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CHEMICAL KINETICS
AND CATALYSIS

A Copper Catalyst on Nonporous Supports Based on Copper Oxalate as a Precursor

Yu. N. Zhitnev, E. A. Tveritinova, F. M. Spiridonov, and V. V. Lunin

Faculty of Chemistry, Moscow State University, Moscow, Russia
e-mail: zhitnevyun@mail.ru

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Abstract—A method for obtaining copper catalysts on nonporous supports by the thermal decomposition of copper oxalate in the absence of oxygen was suggested. The catalytic properties of the catalyst were studied in the model reaction of the conversion of propanol-2 into acetone and propylene. The influence of the content of copper in the catalyst, reaction temperature, and conditions of oxalate decomposition on the degree of alcohol conversion and ratio between reaction channels was studied. Electron photomicrographs were obtained, specific surface areas were measured, and X-ray powder patterns of the catalyst were recorded.

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INTRODUCTION

In recent years, the development of new technologies has increased the demand for methods for the preparation of transition metal nanosized particles, including copper nanoparticles, which are used in electronics and the production of composition materials. The use of copper nanoparticles in catalysis offers promise.

Copper-containing catalysts are extensively used in industrial and laboratory syntheses. They catalyze such important processes as hydrogenation and dehydrogenation, hydration, oxidation, water gas conversion, and neutralization of toxic gases. The methods and conditions of catalyst preparation substantially influence their catalytic activity. Traditional methods for metal deposition on the surface of a support are impregnation of a support with a solution of copper salts followed by annealing and reduction [1–9], ion exchange in the deposition of copper on the surface of a support in the form of various complexes also followed by annealing and reduction [8–10], and the coprecipitation method, when copper catalysts are obtained from insoluble copper salts (oxalates and carbonates) and other metal salts (Zn, Al), which is followed by washing, drying, and precipitate decomposition [11, 12]. The method of chemical reduction is also known. It includes preliminary surface sensitization with tin salts, the deposition of a platinum layer as a catalyst of copper reduction on the surface, and subsequent annealing [13–15].

Nontraditional methods of the preparation of copper-containing catalysts include vapor-phase copper deposition on activated carbon, when the precursor is copper acetylacetonate [16]. In [17], a method for obtaining a copper-carbon catalyst under nonequilibrium conditions by explosive decomposition of copper acetylacetonate in a vacuum was suggested. Copper catalysts in the form of composite films were prepared by low-temperature joint deposition of metal and monomer vapors on a substrate with subsequent low-temperature solid-state polymerization [18]. In [19], an effective copper catalyst was obtained by the deposition of atomic layers.

According to stickler for nontraditional methods for the preparation of copper-containing catalysts, the traditional multistage scheme of synthesis, including adsorption, drying, calcination, and reduction, substantially influences the structure of catalysts and decreases catalytic activity, whereas the direct deposition of metal particles on a support to a greater extent contributes to the formation and conservation of active catalytic centers.

Supports for copper catalysts are most often porous compounds with developed surfaces, largely silica [5, 7, 9, 10, 12], alumina [11, 13, 14], and zinc oxide [6, 11] and also activated carbon [15, 16] and other carbon forms [1–4].

Silica as a support for the synthesis of copper catalysts is used in quite different forms, including silica gel [6, 7, 9, 10], aerosil [8, 21] and its varieties such as cab-o-sil [21] and zeosil [5], and silica obtained by burning rice husk [22]. Copper oxalate is extensively used as a precursor of small-sized copper particles [23, 24]. An analysis of the available data shows that the conditions of oxalate decomposition (temperature, gas atmosphere, rate of heating, etc.) can influence the composition of decomposition products and size of copper particles.

In this work, we studied the catalytic behavior of copper particles prepared by the thermal decomposi-

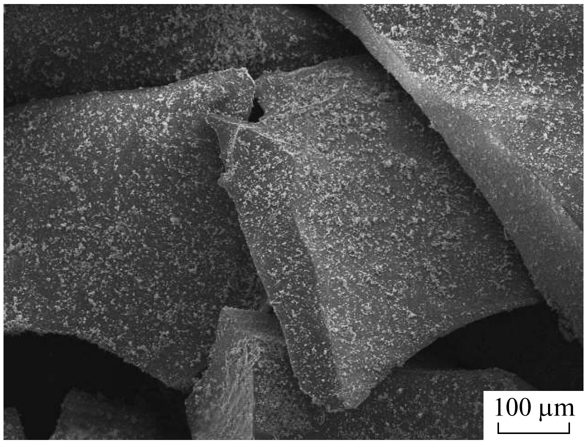

Fig. 1. Photomicrograph of the products of copper oxalate decomposition on the surface of lamp glass particles.

