

## NOTE

# The Selective Hydrogenation of Propyne over a Copper/Silica Catalyst Prepared from a Monolayer Film of Copper 2,2'-Bipyridine Dimer on Cab-O-Sil

The hydrogenation of propyne to propene is a reaction of commercial interest to the polyolefins industry. Currently, a propene-rich stream which contains 2 mol% propyne/propadiene is reduced over supported metal catalysts such as supported Pd or bimetallic Pd with another metal, or promoted Cu/alumina (1). The Pd catalysts convert up to 50% of the propyne/propadiene to propane and this saturate is separated from the olefin to be recycled to the cracking furnace (2). A copper catalyst for this reaction is desirable as the diolefins and alkynes will be saturated to monoolefins only (2, 3). However, one serious side reaction is the oligomerization of C<sub>3</sub> adsorbed species to nonvolatiles called "green oil" by the industry. Zippert and White (4) showed that Cu/silica catalysts which were prepared from Cu(acac)<sub>2</sub>/Cab-O-Sil catalyze the desired reaction with high selectivities to propene (60-90%); however, these catalysts were much less active than the low-dispersion Cu/silica catalysts made by aqueous impregnation. These low-dispersion catalysts (ca., 10-20%) suffered from low selectivities to propene (20%) with the oligomer as the major product. These data suggested to us that the yield of propene was influenced by the type of Cu precursor.

We reported earlier on our efforts to develop controlled reaction environments by decorating an oxide surface with a stable metal complex (5). This methodology permitted us to relate catalyst properties to subtle changes in structure (6) and ensemble size of the precursor (7). We found this technique especially helpful in documenting the effect of ensemble size on the selective reduction of methyl acetate over a family of supported copper catalysts (7). It was of interest to us to examine the catalytic properties of Cu/silica catalysts derived from a dinuclear Cu complex, [Cu(OH)bipy]<sub>2</sub><sup>2+</sup> cation (Fig. 1), supported on silica. These catalysts were characterized previously (8) by NO and N<sub>2</sub>O titrations to show that most of the Cu atoms were in contact with the gas phase. The results of this work suggested to us that the dinuclear Cu complexes interacted with the silica to form a monolayer. Highly dispersed Cu/silica was formed when the supported complex was decomposed in air and we suggested that the Cu ions were in close proximity to each other (8). The catalytic properties of these

catalysts will be compared to those developed by thermolysis of Cu(acac)<sub>2</sub>/silica (4, 9).

Cab-O-Sil (M-5 grade; surface area = 200 m<sup>2</sup>/g silica) was purchased from Cabot Corporation. Acetonitrile, obtained from Fisher, was used without further purification. The gases were (1) extra-dry nitrogen (HoloX), (2) oxygen (HoloX), and (3) 25 vol% hydrogen (Matheson, Inc., balance helium). Each gas was passed through a molecular-sieve, replaceable, gas purifier cartridge (Type 452), held in a Type 450 gas purifier (Matheson). Reagent grade propyne (95.7% propyne, Pfaltz and Bauer) was used without further purification. Propadiene was the major impurity.

The method used to prepare [Cu(OH)bipy]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> was similar to that reported by McWhinnie (10). The elemental analysis for the compound (theoretical values in parenthesis) gave: Cu, 20.0 (18.90); C, 35.79 (35.73); H, 2.74 (2.70); N, 8.27 (8.33); Cl, 10.49 (10.54).

Elemental analyses for carbon, hydrogen, and nitrogen were performed by Atlantic Microlabs, Inc. (Norcross, GA). The copper analyses were performed by Applied Testing Services (Marietta, Ga) using atomic absorption spectrophotometry and inductively coupled plasma techniques.

