Cyclohexane oxidative dehydrogenation over copper oxide catalysts

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Abstract

Here, we report on structure-reactivity trends for cyclohexane oxidative dehydrogenation (ODH) with silica supported copper oxide catalysts as a function of surface structure. Copper oxide was supported on mesostructured KIT-6 silica at low surface densities $<0.2 \text{ Cu/nm}^2$ using copper (II) nitrate, ammonium and sodium copper (II) ethylenediaminetetraacetate, and a hexanuclear copper (I) siloxide complex. Copper oxide surface structures were characterized by X-ray absorption spectroscopy as well as ambient and in situ diffuse reflectance UV-visible (DRUV-vis) spectroscopy to determine trends in copper oxide nuclearity. DRUV-vis spectroscopy identifies three copper species based on Cu^{2+} ligand to metal transfer (LMCT) bands at 238, 266, and $>300 \text{ nm}$ as well as Cu^+ LMCT bands at 235, 296, and 312 nm. Counterintuitively, EXAFS analysis shows that the multinuclear precursor leads to fewer average Cu-Cu interactions than syntheses with mononuclear copper salt precursors. Turnover frequency and selectivity to benzene increase with decreasing copper oxide nuclearity, and thus the multinuclear precursor leads to the highest turnover frequency and benzene production. This work shows the variety of surface species that exist even at extremely low copper surface densities, control of which can improve reactivity of an atypical ODH catalyst up to rates comparable to benchmark vanadia catalysts.

Keywords

Oxidative dehydrogenation; Copper oxide; Cyclohexane; KIT-6

1. Introduction

Oxidative dehydrogenation (ODH) of alkanes is a promising route for producing valuable commodity chemicals such as propylene. The production of H_2O instead of H_2 makes ODH an exothermic reaction, and therefore ODH processes can operate at lower temperatures and pressures than endothermic non-oxidative routes, while not being limited by a low maximum equilibrium production of olefins. ODH processes also have the advantage that oxygen present in the feed stream helps prevent catalyst deactivation by coking. ODH processes are limited to low single-pass conversions to limit over oxidation of products to CO_x . A major goal in alkane ODH is therefore to determine and control the catalyst structural properties that lead to high selectivity to olefins without over-oxidation.

Alkane ODH has been extensively studied over supported VO_x catalysts[1-6] as well as reported over other reducible oxides such as Co_3O_4 [7], MoO_3 [5, 8], WO_3 [5], and MgVO_x [9-12]. Grabowski *et al.*[13] and more recently Carrero *et al.*[14] have compiled kinetic data from more than 100 examples of supported VO_x and other reducible metal oxides and found that alkane ODH occurs by a Mars van Krevelan redox mechanism with rate limiting initial C—H bond activation. This is supported by isotopic studies[6] as well as kinetic studies showing a zero order dependence on oxygen partial pressure along with a positive order dependence on alkane partial pressure[2, 5]. CO_x is formed primarily by consecutive oxidation of the alkane with C—C bond scission, and to a lesser extent by direct oxidation of the alkane[2, 4, 5, 13].

While ODH activity and reaction pathway has been established with a variety of supported reducible oxide catalysts, there is still a major question as to how oxide structure influences ODH activity and selectivity. Dispersed oxide catalysts lend themselves to a distribution of different surface structures with varying numbers of metal-oxygen-support and metal-oxygen-metal bonds as well as the possibility of bulk crystalline phases even at low metal surface densities. These different structures may have different rates of C—H and C—C bond activation, which affects ODH activity and selectivity. Reports of ODH over vanadia agree that crystalline V_2O_5 leads entirely to combustion products while sub-monolayer VO_x structures produce both olefins and CO_x [14]. However, they disagree on whether activity and selectivity are a function of the nuclearity of sub-monolayer structures on a per exposed metal basis. Studies comparing TOF as a function of metal surface density with SiO_2 supported VO_x catalysts report conflicting messages that TOF decreases[15, 16], increases[3, 17], or stays constant[18, 19] over a range of V surface densities. Surface density alone serves as a poor proxy for surface structure nuclearity which is heavily influenced by synthetic method[14]. A more direct comparison between surface structure and reactivity is required to separate catalyst qualities which lead to selective ODH vs. those leading to C—C scission and CO_x .

Cyclohexane ODH is an excellent model reaction for studying structural effects on alkane ODH reactivity[4]. Unlike with propane, all C—C and C—H bonds are equivalent, which simplifies reaction kinetics. Moreover, breaking multiple C—H bonds leads to benzene rather than CO_x like with propane. This allows for separating catalysts' propensity for desired C—H vs. undesired C—C bond scission.

Here, we describe and investigate a new catalyst for cyclohexane ODH consisting of silica-supported copper oxide. Highly dispersed copper(II) oxide should be a promising candidate for cyclohexane ODH. Copper structures are well known for activating O_2 in enzymes and biomimetic zeolite catalysts[20-22], and CuO nanoclusters and highly dispersed Cu^{2+} show remarkable activity

towards cyclohexane oxidation to cyclohexanone and cyclohexanol with molecular oxygen in high pressure batch systems[23-26]. This suggests it should be a good candidate for breaking C—H bonds without C—C bond scission, which is required for cyclohexane ODH. However, there have been virtually no reports of Cu-catalyzed ODH. Cu²⁺ doped strontium hydroxyapatite shows high olefin selectivity for propane ODH[27] compared with non-doped materials, but in that case, the structure of Cu²⁺ in the catalyst is not well understood. In another case, crystalline CuO powder showed up to 85% selectivity to propene in the presence of tetrachloromethane under O₂ limiting conditions, but the selectivity switched to >90% combustion products when tetrachloromethane was not added to the feed[28]. This parallels vanadia catalysts in that bulk crystallites exclusively catalyze combustion rather than selective ODH.

Here, we report on structure-reactivity trends for cyclohexane ODH with copper oxide catalysts as a function of surface structure nuclearity. We have synthesized a series of materials consisting of copper oxide supported on mesostructured KIT-6 silica with varying Cu precursors and copper loadings. In particular, a multinuclear copper siloxide cluster, denoted L₂Cu₆, was utilized as one of the precursors[29] with the goal of synthesizing small clusters. Scheme 1 shows the L₂Cu₆ cluster consists of a hexanuclear Cu⁺ core bound by two tripodal siloxide ligands which are robust and fix the cluster during impregnation, at the same time already providing a mimic of the support environment. In addition, the steric bulk of the siloxide ligands should ensure copper clusters do not aggregate during synthesis of the catalyst. Overall, the different precursors and loadings are intended to generate materials with differing average copper nuclearity, from isolated Cu²⁺ monomers to extended Cu²⁺ aggregates, as illustrated in scheme 2. These materials were characterized by N₂ physisorption, X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and diffuse reflectance UV-visible (DRUV-vis) spectroscopy under ambient and reducing conditions to determine trends in average copper oxide nuclearity. Their reactivity towards cyclohexane ODH is then evaluated to demonstrate how copper oxide structure influences ODH activity and selectivity.

