Catalysis Letters, Vol. 116, Nos. 1–2, July 2007 (© 2007)
DOI: 10.1007/s10562-007-9092-y

Nanoscale Cu supported catalysts in the partial oxidation of cyclohexane with molecular oxygen

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Received 9 March 2007; accepted 15 March 2007

Cu supported catalysts (support: γ-Al_2O_3, Fe_2O_3, TiO_2) have been conveniently prepared by deposition of Cu particles from acetone solvated Cu atoms. The catalysts have been characterized by HRTEM analysis, showing a quite homogeneous Cu particle size distribution. They are active systems for the partial oxidation of cyclohexane to cyclohexanol and cyclohexanone. After the catalytic experiment the Cu/γ-Al_2O_3 and Cu/TiO_2 systems can be reused without valuable loss of activity, while the Cu/Fe_2O_3 system is quite inactive.

KEY WORDS: Cu supported catalyst; cyclohexane oxidation; molecular oxygen; Cu vapour derived nanoparticles.

1. Introduction

The catalytic partial oxidation of hydrocarbons using oxygen or air as oxidant is of great economical and environmental relevance [1,2]. Among various alkanes the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone has an important industrial significance and continues to be an important challenge [3].

Several metal-based homogeneous catalysts have been used [3–7]. Murahashi et al. have recently patented the oxidation of alkanes and cycloalkanes into the corresponding alcohols and ketons in the presence of aldehydes using a Cu-based catalyst and nitrogen containing compounds [8]. Industrially the cyclohexane is oxidized by air (15 Atm) at 160 °C in the presence of cobalt naphtenate as homogeneous catalyst, giving cyclohexanone and cyclohexanol with good selectivity (80 %) at low conversion (1–10 %) [9,10]. Since cyclohexanone and cyclohexanol are more reactive than the cyclohexane reactant, it is difficult to achieve high conversion and selectivity simultaneously.

In the last years, heterogeneous catalysts, which could have a significant industrial impact replacing homogeneous catalysts, have also been largely developed [3,11–13]. Metal aluminophosphates (metal = Mn, Fe, Co, Cu, Cr, V) [14–20] and zeolites encapsulated Fe and Ru phthalocyanine complex [20–24] have been mainly investigated; the catalysts were usually used in the presence of additional solvents and initiators as co-catalysts and their fitness was strongly affected by the large leaching of the metal. Among the various metals studied, copper nanoparticles have been found to be valuable precursors for the activation of molecular oxygen [25, 26].

We report here that nanostructured Cu/γ-Al_2O_3, Cu/Fe_2O_3 and Cu/TiO_2 systems can be easily obtained by deposition of nanoscale Cu particles from solvated Cu atoms. They are valuable catalysts for the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone in the absence of initiators and solvents. The catalysts, which have been characterized by HRTEM analysis show after the first catalytic run, structural rearrangements and different catalytic behaviours, strictly related to the kind of support.

2. Experimental section

2.1. General

All operations involving the metal vapour synthesis (MVS) products were performed under a dry argon atmosphere. The copper loading in solution was determined by Atomic Absorption Spectrometry using a Perkin–Elmer 4100ZL instrument at the Istituto per i Processi Chimico Fisici, CNR, Pisa, Italy. GC analyses were performed on a Perkin–Elmer Autosystem gas chromatograph, equipped with a flame ionisation detector, using a SiO2 "Wide Bore" column (DB1, 30 m_0.53 mm, 5 mL) and helium as carrier gas. GC-MS spectra were recorded on a Perkin–Elmer Q-mass

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910 spectrometer connected with a Perkin–Elmer gas chromatograph, equipped with a “split-splitless” injector, using a SiO2 capillary column and helium as carrier gas.

Electron micrographs were obtained with a JEOL 2000EX microscope equipped with polar piece and top entry stage. Before introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. The histograms of the metal particle size distribution for the Cu samples were obtained by counting at least 300 particles onto the micrographs. The mean particle diameter (d_m) was calculated by using the formula $dm = \mathrm{T}\ d_i n_i/\mathrm{T}\ n_i$, where n_i is the number of particles with diameter d_i.

2.2. Materials

Acetone was dried on $CaSO_4$, distilled and stored under inert atmosphere. Cyclohexane had the highest purity grade from Aldrich. Commercial γ-Al_2O_3 (Chimet product, type 49, surface area 110 m^2/g, mean particle diameter 31 mm), commercial Fe_2O_3 powder (Aldrich product, $<5\ \mu M$, surface area 2.1 m^2/g), commercial TiO_2 powder (Aldrich product, 325 mesh, surface area 5.8 m^2/g) were dried in a static oven before use. Gaseous oxygen, from Rivoira, was 99.99 % pure.