The catalyst preparation was described earlier for supporting the dinuclear Cu complex on silica (8, 11). This sample showed a copper loading of 2.27 wt% Cu with a dispersion of 100% and the moles of Cu/g of solid was 357 μmol/g catalyst (8). Another catalyst was prepared by traditional methods for comparison to the novel catalyst. This sample, obtained from Professor N.W. Cant, was prepared by mixing 23.64 g Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O with 450 cm<sup>3</sup> of H<sub>2</sub>O. The pH of this solution was 3.07. The pH was adjusted to 11.0 with the addition of concentrated ammonia solution (NH<sub>4</sub>OH, aq.). This solution was contacted with 15.0 g of Aerosil 200 with stirring. As the pH decreased to 10.7 more concentrated ammonia solution was added to restore the pH to 11.0 and the solution was stirred for 60 min at room temperature. The suspension was then filtered and resuspended in distilled water, followed by further stirring at room temperature for 20 min. This washing procedure was repeated three times and the pH was measured after each resuspension: after first wash, pH = 10.3; after second wash, pH = 9.9; after third wash, pH = 9.7. The final filter cake was

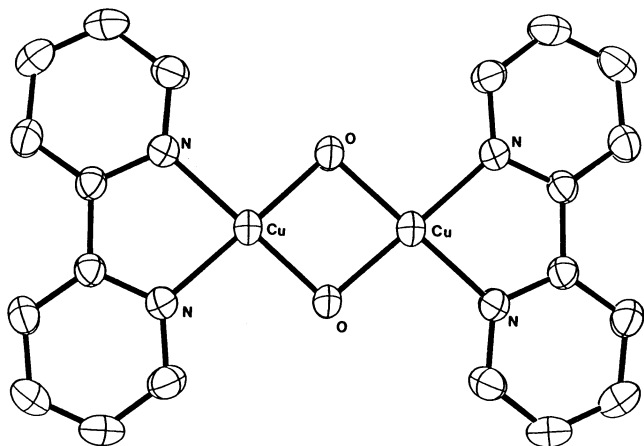


FIG. 1. ORTEP perspective drawing of copper 2,2' bipyridine dimer cation. Hydrogens have been omitted for clarity.

dried overnight at 110°C. Calcination procedure in a tube furnace equipped with flowing air was as follows: 200°C for 1 h, 350°C for 1 h, 500°C for 3 h. The heating rates were 2–4°C/min. This sample showed a dispersion of 12% with a Cu loading of 5.8 wt% Cu (12).

The dispersion of Cu is determined from the isothermal (100°C) pickup of NO measured in a gravimetric device. The technique was reported earlier and is used here to measure the Cu dispersion in the catalyst derived from the dinuclear Cu complex (8, 9). Three of the four catalysts discussed here were characterized by this technique using the same procedures. The dispersion of catalyst supplied by Cant was determined by chemisorption of nitrous oxide on a reduced sample. The reaction to form nitrogen is followed by mass spectrometer and moles of surface copper determined from the stoichiometric reaction.

A description of this reactor appears in the earlier work (4, 9). For one set of runs, only 32.5 mg of Cu/silica (2.27 wt% Cu, 11.6  $\mu\text{mol}$  of exposed Cu) prepared from the dinuclear metal complex was used and the flow rate of carrier gas was 91.3 STP  $\text{cm}^3/\text{min}$ . The space-time based on the  $\text{H}_2/\text{He}$  (25 vol%  $\text{H}_2$ ) carrier gas flow rate was  $0.48 \times 10^{-3}$  g Cu sec/STP  $\text{cm}^3$ . By comparison, we used only 25.4 mg of polycrystalline sample (5.8 wt% Cu) in a separate test with a carrier gas flow rate of 48.6 STP  $\text{cm}^3/\text{minute}$ . The space-time was  $1.82 \times 10^{-3}$  g Cu-sec/STP  $\text{cm}^3$ . This space-time appears to be higher than that used for the dinuclear catalyst except when one considers the lower Cu dispersion in the polycrystalline sample. On that basis, the space-times are as follows: dinuclear catalyst,  $4.85 \times 10^{-4}$  g exposed Cu sec/STP  $\text{cm}^3$ ; polycrystalline catalyst,  $2.18 \times 10^{-4}$  g exposed Cu sec/STP  $\text{cm}^3$ .

