

Supporting Information

The synergistic effect of Cu⁰ and Cu⁺ for one-step synthesis of aviation biofuel from biomass-derived ketones

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1. Experimental

1.1. Catalyst characterizations

To determine the specific surface area and pore distribution of the catalysts, a Micromeritics ASAP 2460 instrument was used to perform N₂ adsorption-desorption analysis. Before the measurement, the samples were outgassed under a vacuum at 200 °C for 6 h. The specific surface areas of samples were calculated using the Brunauer-Emmett-Teller (BET) method. The pore volume and pore size of the samples were calculated using the Barrett-Joyner-Halenda (BJH) method.

The X-ray diffraction (XRD) patterns were acquired using an X-ray powder diffractometer (Smartlab 9kw, Rigaku) with a 2-theta range of 10°-90° and a scanning rate of 5°/min. Small-angle X-ray scattering (SAXS) patterns were obtained with an X-ray small angle scatterometer (Xeuss SAXS, Xenocs SA).

The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo Scientific K-Alpha with Al K α monochromatic radiation (h ν , 1486.6 eV). The C1s peak (284.80 eV) is used to internally calibrate the energy scale.

A HT7700 EXALENS transmission electron microscope (TEM) equipped with an X-ray energy spectrum analyzer (EDS) was used to obtain TEM images. The accelerating voltage is 120 kV. A JEM 2100F field emission transmission electron microscope (FE-TEM) was performed at an accelerating voltage of 200 kV to obtain FE-TEM images.

Hydrogen temperature-programmed reduction (H₂-TPR) was conducted by a chemisorption instrument (BelCata II, Japan). The samples were placed into a tube reactor and heated from room temperature to 300 °C at 10 °C/min under He (30 mL/min) for 1 h. After cooling to 50 °C, the samples were heated to 850 °C at 10 °C/min under 10 vol% H₂/Ar with a flow of 50 mL/min. The H₂ consumption was recorded by a thermal conductivity detector (TCD).

For the characterization and quantification of the catalyst's acidic sites, temperature-programmed desorption of ammonia (NH₃-TPD) analysis was conducted in a Bel Cata II Chemisorption analyzer. The sample was reduced at 500 °C in 10% H₂/Ar flow at a ramp rate of 5 °C/min for 3 h. The sample was purged with Ar flow at 500 °C for 0.5 h and then was cooled to 50 °C in Ar flow. After that, NH₃ was adsorbed for 1 h in 10 vol% NH₃/Ar with a flow of 30 mL/min. Then switched to Ar (30 mL/min) for 1 h to remove the surface physically adsorbed NH₃. The sample was then heated to 900 °C at 10 °C/min. The NH₃ desorption data were recorded using a TCD.

To determine the type and strength of active sites on the catalyst surface, temperature-programmed desorption of hydrogen (H₂-TPD) analysis was conducted in a Bel Cata II Chemisorption analyzer. The sample was reduced at 500 °C in 10% H₂/Ar

flow at a ramp rate of 5 °C/min for 3 h. The sample was purged with Ar flow at 500 °C for 0.5 h, and then was cooled to 50 °C in Ar flow. After that, H₂ was absorbed in 10% H₂/Ar flow for 1 h at 50 mL/min. Then switched to Ar flow (30 mL/min) to purge for 1 h to remove the surface physically adsorbed H₂. After that, the temperature was increased to 800 °C at a rate of 10 °C/min to ensure complete desorption of H₂. The signal change was recorded by TCD.

For the analysis of the basic properties of catalysts, temperature-programmed desorption of carbon dioxide (CO₂-TPD) was carried out in a Bel Cata II Chemisorption analyzer. The catalysts were first reduced at 500 °C in 10% H₂/Ar flow at a ramp rate of 5 °C/min for 3 h. The sample was purged with Ar flow at 500 °C for 0.5 h, and then was cooled to 50 °C in Ar flow. Subsequently, the catalysts were treated with a flow of CO₂ (99% purity, 30 mL/min) for 1 h. The weakly adsorbed CO₂ was removed by flushing catalysts with Ar (30 mL/min) for 1 h. The desorption of CO₂ was measured by heating the catalyst from room temperature to 900 °C at a heating rate of 10 °C/min in Ar flow. The signal change was recorded by TCD.

An EMXplus-9.5/12 electron paramagnetic resonance (EPR) was used to measure the changes in the valence state of the internal Cu species before and after the reaction. The tests were conducted at room temperature. The spectrometer is equipped with a cavity operating at ~9.5 GHz (X band). The EPR intensity is given by the normalized double integral of the EPR signal.

The in-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) characterization was performed on a Nicolet NEXUS 6700 in-situ Infrared spectrometer equipped with an MCT/A detector and Harrick IR reaction cell using CO as a probe. The resolution of the instrument is 4 cm⁻¹. Background spectra were collected after purifying the samples in N₂ flow (100 mL/min) at 280 °C for 1 h. The reaction gas was then switched to CO (50 mL/min). 32 scans were performed per experiment.

The morphology of the fresh and spent catalysts were examined using scanning electron microscopy (SEM, ZEISS Sigma 300). The catalyst power was directly glued to the conductive adhesive. Then ZEISS Sigma 300 scanning electron microscope was used for sample morphology with an accelerated voltage of 3kV.

1.2 Activity test

The screening experiments of catalysts and reaction conditions were carried out in a 50 mL stainless steel autoclave reactor. For a single run, 10 mmol substrate and 0.1 g catalyst were loaded in the reactor. Then the reactor was pressured with H₂ flow to 1 MPa and released three times to get rid of the air. After setting the temperature, rotation

speed, reaction time and pressure, the reaction begins to take place. After the reaction was completed, the gas product was collected by gas bag. The liquid product was dissolved with 10 ml of trichloromethane. The reactor was washed with trichloromethane to remove the residual liquid products. For catalyst regeneration, the spent catalyst was filtered and subsequently calcined at an annealing temperature for 3h in the muffle furnace to remove carbon deposition and possible contaminants. The regenerated catalyst was then reduced under H₂ flow (80 mL/min) at 500 °C (5 °C/min ramping rate) for 3 h in a tube furnace. The catalyst regeneration test was also carried out in the stainless steel autoclave reactor. The specific experimental steps are the same as the catalyst screening process.

