

Mechanism of High-Temperature CO Steam Conversion on Ce–Zr–(La)–O and Pt/Ce–Zr–(La)–O

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Abstract

The dynamics of transient behaviour in the reaction of CO steam conversion at 650 °C on the surface of $\text{Ce}_{0.5-x}\text{Zr}_{0.5-x}\text{La}_{2x}\text{O}_2$ ($x = 0, 0.1$) and platinum catalysts based on them has been studied. The numerical simulation of response curves has demonstrated that all the transformations on the carrier surface occur within the framework of an oxidation-reduction mechanism. The basic contribution into the catalytic activity under steady-state conditions on the surface of catalyst is made by transformations occurring *via* an associative mechanism. The dynamics of transient modes is determined by the oxidation-reduction mechanism.

Key words: CO steam conversion, cerium–zirconium, transient process kinetics simulation

INTRODUCTION

Cerium oxide accumulates and readily gives up significant amounts of oxygen due to the ease of oxidation-reduction process $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ [1], which allows one to employ this substance as a carrier for Pt- and Rh-containing catalysts of the reaction for obtaining synthesis gas *via* partial oxidation of methane [2]. The addition of La_2O_3 allows one to adjust the mobility of oxygen in the lattice [4], whereas the thermal stability of such systems could be increased by adding ZrO_2 and La_2O_3 [3–6]. The development of novel fields of application for the mentioned reaction assumes frequently changing reaction conditions (the processes of starting, stopping, fast changes in the composition of raw material). All this requires for knowing non-steady-state kinetics of the reaction basing on a detailed mechanism. The reaction of CO steam conversion makes a significant contribution to the final composition of the products of partial methane oxidation reaction [7]. Meanwhile, the majority of studies on

the mentioned reaction have been performed for a low-temperature range (150–300 °C) and higher contact time values [8–10].

This paper presents the results of the studies concerning the kinetics of transient modes in the reaction of CO steam conversion on the surface of carriers such as $\text{Ce}_{0.5-x}\text{Zr}_{0.5-x}\text{La}_{2x}\text{O}_2$ ($x = 0, 0.1$), as well as Pt-containing catalysts on their basis. The experiments were carried out under the conditions as much as possible close to the conditions corresponding to the reaction of selective methane oxidation ($T = 650$ °C, the contact time equal to 10^{-2} s). The simulation of response curves has allowed us to reveal a scheme of the reaction mechanism for CO steam conversion and to estimate rate constants for separate stages.

EXPERIMENTAL

The samples of carriers such as $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (Ce–Zr–O) and $\text{Ce}_{0.4}\text{Zr}_{0.4}\text{La}_{0.2}\text{O}_{1.9}$ (Ce–Zr–La–O)

were prepared according to the Peckini method, Pt (the mass fraction amounting to 0.2 or 1.4 %) was applied via impregnation from of H_2PtCl_6 [11]. In order to perform kinetic studies a sample of a carrier or of the catalyst (the fraction of 0.5–1 mm) 0.05 g in mass was placed into a tubular reactor ($L = 300$ mm, $D_{\text{int}} = 3$ mm, layer height: 8 mm) to heat up to 650 °C in a flow of He with a heating rate of 10 °C/min. A thermocouple was fixed on the reactor wall at the level of catalytic layer. Thereupon the sample was subjected to oxidative (2.2 % O_2 in He during 30 min) or regenerative pre-processing (first of all the oxidation as described above, and then the treatment in pure H_2 during 30 min). Before feeding the reaction mixture the system was blown with helium during 2 min. The volume rate of gas mixtures such as (2.55 ± 0.05) % CO + (2.65 ± 0.05) % H_2O in He (for carriers) and (2.45 ± 0.05) % CO + (2.5 ± 0.2) % H_2O in He (for Pt catalysts) amounted to 18 L/h. In order to determine the composition of the reaction mixture at the reactor outlet we employed chromatography and mass spectrometry assays (Stanfords Research Systems QMS200 with the time resolution amounting to 1 s).

