**Supplementary information**

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**Heterogeneous Droplet Catalyst for Selective Oxidation of Methane**

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**Supplementary materials and methods**

**Chemicals**

Gallium, indium, tin, copper and H2O2 (30%) were purchased from Alfa Aesar. PDMS and the curing agent (Sylgard 184 silicone elastomer curing agent) were purchased from Dow Corning Corporation. Deionized water was purified using the Milli-Q System (Millipore, Billerica, MA). All chemicals were used as received.

**Preparation of Cu-HDC@PDMS**

Gallium was first melted at 50 oC in separate beakers. Subsequently, the molten metal was mixed with indium and tin powder in a weight ratio Ga : In : Sn = 7 : 2 : 1, followed by vigorous stirring at 160 oC for several hours. Cupper powder (~2 wt%) was dissolved into the liquid metal alloy under continued stirring and the formed Cu-HDC added dropwise to polydimethylsiloxane (PDMS) to a weight ratio Cu-HDC : PDMS = 1 : 100. The mixture was then stirred until a homogeneous suspension was obtained. Next, the suspension was mixed with the curing agent (in a weight ratio PDMS : curing agent = 10 : 1) and the mixed solution poured onto a Teflon substrate. After standing for several hours, the substrate was heated to 60 oC and held at this temperature for 4 h, aiming to cure the PDMS. The cured PDMS rubber film with embedded M-HDC microspheres could easily be peeled off from the Teflon substrate. The obtained rubber film was used as catalyst after being sheared into 0.5 × 0.5 × 0.1 cm3 chips.

**Catalytic evaluation**

The oxidation of CH4 was performed in a stainless-steel Teflon-lined autoclave with a volume of 100 ml. Typically, about 10 mg of catalyst, 19 ml deionized water and 1 ml H2O2 (30%) were added in the autoclave. The autoclave was flushed three times and then pressurized with methane to the desired pressure (0.5 - 3.0 MPa CH4 (99.999%)). The reaction mixture was subsequently heated to the test temperature (25 - 80 oC), at a rate of 5 oC min-1, and left at this temperature for reaction under stirring at 1,000 rpm for 10 h. The obtained products were cooled in ice-water for 20 min prior to analysis. Liquid products were quantified by 1H and 13C nuclear magnetic resonance (NMR) spectroscopy. Gas products were quantified by gas chromatography. Errors were obtained by repeating the catalytic tests at least five times.

**Catalyst reusability**

10 mg of a fresh catalyst was tested for catalytic performance. Hereafter, the catalyst was separated from the reaction solution by centrifugation and stored in a vacuum desiccator overnight. The dried catalyst was again tested under the same reaction conditions. After 10 cycles of testing, the catalyst was kept under reaction conditions for another 240 h, separated from the reaction solution, stored overnight in the desiccator and subjected to another 10 cycles of testing.

**Kinetic analysis**

The transposed form of the Arrhenius equation reads

(1)

where *k* is the rate constant, *E*a the activation energy, *T* the absolute temperature, *R* is the universal gas constant, and *A* the frequency or pre-exponential factor. In accord with Eq. (1), *E*a is calculated from the slope of vs. 1/*T*.

The reaction rate *r* can be represented by

(2)

(3)

where is the methane partial pressure and *a* the reaction order. Combining equations (1) and (3) gives

(4)

It follows that *E*a can be obtained from the slope of vs. 1/*T* at constant , while the order can be obtained from the slope of vs. at constant temperature *T*.

**Characterization**

The composition of Cu-HDC was checked by inductively coupled plasma mass spectrometry (ICP-MS). X-ray diffraction (XRD) measurements were recorded on a Rigaku Miniflex-600 diffractometer using Cu Kα radiation (λ = 0.15406 nm) with a step size of 0.02° and a counting time of 0.5 s. Transmission elelctron microscopy (TEM) images were recorded on a Hitachi H-7700 operated at 100 kV. Aberration-corrected high-angle annular dark-field - scanning transmission electron microscopy (HAADF-STEM) images and corresponding energy dispersive X-ray (EDS) maps were recorded on a JEOL JEM-2010 LaB6 high-resolution TEM and double Cs-corrected JEOL JEM-ARM200CF STEM, which were operated at 200 kV. Elemental analysis was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Optima 7300 DV spectrometer. Liquid products were quantified by nuclear magnetic resonance (NMR) spectroscopy. Measurements were conducted on a Bruker Avance-Ⅲ 400 spectrometer. 1H NMR spectra were recorded with a 2 s recycle delay, for 64 scans, using dimethyl sulfoxide as an internal standard. 13C NMR spectra were recorded with a 10 s recycle delay, for 2048 scans. Gaseous products were quantified by a gas chromatograph equipped with molecular sieve 5A, Porapak Q 80/100 mesh, SE-30 and HP-Al2O3/S columns using He (ultra high purity) as carrier gas.