The catalytic experiments of cyclopentanone were conducted in a high-pressure continuous flow fixed bed reactor system. A stainless steel tube of 0.5 inch OD (wall thickness 0.049 inches) was used as the reaction zone. Before the experiment, the catalyst was reduced under H₂ flow (80 mL/min) at 500 °C (5 °C/min ramping rate) for 3 h. In a typical run, 2 mL (0.9g±0.05g) of pre-reduced catalysts were loaded in the middle of the tube fixed by the quartz wool. 100 mL/min of H₂ was used as carrier gas. 0.03 mL/min of cyclopentanone was introduced into the system via a syringe pump. The reaction zone and heat preservation zone of the system were preheated to 280 °C and 260 °C, respectively. The circulating water condenser was set to -5 °C to capture condensable products. Gas products were collected hourly with gas bags. All runs were conducted for 6 h at 1.0 MPa H₂ and 280 °C. The WHSV was maintained for 2 h⁻¹.

1.3 Product analysis

The liquid products were quantified by GC/MS (GC: Agilent 8860, MSD: Agilent 5977B) with an HP-5 column. The oven temperature was kept constant at 35 °C for 8 min, then raised to 250 °C at a rate of 3 °C/min. The gas products were quantified by a GC-TCD (GC: Agilent 8860) using a GS-GasPro capillary column. The oven temperature was kept constant at 30 °C for 8 min, then raised to 150 °C at a rate of 5 °C/min. The carbon yield of gas products was calculated by the external standard method. Coke deposited on catalysts was analyzed by an elemental analyzer (Vario MAX cube, Germany). The quantitative results of liquid products were obtained by an internal standard method in this manuscript. Benzene, which was not detected in any of the experiments, with chemical stability was selected as the internal standard. After the reaction was completed, trichloromethane was used as a solvent to dissolve the products. Then 1 mmol of benzene was added as an internal standard to the mixed solution, which was labeled solution A. 1 mL of the evenly mixed solution was extracted, labeled as solution B, and detected by GC/MS. The calibration curves of

standard chemicals were used to determine the content of the specific product in solution B. The ratio of the benzene content in solution B to the actual amount of benzene added was taken as the conversion coefficient. The content of a specific product in solution B is divided by this conversion coefficient to obtain the total content of the specific product in solution A.

The WHSV, carbon yield of products, the selectivity of products, and conversion rate of feedstock were calculated by the equation below:

$$WHSV(h - 1) = \frac{\text{The mass flow of feedstock}}{\text{The mass of catalyst}}$$

$$\begin{aligned} \text{Carbon yield of product}(\%) \\ = \frac{\text{The carbon mass of product}}{\text{The total carbon mass of feedstock}} \times 100\% \end{aligned} \quad \text{Eq. 2}$$

$$\begin{aligned} \text{Selectivity}(\%) \\ = \frac{\text{The carbon mass of specific gas/liquid product}}{\text{The total carbon mass of gas/liquid product}} \times 100\% \end{aligned} \quad \text{Eq. 3}$$

$$\begin{aligned} \text{Conversion}(\%) \\ = \left(1 - \frac{\text{The residual carbon mass of feedstock}}{\text{The total carbon mass of feedstock}} \right) \times 100\% \end{aligned} \quad \text{Eq. 4}$$

In order to enrich aviation biofuel components, it is necessary to promote the conversion of all aldol condensation products with long carbon chains into aviation biofuels through hydrodeoxygenation. In this paper, when the relative value of aldol condensation reaction intensity and hydrodeoxygenation reaction intensity is 1, the aviation biofuel component in the product can be maximized. In order to qualitatively evaluate the catalyst performance, a dimensionless coefficient (*AD/HD*) was established. *AD/HD* represents the ratio of the selectivity of aldol condensation products to the selectivity of hydrodeoxygenation products. This coefficient qualitatively describes the relative strength of aldol condensation and hydrodeoxygenation reactions. When *AD/HD*=1, the efficiency of producing aviation biofuel components is the highest. This coefficient provides an indication for the adjustment of reaction conditions and the optimization of catalysts. The *AD/HD* was calculated by the equation below. In this paper, aldol condensation products include dimer oxygenates, trimer oxygenates, tetramer oxygenates, dimer hydrocarbons, trimer hydrocarbons and tetramer hydrocarbons. Hydrodeoxygenation products include monomer oxygenates, monomer hydrocarbons, dimer hydrocarbons, trimer hydrocarbons and tetramer hydrocarbons.

AD/HD

$$= \left(\frac{\text{The sum of selectivity for aldol condensation prod}}{\text{The sum of the selectivity of Hydrodeoxygenation pr}} \right)$$

Eq. 5

2. Characterization of catalysts

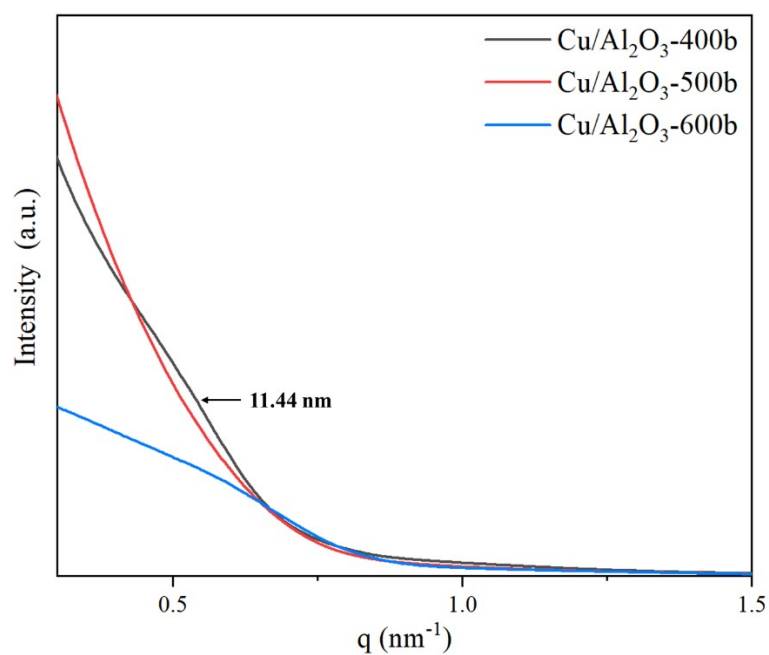


Fig. S1. Small angle SAXS patterns of the *ex-situ* reduced Cu/Al₂O₃ catalysts.