2.3. Preparation of Cu solvated atoms

Copper (500 mg) loaded into a Sylvania tungsten-alumina crucible was evaporated over a 1 h period, under a dynamic vacuum of ca. 10^{-4} Torr, and co-condensed with acetone (100 mL,) at liquid nitrogen temperature, using a typical glass metal atom reactor. The solid red-brown matrix obtained was allowed to melt, and the resulting brown solution was siphoned out under argon into a Schlenk flask and kept in a refrigerator at −40 °C. The content of metal in solution was 0.45 mg Cu/mL.

2.4. Preparation of supported Cu catalysts

In a typical experiment the above brown Cu/acetone reaction solution (44 mL, 20 mg Cu) was added to a suspension of support (2 g) (γ-Al_2O_3, Fe_2O_3, TiO_2) in acetone (20 mL). The mixture was stirred for 12 h at room temperature. The colourless solution was removed and the light-brown solid, containing 1 wt/wt % Cu, was washed with *n*-pentane and dried under reduced pressure.

2.5. Oxidation reactions with supported Cu catalysts

The oxidation experiments were performed under a starting oxygen pressure of 20 Atm using a 75-mL stainless steel autoclave equipped with a Teflon removable cylinder Jacker, a magnetic bar, a stainless steel tap and a manometer (100 atm end scale). The reactions were performed by heating the autoclave in an oil bath. In a typical experiment with Cu solution, the autoclave was charged, under argon atmosphere, with 350 mg of supported Cu and 10 mL of cyclohexane. The autoclave was closed, argon was eliminated and oxygen was introduced. The reaction mixture was stirred (1000 rpm) and heated. The reaction was monitored by GLC analysis of liquid samples using *o*-xilene as internal standard.

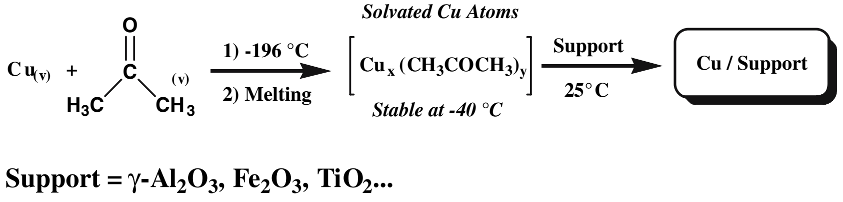
Recycle tests have been performed removing the liquid phase from the reactor, washing with acetone, drying and adding fresh cyclohexane. The reactions are performed under the same experimental conditions of the first run.

3. Results and discussion

The reaction of Cu vapours with acetone at liquid nitrogen temperature affords a red brown solid matrix which gives, on melting, acetone solvated Cu atoms, soluble in the excess of acetone and stable at low temperature (−40 °C) (Scheme 1) [26]. Acetone solvated Cu atoms act as valuable starting material for the gentle deposition of activated Cu particles on solid oxide supports. When added to acetone suspension of inorganic support (γ-Al_2O_3, Fe_2O_3, TiO_2...), the starting brown solution of acetone solvated Cu atoms, rapidly turns clear, with a complete placing of nanosized Cu particles on the support (Scheme 1).

3.1. HRTEM analysis of freshly prepared catalysts

Cu/γ-Al_2O_3, Cu/Fe_2O_3 and Cu/TiO_2 samples with the Cu loading of 1 wt/wt % have been prepared and characterized by HRTEM analysis. For each case one representative image is displayed, accompanied by the histogram of the Cu particle size distribution, obtained on the basis of the collection of taken images for each sample (figure 1).



Scheme 1.

In the case of Cu/γ-Al_2O_3, metal particles, with size in the 3–9 nm range, form quite dense ensemble on the support (figure 1A). Passing to the Cu/Fe_2O_3 system, Cu particles appeared more homogeneously located on the support, and their size distribution, although spread between the same limit values, exhibited a significantly higher presence of particles with size in the 4–7 nm domain (figure 1B). Finally, the Cu/TiO_2 catalyst was found to contain very small Cu particles, highly homogeneously distributed on the TiO_2 grains and with size essentially confined between 1 and 3 nm (figure 1C). In all samples the HRTEM analysis indicated the presence of a narrow distribution of quite small Cu particles, averaging 6.0 nm in diameter in the Cu/γ-Al_2O_3 and Cu/Fe_2O_3 samples and 2.2 nm in the Cu/TiO_2 sample.

The Cu particle sizes are largely are quite small pointing out the powerful of solvated metal atoms in the generation of nanosized supported metal particles homogeneously distributed [27].