***In-situ* X-ray absorption fine structure (XAFS) measurements**

Cu *K*-edge (8,979 eV) XAFS spectra were recorded at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring was operated at 3.5 GeV with a maximum electron current of 250 mA. The hard X-ray beam was monochromatized with a Si(111) double crystal monochromator. For removal of higher order harmonics, a Rh mirror was used. *In-situ* XAFS measurements were performed using a home-made reactor (10 ml) with a vitreous carbon window (Ø = 6 mm; Figure S10). A catalyst-coated carbon fiber paper (~5 mm in diameter) was sealed behind the window. Spectra were collected in the fluorescence mode using a Lytle detector. The spectrum of a Cu metal foil, allowing for internal energy calibration, was collected concomitantly. Three spectra were averaged for each data set.

**XAFS data analysis**

Extended X-ray absorption fine structure (EXAFS) data were processed and analyzed following standard procedures within the ATHENA module implemented in the IFEFFIT library software package. The Cu *K*-edge *k*3-weighted χ(*k*) data in the *k*-space from 2.3 to 12.1 Å−1 (Δ*k*) were Fourier-transformed (FT) to the real space (*R*) with Hanning windows (d*k*= 1.0 Å−1) to separate out EXAFS contributions from different coordination shells. Effective backscattering amplitudes and phase shifts were calculated using the ab initio code FEFF8.054. Quantitative fittings of the spectra in the *R*-space were carried out within the range 1.0 - 2.8 Å (Δ*R*). The number of independent points was: *N*ipt = 2Δ*k* × Δ*R*/π = 2 × (12.1–2.3) × (2.8−1.0) ∕π ≈ 11.

The FT curves for Cu-HDC showed a peak at 2.23 Å assigned to Cu-Ga coordination, and a single-shell structure model with a Cu-Ga scattering path was used for fitting. For Cu-HDC-H2O2 and Cu-HDC-H2O2-CH4, besides peak at 2.23 Å from the Cu-Ga coordination, two distinct peaks at 1.44 Å and 1.61 Å arise due to Cu-O bonds. Consequently, a two-shell structure model with Cu-O and Cu-Ga scattering paths was used to fit the data of both samples.

During curve fittings, the amplitude reduction factor *S*02 was fixed at a value of 0.80 as determined by fitting data of a Cu foil. For the *ex-situ* measured Cu-HDC sample, the Debye–Waller factor (σ2), coordination number (CN), interatomic distance (*R*) and energy shift (Δ*E*0) for the Cu-Ga path were treated as adjustable parameters. The actual number of adjustable parameters, *N*para = 4, is lower than the maximum number *N*ipt = 11. For the *in-situ* measured samples Cu-HDC-H2O2 and Cu-HDC-H2O2-CH4, the corresponding parameters for the Cu-O and Cu-Ga shells were left free. The actual number of adjustable parameters for these samples was *N*para = 4 + 4 = 8. The structural parameters obtained from fitting are listed in Table S1. The *R* factor obtained for every fit is not larger than 0.013, indicating a good quality of the fitting.

**Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)**

NAP-XPS measurements were performed using a system located at the ShanghaiTech University (SHTU). This system was manufactured by SPECS Surface Nano Analysis GmbH, Germany (Figure S11). The facility is composed of a main chamber, a preparation chamber and a load-lock chamber. The analysis chamber is equipped with a PHOIBOS NAP hemispherical electron energy analyzer, a microfocus monochromatized Al Kα X-ray source with a beam size of 300 μm in diameter, a SPECS IQE-11A ion gun, and an infrared laser heater. Cu-HDC was dropped onto a clean silicon wafer and dried at room temperature. After the sample was installed into the analysis chamber, high-purity CH4 was fed into the chamber up to a pressure of 0.4 mbar. After collecting the C1s spectra, 0.9 mbar high-purity O2 was introduced into the chamber, and a new series of C1s spectra was acquired.

