ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 6, pp. 851–854. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.R. Zurnachyan, Kh.V. Manukyan, S.L. Kharatyan, V.A. Matyshak, R.A. Mnatsakanyan, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 6, pp. 873–876.

New Isopropanol Dehydration Catalyst Based on Tungsten Carbide Prepared by Modified Self-Propagating High-Temperature Synthesis

A. R. Zurnachyan[a], Kh. V. Manukyan[a, b], S. L. Kharatyan[a, b], V. A. Matyshak[c], and R. A. Mnatsakanyan[a]

[a] *Nalbandyan Institute of Chemical Physics, Academy of Sciences of Armenia, Yerevan, 0014 Armenia*
[b] *Yerevan State University, Yerevan, 0025 Armenia*
[c] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia*
e-mail: rmnats@rambler.ru

Received July 13, 2010

Abstract—The W_2C/C catalytic system with a high specific surface area (55 m^2/g) was synthesized for the first time using modified self-propagating high-temperature synthesis (SHS). The bulk and surface properties of the synthesized system were characterized using physicochemical methods and a model reaction of isopropanol conversion. It was found that the conversion of the alcohol with 100% selectivity occurs in the direction of dehydration with the formation of propylene and water. It was shown that active centers are the W(VI) surface ions of the carbide, whose activity is higher than the activity of tungsten as a constituent of the phase of WO_3.

DOI: 10.1134/S0023158411060231

INTRODUCTION

Because of its unique properties, tungsten carbide has a wide range of applications as a tool material, jewelry material, heterogeneous catalyst, electrocatalyst, etc. It is well known [1] that tungsten carbides have an isoelectronic structure with platinum; because of this, they are catalytically active in the reactions in which platinum systems are active. This fact explains interest in the development of new methods for the preparation of catalytic systems on their basis. In recent years, in addition to traditional methods [2] for the preparation of tungsten carbide, new methods [3, 4] have been proposed for the production of carbides with high specific surface area and porosity [5] and a specified phase composition [6] or a specific surface structure [7]. Previously [8, 9], we proposed a procedure for the preparation of nanosized tungsten carbides using modified self-propagating high-temperature synthesis (SHS). Traditionally, transition metal carbides are prepared by the SHS method from a mixture of powdered metal and carbon (graphite or carbon black). In spite of a number of advantages [10–12] (low energy intensity, high productivity, and purity of the resulting products), the main disadvantage of the SHS method for the preparation of catalysts is the extremely low specific surface area of products because of the high temperature of the synthesis (1500–3000°C).

The SHS method proposed [8, 9] consists in the preliminary impregnation of carbon (in particular, of Vulcan XC-72R grade) with soluble peroxo complexes of tungsten, which increases contact between the molecules of the peroxo complex and the surface atoms of coal. This improves the homogeneity of the initial mixture and accelerates the reaction of combustion. As compared with soluble tungstates, the use of the peroxo complexes affords more homogeneous and finely grained carbides. With the use of this method, unsupported and carbon-supported WC and W_2C with submicron particle sizes and high specific surface areas were prepared. Note that the pure tungsten carbide W_2C was obtained for the first time with the use of the above-mentioned method under combustion conditions.

The catalytic conversion of isopropanol was considered as a model reaction, which makes it possible to determine [13] the acid–base or redox nature of the active centers of the carbide surface. In this work, the conversion of isopropanol was performed in the presence of a 40% W_2C/C sample. The sample of this composition is characterized by a maximum specific surface area and the presence of only the phase of W_2C as a catalyst constituent.

EXPERIMENTAL

To synthesize tungsten nanocarbide supported on carbon, we used the modified SHS method [8], which includes several stages:

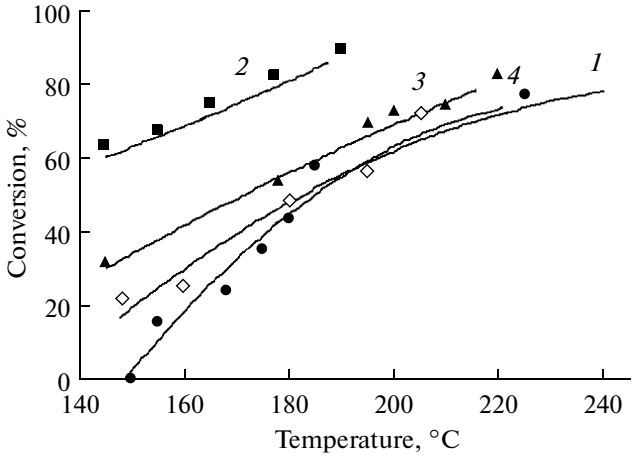

Fig. 1. The temperature dependence of the conversion of isopropanol on (*1*) γ-Al_2O_3, (*2*) 40% W_2C/C, (*3*) 40% W_2C/C (140°C; 40 min in air), and (*4*) 40% W_2C/C (140°C; 80 min in air).