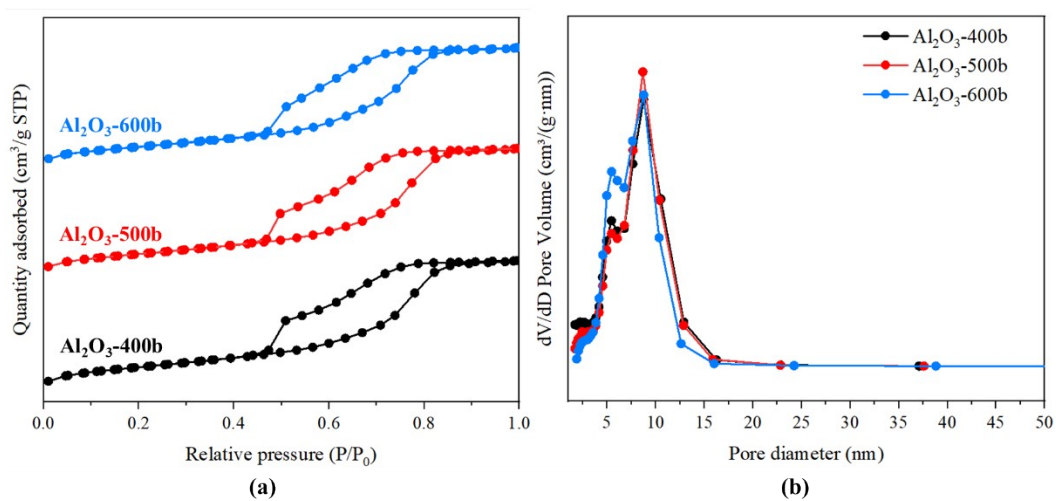


Fig. S2. (a) N₂ adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of Al₂O₃ catalysts.

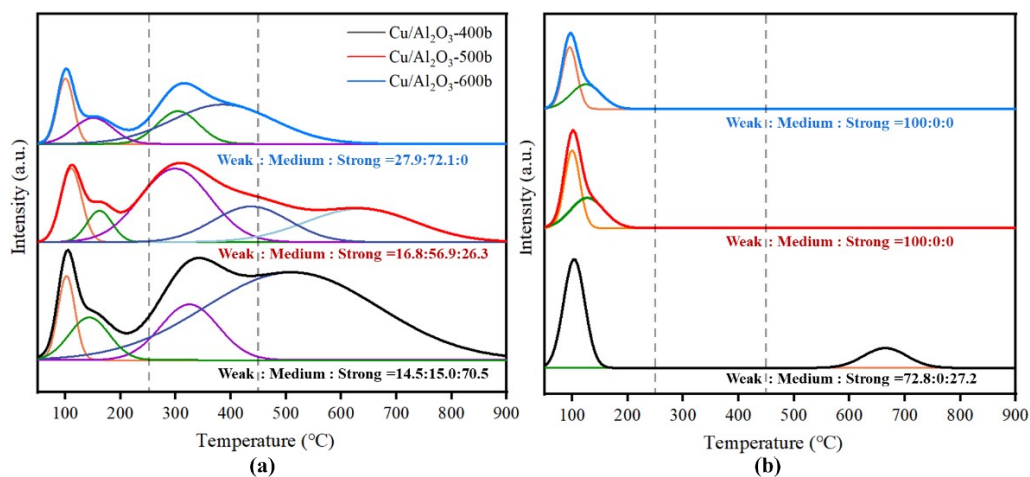


Fig. S3. (a) NH₃-TPD and (b) CO₂-TPD profiles of Al₂O₃ catalysts.



Fig. S4 Bio-oil photography (Reaction condition: 1.0 MPa H₂, reaction temperature 280 °C, 6h, WHSV=2 h⁻¹, cyclopentanone, Cu/Al₂O₃-500b).

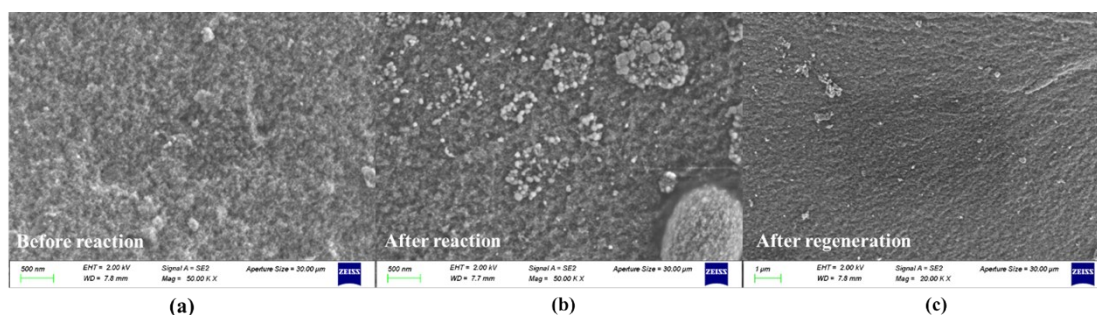
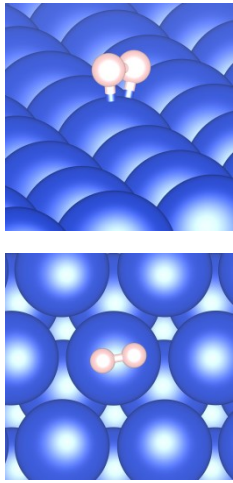
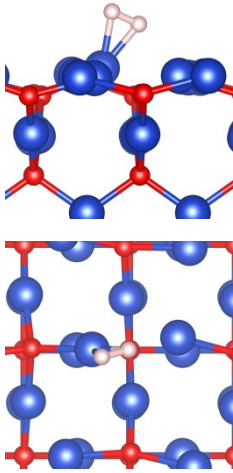
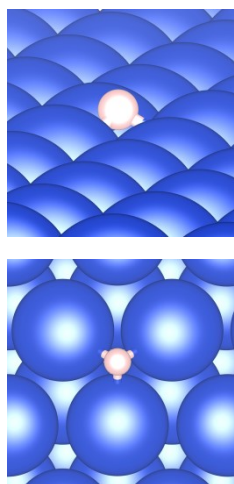


Fig. S5 SEM images of *ex-situ* reduced Cu/Al₂O₃-500b (a), spent Cu/Al₂O₃-500b, and regenerated Cu/Al₂O₃-500b (c).

