

Influence of Crystallite Size on Acetone Hydrogenation over Copper Catalysts[†]

Rajeev S. Rao, Arden B. Walters, and M. Albert Vannice*

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania

Received: February 12, 2004; In Final Form: April 30, 2004

Acetone hydrogenation was studied over a family of Cu/SiO₂ catalysts as well as UHP Cu powder and a Cu chromite catalyst. Oxygen chemisorption via dissociative N₂O adsorption was used to count surface Cu atoms and calculate crystallite sizes, and a microwave absorption technique was used to measure the electrical conductivity of these Cu particles. Under differential reaction conditions at 423 K and 1 atm, all catalysts exhibited deactivation on stream and activities were typically 10–20% of their initial values after 3–4 h on stream. However, initial turnover frequencies (TOFs) varied from 0.056 s⁻¹ on the most highly dispersed Cu catalyst to 0.50 s⁻¹ on Cu powder, with the highest TOF of 2.4 s⁻¹ occurring on 110 nm crystallites. A similar trend with a broader (80-fold) variation was observed in the “steady-state” TOF values. Apparent activation energies varied between 11 and 14 kcal/mol. These initial TOF values are in good agreement with previous results, and a correlation exists between TOF and Cu crystallite size in this reaction, which appears to be structure sensitive. In addition, the electrical conductivity of these dispersed Cu nanoparticles, which was always less than that of bulk Cu, also increased with increasing Cu crystallite size; consequently, the change in this parameter may offer a possible explanation for the increase in TOF.

Introduction

Definitions of structure-sensitive and structure-insensitive reactions were proposed 30 years ago by Boudart.¹ The former reactions exhibit a significant change in turnover frequency (TOF) as metal particle size becomes very small, whereas the latter reactions have a TOF that is relatively invariant with crystallite size. This variation in TOF is routinely associated with surface structure, which depends on the geometry and coordination number of the surface atoms;² however, as the latter properties change with decreasing crystallite size so also do the electronic properties; thus, it is invariably difficult to separate geometric and electronic effects on catalytic behavior so that the influence of only the latter can be determined. To further complicate this situation, there have been few, if any, techniques available to quantitatively measure electrical properties, such as the conductivity of dispersed metal particles, in the size range of interest, i.e., 1–1000 nm. Regardless, there has been considerable interest in trying to elucidate the “electronic factor” in catalysis, and some experimental studies have been devoted to this topic (3–5). In addition, some theoretical studies during the 1990s have tried to correlate adsorptive and catalytic behavior with fundamental electronic, as well as geometric, properties.^{6,7}

We have the unique capability in our laboratory to measure the electrical properties of small solid particles, including dispersed metal crystallites, using novel microwave absorption techniques, and in a recent investigation, it was found that the electrical conductivity of silica-supported copper particles varied more than 2000-fold over a range of 10–180 nm,⁸ as expected from semiclassical quantum confinement arguments.⁹ These very small Cu particles had much lower conductivity than bulk metallic Cu and exhibited a size-induced, metal–insulator

transition (SIMIT) similar to that described in a study of indium particles.⁹ Consequently, it was of interest to examine if changes in this electronic property would be reflected in the catalytic behavior of these catalysts. One postulated mechanism for acetone hydrogenation invokes charge transfer from the Cu surface to the carbonyl bond of the acetone molecule,¹⁰ whereas an alternative mechanism suggests bonding of acetone to copper metal via the lone pair of electrons on the oxygen atom.¹¹ In either case, it might be reasonable to expect that the ease of electron donation (or acceptance) could influence the reaction rate, particularly if charge transfer were associated with a rate determining step. If so, the specific activity would be affected by the ease of charge transfer and would be dependent on the Cu crystallite size if electron conductivity governed this parameter. However, no detailed studies of particle size effects in acetone hydrogenation over supported Cu catalysts could be found, although Golodets and co-workers have reported that particle size does influence the specific reaction rate.¹⁰ Therefore, one goal of this study was to carefully examine acetone hydrogenation over a family of well characterized copper-based catalysts to determine whether specific activity was dependent on Cu crystallite size. To this end, this reaction was conducted over a range of crystallite size obtained with a series of Cu/SiO₂ catalysts, a copper-chromite catalyst, and UHP copper powder. Initial rate data were obtained which allowed comparisons to be made to see if any prevalent particle size effects existed, and the results indicate a turnover frequency that is dependent on Cu particle size.

Experimental Section

Three different SiO₂-supported Cu catalysts were used in this study: 0.5% Cu/SiO₂, 4.8% Cu/SiO₂, and 20.5% Cu/SiO₂, henceforth referred to as 0.5Cu, 5Cu, and 20Cu, respectively. The silica support was high surface area SiO₂ (Davison Grade 57, 300 m²/g, 99.5%) and was calcined in pure oxygen at 773 K for 2 h prior to impregnation to remove any organic contaminants. 5Cu and 20Cu were prepared by a standard

[†] Part of the special issue “Michel Boudart Festschrift”.

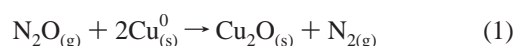
* To whom correspondence should be addressed. Address: Department of Chemical Engineering, 107 Fenske Laboratory, The Pennsylvania State University, University Park, PA 16802. E-mail: mavche@engr.psu.edu.

incipient wetness technique using a precalculated amount of copper nitrate dissolved in distilled, deionized water ($0.9 \text{ cm}^3/\text{g SiO}_2$), whereas 0.5Cu was prepared by an ion-exchange technique, as described by Kohler et al.¹² An aqueous solution of copper nitrate was brought to a pH of 11 by the addition of the required amount of ammonium hydroxide. About 10 grams of silica was added to the solution, the mixture was stirred at room temperature until the copper uptake equilibrium was attained, and the pH was then maintained at the desired value by periodic additions of ammonium nitrate. The suspension was then filtered and given four washings with distilled, deionized water. After impregnation, all catalysts were dried in air overnight in an oven at 423 K, and following the drying step, all catalysts were calcined in pure O_2 at 773 K for 2 h. The catalysts were reduced at either 673 or 873 K for either one or 2 h in pure hydrogen (MG, 99.999%) to completely reduce the copper oxide to metallic copper. In addition to the Cu/SiO₂ catalysts, a commercial copper chromite catalyst (Engelhard, Cu-1800P) and UHP Cu powder (Alfa, 99.999%) were also used.

