

Electronic Supplementary Information

Distinct Activation of Cu-MOR for Direct Oxidation of Methane to Methanol

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Synthesis of a Cu-MOR catalyst

A Cu-MOR catalyst was synthesized via a method established by Lercher et al. [S1]. H-MOR with a Si/Al ratio = 20 was prepared by calcination of NH₄-MOR under excess air at 500 °C for 8h. Ion exchange was performed using H-MOR and an aqueous solution of 0.01 M copper (II) acetate (Junsei). The resultant pale blue powder was collected and washed with excess deionized water with repeated centrifugation. Samples were dried at 70 °C overnight, and then were calcined at 450 °C for 3h (5 °C min⁻¹). The copper content of the catalyst was quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Reaction tests

Reaction tests were carried out using a fixed-bed flow reactor with a thermocouple well. The temperature was measured via a K-type thermocouple placed in the thermocouple well, and was controlled electronically via an external electrical furnace. Then, 0.2 g of a Cu-MOR catalyst was placed on a porous quartz bed, and activation was carried out either by N₂O (9.95% in He) or O₂ flow (total flow rate 20 ml min⁻¹) for 2h at temperatures ranging from 300 to 600 °C (ramping rate = 10 °C min⁻¹). The samples were cooled to 150 °C, and then the remaining O₂ or N₂O was purged with N₂ flow for 30 min. Subsequently, the reaction with pure methane (20 ml min⁻¹) was performed for 1h. After the reaction, the methane was purged under a N₂ flow, and the samples were cooled to 135 °C. The produced methanol was extracted via a steam flow (7% H₂O/N₂ 33 ml min⁻¹), and was quantified by quadruple mass spectrometer (Hiden Analytical QGA).

Characterization

Ultraviolet-visible-near infrared (UV-vis-near IR) spectra were recorded using a Jasco V670 spectrometer equipped with a diffuse reflectance spectroscopy (DRS) unit. The powder samples were loaded into a quartz cell, and the spectra were collected at 10,000 – 42,000 cm⁻¹. The Cu-MOR was treated in N₂, N₂O (9.95% in He, 20 ml min⁻¹) or O₂ flow (20 ml min⁻¹) for 2h at the desired temperature. Subsequently, the recorded activated samples by UV-vis-near IR spectrometer were reacted with a CH₄ flow (20 ml min⁻¹) at 150 °C for 1h and analyzed. The intensity of the collected UV-vis-near-IR spectra was processed in the form of the Kubelka-Munk function.

Cu K-edge X-ray absorption near edge spectra (XANES) were collected in a transmittance mode on a 10C wide XAFS beamline at the Pohang Light Source (PLS) at the 3.0 GeV storage ring with a beam current of ~300 mA. Samples were prepared by activating Cu-MOR with N₂O (9.95% in Helium) at 600 °C or O₂ at 450 °C for 2h. A reference Cu foil was concurrently measured for calibration of the samples. The collected X-ray adsorption spectra were processed using an ATHENA software program.

Temperature programmed desorption of H₂O was carried out using the same system reaction. Prior to the analysis, steam flow (7% H₂O/N₂ 33 ml min⁻¹) was passed through 0.15 g of a Cu-MOR sample held on a quartz bed at 130 °C for 1h. The sample was cooled to room temperature, and then was heated with a temperature-ramping rate of 10 °C min⁻¹. The desorbed H₂O was analyzed using a quadruple mass spectrometer (Hiden Analytical QGA).

