

SHORT
COMMUNICATIONS

Catalytic Properties of a Copper–Carbon System Formed by Explosive Decomposition of Copper Acetylide

Yu. N. Zhitnev, E. A. Tveritinova, and V. V. Lunin

Faculty of Chemistry, Moscow State University, Moscow, Russia

e-mail: zhitnev@kge.msu.ru

Received January 29, 2007

Abstract—The catalytic properties of a copper–carbon system formed by the explosive decomposition of copper acetylide in the propanol-2 dehydrogenation and dehydration reaction were studied by the pulse microcatalytic method over the temperature range 60–350°C. The extent of conversion was as high as 85%. It was established that the ratio between the catalytic conversion channels of propanol-2 depended on the method of acetylide decomposition (explosion in air or in vacuum).

DOI: 10.1134/S003602440801024X

Metal-containing catalysts are traditionally prepared from solutions of the corresponding metal salts followed by their decomposition on a support and reduction of the resulting oxides in a hydrogen atmosphere upon heating. The presence of water and the sequence of thermal processes acting on the starting reactants differently affect the state and size of metal particles in such catalysts, inevitably blocking a portion of active catalytic centers.

In this work, a “dry” one-step method of preparing copper-containing catalyst through the initiation of the explosive decomposition of copper acetylide was investigated. Copper-containing catalysts are quite popular, because they are inexpensive and active in a diversity of chemical processes. They have found wide use in industry and in fine chemical synthesis. Synthesis [1] and oxidation [2] of methanol, NO removal [3], dehydrogenation of alcohols [4–7], and hydrogenation of aldehydes [8] are far from being a full list of the processes where copper is used as an active catalytic component. However, the use of copper-containing catalysts is often restrained, because they are readily deactivated in high-temperature reactions as a result of the agglomeration of low-melting copper particles. The choice of a support is an important problem in catalyst preparation. The carbon-based supports are quite promising. Contrary to the traditionally used silicon and aluminum oxides, carbon supports are stable in both acid and alkaline media, which is quite essential for many chemical processes.

There are several methods of coating carbon surface with copper. In [8], copper was applied to the surfaces of activated carbon, diamond, and graphite by wet impregnation with a solution of copper nitrate followed by drying, annealing, and reduction in a hydrogen flow. In [9], impregnation with an ammonia solution of copper hydrocarbonate was followed by the decomposition

in a vacuum at 503 K. The authors of [10] proposed the method of copper precipitation from a solution of a copper salt. All of these methods are based on the use of aqueous solutions and, often, on a multistep scheme of the thermal accompaniment of reduction reactions, inevitably leading to the partial blocking of the active catalytic centers.

The methods of preparing copper adsorption catalysts by dry metal deposition on a support upon the thermal decomposition of organometallic compounds in a flow of a carrier gas are also known [11]. In this work, vapor of copper acetylacetonate was carried by the nitrogen flow to a column with activated carbon, whereupon heated for a long time at a temperature above 300°C to deposit metallic copper on carbon. This method requires the use of a rather complex apparatus and involves prolonged thermal treatment, which diminishes the “degree of inhomogeneity” in the process of catalyst preparation and leads to the loss of some active centers.

By contrast, a fast one-step synthesis of catalysts ensures high degree of inhomogeneity and, hence, favors the retention of active centers.

Copper acetylide is an exothermic compound stable in the wet state. In the dry state, C_2Cu_2 is a weak explosive. The explosive decomposition of copper acetylide can be initiated by heating above ~120°C, by impact, or by electric spark. The absence of gaseous decomposition products causes a weak explosive power of copper acetylide. When keeping due precautions, C_2Cu_2 is a quite available chemical. The high rate of product formation can guarantee the retention of the defect zones and nonequilibrium phase states in the products, which is essential for the manifestation of catalytic properties. The formation of finely dispersed carbon upon acetylide decomposition can also

affect the copper catalytic activity, because carbon is an efficient support.

Of indubitable interest is the effect of the acetylide explosive decomposition on the state and particle size of the decomposition products and, therefore, on their catalytic activity.