3. DFT results

Table S1 H₂ and H adsorption on Cu(111) and Cu₂O(200)

	Adsorption energy (kJ/mol)	Bond length $d_{\text{H-Cu}}$ (Å)	$d_{\text{H-H}}$
H₂			
Cu(111)	9.7	1.90, 1.90	0.81
			
Cu ₂ O(200)	-39.0	1.67, 1.65	0.87
			
H			
Cu(111)	-25.5	1.74, 1.74, 1.74	-

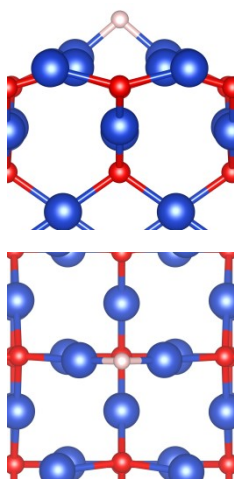


Cu₂O(200)

-114.5

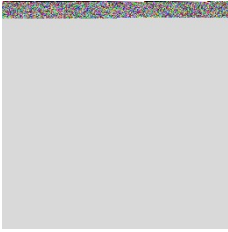
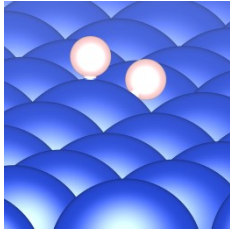
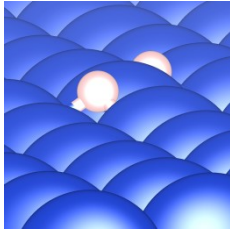

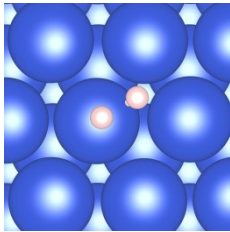
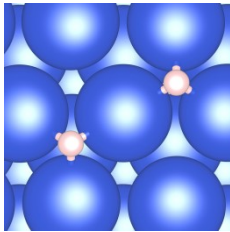

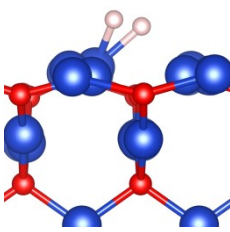
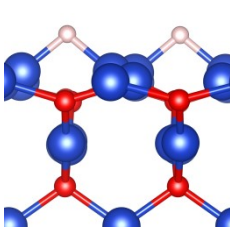

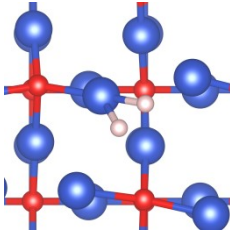
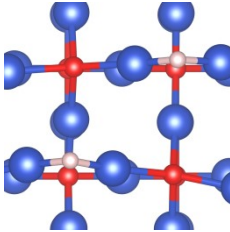
1.59, 1.59

-



The blue, red, and white spheres represent the Cu, O, and H atoms, respectively.

Table S2 H₂ dissociation to H (H₂* → H* + H*) on Cu(111) and Cu₂O(200)

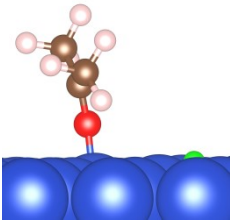
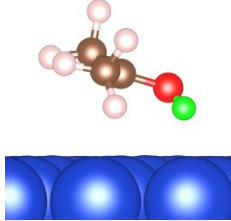
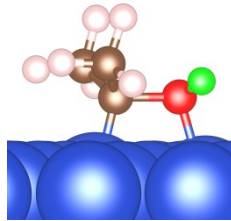
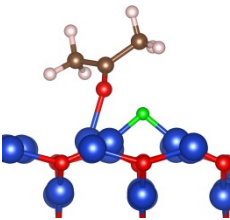
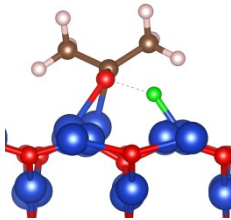
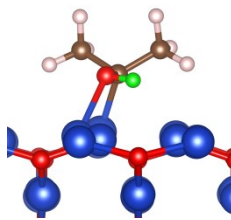
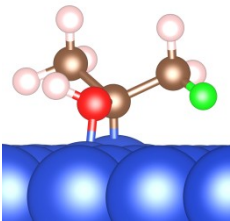
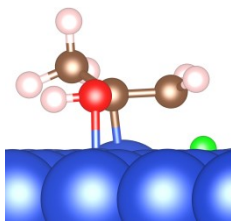
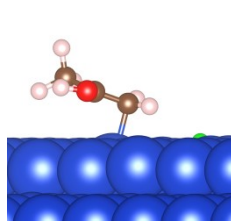
	E_{af}	ΔH	IS	TS	FS
	kJ/mol	kJ/mol			
Cu(111)	30.3	-77.6			
					
			$d_{\text{H-H}} = 0.81 \text{ \AA}$	$d_{\text{H-H}} = 1.23 \text{ \AA}$	$d_{\text{H-H}} = 2.98 \text{ \AA}$
Cu ₂ O(200)	1.5	-186.0			
					
			$d_{\text{H-H}} = 0.87 \text{ \AA}$	$d_{\text{H-H}} = 0.99 \text{ \AA}$	$d_{\text{H-H}} = 4.16 \text{ \AA}$

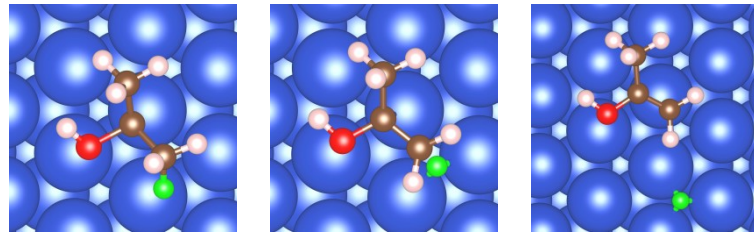
Forward activation energy, E_{af}

Backward activation energy, E_{ab}

The blue, red, and white spheres represent the Cu, O, and H atoms, respectively.