Additional discussion

The products from methane oxidation

Figure S1 shows typical MS signals during the extraction by H₂O of Cu-MOR after N₂O activation and the subsequent reaction with CH₄ flow. The MS signals for a blank test (only H₂O flow without activation and reaction) are also shown. The increase in the signal of CH₃OH (m/z = 31) is clearly recognizable. Dimethyl ether (m/z = 46), a product from the sequential dehydration of methanol, was not detected. The signal of formaldehyde (m/z = 29) was slightly increased when H₂O flow was injected to N₂O-activated Cu-MOR, but blank showed quite similar signal. This indicates that the increase in the formaldehyde signal was attributed to the change in composition of sampling gases, rather than detection of formaldehyde. The signal of CO₂ (m/z = 44) for N₂O-activated Cu-MOR was also comparable to that for blank test. Therefore, methanol was sole product for the oxidation of methane over Cu-MOR catalyst. It was also previously reported that only methanol was produced from Cu-exchanged zeolites [S2].

Effect of the partial pressure of an oxidant on methanol production

The effect of partial pressure of N₂O or O₂ on methanol production is shown in Figure S9. When Cu-MOR was activated under decreased partial pressure of N₂O, the methanol production was merely influenced (98, 102, and 99 μmol/g for 10, 7, and 3% N₂O/He, respectively). In contrast, a decrease in O₂ partial pressure significantly suppressed the methanol production (67 and 35 μmol/g for 100% and 10% O₂, respectively).

These results supported our description for the formation of active sites during N₂O or O₂ activation. The decrease in partial pressure of an oxidant increases the free energy of adsorption (or reaction) about 3-4 kJ/mol (N₂O 10% → 3%: 3.0 kJ/mol, O₂ 100% → 10%: 4.3 kJ/mol) according to a change of the chemical potential of an oxidant as described by the following equation:

$$\mu(T,p) = \mu^0(T,p_0) + \frac{1}{2}RT \ln \frac{p}{p_0}$$

where p is partial pressure, and p₀ is standard atmospheric pressure.

For N₂O activation, the increase in free energy negligibly affects the formation of an active site due to its higher exothermicity. In contrast, in the case of O₂ activation whereby the sign of free energy change is reversed in the temperature range of the reaction tests, the small increase of free energy (4.3 kJ/mol) considerably suppresses the adsorption of O₂. This can lead to a decrease in the formation of active sites and to lower methanol production.

References

- [S1] S. Grundner, M. A. C. Markovits, G. Li, M. Tromp, E. A. Pidko, E. J. M. Hensen, A. Jentys, M. Sanchez-Sanchez and J. A. Lercher, *Nat. Commun.*, 2015, **6**, 7546.
- [S2] T. Sheppard, C. D. Hamill, a Goguet, D. W. Rooney and J. M. Thompson, *Chem. Commun.*, 2014, **50**, 11053.