2. Experimental Methods

2.1. Materials synthesis

KIT-6 mesostructured silica was synthesized using a precipitation method adapted from Ryoo *et al.*[30] using a molar ratio of 195 H₂O : 1.5 mol tetraethyl orthosilicate (TEOS) : 1.7 n-butanol : 1.83 HCl : 0.017 Pluronic® P-123 (Sigma, M_n = 5800 g/mol). Briefly, 17.3 g of 37 wt % aqueous hydrochloric acid (Fischer, ACS grade) and 9.6 g of Pluronic® P-123 were added to 326 mL de-ionized water and stirred at 750 rpm at 308 K for 4 h until complete dissolution of the P-123 polymer. Next, 12.15 g n-butanol (Sigma, 99.0%) was added to the mixture and stirred for 1 h. Then 30.2 g TEOS (Sigma, 99.0%) was added, and the mixture was stirred for an additional 24 h. The mixture was subsequently aged at 373 K for 24 h under reflux without stirring. The white precipitate was filtered hot, washed with ethanol and water, and dried at 373 K for 16 h. The dried powder was calcined at 823 K for 4 h with a 5 K/min ramp rate before use.

Copper oxide catalysts were prepared by incipient wetness impregnation of KIT-6 supports and are denoted by metal weight loading followed by precursor used. KIT-6 was dried at 493 K under dynamic vacuum for 16 h prior to use for all catalysts. The dried support was then impregnated with

aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Strem, 99.5%), Na_2CuEDTA (Sigma, 97.0%), or $(\text{NH}_4)_2\text{CuEDTA}$. The complex $(\text{NH}_4)_2\text{CuEDTA}$ was synthesized following an established procedure[31] and purified by crystallization in methanol. A hexanuclear Cu(I) complex with two tripodal, trisilanol ligands, denoted L_2Cu_6 , was synthesized according to a procedure by Limberg *et al.*[29] L_2Cu_6 catalysts were prepared by impregnating dried KIT-6 with L_2Cu_6 dissolved in THF under oxygen- and moisture-free conditions and let dry for 24 h at room temperature in an argon-filled glove box. THF was prepared by distillation over Na-benzophenone followed by three freeze pump thaw cycles to remove water and dissolved gasses. The L_2Cu_6 catalysts were then dried for an additional 24 h at room temperature under dynamic vacuum before exposure to air to remove additional physisorbed solvent. Note that L_2Cu_6 is sparingly soluble in many solvents, and that its comparatively high solubility in THF limits the amount of Cu deposition possible in a single round of incipient wetness impregnation. A vanadia catalyst was prepared by a grafting procedure adapted from Du *et al.*[32]. First, 0.0823 g $\text{VCl}_3 \cdot 3\text{THF}$ (Strem) was suspended in 130 mL dry toluene under N_2 atmosphere forming an orange solution. Next, 20 mL ethanol was added at which point the solution turned light green. Excess ethanol was distilled out of the solution at 383 K at which point 1 g KIT-6 support suspended in toluene was added to solution. The solution was refluxed at 383 K for 24 h, filtered, washed with 150 mL toluene, and dried overnight. All catalysts were then calcined at 823 K for 4 hr with a 5 K/min ramp rate, with the exception of the L_2Cu_6 catalyst, which was left as synthesized.

2.2. Catalyst characterization

Nitrogen adsorption-desorption isotherms were collected using a Micromeritics ASAP 2010 instrument. Prior to measurement, samples were degassed at 473 K under dynamic vacuum until pressure stabilized at 5×10^{-6} bar, typically 8-16 h. The surface area of the samples was calculated from the adsorption isotherm using the BET method, while mesopore size distribution and volume was calculated from the desorption isotherm using the Barrett-Joyner-Halenda (BJH) method. The metal content was determined using ICP-OES (Thermo iCAP 7600) calibrated with Cu and V standards of known concentration. Samples were digested with 48 wt % HF then diluted ten-fold with 0.9 wt % HNO_3 and shaken at 300 rpm at room temperature for 24 h prior to analysis. X-ray diffraction (XRD) spectra were collected using a Rigaku ATXG X-ray diffractometer over the range $1-3^\circ 2\theta$ for KIT-6 diffraction patterns and $20-80^\circ 2\theta$ for CuO diffraction patterns, using $\text{Cu K}\alpha$ radiation. Thermogravimetric analysis with mass spectrometer (TGA-MS) were conducted on a TA Instruments TGA Q500 attached to a Pfeiffer ThermoStar 301T mass spectrometer in high-resolution mode with a 10 K/min ramp up to 873 K under a flow of dry synthetic air. Temperature programmed reduction experiments were performed on an Altamira AMI-2000 chemisorption instrument in the CleanCat user facility at Northwestern University.

Diffuse reflectance UV-visible spectra were collected with a Shimadzu UV-3600 spectrophotometer equipped with a Harrick Praying Mantis diffuse reflectance accessory and reaction cell for in situ measurements. Polytetrafluoroethylene was used as the baseline white standard, and reflectance data were transformed to pseudo-absorbance using the Kubelka-Munk function, $F(R_\infty)$, using the KIT-6 support as the reference as in equations 1 and 2.

$$R_\infty = \frac{R_{\text{sample}}}{R_{\text{KIT6}}} \quad \text{Eq. 1}$$

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} \propto \frac{\alpha \text{ (absorption coefficient)}}{S \text{ (scattering coefficient)}} \quad \text{Eq. 2}$$

All samples are diluted with KIT-6 support to achieve similar $F(R_{\infty}) < 1.5$ to avoid non-linearity issues in the Kubelka-Munk transformation for highly absorbing samples. Pseudo-absorbance spectra are treated with a Savitzky-Golay filter with polynomial degree 2 and 11 point frame to increase signal to noise ratio at the expense of minor signal distortion. Absorption edge energies are estimated from the x-intercept of a linear fit of the rising absorption edge in a plot of $(F(R_{\infty})h\nu)^{1/n}$ where $n=1/2$ for direct allowed transitions as in copper oxide catalysts and $n=2$ for indirect allowed transitions as in the vanadia catalyst.

