ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 3, pp. 409–413. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © A.V. Vosmerikov, G.V. Echevskii, L.L. Korobitsyna, N.V. Arbuzova, E.G. Kodenev, L.M. Velichkina, C.P. Zhuravkov, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 3, pp. 432–437.

Nonoxidative Methane Conversion into Aromatic Hydrocarbons on Tungsten-Containing Pentasils

A. V. Vosmerikov[a], G. V. Echevskii[b], L. L. Korobitsyna[a], N. V. Arbuzova[a], E. G. Kodenev[b], L. M. Velichkina[a], and C. P. Zhuravkov[c]

[a] *Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk, 634021 Russia*
[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[c] *Institute of Strength Physics and Materials Science, Siberian Branch, Russian Academy of Sciences, Tomsk, 634021 Russia*
e-mail: pika@ipc.tsc.ru

Received June 17, 2005

Abstract—The effects of the tungsten concentration and of the method of tungsten introduction into ZSM-5 pentasils with different SiO_2/Al_2O_3 molar ratios on the acidity and the activity of the resulting catalysts in nonoxidative methane conversion into aromatic hydrocarbons are considered. The catalysts obtained from the SiO_2/Al_2O_3 = 40 pentasil and a nanosized tungsten powder are the most active and the most stable. The maximum methane conversion and the highest yield of aromatic hydrocarbons are achieved on the zeolite containing 8.0 wt % tungsten nanopowder.

DOI: 10.1134/S002315840703010X

INTRODUCTION

Recently, researchers have given considerable attention to studies of methane dehydroaromatization (DHA) under nonoxidative conditions on zeolite catalysts modified with transition metal ions as a promising method of natural gas conversion to valuable chemical products. Zeolites of the pentasil-type (ZSM-5 zeolites) modified with molybdenum and tungsten were found to be the most efficient in this reaction [1–3]. The W/ZSM-5 catalysts have several advantages over the Mo-containing pentasils due to their higher thermal stability and carburizing resistance at high temperatures [4]. At the same time, systematic studies of the W-containing pentasils have been begun quite recently and, as a consequence, very limited data characterizing the activity of these catalysts in methane conversion and the influence of different factors on their properties are available from the literature.

The purpose of the present work is to study the influence of the method of W introduction into the zeolite matrix and of the catalyst composition on the acidic properties and activity of the catalyst in methane dehydroaromatization.

EXPERIMENTAL

Zeolite ZSM-5 with SiO_2/Al_2O_3 (M) equal to 40, synthesized at the Boreskov Institute of Catalysis (Siberian Branch, Russian Academy of Sciences, Novosibirsk), and pentasils with M = 30, 60, and 80 were used for catalyst preparation. Catalyst samples were prepared as follows:

(1) WP-1, by mechanical mixing in a vibrating mill (2 h) of a zeolite powder with a nanosized powder (NSP) of W prepared by electroexplosion of a metallic wire in argon [5];

(2) WP-2, by mechanical mixing in a vibrating mill (2 h) of a zeolite powder with WO_3 (reagent grade);

(3) WP-3, by zeolite impregnation with an aqueous solution of ammonium tungstate $(NH_4)_{10}W_{12}O_{41} \cdot H_2O$ acidified with H_2SO_4 to pH 2;

(4) WP-4, by mechanical mixing in a vibrating mill (2 h) of a zeolite powder with dry $(NH_4)_{10}W_{12}O_{41} \cdot H_2O$.

The calculated tungsten content of the catalysts prepared by methods (1–4) was 4.0 wt %.

Catalysts with different tungsten contents were prepared by mechanical mixing in a vibrating mill of the M = 40 zeolite and the nanosized W powder (3.0–10.0 wt %).

Samples with SiO_2/Al_2O_3 = 30–80 (mol/mol) containing 8.0 wt % W NSP were prepared by mechanical mixing to estimate the effect of the M value on the properties of the W/ZSM-5 catalysts.

All catalyst samples were treated with air at 550°C (5 h) and pressed into pellets. The 0.25–0.50 mm fraction was used in the studies.

