Journal of Engineering Physics and Thermophysics, Vol. 69, No. 1, 1996

EFFECTIVE THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF CATALYSTS AND THEIR SUPPORTS AS FUNCTIONS OF TEMPERATURE IN VARIOUS GASEOUS MEDIA AND IN VACUUM.
II. THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF GRANULATED POROUS CATALYSTS AS FUNCTIONS OF INTERNAL AND EXTERNAL FACTORS

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UDC 536.21

It is established in studies of the thermal conductivity λ and thermal diffusivity a of granulated porous catalysts and their supports that in gaseous mixtures λ and a for a catalyst load is determined by the properties of the main component of the mixture, and an increase in λ and a of catalysts under investigation is observed in the region of stresses that disintegrate the granules. The quantities λ and a of a load of a catalysts and support increase with increasing thermal conductivity of the filling gas, granule dimensions, concentration, and thermal conductivity of metallic additives. The values of λ and a of a catalyst load decrease linearly with increasing total volume of pores and specific surface.

Various fuels decompose during chemical reactions with catalysts in reactors into gas mixtures consisting of various components. In order to model processes that take place in reactors one should know the thermophysical properties of the catalysts in the atmosphere of the gas mixture created as a result of decomposition of the fuel. Taking this fact into consideration, we studied the thermal conductivity and thermal diffusivity of catalysts as functions of temperature in vacuum, various gaseous media, and in media of gaseous mixtures with various concentrations of components: $0.2\ NH_3 + 0.3\ N_2 + 0.5\ H_2$; $0.1\ NH_3 + 0.9\ N_2O$; $0.3\ NH_3 + 0.7\ N_2O$; $0.1\ N_2 + 0.9\ N_2O$; $0.2\ N_2 + 0.8\ N_2O$; $0.3\ N_2 + 0.7\ N_2O$; $0.05\ CO_2 + 0.95\ N_2O$; $0.1\ CO_2 + 0.9\ N_2O$; $0.15\ CO_2 + 0.85\ N_2O$.

Measurements were carried out within the temperature range of 293–1073 K at atmospheric pressure.

The data on the thermal conductivity and thermal diffusivity of a catalyst deposited on an N-1 support, which contains 20% ruthenium with granule dimensions of 0.8–2 mm, are presented in Tables 1, 2. According to the data, λ and a vary linearly with temperature, i.e., these dependences virtually repeat dependences of λ and a of catalysts for pure gases.

Investigations have shown that in gaseous mixtures that contain components with high thermal conductivity, the catalysts loads have high values of thermal conductivity and thermal diffusivity. For example, in a gaseous mixture that contains 50% hydrogen, the catalyst have the highest values of λ and a, as compared with other mixtures.

An investigation of the thermal conductivity and thermal diffusivity of catalyst in a gaseous mixture that containing nitrogen oxide as the main component has shown that the addition of a component with a high molecular weight leads to insignificant changes in λ and a of the catalysts. For example, in a mixture of $0.3\ NH_3 + 0.7\ N_2O$, the thermal conductivity of a catalyst deposited on an N-4 support that contains 0.5% platinum and 0.5% iridium with granule dimensions of 2–4 mm increases at a temperature of 293 K from 0.160 W/(m·K) (in nitrogen oxide) to 0.180 W/(m·K). At the same time, in a $0.3\ N_2 + 0.7\ N_2O$ mixture, $\lambda = 0.168$ W/(m·K).

K. Dzhuraev Pedagogical University, Dushanbe, Tadjikistan. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 1, pp. 141-150, January-February 1996. Original article submitted October 25, 1994; revision submitted April 4, 1995.

1062-0125/96/6901-0120$15.00

TABLE 1. Thermal Conductivity ($\lambda \cdot 10^3$, W/(m·K) of a Catalyst on N-1 Support Containing 20% Ruthenium with Granule Sizes of 0.8–2 mm as a Function of the Temperature of the Gaseous Mixture.

