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Selective Oxidation of CO under Conditions of Catalyst Surface Ignition

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Abstract—The oxidation of CO in the presence of an excess of hydrogen and to 20% CO_2 and H_2O in the starting mixture was studied in flow reactors with high and low rates of heat removal. The ignition of the catalyst surface was observed in the reactor with a low rate of heat removal; catalyst surface ignition initially occurred at a “hot” spot (section) of the catalyst bed and gradually propagated along the bed. Experimental data on the relaxation dynamics of residual CO concentration and temperature in a catalyst bed under conditions of small heater temperature disturbances near and at the critical temperature of ignition and the effect of oxygen concentration in the starting mixture on this process are reported. It was found experimentally that the ignition regime in the tested cases was more favorable for the selective oxidation of CO in an excess of hydrogen than the reaction in an isothermal reactor; this was likely due to the more favorable temperature distribution over the length of the catalyst bed.

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INTRODUCTION

The catalytic oxidation of CO in the presence of hydrogen (selective oxidation of CO) has been widely used as a method for hydrogen purification. This reaction has been studied in the past decade in the context of pure hydrogen production for fuel cells (e.g., see [1, 2] and references therein). The oxidation of CO on supported Pt catalysts seems best studied. However, in spite of numerous publications, the nature of processes that occur in the oxidation of CO (even in the absence of H_2) remains unclear.

A high-rate (high temperature and/or high O_2/CO ratio) or low-rate reaction branch is observed on supported platinum catalysts, depending on temperature and the partial pressures of the components (see, e.g., [2]). It is believed that the surface was covered with CO or oxygen at low or high temperatures, respectively. This is consistent with the apparent orders of reaction: at high and low temperatures, the orders of reaction with respect to CO were equal to +1 and a negative value (to –1.5), respectively, and the orders of reaction with respect to O_2 were equal to 0 and +1, respectively.

Indeed, CO is strongly adsorbed mainly in a linear form on the surface of platinum metal. Oxygen is bound to surface sites more strongly than CO; however, it is not sorbed on the surface of Pt covered with CO. Oxygen does not displace preadsorbed CO, although it can react with CO to form CO_2 [2–5].

On the contrary, Venderbosch et al. [6] believed that external diffusion inhibition was responsible for special features of the reaction, in particular, variable reaction orders. The low-rate and high-rate modes corresponded to the occurrence of the reaction in the kinetic and external diffusion regions, respectively.

The experimental measurements of the temperature dependence of CO conversion in the course of oxidation on various catalysts lead to problems. Thus, it was found [7–9] that the curve of CO conversion plotted as a function of temperature on heating a reactor was shifted to the region of higher temperatures, as compared with an analogous curve obtained on cooling (it described a hysteresis loop). According to Yakerson et al. [7, 8], it is evident that the observed phenomena are inconsistent with the hypothesis that multiple steady states are responsible for hysteresis. Note that, on the contrary, it is our opinion that the classical interpretation of hysteresis as a consequence of catalyst surface ignition (the term introduced by Frank-Kamenetskii [10]) is adequately correct (for more details, see below).

Additional problems arise in the oxidation of CO in complex mixtures, in particular, in an excess of hydrogen and, especially, in the presence of CO_2 and H_2O, which are gas mixture constituents after various types of hydrocarbon steam reforming. In this case, selectivity is the most important requirement imposed on a catalytic system; in turn, selectivity is a function of macrokinetic reaction characteristics.

In a detailed study performed by Snytnikov et al. [1, 11], a 1% Ru/C catalyst was found more active than 1% Pt/C in the oxidation of CO in an excess of hydrogen: the conversion of CO on the former catalyst was equal to that on the latter at temperatures several tens of degrees lower. However, the 1% Ru/C catalyst decreased the concentration of CO to 500 ppm at 110–120°C (a mixture of 1.0 vol % CO, 1.5 vol % O_2, 65 vol % H_2, 10 vol % H_2O, and 20 vol % CO_2; a space velocity of 7500 h^{-1}), whereas the 1% Pt/C catalyst decreased this concentration to ~20 ppm. On the other hand, according to [12], the selectivity of ruthenium catalysts in the oxidation of CO in an excess of hydrogen was higher than the selectivity of platinum catalysts. It is likely that these contradictions are due to macrokinetic reaction parameters.

The majority of special features in the oxidation of CO depend on the high activity of catalysts used in combination with the high exothermicity of the reaction. In this case, a stepwise change of the reaction to the external diffusion region is almost inevitable. In actual practice, it has been repeatedly observed experimentally as an anomalously high temperature dependence of the rate of reaction. According to [2], this suggests ignition. The temperature at which a gradient in the curve of the temperature dependence of CO conversion reaches a maximum is taken as the ignition temperature. Such an approach can be considered a purely formal interpretation of experimental observations. As will be demonstrated below, this rapid growth is actually due to a spontaneous change of the reaction to the external diffusion region with corresponding conversion and temperature jumps in the catalyst bed. Of course, the "ignition temperature" in [2] (and in corresponding sources) is not related to the real surface ignition temperature according to Frank-Kamenetskii [10] and, generally, it has no direct physical meaning.