Pulses of propyne (8.6  $\mu\text{mol}$ ) were introduced to the reactor by directing the  $\text{H}_2/\text{He}$  carrier gas into a gas sampling valve having a volume of 0.21  $\text{cm}^3$ . Prior to pulsing the reactor, the sample valve was filled by passing propyne at 1 atm

pressure and room temperature through it for 1 min. Under these conditions, the amount of propyne per pulse passing over the catalyst was 0.74 mol propyne/mol total Cu. We pass 10–15 pulses of propyne over the catalyst during a typical run so that the integrated moles of propyne converted per mol of total Cu is 5. This turnover suggests that the solid is catalytic toward the reactant propyne. The total pressure at the reactor was 65 psig.

The temperature was increased after each pulse of propyne for half of the pulses (ca. 5–7 pulses) so as to attain the maximum conversion and then the temperature was decreased for the remaining pulses so as to end the run at the initial temperature. Permanent changes in catalyst activity during a run would be manifest by methodical changes in specific activity at replicate data for different times during the run.

The conversion of reactant and selectivity to propene were calculated from the average of several pulses using the peak areas of unreacted propyne and product propene. The GC response factors used to convert data of peak area to moles of species were as follows: 1.00/0.957/0.886 for propane/propene/propyne. The moles of propyne fed to the pulse reactor were estimated in a separate experiment for which the sample loop was filled with aliquots of propene at the same conditions for which the loop was filled with propyne. It has been determined that propene is not converted over the catalysts under the reaction conditions.

The properties of the catalyst were examined for which the mass of catalyst was constant and the temperature was changed to adjust the conversion. The data in Figs. 2 and 3 show that the specific activity describes a single line for the data collected when the temperature was either increasing or decreasing. Consider the specific conversion

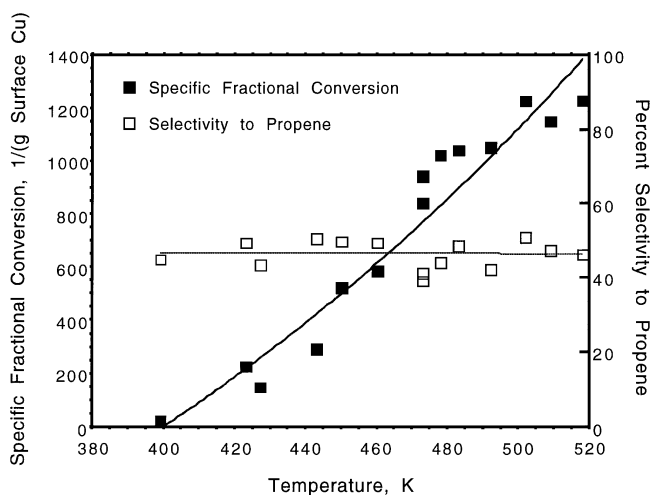
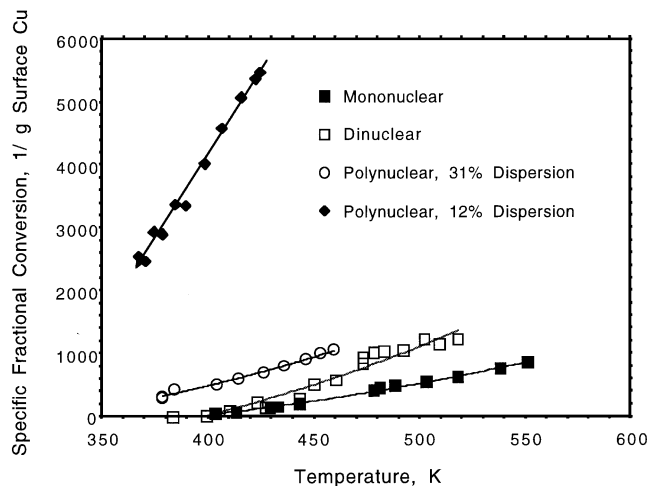


FIG. 2. Specific fractional conversion/selectivity for the hydrogenation of propyne over Cu/silica. 32.5 mg of Cu/silica (2.27 wt% Cu, 100% dispersion); 91.3 STP  $\text{cm}^3/\text{min}$  He/ $\text{H}_2$  (25 mol%  $\text{H}_2$ ) carrier gas flow rate; 8.6  $\mu\text{mol}$  pulse propyne total pressure = 65 psig (101.5 kPa/14.7 psig).