Cu K-edge X-ray absorption spectroscopy (XAS) was performed at Sector 5 of the Advanced Photon Source, Argonne National Laboratory, on the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) bending magnet D beamline. The beam energy was controlled by a Si(111) monochromator with resolution $\Delta E/E \approx 1.3 \times 10^{-4}$ eV. Incident and transmitted intensities were measured with Canberra ionization chambers while fluorescence measurements were measured using a four-channel SII Vortex-ME4 detector. Energies were calibrated in transmission mode against a Cu foil, setting the first inflection point at the known Cu edge energy of 8979 eV. Dried Cu catalysts were pressed into 0.05 g pellets under oxygen and moisture free conditions and mounted into a 9-pellet controlled atmosphere cell with flowing N_2 . Catalysts were mounted at an incident angle of $\theta = 45 \pm 5^\circ$ with respect to the beam and fluorescence detectors, and spectra were collected in fluorescence mode. For EXAFS analysis, XAS spectra were normalized in Athena and background removed using the AUTOBK algorithm. The Fourier transform was computed over the wavenumber range $k = 3.0 - 10.0 \text{ \AA}^{-1}$ using a Hanning window function with width $dk = 0.5 \text{ \AA}^{-1}$, and fits to the EXAFS function were computed using the real and imaginary components of the Fourier transformed k^2 -weighted $\chi(k)$ function over the range $R = 1.0 - 3.0 \text{ \AA}$ giving a total of 8.91 independent points by the Nyquist criterion. The many-body amplitude reduction factor, S_0^2 , was set to 0.8 for all fits. The first two coordination shells were fit using Cu-O and Cu-Cu scattering paths generated from CuO crystallographic data using FEFF 6.0. Real and imaginary components of the forward Fourier transform of the k^2 -weighted χ function as well as model fits are given in figure S1. The Debye-Waller factor and coordination number are typically highly correlated for any scattering path. To determine model sensitivity, Cu-O and Cu-Cu coordination numbers were varied while maintaining an R-factor model error within 20% of the error of the best fit model.

2.3. Measurements of catalytic activity

Catalytic measurements were conducted in a packed-bed quartz microreactor using 0.01-0.1 g catalyst diluted with KIT-6 support to a total bed mass of 0.1 g to ensure similar flow characteristics. Bed heights measured 3-5 mm in height to minimize pressure and temperature gradients. He (Airgas, 99.999%) and O_2 (Airgas, 99.999%) flows were supplied by mass flow controllers. Cyclohexane was supplied by bubbling He through a cyclohexane saturator with a fixed pressure of 1.44 bar and fixed temperature 296 K to achieve a known cyclohexane molar flow rate. Reactions were performed using a cyclohexane: O_2 : He molar composition of 1: 4.7: 94.3 with a total flow rate of 31.6 $\mu\text{mol/s}$. All lines were heated to 363 K to avoid condensation of vapors. Catalysts were dried in a 5% O_2 in He stream at 523 K for 1 h prior to reaction, and reactions were carried out at atmospheric pressure over the

temperature range 523-623 K. Products were analyzed using an Agilent GC 6890 with capillary column (HP-Innowax, 30 m x 320 μm x 0.5 μm) and flame ionization detector (FID). Conversion was measured relative to the cyclohexane detected when the flow bypassed the reactor and was maintained below 2% in all catalytic tests and all temperatures. Negligible cyclohexane conversion was observed up to 623 K with a blank reactor or with 0.1 g KIT-6 support. Mass balance is defined with respect to carbon as the sum of C_6 species detected during a reaction divided by the sum of cyclohexane detected when the flow bypassed the reactor, and mass balances measured $98\pm5\%$ for all reactions at all temperatures. ODH selectivity is reported as:

$$S_{\text{Benzene}} = \frac{\text{Benzene rate}}{\text{Cyclohexene} + \text{Benzene rate}} \quad \text{Eq. 3}$$

3. Results

3.1. Support and catalyst characterization by nitrogen physisorption

KIT-6 mesoporous silica was used as the catalyst support instead of other mesostructured silicas, in part because its open pore geometry and narrow mesopore size distribution make it ideal for impregnating bulky precursors such as L_2Cu_6 . Small angle powder XRD shows the (211) and (220) peaks characteristic of KIT-6's $Ia\bar{3}d$ pore structure[30] (Fig. S2). Table 1 shows characterization results of catalysts and their KIT-6 supports. Surface areas varied batch to batch from 800-1000 m^2/g , and all KIT-6 used has mesopore diameters of 5.2 ± 0.2 nm large enough to accommodate the L_2Cu_6 precursor with a diameter of ~ 2 nm. Mesopore volume decreased roughly 10% upon impregnation and calcination which confirms the pore structure is stable after calcination up to 823 K. This pore volume decrease is less than the 25-35% pore volume decrease typical for SBA-15 supported catalysts[4, 33, 34] and is attributed to the open pore geometry of KIT-6.

Catalyst metal loadings in table 1 were determined by ICP-OES and used to calculate metal surface density. All catalysts have a low surface density of 0.12 Cu/nm^2 for 1.4- $\text{Cu}(\text{NO}_3)_2$ and 0.014 ± 0.002 Cu/nm^2 for 0.14 wt % Cu catalysts. Even the highest loading is <2% of the reported 6.5 Cu/nm^2 geometric monolayer coverage[35], and Cu ions are statistically likely to be isolated. However, studies on several supported metal oxides show that catalysts with coverage well below a statistical monolayer may possess a range of non-isolated structures[36, 37] as well as bulk metal oxide crystallites. In particular, oligomeric and bulk crystalline CuO were identified in MCM-41 supported copper oxide catalysts with copper surface densities as low as 0.05 Cu/nm^2 [38, 39]. Powder XRD, figure S3, shows no diffraction lines associated with CuO, which indicates the absence of bulk CuO crystallites >3 nm in size. Characterization by techniques such as DRUV-vis and X-ray absorption spectroscopy were next used to gain further insight into the Cu oxide structure.