Additional Figures

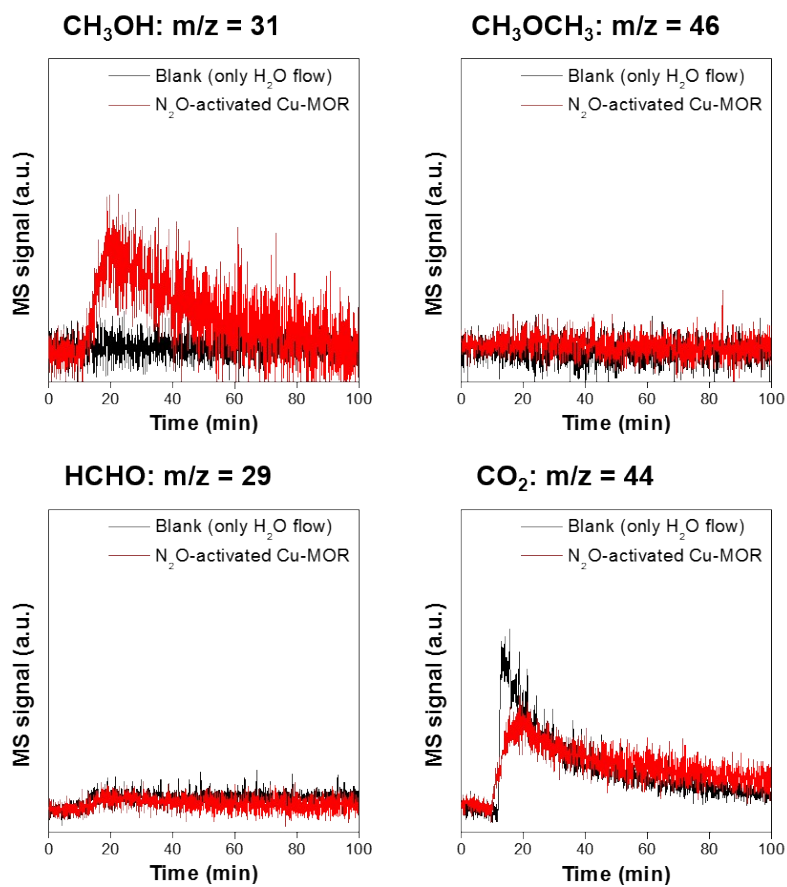


Figure S1. MS signals during extraction by H₂O of N₂O-activated Cu-MOR.

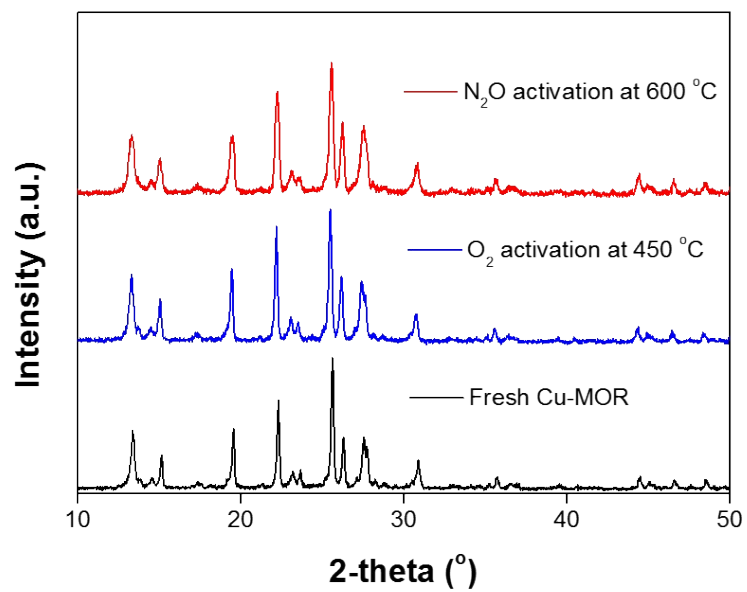


Figure S2. XRD patterns for Cu-MOR catalyst after activation by N₂O or O₂.