Gaseous mixture			Gaseous mixture							
T, K	$0,2NH_3 + 0,3 N_2 + 0,5 H_2$	$0,3NH_3 + 0,7N_2O$	T, K	$0,1NH_3 + 0,9N_2O$	$0,1N_2 + 0,9N_2O$	$0,2N_2 + 0,8N_2O$	$0,3N_2 + 0,7N_2O$	$0,05CO_2 + 0,95N_2O$	$0,1CO_2 + 0,9N_2O$	$0,15CO_2 + 0,85N_2O$
296,2	311	224	295,3	215	204	205	208	202	199	197
369,5	329	240	457,2	250	234	240	235	230	235	230
488,9	360	270	620,3	285	267	270	268	264	267	265
582,1	383	300	703,3	306	288	290	287	283	284	286
660,0	400	318	812,4	330	307	305	309	304	309	306
779,2	428	340	935,9	356	324	331	336	327	333	339
866,1	449	365	1055,7	390	354	359	363	353	363	368
981,2	470	398								

TABLE 2. Thermal Diffusivity ($a \cdot 10^4$, m^2/sec) of a Catalyst on N-1 Support Containing 20% Ruthenium with Granule Sizes of 0.8–2 mm as a Function of the Temperature of the Gaseous Mixture.

Gaseous mixture			Gaseous mixture							
T, K	$0,2NH_3 + 0,3N_2 + 0,5H_2$	$0,3NH_3 + 0,7N_2O$	T, K	$0,1NH_3 + 0,9N_2O$	$0,1N_2 + 0,9N_2O$	$0,2N_2 + 0,8N_2O$	$0,3N_2 + 0,7N_2O$	$0,05CO_2 + 0,95N_2O$	$0,1CO_2 + 0,9N_2O$	$0,15CO_2 + 0,85N_2O$
295,1	2,77	1,93	297,1	1,86	1,79	1,80	1,81	1,75	1,77	1,73
338,9	2,87	2,05	431,5	2,00	1,88	1,87	1,88	1,86	1,84	1,87
520,1	2,97	2,17	579,5	2,15	2,00	2,04	1,99	1,96	1,96	1,95
691,5	3,12	2,36	709,9	2,29	2,13	2,14	2,15	2,08	2,12	2,08
796,2	3,23	2,42	835,1	2,39	2,20	2,17	2,24	2,20	2,17	2,20
873,5	3,27	2,55	965,2	2,50	2,28	2,33	2,35	2,39	2,32	2,34
972,6	3,31	2,66	1070,7	2,64	2,39	2,42	2,40	2,31	2,40	2,42
1070,2	3,46	2,72								

In mixtures that contain nitrogen and nitrogen oxide, carbon dioxide, and nitrogen oxide, variations in the N_2 concentration of from 10 to 30% and in the CO_2 concentration of from 5 to 15% barely affect the thermal conductivity and thermal diffusivity of the catalysts within the entire temperature range, as compared with an atmosphere of nitrogen oxide (see curve 3, Fig. 1).

Thus, thermal conductivity and thermal diffusivity of catalysts in binary mixtures are determined by the properties of the main component. In a gas mixture that contains ammonia and nitrogen oxide, the values of λ and a increase with ammonia content.

Using the experimental installations shown in Figs. 2 and 3 we measured the thermal conductivity and thermal diffusivity of catalysts containing 30% nickel and 13% irridium on an N-1 support within the temperature range of 293–673 K in an atmosphere of saturated vapor with a pressure of from $0.02 \cdot 10^5$ to $56 \cdot 10^5$ Pa. The measurements were carried out for loose loading.

The experimental installations consist of a cylindrical bicalorimeter and a cylindrical acalorimeter, a vessel for production of saturated vapor at various temperatures and pressures, a tube for liquid filling, an evacuation system, a system for gas filling, and an electric measuring system. These installations make it possible to measure the thermal conductivity and thermal diffusivity of granulated and powdered materials under saturated-vapor pressure and in an atmosphere of pure gases as functions of temperature and pressure.

The main characteristics and thermophysical properties of the objects under investigation at a temperature of 293 K are presented in Table 3.

The experimentally obtained values of thermal conductivity of the catalyst loads under investigation are listed versus the temperature and saturated-vapor pressure in Table 4. According to the table, the thermal conductivity and thermal diffusivity of the objects under investigation increase with temperature and saturated-vapor pressure.