RESULTS AND DISCUSSION

Activity of Ce–Zr–(La)–O and Pt/Ce–Zr–(La)–O and the dynamics of transient modes in the reaction of CO steam conversion

The catalytic activity of the samples of Ce–Zr–O and Ce–Zr–La–O carriers is close to each other being characterized by almost identical values of CO conversion level under steady-state

conditions – 11 and 12 %, respectively (Table 1). The applying of platinum results in a considerable increase in the activity in spite of a decrease in the specific surface area of samples. At the same time, with the increase in the mass fraction of platinum in a sample from 0.2 to 1.4 % the conversion level almost does not vary. We believe that such a low sensitivity of catalytic properties with respect to the content of platinum in a sample is caused by the fact that the reaction proceeds under the conditions close to thermodynamic equilibrium. Indeed, at 650 °C for the equimolar CO and H_2O mixture the equilibrium CO conversion level under the conditions of thermodynamic equilibrium should amount to about 57 % [12].

Ce–Zr–(La)–O. The dynamics of establishing the steady state condition for both samples (Ce–Zr–O and Ce–Zr–La–O) is determined mainly by their initial condition. So, with feeding the mixture to a preliminary oxidized sample of Ce–Zr–O (Fig. 1, a) one can observe fast CO_2 evolution and a subsequent slow (during 300 s) decrease of its concentration up to steady-state value. Hydrogen appears with a certain delay with respect to CO_2 , and its concentration monotonously increases, reaching the steady-state values in ~ 100 s. On a reduced sample, on the contrary, first of all H_2 is formed and then, with a considerable delay the formation of CO_2 is observed (see Fig. 1, b). The differences in the dynamics of CO_2 and H_2 formation on a reduced sample is not such significant as on an oxidized sample, and the steady state condition is reached much faster by this system (in ~ 15 s).

Since the processes of CO_2 and H_2 formation are not synchronized, the reaction, most

TABLE 1

Steady-state conversion CO level and total amount of strongly adsorbed C-containing compounds formed under interaction the reaction mixture with oxidized and reduced samples Ce–Zr–(La)–O and Pt/Ce–Zr–(La)–O

Sample	S_{sp} , m^2/g	CO conversion level, %	Amount of strongly adsorbed compounds, monolayers*	
			Oxidized	Reduced
Ce–Zr–O	65	11	2.3	1.5
Ce–Zr–La–O	66	12	1.65	8.3
1.4 % Pt/Ce–Zr–O	33	56	1.4	3.0
1.4 % Pt/Ce–Zr–La–O	29	57	2.2	7.17
0.2 % Pt/Ce–Zr–O	54	54–57	1.9	3.0

*One monolayer is equal to $1 \cdot 10^{19}$ at./ m^2 .