The catalytic properties of the W/ZSM-5 samples were studied in a flow reactor at 750°C; a methane space velocity of V_s = 500, 1000, and 1500 h^{-1}; and atmospheric pressure. A catalyst sample (1.0 cm^3) was placed in a quartz reactor 12 mm in diameter. Before the reaction, the catalyst was heated in flowing helium to 750°C and was held at this temperature for 10–20 min. Thereafter, methane (99.9%) was fed. The first

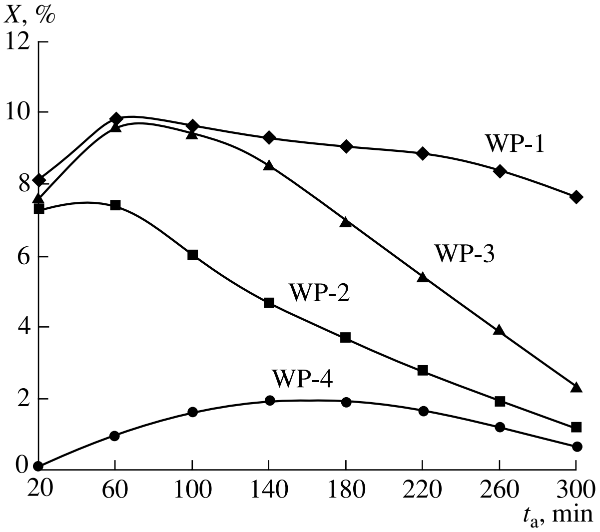

Fig. 1. Changes in the methane conversion during DHA on the pentasil (M = 40) modified with tungsten (4.0%) using different methods (T = 750°C, V_s = 1000 h^{-1}).

GC analysis of the methane conversion products was carried out after 20 min. Analyses were made at 40-min intervals over 300–340 min. The experimental and product analysis procedures are detailed elsewhere [6].

The acidic properties of the samples were studied by temperature-programmed thermal desorption (TPD) of ammonia. This made it possible to determine the acid site strength distribution and the number of acid sites [7].

RESULTS AND DISCUSSION

The methane conversion curves for W pentasils prepared by different methods are presented in Fig. 1. The catalyst prepared by zeolite mixing with the nanosized W powder exhibited the highest activity. With this catalyst, the methane conversion reached its maximum (9.8%) in 60 min and then gradually decreased. The catalyst obtained by zeolite impregnation with an acidified solution of $(NH_4)_{10}W_{12}O_{41}$ was somewhat less active, and the lowest activity was observed for the catalyst prepared by dry mixing of the zeolite with ammonium paratungstate.

The results of investigating the effect of the method of W introduction into the zeolite on the yield of the major liquid products of methane conversion (benzene and naphthalene) are presented in Table 1. The largest amount of aromatic hydrocarbons (ArH) is formed on the catalyst containing the nanosized W powder at a gas space velocity of 500 h^{-1}. After catalyst development for 60 min, the yield of the aromatic products (~10%) is invariable for another 160 min, and then the ArH concentration begins to gradually decrease. Similar values of the ArH yield for 60-min operation were obtained on the catalyst prepared by pentasil impregnation. As the on-stream time of this catalyst (t_a) was extended, the yield of ArH decreased more sharply as compared to that for the WP-1 catalyst. For the WP-2 and WP-4 catalysts, the products contained substantially smaller amounts of benzene and naphthalene. For instance, the highest yield of the arenes on the WP-2 sample after 100-min operation was ~5% at V_s = 500 h^{-1}, whereas, on the WP-4 catalyst, the maximum amount of ArH

Table 1. Influence of the method of W introduction and of the on–stream time on the benzene and naphthalene yields during methane DHA at different space velocities (V_s) of methane (T = 750°C)