(1) dissolution of tungsten metal or tungsten carbide (ATI Alldyne, WC-I) in a 15% solution of hydrogen peroxide to obtain a peroxo complex of tungsten;

(2) supporting of the peroxo complex from the solution on Vulcan XC-72R carbon with high electrical conductivity (specific surface area of 250 m^2/g) to obtain 40% W_2C/C;

(3) drying of the resulting mixture at 120°C and calcination at 250°C;

(4) mixing with magnesium powder in a molar ratio of WO_3 : 3Mg;

(5) SHS process performed in argon at 20 atm;

(6) washing with hydrochloric acid and drying.

The structure of carbide phases was studied by X-ray diffraction (XRD) analysis on a DRON-3 diffractometer with the use of CuK_α radiation. The X-ray photoelectron spectra (XPS) were measured on an XSAM-800 spectrometer with the use of MgK_α radiation (1253.6 eV). The binding energy (E_b) of W_{4f} was determined from the position of its lines relative to the C_{1s} line (E_b = 284.2 eV), which belongs to the carbon support (internal standard). Before the measurement of the spectra, the samples were kept in a high vacuum for 180 min. The surface concentration of tungsten was calculated taking into account the integrated line intensity with the use of photoionization cross section [14].

The specific surface areas of the samples were measured by the BET method using the adsorption of nitrogen on a Gazometr-1 instrument. The specific surface area of the 40% W_2C/C supported catalyst was 55 m^2/g.

The catalytic conversion of isopropanol was determined in a flow system with a quartz reactor (the catalyst sample weight was 0.17 g) at atmospheric pressure and an alcohol partial pressure of 33 Torr. An LKhM-80 chromatograph with a thermal conductivity detector and Reoplex/Chromaton N-AW and Polysorb-1 columns 3 m in length with an inside diameter of 3 mm was used for analysis. Helium was used as a carrier gas (40 ml/min); the column oven temperature was 80°C. Before passing the alcohol vapor, tungsten carbide in the reactor was blown with high-purity helium at a temperature of 250°C for 2 h.

For comparison, the activity of γ-Al_2O_3 (Rhône Poulenc; specific surface area of 200 m^2/g) and tungsten trioxide (specific surface area of 3.5 m^2/g) was measured under analogous conditions; the catalyst sample weight was 0.17 g.

RESULTS AND DISCUSSION

It is well known that the conversion of isopropanol in the presence of heterogeneous catalysts can occur via two reaction paths: dehydration with the formation of propylene and water or dehydrogenation with the formation of acetone and hydrogen. The former reaction path is usually related to the presence of acid sites on the catalyst surface, whereas the latter is related to the occurrence of redox or basic sites [15, 16]. It is well known that isopropanol is mainly converted into acetone and hydrogen on metallic and semiconductor catalysts. Based on the fact that tungsten carbide and carbon are conductors, it was possible to assume that the reaction occurs with the formation of acetone in the presence of tungsten carbide. However, our experiments showed that the conversion of isopropanol in the presence of 40% W_2C/C occurs toward the formation of propylene and water with 100% selectivity. Figure 1 (curve *2*) shows the temperature dependence of the degree of conversion of the alcohol on 40% W_2C/C.

Because aluminum oxide is considered as a typical catalyst for isopropanol dehydration [17], we compared the activity of the carbide catalyst with the activity of γ-Al_2O_3 (Fig. 1, curve *1*). It can be seen that the activity of the carbide catalyst is higher than the activity of aluminum oxide by a factor of 2–3 over the entire temperature range. Figure 1 shows the temperature range in which reproducible data were obtained.