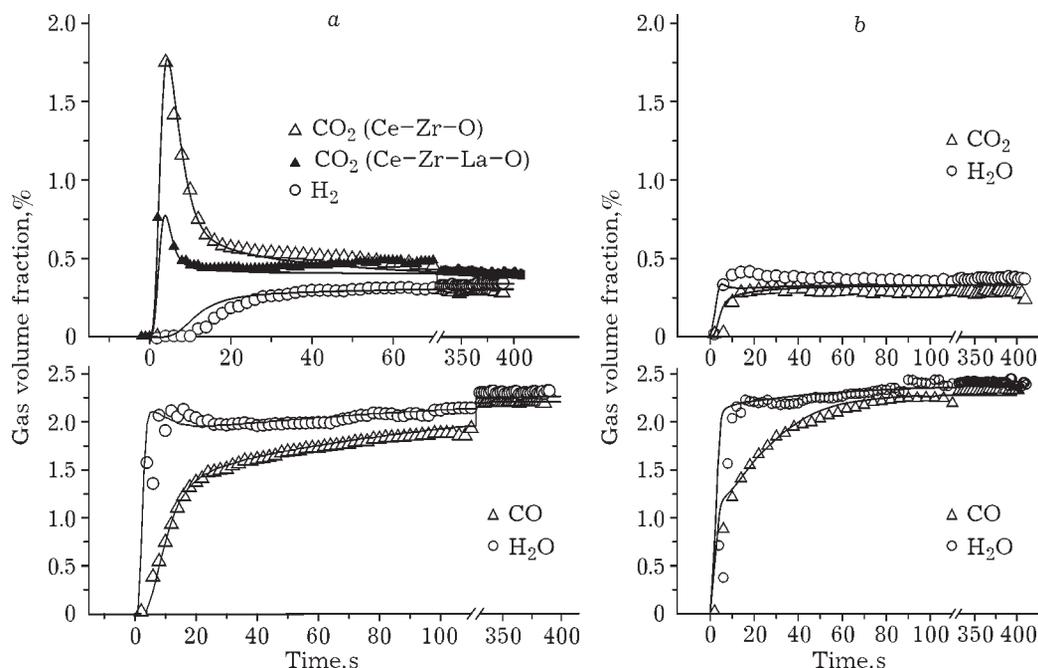


Fig. 1. Experimental (symbols) and calculated according to oxidation-reduction mechanism curves corresponding to the response due to switching from He to CO + H₂O for preliminary oxidized (a) and reduced (b) samples of Ce-Zr-O and Ce-Zr-La-O (only CO₂).

likely, proceeds according to the oxidation-reduction mechanism. Carbon monoxide reacting with the oxidized centres of the carrier yields CO₂. In turn, water causes the catalyst to be reoxidized with the formation of hydrogen.

Since the steady-state concentration of CO₂ is much lower than the value observed under the interaction between the reaction mixture and an oxidized sample, one can believe that the steady-state condition of Ce-Zr-O is close to

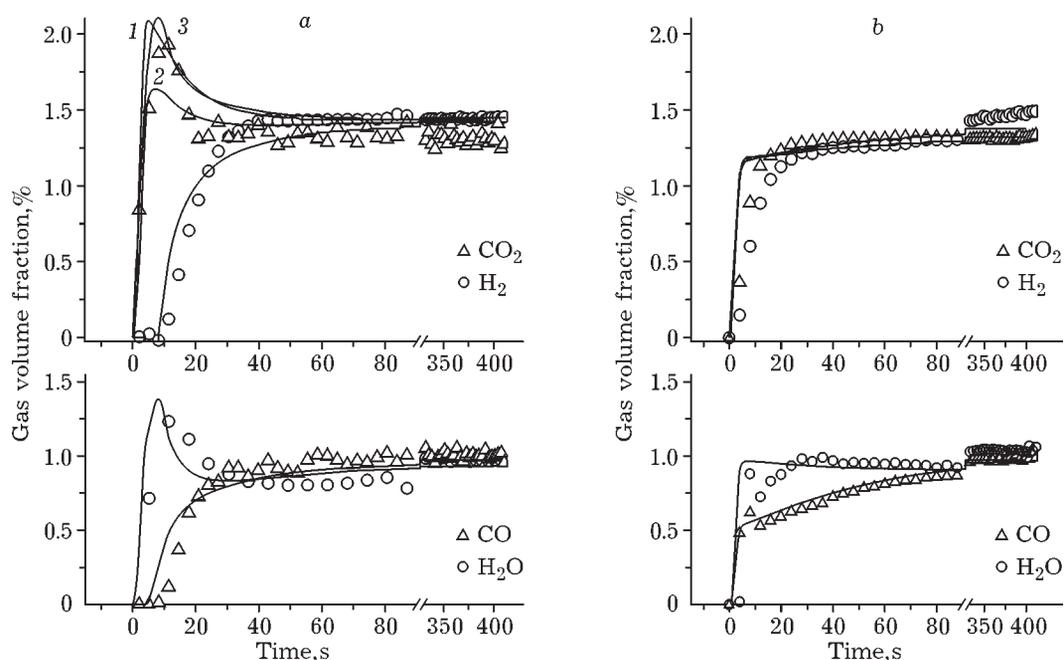


Fig. 2. Experimental (symbols) and calculated according to oxidation-reduction mechanism curves corresponding to the response due to switching from He to CO + H₂O for preliminary oxidized (a) and reduced (b) samples of 1.4 % Pt/Ce-Zr-O. In the case of CO₂, lines designate the variants corresponding to different mechanisms such as OR (1), A (2), OR + A (3); for the other components of the mix the calculation was performed according to OR + A mechanism.

the reduced condition, whereas the overall reaction rate, correspondingly, is determined by the rate of surface reoxidation by water.