X-ray diffraction spectra were obtained ex situ using a Rigaku Geigerflex diffractometer equipped with a Cu K α radiation source and a graphite monochromator. Each sample was given one of the pretreatments mentioned above and then passivated by exposure to a 1% O_2 in He mixture at 300 K prior to handling in air.

Prior to the reaction, 0.5Cu was reduced at 873 K for 2 h, whereas 5Cu and 20Cu were reduced at 673 K for 2 h in flowing H_2 . Cu-1800 P was reduced in flowing H_2 for 4 h at 673 K, whereas the Cu powder was heated in He at 673 K for 30 min and then reduced in H_2 at 673 K for 2 h prior to reaction. In one run, the copper powder was heated in oxygen for 10 h at 673 K to clean the surface and then reduced in the reactor at 673 K for 4 h prior to the reaction.

The copper dispersion ($D = \text{Cu}_s/\text{Cu}_{\text{total}}$) and thereby the Cu crystallite size were determined by O chemisorption via dissociative N_2O decomposition at 363 K, as discussed elsewhere^{8,13} according to the equation



where Cu_s is a surface Cu atom. The oxygen uptake was measured in a Perkin-Elmer TGS2 TGA apparatus after 20–40 mg of catalyst was reduced in situ in accordance with one of the pretreatments described above. After reduction in H_2 , the catalyst was cooled to 363 K in Ar and purged in Ar for 30 min at 363 K. The gas was switched to a 50% $\text{N}_2\text{O}/50\%$ Ar mixture, and the weight was monitored until it reached a steady value, and then the sample was purged in pure Ar to remove any weakly adsorbed species. The difference in weight before and after exposure to N_2O was used to determine the oxygen uptake, from which the number of exposed copper atoms and hence the Cu dispersion were calculated. From the dispersion, D , the average crystallite size, \bar{d} , in nm was calculated from the relationship $\bar{d} = 1.1/D$.¹³ Identical runs with the pure silica support showed that oxygen uptake on silica was negligible; hence, the measured oxygen uptake was attributed only to the copper.

Vapor-phase rate measurements were conducted at atmospheric pressure in a Pyrex reactor which was placed in a heating mantle equipped with a temperature controller (Omega, model CN2011). The catalyst was subjected to one of the pretreatments mentioned previously and cooled under flowing H_2 to the reaction temperature. A constant flow of degassed acetone (Sigma, 99.99%) was established by bubbling another H_2 carrier gas stream through a saturator containing pure liquid acetone,

TABLE 1: Oxygen Uptakes, Dispersions, and Crystallite Sizes for Copper Catalysts

catalyst	Cu content (wt. %)	pretreatment	uptake (μmol of O/ g cat)	dispersion (D)	d_p (nm)
0.5Cu	0.5	2 h, 873K	29.5	0.75	1.5
5Cu	4.8	2 h, 673 K	30.7	0.081	14
20Cu	20.5	2 h, 673 K	16	0.010	110
Cu-1800P	42	4 h, 673 K	1240	0.366	3.0
Cu powder	100.0	2 h, 673 K	1	1.2×10^{-4}	9000

which was kept in a constant-temperature bath comprised of ethylene glycol and water to control the partial pressure of the acetone. The flow rates of hydrogen were regulated by mass flow controllers (Tylan, model FC-260). All stainless steel lines downstream from the saturator to the gas chromatograph were heated to 373 K to ensure that no condensation of either the reactant or products occurred. Kinetic runs were performed at 1 atm under differential reactor conditions, with conversions routinely below 10% and the acetone partial pressure maintained at either 40 or 180 Torr. There was no detectable reaction in the absence of the catalyst. Arrhenius runs were performed at 40 Torr acetone between 323 and 423 K to measure and compare apparent activation energies (E_{app}) for acetone hydrogenation over these different catalysts. Prior to the commencement of each Arrhenius run, the catalyst was left on stream for at least 150 min to achieve a relatively stable, pseudo “steady-state” activity, and then data were acquired first in a decreasing temperature sequence, with each change in the reaction temperature followed by a 30 min waiting period to allow for the reaction to again reach steady state before sampling and then in an increasing temperature sequence back to the initial temperature so that any deactivation during the time period on stream could be detected. Product analysis was carried out using a gas chromatograph (Hewlett-Packard 5730A) equipped with a 10-ft column packed with Carbowax 20M on 80/100 Supelcoport. After passivation under 1% O_2 at 300 K, XRD measurements were conducted to determine Cu phases and crystallite sizes via line broadening.⁸

The electrical conductivity measurements were made using a microwave frequency cavity absorption technique described in previous publications.^{14,15} This microwave cavity technique is especially suited to measuring the electrical properties of small, dispersed particulate materials because it does not use electrical contacts and significantly reduces charge-carrier interparticle hopping, grain boundary resistances, and electrical polarization effects. The accuracy of the conductivity measurements made using the TE102 rectangular bimodal X-band microwave cavity is estimated to be at least within a factor of 2 of the actual values. Greater reliance can be placed on relative conductivity values because the causes of experimental error are systematic and shared in all measurements. Prior to the electrical conductivity measurements, the average Cu crystallite size was altered by sintering in H_2 using different time/temperature combinations, as noted in Table 3.