Carlsson et al. [13] demonstrated (using Fourier transform IR spectroscopy) a change in the composition of an adsorbed layer on Pt as the temperature of CO oxidation was increased. Nevertheless, as found by Carlsson et al. [14], catalyst surface ignition was the origin of the temperature jump and the change of the regime. Carlsson et al. [14] used an original technique of the stepwise change of oxygen concentration in the starting mixture (0.5, 1, 2, 4, and 8 vol % O_2) at a constant CO concentration (1 vol %). As a result of this, they managed to detect both ignition and extinction of the surface of a honeycomb Pt catalyst in a quartz flow reactor. With a stepwise increase in the oxygen content of a mixture containing 1 vol % CO, ignition was observed at an oxygen concentration of 8 vol %. On the subsequent stepwise decrease in the oxygen content, surface extinction was observed at a much lower O_2 concentration of 1 vol %, which corresponds to the occurrence of a hysteresis loop. Carlsson et al. [14] simulated the dynamics of ignition; however, the constants of rate equations should be changed by more than one order of magnitude to describe surface extinction. It is likely that this partial failure was a consequence of incorrect concepts of the reaction mechanism (the Langmuir–Hinshelwood mechanism was accepted), which affected the kinetic block of the corresponding program.

In our preliminary communication [15], we demonstrated that the reaction of selective CO oxidation performed under conditions of catalyst surface ignition considerably (by an order of magnitude) decreased the residual concentration of CO, as compared with an ordinary reaction in an isothermal reactor. The effect was observed even at a relatively low O_2/CO ratio of 1.

The aim of this work was to consider in more detail macrokinetic parameters and experimental results for the reaction of selective CO oxidation under conditions of catalyst surface ignition. First, we shall dwell briefly on the phenomenon of surface ignition.

THEORETICAL FUNDAMENTALS OF THE MACROKINETICS OF HETEROGENEOUS CATALYTIC REACTIONS: THERMAL REACTION CONDITIONS: CATALYST SURFACE IGNITION

To avoid misunderstandings, note that, as a rule, the ignition of a gas mixture cannot occur in heterogeneous catalysis because of the high rates of heterogeneous disappearance of radicals and atoms. At the same time, a process that simulates ignition (the spontaneous transition of the reaction to the external diffusion region) can be implemented. According to Frank-Kamenetskii [10], this transition can be observed in strongly exothermic catalytic reactions in the case that the positive heat flow q^+ due to the reaction is equal to the negative heat flow q^- related to heat removal, $q^+ = q^-$, and the growth of the positive heat flow with temperature is higher than the growth of the negative heat flow, $dq^+/dT > dq^-/dT$. Then, as the temperature is increased, the heat removal power becomes insufficient for the complete removal of heat released in the reaction. The combination of conditions becomes crucial, and the reaction abruptly changes to the external diffusion region; this is accompanied by a spontaneous increase in the reaction temperature. Frank-Kamenetskii designated this transition as *catalyst surface ignition* and the minimum surface temperature at which the ignition is observed as *the critical ignition temperature.*

Based on the heat explosion theory, Frank-Kamenetskii [10] developed a mathematical apparatus for describing surface ignition; this mathematical apparatus allowed him to find critical conditions for ignition and definition parameters. This mathematical apparatus was difficult to use because the catalyst surface temperature, which usually cannot be measured experimentally (under conditions of a gas flow through a granular catalyst bed, a sensor usually measures the temperature of the surrounding gas mixture), was used as the main variable. Rozovskii [16] used the approach of Frank-Kamenetskii in order to describe the phenomenon of surface ignition based on the temperature of the gas mixture that contacts with a catalyst and to find a relationship between the kinetic parameters of the process and the critical temperature of a gas.

Physically, the effect of ignition is due to the fact that the constants responsible for the rate of reaction and the heat flow, which is proportional to this rate, exponentially increase with temperature, whereas the heat removal is approximately proportional to the difference between the temperature of the reaction gas mixture supplied to the system and the temperature in the reaction zone. For strongly exothermic reactions, when the equality of positive and negative heat flows is reached, the above derivative inequality holds automatically; this leads to a disruption of macrokinetic reaction conditions (ignition) as the temperature is increased: an increase in the temperature causes an exponential increase in the rate of reaction, which implies a further increase in the temperature. This unrestrained increase continues until the supply of reacting molecules to the catalyst surface becomes a rate-limiting step. Under new steady-state conditions, the reaction occurs in the external diffusion region.

Although the major portion of heat released in the course of the reaction is consumed for heating the gas mixture, a portion of heat is removed through the reactor walls. In this case, the heater (furnace) actually becomes a cooler. Macrokinetic conditions can be controlled within a limited range by varying the intensity of heat removal through walls and heat supply due to the reaction (by changing the space velocity and composition of the mixture).

A change from the kinetic region to the external diffusion region can occur either gradually or abruptly depending on the catalyst activity, heat of reaction, and other parameters. According to Rozovskii [16], the condition for the stability of a process on a catalyst grain can be written in the form

$$\frac{Qk_0\exp(-E/RT_0)}{\alpha} < \frac{RT_0^2}{E}\left(\frac{1+b+b^2}{\mathrm{e}}\right), \tag{1}$$

where Q and E are the heat and activation energy of the reaction, respectively; k_0 is a preexponential factor (which includes a function of concentration in the general case); α is a heat-transfer factor; $b = RT_0/E$, T_0 is the gas mixture temperature; and e is the natural logarithmic base.

The invalidity of this inequality automatically leads to surface ignition.

A more rigid situation is characterized by the following inequality [16]:

$$Q\beta CE/\alpha RT_0^2 < 1 + 2b + 5b^2 \tag{2}$$

(where β is a mass-transfer factor, and C is the concentration of a key reactant in a gas-flow core). If this inequality is valid, critical phenomena are impossible and only a smooth change from the kinetic region to the transition and external diffusion regions can occur.