**FIG. 3.** Effect of copper precursor and dispersion on conversion. Varying amounts of Cu/silica catalysts [mononuclear = 34.4 mg, dinuclear = 32.5 mg, polynuclear (31% dispersion) = 34.4 mg, polynuclear (12% dispersion) = 25.4 mg]; varying flow rates of He/H<sub>2</sub> carrier gas (25 mol% H<sub>2</sub>) [mononuclear = 66.3 STP cm<sup>3</sup>/min, dinuclear = 91.3 STP cm<sup>3</sup>/min, polynuclear (31% dispersion) = 66.3 STP cm<sup>3</sup>/min, polynuclear (12% dispersion) = 48.6 STP cm<sup>3</sup>/min], 8.6 μmol pulse of propyne; total pressure = 65 psig (101.5 kPa/14.7 psig).

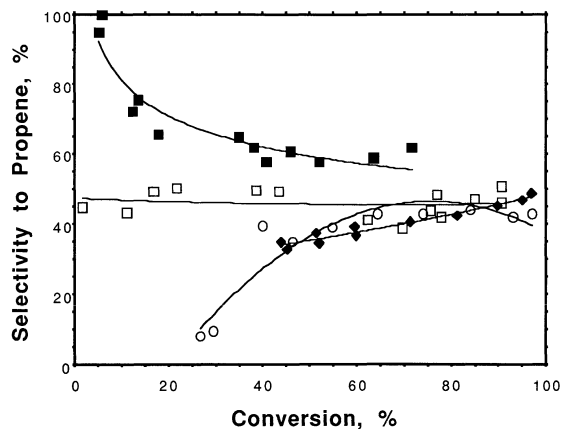
data for the supported dinuclear metal complex/silica for which no systematic change is observed with pulses at similar reaction conditions (Fig. 2). The uncertainty in specific activity is 10% for the data at 473 K. The data for the other catalysts (mononuclear and polynuclear (31%)) also show good agreement (3–10%) between the data collected when the temperature was either increasing or decreasing. However, a small systematic error in specific conversion is noted for the data of the polynuclear (12% dispersion) catalyst (Fig. 3) as made evident in the low-temperature data (370 K). For these data, the lack of agreement is 8–10%.

The data for the catalyst derived from the Cu(bipy) dimer/silica (Fig. 2) show that percentage selectivity to propene was constant over the range of temperatures 390–523 K. The specific fractional conversion is shown in the same figure. Propene was the only gaseous product for temperatures less than 443 K, whereas low selectivities to methane and ethene (5% and 2%, respectively) were observed also for temperatures greater than 443 K (not shown on Fig 2). Minor C<sub>6</sub>-products (<1% selectivity) were detected as the temperature was increased to 573 K.

We show in Fig. 3 the specific fractional conversion of propyne over four catalysts which were developed from different precursors. Two of the catalysts were developed from thermolysis of monolayer films of Cu(acac)<sub>2</sub>/silica (2.4 wt% Cu) or Cu(bipy) dimer/silica (2.2 wt% Cu). Both of these catalysts showed 100% Cu dispersion. The other two catalysts were developed from either aqueous impregnation of the copper salt (12% Cu dispersion) (12) or from thermolysis of multiple layers Cu(acac)<sub>2</sub>/silica (31% disper-