Table S3 Aldol condensation of acetone on Cu(111) and Cu₂O(200)

	E_{af}	ΔH	IS	TS	FS
	kJ/mol	kJ/mol			
R 1					
Cu(111)	112.9	58.0			
			$d_{O-H}=3.53 \text{ \AA}$	$d_{O-H}= 1.00 \text{ \AA}$	$d_{O-H}= 0.98 \text{ \AA}$
Cu ₂ O(200)	234.2	102.8			
			$d_{O-H}= 3.52 \text{ \AA}$	$d_{O-H}= 1.69 \text{ \AA}$	$d_{O-H}= 0.98 \text{ \AA}$
R 2					
Cu(111)	96.7	-10.8			



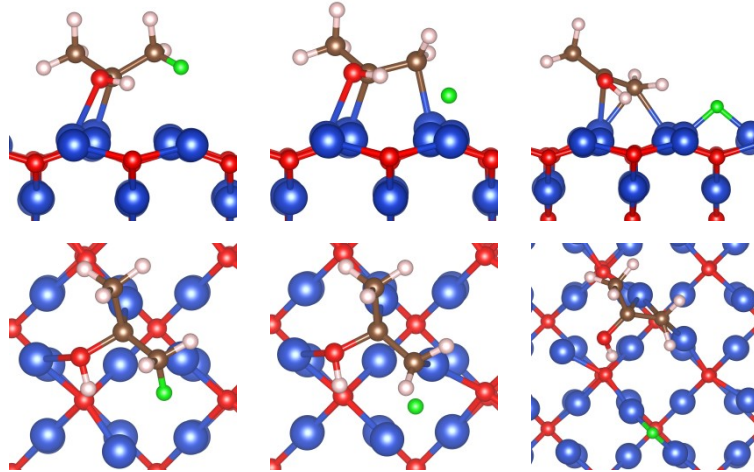
$d_{C-H} = 1.10 \text{ \AA}$

$d_{C-H} = 1.57 \text{ \AA}$

$d_{C-H} = 3.66 \text{ \AA}$

Cu₂O(200) 96.9 -

115.8



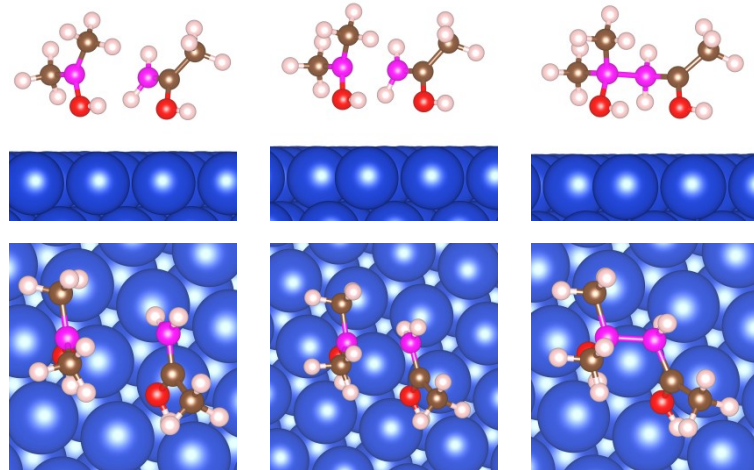
$d_{C-H} = 1.10 \text{ \AA}$

$d_{C-H} = 1.66 \text{ \AA}$

$d_{C-H} = 4.63 \text{ \AA}$

R 3

Cu(111) 12.4 -62.9

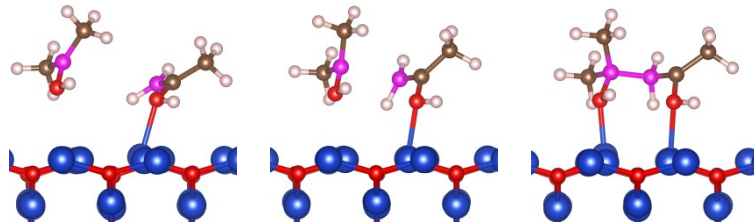


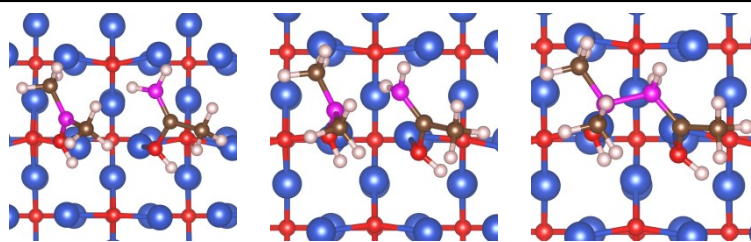
$d_{C-C} = 3.30 \text{ \AA}$

$d_{C-C} = 2.41 \text{ \AA}$

$d_{C-C} = 1.57 \text{ \AA}$

Cu₂O(200) 27.1 -59.8





$$d_{C-C} = 3.81 \text{ \AA}$$

$$d_{C-C} = 2.38 \text{ \AA}$$


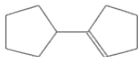
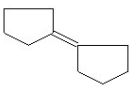
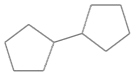
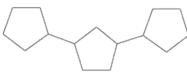
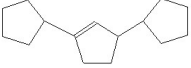
$$d_{C-C} = 1.56 \text{ \AA}$$

The blue, red, brown, white, purple, and green spheres represent the Cu, O, C, H, activated C, and activated H, respectively.

4. Detailed information about liquid products

Detailed information about liquid products from cyclopentanone, acetone, 2-pentanone, and cyclohexanone catalytic conversion over Cu/Al₂O₃-500b are shown in **Table S4-9** and **Fig. S6-11**, respectively.

Table S4 Detailed information about liquid products from cyclopentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclopentanone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Name	Molecular formula	Structural formula
Monomer hydrocarbon		
Cyclopentene	C ₅ H ₈	
Dimer hydrocarbon		
1-Cyclopentylcyclopentene	C ₁₀ H ₁₆	
Bicyclopentylidene	C ₁₀ H ₁₆	
1,1'-Bicyclopentyl	C ₁₀ H ₁₈	
Trimer hydrocarbon		
1,1':3',1''-Tercyclopentane	C ₁₅ H ₂₆	
1,3-Bis(cyclopentyl)-1-cyclopentene	C ₁₅ H ₂₄	