EXPERIMENTAL

Copper acetylide was prepared by bubbling acetylene through a solution of copper(I) ammonia complex obtained by dissolving copper(I) chloride in a concentrated aqueous solution of ammonia. Copper(I) chloride was prepared by the procedure described in [12]. The explosive decomposition of room-temperature dried copper acetylide was initiated by two methods: (i) heating in a porcelain crucible in air and (ii) spark-induced explosion of a sample evacuated to 5 Pa. Air decomposition of acetylide was accompanied by a shrill sound and slight scatter of the particles formed, while the evacuated samples were decomposed almost soundlessly. The decomposition products were a black-colored powder mass.

X-ray diffraction analysis of the copper acetylide decomposition products (Cu + C system) was carried out on a DRON-3M diffractometer with step-by-step scanning (scan step 0.05° – 0.1° , scan time 3–10 s). Electron microscopic study of the Cu + C system was performed with a Cam Scan Series 2 scanning microscope. The specific surface of the Cu + C system was determined chromatographically from low-temperature nitrogen adsorption/desorption on a GKh-1 gasometer.

Catalytic activity of the thermal decomposition products of copper acetylide was examined using the

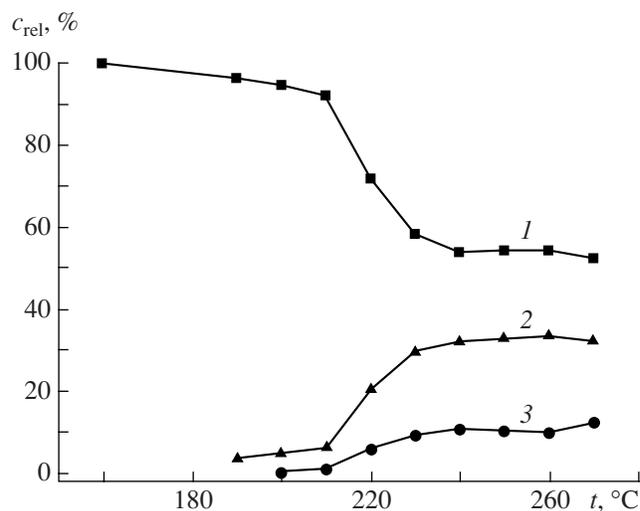


Fig. 1. Temperature dependence of the composition of reaction mixture ((1) alcohol, (2) acetone, (3) propylene) in the reaction of propanol-2 on catalyst A (product of copper acetylide explosion through heating in air).

pulse microcatalytic method [13]. A batch of the catalyst (~50 mg) was placed between two fiberglass layers inside a reactor representing a quartz tube of length 15 cm and diameter 0.5 cm. The reactor was placed in a metallic jacket with holes for the injection of inert gas and substrate (propanol-2). The jacketed reactor was screwed on the inlet in a chromatography column. On the outside, the jacket was heated with a furnace, whose temperature was controlled by a TRM-10 temperature gauge and maintained with an accuracy of 1 K. The temperature of the catalytic reactor was varied in the range 60–350°C.