3.2. Cu catalysts characterized by DRUV-vis spectroscopy

Diffuse reflectance UV-visible (DRUV-vis) spectroscopy gives valuable insight into metal oxide dispersion, coordination geometry, and oxidation state. First, a d-d transition band is found between 600-900 nm for octahedrally coordinated Cu^{2+} or 1300-1600 nm for Cu^{2+} in a tetrahedral coordination environment based on coordination geometry^[40-42], while bulk, crystalline CuO displays a single broad band centered around 650 nm^[40]. The d orbitals of Cu^+ and Cu^0 are filled, and therefore they do not

display d-d transitions[36]. Figure 1 shows normalized DRUV-vis spectra of fresh Cu catalysts. All catalysts exhibit a peak in the d-d transition region (Fig. 1 inset) around 720-760 nm, indicative of Cu^{2+} in an octahedral field[40]. The low d-d band absorption intensity of 0.14- L_2Cu_6 compared with other catalysts indicates that it remained primarily as a Cu^+ species after synthesis, with only a minority Cu^{2+} species upon exposure to air.

Additionally, non-crystalline Cu^{2+} species exhibit an $\text{O}_{2p} \rightarrow \text{Cu}_{3d}$ ligand to metal charge transfer (LMCT) band in the range 240-350 nm. The wavelength of the LMCT peak maximum of metal oxides is often correlated with average metal oxide nuclearity. Isolated cations have the shortest wavelength LMCT which red shifts as metal oxide nuclearity increases and discrete energy levels hybridize into a band structure[43, 44]. The 0.14 wt % Cu^{2+} catalysts have similar DRUV-vis spectra well described by a two-Gaussian fit with a majority peak centered at $\lambda = 238 \pm 3$ nm (5.2 eV) and a minority species centered at $\lambda = 266 \pm 2$ nm (4.7 eV), while 1.4- $\text{Cu}(\text{NO}_3)_2$ has one peak centered at $\lambda = 266$ nm with a tail at higher wavelengths. A LMCT band with $\lambda_{\text{max}} < 250$ nm is assigned to an isolated Cu^{2+} cation in an octahedral field, while LMCT bands with $\lambda_{\text{max}} > 250$ nm are assigned to sub-nanometer Cu^{2+} clusters and larger aggregates, based on comparison between the LMCT peak wavelength and fraction of EPR-active Cu in supported Cu catalysts by Tanaka *et al*[37]. Based on these assignments, fresh 0.14- $\text{Cu}(\text{NO}_3)_2$, 0.14- $(\text{NH}_4)_2\text{CuEDTA}$, and 0.14- Na_2CuEDTA consist of primarily isolated Cu^{2+} cations and small Cu^{2+} clusters, while 1.4- $\text{Cu}(\text{NO}_3)_2$ consists of larger Cu^{2+} aggregates despite its low Cu surface density of 0.12 Cu/nm^2 .

The fresh 0.14- L_2Cu_6 catalyst exists primarily as Cu^+ at room temperature shown *vide infra*, and therefore its DRUV-vis spectrum in figure 1 cannot be compared with Cu^{2+} catalysts. The peak at 260 nm in 0.14- L_2Cu_6 is assigned as a phenyl $\pi \rightarrow \pi^*$ transition in phenyl groups attached to the siloxide ligand. TGA-MS, figure S4, indicates that the siloxide ligand stays intact after L_2Cu_6 deposition. A sharp peak at 220 nm and a broad band around 320 nm are both assigned to the $\text{O}_{2p} \rightarrow \text{Cu}_{4s}$ transition[36] and indicate the presence of at least two populations of Cu^+ species.

3.3. X-ray absorption spectroscopy of Cu catalysts

X-ray absorption spectroscopy gives insight into the oxidation state and local coordination environment of supported Cu catalysts. Figure 2 presents XANES spectra of the L_2Cu_6 precursor, a supported $\text{Cu}(\text{NO}_3)_2$ catalyst, and a supported L_2Cu_6 catalyst before and after calcination at 823 K. Relevant transitions and edge energies, defined as the first inflection point in the near edge region, are listed in Table 2. Cu^+ and Cu^{2+} references exhibit a $1s \rightarrow 4p$ transition at 8997 eV, while ligand field effects split the 4p orbitals in Cu^+ creating a second, lower energy transition at 8983 eV whose normalized height depends on Cu-O coordination number[45]. Cu^+ in the L_2Cu_6 precursor is bound to two oxygen atoms in a linear configuration[29] and consequently exhibits a large feature at 8983 eV. Decreased absorption height at 8983 eV in the supported L_2Cu_6 catalyst is consistent with increased Cu-O coordination as L_2Cu_6 interacts with the support. A weak dipole-forbidden $1s \rightarrow 3d$ feature at 8978 eV and a shoulder at 8986 eV attributed to the $1s \rightarrow 4p$ with ligand to metal “shake down” transition[46, 47] are characteristic of Cu^{2+} ($3d^9$) compounds. The lack of absorption at 8978 eV in figure 2 inset in supported L_2Cu_6 , along with the characteristic Cu^+ transition at 8983 eV and low edge energy below 8982 eV prove supported L_2Cu_6 exists primarily in the +1 oxidation state.

Upon calcination at 823 K, the supported L_2Cu_6 largely oxidizes to Cu^{2+} , seen by the absorption edge shift to 8985 eV, but some Cu^+ may still be present as indicated by the weak band at 8983 eV. The

resulting spectrum is nearly identical to supported $\text{Cu}(\text{NO}_3)_2$ indicating the L_2Cu_6 catalyst oxidizes to form structures similar to those present in other low surface density supported $\text{Cu}(\text{NO}_3)_2$ catalysts.

Figure 3 presents the magnitude of the k^2 -weighted Fourier transformation of the $\chi(k)$ function for the L_2Cu_6 precursor, a supported $\text{Cu}(\text{NO}_3)_2$ catalyst, and a supported L_2Cu_6 catalyst before and after calcination at 823 K. The first two coordination shells of supported catalysts were fit to determine Cu-O and Cu-Cu bond lengths and coordination numbers and results are presented in table 3. Bond lengths and coordination numbers for the L_2Cu_6 precursor are known from X-ray crystallographic data[29] and are also presented in table 3 for comparison. Each material has a large peak centered at 1.41-1.47 Å in figure 3 attributed to Cu-O backscattering whose magnitude is related to Cu-O coordination number and whose position is related to Cu-O bond length. The supported L_2Cu_6 catalyst has an increased Cu-O coordination number of 3.4 and increased Cu-O bond length of 1.918 Å compared to the crystallographic data for the L_2Cu_6 precursor. This is consistent with XANES data and provides further evidence for interaction between L_2Cu_6 clusters and oxygens in the support. The Cu-O backscattering peak increases in magnitude upon calcination in air at 823 K as average Cu-O coordination number increases to 4.2. The Cu-O coordination number and bond length of calcined L_2Cu_6 catalyst are comparable to the $\text{Cu}(\text{NO}_3)_2$ catalyst suggesting that synthesis using either precursor leads to a similar Cu-O coordination environment after aggressive oxidation.

