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Reaction of carbon tetrachloride with the nanoscale particles of silver and copper in a liquid phase

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The nanoscale particles of silver and copper coated with amorphous carbon (Ag/C and Cu/C) react with liquid carbon tetrachloride at 25–30 °C to selectively form hexachloroethane in 60% yield.

Reactions of nano- and subnanoscale metal particles in condensed media in a broad range of temperatures are carried out in order to establish the factors that determine their reactivity and to reveal the dimensional effects.[1–6] Such processes simulate the interaction of molecules with active sites on the surfaces of metal catalysts and the specifics of unusual chemical reactions with small-scale particles. Some inert small molecules, such as nitrogen, carbon monoxide and dioxide and lower polyhaloalkanes, have been activated using metal nanoparticles.[6–8] In this work we chose carbon tetrachloride, which does not react at room temperature with compact metals such as silver and copper, as the model reagent. It has been shown previously[9–11] that atoms and small clusters of silver and copper react with carbon tetrachloride at low temperatures. Thus, it was the purpose of this work to find out whether it is possible to activate carbon tetrachloride in liquid phase in reactions with nanoscale silver and copper particles at room temperature and to study the selectivity of this reaction.

Silver and copper nanopowders coated with amorphous carbon were obtained at the Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences using the metal droplet evaporation technique (T = 1500 °C) in an inert gas stream containing a hydrocarbon.[12] The metal was heated using a high-frequency induction generator. The particle size was controlled by the inert gas pressure and the gas flow rate in the vicinity of the evaporation zone. The particle composition was determined by chemical analysis and X-ray diffraction methods. Typical electron micrographs of specimens of silver and copper particles are presented in Figure 1. The sizes of silver and copper particles range from 20 to 50 nm. The carbon layer on silver and copper particles is well visible. In addition, twin defects are observed in copper particles.

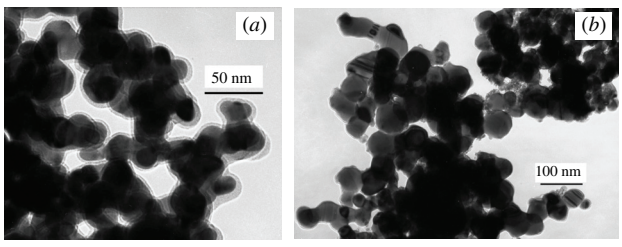

Figure 1 TEM images of (*a*) silver nanopowder and (*b*) copper nanopowder coated with carbon.

Table 1 Compositions of reaction mixtures for some of the specimens.

Specimen	Metal/μmol	CCl_4/μmol	Metal concentration (mol%)
Cu1	357.5	10.67	3.4
Cu2	430.0	11.48	3.7
Ag1	282.4	13.75	2.1
Ag2	272.2	13.64	2.0

In this work, we studied specimens with copper and silver nanoparticles in excess carbon tetrachloride, where the metal concentration amounted to a few mole percent (Table 1).†

GLC revealed a single product, hexachloroethane (C_2Cl_6), in the reaction mixture. No formation of tetrachloroethylene (C_2Cl_4), which was previously established in reactions of magnesium atoms and clusters in combined low-temperature condensates with CCl_4,[13,14] was found under our experimental conditions. The formation of hexachloroethane suggests that the process occurs by a radical mechanism. The reaction initiation and the initial formation of trichloromethyl radicals may occur due to

† The reaction mixtures were prepared from analytical grade carbon tetrachloride. The reagent was additionally purified and distilled (bp 76.8 °C); the purity was checked by gas chromatography. Weighed specimens of Ag/C and Cu/C nanoparticles and a known amount of carbon tetrachloride were placed under argon into ampoules, which were then hermetically sealed and exposed to ultrasonic treatment for 10–20 min (power, 45 W; frequency, 50 kHz) to disintegrate nanoparticle agglomerates and to stir the mixture vigorously. After that, the reaction mixtures were kept in a thermostat at 30 °C with stirring for 10–200 h, samples were regularly withdrawn in order to monitor the compositions of the reaction mixtures.

After the experiment was completed, the solid phase was separated by centrifugation and analysed by X-ray diffraction. Structural studies were performed using powders or pellets ~10 mm in diameter. X-ray diffraction spectra were recorded with a DRON-6 diffractometer using CrKα irradiation and stepped scanning with steps of 0.02 or 0.05° (2θ) and a scanning time of 5 s at each point. Calculation of the crystal lattice parameters and phase composition, quantitative analysis and assessment of coherent scattering block sizes were carried out using the PDWin-4.0 software ('Burevestnik', St. Petersburg).