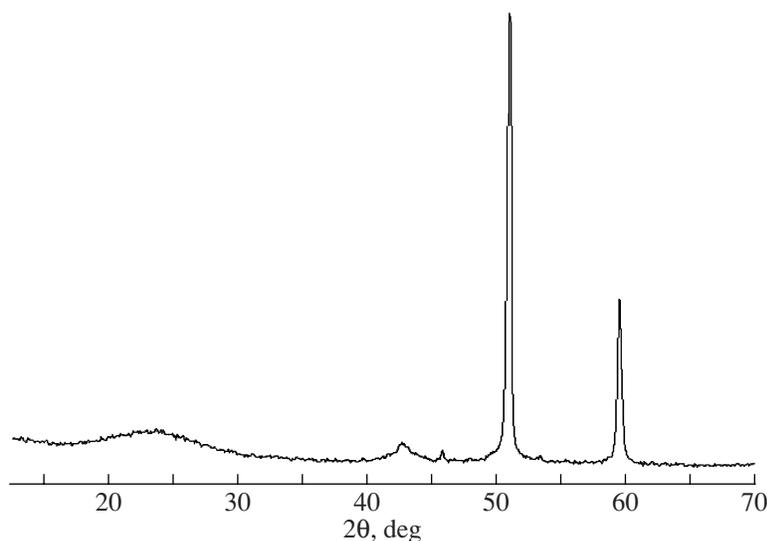


Fig. 2. X-ray diffraction pattern of catalyst A.

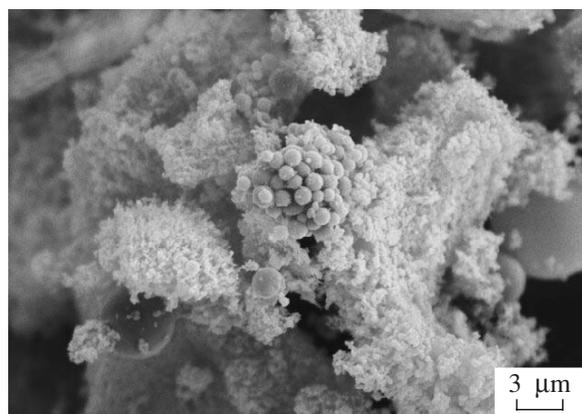


Fig. 3. Electron micrograph of catalyst **A**.

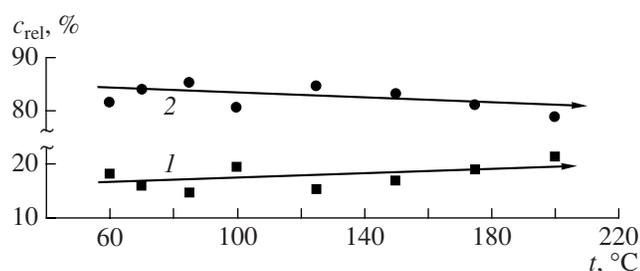


Fig. 4. Temperature dependence of the composition of reaction mixture ((1) alcohol, (2) acetone) in the reaction of propanol-2 on catalyst **B** (product of spark-induced explosion of copper acetylide evacuated to 5 Pa).

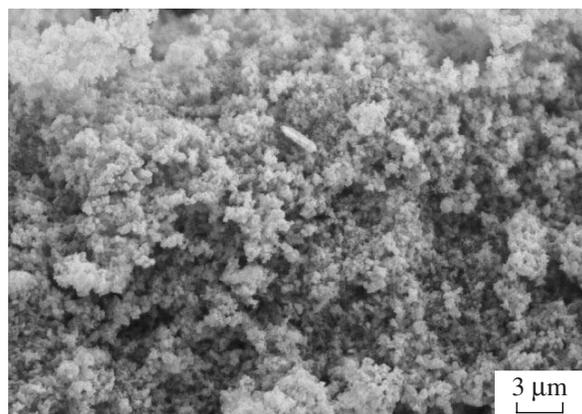


Fig. 5. Electron micrograph of catalyst **B**.

Chromatographic analysis was performed on a Chrom-5 chromatograph with a flame ionization detector. The areas of chromatographic peaks were measured using a C 1-100 integrator. The reactant (5 ml of propanol-2 vapor) was injected into the reactor using syringe. The velocity of nitrogen carrier gas was 30 ml/min at room temperature. Glass column (1.3 m in length and 0.5 cm in diameter) filled with fluorinated carbon [14] was used.

RESULTS AND DISCUSSION

The dependence of the composition of reaction mixture on temperature in the reaction of propanol-2 on catalyst **A** (product of copper acetylide explosion through heating in a porcelain crucible in air) is demonstrated in Fig. 1. The detectable alcohol conversion starts at $\sim 180^\circ\text{C}$, and it achieves 40% at $\sim 230^\circ\text{C}$. The dehydrogenation reaction affording acetone and the dehydration reaction affording ethylene proceed simultaneously with a small difference in their rates.