In addition to the Cu-O backscattering peak around 1.45 Å, all materials exhibit Fourier peaks between 2-3 Å due to Cu-Cu scattering contributions. The L_2Cu_6 precursor has two Cu-Cu interactions at an average bond distance of 2.66 Å which manifests as a Cu-Cu scattering peak at 2.12 Å in figure 3. Upon supporting the L_2Cu_6 precursor, this peak shifts to longer scattering distances and decreases in magnitude, consistent with a bond distance of 2.95 ± 0.01 Å and average Cu-Cu coordination number of 1.1 indicating some restructuring of the Cu_6 cluster on the support. After calcination, the supported L_2Cu_6 Cu-Cu scattering peak increases in magnitude and is nearly identical to supported $\text{Cu}(\text{NO}_3)_2$ with an average Cu-Cu coordination number of 5.0. The supported L_2Cu_6 and $\text{Cu}(\text{NO}_3)_2$ catalysts used for EXAFS analysis have a Cu surface density of 0.017 Cu/nm^2 , or about 0.3% of a copper oxide monolayer, at which loading few Cu-Cu interactions are expected and supported by the DRUV-vis spectra in figure 1. Therefore, we assign the structure of these materials as predominantly small clusters or dimers, as illustrated in Scheme 2.

3.4. Catalyst Reducibility

Diffuse reflectance spectra in figure 4 taken during temperature programmed reduction (TPR) up to 573 K in 5% H_2/Ar gives structural as well as reducibility information about the species present in these copper oxide catalysts that are most relevant for ODH catalysis. Reduction events are distinguished by tracking the Cu^{2+} d-d transition band between 600-800 nm[40] as well as metallic interband transitions between 200-800 nm[48]. All of the catalysts except 0.14- Na_2CuEDTA show complete disappearance of Cu^{2+} evidenced by the complete disappearance of the d-d absorption band at 760 nm, but only the 1.4- $\text{Cu}(\text{NO}_3)_2$ catalyst exhibited some reduction to Cu metal by 573 K based on the absorption intensity at 500 nm in figure 4 insets. In addition, the low intensity d-d band in 0.14- L_2Cu_6 completely disappears by 573 K which confirms the presence of a minor Cu^{2+} fraction for this catalyst in addition to the majority Cu^+ species identified by XANES. In contrast, 0.14- Na_2CuEDTA exhibits incomplete reduction of Cu^{2+} at 573 K seen in the inset of figure 4e. This low reducibility

compared to other catalysts is attributed to the Na^+ ion and is consistent with other reports that alkali doping decreases metal oxide reducibility[49, 50]. These results are consistent with H_2 -TPR profiles in figure S5. All but the 0.14- Na_2CuEDTA catalyst exhibit a peak centered between 480-500 K, which corresponds to a reduction from $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ based on DRUV-vis results. The 0.14- Na_2CuEDTA catalyst exhibits broad, weak reduction from 423-823 K consistent with incomplete disappearance of the d-d absorption band by 573 K.

The reduced catalysts differ in Cu^+ speciation based on their charge transfer bands in the main plots of figure 4. The single apparent LMCT of the starting Cu^{2+} catalyst splits into two distinct absorption bands at 230-240 nm and 295-300 nm in all 0.14 wt % Cu catalysts concurrent with reduction to Cu^+ . The relative intensity of these two bands is different between catalysts, indicating the bands arise from transitions in two different Cu^+ structures, rather than two different transitions arising from the same Cu^+ species. The 1.4- $\text{Cu}(\text{NO}_3)_2$ catalyst exhibits a single, lower energy band at 312 nm by 573 K concurrent with the reduction of all Cu^{2+} . The total absorption of each of these 3 bands is comparable to that in the symmetry allowed Cu^{2+} LMCT band, which suggests that they also arise from a symmetry allowed transition. Based on the energy levels for a $3d^{10}$ metal in a distorted octahedral field, we assign the Cu^+ bands at 240, 300, and 312 nm to an $\text{O}_{2p} \rightarrow \text{Cu}_{4s}$ transition in structures with increasing Cu^+ nuclearity. This is consistent with room temperature DRUV-vis spectra of fresh and spent catalysts which indicate 0.14 wt % catalysts are composed of isolated cations and small Cu^{2+} clusters while 1.4- $\text{Cu}(\text{NO}_3)_2$ is composed of higher nuclearity Cu^{2+} aggregates than those of the lower surface density materials. The molar absorptivity of each band is unknown, but we posit that the ratio of pseudo-absorbances at 240 and 300 nm at 573 K gives information about the fraction of cations or small clusters present in 0.14 wt % catalysts. The ratios of pseudo-absorbance at 240 nm to 300 nm follow the order $F(R_{240})/F(R_{300}) = 1.33$ (0.14- L_2Cu_6) > 1.00 (0.14- $\text{Cu}(\text{NO}_3)_2$) > 0.48 (0.14- $(\text{NH}_4)_2\text{CuEDTA}$), and therefore 0.14- L_2Cu_6 is expected to have the greatest number of isolated cations, followed by 0.14- $\text{Cu}(\text{NO}_3)_2$ and 0.14- $(\text{NH}_4)_2\text{CuEDTA}$ respectively.

3.5. Catalytic properties of supported Cu oxide catalysts for ODH of cyclohexane

Catalytic tests were performed to determine how differences in Cu^{2+} nuclearity affect cyclohexane ODH chemistry. Additionally, a 1.1 wt % V catalyst, denoted 1.1- VO_x , was synthesized and tested to compare Cu^{2+} activity with a typical vanadia catalyst. C_6 hydrocarbon yields account for $98 \pm 5\%$ of the total carbon content expected by mass balance for all reactions, indicating little CO_x production. The two major products were cyclohexene and benzene, and selectivity is defined as in equation 3 as benzene production rate divided by cyclohexene and benzene rate. All catalysts deactivated upon use with no steady state attained after 36 h (Fig. S6), and all given rates and selectivities are initial rates and initial selectivities extrapolated back to zero time before deactivation. Turnover frequency (TOF) is calculated by normalizing measured product production rates by total metal content determined by elemental analysis, and apparent activation energies are calculated with respect to the consumption of cyclohexane.