V_s, h^{-1}	Sample	On-stream time, min															
		20		60		100		140		180		220		260		300	
		Yield, %															
		C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$	C_6H_6	$C_{10}H_8$
500	WP-1	2.87	2.21	5.49	3.79	5.68	4.24	5.88	4.34	6.06	3.94	6.13	3.77	5.68	3.35	4.88	2.70
	WP-2	0.02	0.03	1.49	1.56	1.59	3.39	1.42	2.70	1.23	2.63	1.07	2.27	0.73	0.71	0.51	1.13
	WP-3	2.78	2.26	4.78	4.30	4.94	4.67	5.02	4.65	3.97	4.23	3.84	3.88	3.39	3.15	2.79	2.82
	WP-4	0	0	0.07	0.19	0.40	0.96	0.47	1.29	0.70	1.31	0.61	1.25	0.48	1.08	0.27	0.86
1000	WP-1	2.84	2.82	4.67	3.05	4.46	2.86	4.24	2.63	4.07	2.58	3.97	2.46	3.62	2.34	3.20	2.01
	WP-2	2.14	3.64	2.18	3.74	1.48	2.29	1.24	1.57	1.02	1.17	0.57	0.68	0.24	0.31	–	–
	WP-3	3.11	3.17	3.91	3.63	3.64	3.48	3.45	3.17	2.51	2.45	1.68	1.45	0.80	0.76	0.36	0.40
	WP-4	0	0	0.06	0.26	0.23	0.95	0.27	1.11	0.27	1.04	0.25	0.65	0.10	0.25	–	–
1500	WP-1	3.29	1.92	2.68	1.54	1.96	1.16	1.48	0.79	0.84	0.55	0.74	0.49	–	–	–	–
	WP-2	0.83	1.61	0.87	2.51	0.52	2.22	0.50	1.33	0.22	0.70	–	–	–	–	–	–
	WP-3	0.93	0.88	1.20	1.06	0.95	0.84	0.80	0.76	0.55	0.50	0.31	0.30	–	–	–	–
	WP-4	0.03	0.05	0.07	0.18	0.10	0.71	0.09	0.62	–	–	–	–	–	–	–	–

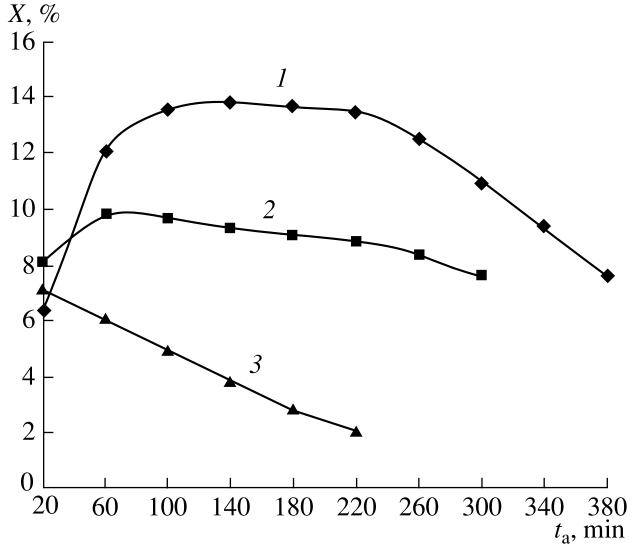

Fig. 2. Changes in methane conversion during DHA at 750°C on the 4.0% W(NSP)/ZSM-5 catalyst at V_s = (*1*) 500, (*2*) 1000, and (*3*) 1500 h^{-1}.

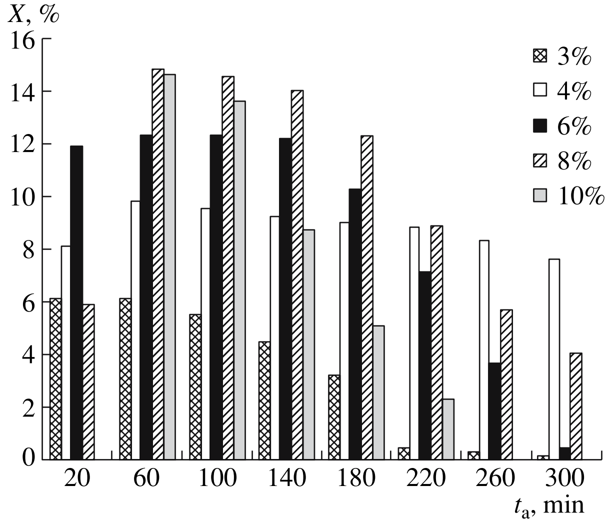

Fig. 3. Diagram of the changes in methane conversion during DHA on the pentasils (*M* = 40) containing different amounts of W NSP (*T* = 750°C, V_s = 1000 h^{-1}).