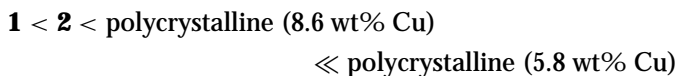
sion) (4, 9). We refer to these last two catalysts as polycrystalline having 5.8 and 8.6 wt% Cu, respectively. We adjusted the mass of catalyst in the reactor so that the space-times of the catalysts were similar when expressed as *g exposed Cu-sec/STP cm<sup>3</sup>*: mononuclear precursor,  $7.5 \times 10^{-4}$ ; dinuclear precursor,  $4.8 \times 10^{-4}$ ; polycrystalline (5.8 wt% Cu),  $2.2 \times 10^{-4}$ ; and polycrystalline (8.6 wt% Cu),  $8.3 \times 10^{-4}$  [4]. The conversion of propyne is smallest with the sample showing 100% dispersion of copper ions which were prepared from a mononuclear precursor, Cu(acac)<sub>2</sub> (9). We showed in earlier manuscripts (9, 13) that the Cu species in these catalysts were “isolated” using two probe reactions: N<sub>2</sub>O decomposition and ethanol dehydrogenation. The decomposition of nitrous oxide occurs readily on polycrystalline Cu (14) and supported Cu/silica developed by thermolysis of supported Cu(bipy) dimer (8). Ethanol will form ethyl acetate over polycrystalline supported Cu (13). We found no evidence of reactivity to the reactant N<sub>2</sub>O (9) nor any evidence of oligomerization activity for ethanol to ethyl acetate (13) over the catalysts prepared from mononuclear precursors. These results support our claim that the Cu species in these samples are “isolated.” Slightly higher conversion is observed for the catalyst prepared from the dinuclear precursor which also shows a dispersion of 100%. The two polycrystalline Cu samples show higher conversions of propyne with the more active sample showing the lower dispersion (12%).

The selectivity to propene data for these catalysts are reported in Fig. 4. The two polycrystalline catalysts show very similar selectivity vs conversion behavior with the well-dispersed catalyst having “isolated” Cu atoms showing the highest selectivity to propene (60–90%). The catalyst developed from the dinuclear precursor shows a selectivity intermediate (40–50%) to the “isolated” Cu catalysts and the polycrystalline catalyst for conversions less than 40%. At high conversions of propyne all catalysts show about the same selectivity (50%).



**FIG. 4.** Comparison of selectivity vs conversion over Cu/silica catalysts. Reaction conditions stated in caption for Fig. 3.

The data of catalyst activity for the four catalysts permit us to develop a sequence of catalyst activity as shown below:



where the catalysts prepared from mononuclear and dinuclear Cu complexes, denoted here **1** and **2**, show lower activity than the two polycrystalline catalysts having Cu loadings of 8.6 and 5.6 wt%. The two polycrystalline show the following Cu dispersions: 8.6 wt% Cu—31% and 5.8 wt% Cu—12%. We showed earlier that catalysts **1** and **2** display 100% Cu dispersion, but the Cu species in catalyst **1** were “isolated” so that N<sub>2</sub>O would not decompose. Catalyst **2** shows Cu species sufficiently close to catalyze the N<sub>2</sub>O decomposition. The N<sub>2</sub>O probe reaction permits us to discriminate between the two model catalysts (**1** and **2**) even though NO titration suggests that both catalysts show 100% Cu dispersion. Moreover, the results of the probe reaction suggests that the Cu species are closer together in catalyst **2** than in catalyst **1**. It appears that the hydrogenation of propyne over these model Cu catalysts is a structure-sensitive reaction for which the propyne is less reactive over small ensembles (1–2 Cu atoms) than over larger ensembles (>10 Cu atoms).