Initial TOF and selectivity to benzene as a function of temperature are shown in figure 5 with select initial TOFs and apparent activation energies for the disappearance of cyclohexane calculated from the slope of $\ln(\text{TOF})$ vs. $1/T$ reported in table 4. Copper catalysts exhibit promising initial TOFs comparable to the vanadia catalyst, though the authors acknowledge that other factors such as stability

or maximum metal loading influence the industrial viability of any given catalyst for ODH. All copper oxide catalysts have apparent activation energies of 60-70 kJ/mol, consistent with the activation energies of other reducible oxide catalysts on silica[14]. Similar apparent activation energies indicate that the rate limiting step for cyclohexane ODH is the same over all active Cu^{2+} species, and therefore differences in TOF primarily arise due to a difference in the *number* of active Cu^{2+} species per total Cu in each catalyst. Alkane ODH is reported to scale with the number of reducible sites[14]. Consistent with this, the 0.14- Na_2CuEDTA catalyst which contains a large fraction of unreducible Cu^{2+} (figure 4e inset) is least active for cyclohexane ODH. The activity of all other copper oxide catalysts scales with the fraction of isolated cations and small clusters as determined from the absorption intensity of Cu^+ bands at 240, 300, and 312 nm in figure 4. This fraction is quantified by the ratio of pseudo-absorbance at 240 nm to 300 nm, $F(R_{240})/F(R_{300})$, for catalysts reduced at 573 K and presented in table 4. The TOF of reducible copper oxide catalysts is proportional to $F(R_{240})/F(R_{300})$ at both temperatures tested, which indicates that cyclohexane ODH activity scales inversely with copper oxide nuclearity.

Selectivity to benzene in figure 5b is insensitive to temperature at constant space velocity. Conversions vary by an order of magnitude over the temperature range tested, and it is not readily apparent from figure 5b whether the apparent constant selectivity with temperature is an intrinsic property or due to compensating effects of temperature and conversion. With the exception of the largely redox inactive 0.14- Na_2CuEDTA catalyst, all the Cu oxide catalysts have a similar, high selectivity to benzene compared with 1.1- VO_x , despite having slightly different fractions of isolated cations and low nuclearity Cu^{2+} clusters. The reaction network is examined next to understand the origin of these apparent selectivity differences.

Alkane ODH proceeds by rate limiting C—H bond abstraction followed by one or more additional C—H abstractions to form cyclohexene or benzene directly[14]. Cyclohexene can also readsorb on a second active site and form benzene in a sequential reaction. This reaction network is depicted in scheme 3. Assuming pseudo-first order kinetics in cyclohexane, the reactant and product rates are given by:

$$\frac{d[C_6H_{12}]}{dt} = -(k_1 + k_2)[C_6H_{12}] \quad \text{Eq. 4}$$

$$\frac{d[C_6H_{10}]}{dt} = k_1[C_6H_{12}] - k_3[C_6H_{10}] \quad \text{Eq. 5}$$

$$\frac{d[C_6H_6]}{dt} = k_2[C_6H_{12}] + k_3[C_6H_{10}] \quad \text{Eq. 6}$$

Substituting benzene and cyclohexene rates in equations 5 and 6 into the definition of selectivity in equation 3 gives the selectivity to benzene as a function of cyclohexene concentration:

$$S_{\text{Benzene}} = \frac{k_2}{k_1 + k_2} + \frac{k_3}{k_1 + k_2} \frac{[C_6H_{10}]}{[C_6H_{12}]} \quad \text{Eq. 5}$$

Selectivity to benzene therefore critically depends on the kinetics of competing pathways in scheme 3. Direct pathway selectivity, k_2/k_1 , can be calculated from $k_2/(k_1 + k_2)$ using equations S3 and S4 while selectivity due to sequential oxidation reactions depends on k_3 and product yield through the concentration of cyclohexene.

Catalysts were tested at constant temperature and cyclohexane concentration while varying space velocity to measure selectivity changes with product yield. As seen in figure 6, all catalysts exhibit a non-zero intercept and increasing selectivity with product yield, indicating that direct and sequential pathways both influence benzene selectivity. The 1.4- $\text{Cu}(\text{NO}_3)_2$, 0.14- $\text{Cu}(\text{NO}_3)_2$, and 0.14- $(\text{NH}_4)_2\text{CuEDTA}$

catalyst selectivities fall along the same curve, indicating they have the same intrinsic selectivity, and any apparent differences between them in figure 5b are due to differences in conversion at the same space velocity. Direct pathway selectivity, k_2/k_1 , is calculated from figure S7 and presented in table 4. With the exception of 0.14-L₂Cu₆, all other copper and vanadia catalysts have the same direct benzene selectivity of 5 – 10 % within experimental error. The low direct benzene selectivity is in agreement with Feng *et al.* who found that direct benzene selectivity decreases with decreasing metal surface density for alumina supported vanadia catalysts[4]. The 0.14-L₂Cu₆ catalyst exhibits a higher direct benzene selectivity of about 24 % in addition to lower sequential benzene production and by extension lower k_3 than other Na free copper catalysts. This increased k_2/k_1 and decreased k_3 may be due to an electronic effect of nearby phenyl groups left over from the siloxide ligand, since these groups are found to be stable at reaction temperatures by TGA-MS as seen in figure S4. The 0.14-Na₂CuEDTA catalyst exhibits a lower TOF and lower sequential oxidation capacity than other copper catalysts indicating k_1 , k_2 , and k_3 are all lowered on addition of Na. This is consistent with the less redox active catalyst being less able to activate the C—H bond for ODH. The 1.1-VO_x catalyst exhibits a TOF similar to non-doped copper catalysts, but it differs from copper by having much lower sequential oxidation capacity as seen by the low slope in figure 6. This may be due to lower readsorption of cyclohexene onto vanadia sites than on copper catalysts.