(2%) was obtained after 180 min. The highest yield of benzene on the WP-3 catalyst was 5.0%, and that on the WP-2 and WP-4 samples was 1.6 and 0.7%, respectively. At V_s = 1000 h^{-1}, the largest amount of benzene during the first 20 min of the reaction is formed on the WP-3 catalyst. However, as t_a is further extended, much more benzene is formed on the zeolite containing the nanosized W powder and the naphthalene yield forming on the W-containing pentasils examined passes through a maximum. At the early stages of the reaction at space velocities of 500 and 1000 h^{-1}, considerably more naphthalene is formed on the WP-3 catalyst than on the WP-1 sample. As V_s is increased to 1500 h^{-1}, more benzene and naphthalene are formed on the WP-1 catalyst even after 20-min catalyst operation. The maximum yield of ArH at 1500 h^{-1} was observed for the WP-1 and WP-2 catalysts; for the latter, the naphthalene content of the reaction products exceeded considerably the benzene content.

Thus, our study showed that the activity, selectivity, and stability of the catalysts prepared by different methods differ substantially despite the fact that the same amount of tungsten was introduced into the pentasil. This is likely due to W being in different states in both the starting substances used for catalyst preparation and the catalytic systems obtained after calcination.

The results of studies of the dependence of the methane conversion on t_a of the WP-1 catalyst at different space velocities are presented in Fig. 2. The methane conversion increases with decreasing V_s. For example, the maximum conversion at V_s = 500 h^{-1} (13.8%) is achieved at t_a = 140 min; as the feed space velocity is increased to 1000 and 1500 h^{-1}, the conversion decreases to 9.8 and 7.3%, respectively. Both the catalyst preparation method and the reaction conditions substantially affect the induction period of DHA. The shortest induction period was observed for the WP-1 and WP-2 catalysts, and the WP-4 sample exhibited the longest induction period (Fig. 1). An increase in V_s shortens the induction period, and this effect is most pronounced for the WP-1 catalyst (Fig. 2). The maximum methane conversion time decreases from 140 min at 500 h^{-1} to 20 min at 1500 h^{-1}. The results obtained agree with the conclusion that the induction period is related to the formation of the WC_x phase as clusters upon the interaction of W with methane during the reaction [8]. The studies showed that the state of W and its distribution in the elements of the pentasil structure have a substantial effect on the formation rate of this phase. Tungsten carbide forms most rapidly on the pentasil modified by the nanosized W powder.

A diagram illustrating the influence of the nanosized W powder concentration in the pentasil on its catalytic activity and stability in methane DHA is shown in Fig. 3. It can be seen that the amount of the nanosized W powder introduced into the zeolite substantially affects the methane conversion and the duration of stable catalyst service. The methane conversion as a function of t_a passes through an extremum throughout the concentration range examined, and the maximum conversion is achieved in 60 min. The highest conversion (14.8%) and the longest duration of stable service (300 min) are achieved with the pentasil containing 8.0 and 4.0 wt % W NSP. A lower activity and stability were observed for the zeolites containing 3.0 and 6.0 wt % W. The 10.0% W/ZSM-5 catalyst was most active in the on-stream time interval from 60 to 100 min, after which its activity decreased sharply. The largest amount of benzene (6.2%) at t_a = 100 min was obtained with the catalyst

Table 2. Methane conversion on the 8.0% W/ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios (T = 750°C, V_s = 1000 h^{-1})