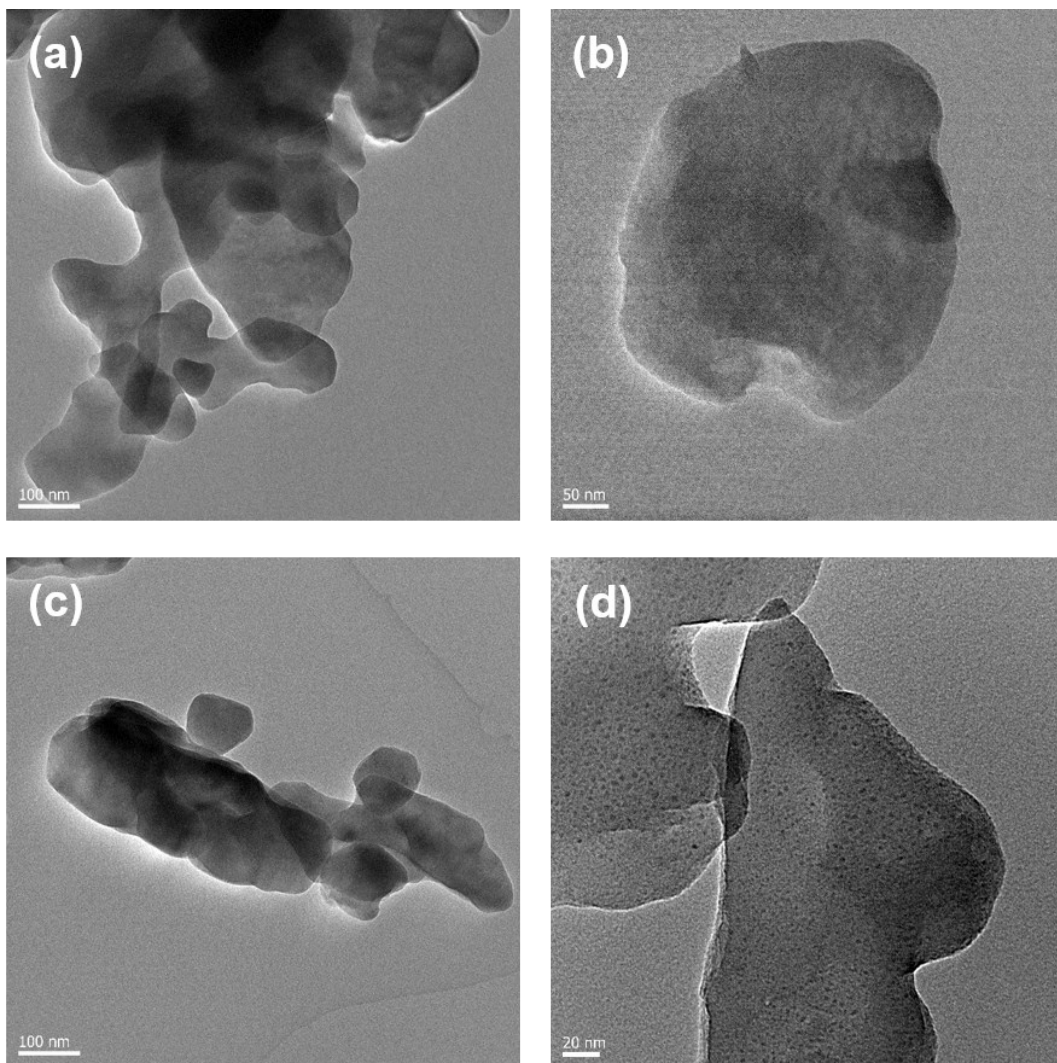


Figure S3. TEM images of fresh Cu-MOR (a), after N_2O activation (b), and after O_2 activation (c). When electron beam was focused (high magnification), Cu particles were observed after few seconds due to agglomeration (d).