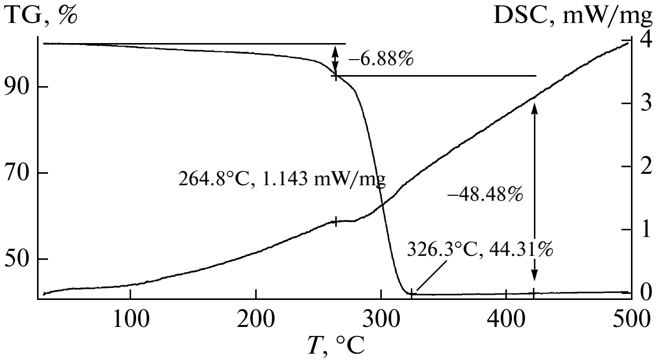

Fig. 2. Thermogram of copper oxalate (in argon atmosphere).

tion of copper oxalate deposited on nonporous materials, such as crystalline quartz, quartz glass, and usual glass of luminescent lamps (the latter contains K, Na, and Mg oxides in addition to silica). Such a method for copper deposition allows the content of copper to be varied over a wide range. The use of nonporous supports minimized the role played by supports in catalytic reactions and allowed the catalytic behavior of copper itself to be studied in more detail. The catalytic activity of the products synthesized was studied for the example of the conversion of propanol-2 into propylene and acetone.

EXPERIMENTAL

Support samples without preliminary chemical treatment were prepared by grinding in a porcelain mortar. Fractions of 0.5–1.0 mm particles were used in experiments. Copper oxalate was deposited on the surface of a nonporous support by pouring together equimolar copper sulfate and oxalic acid solutions. The precipitate was centrifuged and washed with distilled water to a negative reaction for sulfate ions. Copper oxalate deposited on the surface of supports was dried and loaded into an ampule for evacuation placed into an electric furnace with controlled temperature. Evacuation was performed first at room temperature to a pressure of 7 Pa. The selected decomposition temperature was then established, and evacuation continued to complete copper oxalate decomposition (~2 Pa). Copper oxalate + support mixtures had the compositions 0.5, 1.0, 5.0, and 10% (recalculated to pure copper). The decomposition temperature was varied from 280 to 450°C. Copper oxalate deposited on surfaces and the products of copper oxalate thermal decomposition were fairly firmly held by surfaces. The microelectronic photograph (Fig. 1) shows that the surface of lamp glass was fairly uniformly covered by copper particles.

X-ray diffraction patterns of catalyst samples were obtained on a TROE diffractometer, the specific surface area of supports and catalysts was determined by the Brunauer–Emmett–Teller method from the low-temperature adsorption of nitrogen on a GKh-1 gasometer. Electron photomicrographs of catalyst samples were obtained using a JSM-6390LA IEOL scanning electron microscope.

The catalytic activity of copper catalysts was studied by the pulsed microcatalytic method [17] in the dehydrogenation and dehydration of propanol-2. The temperature of the catalytic reaction was maintained constant to within 1 K and varied from 120 to 350°C. Catalytic transformation products were analyzed chromatographically on a Chrom-5 chromatograph with a flame ionization detector and a column with Porapak-N. The thermogram of the decomposition of copper oxalate was recorded on a NETZSCH STA 409 PC/PG thermoanalyzer.

RESULTS AND DISCUSSION

The catalysts were comparatively estimated according to two parameters, the degree of initial alcohol conversion and reaction selectivity with respect to the yield of acetone (the dehydrogenation channel). The specific surface areas of the nonporous materials used almost coincided and were of 0.15 ± 0.03 m^2/g, which allowed them to be used as fairly inert diluents. Estimates of the effectiveness of catalyst samples on these supports under comparable conditions showed the absence of support nature effects. All subsequent studies were therefore performed using luminescent lamp glass as a support.