After the surface ignition took place, a decrease in the heater temperature below the critical ignition temperature within the temperature range did not cause extinction: the upper steady-state mode, which corresponds to the external diffusion region of the reaction, was retained. Nevertheless, a further decrease in the temperature finally causes the next disruption (surface extinction), at which the reaction abruptly changed to the kinetic region once again. Correspondingly, the occurrence of hysteresis is characteristic in the situation of catalyst surface ignition–extinction (for more details, see [10, 16]).

Yakerson et al. [7, 8] proposed an alternative explanation for the hysteresis phenomena observed: a local overheating of active sites as a consequence of hindered reaction-heat removal. At the same time, the probability of the local overheating of active sites is lower than the probability of catalyst surface ignition by several orders of magnitude. This directly follows from ratios between heat-conductivity factors and heat-transfer lengths for the solid–gas-flow core system on the one hand and the active site set–support system on the other hand. Subbotin et al. [7], who criticized the hypothesis that multiple steady states are responsible for hysteresis, noted that, according to these concepts, a qualitative change (leap) of the system from one state to another will occur at a point in time in the course of a gradual temperature change and these transitions will take place instantaneously. This argumentation does not stand up under scrutiny because a leap of this kind can occur only at a spot (in a particular section of the bed), whereas a new regime can propagate to the catalysts bed (non-steady-state process) for a rather long time depending on experimental conditions. At the same time, a leap in the catalyst bed is easy to detect by measuring the steady-state values of the rate of reaction, conversion, etc., under changes in experimental conditions.

EXPERIMENTAL

Here, we report the results obtained with a 0.1% (Pt, Ru)/ceramic support catalyst provided by Haldor Topsøe.

To characterize macrokinetically the reaction system in more detail, we studied the selective oxidation of CO in an excess of hydrogen in flow setups with dramatically different conditions of heat removal from the reaction zone. In one of these setups, a nearly isothermal reactor (henceforth referred to as the isothermal reactor) was used, whereas a reactor with a low intensity of heat removal (henceforth tentatively referred to as the adiabatic reactor) was used in the other setup. In order to simulate practically important cases, the oxidation was performed in the presence of CO_2 and water vapor at concentrations to 20 vol %.

The starting gas mixtures (H_2, CO, O_2, CO_2, and N_2) were prepared in a special gas cylinder and supplied to a setup with the use of special devices (see below); water was supplied independently with a pump through an evaporator.

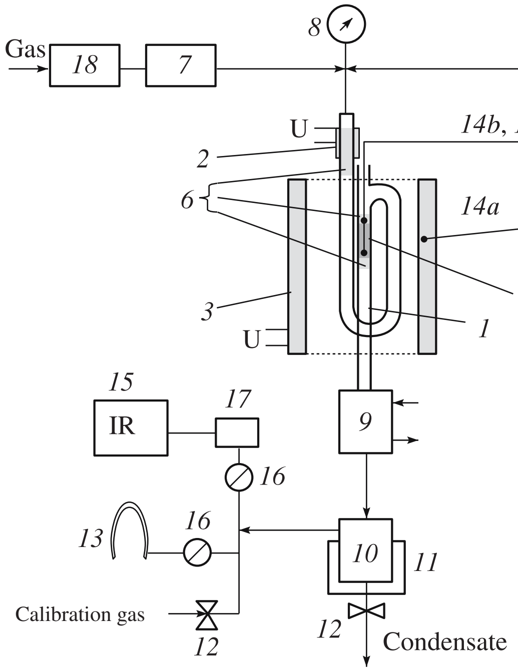

Fig. 1. Schematic diagram of the setup with the adiabatic reactor: (*1*) reactor, (*2*) evaporator, (*3*) furnace, (*4*) water pump, (*5*) catalyst, (*6*) porous quartz, (*7*) gas flow meter, (*8*) pressure gage, (*9*) water cooler, (*10*) separator, (*11*) cooler (0°C), (*12*) stop valves, (*13*) chromatograph, (*14a–14c*) thermocouples, (*15*) IR analyzer, (*16*) control valves, (*17*) trap with silica gel, (*18*) gas flow regulator, and (*19*) processor.

A catalyst fraction of 0.250–0.315 mm was used. Reduction with hydrogen at 500°C was performed immediately in the reactor.

Adiabatic Reactor

Figure 1 shows a schematic diagram of the setup with the adiabatic reactor. Quartz reactor *1* was made of a curved tube (5.5 mm in i.d.); porous quartz *6* was placed at the reactor inlet (water evaporation zone *2* heated with an electric coil). The reactor was arranged in cylindrical electric furnace *3* (~50 mm in i.d.). Catalyst sample *5* (~0.2 g) was placed without dilution between porous quartz plugs *6* in the reactor. Two measuring Chromel–Copel thermocouples *14b* and *14c* were introduced into the reactor through a ground-glass joint (the stainless-steel thermocouple shield diameter was 1 mm; the temperature of the gas mixture was measured to within 0.1 K). As a rule, the thermocouples were arranged with respect to the catalyst bed in the following manner: the lower thermocouple was 1–2 mm higher than the bed outlet, and the upper thermocouple was approximately 1–2 mm higher than the bed inlet. The catalyst bed height was 11–12 mm.

The furnace temperature was specified and measured using multichannel processor *19* with adjusting thermocouple *14a*, which was arranged in the furnace tube near the heating coil. This processor also detected the temperatures of thermocouples *14b* and *14c*.