3.2. Catalytic experiments

The supported Cu/γ-Al_2O_3, Cu/Fe_2O_3 and Cu/TiO_2 systems have been tested in the oxidation of cyclohexane, an attractive reference substrate from the industrial point of view because its products are the intermediates for the manifacture of Nylon-6 and Nylon-6-6 [28]. The reactions have been performed at 120 °C under an oxygen starting pressure of 20 atm, in the absence of solvents and initiators or co-catalysts. The results are summarized in table 1.

Using Cu/γ-Al_2O_3 as catalysts the reaction affords after 24 h a mixture of cyclohexanone (I) and cyclohexanol (II) (1.4:1 ratio) in yields of 9.2 %, with a specific catalytic activity (mol products/g atom Cu) of 155. The catalyst can be reused without valuable loss of activity. Under the same reaction conditions the Cu/Fe_2O_3 catalyst gives cyclohexanone and cyclohexanol (1:1.5 ratio) with comparable yields (9.85 %) and a specific catalytic activity of 165. The life of this catalyst, however, is quite poor: in the second experiment (run 5) the yields dramatically decrease to 1.9 % and the catalyst turns quite inactive (run 6). The Cu/TiO_2 sample is also active in the oxidation of cyclohexane to cyclohexanone and cyclohexanol with good yields (7.2 %) and high selectivity to cyclohexanone (12:1). The catalyst maintains its activity when reused, while the molar

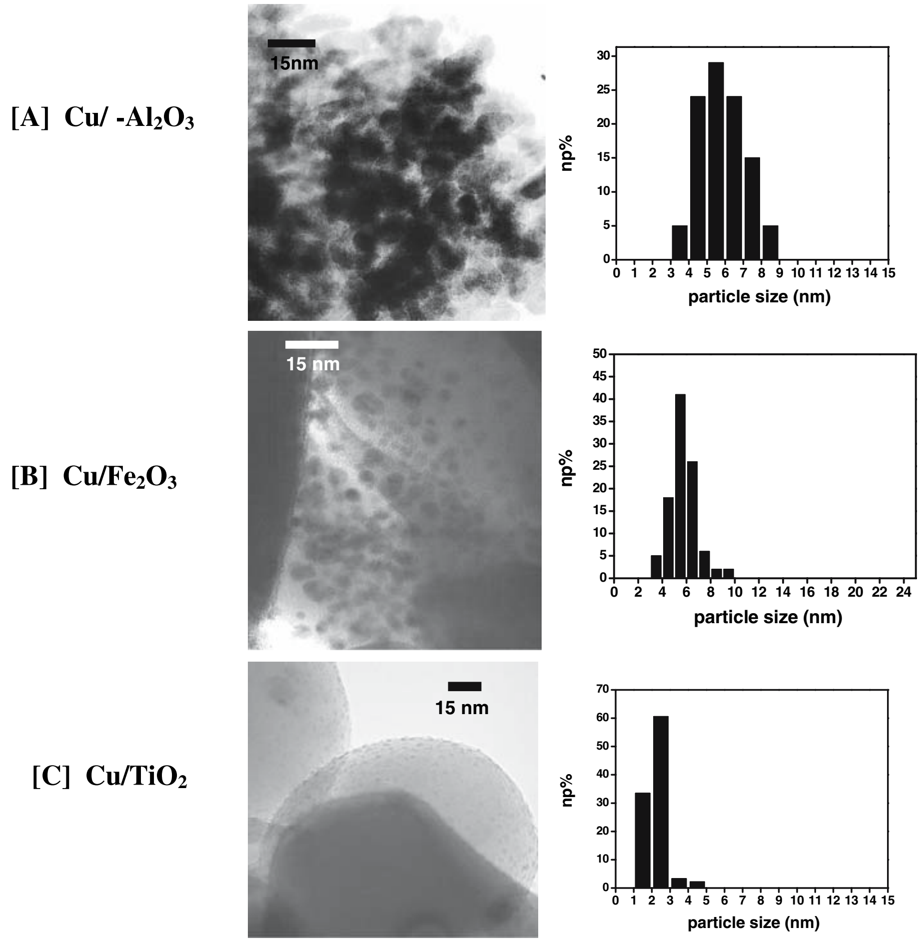
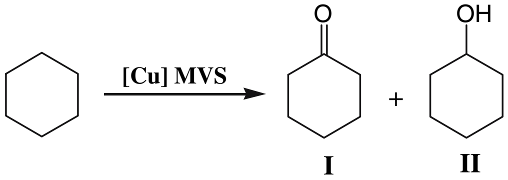


Figure 1. TEM images (original magnification: × 300,000) and related histograms of size distribution of supported Cu particles (Cu loading: 1 wt/wt %) of: Cu/γ-Al_2O_3, [A]; Cu/Fe_2O_3, [B]; Cu/TiO_2, [C] in the fresh form.