The reaction products were analysed by gas-liquid chromatography (GLC) using a Chrom-5 instrument with polyethylene glycol (PEG) as the liquid phase and a flame ionization detector. For this purpose the samples were centrifugated and 2 μl of the liquid phase was withdrawn to perform each GLC analysis. The concentrations of the reaction products were determined by comparison with reference solutions; the determination error was no higher than 2%.

dissociative interaction of carbon tetrachloride with metal nanoparticles accompanied by formation of a metal monochloride:

$$M + CCl_4 = MCl + CCl_3. \quad (1)$$

The subsequent recombination of trichloromethyl radicals results in the final reaction product, *viz.*, hexachloroethane:

$$\cdot CCl_3 + \cdot CCl_3 = C_2Cl_6. \quad (2)$$

The probable overall stoichiometric reaction equation is

$$2M + 2CCl_4 = 2MCl + C_2Cl_6. \quad (3)$$

If the process occurs completely, 0.5 mol of hexachloroethane should be formed per a mole of consumed metal. X-ray diffraction data (Figure 2) suggest that almost 100% silver nanoparticles are converted into silver monochloride. The possibility of oxidation of nanoscale silver particles ($Ag \rightarrow Ag^+$) with CCl_4 has also been shown elsewhere.[15] The yield of hexachloroethane is somewhat lower than the theoretical value with respect to the metal; it depends on the metal concentration in a complex way. The yield of hexachloroethane increases up to 2–3 mol% with an increase in the metal concentration in the reaction system containing excess carbon tetrachloride (Table 2). A further increase in the metal concentration does not increase the product yield, presumably due to secondary reactions occurring on the surfaces of nanoparticles.

Table 3 shows the yields of the reaction product (C_2Cl_6) as a function of the reaction time. The maximum yield of hexachloroethane is 60–70% for specimens containing 1–2 mol% silver; it is almost reached in 50 h at 30 °C. For copper specimens (3–4 mol% of the metal) the yield is up to 1% under the conditions used.

The small yield of hexachloroethane in copper-containing specimens may be due to side reactions of nanoscale copper and to the presence of reaction products with dissolved oxygen; these partially consist of copper oxide, which can react with carbon tetrachloride to give carbon dioxide.[16] The Debye crystallogram of a specimen of copper nanoparticles after exposure to carbon tetrachloride shows a small percentage of the copper monochloride (CuCl) phase. However, the strongest phase of the anticipated copper dichloride ($CuCl_2$) phase is not observed. The other strong lines observed in the Debye crystallograms are close to the lines of mixed copper hydroxychloride $Cu_2(OH)_3Cl$; moreover, weak lines of metallic Cu and copper monoxide Cu_2O are present.

Thus, it has been shown for the first time that, unlike the compact metals, nanoscale particles of silver and copper react with carbon tetrachloride in a liquid phase at room temperature to give hexachloroethane. The process selectivity is close to 100%. The product yield with respect to the metal ranges from a few percent for copper nanoparticles to 60–70% for silver nanoparticles. It increases with an increase in the metal concentration from 0.4 to 2 mol% silver and from 1 to 3 mol% copper.

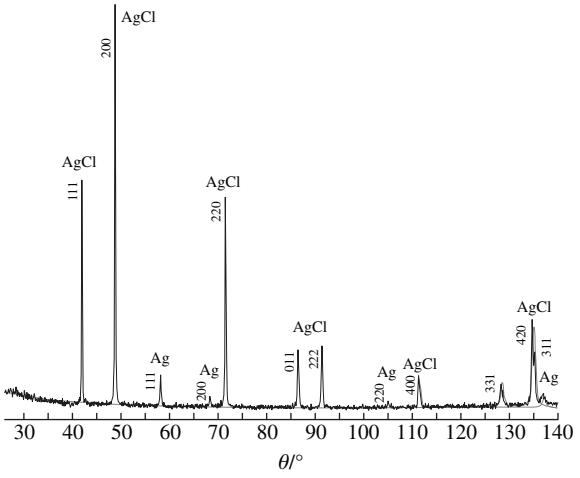

Figure 2 X-Ray diagram of the solid phase of the reaction mixture of silver nanoparticles with carbon tetrachloride. Phase composition: AgCl, 97.4%; Ag, 2.6%.

Table 2 Yield of C_2Cl_6 depending on the metal concentration (mol%) in the specimen (reaction time, 30 h; T = 30 °C).

Silver		Copper	
Metal concentration (mol%)	Yield (%) with respect to theory	Metal concentration (mol%)	Yield (%) with respect to theory
0.41	25	1.7	0.60
0.78	49	3.0	1.0
2.0	48	3.4	0.82

Table 3 Yield of C_2Cl_6 depending on the reaction time (T = 30 °C).[a]

Time/h	Cu1 Yield (%) with respect to theory	Cu2 Yield (%) with respect to theory	Ag1 Yield (%) with respect to theory	Ag2 Yield (%) with respect to theory
0	0	0	0	0
10	—	0.37	12.0	11.5
20	—	0.70	24.0	23.8
30	0.82	0.84	44.2	48.3
50	1.09	—	60.6	62.6
200	1.12	—	67.0	68.2

[a]For compositions of the specimens, see Table 1.

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