The thermogravimetric curve of copper oxalate is shown in Fig. 2. This curve was used to select the temperature interval for decomposition (250–450°C). Catalyst samples containing 1% copper were used to study the influence of the temperature of precursor

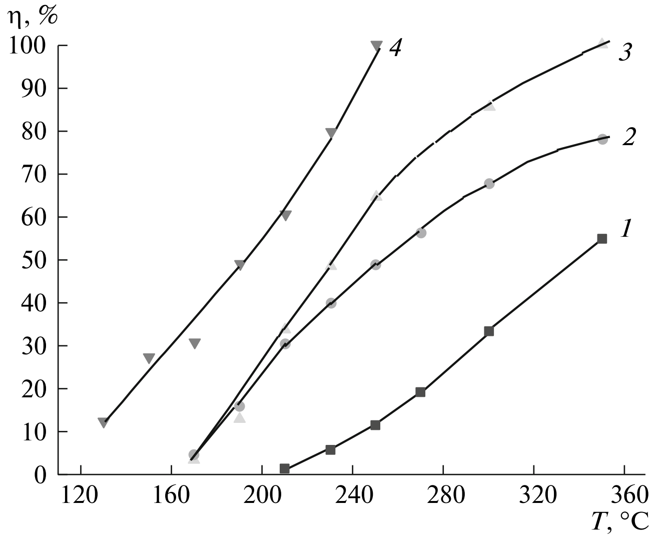

Fig. 3. Temperature dependences of the degree of conversion (η) of propanol-2 on catalysts containing (*1*) 0.5, (*2*) 1, (*3*) 5, and (*4*) 10% copper.

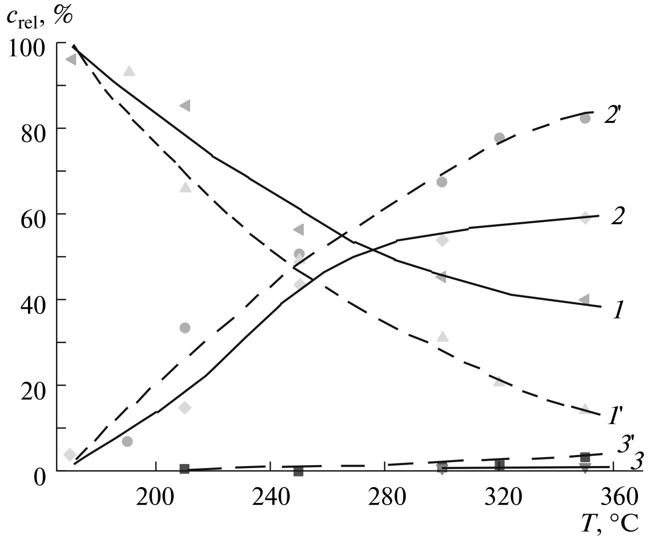

Fig. 4. Reaction temperature dependence of the relative contents of reagents (c_{rel}) in the reaction medium for (*1*–*3*) 1 and (*1'*–*3'*) 5% catalysts; (*1*, *1'*) propanol-2, (*2*, *2'*) acetone, and (*3*, *3'*) propylene.

(copper oxalate) decomposition (T_{decomp}) on alcohol conversion (η) at 250°C:

T_{decomp}, °C	280	330	360	450
η, %	25	44	37	0

Alcohol conversion is maximum for catalysts obtained by the decomposition of copper oxalate at 330°C.

Data on catalytic conversion of propanol-2 with catalyst samples containing 0.5, 1.0, 5.0, and 10.0% copper under comparable conditions (Fig. 3) show that conversion increases as the content of copper grows. Conversion for the sample with 1% copper reaches ~50% at 250°C (at a 100% selectivity for the dehydrogenation channel).

Typical dependences of the yields of products and the degree of alcohol conversion on reaction temperature for catalysts containing 1 and 5% copper are shown in Fig. 4. We see that catalytic alcohol conversion is observed already at 170°C and reaches 50% (75%) at 250°C with a high reaction selectivity with respect to acetone (the dehydrogenation channel). No propylene (the dehydration channel) was observed in the reaction with the catalyst containing 1% copper over the temperature range 210–330°C. Electron photomicrographs show that copper is largely formed as particles with a porous structure and size from 150 nm to several μm (Fig. 5).

The efficient activation energy calculated from the temperature dependence of the degree of propanol-2 conversion for catalysts with different copper contents was ~28 and 82 kJ/mol. The dependence shows the occurrence of the transition from kinetically to diffusion controlled conditions, which can be caused by the porous structure of copper crystallites.