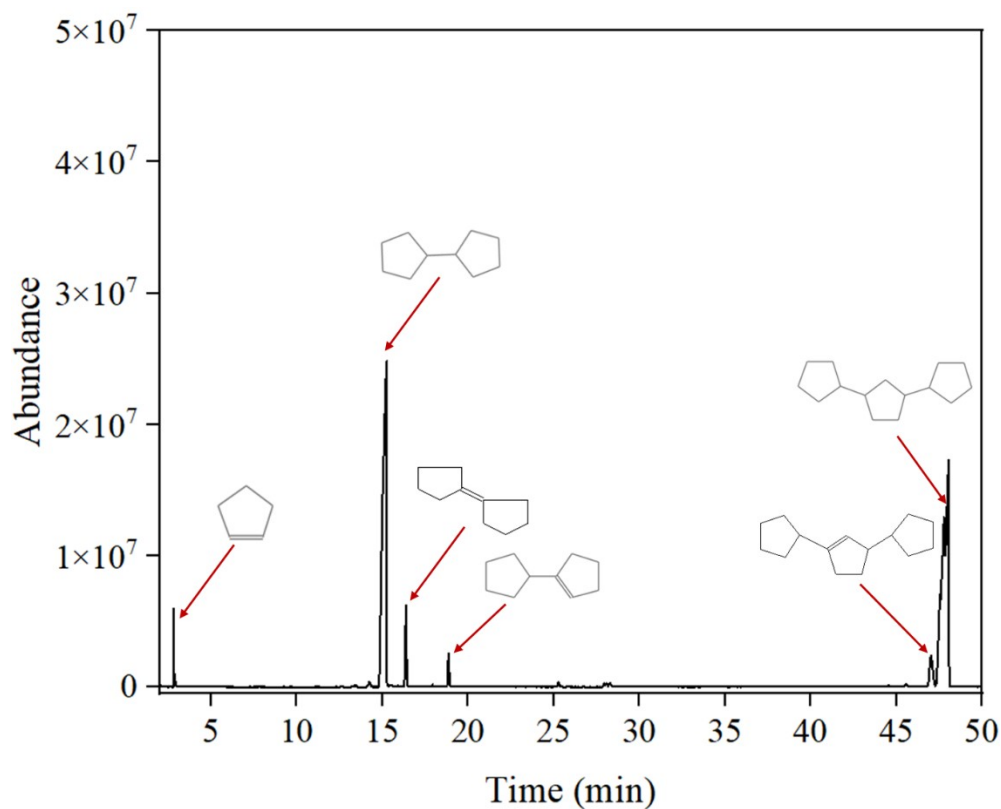
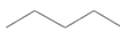
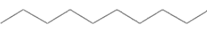
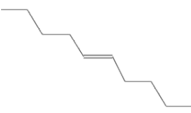
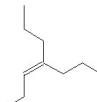



Fig. S6 Detailed information about liquid products from cyclopentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclopentanone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Table S5 Detailed information about liquid products from 2-pentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol 2-pentanone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Name	Molecular formula	Structural formula
Monomer hydrocarbon		
Pentane	C ₅ H ₁₂	
Dimer hydrocarbon		
Decane	C ₁₀ H ₂₂	
5-Decene, (E)-	C ₁₀ H ₂₀	
3-Heptene, 4-propyl-	C ₁₀ H ₂₀	
Trimer hydrocarbon		
Pentadecane	C ₁₅ H ₃₂	

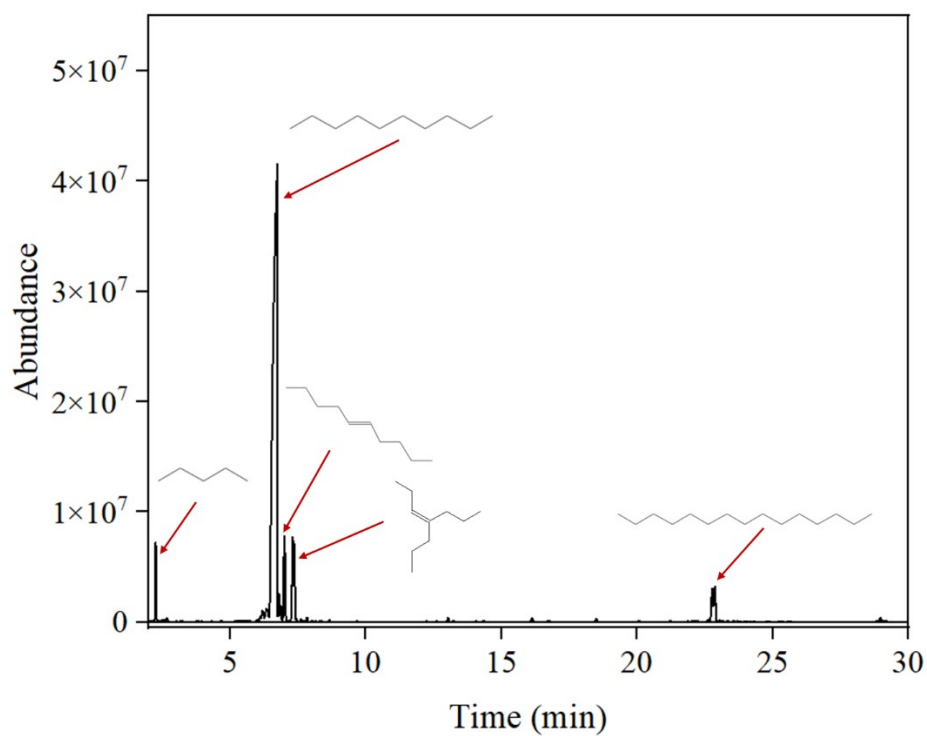


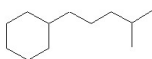
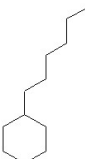
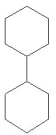
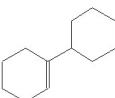
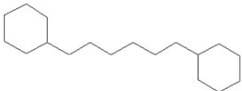

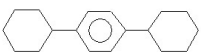



Fig. S7 Detailed information about liquid products from 2-pentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol 2-pentanone, 0.1 g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Table S6 Detailed information about liquid products from cyclohexanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclohexanone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Name	Molecular formula	Structural formula
Monomer hydrocarbon		
Cyclohexane	C ₆ H ₁₂	
Cyclohexene	C ₆ H ₁₀	
Dimer hydrocarbon		
Cyclohexane, (4-methylpentyl)-	C ₁₂ H ₂₄	
Cyclohexane, hexyl-	C ₁₂ H ₂₄	
1,1-Bicyclohexane	C ₁₂ H ₂₂	
1-Cyclohexyl-cyclohexene	C ₁₂ H ₂₀	
Trimer hydrocarbon		
1,6-Dicyclohexyl-hexane	C ₁₈ H ₃₄	
1,1':4',1''-Tercyclohexane	C ₁₈ H ₃₂	
1,4-Dicyclohexylbenzene	C ₁₈ H ₂₆	
1,1':3',1''-Tricyclohexane	C ₁₈ H ₃₂	