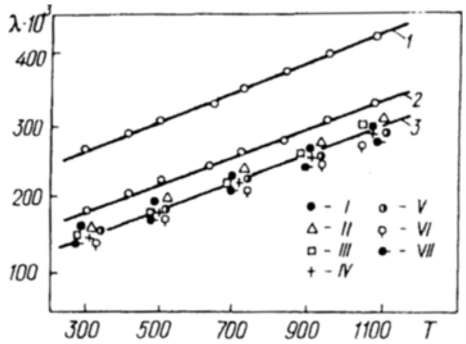

Fig. 1. Thermal conductivity of load of catalyst on N-4 support containing 0.5% platinum and 0.5% iridium with granule sizes of 2–4 mm as a function of temperature in mixtures of gases: 1) 0.2 NH_3 + 0.3 N_2 + 0.5 H_2; 2) 0.3 NH_3 + 0.7 N_2O; 3: I) 0.1 NH_3 + 0.9 N_2O; II) 0.1 N_2 + 0.9 N_2O; III) 0.2 N_2 + 0.8 N_2O; IV) 0.3 N_2 + 0.7 N_2O; V) 0.05 CO_2 + 0.95 N_2O; VI) 0.1 CO_2 + 0.9 N_2O; VII) 0.15 CO_2 + 0.85 N_2O. λ, W/(m·K); T, K.

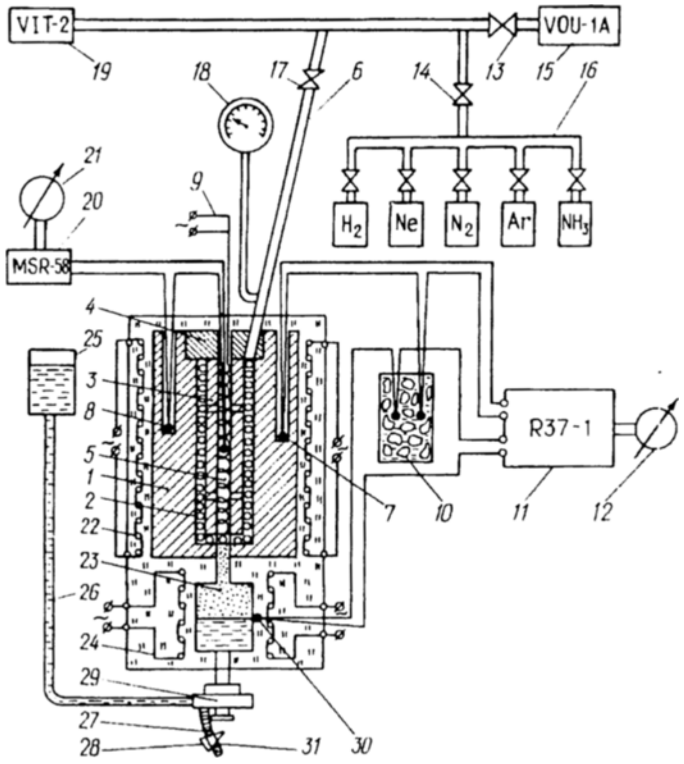

Fig. 2. Experimental setup for measurement of thermal conductivity of granulated catalysts under saturated-vapor pressure in various gaseous media: 1) external cylinder of cylindrical bicalorimeter; 2) internal cylinder (core of bicalorimeter); 3) compensation cylinders; 4) stopper; 5, 6) tubes; 7, 8, 30) thermocouple junctions; 9) electric heater; 10) thermos with melting ice; 11) potentiometer; 12, 21) mirror galvanometers; 13, 14, 17, 29) valves; 15) exhaust unit; 16, 26, 27) pipelines; 18) manometer; 19) vacuum meter; 20) resistance box; 22, 24) electric ovens; 23) vessel for production of saturated vapor; 25) cup; 28) pinch-cock; 31) rubber pipe.

The thermal conductivity and thermal diffusivity of several catalysts were studied as functions of mechanical stress.