The X-ray diffraction pattern of catalyst **A** (Fig. 2) exhibits characteristic copper peaks, very small copper(I) and copper(II) oxide peaks, and a diffuse region characteristic of the carbon amorphous phase. One can clearly see spherical copper particles on the electron micrograph of catalyst **A** (Fig. 3). The carbon particles have a well-defined porous structure. The specific surface of catalyst **A** is $\sim 50\text{ m}^2/\text{g}$.

In Fig. 4, the temperature dependence of the composition of reaction mixture is shown for propanol-2 conversion on catalyst **B** (product of spark-induced explosion of copper acetylide evacuated to 5 Pa). The following distinctions from the reaction with catalyst **A** are seen: (i) a low temperature reaction threshold ($\sim 50^\circ\text{C}$); (ii) a high catalyst activity ($\sim 85\%$ conversion of alcohol); and (iii) a high selectivity (the alcohol dehydration channel is absent in the temperature range $60\text{--}210^\circ\text{C}$).

No spherical copper particles are seen in the electron micrograph of catalyst **B** (Fig. 5), while a finely structured porous mass of the components formed upon copper acetylide decomposition is clearly seen.

The X-ray pattern of catalyst **B** is virtually not different from **A**. The specific surface of **B** is $\sim 130\text{ m}^2/\text{g}$.

Thus, a copper-containing Cu + C product obtained upon the dry one-step synthesis through the spark-induced explosive decomposition of copper acetylide showed high catalyst activity below 60°C and displayed a high selectivity in propanol-2 conversion to acetone over the temperature range from 60 to 200°C .

ACKNOWLEDGMENTS

We are thankful to F.M. Spiridonov, S.N. Torbin, Yu.D. Ivakin, and E.P. Chinennikova for assistance in measurements. This work was supported by the Federal Scientific and Technical Program (project no. 2005-R1-112.0/001/056) and the Russian Foundation for Basic Research (project no. 06-03-32933).

REFERENCES

1. E. M. Kalvery and K. J. Smith, *J. Catal.* **130**, 616 (1991).
2. R. M. Navarro, M. A. Pena, C. Merino, and J. L. G. Ferro, *Topics Catal.* **30/31**, 481 (2004).
3. C. Margues-Alvarez, J. Rodriguez-Ramos, and A. Guerrero-Ruiz, *Carbon* **34** (3), 339 (1996).

4. F.-W. Chang, W.-Y. Kuo, and K.-C. Lee, *Appl. Catal.* **246**, 353 (2003).
5. Z. Wang, H. Ma, W. Zhu, and G. Wang, *React. Kinet. Catal. Lett.* **76**, 271 (2002).
6. T. P. Minyukova, I. I. Simentsova, A. V. Khasin, et al., *Appl. Catal., A* **237**, 171 (2002).
7. Y. Han, J. Shen, and G. Chen, *Appl. Catal., A* **205**, 79 (2001).
8. R. S. Rao, T. K. Baher, and M. A. Vannice, *Catal. Lett.* **60**, 51 (1999).
9. T. Tsoncheva, S. Vankova, and D. Mehandjiev, *React. Kinet. Catal. Lett.* **80** (2), 383 (2003).
10. S.-J. Park and Jun-Shin, *J. Porous Mater.* **11**, 15 (2004).
11. L. Y. Frank and H. H. Lam, *Chem. Eng. Sci.* **58**, 687 (2003).
12. Yu. V. Karyakin and I. I. Angelov, in *Pure Chemical Reagents* (Goskhimizdat, Moscow, 1955), p. 355 [in Russian].
13. D. W. Bassett and H. W. Habgood, *J. Phys. Chem.* **64** (6), 769 (1960).
14. T. M. Roshchina, A. A. Kaz'mina, O. V. Kokhanov, et al., in *Proceedings of All-Russia Conference "Chemical Analysis of Substances and Materials"* (Moscow, 2000), p. 218 [in Russian].