The residual concentration of CO in the dried gas mixture was measured (and recorded) in an on-line mode with the use of BINOS 100 IR analyzer *15* (error of <1 ppm). Drying was performed successively in coolers *9* and *10* and silica gel trap *17*. The flow rate of a gas mixture was specified with flow controller *18* and measured with digital meter *7* (IRG-1000). The gas composition at the reactor outlet (CO, O_2) was monitored by chromatography (zeolite 13X). As a rule, the reactor pressure was no higher than 0.12 MPa. Usually, the catalyst was heated to 200°C in a flow of H_2; after a 0.5-h exposure, the temperature was decreased to 110–120°C and water was supplied; next, H_2 was replaced with a gas mixture.

After performing an experiment and cooling to ~110°C, the pump was turned off and the catalyst was cooled in hydrogen.

Isothermal Reactor

The setup with the isothermal reactor was based on a KL-3d catalytic setup (Special Design Bureau of the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences). In this setup, the reactor was nearly isothermal (high rate of heat removal); it was made of a coaxially arranged metal cylindrical tube and thermocouple pocket with a gap of 3–3.5 mm between them. A weighed portion of the catalyst was diluted with an inert material in a ratio of 1 : 10 and loaded in the annular gap. The bed height was about 15 mm. The setup was equipped with a sampler for the on-line chromatographic analysis of the vapor–gas mixture (without water condensation and separation). The following chromatographs were used: 3700 (column with Porapak T for the determination of water concentrations) and Chrom 5 (columns with Polysorb for the determination of CO_2 and with zeolite 13X for the determination of O_2, N_2, and CO). In a number of experiments, a BINOS 100 IR analyzer was used for the determination of the residual concentrations of CO. As a rule, the reactor pressure was no higher than 0.17 MPa.

Only CO_2 and H_2O were detected as the products of reactions occurring over the tested temperature range (≤250°C).

RESULTS AND DISCUSSION

Figure 2 shows a typical curve of the temperature dependence of CO conversion in the isothermal reactor. As can be seen, this is an ordinary shaped smooth curve up to nearly complete degrees of conversion. Because the reaction on fine grains in the isothermal reactor is characterized by high transfer coefficients, stepwise changes in the macrokinetic regime are unlikely in this reactor. Even without special calculations, it is expected that, even through the reaction changes to the external diffusion region, this change occurs gradually

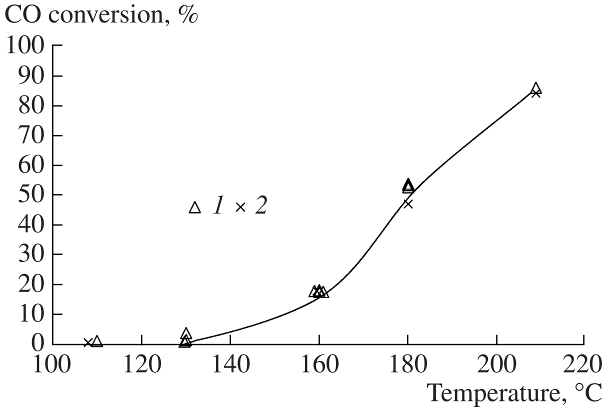

Fig. 2. Typical temperature dependence of CO conversion for CO oxidation in the isothermal reactor. Reaction mixture, vol %: CO, 0.87; O_2, 1.04; CO_2, 17; H_2, 34; H_2O, 17; and the balance N_2. Flow rate: (*1*) 45 or (*2*) 42 l (g Cat)$^{-1}$ h^{-1}.

without regime disruptions. Indeed, the effect of the linear velocity of a gas flow (and, correspondingly, the effect of external diffusion inhibition) on the rate of CO oxidation becomes noticeable only at low linear velocities, which are lower than those used in the experiments.

Figure 3 shows a typical curve of the temperature dependence of CO conversion for the reaction in the adiabatic reactor, in which catalyst surface ignition was observed. To obtain another point in the temperature dependence after reaching about 10% conversion, the furnace temperature was increased by 1 K, a period was allowed to elapse in order to reach a steady-state rate of oxidation, the temperature was increased by 1 K once again, etc. As can be seen in Fig. 3, a spontaneous increase in the conversion of CO with a corresponding increase in the catalyst bed temperature (shown with a dashed line in Fig. 3) was observed at a certain temperature (critical ignition temperature) after a regular increase in the furnace temperature. As the furnace temperature was further increased, the conversion of CO changed only slightly. It can also be seen that ignition was observed at conversions to 30%.

The dynamics of changes in the concentration of CO at the reactor outlet and in the temperatures of the furnace and the gas mixture at the inlet and outlet of the catalyst bed can be seen in Fig. 4, which shows a fragment of data recorded in the course of a particular experiment. As noted above, the experiment was performed at the stepwise increase of the temperature with a step of 1 K. It can be seen in Fig. 4 that, at temperatures lower than the critical temperature, an increase in the furnace temperature by 1 K resulted in a small increase in the gas mixture temperatures at the inlet and outlet of the catalyst bed and a decrease in the concentration of CO in the effluent gas. All of the segments have the shapes of saturation curves; the time taken to reach a steady-state regime was about 10 min.

