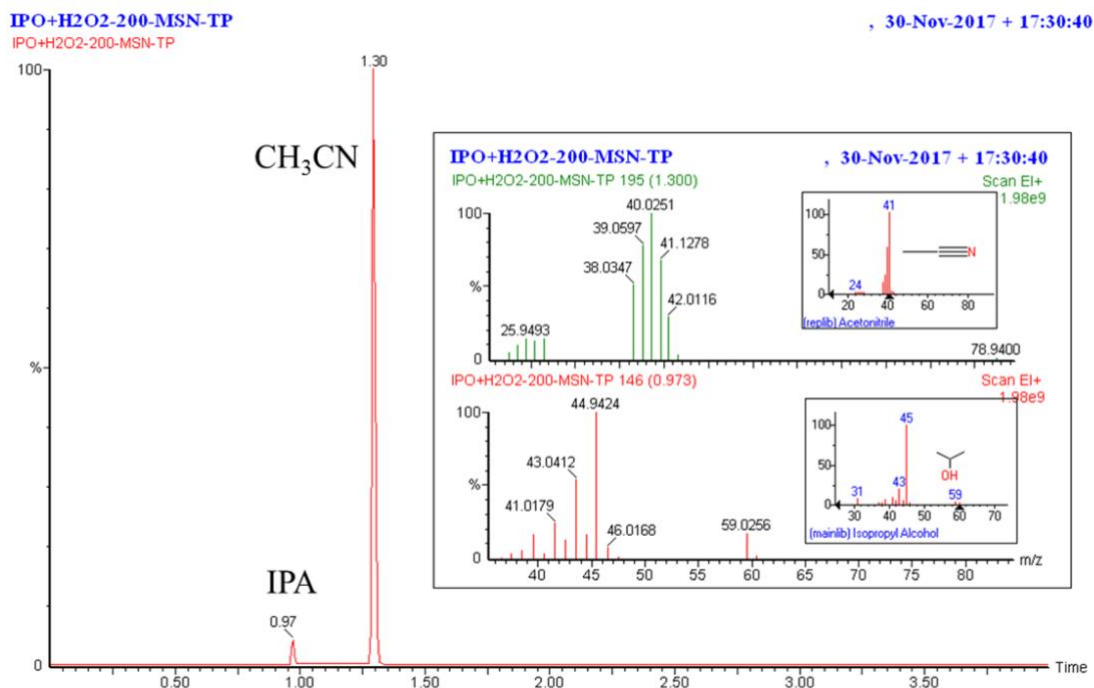
**Figure S8.** GC-MS spectra of the products observed in the (a) ethane and (b) propane oxidations attempted using the bare MSN-TP (20 mg) for 3 h. The starting amount of alkane gas ( $C_2H_6$  or  $C_3H_8$ ) in each of the experiments is 4.1 mmol. These control experiments were performed according to the same procedures used in the ethane and propane oxidation reaction mediated by the **CuEtp@MSN-TP** catalyst shown in the text. No oxidation products were observed. *Inset:* The fitted MS spectrum from the built-in MS database software.



