



# 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  $\text{Cu}^{2+}$  ligand to metal transfer (LMCT) bands at 238, 266, and  $>300 \text{ nm}$  as well as  $\text{Cu}^+$  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.

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## 1. Introduction

Oxidative dehydrogenation (ODH) of alkanes is a promising route for producing valuable commodity chemicals such as propylene. The production of  $\text{H}_2\text{O}$  instead of  $\text{H}_2$  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  $\text{CO}_x$ . 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  $\text{VO}_x$  catalysts [1–6] as well as reported over other reducible oxides such as  $\text{Co}_3\text{O}_4$  [7],  $\text{MoO}_3$  [5,8],  $\text{WO}_3$  [5], and  $\text{MgVO}_x$  [9–12]. Grabowski et al. [13] and more recently Carrero et al. [14] have compiled kinetic data from more than 100 examples of supported  $\text{VO}_x$  and other reducible metal oxides and found that alkane ODH occurs

by a Mars–van Krevelen 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].  $\text{CO}_x$  is formed primarily by consecutive oxidation of the alkene 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 pathways have 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  $\text{V}_2\text{O}_5$  leads entirely to combustion products while sub-monolayer  $\text{VO}_x$  structures produce both olefins and  $\text{CO}_x$  [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  $\text{SiO}_2$  supported  $\text{VO}_x$  catalysts report conflicting messages that TOF decreases [15,16], increases [3,17], or stays

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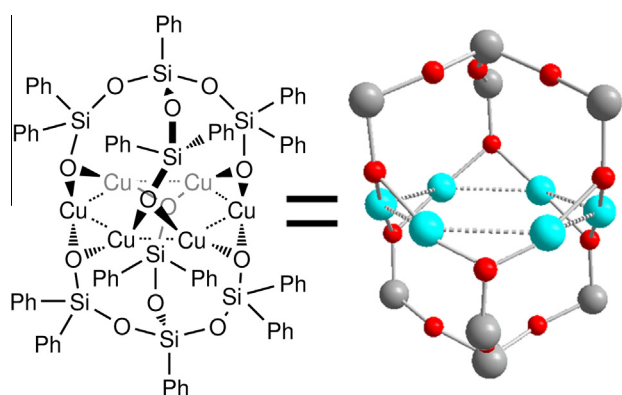
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constant [18,19] over a range of V surface densities. Surface density alone serves as a poor proxy for surface structure nuclearity which is heavily influenced by synthetic method [14]. A more direct comparison between surface structure and reactivity is required to separate catalyst qualities which lead to selective ODH vs. those leading to C–C scission and CO<sub>x</sub>.

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<sub>x</sub> 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<sub>2</sub> in enzymes and biomimetic zeolite catalysts [20–22], and CuO nanoclusters and highly dispersed Cu<sup>2+</sup> show remarkable activity toward 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. Cu<sup>2+</sup> doped strontium hydroxyapatite shows high olefin selectivity for propane ODH [27] compared with non-doped materials, but in that case, the structure of Cu<sup>2+</sup> 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 O<sub>2</sub> 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 Cu loadings. In particular, a multinuclear copper siloxide cluster, denoted L<sub>2</sub>Cu<sub>6</sub>, is utilized as one of the precursors [29] with the goal of synthesizing small clusters. Scheme 1 shows the L<sub>2</sub>Cu<sub>6</sub> cluster consists of a hexanuclear Cu<sup>+</sup> 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



**Scheme 1.** Structure of L<sub>2</sub>Cu<sub>6</sub> (left) and core motif (right) showing Si (gray), O (red), and Cu (cyan) atoms with phenyl ligands omitted for clarity.

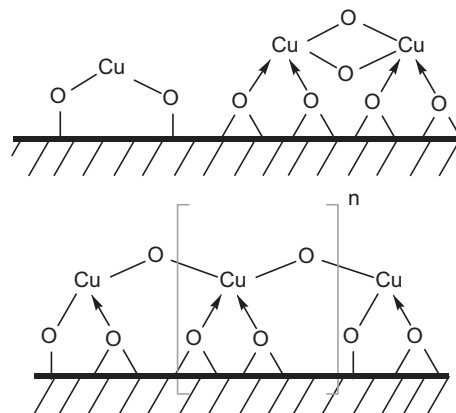
average copper nuclearity, from isolated Cu<sup>2+</sup> monomers to extended Cu<sup>2+</sup> aggregates, as illustrated in Scheme 2. These materials are characterized by N<sub>2</sub> physisorption, X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES), extended X-ray absorption fine 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 toward 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 H<sub>2</sub>O:1.5 mol tetraethyl orthosilicate (TEOS):1.7 *n*-butanol:1.83 HCl:0.017 Pluronic<sup>®</sup> P-123 (Sigma, *M<sub>n</sub>* = 5800 g/mol). Briefly, 17.3 g of 37 wt% aqueous hydrochloric acid (Fischer, ACS grade) and 9.6 g of Pluronic<sup>®</sup> 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 Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Strem, 99.5%), Na<sub>2</sub>CuEDTA (Sigma, 97.0%), or (NH<sub>4</sub>)<sub>2</sub>CuEDTA. The complex (NH<sub>4</sub>)<sub>2</sub>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<sub>2</sub>Cu<sub>6</sub>, was synthesized according to a procedure by Limberg et al. [29] L<sub>2</sub>Cu<sub>6</sub> catalysts were prepared by impregnating dried KIT-6 with L<sub>2</sub>Cu<sub>6</sub> 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<sub>2</sub>Cu<sub>6</sub>



**Scheme 2.** Potential supported Cu<sup>2+</sup> species, including monomer, dimer, and oligomeric species.

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