**Density functional theory (DFT) calculations**

The Vienna *ab initio* simulation package (VASP)1,2 was employed for spin-polarized DFT calculations using the Perdew-Burke-Ernzerhof (PBE)3 generalized gradient approximation. The projector augmented wave (PAW)4 was used to describe the core electrons. An *ab initio* molecular dynamics (AIMD) simulation was performed, starting from a cubic unit cell (30 × 30 × 30 Å3), consisting of 125 Ga atoms and 1 Cu atom. A simulation of 10 ps was carried out in the constant temperature, constant volume (NVT) ensemble using the Nosé-Hoover thermostat5,6 at *T* = 323.15 K with a time step of 2 fs. The liquid cluster model was extracted from the AIMD trajectory and structurally relaxed. To reduce computational time, all Ga atoms more than two bonds away from the Cu atom were fixed during optimization. The Brillouin zone was sampled using a 1 × 1 × 1 Monkhorst-Pack grid. For comparison, we built a Cu(111) slab model with 4 layers of Cu atoms. The top 2 layers were allowed to relax during optimization. A 5 × 5 × 1 Monkhorst-Pack grid to sample the Brillouin zone. In order to eliminate spurious interactions between images, a 15 Å vacuum spacing was added in the z-direction. For the z-direction dipole correction, a quadratic electrostatic potential was added to the total energy7. For both model systems, the energy cutoff was set to 500 eV, and the convergence criteria of energy and force were set to 1 × 10-5 eV and 0.02 eV Å-1, respectively. The DFT-D3 method, with a Becke-Johnson damping8,9, was incorporated to correct for the dispersion forces during adsorption. Transition states were determined by the climbing image nudged elastic-band (CI-NEB)10 and the dimer11 method with a force criterium set to 0.03 eV Å-1. The LOBSTER 4.0 package12 with the pbeVaspFit2015 basis set 13,14 was used to calulate the crystal orbital Hamiltonian population (COHP). The VESTA program15 was used for visualization of coordinates and charge data.

**Supplementary figures and tables**



**Figure S1**. (A, B) Magnified HAADF-STEM images of droplet edges of Cu-HDC.



**Figure S2**. XRD patterns of Cu-HDC samples with different Cu loadings (wt%) in comparison with the standard pattern of CuGa2 (JCPDS No. 25-0275).

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**Figure S3**. Cu K-edge EXAFS spectra in the *R* space of (A) Cu foil, (B) Cu-HDC, (C) Cu-HDC-H2O2 and (D) Cu-HDC-H2O2-CH4(D). Cu K-edge EXAFS spectra in the *q* space of (E) Cu foil, (F) Cu-HDC, (G) Cu-HDC-H2O2 and (H) Cu-HDC-H2O2-CH4. The red lines are for the fitted curves.

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**Figure S4**. Contact angle between (A) Cu-HDC and H2O, (B) Cu-HDC and CH3OH, (C) Cu-HDC@PDMS and H2O, and (D) Cu-HDC@PDMS and CH3OH.

**Figure S5**. EDX analysis of used Cu-HDC catalyst. Note that the signal intensity of C is close to that of the background, confiriming that no carbon deposition occurred during reaction.

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**Figure S6**. Production rate of primary oxygenates as a function of methane partial pressure (). Data were collected after 10 h of reaction at 50 oC. The dashed red line represents the best-fit from linear regression analysis (*R2*= 0.960). Linearity shows that the reaction order (α) in methane is close to unity.

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**Figure S7**. Production rate of primary oxygenates as a function of inverse temperature. Data were collected after 10 h of reaction at the reaction temperature in the autoclave pre-pressurized to 2.0 MPa CH4. The dashed red line represents the best-fit from linear regression analysis (*R2* = 0.974).The apparent activation energy (*E*a) derived from the slope of the plot is 31.3 ± 1.7 kJ mol-1).



**Figure S8**. Amount of primary oxygenates formed as a function of reaction time. Data were collected after different reaction times at reaction temperature of 50 oC, the autoclave being pre-pressurized to 2.0 MPa CH4. The dashed red line represents the best-fit from linear regression analysis (*R2* = 0.986), confirming linearity of the reaction versus reaction time.