The selectivity to propene observed over the catalysts prepared from the dinuclear precursor appears to be intermediate to that of the “isolated” Cu catalysts and the polycrystalline solids (Fig. 4). As with the activity, these catalysts appear to form a sequence in which the selectivity to propene is related to ensemble size with the small ensembles producing higher selectivity to propene than the larger ensembles. Thus, the more active catalysts (polycrystalline) show poorer yields of desired products than the catalysts having well-dispersed Cu in small ensembles. The difference in reactivity and selectivity suggest that the small ensemble catalysts are more efficient in converting propyne to propene. These results imply that different reactions are catalyzed on different reaction sites, otherwise the selectivity vs conversion data would follow the same curve for all catalysts. The results of Fig. 4 clearly show that the conversion-selectivity characteristics of the high-dispersion catalysts (samples **1** and **2**) are different from conversion-selectivity characteristics of the low-dispersion catalysts. The differences between all catalysts become smaller at high conversion as a result of the high temperatures necessary to attain these conversion levels.

These results can be viewed best as shown in Fig. 5 for which we plot the yield of propene vs conversion. The catalyst prepared from the mononuclear precursor gives the highest yield of propene over the range of conversions we report here. The catalyst formed from the dinuclear precursor shows yields of propene higher than the two polycrystalline catalysts at conversions less than 60%.

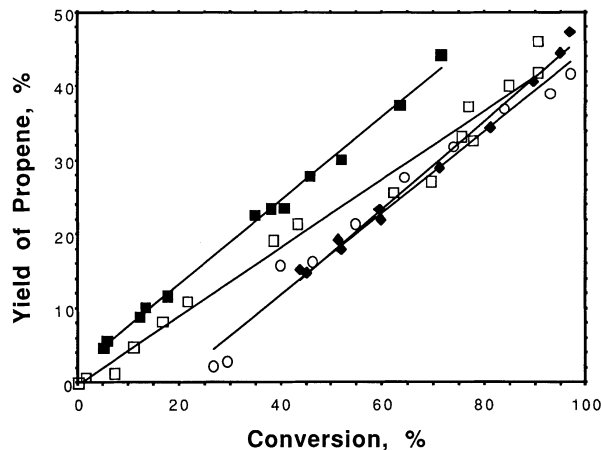
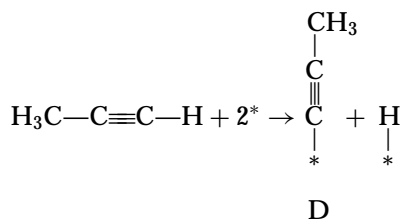


FIG. 5. Yields of propene over Cu/silica catalysts. Reaction conditions stated in caption for Fig. 3.

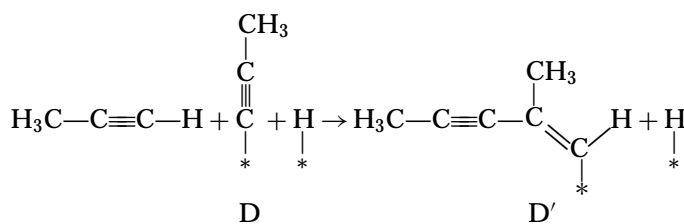
We interpret these results in the light of the mechanism advanced by others. Bond proposed associative adsorption of propyne on Ni, Pd, and Pt as an ethylene-like and an acetylene-like species (15–19) and several reviews have appeared which comment on alkene and alkyne hydrogenation reactions (20, 21). The hydrogenation of alkynes is proposed to occur by the Horiuti–Polanyi mechanism involving a “half-hydrogenated state” of the alkyne as an intermediate and the reaction scheme on copper is of the same type as on palladium (22). Ossipoff and Cant (23) explained their data by a mechanism (Scheme 1 therein) which involved the adsorption of propyne as five different species. One species is propyne adsorbed across two adjacent Cu ions (species A). The other four species were the vinyl-type, half-hydrogenated propyne; two of these were radicals with the extra electron residing on the acetylenic carbon (R<sub>1</sub>) or the internal carbon (R<sub>2</sub>). The nonradical species are distinguished by the point of the Cu adsorption site: B<sub>1</sub>, sorbed to surface via acetylenic carbon; B<sub>2</sub>, sorbed to surface via internal carbon. The formation of these species requires sites having at least 2 metal atoms. Propene is the result of adding another H atom to either R<sub>1</sub>, R<sub>2</sub>, B<sub>1</sub>, or B<sub>2</sub>. However, if species A combines with either of the radical species, then a C<sub>6</sub> radical is the expected product. A stable C<sub>6</sub> is expected with the addition of a H atom or the polymerization may continue. Ossipoff and Cant discuss in detail the mechanism by which linear hexadienes, methyl-pentadienes, and dimethyl butadienes are formed. These C<sub>6</sub> species require sites having at least 4 metal atoms.