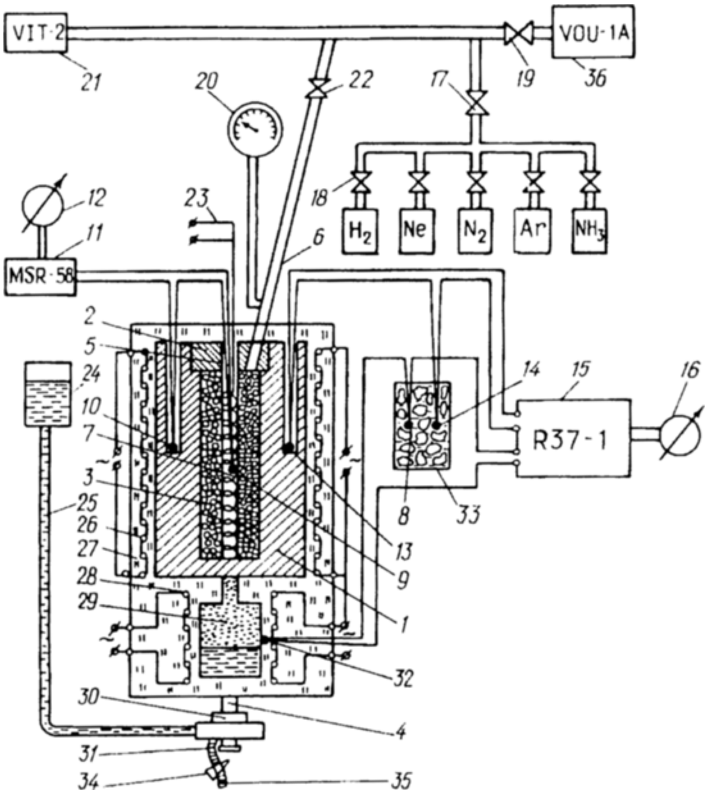

Fig. 3. Experimental setup for measurement of thermal diffusivity of granulated catalysts under saturated-vapor pressure in various gaseous media: 1) acalorimeter; 2, 15) stoppers; 3) object under investigation; 4, 25, 31) pipelines; 5, 6) tubes; 7) cylindrical hole; 8, 9, 10, 13, 14, 32) thermocouple junctions; 11) resistance box; 12, 16) mirror galvanometers; 15) potentiometer; 17, 18, 19, 22, 30) valves; 20) manometer; 21) vacuum meter; 23) electric heater; 24) cup; 26, 28) electric ovens; 27) thermoinsulator; 29) vessel for production of saturated vapor; 33) thermos with melting ice; 34) pinch-cock; 35) rubber pipe.

In order to study the effective thermal conductivity of catalyst loads in air as a function of mechanical stress we built an experimental setup based on the cylindrical bicalorimeter (Fig. 4). The bicalorimeter consists of an outer copper cylinder 90 mm in diameter in which a cylindrical cavity (1) 30 mm in diameter is drilled. A copper kernel 2 15 mm in diameter is introduced into the cavity. A thin steel tube 12 with guard cylinders 3 and a stopper 15 is placed in the center of the kernel. A low-power heater 4 and the hot junction of a measuring thermocouple 5 are inserted into the tube. The cold junction of a differential thermocouple 14 is mounted in a special hole drilled in the wall of the bicalorimeter. The lengths of the kernel and guard cylinders are 140 and 15 mm, respectively. The guard cylinders are separated from the kernel by a thin mica layer. The ends of the steel tube, which extend beyond the guard cylinders and the stopper 15, are used to center the kernel with respect to the internal cavity of the bicalorimeter. For compression of the sample under the action of external stress, a piston 6 is situated in the upper portion of the installation. The outer surface of the piston slides past the walls of the bicalorimeter, since its outer diameter is 0.05–0.06 mm smaller than that of the internal cavity of the bicalorimeter. Weights 7 are placed on top of the piston 6. The steel tube 12, which slides freely past the runner, is situated in the middle of the piston.

The space between the kernel and the internal cavity of the bicalorimeter is filled with the sample 13. A stopper is placed in the upper open portion of the internal cavity of the bicalorimeter, so that the lower end of the stopper rests on the sample and the upper end extends beyond the bicalorimeter. By applying a pressure to the upper end of the stopper, one can apply an external pressure to the sample, which fills the bicalorimeter, and thus

TABLE 3. Main Characteristics and Thermophysical Properties of Catalysts on N-1 Support in Air at a Temperature of 293 K

Granule size, mm	Active metal	Concentration, %	Specific surface, m^2/g	Total pore volume, cm^3/g	Loading density, g/cm^3	$\lambda \cdot 10^3$, W/(m·K)	$a \cdot 10^7$, m^2/sec	c_p, J/(kg·K)
2–3	Ni	30	89	0.2	1600	240	2.13	705
3–4	Ir	13	20	0.08	1755	226	2.04	631

