Supporting Information

1. Experimental Section

Synthesis of $Cu_{12}Ag_{17}(SR)_{12}(PPh_3)_4$: $Cu_{12}Ag_{17}(SR)_{12}(PPh_3)_4$ (SR=1,3-benzenedithiol) cluster was synthesized according to the previous work.[S1,S2] First, 10 mg $AgNO_3$ and 6 mg $Cu(C_5H_7O_2)_2$ were ultrasonically dissolved in methanol to obtain solution A; 13.5 μL1,3-benzenedithiol was added to 10 mL CH_2Cl_2 to obtain solution B. Then, added solution A to solution B and kept stirring. 0.2 g PPh_3 was dissolved in 1 mL CH_2Cl_2 and added to the above mixed solution. After stirring for 10 minutes, dissolved 0.0105 g $NaBH_4$ in 0.5 mL ultra-pure water, quickly added to the above mixture and kept stirring for 12 h. After the reaction, the mixture was centrifuged at high speed and collected solids, then washed with ethanol for many times and obtained the $Cu_{12}Ag_{17}(SR)_{12}(PPh_3)_4$ clusters.

Catalytic test: Catalytic hydrogenation of nitrocyclohexane (NCH) was performed in a 50 mL stainless-steel autoclave. Typically, 3 mg catalyst, 5 mL solvent and 0.3 mmol NCH were added into autoclave. First, the reactor was purged several times with N_2 to replace the air in the system, then purged several times with H_2 and pressurized. The reaction system was heated to 100 ºC and kept for 24 h with a stirring rate of 1000 r/min. After the reaction, the reaction system was cooled to room temperature. The reaction liquid was centrifuged and collected the catalyst. The cluster catalyst was washed with methanol for many times and dried at 50 ºC for next use. The products were analyzed by gas chromatograph (GC-9860) instrument equipped with a thermal conductivity detector with a TDX-1 column and a flame ionization detector with an FFAP and PLOT-Q capillary column, dodecane as the internal standard. GC-MS (QP2020 NX/GC-2023) was used to further analyze the products. The carbon balance was close to 98-99% on the basis of the detected compounds of NCH, CHO and CHone. All data were repeated three times to obtain the average. The NCH conversion and product selectivity were calculated according to the following equation:

$$Conversion\ (\%) = \frac{moles\ of\ nitrocyclohexane\ input - moles\ of\ nitrocyclohexane\ output}{moles\ of\ nitrocyclohexane\ input} * 100$$

$$Selectivity\ (\%) = \left(\frac{moles\ of\ specific\ product}{total\ moles\ of\ all\ product}\right) * 100$$

Characterizations

The UV-vis optical spectra were characterized by a SHIMADZU UV-1800 spectrometer.

X-ray photoelectron spectroscopy (XPS) analyses were performed on an X-ray photoelectron spectrometer (ESCALAB 250Xi) to detect the elemental compositions, and the electron binding energy scale of all spectra was calibrated using C 1s at 284.8 eV.

In situ infrared Fourier transform (FTIR) spectra of the clusters with time at 100 °C were recorded by a Thermo Scientific Nicolet iS50 FTIR instrument equipped with a high-temperature/pressure reaction chamber, and spectra were recorded after 32 scans at a resolution of 4 cm^{-1}. KBr disk was scanned as a background spectrum under N_2 flow, the clusters were ultrasonically dispersed in ethanol solvent and then dripped onto KBr disk and dried by an infrared lamp. FTIR spectra were collected at certain time intervals when the temperature was kept at 100 °C.

In situ FTIR experiments of testing metal-H bond were conducted on a Thermo Scientific Nicolet iS50 FTIR instrument. Firstly, the clusters were ultrasonically dispersed in ethanol solvent and then dripped onto KBr disk and dried by an infrared lamp. Before measurement, the sample was heated in N_2 at 100 °C for 3 h to remove impurities on the sample surface, and then cooled to room temperature. After the background spectrum was recorded, H_2 was injected at a flow rate of 50 mL/min. After 30 min, H_2 was removed and N_2 was injected for 30 min. FTIR spectra of the samples were collected at specific times.