Results

Oxygen uptakes, Cu dispersions, and the crystallite sizes calculated from the oxygen adsorption experiments for the catalysts following various pretreatments are shown in Table 1. It was verified by X-ray diffraction, as reported elsewhere,⁸ that all detectable copper was present in the Cu^0 phase in these catalysts following the corresponding pretreatments. The thin (ca. 1 nm) surface layer of Cu_2O created during passivation could not be detected by XRD, consistent with previous

TABLE 2: Rates, TOFs, and Deactivation Constants in Acetone Hydrogenation over Copper Catalysts $T = 423$ K, $P_{\text{total}} = 1$ atm

catalyst	P_{acc} (Torr)	k_0 (g s/ μmol)	k_1 (g/ μmol)	initial activity ($\mu\text{mol/s g}$)	initial TOF (s^{-1})	"steady-state" TOF ^a (s^{-1})	E_{app} (kcal/mol)
0.5 Cu	180	0.29	0.0056	3.41	0.056	0.011	14.3 ± 0.7
	40	0.64	0.0008	1.6	0.027		
Cu-1800P	180			290	0.12	0.006	14.3 ± 1.5
	40	0.08	0.0001	13	0.0052		
5 Cu	180	0.096	0.0034	10	0.17	0.03	10.5 ± 2.5
20 Cu	180	0.013	0.002	77	2.4	0.47	13.8 ± 1.2
	40	0.20	0.0008				
Cu powder	180	1.3	0.113	0.75	0.37	0.05	10.6 ± 1.7
Cu powder ^b				1.0	0.50	0.08	

^a After ca. 200 min on stream. ^b After cleaning in pure O₂ for 10 h at 673 K followed by reduction in H₂ for 4 h at 673 K.

TABLE 3: Copper Particle Electrical Conductivity, σ , vs Copper Particle Size at 298 K

catalyst (reduction time/temp.)	d_p (nm)	measured σ for composite catalyst, ($\Omega\text{-m}$) ⁻¹	calculated σ for copper particles, ($\Omega\text{-m}$) ⁻¹
0.5 Cu (2h/873K)	1.5	$<0.007^a$	$<0.2^d$
5 Cu (2h/673K)	14	0.009^a	0.3^d
20 Cu (1h/873K)	64	$30^{b,c}$	490^d
20 Cu (2h/673K)	110	$116^{b,c}$	1900^d
20 Cu (2h/873K)	176	$230^{b,c}$	3760^d

^a Low conductivity formula, refs 8, 14, and 15. ^b Intermediate conductivity formula, refs 8, 14, and 15. ^c With skin depth correction, refs 8, 14, and 15. ^d Using formula for linear volume fraction relationship, $\sigma = \nu_{\text{Cu}}\sigma_{\text{Cu}} + \nu_{\text{SiO}_2}\sigma_{\text{SiO}_2}$.

characterization of these Cu/SiO₂ catalysts.¹³ Therefore, oxygen adsorption on reduced Cu via N₂O decomposition should provide an accurate count of the total amount of surface copper atoms, which can be used to calculate crystallite size and turnover frequencies.¹³

A comparison of catalytic activity was made at a reaction temperature of 423 K. All of the catalysts utilized in this study exhibited considerable deactivation during acetone hydrogenation, and 2-propanol was the dominant product (>99%). In the case of 5Cu, 20Cu, and Cu-1800P, a small amount (<1%) of a light gaseous product (possibly a light hydrocarbon) was observed during the first few minutes on stream, whereas for 0.5Cu and Cu powder, isopropyl alcohol was the only detectable product throughout the duration of the reaction. This is consistent with other studies of acetone hydrogenation in which the only reported product was isopropyl alcohol,^{10,16–19} although in one case aldol condensation-type products were reported at temperatures above 473 K.²⁰

To make proper activity comparisons and facilitate the observation of any particle size effects, it is important to determine initial activities in addition to steady-state activities. Most published reports have not clearly distinguished whether the reported rates are initial or steady-state, nor do they mention the rates of deactivation in general;²¹ consequently, a thorough investigation of the deactivation behavior of all of the catalysts during acetone hydrogenation was undertaken in order to obtain initial activities. The acetone hydrogenation activity as a function of time was monitored at 423 K and an acetone pressure of 180 Torr, although deactivation profiles were also obtained for some catalysts at 40 Torr acetone.⁸ Deactivation curves for 0.5Cu, 5Cu, and 20Cu are illustrated in Figures 1–3, respectively, and it was found that the inverse of the rate was varied linearly as a function of time on stream for all catalysts except

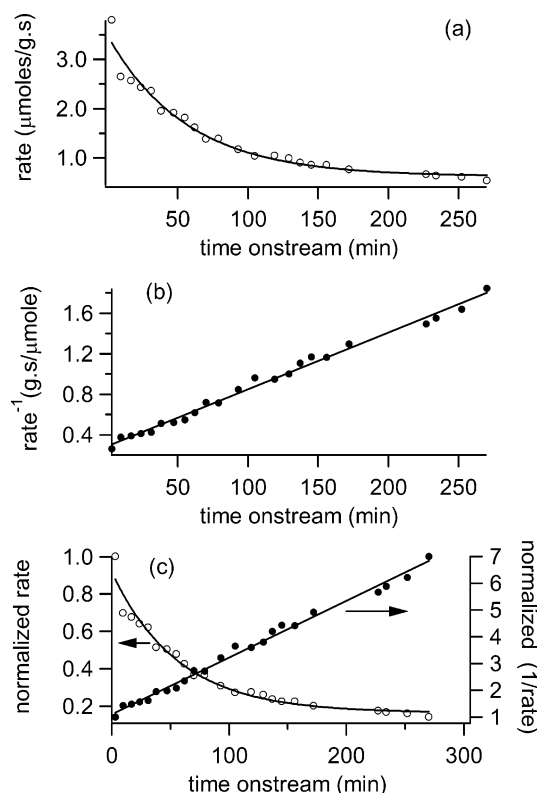


Figure 1. Acetone hydrogenation over 0.5% Cu/SiO₂ at 423 K, $P_{\text{acc}} = 180$ Torr, $P_{\text{H}_2} = 560$ Torr: (a) activity maintenance, (b) inverse rate vs time on stream, (c) normalized plots of (a) and (c).