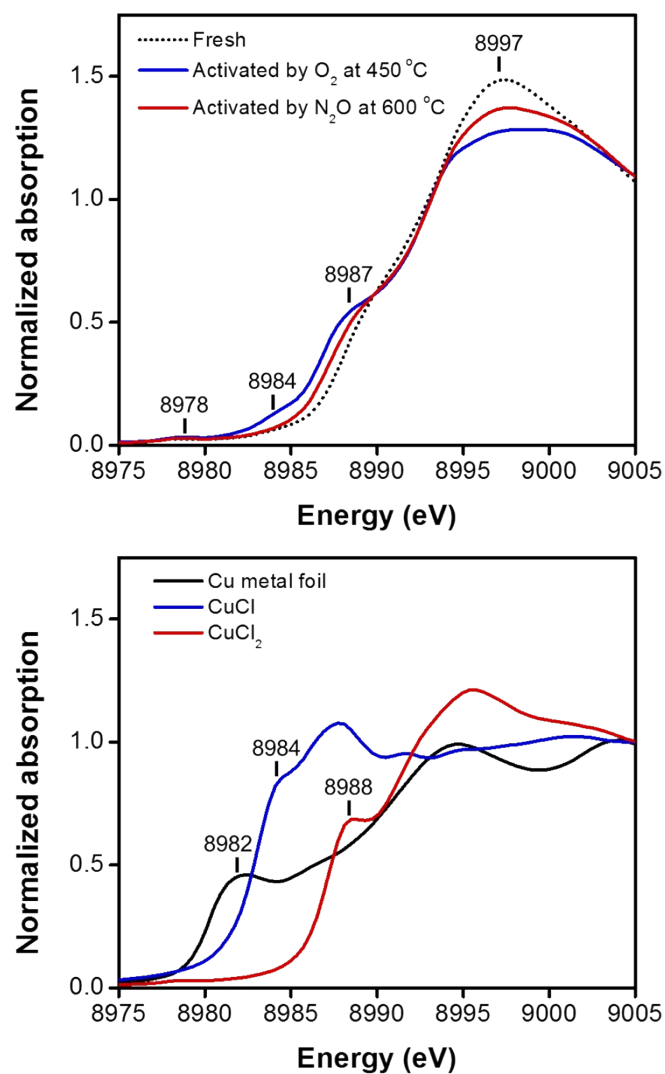


Figure S4. X-ray absorption near edge spectra (XANES) for Cu-MOR samples and reference materials. Characteristic absorptions for Cu-MOR samples and pre-edge features of reference materials are indicated.

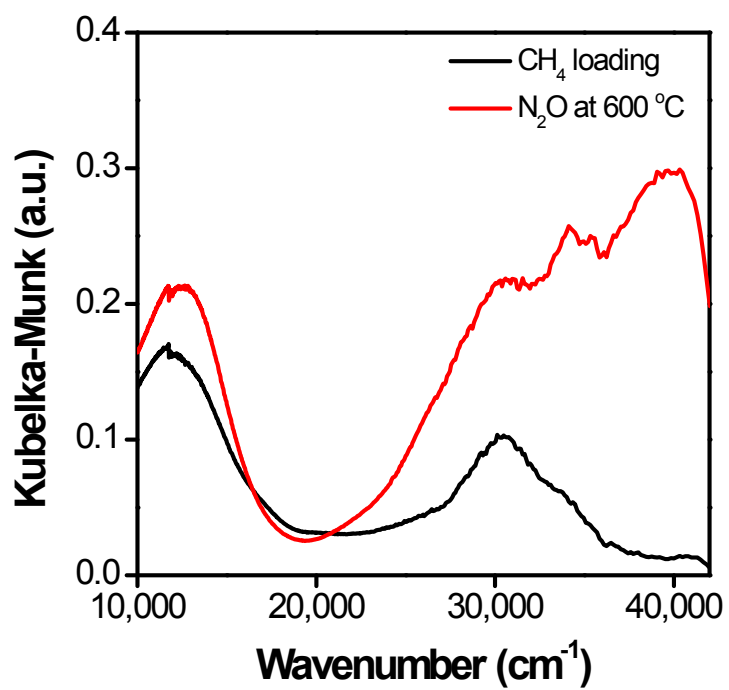


Figure S5. UV-vis-NIR spectra for Cu-MOR samples: after N₂O activation at 600 °C for 2h (red) and subsequent reaction with CH₄ (black).