Under the interaction of the reaction mixture both with oxidized and with reduced samples, a considerable disbalance was observed concerning carbon (see Table 1). We consider this fact to be connected with the formation of stable carbonates and/or formiates under CO interaction with oxidized centres and/or hydroxyl groups of the carrier [6, 9, 10]. Their amount exceeds to a considerable extent the value corresponding to monolayer covering of the surface. However, the formation of multilayer carbon-containing compounds or their accumulation in the bulk of the carrier [13] does not influence the rate of formation CO_2 , especially on the surface of a reduced sample (see Fig. 1), therefore the mentioned process could be considered to be a side reaction with the participation centres those are not involved in the catalytic cycle.

The nature of mixed oxides such as Ce-Zr-O allows such systems to accumulate superstoichiometrical oxygen [14] wherefrom after the oxidative treatment a lot of oxidized centres are formed on the surface. The substitution of a part of Ce by La causes reduces their maximal possible concentration to be reduced [3], which results in a less intense CO_2 formation under the interaction of the reaction mixture with oxidized Ce-Zr-La-O sample (see Fig. 1, a).

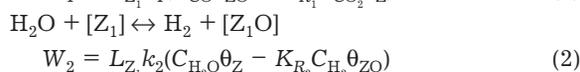
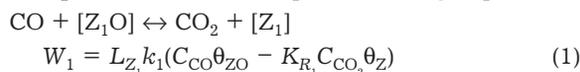
Pt/Ce-Zr-(La)-O. Applying Pt onto carriers does not cause any fundamental change in the dynamics of transient processes for carriers under the interaction of the reaction mixture both with oxidized and with reduced samples (Fig. 2), except for a faster, as compared to the carrier, establishing of the steady-state condition on the surface an oxidized sample. Since the direct platinum reoxidation by water is impossible [15], a question arises: due to what does the increase in the activity occur? Notwithstanding the fact that the nature of the reaction intermediates and the basic routes of the reaction course are still far from understanding, the two reaction mechanisms such as oxidation-reduction and associative are usually under consideration for Pt-containing systems based on CeO_2 and ZrO_2 the range of low (up to 300 °C) temperature values. The oxidation-

reduction mechanism assumes that CO and H_2 are adsorbed onto platinum and then they are oxidized by oxygen delivered from the carrier through the metal carrier interface [8–10], to produce CO_2 and H_2O , respectively. However, even at a very high rate of oxygen transfer from the carrier to platinum, the conversion of CO fundamentally cannot grow without an increase in the reaction rate for the carrier reoxidation by water, since the latter determines the overall reaction rate. The studies on oxygen isotope exchange kinetics within the mentioned systems have demonstrated that the rate of exchange between gas phase oxygen and the surface in the presence of Pt is much higher than that observed for pure carrier [16]. This fact is caused by a considerable increase in the amount of oxygen accumulated onto structural defects those arise within surface and near-surface layers of the carrier at the interface between the metal and the carrier resulting from the incorporation of platinum clusters [17]. It is reasonable to assume that the concentration of structural defects increases with the increase in the amount of platinum added. This, in turn, should result in an increase in the surface reoxidation rate as well as in the growth of conversion level, which was not observed in the experiment (see Table 1).

According to the associative mechanism, CO, being adsorbed at the interface between Pt and the carrier reacts with hydroxyl groups of the carrier with the formation of surface formiates those decompose to produce CO and H_2 in the presence of water vapour. It is supposed that platinum promotes the decomposition of formiates to yield CO and $-\text{OH}$ and thereby causes the regeneration rate of active centres to increase [8]. Within the framework of such a mechanism, both the rate of intermediate species formation and the rate of their decomposition exhibit an increase with the increase in the concentration of platinum; therefore in general the conversion level should not depend on the concentration of platinum. In order to understand what the mechanism among the mentioned ones determines the transformations on the platinum centres, we performed a numerical analysis of the response curves obtained both for Ce-Zr-(La)-O, and for Pt/Ce-Zr-(La)-O.