According to available data [18, 19], the catalytic activity in isopropanol dehydration on γ-Al_2O_3 and mixed oxide systems is proportional to the total surface acidity determined by the adsorption of ammonia or *n*-butylamine. Alvarez-Merino et al. [20] obtained an analogous correlation for the conversion of isopropanol on tungsten carbide; they determined the total acidity by the adsorption of ammonia. It is reasonable to assume that the activity of a carbide catalyst is caused by the presence of an oxide phase with acid sites on the carbide surface. To determine the nature of active centers on the synthesized tungsten carbide, we

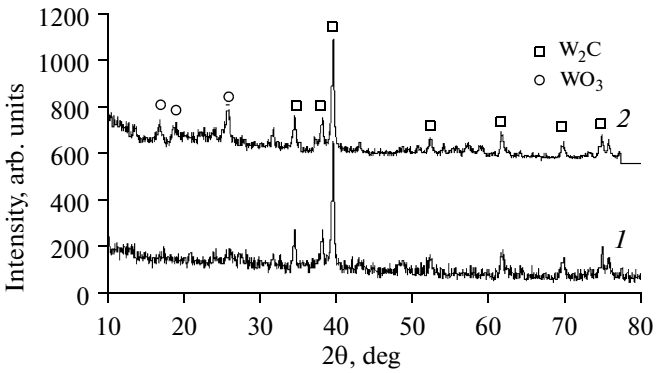

Fig. 2. Diffraction patterns of 40% W_2C/C (*1*) before oxidation and (*2*) after oxidation at 140°C for 40 min.

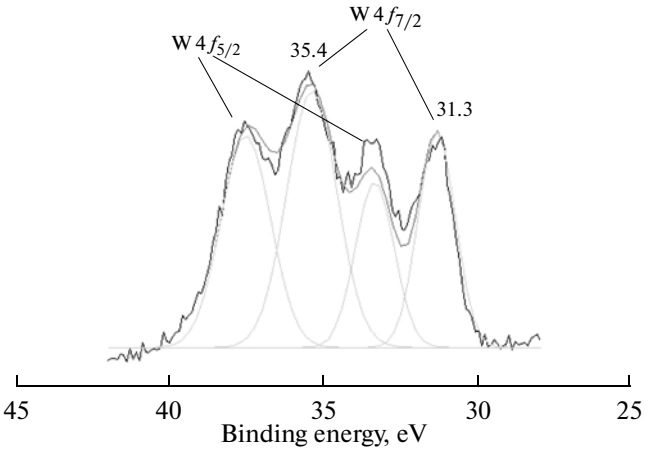

Fig. 3. X-ray photoelectron spectrum of a freshly prepared sample.

performed the mild oxidation of its surface in this work. After the first testing of a fresh catalyst in the specified temperature range (Fig. 1, curve *2*), the catalyst was treated with air at a temperature of 140°C for 40 min. Figure 1 (curve *3*) indicates that the conversion of isopropanol decreased after this treatment. The repeated treatment with air under the same conditions led to an even greater decrease in the conversion (Fig. 1, curve *4*).

Kirakosyan et al. [8] found that tungsten carbide obtained by the above method is nanosized. Therefore, the above effect oxygen on the activity is because tungsten nanocarbide is oxidized at sufficiently low temperatures unlike bulk tungsten carbide, which possesses high thermal stability to oxidation. A study of the effect of oxidation on the phase composition of tungsten carbide showed that a tungsten oxide phase is formed in this case, as evidenced by the appearance of a corresponding wide reflection line in the diffraction pattern (Fig. 2b). These results suggest that the passivation of the catalyst is related to the appearance of tungsten oxide on the carbide surface. To confirm this assumption, we investigated the conversion of isopropanol in the presence of tungsten trioxide ($S_{sp} = 3\ m^2/g$). The reaction was performed under the conditions described above. Indeed, in this case, the conversion of isopropanol into propylene came into play at 280°C, and it was as low as 20% at 300°C. This means that WO_3 is inferior to both tungsten carbide and γ-Al_2O_3 in terms of activity.

Figure 3 shows the XPS spectrum of freshly prepared 40% W_2C/C. It can be seen that W(VI) was present on the sample surface from the very beginning to the preliminary oxidation. Comparing Fig. 2a with Fig. 3, we can hypothesize that oxidized tungsten was initially present as isolated ions stabilized by interstitial oxygen atoms in the carbide rather than as an individual oxide phase [21]. This was supported by the presence of corresponding W(VI) lines in the XPS spectrum and the absence of lines due to the tungsten oxide phase from the diffraction pattern. Oxidation with air led to the appearance of reflection lines from the tungsten oxide phase in the diffraction pattern (Fig. 2b), a decrease in the W(0)/W(VI) ratio from 0.61/1 to 0.54/1, and a decrease in the activity. Note that oxidation even at a low temperature did not lead to the appearance of tungsten in intermediate oxidation states: tungsten immediately changed from the state W(0) (in tungsten carbide) to the state W(VI) (in tungsten trioxide).