Cu chromite (Cu-1800P). Thus, expressing the inverse of the rate as a linear function of time on stream

$$1/\text{rate} = k_0 + k_1 t \quad (2)$$

provides k_0 , the inverse of the initial rate at time $t = 0$, and k_1 , a constant associated with the rate of deactivation. Values for these constants are listed in Table 2. Both the rates and their inverse values can be normalized by dividing the instantaneous values of these parameters by the initial value of k_0 or its reciprocal value, and these normalized data are also plotted in Figures 1–3. Similar plots are shown elsewhere for Cu-1800P and Cu powder.⁸ For Cu-1800P, the inverse of the rate was not a linear function of time on stream, so the initial rate was determined by fitting the deactivation curve to a polynomial function and extrapolating to zero time.⁸

Initial activities as well as both initial and "steady-state" turnover frequencies (TOFs) based on surface Cu atoms, i.e., molecule/s/Cu_s, assuming a Cu_s:O stoichiometry of 2:1 are also summarized in Table 2. It is apparent that TOFs for acetone hydrogenation vary significantly on these copper catalysts, as

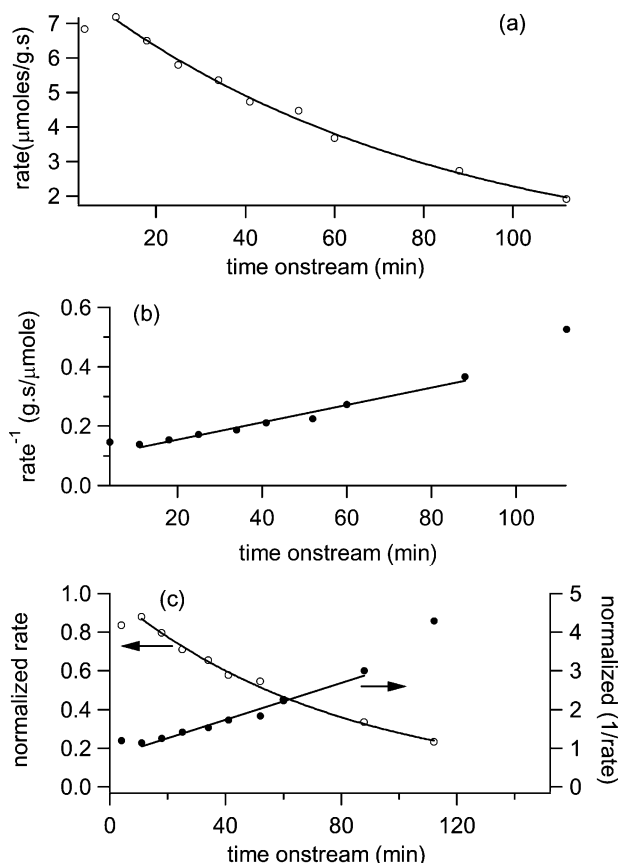


Figure 2. Acetone hydrogenation over 4.8% Cu/SiO₂ at 423 K, $P_{\text{ace}} = 180$ Torr, $P_{\text{H}_2} = 560$ Torr: (a) activity maintenance, (b) inverse rate vs time on stream, (c) normalized plots of (a) and (c).

a 40-fold variation in initial TOF and an 80-fold variation in “steady-state” TOF occurred, with the TOFs increasing with increasing particle size for the supported catalysts. The Cu powder, which is comprised of the largest copper particles, did not exhibit the highest TOF, however. A similar dependence on particle size was reported by Tripol’skii et al., who studied acetone hydrogenation over both Cu/Al₂O₃ and Cu/Cr₂O₃ catalysts and found that the rate on Cu/Cr₂O₃, with an average copper particle size of 23 nm, was six times higher than the rate on Cu/Al₂O₃, which had an average particle size of 3 nm.¹⁰

The Arrhenius runs with these copper catalysts are plotted in Figure 4, and the apparent activation energies (E_{app}) are listed in Table 2 along with their uncertainty, represented by 95% confidence limits. From the data provided by Tripol’skii et al.¹⁰ and Babkova et al.,¹⁷ one can calculate apparent activation energies of 9.5 kcal/mol for Cu/Cr₂O₃ and Cu/Al₂O₃ and 10.5 kcal/mol for Cu powder. These latter values were calculated assuming that rate measurements were made under differential conditions. Valarivan et al. reported an activation energy of 6 kcal/mol for a copper–magnesium intermetallic compound, but admitted that their value may lack accuracy due to high conversion and high contact times.¹⁹ The E_{app} values of 11–14 kcal/mol from this study are smaller than, but comparable to, the apparent activation energies of 15–18 kcal/mol measured for acetone hydrogenation over a variety of platinum catalysts.²²

The X-band microwave electrical conductivities measured for the Cu/SiO₂ catalysts at 298 K are presented in Table 3. The conductivity values for the 0.5Cu and the 5Cu catalysts were obtained using the formula for low conductivity materials, whereas the values for the 20Cu catalysts were obtained using the intermediate conductivity formula with skin depth correction for the Cu particles.¹⁵ There is a steady increase in electrical

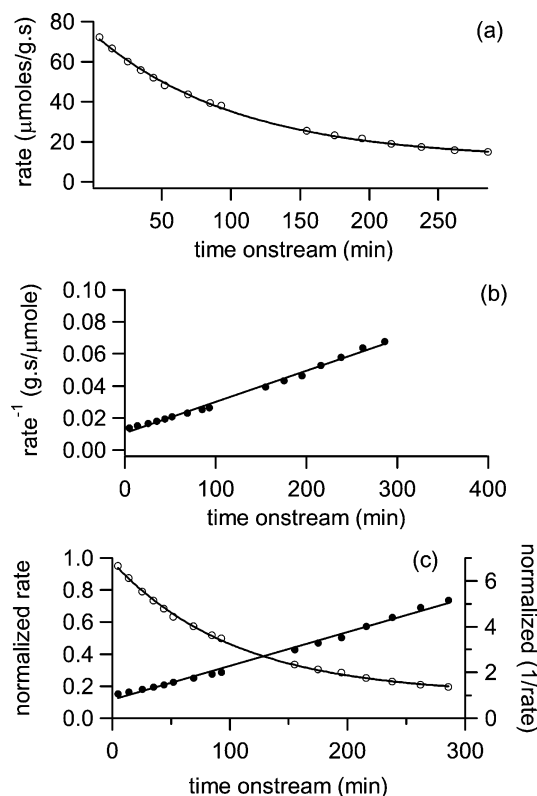


Figure 3. Acetone hydrogenation over 20.5% Cu/SiO₂ at 423 K, $P_{\text{ace}} = 180$ Torr, $P_{\text{H}_2} = 560$ Torr: (a) activity maintenance, (b) inverse rate vs time on stream, (c) normalized plots of (a) and (c).