Table 1
Oxidation of cyclohexane with supported Cu MVS catalyst[a]



Run	Catalyst (Cu 1 wt %)	Conv. (%)[b]	Yields (%) [c]	Products(%)		Specific Activity (mmol products / mg at. Cu)
				I	II	
1	Cu/γ-Al_2O_3	13.7	9.2	58	42	155
2	Recycled from run 1	13.2	8.9	63	37	156
3	Recycled from run 2	12.5	8.1	64	36	142
4	Cu/Fe_2O_3	14.2	9.8	34	66	165
5	Recycled from run 4	3.2	1.9	52	48	34
6	Recycled from run 5	1.9	traces	–	–	–
7	Cu/TiO_2	11.5	7.2	92	8	121
8	Recycled from run 7	11.8	7.8	88	12	133
9	Recycled from run 8	12.7	8.0	75	25	136

[a] Reaction condition: cyclohexane = 10 mL, catalyst = 350 mg, substrate/catalyst ratio = 1680, $P(O_2)$ = 20 atm, T = 120 °C, t = 24 h.
[b] Determined by analysis using internal standard.
[c] Determined by GC analysis; the identity of the products were verified by co-injection with authentic samples and GC-MS analysis.

ratio cyclohexanone/cyclohexanol changes from 7.3:1 (run 8) to 3.1:1 (run 9).

The leaching of Cu from freshly prepared and recycled catalysts has been also valuated by atomic absorption analysis of the reaction mixture. The results are summarized in table 2.

The Cu leaching during the first catalytic run is 1.2 % for the Cu/TiO_2 sample and increases to 4.0 % and 6.5 % for the Cu/γ-Al_2O_3 and Cu/Fe_2O_3 catalysts, respectively. It also appears from the reported data that the Cu leaching in the second catalytic run, is, from all the catalysts, largely lower suggesting that, the Cu erosion could be mainly related to Cu particle of the freshly prepared samples weakly bonded to the solid oxide support. The Cu leaching is, in any cases, more consistent for the Cu/Fe_2O_3 sample: however, it appears not enough to justify the dramatic loss of activity of the catalyst when recycled.

Table 2
Cu leaching during the catalytic runs[a]

Catalysts (mg)	Cu-leaching (%) after the 1° cycle	Cu-leaching (%) after the 2° cycle
Cu/γ-Al_2O_3 (350 mg)	4.0%	0.2%
Cu/Fe_2O_3 (350 mg)	6.5%	0.4%
Cu/TiO_2 (350 mg)	1.2%	0.09%

[a] Determined by atomic absorption analysis after filtration of the reaction mixture through PTFE membrane (0.45 μm).

In order to get a better insight on the matter, HRTEM analysis on Cu samples after catalytic experiments have been also performed.

3.3. *HRTEM analysis of the Cu samples after the catalytic test*

Representative images and corresponding histograms of Cu/γ-Al_2O, Cu/Fe_2O_3, Cu/TiO_2 after one catalytic run are reported in figure 2.

It appears that the Cu/γ-Al_2O_3 recycled sample shows the same features of the freshly prepared catalysts (see infra figure 1 A). The only difference was a single broadening of the size distribution toward larger values (figure 2 A'). Passing to the Cu/Fe_2O_3 system, the occurrence of the reaction deeply modified the state of supported metal, resulting in the formation of much larger Cu particles, with a consequent relevant broadening and flattering of their size distribution over 4–24 nm range (figure 1B'). Finally the Cu/TiO_2 catalysts was found to exhibit a third type of distinct features. After the reaction no supported metal particles were longer observed (figure 2 C'). However, by prolonging the exposure to the electron beam for some minutes supported metal Cu particles appeared (figure 2 C''), likely resulting from the sintering of supported Cu species so small in size the escape detection by TEM. These very small Cu particles were probably present in the freshly prepared catalyst and/or generated by erosion of previously detectable Cu particles by O_2 to form Cu oxide species during the catalytic experiment.