TABLE 4. Experimental Values of Thermal Conductivity of Catalyst Load as a Function of Saturated-Vapor Pressure and Temperature

Catalyst containing 30% nickel			Catalyst containing 13% iridium		
T, K	$P \cdot 10^5$, Pa	$\lambda \cdot 10^3$, W/(m·K)	T, K	$P \cdot 10^5$, Pa	$\lambda \cdot 10^3$, W/(m·K)
293.0	0.02	235	293.5	0.02	227
407.1	3.3	393	375.5	1.2	288
492.5	25.8	515	432.2	3.9	323
521.1	39.0	566	518.9	29.4	358
			556.7	56.8	358

measure the thermal conductivity of the sample at various stresses. Standard disks 7 from an MP-2500 weight-piston manometer are used as weights.

The low-power heater 4 is operated from the line (~200 V) through an isolation transformer 9 and a variable-ratio autotransformer 10. The cooling rate of the kernel of the bicalorimeter is determined by an M17/4 mirror galvanometer 8. The voltage is measured by a voltmeter 11.

In order to verify the operation of the installation, the thermal conductivity of Al_2O_3 (irregularly shaped grains with dimensions of 2–3 mm) was measured at atmospheric pressure. The data obtained on the thermal conductivity of the reference sample at a temperature of 293 K in air agree well with the data from [1].

In order to measure the thermal conductivity of a catalyst as a function of mechanical stress, we used a cylindrical acalorimeter (Fig. 5). It consisted of a thick-wall copper cup (1) 90 mm in diameter and 260 mm in height, along the axis of which the thin steel tube 12 was placed, in which the low-power heater 4 and the hot junction of the measuring differential thermocouple 3 were inserted. The cavity of the acalorimeter was 30 mm in diameter and 127 mm in depth.

In order to apply the mechanical stress, a piston 5 sliding along its outer side surface past the inner side surface of the cup and a metal tube fixed within it is centered by a hole drilled in the lower portion of the cup; the tube can move up and down within certain limits with respect to the cup with the sample.

In order to verify the correct functioning of the setup we measured the thermal diffusivity of aluminum oxide powder at atmospheric pressure. The data on the thermal diffusivity of the aluminum oxide powder in air at a temperature of 293 K coincide with Kraev's data [2] with an error of 1–2.5%.

By varying the stress at the piston one can vary the axial pressure on the sample within rather wide limits. Standard disks 6 from an MP-2500 weight-piston manometer were used as weights.

In the measurements of thermal conductivity and thermal diffusivity on these installations the mechanical stress imposed on the granules was varied up to 140 N per granule.

We also measured the thermal conductivity and thermal diffusivity of catalyst containing 30% nickel and 13% iridium on an N-1 support at a temperature of 293 K as functions of mechanical stress. According to the results obtained, no noticeable variation in thermal conductivity or thermal diffusivity takes place within the range of mechanical stress of from 0 to 60–70 N per granule.

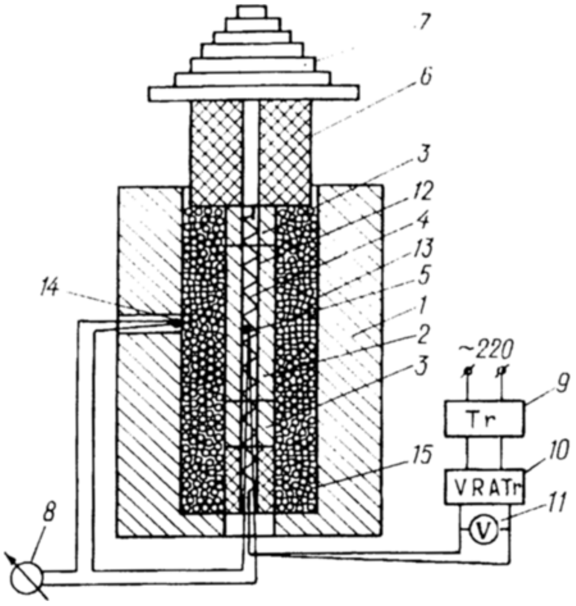

Fig. 4. Experimental setup for measurement of effective thermal conductivity of catalyst load as a function of mechanical stress: 1) external cylinder of cylindrical bicalorimeter; 2) internal cylinder (core of bicalorimeter); 3) compensation cylinders; 4) heater; 5) hot junction of the measuring thermocouple; 6) piston; 7) weights; 8) mirror galvanometer; 9) isolation transformer; 10) variable-ratio autotransformer; 11) voltmeter; 12) tubes; 13) sample (object under investigation); 14) add junction of measuring thermocouple.