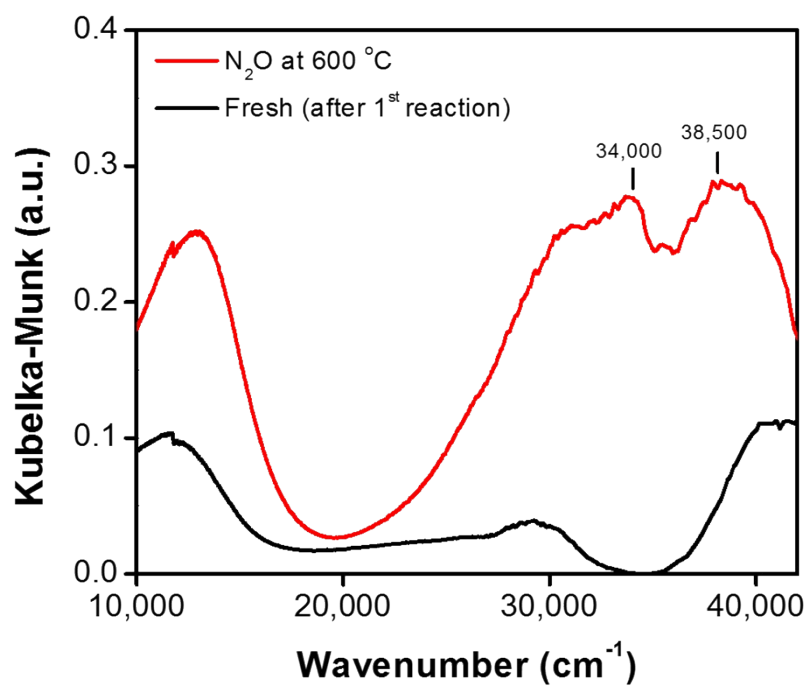


Figure S6. UV-vis-NIR spectra for Cu-MOR samples: after the first reaction cycle (black) and subsequent N₂O activation at 600 °C for 2h (red).

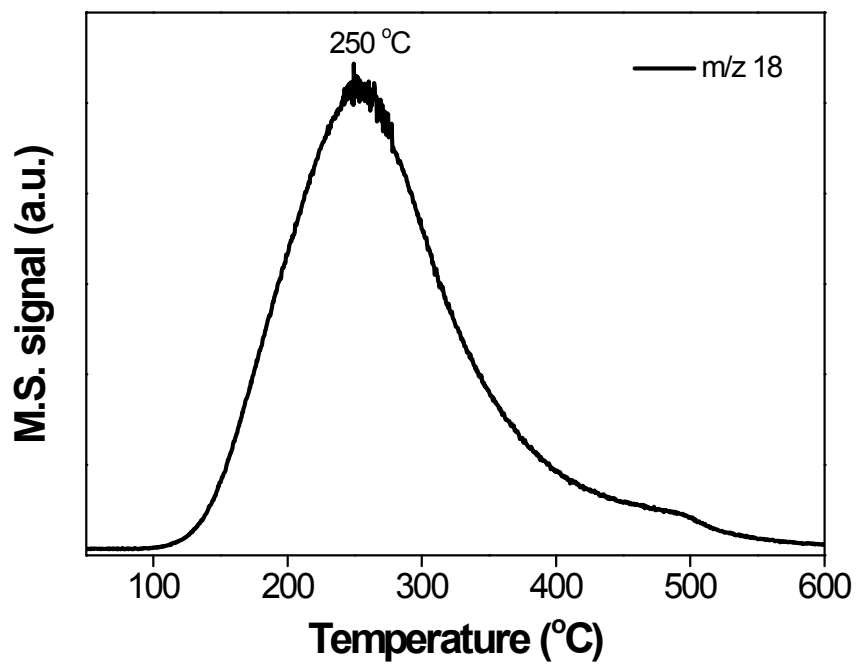


Figure S7. Temperature-programmed desorption of H₂O for a freshly hydrated Cu-MOR sample.