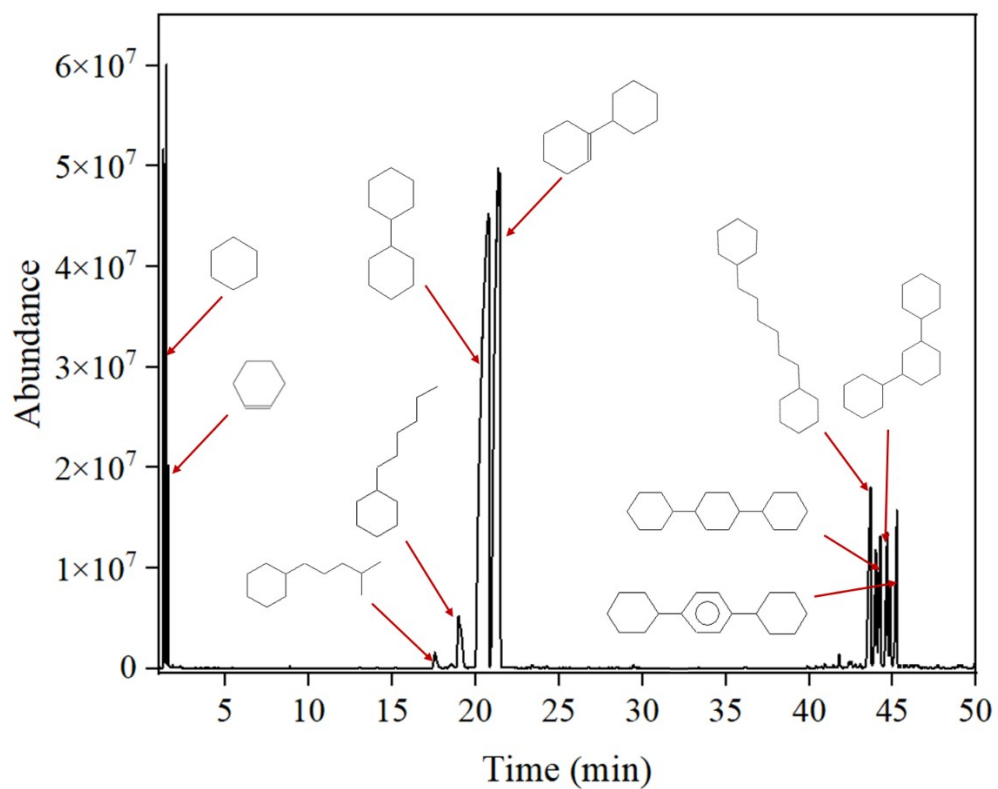
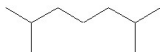
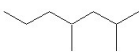
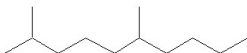


Fig. S8 Detailed information about liquid products from cyclohexanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclohexanone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8h.)

Table S7 Detailed information about liquid products from acetone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol acetone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8 h.)

Name	Molecular formula	Structural formula
Trimer hydrocarbon		
Heptane, 2,6-dimethyl-	C ₉ H ₂₀	
Heptane, 2,4-dimethyl-	C ₉ H ₂₀	
Tetramer hydrocarbon		
2,6-Dimethyldecane	C ₁₂ H ₂₆	

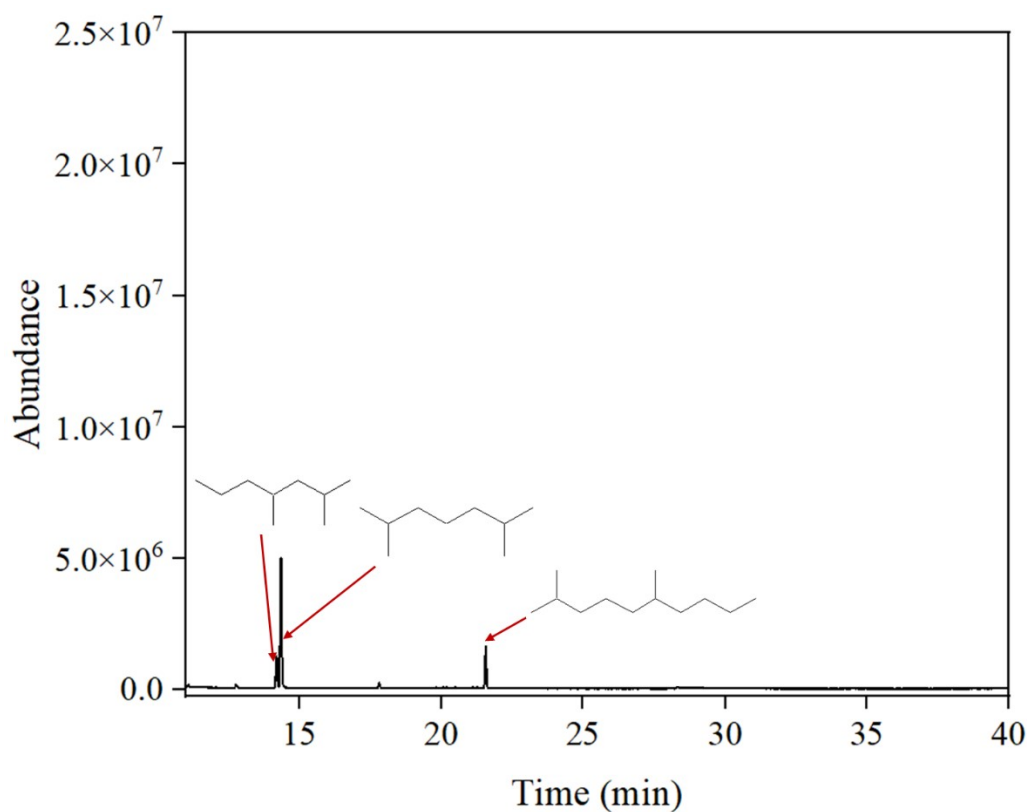
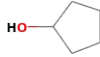
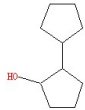
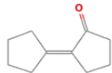
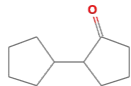
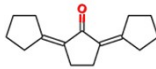


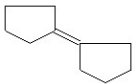
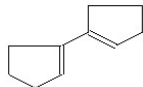


Fig. S9 Detailed information about liquid products from acetone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol acetone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 280 °C, 8 h.)

Table S8 Detailed information about liquid products from cyclopentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclopentanone, 0.1g Cu/Al₂O₃-500b, 0.1 MPa H₂, 280 °C, 4 h.)