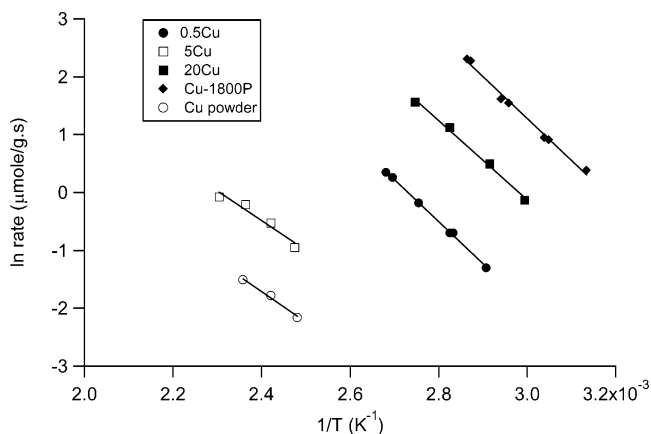


Figure 4. Arrhenius plots for acetone hydrogenation over copper catalysts: $P_{\text{ace}} = 40$ Torr, $P_{\text{H}_2} = 700$ Torr.

conductivity of the Cu/SiO₂ catalysts with increasing Cu crystallite size. The values in Table 3 calculated for the electrical conductivity, i.e., σ , of the Cu crystallites were obtained from the ideal relationship for the electrical conductivity of composite materials, $\sigma = v_{\text{Cu}}\sigma_{\text{Cu}} + v_{\text{SiO}_2}\sigma_{\text{SiO}_2}$, where v_i is the volume fraction on component i . Any significant nonideality would require a different relationship than the ideal formula used, but a detailed investigation of Cu/SiO₂ electrical conductivity nonideality is beyond the scope of this work; however, even if the Cu-crystallite electrical conductivity values possess some inaccuracy due to nonideality, their relative values will remain valid.

The electrical conductivity values in Table 3 for Cu crystallites approximately increase as the square of the Cu crystallite diameter (d^2). This is different from the increase of conductivity with the cube of the particle diameter (d^3) expected for the quantum confinement model.⁹

Discussion

Acetone hydrogenation has been studied over a number of different copper-containing catalysts, and many years ago Bond summarized this reaction over different metals.¹¹ He included two studies of acetone hydrogenation over Cu: one in the vapor phase on Cu powder²³ and one in the liquid phase on Raney copper.²⁴ In both cases, the only observed product was 2-propanol. Babkova and co-workers have reported the results of a comprehensive vapor-phase study of acetone hydrogenation below 373 K over bulk copper¹⁷ as well as over a series of Ni–Cu alloys.²⁵ Again, the only observed product was 2-propanol, and they found that the acetone hydrogenation kinetics for both Ni and Ni–Cu alloys were quite similar to the kinetics observed on copper. More recently, Tripol'skii et al. studied vapor-phase acetone hydrogenation over Cu/Al₂O₃ and Cu/Cr₂O₃ catalysts and also reported 2-propanol as the only detectable product.¹⁰ Cunningham and co-workers have examined this reaction over copper catalysts in some detail in an attempt to explain the surface synergism between copper and its oxides in catalytic 2-propanol-acetone interconversions,^{16,18} and they have also investigated the use of TiO₂-supported Cu catalysts for acetone hydrogenation.²⁰

Surprisingly, not all of the studies listed above mention catalyst deactivation, which must be considered in this reaction system to obtain an accurate assessment of intrinsic activity. Babkova and co-workers do not indicate any deactivation in their reports on acetone hydrogenation below 373 K over either copper¹⁷ or Cu–Ni alloys.²⁵ Similarly, deactivation is not addressed by Tripol'skii et al. in their study of acetone hydrogenation below 373 K over Cu/Al₂O₃ and Cu/Cr₂O₃¹⁰ or by Valaraivan et al. in their study of this reaction over Mg–Cu intermetallics.¹⁹ However, Cunningham and co-workers do mention a continuous decline in the activity of copper powder for acetone hydrogenation at 423 ± 5 K and 0.05 atm acetone.¹⁸ Deactivation can be caused by a variety of factors. Site blockage due to the presence of carbonaceous material is a likely possibility. A reduction in the active metal surface area due to Cu sintering is another possibility, although this seems quite unlikely given the relatively low reaction temperatures (423 K) employed in this study and the high reduction temperatures used (>673 K) to pretreat the catalysts. Another possible cause of deactivation is a progressive change in the oxidation state of the metal during the course of the reaction; however, in the catalysts used here, the copper was initially in the zerovalent state and the possibility of its oxidation under the clearly reducing conditions used in this study appears remote. To test if the observed deactivation were reversible, a sample of deactivated Cu powder was heated in pure H₂ at 673 K for 2 h and then reused in the reaction. The regenerated sample had 70% of the initial activity in the earlier run and displayed similar deactivation behavior. It is likely that the treatment in H₂ after the first run and prior to the second run removed carbonaceous deposits or deactivating intermediates from the Cu surface and made it more accessible to the vapor-phase reactants. However, the possibility of pore blockage in the supported catalysts as a cause of the deactivation due to formation of carbonaceous deposits cannot be ruled out.

The lack of any mention of deactivation in these previous studies^{10,17,19,25} is rather puzzling based upon the observations in this study. The idea was considered that perhaps the lower reaction temperatures employed in some of those studies (below 373 K) were in some way preventing or minimizing deactivation, thereby preventing its detection. Therefore, the activity maintenance of three of the catalysts was also monitored at lower

TABLE 4: Ratio of Rates after 100 min Onstream (r_{100}) to Initial Rates (r_0)^a in Acetone Hydrogenation over Copper Catalysts $T = 423$ K, $P_{\text{ace}} = 180$ Torr, Balance H₂

catalyst	ratio (r_{100}/r_0)
0.5 Cu	0.29
5 Cu	0.28
20 Cu	0.43
Cu-1800P	0.32 ^a
Cu powder	0.15

^a Obtained directly from deactivation curve.