Time-resolved in situ FTIR spectra of the NCH with H_2 over the catalysts were monitored using a temperature-controlled gas-solid cell. Firstly, KBr disk were prepared, and then the ethanol solution of clusters was dripped onto KBr disk and dried by an infrared lamp. In the measurement, the sample was pressed into a 13 mm diameter disk and placed in a gas-solid cell. Before testing, N_2 was injected at 100 °C to remove excess gas and water. After the background spectrum was recorded, the NCH was bubbled into the gas-solid cell, and then filled with 3 MPa H_2, the reaction temperature was performed at 100 °C.

2. Supporting Figures and Tables

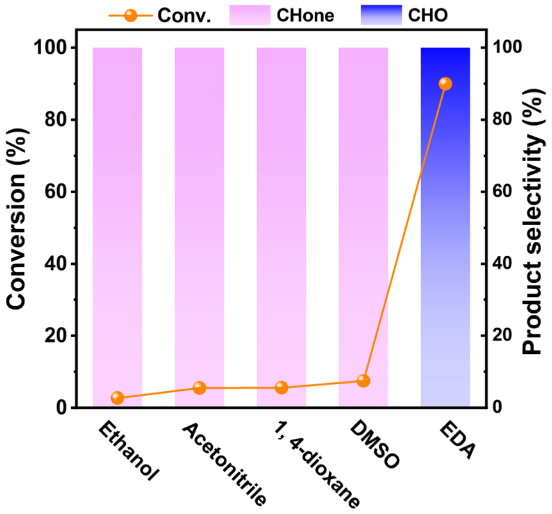

Fig. S1 Catalytic performances of $Cu_{12}Ag_{17}$ cluster catalysts for the NCH hydrogenation in different solvents. DMSO: dimethyl sulfoxide. Reaction conditions: 3 mg catalyst, 0.3 mmol NCH, 5 mL solvent, 3 MPa H_2, 100 °C for 20 h. All the data were the average of the three reactions.

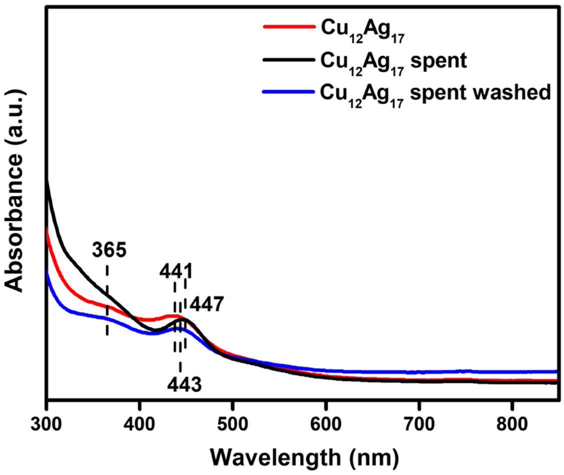

Fig. S2 UV-vis spectra of fresh and spent $Cu_{12}Ag_{17}$ clusters. The used catalyst was washed several times with methanol to obtain $Cu_{12}Ag_{17}$ spent washed catalyst.

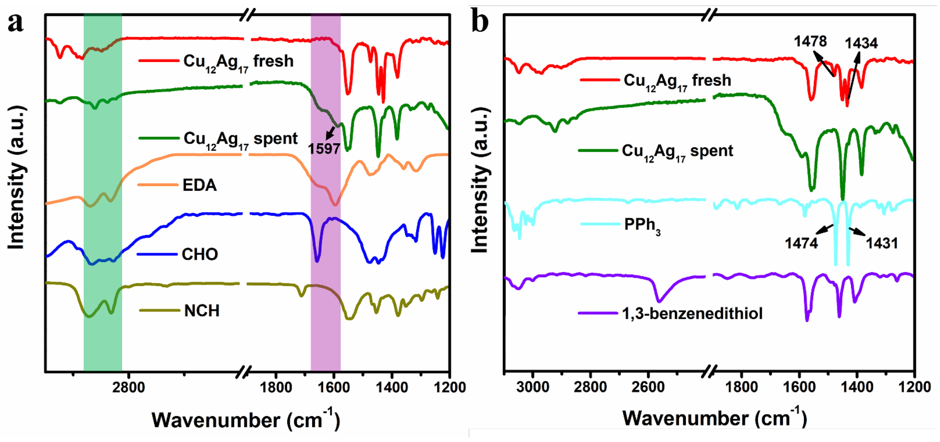

Fig. S3 (a) FTIR spectra of fresh and spent $Cu_{12}Ag_{17}$ clusters, EDA, CHO and NCH. (b) FTIR spectra of fresh and spent $Cu_{12}Ag_{17}$ clusters, PPh_3 and 1,3-benzenedithiol. The spent clusters involved herein were washed with methanol, all of those mentioned next as well.