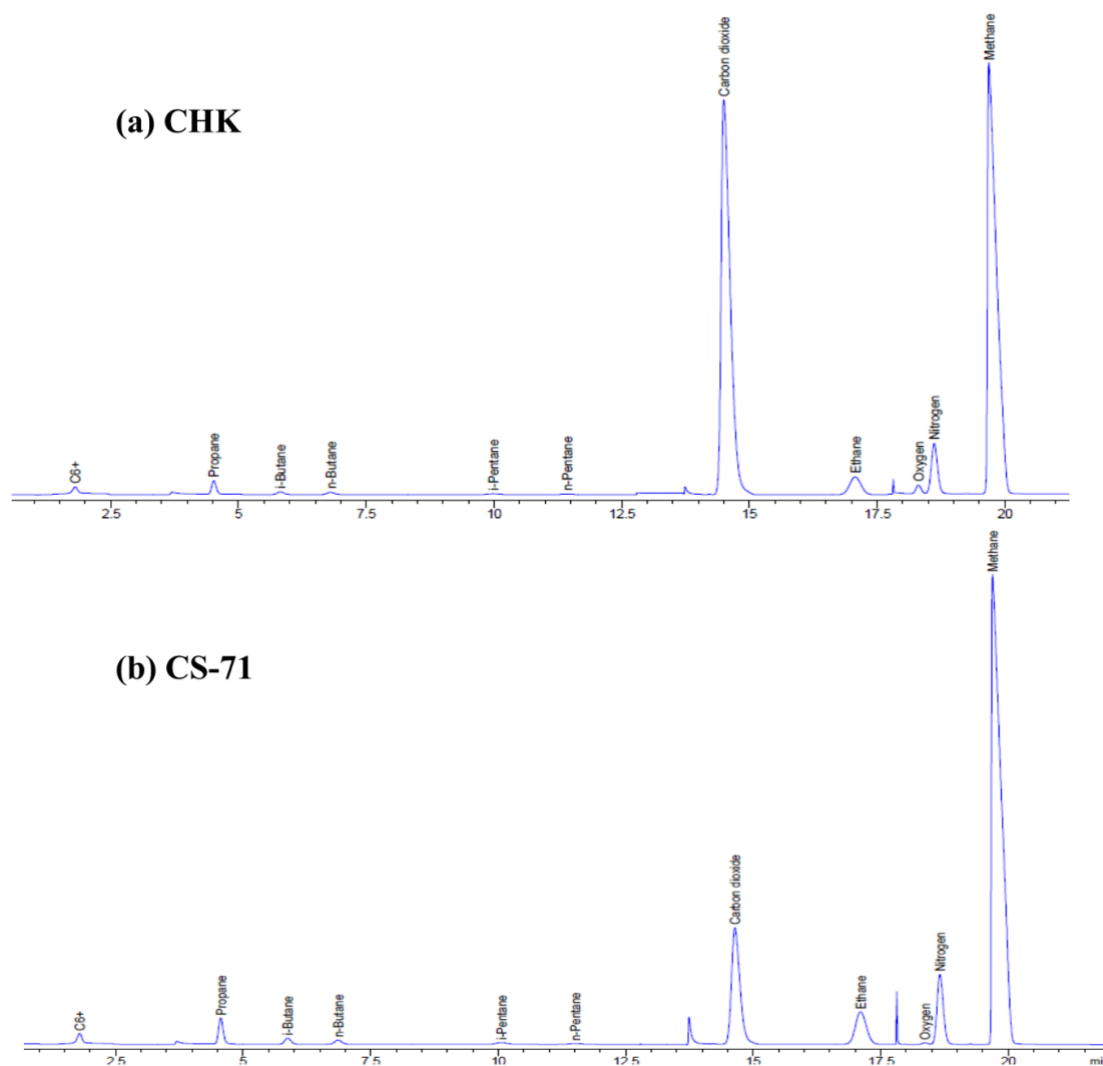
**Figure S9.** Time course of the product TONs in the (a) ethane and (b) propane oxidations catalyzed by the **CuEtp@MSN-TP** catalyst at room temperature initiated with 200 equiv. of  $\text{H}_2\text{O}_2$  (black line). The starting amount of alkane gas ( $\text{C}_2\text{H}_6$  or  $\text{C}_3\text{H}_8$ ) in each of the experiments is 4.1 mmol; and the quantity of the tricopper complex immobilized in the MSN-TP is 2.28  $\mu\text{mole}$ . In each case, a parallel experiment was also conducted under the same conditions except that the catalytic turnover was interrupted 40 minutes into the experiment to quickly separate and remove the **CuEtp@MSN-TP** catalyst from the liquid phase by centrifugation. Measurement of the catalytic activity was then continued on the supernatant until the end of the 3-h experiment (red line). No catalytic activity was observed for the supernatant.



**Figure S10.** Comparison of the time courses of the (a) ethane and (b) propane oxidations mediated by the **CuEtp@MSN-TP** catalyst at room temperature in the absence (*black* line) and presence (*red* line) of the radical trapping agent 2,6-di-tert-butyl-p-cresol (1 equiv., based on the amounts of the immobilized tricopper complexes in the MSN-TP sample). The starting amount of alkane gas ( $C_2H_6$  or  $C_3H_8$ ) in each of the experiments is 4.1 mmol; and the quantity of the tricopper complex immobilized in the MSN-TP is 2.28  $\mu$ mole. The TONs of the products are expressed in terms of the moles of product formed per mole of the tricopper complex in each case.



**Figure S11.** The GC-MS spectrum of isopropanol oxidation catalyzed by the bare MSN-TP sample (20 mg) for 3 h at room temperature in the presence of 200 equiv. of H<sub>2</sub>O<sub>2</sub>. The starting amount of isopropanol is 4.1 mmol. No catalytic activity was detected with the bare MSN-TP sample, indicating that the conversion of isopropanol to acetone is intrinsic to the active tricopper complex immobilized in the MSN-TP when the **Cu<sub>3</sub>(7-*N*-Etpyz)** complex is activated by O<sub>2</sub> and the catalytic turnover is driven by H<sub>2</sub>O<sub>2</sub>.



**Figure S12.** The GC spectra of natural gas samples collected by the China Petroleum Corp. (CPC) from different locations in Miao-li County in Taiwan: (a) CHK, and (b) CS-71. Gas analyses were provided by the CPC.

## References

1. Liu, C.-C.; Mou, C.-Y.; Yu, S. S. F.; Chan, S. I., Heterogeneous formulation of the tricopper complex for efficient catalytic conversion of methane into methanol at ambient temperature and pressure. *Energy Environ. Sci.* **2016**, *9*, 1361-1374.
2. Liu, C.-C.; Ramu, R.; Chan, S. I.; Mou, C.-Y.; Yu, S. S. F., Chemistry in confined space: a strategy for selective oxidation of hydrocarbons with high catalytic efficiencies and conversion yields under ambient conditions. *Catal. Sci. Tech.* **2016**, *6*, 7623-7630.

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