A comparison of the fraction of the residual copper oxalate mass from the thermogram (Fig. 2) obtained in the argon atmosphere (44.31%) with that theoretically calculated for copper oxalate on the assumption that, in the absence of oxygen, oxalate decomposes thermally to free copper and carbon dioxide only (41.91%) shows that real oxalate decomposition products contain copper oxides in addition to free copper. The presence of oxides also follows from the X-ray pattern of the products of copper oxalate pyrolysis (Fig. 6).

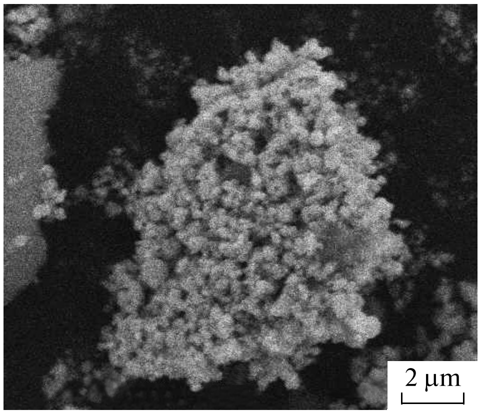

Fig. 5. Electron photomicrograph of a copper crystallite.

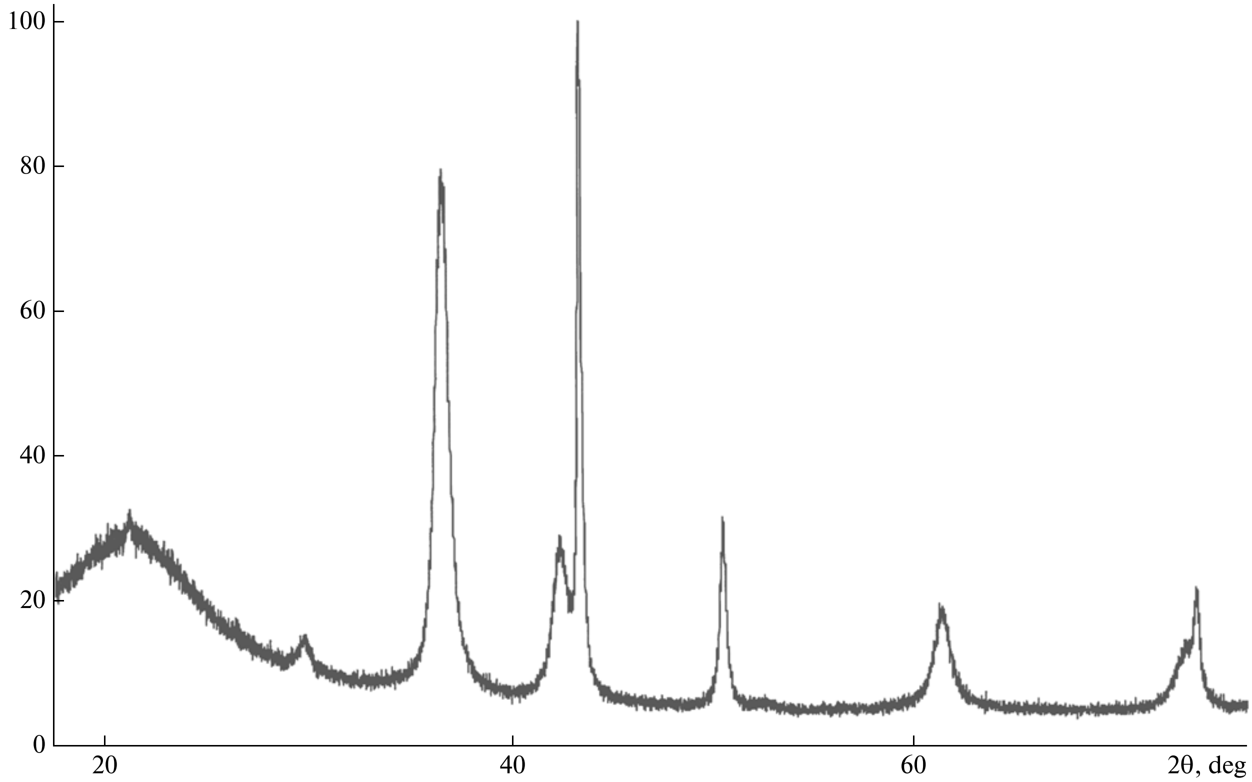

Fig. 6. X-ray pattern of copper oxalate pyrolysis products obtained under dynamic vacuum conditions (residual pressure ~2 Pa).