The formation of oligomers demands that species A and R<sub>1</sub> or R<sub>2</sub> be in close proximity thus demanding a site of ensemble size ≥4. They reported an additional process by which propyne was adsorbed to two adjacent Cu atoms to form species D. This mechanism could occur on the dinuclear catalyst with each \* representing a copper ion. If species D reacted with propyne taking the H adsorbed on

the adjacent Cu, then hex-2-yne-4-ene would be the result on H-addition to species (D') which we did observe over the catalyst formed from Cu(bipy) dimer at 573 K. This mechanism suggest that a C<sub>6</sub> diene can be formed on catalysts having ensembles as small as two Cu atoms; whereas, the formation of methyl-pentadienes, dimethyl-butadienes, and hexadienes by the mechanisms shown in (14) appear to require four adjacent sites.



We believe that the subject catalyst does not show many sites having ensemble sizes  $>4$  Cu atoms. Catalytic sites having large Cu ensembles can accommodate more than one C<sub>3</sub> intermediate and therefore can produce the oligomers. We believe that the low-dispersion, polycrystalline catalysts show surface environments conducive to the formation of species such as A and R in close proximity, whereas the "isolated" Cu ions in the well-dispersed catalysts have fewer of these sites in close proximity. The large Cu ensembles rapidly form oligomers so that the apparent reaction rate to consume propyne is large for these catalysts relative to the propyne reaction rate over the mononuclear and dinuclear catalysts.



Taghavi and co-workers reported on the hydrogenation of cyclopentadiene to cyclopentene over supported copper catalysts where the support was alumina, silica, or magnesia (24, 25). The catalysts were prepared using a copper hydroxide ammine complex in either a water or a methanol solvent. They showed that the hydrogenation rate of cyclopentadiene to cyclopentene increases proportionally with the size of the Cu particle (24). The range of particle sizes in this study (24) varied from 30–500 Å, whereas particle sizes in our study were  $<5$  to 90 Å. Taghavi and co-workers suggest that the reaction occurred on the copper atoms on the periphery of the Cu particles with the participation of the support. As a result they suggest that this reaction demonstrates a novel type of structure sensitivity. Our results for the Cu/silica also show increasing reactivity for increasing particle size (Fig. 4); however, we explain the variation in catalyst activity with particle size as a consequence

the larger Cu ensembles catalyzing the oligomerization reactions in addition to the hydrogenation reaction. These authors described in an earlier article (25) that the reaction rate was developed from the rate of disappearance of reactant. Although they stated that the selectivity to cyclopentene was 100%, the authors did not comment on the formation of oligomer as we have observed in our data. We believe that their results are consistent with ours; however, we are able to draw clear conclusions regarding the effects of ensemble size as a result of our catalyst synthesis technology which affords to us a picture of the catalytic sites on the surface.

Model Cu catalysts were used to understand the relationship between structure and catalytic properties. The results of this work suggest that the propyne reactions over copper are demanding with the simple hydrogenation propene occurring on Cu ensembles  $\geq 1$ . We speculate that the rapid formation of oligomers occurs on sites having  $\geq 2$  Cu atoms.

### ACKNOWLEDGMENTS

We gratefully acknowledge the support from Georgia Institute of Technology for partial support of this project through the auspices of the Focused Research Program in Surface Science and Catalysis. We thank Professor N. W. Cant (Mcquarrie University, New South Wales, Australia) for the polycrystalline catalysts prepared from the aqueous nitrate and for his suggestion to begin this line of research.

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Received January 12, 1996; revised August 21, 1996; accepted August 23, 1996

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