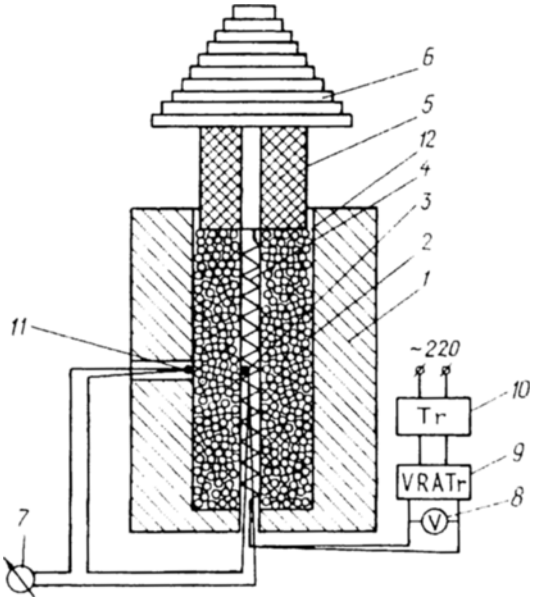

Fig. 5. Experimental setup for measurement of thermal diffusivity of catalysts as a function of mechanical stress: 1) calorimeter; 2) object under investigation; 3) hot junction of measuring thermocouple; 4) electric heater; 5) piston; 6) weights; 7) mirror galvanometer; 8) voltmeter; 9) variable-ratio autotransformer; 10) isolation transformer; 11) cold junction of measuring thermocouple.

In the region of high stresses that are close to those at which the granules disintegrate, an increase in thermal conductivity and thermal diffusivity is observed, which is due to an increase in the contact area of the catalysts.

As follows from the experimental data, the thermal conductivity and thermal diffusivity of supports and catalysts on their basis are insignificant in vacuum, as compared with λ and a in an atmosphere of filling gases. This indicates that heat transfer proceeds mainly via the gas medium that fills the pores of the samples and the free space between granules and much less via contacts of the solid phase. The gas that fills pores and space between the granules of the supports and catalysts contributes somewhat to the thermal conductivity and thermal diffusivity of the layer of objects under investigation.

Thus, the absence of gas in the pores increases substantially the thermal resistance of the layer of samples and correspondingly decreases the thermal conductivity.

Investigations have shown that the effective heat conductivity of samples depends considerably on the gas that fills their pores and to a lesser degree is determined by the gas that fills the space between the granules of catalysts and supports. For example, if the bicalorimeter is filled with argon subsequent to deep evacuation, the value of the effective thermal conductivity equals 0.167 W/(m·K) for a copper catalyst containing 4.5% metal with granule sizes of 0.8–1.25 mm at 293 K. When the gas is evacuated from the bicalorimeter (not deeply, so that argon remains in pores) the latter is filled with a gas, e.g., helium. After measurements we obtain results close to the effective thermal conductivity when the bicalorimeter is filled with argon. This indicates the small effect on the effective heat conductivity of the gas that fills the bicalorimeter, and the preferential effect of the gas that fills the pores of the catalysts and supports.

The thermal conductivity and thermal diffusivity of catalysts and supports increase with increasing thermal conductivity of the filling gas. The highest values of thermal conductivity and thermal diffusivity were obtained in a hydrogen atmosphere; the lowest, in argon and carbon dioxide.

The smallest increase in thermal conductivity with temperature is observed in vacuum for all samples. As the heat conductivity of the filling gas increases, the heat conductivity of the samples grows faster with temperature. For example, when a catalyst containing 3.1 wt.% iridium with granule sizes of 2–3 mm on an N-1 support is heated by 1 degree, its heat conductivity increases: in vacuum by $6.8 \cdot 10^{-5}$; in argon by $20.1 \cdot 10^{-5}$; in nitrogen by $20.7 \cdot 10^{-5}$; in helium by $29.8 \cdot 10^{-5}$, and in hydrogen by $31.5 \cdot 10^{-5}$ W/(m·K).