Name	Molecular formula	Structural formula
By-products		
Cyclopentanol	C ₅ H ₁₀ O	
[1,1'-Bicyclopentyl]-2-ol	C ₁₀ H ₁₈ O	
Cyclopentanone, 2-cyclopentylidene-	C ₁₀ H ₁₄ O	
[1,1'-Bicyclopentyl]-2-one	C ₁₀ H ₁₆ O	
Cyclopentanone, 2,5-dicyclopentylidene-	C ₁₅ H ₂₀ O	
Aviation biofuels		
1,1'-Bicyclopentyl	C ₁₀ H ₁₈	
1-Cyclopentylcyclopentene	C ₁₀ H ₁₆	
Bicyclopentylidene	C ₁₀ H ₁₆	
Bicyclopentyl-1,1'-diene	C ₁₀ H ₁₄	

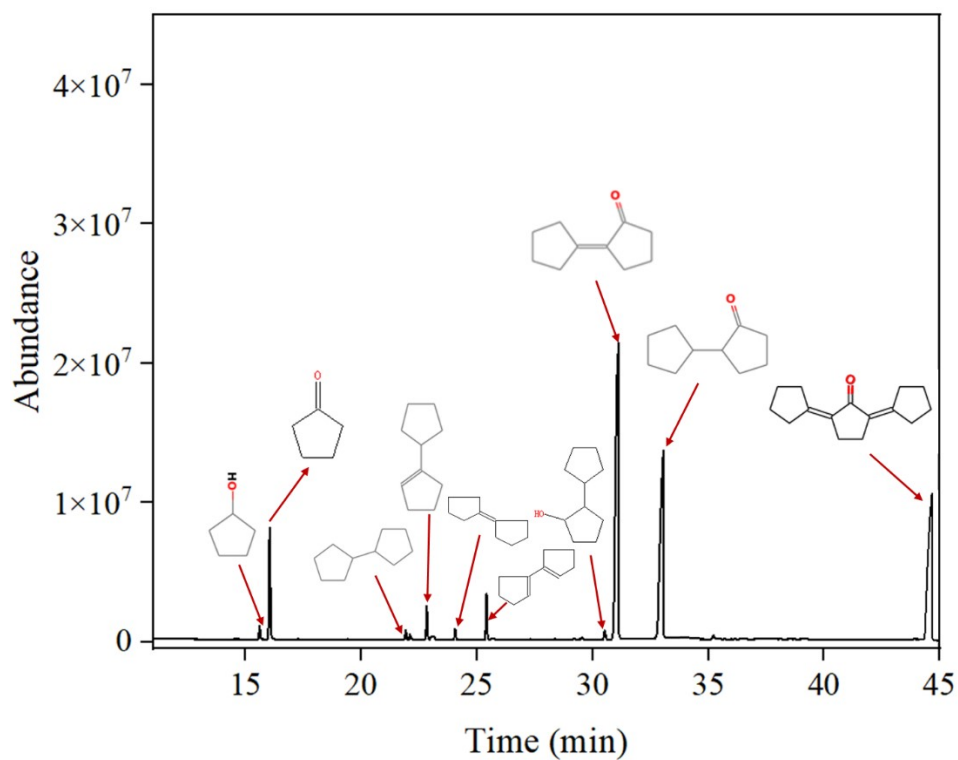

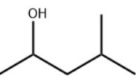


Fig. S10 Detailed information about liquid products from cyclopentanone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol cyclopentanone, 0.1g Cu/Al₂O₃-500b, 0.1 MPa H₂, 280 °C, 4 h.)

Table S9 Detailed information about liquid products from acetone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol acetone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 150 °C, 4 h.)

Name	Molecular formula	Structural formula	Selectivity (%)
Monomer oxygenate			
2-Propanol	C ₃ H ₈ O		93.8%
Dimer oxygenate			
2-Methyl-4-pentanol	C ₆ H ₁₄ O		6.2%

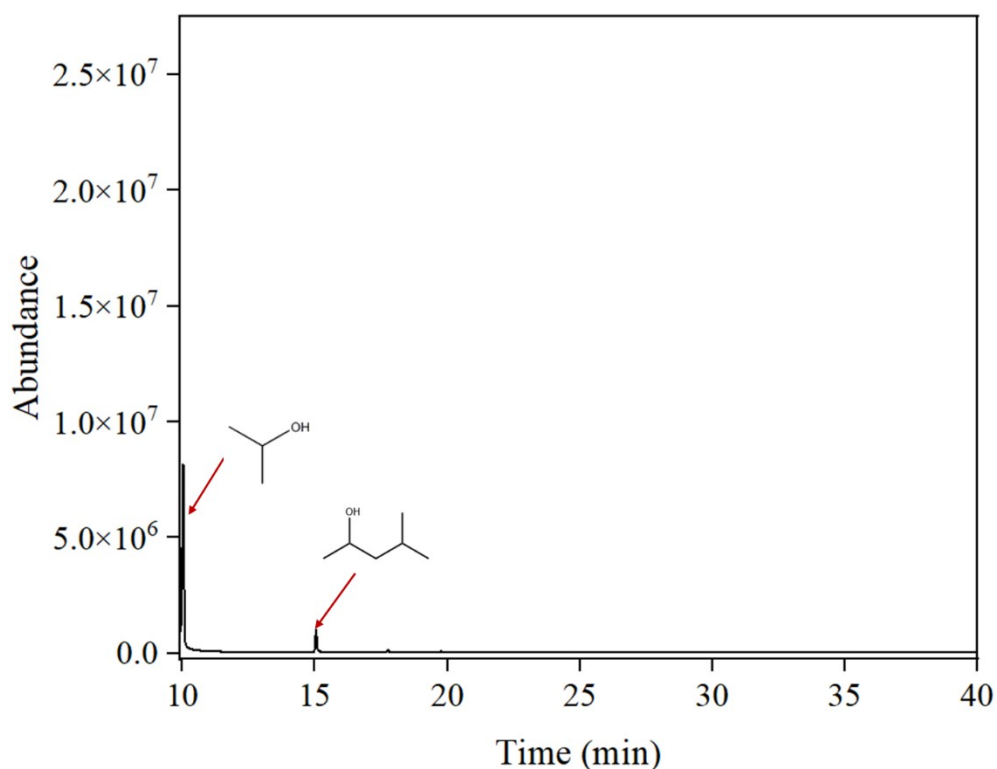


Fig. S11 Detailed information about liquid products from acetone catalytic conversion over Cu/Al₂O₃-500b catalyst. (10 mmol acetone, 0.1g Cu/Al₂O₃-500b, 1.0 MPa H₂, 150 °C, 4 h.)