The experimental results show that two types of W(VI) can coexist in the synthesized carbide: one as the constituent of a carbide phase with interstitial oxygen and the other as the constituent of tungsten trioxide. The former is stabilized by surface oxygen, and the latter is formed upon additional oxidation. An increase in the concentration of W(VI) of the second type leads to the loss of activity; therefore, it is possible to consider that W(VI) of the first type is responsible for the catalytic conversion of isopropyl alcohol into propylene and water. The occurrence of this type of centers is related to stabilization with surface oxygen, which is strongly bound to the lattice of tungsten carbide [21]. As a result, strong acid sites are formed on the surface and the chemisorption of ammonia occurs at these sites [22].

ACKNOWLEDGMENTS

We are grateful to ATI Alldyne and Cabot Corporation for gratuitously providing us with tungsten carbide and carbon, respectively.

REFERENCES

1. Oyama, S., T, *Catal. Today*, 1992, vol. 15, p. 179.
2. Medeiros, F.F.P., Oliveira, S.A., De Souza, C.P., and Da Silva, A.G.P., *Mater. Sci. Eng., A*, 2001, vol. 315, nos. 1/2, p. 58.
3. Borovinskaya, I.P., Ignat'eva, T.I., Vershinnikov, V.I., and Sachkova, N.V., *Inorg. Mater.,* 2004, vol. 40, no. 10, p. 1043.
4. Löfberg, A., Seyfried, L., Blehen, P., Decker, S., Bastin, J.M., and Frennet, A., *Catal. Lett.*, 1995, vol. 33, p. 165.
5. US Patent 4667068.
6. Zalite, I., Grabis, J., and Angerer, P., *Powder Metall. Met. Ceram.*, 2008, vol. 47, p. 11.
7. Weigert, E.C., Zellner, M.B., Stottlemyer, A.L., and Chen, J.G., *Top. Catal.*, 2007, vol. 46, p. 349.
8. Kirakosyan, Kh.G., Manukyan, Kh.V., Kharatyan, S.L., and Mnatsakanyan, R.A., *Mater. Chem. Phys.,* 2008, vol. 110, p. 454.
9. Manukyan, Kh.V., Zurnachyan, A.R., Kharatyan, S.L., and Mnatsakanyan, R.A., *Int. J. SHS*, 2011, vol. 20, no. 1, p. 1.
10. Merzhanov, A.G., *Combustion and Plasma Synthesis of High-Temperature Materials*, Munir, Z.A. and Holt, J.B., Eds., New York: VCH, 1990, p. 1.
11. Merzhanov, A.G., *J. Mater. Process. Technol.*, 1996, vol. 56, p. 222.
12. Abovyan, L.S., Nersisyan, H.H., and Kharatyan, S.L., *Chem. Phys. Rep.*, 1995, vol. 13, no. 10, p. 1740.
13. Turek, W., Stochmal-Pomarzanska, E., Pron, A., and Haber, J., *J. Catal.*, 2000, vol. 189.
14. Scoffield, J.H., *J. Electron Spectrosc. Relat. Phenom.*, 1979, vol. 17, p. 275.
15. Krylov, O.V., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Akademkniga, 2004.
16. Turek, W., Haber, J., and Krowiak, A., *Appl. Surf. Sci.*, 2005, vol. 252, no. 3, p. 823.
17. Jagdish Rai Jain and Pillai, C.N., *J. Catal.,* 1967, vol. 9, p. 322.
18. Jayamani, M., Viswanathan, B., and Pillai, C.N., *J. Catal.*, 1984, vol. 89, p. 560.
19. Berteau, P. and Delmon, B., *Catal. Today*, 1989, vol. 5.
20. Alvarez-Merino, M.A., Carrasco-Marin, F., Fierro, J.L.G., and Moreno-Castilla, C., *J. Catal.*, 2000, vol. 192, p. 363.
21. Muller, A., Keller, V., Ducros, R., and Maire, G., *Catal. Lett.*, 1995, vol. 35, p. 65.
22. Ribeiro, F.H., Dalla Betta, R.A., Guskey, G.J., and Boudart, M., *Chem. Mater.*, 1991, vol. 3, p. 805.