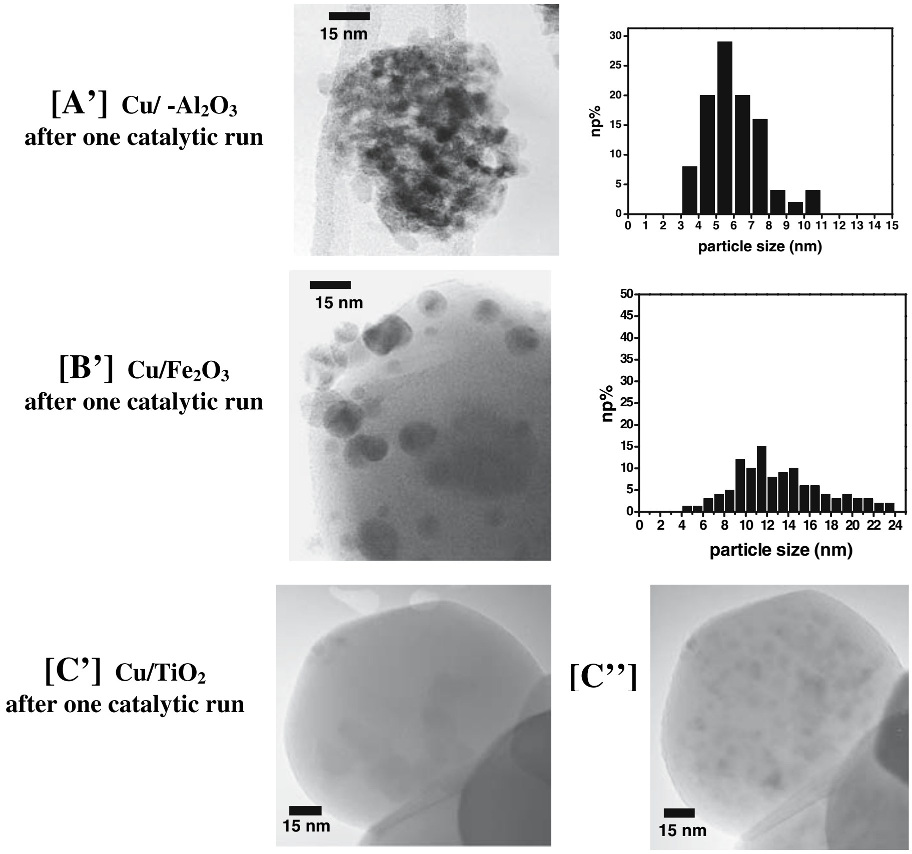


Figure 2. TEM images (original magnification: × 300,000) and related histograms of sizedistribution of supported Cu particles of Cu/γ-Al_2O_3 [A'], Cu/Fe_2O_3 [B'], Cu/TiO_2 [C'] after one catalytic run. [C''] obtained by prolonging the exposure of the sample Cu/TiO_2 [C'] to the electron beam for some minutes.

4. Conclusions

The results here reported indicate in the deposition of copper particles from acetone solvated Cu atoms, a valuable method for the preparation of Cu supported catalysts. Compared to other Cu weakly stabilizing organic ligands (toluene, THF, *n*-pentane,...) the acetone allows to easily handle the resulting solvated Cu solutions, without inside clustering processes to large and insoluble Cu particles, before treatment with supports [25, 29]. Toluene solvated Cu atoms, for instance, which have been used to prepare Cu/CeO_2 catalysts, are thermally unstable even at −100 °C [26]. It has been recently reported that they give, by clustering at room temperature, ultra fine Cu powders, containing Cu particles ranging 20 nm in diameter. Acetone solvated Cu atoms, on the contrary, are thermally stable at −30 °C for several hours and give, by clustering at room temperature, very small Cu particles ranging 3.6 nm in diameter [26].

The Cu/γ-Al_2O_3, Cu/Fe_2O_3 and Cu/TiO_2, prepared samples are good catalysts for the partial oxidation of cyclohexane to cyclohexanol and cyclohexanone. The life of the catalyst, however, is greatly depending on the kind of support: after the first catalytic experiment, while the Cu/γ-Al_2O_3 and Cu/TiO_2 catalysts are still active, the Cu/Fe_2O_3 sample became quite inactive likely as result of the clustering process of the Cu particles to large aggregates with a broad size distribution (see infra); this singular behaviour of Cu particles of difference size should also provide an interesting new example of size-depending chemistry [30].

The results reported for the oxidation of cyclohexane to cyclohexanol and cyclohexanone have not been optimised: experiments presently in progress indicate that Cu/γ-Al_2O_3 and Cu/TiO_2 systems with lower Cu loading (0.3 %) are even more efficient catalysts for the above reaction, with catalytic efficiency (mol product/g.atom Cu) ≥ 500 and can be reused without loss of activity and appreciable metal leaching. It should make the development of these heterogeneous catalysts for the oxidation of organic substrates with molecular oxygen, in the absence of solvents and initiators or co-catalysts of close potential relevance.

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