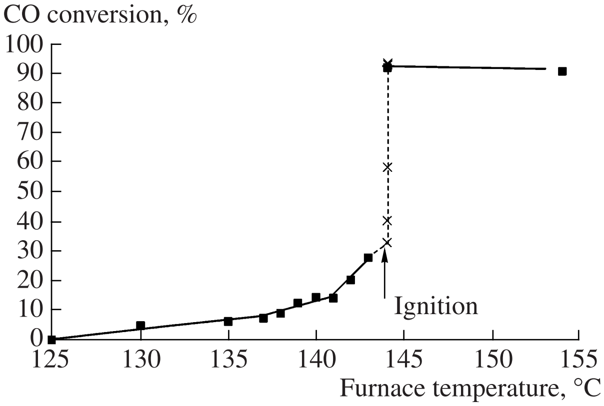

Fig. 3. Typical temperature dependence of CO conversion for CO oxidation in the adiabatic reactor. Gas mixture composition, vol %: CO, 0.83; O_2, 1.33; H_2, 34; CO_2, 17; H_2O, 17; and the balance N_2. Flow rate: 98 l (g Cat)$^{-1}$ h^{-1}. Nonsteady-state values measured in the course of a spontaneous heating of the catalyst bed (surface ignition) are marked with crosses.

As the critical ignition temperature (T_0) was reached, the initial segment of the curve for the gas temperature at the reactor inlet retained the same shape. This trend was also observed in the curve for gas temperature at the reactor outlet in the first several minutes; however, it rapidly disappeared and changed to an accelerating increase to a steady-state temperature in the ignition regime. The curve of CO concentration changes has practically the shape of a mirror reflection of the curve of gas temperature at the outlet: both of these curves reflect a gradual propagation of the regime

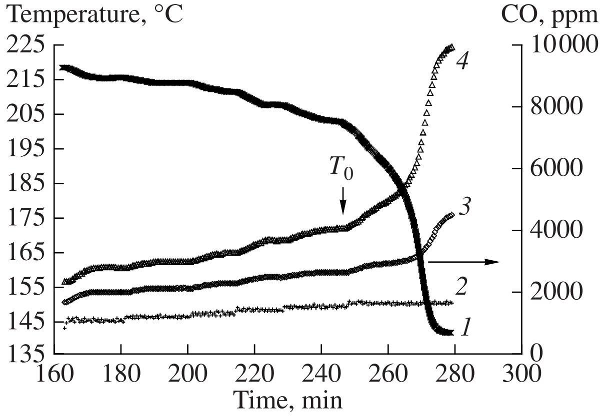

Fig. 4. Fragment of the recordings of the temperature and residual concentration of CO under a stepwise increase in the furnace temperature: (*1*) residual CO concentration; (*2–4*) furnace, bed inlet, and bed outlet temperatures, respectively. T_0 is the critical ignition temperature. Gas mixture composition, vol %: CO, 0.80; O_2, 0.80; H_2, 33; CO_2, 17; H_2O, 17; and the balance N_2. Consumption: 91 l (g Cat)$^{-1}$ h^{-1}.

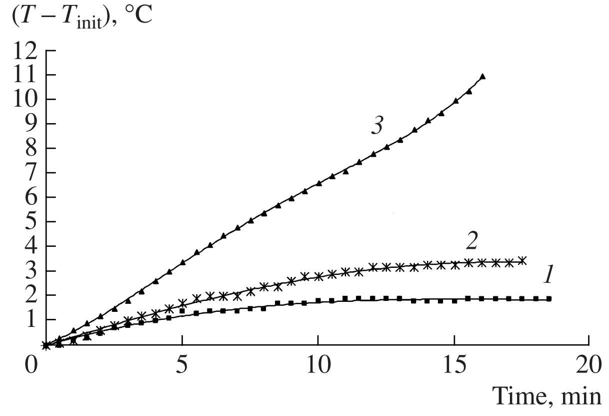

Fig. 5. Dynamics of gas heating at the outlet of the catalyst bed under a stepwise increase in the furnace temperature with a step of 1 K: (*1*) 145 ⟶ 146°C, (*2*) 148 ⟶ 149°C, and (*3*) 149 ⟶ 150°C. Gas mixture composition, vol %: CO, 0.8; O_2, 0.8; H_2, 33; CO_2, 17; H_2O, 17; and the balance N_2. Flow rate: 91 l (g Cat)$^{-1}$ h^{-1}.

along the catalyst bed. The final portion of the curve of the gas mixture temperature at the inlet of the catalyst bed also exhibited an additional growth due to longitudinal heat exchange.

A more detailed pattern of the initial stage of catalyst surface ignition can be seen in Fig. 5, which shows the initial portions of temperature buildup curves for the gas mixtures at the outlet of the catalyst bed with a stepwise increase in the furnace temperature by 1 K. It can be seen that, as the temperature was increased by 1 K from 145 or 148°C, heating somewhat increased (by ~2 K) in accordance with an increase in conversion and the gas temperature reached a steady-state value after ~10 min. At 149°C, the situation changed dramatically: progressive heating was observed, which ended (as seen in Fig. 4) in the establishment of a new steady-state regime of catalyst surface ignition.

Figure 6 shows a full cycle: sample heating to catalyst surface ignition (and above) followed by a decrease in the temperature up to surface extinction. An analogous behavior was observed at a lower O_2/CO ratio of 1 : 1 [15]. In both cases, hysteresis was clearly defined in both the curve of gas temperature changes in the catalyst bed and the curve of the residual CO concentration.

The relatively long relaxation of the system upon surface ignition was due to the fact that ignition conditions initially occurred in a section of the bed (in the neighborhood of a hot spot). An additional heat flow due to an increase in the temperature in the ignition zone was favorable for its propagation to adjacent regions and the bed as a whole. Because the major portion of heat was removed from the system by heating the gas flow, the propagation of ignition along the direction opposite to gas motion (establishment of a steady-state regime) occurred slowly for an outside observer.