As mentioned above, these copper catalysts deactivate continuously over 36 h, as can be seen in figure S6, where cyclohexene and benzene TOF both decline. The vanadia catalyst is much more stable than either 0.14-L₂Cu₆ or 1.4-Cu(NO₃)₂, losing only about 10% activity over 36 h compared with the loss of over 50% activity for either copper catalyst. Benzene TOF decreases much more quickly than cyclohexene TOF with time on stream for 0.14-L₂Cu₆ and 1.4-Cu(NO₃)₂. However, the decrease in benzene TOF with decreasing yield is consistent with the selectivity vs. product yield curve for 0.14-L₂Cu₆ and 1.4-Cu(NO₃)₂ in figure 6. This indicates the intrinsic selectivity of the catalysts does not change during deactivation, and the effect of agglomeration is to change the *number* of active Cu²⁺ species per total Cu rather than to a change the mechanism or kinetics of ODH. The origin of this change can be assigned to either coking or a structural rearrangement. Figure S8 shows TGA-MS profiles of m/z =44 (carbon dioxide) during calcination of spent catalysts. Integrating the mass loss associated with CO₂ gives an upper bound of 0.05 wt % carbon on the catalyst surface after reaction, which suggests coking is not a significant source of deactivation. Alternately, the change in activity can be associated with a change in the distribution of isolated, clustered, and aggregated Cu²⁺ under ODH reaction conditions as high energy structures agglomerate into lower energy ones. Normalized DRUV-vis spectra of spent catalysts in figure S9 show the LMCT transfer bands generally redshift 0.3-0.6 eV after being subjected to ODH conditions. The spectra also exhibit a low energy tail, suggesting the presence of a minority distribution of Cu²⁺ structures larger in extent than the majority species determined by the charge transfer peak wavelength. The peak wavelength redshift and long tail indicate that Cu structures initially present in fresh catalysts are not thermally stable and tend to agglomerate during reaction. The exception is again the 0.14-Na₂CuEDTA, which is stable, but less active. In spite of the shift in the DRUV-vis, there are no diffraction lines present in powder XRD of 1.4-Cu(NO₃)₂ after cyclohexane ODH in figure S10. This indicates that Cu²⁺ crystallites are <3.0 nm even after reaction, and crystallites present in 0.14 wt % Cu catalysts are likely even smaller.

4. Conclusions

Here we demonstrate the first report of nanostructured copper oxide activity towards ODH of alkanes. DRUV-vis and X-ray absorption spectroscopy of fresh catalysts show structural differences between catalysts with different loadings and precursors despite metal surface densities $<0.2 \text{ Cu/nm}^2$. At least three copper species are identified by DRUV-vis based on Cu^{2+} LMCT bands at 238, 266, and $>300 \text{ nm}$ as well as Cu^+ LMCT bands at 235, 296, and 312 nm after reduction. The fraction of each copper species can be tuned by synthesis method, and use of the multinuclear L_2Cu_6 precursor led to the highest fraction of low nuclearity copper species. This is likely due to L_2Cu_6 depositing as small copper oxide domains with steric bulk from the siloxide ligand enforcing a minimum distance between deposited clusters.

Nuclearity trends combined with cyclohexane ODH studies show that activity scales inversely with copper oxide nuclearity. Selectivity to benzene is a function of the relative kinetics of direct and sequential pathways in scheme 3 as well as product yield, and it appears to be influenced by transition metal identity, alkali dopants, and the local ligand environment. All supported copper oxide catalysts exhibit high selectivity to selective oxidation products with negligible CO_x , in contrast to bulk, crystalline CuO which exhibited over 90% selectivity to CO_x in the ODH of propane without additives such as tetrachloromethane[28]. Copper oxide catalysts exhibit comparable activity and higher subsequent C—H bond abstraction at the same conversion as a typical vanadia catalyst, apparently due to much faster sequential oxidation reactions, but their tendency to agglomerate during reaction will need to be overcome for industrial application. Potential methods for improving stability are to use a different support for which Cu^{2+} has a higher affinity or using a physical overcoat of secondary metal oxide, such as has been shown to improve stability of metallic Cu nanoparticles during liquid phase hydrogenation reactions[51, 52]. Additional studies on the kinetics of these and related catalysts are currently under way.

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Table Titles and Scheme / Figure Captions.

Table 1. Catalyst and KIT-6 support properties

Table 2. Cu K edge energies and relevant transitions

Table 3. Fitting results for supported copper oxide catalysts

Table 4. Apparent activation energies, TOFs, and direct pathway selectivity of copper and vanadium oxide catalysts.

Scheme 1. Structure of L_2Cu_6 (left) and core motif (right) showing Si (gray), O (red), and Cu (cyan) atoms with phenyl ligands omitted for clarity.

Scheme 2. Potential supported Cu^{2+} species, including monomer, dimer, and oligomeric species

Scheme 3. Cyclohexane ODH reaction network

Figure 1. DRUV-vis spectra of fresh Cu catalysts. 0.14- L_2Cu_6 (red), 0.14- $Cu(NO_3)_2$ (cyan), 0.14- $(NH_4)_2CuEDTA$ (orange), 0.14- $Na_2CuEDTA$ (green), 1.4- $Cu(NO_3)_2$ (blue). Inset shows the lower-energy d-d transition region.

Figure 2. Cu K edge XANES spectra of L_2Cu_6 precursor (black), 0.2- L_2Cu_6 catalyst (red), 0.2- L_2Cu_6 catalyst calcined 823 K in air (red dashed), and 0.2- $Cu(NO_3)_2$ catalyst (cyan) with edge energy marked with an X for clarity. Vertical dashed lines mark transitions associated with Cu^+ and Cu^{2+} at 8983 and 8987 eV respectively. Inset marks $1s \rightarrow 3d$ transition.

Figure 3. Magnitude of the Fourier transformed k^2 -weighted EXAFS function.

Figure 4. DRUV-vis spectra of catalysts under 3.7 $\mu\text{mol/s}$ flow of 5% H_2 / He between 333-573 K. Main figures show LMCT region while insets show d-d transition region. A) 0.14- L_2Cu_6 , B) 1.4- $Cu(NO_3)_2$, C) 0.14- $Cu(NO_3)_2$, D) 0.14- $(NH_4)_2CuEDTA$, E) 0.14- $Na_2CuEDTA$

Figure 5. Temperature dependence of cyclohexane ODH (a) turnover frequency and (b) selectivity to benzene. Reaction conditions: $C_6H_{12}:O_2:He = 1:4.7:94.3$, space velocity = 540 mol C_6H_{12} / (mol metal * hr), $P = 1.01$ bar, $v_{\text{total}} = 31.6$ $\mu\text{mol/s}$ gas.

Figure 6. Selectivity to benzene as a function of product yield. Reaction conditions: $T = 573$ K, $C_6H_{12}:O_2:He = 1:4.7:94.3$, space velocity = 230-1770 mol C_6H_{12} / (mol metal * hr), $P = 1.01$ bar, $v_{\text{total}} = 16.6$ -64.0 $\mu\text{mol/s}$ gas.