According to [3], the thermal conductivities of helium and hydrogen grow faster with temperature than those of argon and nitrogen. Therefore, the effective thermal conductivity of catalysts and supports in helium and hydrogen amospheres grows faster than in nitrogen and argon media.

Hydrogen and helium have the highest thermal conductivities [3]; therefore, in these media the effective thermal conductivity of the catalysts and supports under investigation is higher than in other gas media.

To determine the effect of the concentration and nature of metallic particles on the thermal conductivity and thermal diffusivity of objects under investigation we studied catalysts containing various amounts of copper, nickel, cobalt, ruthenium, iridium, and rhodium.

The thermal conductivity of a catalyst load increases with the amount of metallic additives in all gaseous media and in vacuum within the entire temperature range under investigation. An increase in λ and a with the concentration of metallic additives was observed for all catalysts under investigation.

Our studies have shown that the thermal conductivity and thermal diffusivity of catalysts with the same support depend on the nature of the metallic additives, and catalysts with metallic additives with higher thermal conductivity and thermal diffusivity have higher values of effective thermal conductivity and thermal diffusivity. Catalysts that contain cobalt on an N-1 support have the highest values of thermal conductivity and thermal diffusivity.

According to [4, 5], copper has the highest thermal conductivity and thermal diffusivity, whereas cobalt has the lowest values of these quantities.

Thus, the thermal conductivity and thermal diffusivity of the catalysts under investigation depend on both the concentration of metallic additives and their nature.

Investigations have shown that the thermal conductivity and thermal diffusivity of catalysts depend on the granule size. According to the results obtained, the value of λ increases somewhat with granule size within the entire temperature range. An increase in the thermal conductivity and thermal diffusivity of catalysts with granule size is observed in all gaseous media and in vacuum.

In order to reveal the effect of the support on thermophysical properties, we studied the thermal conductivity and thermal diffusivity of catalysts on various supports (N-1, N-2, N-3, and N-4) with different granule sizes as functions of temperature in gaseous media and vacuum. Catalysts that contain one and the same metal with the same weight concentration of metal particles introduced in different supports, have different values of thermal conductivity and thermal diffusivity.

Catalysts have the highest value of thermal conductivity on an N-3 support, whereas a catalyst on an N-1 support has the lowest value of this quantity. The highest values of λ and a were obtained for catalyst load on an N-3 support. Hence, it follows that catalysts that have supports with high values of λ and a have high values of thermal conductivity and thermal diffusivity.

We studied the temperature dependences of the thermal conductivity and thermal diffusivity of catalysts that have differing total volumes of pores and contain metallic additives on various supports in gaseous mixtures of various compositions and in vacuum.

The investigation showed that the thermal conductivity and thermal diffusivity of all catalysts considered decrease linearly with increasing pore volume.

The sharpest drop in thermal conductivity and thermal diffusivity with increasing total pore volume is observed for a deposited copper catalyst and the slowest drop is observed for a deposited cobalt catalyst. According to the results obtained, the higher the values of λ and a for a catalyst load, the faster the thermal conductivity and thermal diffusivity drop with increasing total pore volume.

The investigation has shown that the thermal conductivity and thermal diffusivity of catalysts depend on their specific surface s. In order to find the particular form of the dependence we plotted $\lambda(s)$ vs $a(s)$ for the catalysts under investigation. According to the experimental data, the value of λ decreases linearly with increasing specific surface for all catalysts within the entire temperature range. A linear decrease in thermal conductivity and thermal diffusivity of catalysts with increasing specific surface is also observed in all gaseous media and in vacuum.

In hydrogen and helium media, the thermal conductivity and thermal diffusivity decrease faster than in other gaseous media or in vacuum. For catalysts with different granule sizes, the thermal conductivity and thermal diffusivity decrease almost identically with the specific surface.

It should be pointed out that among the catalysts studied with granule sizes of 0.8–1.25 mm, the smallest drop in λ with increasing specific surface is observed for cobalt catalysts; the greatest, for copper catalysts.

Thus, the higher the thermal conductivity of the catalysts, the sharper the drop in thermal conductivity and thermal diffusivity with increasing specific surface.

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