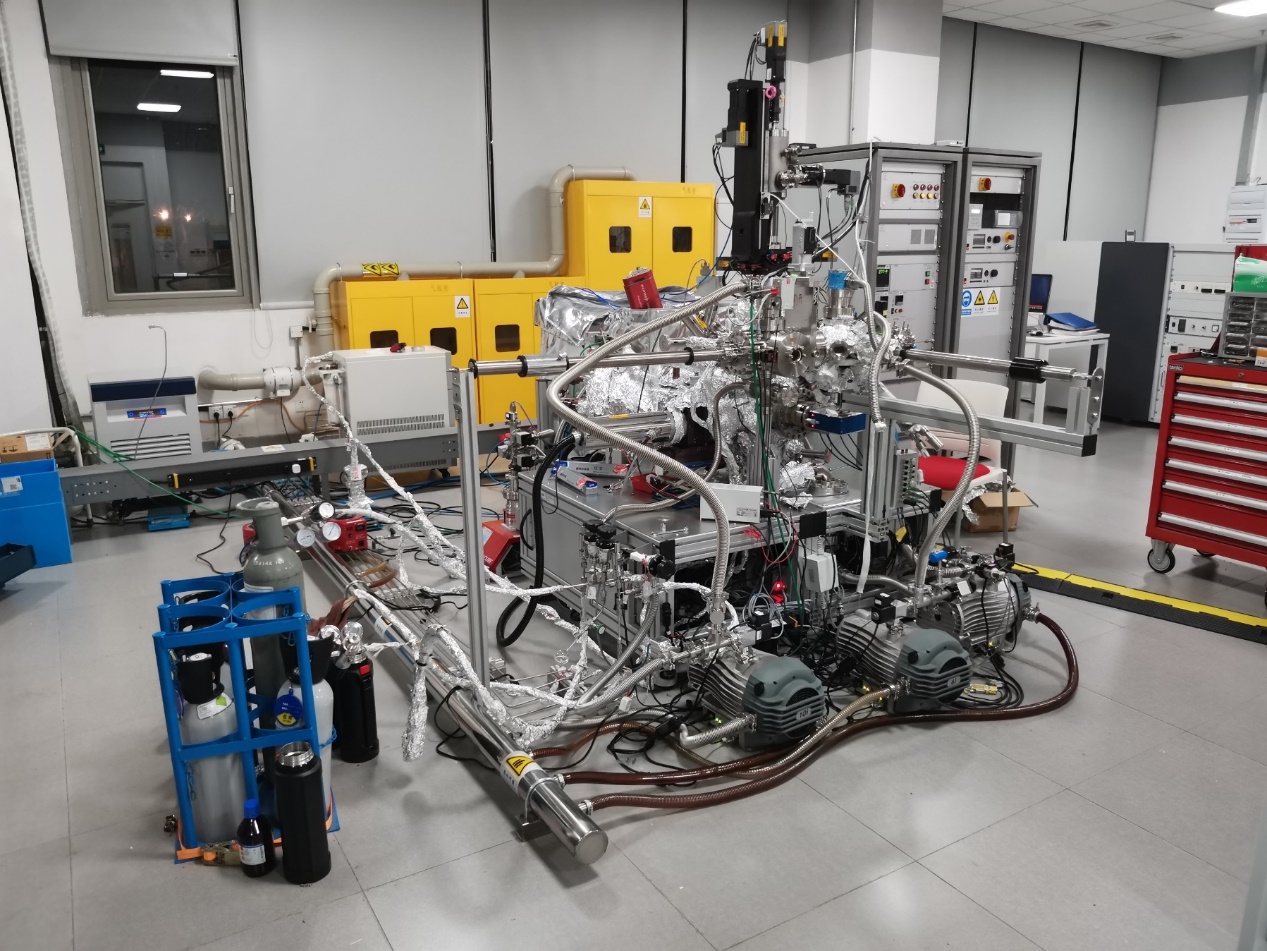


**Figure S9**. (A) 13C NMR spectrum (colored red) of products. The peaks at 65 and 93 are assigned to CH3OOH and HOCH2OOH, respectively16. The blue and orange colored spectra were recorded replacing 2MPa 13CH4 by 2MPa 12CH4 and 2MPa Ar, respectively. (B) 1H NMR spectrum (colored red) of products. The peaks at 3.93 and 3.43 are assigned to CH3OOH and CH3OH, respectively16. The blue spectra were recorded replacing 2MPa 13CH4 by 2MPa Ar.

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**Figure S10**. Home-made reactor (10 ml) equipped with a vitreous carbon window (Ø = 6 mm) for *in situ* XAFS experiments.



**Figure S11**. Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at the ShanghaiTech University (SHTU).

Diagram

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**Figure S12**. Liquid cluster models of Cu-HDC for reaction pathway calculations of methane oxidation. (A) The model extracted from the trajectory of AIMD simulations (*T* = 323.15 K, simulation time exceeds 10 ps) and structurally relaxed. The Cu atom is found in the subsurface of the CuGa125 alloy cluster17. (B) The model with Cu atom located at the surface, which is required for the catalytic act, i.e., for adsorption of a reactant or intermediate. The used color scheme is: copper is yellow and gallium is silver. (C) The transformation between Cu in subsurface (Cu\_subsurface) and surface (Cu\_surface) regions displays an activation energy of 0.14 eV, indicating that diffusion of Cu from the bulk of the Cu-HDC droplet to the surface is viable at ambient conditions.