SiO_2/Al_2O_3, mol/mol	On-stream time, min								
	20	60	100	140	180	220	260	300	340
30	5.2	10.5	11.0	11.1	8.5	5.9	5.0	3.5	2.4
40	5.9	14.8	14.5	14.0	12.3	8.9	5.7	4.0	2.9
60	5.0	8.3	7.8	6.5	6.0	5.2	4.5	3.4	2.0
80	4.6	8.0	7.1	6.2	5.3	4.7	3.7	3.1	1.6

Table 3. Acidic characteristics of the pentasils with M = 40 containing different amounts of W NSP

W content, wt %	T_{max}, °C		Concentration, μmol/g		
	T_I	T_{II}	C_I	C_{II}	C
–	235	450	551	424	975
3.0	220	430	364	183	547
4.0	210	375	262	99	361
6.0	210	340	248	74	322
8.0	210	365	267	127	394
10.0	210	375	279	152	431

Note: T_I and T_{II} are the temperatures of the peaks for forms **I** and **II**; C_I, C_{II}, and C are the concentrations of acid sites in forms **I** and **II** and the total concentration, respectively.

containing 8.0% W NSP. The benzene content decreased and the naphthalene fraction increased with an increase in the W content of the zeolite to 10.0%. Thus, the pentasil containing 8.0 wt % W NSP is the most active and selective in benzene formation. The oxidative regeneration of the 8.0% W(NSP)/ZSM-5 catalyst did not restore its primary activity: the methane conversion and the yield of ArH in the second reaction cycle decreased by ~2 times. For instance, the conversion was 14.5 and 7.2% at t_a = 100 min before and after regeneration, while the conversion at t_a = 300 min was 4.0 and 2.2%, respectively.

The data obtained on the effect of the W concentration in the zeolite on the stability of its operation also show the presence of an induction period of the process. The catalysts with a high W content (8.0–10.0%) exhibit relatively low activity at V_s = 1000 h^{-1} over the first 20 min, which increases sharply after 60-min treatment with methane (Fig. 3). The catalysts with a lower W content (3.0–6.0%) are active already at the early stages of the reaction, and their activity increases to a lesser extent in the time interval of t_a = 60 min. As for the above described samples, the induction period of the reaction shortened with an increase in V_s, and at V_s = 1500 h^{-1} the maximum conversion on these catalysts was observed already at an on-stream time of 20 min. Thus, the induction period of the reaction depends on the method of catalyst preparation and process conditions, as well as on the composition of the W/pentasil system.

To confirm the above inference, we prepared the catalysts with different M values and the same amount of W NSP. It follows from the results presented in Table 2 that the SiO_2/Al_2O_3 = 40 zeolite manifests the highest activity; the closest conversion values were obtained for the catalyst with M = 30, and the W/pentasils with M = 60 and 80 were less active.

Nonoxidative methane conversion catalysts are bifunctional systems in which acid sites of the zeolite itself play an important role along with transition metals. For instance, there is an optimum Mo/[H^+] ratio for the Mo/ZSM-5 catalysts, which can be controlled by varying either the SiO_2/Al_2O_3 molar ratio or the amount of Mo added [9]. It is believed that Mo_2C carbide particles formed after the methane treatment are responsible for methane dehydrogenation and for the formation of C_2 fragments, whereas ethylene is oligomerized and benzene and other ArH are formed on the Brønsted acid sites in the zeolite channels. Furthermore, the number of Brønsted acid sites in the Mo/ZSM-5 catalyst depends strictly on its activity in benzene formation. For this reason, the acidic characteristics of the SiO_2/Al_2O_3 = 40 pentasil containing different amounts of W NSP and of the W/ZSM-5 catalysts with different M values were studied by ammonia TPD.