We estimated the size of elementary crystallites from the X-ray diffraction patterns. This gave ~40–60 nm for copper and ~40 nm for copper oxide. It was shown that copper oxalate thermal decomposition products deposited on the surface of a nonporous support exhibited fairly high catalytic activity and selectivity (with respect to the dehydrogenation channel) already at moderate temperatures (200–250°C) in propanol-2 dehydrogenation and dehydration. The reactivity of these catalysts depended strongly on the conditions of copper oxalate thermal decomposition.

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REFERENCES

1. C. Marquez-Alvarez, I. Rodriguez-Ramos, and A. Guerrero-Ruiz, Carbon **34**, 339 (1996).
2. C. Marquez-Alvarez, I. Rodriguez-Ramos, and A. Guerrero-Ruiz, Carbon **34**, 1509 (1996).
3. R.S. Rao, R. T. K. Baker, M. A. Vannice, Catal. Lett. **60**, 51 (1999).
4. J. Ma, N. M. Rodriguez, M. A. Vannice, and R. T. K. Baker, Topics Catal. **10**, 27 (2000).
5. Gyung Soo Jeon, Gon Seo, and Jong Shik Chung, Korean J. Chem. Eng. **13**, 412 (1996).
6. Zhenlu Wang, Hongchao Ma, Wanchun Zhu, and Guojuia Wang, Reakt. Cinet. Catal. Lett. **769**, 271 (2000).
7. Rong Zhang, Yuhan Sun, and Shaoyi Peng, Fuel. **81**, 1619 (2002).
8. T. Toupance, M. Kermarec, and C. Louis, J. Phys. Chem. B **104**, 965 (2000).
9. E. D. Guerreiro, O. F. Gorriz, J. B. Rivarolla, and L. A. Arrua, Appl. Catal. A: Gen. **165**, 259 (1997).
10. E. D. Guerreiro, O. F. Gorriz, G. Larsen, and L. A. Arrua, Appl. Catal. A: Gen. **204**, 33 (2000).
11. Deng Jingfa, Sun Qi, Zhang Yulong, Chen Songying, and Wu Dong, Appl. Catal. A: Gen. **139**, 75 (1996).
12. Zhifei Wang, Weiping Wang, and Gongxuan Lu, Int. J. Hydrogen Energy **28**, 151 (2003).
13. Hsin-Fu Chang, M. Abu Saleque, Wen-Su Hsu, and Wen-Hsiung Lin, J. Mol. Catal. A: Chem. **109**, 249 (1996).
14. Wen-Hsiung Lin, Chien-Yao Hwang, and Hsin-Fu Chang, Appl. Catal. A: Gen. **162**, 71 (1997).
15. Soo-Jin Park and Jun-Sik Shin, J. Porous Mater. **11**, 15 (2004).

16. Frank L. Y. Lam and Xijun Hu, Chem. Eng. Sci. **58**, 687 (2003).
17. Yu. N. Zhitnev, E. A. Tveritinova, and V. V. Lunin, Zh. Fiz. Khim. **82**, 157 (2008) [Russ. J. Phys. Chem. A **82**, 140 (2008)].
18. L. I. Trakhtenberg, G. N. Gerasimov, V. K. Potapov, et al., Vestn. Mosk. Univ., Ser. Khim. **42**, 325 (2001).
19. Ching-Shiun Chen, Jarrn-Horng Lin, Tzu-Wen Lai, and Bao-Hui Li, J. Catal. **263**, 155 (2009).
20. N. Ravasio, F. Zaccheria, M. Gargano, et al., Appl. Catal. A **233**, 1 (2002).
21. Yuwang Han, Jianyi Shen, and Yi Chen, Appl. Catal. A: Gen. **205**, 79 (2001).
22. Feg-Wen Chang, Wen-Yao Kuo, and Kuen-Chan Lee, Appl. Catal. A: Gen. **246**, 253 (2003).
23. Masound Salavati-Niasari, Fatemeh Davar, and Noshin Mir, Polyhedron. **27**, 3514 (2008).
24. J. Romann, V. Chevallier, A. Merlen, and J.-Ch. Valmalette, J. Phys. Chem. C **113**, 5068 (2009).