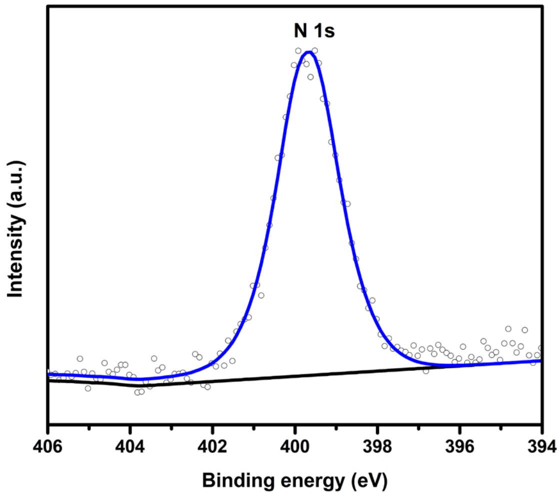

Fig. S4 N 1s XPS spectra of spent $Cu_{12}Ag_{17}$ clusters.

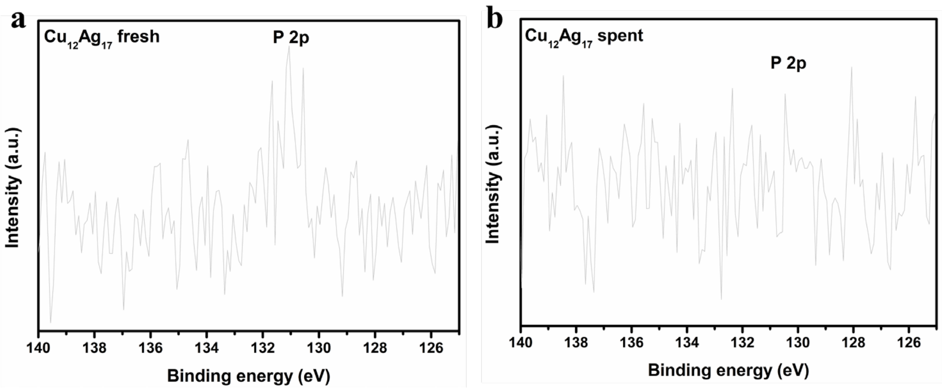

Fig. S5 P 2p XPS spectra of (a) fresh $Cu_{12}Ag_{17}$ clusters and (b) spent $Cu_{12}Ag_{17}$ clusters.

Table S1. Comparison of the activity and CHO selectivity for the NCH hydrogenation on the reported catalysts and the $Cu_{12}Ag_{17}$ catalyst.

Catalyst	Solvent	NCH conversion (%)	CHO selectivity (%)	Reference
$Cu_{12}Ag_{17}$	EDA	90	100	This work
Ni@DC-0.06	EDA	95.2	97.2	S3
Au/Al-2.5	EtOH	100	83	S4
NiTi-LDH	EDA	99.8	90.7	S5
(Pt-Na)/TiO_2	Solvent free	95	85	S6
1%Cu-20%Ni/AC	EDA	99.6	87.8	S7
15Cu/SiO_2-AE	EDA	74	92	S8
Pd/SWCNTs-2	EDA	96	96.4	S9
5% Pd/HMC-1	EDA	99.4	82.8	S10
Pd/SWCNTs	EDA	97.3	94.6	S11
Pd/CNT	EDA	97.6	85.9	S12
EDA-Pt/In_2O_3	EDA	100	100	S13
Pd/C	EDA	100	84.2	S14
CuFeAl-LDH	EDA	100	93.4	S15
Ni_1Co_2@NC-APTES	EDA	94.5	93.6	S16

Table S2. The relative amount of different components form Cu LMM XAES.

Sample	Kinetic energy (eV)		Relative amount of Cu species	
	Cu^0	Cu^+	Cu^0	Cu^+
$Cu_{12}Ag_{17}$ fresh	917.10	914.30	40.8%	59.2%
$Cu_{12}Ag_{17}$ spent	917.10	914.28	45.1%	54.9%

Supporting References

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