**Figure S13**. DFT calculated reaction pathway for methane oxidation on Cu-HDC. The transition states are denoted by TSn. The relative activation energies (in electronvolts) are given in parentheses.



**Figure S14**. DFT calculated reaction pathway for methane oxidation on Ga. The transition states are denoted by TSn. The relative activation energies (in electronvolts) are given in parentheses.



**Figure S15**. DFT calculated reaction pathway for methane oxidation on Cu(111). The transition states are denoted by TSn. The relative activation energies (in electronvolts) are given in parentheses.

**Table S1.** Best fit parameters of the *k*3-weighted EXAFS spectra. CN is the coordination number, *R* is the interatomic distance, σ2 is the Debye–Waller factor and Δ*E*0 is the energy shift.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **Path** | **CN** | ***R* (Å)** | **σ2 (10-3)** | **Δ*E*0 (eV)** |
| Cu Bulk | Cu-Cu | 12.0 | 2.53 | 7.5 | 3.1 |
| Cu-HDC | Cu-O | - | - | - | - |
| Cu-Ga | 6.2 | 2.56 | 8.3 | -1.5 |
| Cu-In | 6.3 | 2.59 | 7.6 | -35.1\* |
| Cu-Sn | 6.3 | 2.62 | 8.1 | -26.9\* |
| Cu-HDC-H2O2 | Cu-O | 1.3 | 1.90 | 6.5 | -9.1 |
| Cu-Ga | 5.9 | 2.57 | 9.7 | 0.7 |
| Cu-HDC -H2O2-CH4 | Cu-O | 1.5 | 2.02 | 5.2 | -9.6 |
| Cu-Ga | 5.8 | 2.56 | 9.6 | -0.7 |

\* Obtained values indicate that formation of Cu-In and Cu-Sn bonds can be excluded.

**Table S2.** EDX analysis of used Cu-HDC catalyst.

|  |  |  |
| --- | --- | --- |
| **Element** | **mass fraction**  **(wt%)** | **atom fraction**  **(at%)** |
| Cu | 0.97 | 1.24 |
| Ga | 63.05 | 73.54 |
| In | 24.01 | 17.01 |
| Sn | 11.97 | 8.21 |
| C | 0.00 | 0.00 |

**Table S3**. List of some existing catalysts for CH4 oxidation.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | TOF\*  (mol·molmetal-1·h-1) | Selectivity (%) | Temperature (℃) | CH4 pressure (Mpa) | | Ref |
| Cu-HDC | 626.6 | 93.6 | 50 | 2 | This work | |
| Cu-HDC | 123.3 | 99.4 | 25 | 1.5 | This work | |
| Rh-CeO2 | 80.914  126.749 | 91.4  93.9 | 30  50 | 0.5 | | 18 |
| Rh-ZSM-5 | 0.73(CH3COOH) | 60.2 | 150 | 2.7 | | 19 |
| Rh-ZrO2 | 2.62 | 78.4 | 70 | 3 | | 20 |
| Fe-NC SA | 0.194 | 38.6 | 25 | 2 | | 16 |
| Cr/TiO2 | 10.867 | 47.6 | 50 | 3 | | 21 |
| Cu-MOR | 0.204 | 97 | 200 | 0.7 | | 22 |
| Cu/silicalite-1 | 70 | 93 | 70 | 0.3 | | 23 |
| Cu-NU-1000 | 0.00323 | 70 | 150 | 0.1 | | 24 |

\* Turn over frequency

**Table S4**. The integral of pCOHP for *d*-*p*total, *d*-*p*x, *d*-*p*y and *d*-*p*z interactions between Cu and C atoms in Cu-HDC\_TS1, Cu-HDC\_\*CH3, Cu(111)\_TS1, and Cu(111)\_\*CH3 complexes.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **pCOHP** | **Cu-HDC\_TS1** | **Cu-HDC\_\*CH3** | **Cu(111)\_TS1** | **Cu(111)\_\*CH3** |
| *d*-*p*total | 0.26 | 0.62 | 0.04 | 0.73 |
| *d*-*p*x | 0.00 | 0.04 | 0.00 | 0.16 |
| *d*-*p*y | 0.03 | 0.04 | 0.00 | 0.08 |
| *d*-*p*z | 0.24 | 0.55 | 0.03 | 0.49 |

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