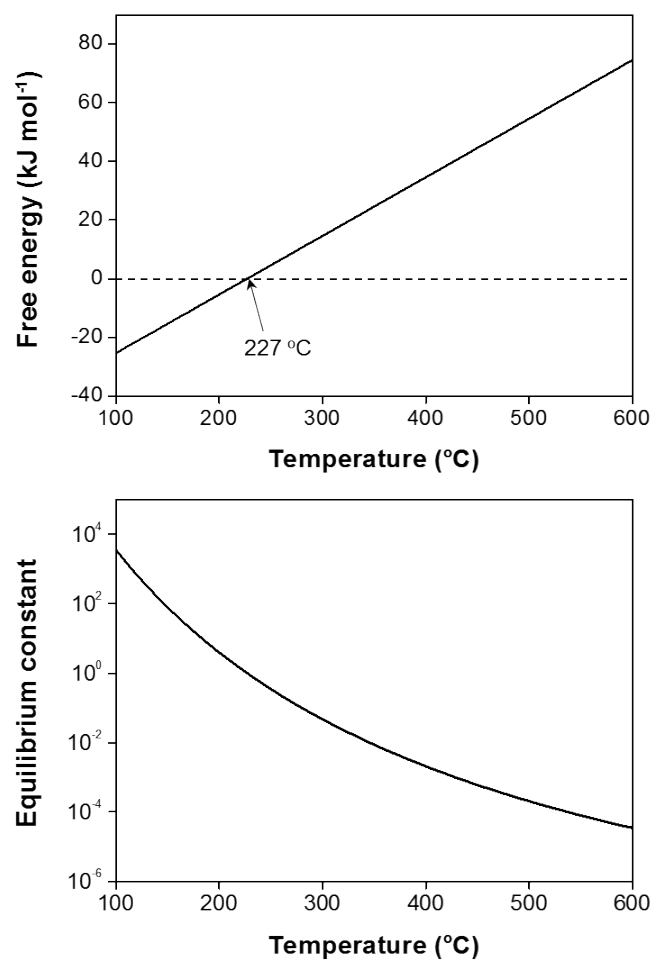


Figure S8. Free-energy change and corresponding equilibrium constant as a function of temperature for the formation of the intermediate site during O₂ activation ($\text{Cu} + \text{O}_2 \leftrightarrow \text{Cu} + \text{O}_2$).

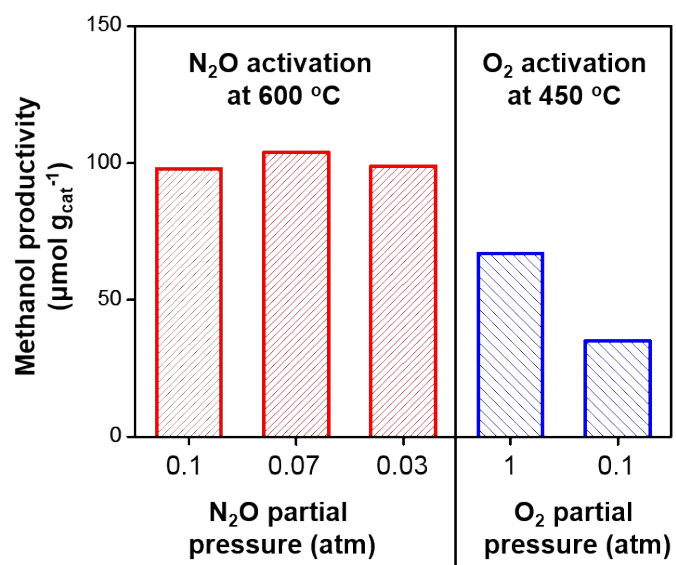


Figure S9. Effect that the partial pressure of oxidants exerts on methanol production.

Additional Tables

Table S1. The atomic ratio of copper to aluminum in Cu-MOR catalyst after activation by N₂O or O₂ measured by ICP-AES.

Sample	Cu/Al atomic ratio
Fresh Cu-MOR	0.385
O ₂ -activated Cu-MOR	0.386
N ₂ O-activated Cu-MOR	0.387

Table S2. The utilized fraction of copper atoms for the formation of active copper species. It was assumed that trimeric copper oxo clusters were active site, and stoichiometrically converted one methane into one methanol.

Temperature (°C)	N ₂ O-activated Cu-MOR (%)	O ₂ -activated Cu-MOR (%)
300	32	11
350	35	21
400	29	42
450	48	66
500	61	54
600	94	54