Table 1. Catalyst and KIT-6 support properties

	Support properties		Catalyst properties			
	Surface area	Pore volume	M loading	Surface density	Surface area	Pore volume
Catalyst	(m ² /g)	(cm ³ /g)	(wt %)	(M/nm ²)	(m ² /g)	(cm ³ /g)
0.14-L ₂ Cu ₆	900	0.84	0.12%	0.012	1000	0.90
1.4-Cu(NO ₃) ₂	1100	1.0	1.30%	0.12	890	0.89
0.14-Cu(NO ₃) ₂	900	0.84	0.14%	0.014	960	0.89
0.14-(NH ₄) ₂ CuEDTA	830	0.88	0.17%	0.015	800	0.86
0.14-Na ₂ CuEDTA	830	0.88	0.14%	0.014	600	0.75
1.1-VO _x	830	0.88	1.1%	0.15		

Table 2. Cu K edge energies and relevant transitions

Material	E ₀ (eV)	1s→4p ₁ (eV)	1s→4p ₂ (eV)	1s→3d (eV)
L ₂ Cu ₆ precursor	8981.9	8994.3	8982.3	
0.2-L ₂ Cu ₆	8981.5	8997.3	8982.8	
0.2-L ₂ Cu ₆ , Δ 823 K	8985.3	8997.8	8982.8	8977.5
0.2-Cu(NO ₃) ₂	8985.4	8997.8	8982.8	8977.5

Table 3. Fitting results for supported copper oxide catalysts

Material	Shell	CN ^a	R (Å) ^b	σ ² (Å ²) ^c	ΔE ₀ (eV) ^d	R-factor ^e
L ₂ Cu ₆ precursor ^f	Cu-O	2	1.839 ^g			
	Cu-Cu	2	2.66 ^h			
0.2-L ₂ Cu ₆	Cu-O	3.4	1.918	0.0072	8.32	0.0013
	Cu-Cu	1.1	2.941	0.0074	8.41	0.0013
0.2-L ₂ Cu ₆ Δ 823 K	Cu-O	4.2	1.925	0.0060	4.05	0.0023
	Cu-Cu	5.0	2.962	0.0164	8.28	0.0031
0.2-Cu(NO ₃) ₂	Cu-O	4.1	1.913	0.0051	2.84	0.0003
	Cu-Cu	5.3	2.952	0.0110	7.82	0.0018

^a Coordination number. ^b Fitted radial distance. ^c Debye-Waller factor. ^d Energy reference shift. ^e R-factor defined in eq S2. ^f Coordination numbers and bond lengths taken from crystallographic data. ^g Average of 1st Cu-O shell distances. ^h Average of 1st Cu-Cu shell distances.

Table 4. Apparent activation energies, TOFs, and direct pathway selectivity of copper and vanadium oxide catalysts.

Catalyst	$F(R_{240})/$ $F(R_{300})^a$	E_A (kJ/mol)	$10^4 \cdot \text{TOF (s}^{-1}\text{)}$		k_2/k_1
			523 K	623 K	
0.14-L ₂ Cu ₆	1.33	64.	2.3	32.4	0.24
0.14-Cu(NO ₃) ₂	1.00	64.	2.2	19.6	0.04
0.14-(NH ₄) ₂ CuEDTA	0.48	70.	1.7	14.9	0.11
1.4-Cu(NO ₃) ₂	0.14	61.	1.1	9.8	0.10
1.1-VO _x	---	83.	0.6	13.5	0.08
0.14-Na ₂ CuEDTA	0.77 ^b	69.	0.5	5.7	0.03

^a ratio of pseudo-absorbance at 240 nm to 300 nm for catalysts reduced at 573 K under 3.7 $\mu\text{mol/s}$ flow of 5% H₂ / He. ^b Ratio of selectivity to benzene vs. cyclohexene from direct reaction of cyclohexane. ^c LMCT from large fraction of unreducible Cu²⁺ included in ratio.

Scheme 1. Structure of L_2Cu_6 (left) and core motif (right) showing Si (gray), O (red), and Cu (cyan) atoms with phenyl ligands omitted for clarity.

Scheme 2. Potential supported Cu^{2+} species, including monomer, dimer, and oligomeric species

Scheme 3. Cyclohexane ODH reaction network.

Figure 1. DRUV-vis spectra of fresh Cu catalysts. 0.14- L_2Cu_6 (red), 0.14- $Cu(NO_3)_2$ (cyan), 0.14- $(NH_4)_2CuEDTA$ (orange), 0.14- $Na_2CuEDTA$ (green), 1.4- $Cu(NO_3)_2$ (blue). Inset shows the lower-energy d-d transition region.

Figure 2. Cu K edge XANES spectra of L_2Cu_6 precursor (black), 0.2- L_2Cu_6 catalyst (red), 0.2- L_2Cu_6 catalyst calcined 823 K in air (red dashed), and 0.2- $Cu(NO_3)_2$ catalyst (cyan) with edge energy marked with an X for clarity. Vertical dashed lines mark transitions associated with Cu^+ and Cu^{2+} at 8983 and 8987 eV respectively. Inset marks $1s \rightarrow 3d$ transition.

Figure 3. Magnitude of the Fourier transformed k^2 -weighted EXAFS function.

Figure 4. DRUV-vis spectra of catalysts under 3.7 $\mu\text{mol/s}$ flow of 5% H_2 / He between 333-573 K. Main figures show LMCT region while insets show d-d transition region. A) 0.14- L_2Cu_6 , B) 1.4- $\text{Cu}(\text{NO}_3)_2$, C) 0.14- $\text{Cu}(\text{NO}_3)_2$, D) 0.14- $(\text{NH}_4)_2\text{CuEDTA}$, E) 0.14- Na_2CuEDTA

Figure 5. Temperature dependence of cyclohexane ODH (a) turnover frequency and (b) selectivity to benzene. Reaction conditions: $\text{C}_6\text{H}_{12}:\text{O}_2:\text{He} = 1:4.7:94.3$, space velocity = $540 \text{ mol C}_6\text{H}_{12} / (\text{mol metal} \cdot \text{hr})$, $P = 1.01 \text{ bar}$, $v_{\text{total}} = 31.6 \mu\text{mol/s gas}$.

Figure 6. Selectivity to benzene as a function of product yield. Reaction conditions: $T = 573 \text{ K}$, $\text{C}_6\text{H}_{12}:\text{O}_2:\text{He} = 1:4.7:94.3$, space velocity = $230\text{-}1770 \text{ mol C}_6\text{H}_{12} / (\text{mol metal} \cdot \text{hr})$, $P = 1.01 \text{ bar}$, $v_{\text{total}} = 16.6\text{-}64.0 \mu\text{mol/s gas}$.

Cyclohexane oxidative dehydrogenation over copper oxide catalysts

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Graphical Abstract