The data presented in Table 3 show that the introduction of W NSP into the pentasil decreases the concentration and strength of its acid sites. The shift of both peaks to lower temperature regions indicates that the strength of the acid sites decreases with increasing W NSP content of the zeolite from 1.0 to 6.0 wt %. The

Table 4. Acidic characteristics of the initial and W-containing pentasils with different M values

SiO_2/Al_2O_3, mol/mol	T_{max} of form, °C				Concentration, μmol/g					
	HZSM-5		8.0% W/HZSM-5		HZSM-5			8.0% W/HZSM-5		
	T_I	T_{II}	T_I	T_{II}	C_I	C_{II}	C	C_I	C_{II}	C
30	240	465	215	410	551	431	982	356	174	530
40	235	450	210	365	551	424	975	267	127	394
60	225	440	200	360	549	409	958	211	106	317
80	220	425	190	345	509	392	901	196	74	270

Note: T_I and T_{II} are the temperatures of the peaks for forms **I** and **II**; C_I, C_{II}, and C are the concentrations of acid sites **I** and **II**, and the total concentration, respectively.

concentration of acid sites of both types in these catalysts also decreases. The smallest number of acid sites is observed for the samples containing 6.0% W NSP and is 322 μmol/g, which is 2.8 times smaller than the number of acid sites in the initial pentasil. When 8.0 and 10.0% W NSP are added to the zeolite, the concentration of both types of acid sites increases and their strength is enhanced. The acidity decrease common for all pentasils upon W introduction into the pentasils can be explained by the formation of new acid sites containing tungsten atoms and by the formation of active forms on the outer surface of zeolite crystals at a relatively large amount of W introduced.

The introduction of W NSP into the pentasils leads to a noticeable shift of the high-temperature peaks to lower temperatures, indicating a decreased strength of the acid sites in the modified catalysts (Table 4). Furthermore, the concentration of acid sites decreases, particularly the concentration of strong sites. This change in the acidic characteristics of W/pentasils is likely caused by the fact that, upon calcination during catalyst preparation, the W atoms migrate into the zeolite pores, where they substitute for the bridging hydroxyl groups to form aprotic acid sites. In this case, as was shown by experiments, there is an optimum ratio between the amount of introduced W and the acid site concentration in the zeolite, at which the catalyst manifests the highest activity in methane DHA. The most efficient is the $SiO_2/Al_2O_3 = 40$ pentasil containing 8.0 wt % W NSP (in the catalysts, W/Al = 1 : 2). In addition, the method of W introduction into the zeolite is important for the preparation of the W/ZSW-5 catalysts. The most active catalyst samples were obtained with nanosized W powder, which is probably due to its more uniform distribution on the zeolite surface upon mechanical stirring and to its small particle size, facilitating its penetration into the zeolite channels during calcination and during the DHA reaction. Further studies using a complex of modern analytical methods are required to confirm these assumptions.

REFERENCES

1. Xu, Y. and Lin, L., *Appl. Catal., A*, 1999, vol. 188, p. 53.
2. Shu, Y. and Ichikawa, M., *Catal. Today*, 2001, vol. 71, p. 55.
3. Zhou, T., Lui, A., Mo, Y., and Zhang, H., *J. Phys. Chem. A*, 2000, vol. 104, p. 4505.
4. Zeng, J.-L., Xiong, Z.-Y., Zhang, H.-B., Lin, G.-D., and Tsai, K.R., *Catal. Lett.*, 1998, vol. 53, p. 119.
5. Gusev, A.I., *Nanokristallicheskie materialy: Metody polucheniya i svoistva* (Nanocrystalline Materials: Preparation and Properties), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1998.
6. Vosmerikov, A.V., Echevskii, G.V., Korobitsyna, L.L., Barbashin, Ya.E., Arbuzova, N.V., Kodenev, E.G., and Zhuravkov, S.P., *Kinet. Katal.*, 2005, vol. 46, no. 5, p. 769 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 5, p. 724].
7. Vosmerikov, A.V. and Erofeev, V.I., *Zh. Fiz. Khim.*, 1995, vol. 69, no. 5, p. 787.
8. Ding, W., Meitzner, G.D., Marler, D.O., and Iglesia, E., *J. Phys. Chem. B*, 2001, vol. 105, p. 3928.
9. Su, L., Xu, Y., and Bao, X., *J. Natur. Gas Chem.*, 2002, vol. 11, p. 18.