TABLE 5: Turnover Frequency for Acetone Hydrogenation on Cu Catalysts $T = 363$ K, $P_{\text{ace}} = 180$ Torr, Balance H₂

catalyst	d_p (nm)	TOF (s ⁻¹) ^a	ref
0.5 Cu	1.5	0.0033	b
Cu-1800P	3	0.0072	b
5 Cu	14	0.0216	b
20 Cu	110	0.152	b
Cu powder	9000	.046	b
Cu powder	(~250)	0.11	25
Cu/Al ₂ O ₃	3	0.024	10
Cu/Cr ₂ O ₃	23	0.12	10

^a Initial activity (from $1/k_0$). ^b This study.

reaction temperatures, i.e., Cu-1800P at 348 K, 20Cu at 353 K, and 0.5Cu at 373 K, and plots similar to those in Figures 1–3 showed that these catalysts still exhibited detectable levels of deactivation;⁸ therefore, deactivation is not restricted to higher temperatures. Table 4 lists the ratios of the rate after the catalyst is onstream for 100 min to the initial rate at reaction conditions of 423 K and 180 Torr acetone. All catalysts except the copper powder exhibit ratios of 0.3–0.4.

From the data available for rates of acetone hydrogenation over Cu powder²⁵ and over Cu/Al₂O₃ and Cu/Cr₂O₃,¹⁰ an effort was made to calculate TOFs and compare them with the values obtained in this study. This endeavor is difficult because there is no mention of whether the previously reported rates are initial or “steady-state” values; nevertheless, it is still useful to make such a comparison. As the specific activities in the previous studies are reported per m² Cu, a site density of 1.4×10^{19} Cu atoms/m²²⁶ was used to calculate TOFs, and these values for acetone hydrogenation at 363 K and 180 Torr acetone over the catalysts in this study as well as those in the two previous studies are listed in Table 5. The value for each catalyst was extrapolated using the rate measured at 423 K and the apparent activation energy. For the Cu/Al₂O₃ and Cu/Cr₂O₃ catalysts,¹⁰ the TOFs are about 3-fold higher than the initial TOFs measured on similar sized copper particles in this study. The TOF on the copper powder used by Babkova et al.²⁵ is slightly lower than that for 20Cu, which was the catalyst with an average particle size closest to their catalyst, and it is twice as high as the TOF on the Cu powder studied here. This behavior is consistent with the trend exhibited in our study, in which the Cu powder with a much larger average particle size exhibited a noticeably lower TOF than that for 20Cu. The results in Table 5 indicate that the initial specific activity is dependent on the copper particle size, with the TOF increasing with increasing crystallite size although the bulk Cu powder shows a somewhat lower TOF than that for 20Cu, which had the highest value. The work of Tripol'skii et al. also indicated higher TOFs on larger Cu crystallites over a range of 3–25 nm, but they were not able to detect any activity with a Cu powder sample.¹⁰ The TOF values for acetone hydrogenation on these Cu particles are plotted as a function of Cu crystallite size in Figure 5.

The x-band microwave cavity absorption measurements of electrical conductivity at 298 K for the family of Cu/SiO₂ catalysts presented in Table 3 show a steady increase in

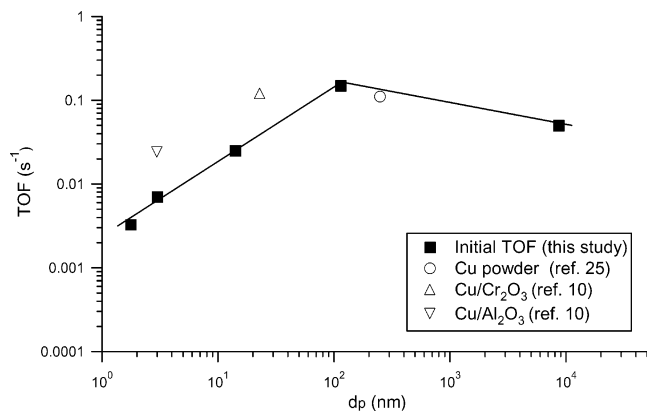


Figure 5. Turnover frequency for acetone hydrogenation versus copper crystallite size. Reaction conditions: 363 K, 180 Torr acetone, 560 Torr H₂.

conductivity with increasing Cu particle size. This correlates positively with the measured increase in TOF values at 423 K in Tables 2 and 363 K in Table 5. Although the Cu particle conductivities were not measured at the same temperatures used for obtaining TOF values, it is expected that the same steady increase in Cu particle conductivity would occur at both 363 and 423 K. As stated earlier, the Cu crystallite size in the 20 Cu catalyst was varied by sintering.

The d^2 dependence of the electrical conductivity values in Table 3 conflicts with the d^3 dependence predicted by the quantum confinement model and reported for the electrical conductivity of mesoscopic indium particles.⁹ The reasons for this difference in particle size dependence between the Cu particles in this study and the indium particles reported earlier is not known, although one possible factor could be differences in particle size distributions. Larger metal particles would dominate the measured conductivity for supported metal particles skewing the calculated conductivity values upward. No correction can be attempted for this effect because the metal particle size distributions for the Cu particles in this study and for the indium particles in ref 9 are not known.

There have been many reports of crystallite size effects on adsorption and catalysis and they have been nicely summarized in a number of reviews dealing with this topic.^{21,27–30} As these reviewers have correctly pointed out, comparing data from different laboratories and research groups is no small task, given that there are often significant variations in reaction conditions, catalyst preparation and pretreatment, and catalyst composition. However, one of the principal reasons Boudart has urged the use of TOFs is to allow such comparisons. It has been clearly demonstrated that several classes of reactions exist which do show a genuine crystallite size effect after accounting for all experiment artifacts which could lead to spurious results, and the original classification of Boudart^{1,2} has been expanded to place reactions into four categories depending on how the TOF varies as a function of the particle size,²⁷ i.e., category 1, the TOF of structure-insensitive or facile reactions does not depend on particle size. The TOF of structure-sensitive or demanding reactions may vary in two opposite ways, i.e., category 2, the TOF decreases as the particle size decreases, which is termed an antipathetic structure sensitivity, or category 3, it increases with decreasing particle size, which is called sympathetic structure sensitivity. Finally, in category 4, the TOF passes through a maximum. These data for acetone hydrogenation on Cu show that the initial TOF varies by a factor of 40 and that this reaction appears to be most appropriate in category 2 although the TOF may pass through a shallow maximum. Che

and Bennett have stated that if a true particle size effect is to be evidenced, the metal particles must meet the following criteria to as great an extent as possible,²⁸ i.e., the crystallites must be (a) monodisperse (ideally), (b) fully reduced, (c) unpoisoned, (d) unperturbed by the carrier gas, and (e) unpromoted. They have also cited some potentially complicating factors, and these authors have also described structure-sensitive reactions as either “limited” or “extended” depending on whether the structure-sensitivity of a particular reaction-catalyst system is confined to below 5 nm or is also observed for particles much larger than 5 nm.²⁸