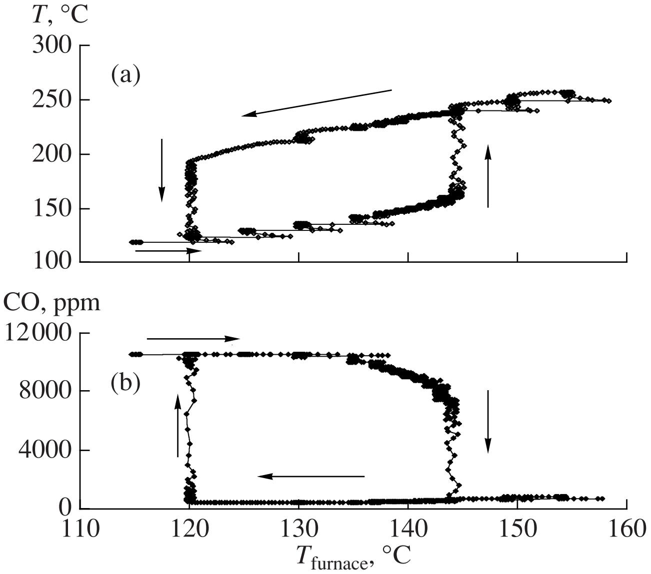

Fig. 6. Hysteresis in the dependence of (a) the gas temperature in the catalyst bed and (b) the residual concentration of CO on the furnace temperature. Gas mixture composition, vol %: CO, 0.83 O_2, 1.33; H_2, 34; CO_2, 17; H_2O, 17; and the balance N_2. Flow rate: 98 l (g Cat)$^{-1}$ h^{-1}.

Note that experimental conditions (a slow increase in the temperature with a step of 1 K) were oriented to minimize differences between heat input and removal on catalyst surface impregnation. In the case of large steps, these differences can be great and the ignition regime propagates very rapidly to the catalyst bed.

An increase in the concentration of oxygen in the gas mixture gave an analogous effect with the specified experimental procedure (a stepwise increase in the furnace temperature by 1 K) because of an increase in the growth of a positive heat flow at a single step. In turn, this shortened the non-steady-state period under changes of conditions, as observed experimentally (Fig. 7).

Let us consider the distribution of temperature along the bed on slowly heating the reactor to the critical temperature of ignition. For strongly exothermic reactions, a change to the regime of catalyst surface ignition occurred at low conversions, at least of no more than 0.3 [16]. At low conversions, if the reaction is not inhibited by products, a hot spot occurs at the end of the catalyst bed; that is, the reaction occurs at a temperature that increases along the catalyst bed and, correspondingly, at an increasing rate of reaction.

If the temperature of the inlet gas mixture was much higher than the critical temperature of ignition, the hot spot approached the frontal section of the bed.

From the above, it follows that, for the reliable determination of the critical ignition temperature of a given mixture, the reaction temperature should be increased and the gas temperature should be measured

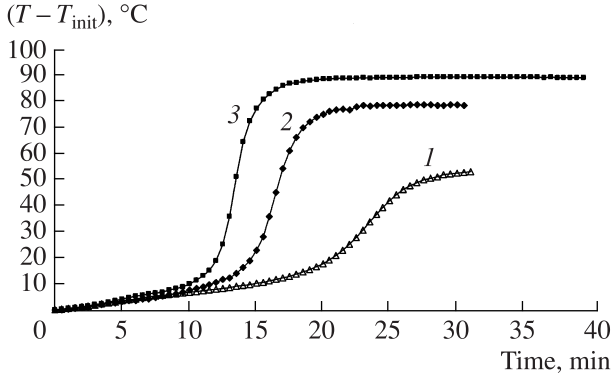

Fig. 7. Effect of the concentration of oxygen in the initial gas mixture on the relaxation curves of gas temperature at the outlet of the catalyst bed after ignition at an O_2/CO ratio of (*1*) 1.0, (*2*) 1.3, or (*3*) 1.6. Gas mixture composition, vol %: CO, 0.80; O_2, (0.80–1.30); H_2, 33; CO_2, 17; H_2O, 17; and the balance N_2. Flow rate: (*1*) 91 or (*2, 3*) 96 l (g Cat)$^{-1}$ h^{-1}.

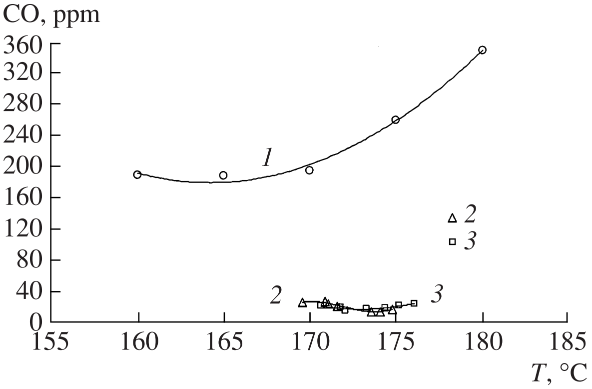

Fig. 8. Residual concentrations of CO upon oxidation in the (*1*) isothermal and (*2*, *3*) adiabatic (ignition mode) reactors. Gas mixture composition, vol %: CO, 0.85; O_2, 0.85; H_2, 33; CO_2, 17; H_2O, 17; and the balance N_2. Space velocity × 10^3: (*1*) 13.5, (*2*) 12.8, or (*3*) 14.2 h^{-1}.

at the end of the catalyst bed starting with not very high conversions at a small step near the ignition temperature. The ignition temperature can be tentatively evaluated in preliminary experiments performed with a great temperature step.