Numerical simulation of transient modes

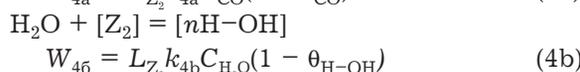
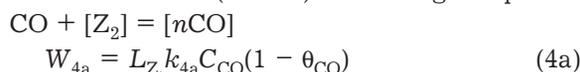
Ce-Zr-(La)-O. The numerical analysis of transient regimes on the surface of carrier samples was carried out within the framework of a simplest oxidation-reduction scheme where it is supposed that all the complexes adsorbed participating in the catalytic cycle are in quasi-equilibrium with respect to the gas phase:



Alongside with the stages of catalytic cycle we also took into account the diffusion of oxygen from the bulk of the carrier:



as well as the stage of the formation of strongly adsorbed C- and (H-OH)-containing complexes:



The present model in a quite adequate manner describes the dynamics of the response observed with flooding the CO + H₂O reaction mixture onto oxidized and reduced samples of the carrier (see Fig. 2); it is also very sensitive with respect to the initial sample condition. So, reducing the initial concentration of [Z₁O] centres on the oxidized sample and the rate of oxygen diffusion (the case of CeZrLa), one can considerably reduce the intensity of CO₂ re-

sponse at the initial moment on the oxidized sample (see Fig. 1, a).

In determining the parameters of the model we took into account that the equilibrium constants for stages (1) and (2) are connected by the relationship: $K_{R_1} K_{R_2} = C_{\text{CO}}^{EQ} C_{\text{H}_2\text{O}}^{EQ} / (C_{\text{CO}_2}^{EQ} C_{\text{H}_2}^{EQ})$, where C_i^{EQ} is the concentration of reagents corresponding to the conditions of thermodynamic equilibrium (at the given temperature and equimolar proportion between CO and H₂O in the initial mixture $C_{\text{CO}}^{EQ} / C_{\text{CO}_2}^{EQ} = C_{\text{H}_2\text{O}}^{EQ} / C_{\text{H}_2}^{EQ} \approx 0.65$). The number of active centres L_{Z_1} was accepted to be equal to the limiting concentration of oxygen on the surface. The latter, basing on the fact that only cerium in participates oxidation-reduction transformations, amounts to a half of monolayer ($0.5 \cdot 10^{19}$ at./m²). The number of L_{Z_2} centres whereon the formation of strongly bound C and (H-OH) complexes was preset in an arbitrary manner; this value also amounted to a half of monolayer. The obtained estimations of the rate constant for the reaction stages as well as the diffusion for oxygen are presented in Table 2. The rate constants for stages (4a) and (4b), as well as the diffusion coefficient for Pt/Ce-Zr-O are somewhat higher as compared to Ce-Zr-O and vary depending on the oxidation level, thus there is only an order of magnitude for these values presented in Table 2.

The rate constant for the stage of CO interaction ZO (k_1) determined according to the rate of CO₂ formation on an oxidized sample during the initial moment of time is more than

TABLE 2
Rate constants of reaction stages

Stage	k_i^* , s ⁻¹	K_{R_i}
1 CO + [Z ₁ O] ↔ CO ₂ + [Z ₁]	40	0.01
2 H ₂ O + [Z ₁] ↔ H ₂ + [Z ₁ O]	1.5	42
3 [Z ₁ O] ↔ {O _{bulk} } (diffusion)	$D/L^2 \approx 10^{-1}$	–
4a CO + [Z ₂] → [nCO]	$\approx 10^0$	–
4b H ₂ O + [Z ₂] → [nH-OH]	$\approx 10^0$	–
5 [Pt] + [Z ₁ O] ↔ [PtO] + [Z ₁]	$> 10^2$	–
6 [PtO] + CO ↔ CO ₂ + [Pt]	$3 \cdot 10^2$	< 0.01
7 [PtO] + H ₂ → H ₂ O + [Pt]	$< 1 \cdot 10^2$	–
8 [Pt] + CO + H ₂ O ↔ CO ₂ + H ₂ + [Pt]	$> 10^4$	0.42

*Data are presented at the rate for one active centre (L_{Z_1} for stages (1)–(4) and L_{Pt} for stages (5)–(8).

an order of magnitude higher than the rate constant for the reoxidation stage (k_2). As a consequence, the increase in k_2 results in a considerable increase in the calculated conversion level. This fact confirms that the steady state reaction rate on the carrier at the given concentration of reagents and the temperature is determined by the reoxidation stage.

1.4 % Pt/Ce-Zr-O. The above mentioned scheme of reaction on the carrier (stages (1)–(4)) together with the obtained estimations of rate constant of the stages has been used as a basis for the model of the processes on Pt-containing sample. Different variants of the reaction mechanisms on platinum centres are considered: oxidation-reduction reaction (OR), associative reaction (A) as well as the combination of these mechanisms (OR + A). Here it was proposed that the concentration of complexes adsorbed on platinum is also quasi-equilibrium with respect to the gas phase.