The earliest examples of structure sensitivity dealt with the breaking of C–C bonds (hydrogenolysis) and N–N bonds (ammonia synthesis), whereas the formation of C–H bonds (hydrogenation) was typically found to be structure insensitive.² However, since these early studies, the hydrogenation of butyne, butadiene, and isoprene,³¹ of aromatic nitro compounds,³² and of acetylene to ethylene³³ over Pd catalysts has been reported to be structure sensitive, and Arai and co-workers have found recently that the initial TOF for acetonitrile hydrogenation was lower on smaller Pt crystallites.⁵ Benzene hydrogenation over Ni catalysts has been reported to be structure insensitive,^{34–36} and this same behavior was found with Pt catalysts;³⁷ although Flores and co-workers have considered benzene hydrogenation over Pt/Al₂O₃ to be structure sensitive when the catalyst is reduced at temperatures below 573 K because of a 5-fold decrease in TOF with increasing dispersion, but there was no significant difference in the apparent activation energies.⁴ However, variations in TOF values of 5- to 10-fold or less should probably be considered to represent structure insensitivity unless the uncertainty and reproducibility of the data clearly warrant such a conclusion. A similar trend with activation energy is apparent in this study as all of the apparent activation energies fall between 11 and 14 kcal/mol and were similar to the values reported by Tripol’skii.¹⁰

The variation in the TOFs for acetone hydrogenation found in this study may be due to a change in the adsorption strength of the acetone molecule on the copper particles; therefore, it is illustrative to examine acetone adsorption on copper. Two alternative models describe acetone adsorption on copper and other transition metals. The first involves the formation of a donor–acceptor bond in which π electrons are transferred from the ketone molecule to a free d orbital of the metal (type I). The second model invokes a dative interaction in which the d electrons of the copper are localized in the antibonding orbitals of the carbonyl group (type II). In this regard, it is useful to examine the heat of adsorption of acetone on these different catalysts to get some idea of the bond strength. Tripol’skii et al. calculated the heat of adsorption for acetone on Cr₂O₃- and Al₂O₃-supported Cu based on their kinetic parameters and reported respective values of 19 and 9.2 kcal/mol,¹⁰ indicating that acetone adsorbed more strongly on the smaller copper particles. There may be some uncertainty about these values because their kinetic model assumed molecular, rather than dissociative, H₂ adsorption; nevertheless, the values are illustrative and the trend is similar to that observed for acetonitrile hydrogenation.⁵ A stronger bond on smaller copper crystallites would seem to support acetone adsorption via the type I model because smaller copper particles would have a less “metallic” character, as evidenced from the electrical conductivity measurements and, therefore, have less capability to donate electrons to a ketone compared to bulk Cu. As Baetzold has discussed, larger metal clusters have a smaller ionization potential and hence a greater capability to donate electrons.³⁸ This might

explain why hydrogenation rates on small Cu particles are much lower because the increased strength of acetone adsorption could make C–H and O–H bond formation more difficult. However, the increased strength of acetone adsorption could also cause more of the Cu surface sites to be covered, thus approaching saturation coverage and leaving fewer sites available for hydrogen adsorption, thereby decreasing activity.

Because the average coordination number of surface atoms changes little on larger metal crystallites, it is difficult to explain why particles which are greater than about 5 nm should show any significant structure sensitivity based only on geometric considerations. Electronic properties for metal particles are frequently assumed to exhibit bulklike behavior once crystallite sizes have reached 5–10 nm, and there is now a general consensus, despite disagreement on details, that clusters containing several hundred metal atoms can show almost bulklike behavior, and properties such as the density of states, energy bandwidth, ionization potential, electron affinity, and binding energy for metal particles ~ 5 nm resemble bulk values.²⁷ For example, Baetzold has obtained UPS He(I) spectra for Ag or Cu clusters deposited on carbon which indicate that ~ 150 atoms per cluster give a spectrum similar to that of the bulk metal.³⁸ Although one can associate particle size effects with crystallites smaller than 5 nm to structural changes, which can alter both geometric and electronic properties, large variations in the TOF for crystallites greater than 5 nm are more difficult to explain. Two other reactions where particle size effects have been reported for sizes up to 100 nm are CO hydrogenation over several different metals and ethylene partial oxidation over silver catalysts, and both of these reactions have been discussed by Che and Bennett.²⁸

Variations associated with crystallite size are frequently explained by invoking ensemble arguments impacting on the geometry of surface atoms, and electronic considerations typically are not of paramount importance. However, Nimtz and Marquardt have questioned whether the positive dielectric response of small metal particles, as opposed to the negative low-frequency dielectric response of bulk metals, could have consequences for their catalytic activity.³⁹ They suggest that a catalyst with a large positive dielectric function could reduce the long-range repulsive forces of reactants and thereby alter the rate of reaction. Table 3 indicates that electrical conductivity can vary by orders of magnitude as crystallite size decrease, and even 1μ Cu crystallites may have a conductivity significant lower than the bulk value; thus, the possibility exists that electronic properties are responsible for crystallite size effects observed with particles larger than 5–10 nm, for which surface coordination numbers do not change significantly. Although this can be considered, there appear to be no data reported to either validate or disprove this line of reasoning. The positive correlation observed here between electrical conductivity and TOF values extends over a wide range of conductivity and it offers a possible explanation for the increase in TOF. Thus, these results may provide some insight regarding the decades-old discussion about the role of electronic properties in catalytic reactions.

Summary

Acetone hydrogenation has been studied over a number of copper catalysts, all of which showed considerable deactivation, most likely due to coverage by inactive carbonaceous species. Consistent with previous studies, 2-propanol was the only product detected, and TOFs were in reasonable agreement with those calculated for similar-sized copper crystallites. The E_{app} values for acetone hydrogenation varied from 11 to 14 kcal/mol and were slightly higher than values reported previously.