The residual concentration of CO in the gas mixture is one of the most important characteristics of the selective oxidation of CO. It usually passes through a minimum (so-called window) depending on the oxidation temperature: activity is insufficient at low temperatures, whereas an excess of oxygen is consumed for the oxidation of hydrogen at high temperatures.

Figure 8 compares the residual concentrations of CO after oxidation in the isothermal and adiabatic (ignition mode) reactors. As can be seen, the ignition mode is much more favorable for the selective oxidation of CO. In this case, the residual concentration of CO in the adiabatic reactor decreased by approximately one order of magnitude, as compared with that in the isothermal reactor. The temperature in the isothermal reactor was maintained close to the gas temperature at the bed outlet in the adiabatic reactor. It can also be seen in Fig. 8 that, in both of the reactors, the residual concentrations of CO occurred in a valley region.

It is well known that, in the general case, an increase in the reaction temperature impairs the selectivity of oxygen consumption: the fraction of reacted oxygen consumed for the oxidation of CO decreases. Correspondingly, it is believed that the above temperature distribution along the catalyst bed is a factor favorable for the selective oxidation of CO under conditions of catalyst surface ignition resulting in low residual concentrations.

As mentioned above, the heat of reaction was mainly consumed for heating the reaction gas mixture and only a portion was removed through reactor walls. Nevertheless, with maximized heat removal, as was the case in the isothermal reactor (fine catalyst grains in the annular gap between metal tubes at a tenfold dilution with an inert material), this portion can be sufficiently high for affecting the macrokinetic situation in the reactor. This is responsible for the occurrence of a strongly exothermal reaction under nearly isothermal conditions. The intensity of positive heat flow q^+ depends on the rate of reaction. Decreasing the space velocity of a gas mixture for reactions whose overall orders are lower than unity, we can decrease q^+ by somewhat decreasing also the intensity of heat removal (because of a decrease in the heat transfer coefficient with decreasing the linear velocity of a gas flow). In this case, the fraction of heat transfer through reactor walls increased; finally, this affected the macrokinetic characteristics of the system.

Determination of the Apparent Activation Energy

The calculation of kinetic parameters for the reaction of CO oxidation from data obtained in experiments with ignition and a comparison of the resulting values with values found using a traditional procedure can serve as an indirect test for the correctness of the approach used. Because the critical temperature of surface ignition is related to the kinetic parameters of the reaction, these kinetic parameters can be determined using the experimental temperatures of ignition found by varying the following conditions: gas flow rate, concentration, etc. For example, if the rate of the gas flow was varied in two experiments in order to obtain the ignition temperatures $T_{0(1)}$ and $T_{0(2)}$, the apparent activation energy can be determined from the equation [16]

$$E = \frac{RT_{0(1)}T_{0(2)}[\ln(\alpha_1/\alpha_2) + 2\ln(T_{0(1)}/T_{0(2)})]}{T_{0(1)} - T_{0(2)}}. \quad (3)$$

Table 1. Determination of the activation energy from the critical ignition temperatures (adiabatic reactor)

Experiment no.	Feed rate, l/h (NTP)	Mass rate v, g/h	Ignition temperature, °C		Activation energy, kcal/mol
			gas in the catalyst bed (T_0)	furnace	
First reduction*					
1	19.9	17.9	166.1	146	14.8
3	19.1	17.3	164.3	146	
4	19.2	17.3	163.3	147	
Average	**19.4**	**17.5**	**165.6**	**146**	
2	**35.4**	**32**	**176.3**	**154**	
Second reduction*					
5	18.7	16.9	170.3	144	14.4
6	18.6	16.8	167.5	145	
8	18.5	16.7	168.6	148	
Average	**18.6**	**16.8**	**168.8**	**146**	
7	**60.9**	**54.9**	**193.9**	**170**	

Note: The values of v and T_0 set in bold were used in the calculations.
* Reduction with H_2 at 500°C for 2.5 h.

Because the ratio between heat-transfer coefficients (α) can be replaced by the ratio between mass rates (v)

$$\alpha_1/\alpha_2 = (v_1/v_2)^{0.65},$$

it is not difficult to calculate E.

The availability of reactors that are dramatically different in the intensities of heat removal allowed us to determine the apparent activation energy both by a traditional procedure and under conditions of a disruption of the regime in terms of critical ignition temperatures. A comparison between the resulting values allowed us to judge the correctness of the approach used.

It is easy to demonstrate that, with an unknown rate equation, the temperature dependence of contact times required for reaching equal conversions at different temperatures can be used to determine the apparent activation energy in the isothermal flow reactor.

The determination of the activation energy from the critical temperatures of ignition from experimental data obtained in the adiabatic reactor, in which the reaction mixture temperature changes along the reactor, is less obvious.

As follows from the above discussion, the critical temperature of ignition can be detected by a stepwise change in the heater (furnace) temperature with the continuous measurement of the gas temperature at the end of the catalyst bed. In this case, the smaller the step, the higher the accuracy of the determination of the critical ignition temperature and activation energy.