Initial TOF values clearly indicate that the reaction is structure sensitive, and an extended structure-sensitivity is observed with supported crystallites up to 110 nm. It may be that the particle-size effect is due primarily to electronic properties because a correlation exists between the TOF and the electrical conductivity of these Cu crystallites, and this latter property is still less than the bulk value for relatively large (1μ) crystallites. Acetone has been reported to adsorb more strongly on smaller Cu particles and this may be why it is more difficult to hydrogenate on these smaller crystallites, i.e., the coverage of adsorbed hydrogen is decreased, but the occurrence of simultaneous rate inhibition complicates the study of this reaction.

Acknowledgment. Financial support for this study was provided by the National Science Foundation via Grant #CTS-9415335.

References and Notes

- (1) Boudart, M. *Adv. Catal. Relat. Subj.* **1969**, 20, 153.
- (2) Boudart, M. *Proc. 6th Int. Congr. Catal.*; Bond, G. C., Weller, P. B., Tompkins, F. C., Eds.; The Chem. Soc.: London, 1977; Vol. 1, p. 1.
- (3) Ruban, A.; Hammer, B.; Stoltze, P.; Skriver, H. L.; Norskov, J. K. *J. Mol. Catal. A* **1997**, 115, 421.
- (4) Flores, A. F.; Burwell, R. L., Jr.; Butt, J. B. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 1191.
- (5) Arai, M.; Takada, Y.; Nishiyama, Y. *J. Phys. Chem. B* **1998**, 102, 1968.
- (6) Norskov, J. K. *Prog. Surf. Sci.* **1991**, 38, 103.
- (7) *Electric Processes in Catalysis: A Quantum Approach to Catalysis*, Yoshida, S., Sakaki, S.; Kobayashi, H., Ed.; VCH: Tokyo, 1994.
- (8) Rao, R. S., Ph.D. Thesis, The Pennsylvania State University, 1998.
- (9) Marquardt, P.; Nimtz, G.; Muhlschlegel, B. *Sol. State. Comm.* **1988**, 65, 539.
- (10) Tripol'skii, A. I.; Pavlenko, N. V.; Golodets, G. I. *Kinet. Catal.* **1985**, 26, 976.
- (11) Bond, G. C. *Catalysis by Metals*; Academic Press: London, 1962.
- (12) Kohler, M. A.; Lee, J. C.; Trimm, D. L.; Cant, N. W.; Wainwright, M. S. *Appl. Catal.* **1987**, 31, 309.
- (13) Dandekar, A.; Vannice, M. A. *J. Catal.* **1998**, 178, 621.
- (14) Na, B.-K.; Kelly, S. L.; Vannice, M. A.; Walters, A. B. *Meas. Sci. Technol.* **1991**, 2, 770.
- (15) Na, B.-K.; Vannice, M. A.; Walters, A. B. *Phys. Rev. B* **1992**, 46, 12226.
- (16) Cunningham, J.; McNamara, D.; Fierro, J. L. G.; O'Brien, S. *Appl. Catal.* **1987**, 35, 381.
- (17) Babkova, P. B.; Avetisov, A. K.; Lyubarskii, G. D.; Gel'bshtein, A. I. *Kinet. Catal.* **1970**, 11, 1209.
- (18) Cunningham, J.; Al-Sayyed, G. H.; Cronin, J. A.; Healy, C.; Hirschwald, W. *Appl. Catal.* **1986**, 25, 129.
- (19) Valarivan, R.; Pillai, C. N.; Swamy, C. S. *React. Kinet. Catal. Lett.* **1994**, 53, 419.
- (20) Cunningham, J.; Hickey, J. N.; Brown, N. M. D.; Meenan, B. J. *J. Mater. Chem.* **1993**, 3, 743.
- (21) Bond, G. C. *Surf. Sci.* **1985**, 156, 966.
- (22) Vannice, M. A.; Sen, B. *J. Catal.* **1988**, 113, 52.
- (23) Federer-Luetic, P.; Brihta, I. *Croat. Chem. Acta* **1959**, 31, 75.
- (24) van Mechelen, C.; Jungers, J. C. *Bul. Soc. Chim. Belg.* **1950**, 59, 597.
- (25) Babkova, P. B.; Avetisev, A. K.; Lyubarskii, G. D.; Gel'bshtein, A. I. *Kinet. Catal.* **1970**, 13, 309.
- (26) Parris, G. E.; Klier, K. J. *Catal.* **1986**, 97, 374.
- (27) Burch, R. A Specialist Periodical Report. In *Catalysis*; Bond, G. C., Webb, G., Eds.; The Royal Society of Chemistry: London, 1985; Vol. 7.
- (28) Che, M.; Bennett, C. O. *Adv. Catal.* **1989**, 36, 55.
- (29) Bond, G. C. *Chem. Soc. Rev.* **1991**, 20, 441.
- (30) Bond, G. C. *Acc. Chem. Res.* **1993**, 26, 490.
- (31) Boitiaux, J. P.; Cosyns, J.; Vasudevan, S. *Appl. Catal.* **1983**, 6, 41.
- (32) Carturan, G.; Facchin, G.; Cocco, G.; Navazio, G.; Gubitosa, G. J. *Catal.* **1983**, 82, 56.
- (33) Gigola, C. E.; Aduriz, H. R.; Bodnariuk, P. *Appl. Catal.* **1986**, 27, 133.
- (34) Coenen, J. W. E.; Schats, W. M. T. M.; Van Meerten, R. Z. C. *Bull. Soc. Chim. Belg.* **1979**, 88, 439.
- (35) Martin, G. A.; Dalmon, J. A. *J. Catal.* **1982**, 73, 233.
- (36) Nikolajenko, V.; Bosacek, V.; Danes, V. L. *J. Catal.* **1963**, 2, 127.
- (37) Vannice, M. A.; Lin, S. D. *J. Catal.* **1993**, 143, 539.
- (38) Baetzold, R. C. *Surf. Sci.* **1981**, 106, 243.
- (39) Nimtz, G.; Marquardt, P. *Philos. Mag. Lett.* **1991**, 61, 235.