The problem of the use of relations from [16], which are applicable, strictly speaking, to a spot or section of the catalyst bed in the adiabatic reactor, for this purpose is open to question. In terms of the previous approach [16], this problem is reduced to the choice of a cooler temperature. In a real experiment, heat is removed from the reaction zone in several steps: from the gas flow core to the inner reactor surface; from the latter to the outer wall; and, finally, from the reactor wall through an air layer to the inner furnace surface, which plays the role of a cooler in the case of ignition. Because the intensity of all of these processes is a linear function of the temperature difference between heat-exchanging bodies, it is clear that the final amount of removed heat is also a linear function of the difference between temperatures at the ends, that is, at the gas flow core and at the furnace wall. Hence, it follows that the relations [16] are also valid in the case under consideration. However, it should be taken into account that heat-transfer coefficients for constituent steps are involved in the overall coefficient with weight fractions corresponding to the contributions of the given steps to the overall heat-transfer process. Therefore, the direct calculation of transfer coefficients from experimental data is impossible. Moreover, errors can occur because of deviations from linearity in the distribution of temperature across the catalyst bed. However, the resulting distortions can be ignored because of the high intensities of gas-flow stirring in the layer of a grain material and the short length of cross-sectional transfer.

Thus, Eq. (3) can be directly used for calculating the apparent activation energy.

In this work, to determine activation energies from critical ignition temperatures, these latter were determined in experiments with various feed rates of the initial gas mixture in terms of the above procedure (stepwise heating by 1 K). The gas temperature in the catalyst bed at which a disruption of the regime occurred was taken as the ignition temperature. Table 1 summarizes the corresponding data.

Table 2. Determination of the activation energy by a traditional method (isothermal reactor)

Feed rate, l/h (NTP)	Temperature, °C		Conversion of CO, %	Activation energy, kcal/mol
	furnace	catalyst		
9.2	–	180	62	12.5
13.8	–	180	51	
20.2	–	180	40	
13.7	193	195	62	
21.3	–	195	51	
33.5	190	195	40	
21.0	205	210	62	
34.0	–	211	51	
51.0	200	211	40	

Table 2 summarizes data obtained using a traditional method in the selective oxidation of CO in the isothermal reactor.

The flow-rate ranges 19.1–60.9 and 9.2–51 l/h for the adiabatic and isothermal reactors correspond to the linear-velocity ranges 22–70.5 and 2.6–14.4 cm/s, respectively.

The above data indicate that the resulting values of *E* are consistent within the limits of experimental and calculation errors; this evidences the correct interpretation of the observed phenomena.

CONCLUSIONS

In this work, we studied the oxidation of CO in the presence of an excess of hydrogen in a starting mixture containing up to 20% CO_2 and H_2O in reactors with high (isothermal reactor) and low (tentatively adiabatic reactor) rates of heat removal. In the reactor with a low rate of heat removal, a disruption of the regime (catalyst surface ignition), which is characteristic of strongly exothermic reactions, was observed as the oxidation temperature was increased. Surface extinction with decreasing temperature also occurred stepwise. In this case, the extinction temperature was lower than the ignition temperature; that is, a characteristic hysteresis was observed. In a flow reactor, the critical conditions of ignition initially occurred at a hot spot (section) in the catalyst bed; then, the ignition regime gradually propagated along the bed. The time taken to reach steady-state conditions depended on the disturbance caused in the regime of the reaction under near-critical conditions, which is responsible for the difference between heat input and heat removal on ignition and, correspondingly, the rate of regime propagation along the catalyst bed.

For indirectly testing the correctness of this approach, the apparent activation energies were determined from data obtained in the isothermal reactor and from the dependence of the critical ignition temperature in the adiabatic reactor on the feed rate of the gas mixture. The found activation energies were consistent within the limits of experimental error.

Experimental data are given to demonstrate the dynamics of changes in the regimes: the relaxation of the catalyst bed temperature and the residual concentration of CO under small disturbances of the heater temperature near (up to) the ignition temperature and at the critical ignition temperature, as well as the effect of the concentration of oxygen in the starting mixture on the dynamics of catalyst surface ignition. In the contest of these data, the interpretation of nontrivial properties of the selective oxidation of CO given in a number of publications seems insufficiently correct.

Phase transitions on the surface or in the bulk of a catalyst, as well as surface ignition, can be responsible for a stepwise change in macrokinetic reaction conditions. However, the following differences in the behaviors of reaction systems in the cases of phase transitions (on the surface, in an adsorption layer, or in the bulk of the catalyst) and stepwise changes in macrokinetic reaction conditions can be noted:

- The critical temperatures of surface ignition and extinction depend on the rate of the gas flow: they increase with the rate, and this increase is not observed in the case of phase transitions. Moreover, a change from low to high conversions (and vice versa) can occur either with or without a disruption of the regime depending on the gas flow rate.
- The critical temperatures of ignition and extinction depend on catalyst activity: the higher the activity, the lower the values of both of the above temperatures. In a surface phase transition, the transition temperature is fixed at least over a limited range.
- Phase transitions occur at a certain combination of conditions (temperature, concentrations, etc.) and do not depend on the intensity of heat exchange. On the contrary, the intensity of heat removal can play a crucial role in surface ignition, so that the conditions of ignition vary in various reactors, on the dilution of a catalyst with an inert material, etc. Moreover, in principle,

the same reaction with the same mixture can be performed either with a disruption of the regime or without it by varying the intensity of heat removal; however, this is practically impossible in the case of phase transitions.

Correspondingly, in the general case, the choice between the above alternative interpretations is unambiguous.

In this work, we found experimentally that the ignition mode in the test cases is much more favorable for the selective oxidation of CO in an excess of hydrogen, as compared with the reaction in the isothermal reactor. This is likely due to a more favorable temperature distribution along the catalyst bed.

The almost complete removal of CO from hydrogen-containing mixtures (1% CO and O_2 and to 20% CO_2 and H_2O) can be implemented by combining an adequately chosen catalyst with optimized macrokinetic reaction conditions even at a consumption of about 100 l (g Cat)$^{-1}$ h^{-1}. The corresponding results will be reported elsewhere.

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