The feature of the reaction scheme corresponding to the oxidation-reduction mechanism consists in the fact that reaction of H_2 oxidation is irreversible, whereas the reoxidation of platinum centres occurs due to oxygen transfer from the carrier on platinum: $[Pt] + [Z_1O] \leftrightarrow [PtO] + [Z_1]$

$$W_5 = L_{Pt}k_5(\theta_{ZO} - \theta_{PtO}) \quad (5)$$

$$[PtO] + CO \leftrightarrow CO_2 + [Pt]$$

$$W_6 = L_{Pt}k_6(C_{CO}\theta_{PtO} - K_{R_6}C_{CO_2}\theta_{Pt}) \quad (6)$$

$$[PtO] + H_2 \rightarrow H_2O + [Pt]$$

$$W_7 = L_{Pt}k_7C_{H_2}\theta_{PtO} \quad (7)$$

The present model adequately reflects the dynamics of transient regimes on such samples as Pt/Ce-Zr-(La)-O only for an increase much higher than one order of magnitude in the rate constant of carrier reoxidation by water (see Fig. 2) as well as provided that it does not depend on the concentration of platinum (the latter is unlikely). Since the model does not satisfy the main principle of thermodynamic equilibrium such as the reversibility of all the stages, changing the rate constants of separate stages or the values of preset model parameters is enough to disturb the equilibrium. So, for example, with an increase in the weighed sample portion the conversion level could become even higher than the equilibrium value, which is from inadmissible the physical point of view (Fig. 3, a).

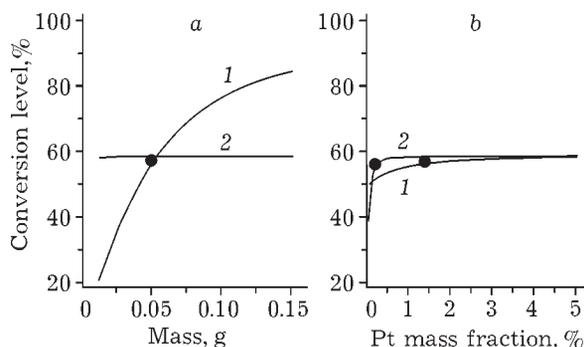
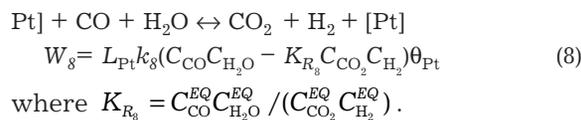


Fig. 3. Conversion level for Pt/Ce-Zr-(La)-O depending on weighed sample portion (a) and Pt content (b), calculated according to the models corresponding to mechanism OR (1) and OR + A (2). Points stand for experimental values.

As opposed to the oxidation-reduction mechanism, the associative mechanism is not accompanied by changing the oxidation level of active centres, and within the frameworks of quasi-steady-state approximation with respect to all the other intermediate species the reaction scheme for this mechanism could be written in one stage:



In this case, with no changing in the rate constant of stages (1)–(4) occurring on the carrier surface, we can increase the calculated conversion level up to the values observed in the experiment, only at the expense of stage (8). At sufficiently great k_8 values the conversion level does not depend on changing in rate constants of stages, in number of active centres, in weighed sample portion and in the contact time, which is inherent in thermodynamic equilibrium. At the same time the present model somewhat worse describes the transient regime on the surface of an oxidized sample to result in a considerable underestimation of CO_2 formation rate at the initial period of time (see Fig. 2).

Having included in the model both stages (5)–(7), corresponding to the oxidation-reduction mechanism (k_{4b} in this case remained constant), and stage (8) corresponding to the associative mechanism, we simultaneously increased the rate of CO_2 formation on the surface of oxidized sample and the steady-state reaction

rate. As a result, a good enough description of transient and steady-state modes (see Fig. 2) has been obtained. At $k_8 > 10^4$, thermodynamic equilibrium is attained: the calculated conversion level almost does not change with varying (down to the certain bottom limit) the rate constants of stages, as well as the number of active centres, including platinum (see Fig. 3, b) and the weighed portion of catalyst (see Fig. 3, a). The estimates of rate constants for the stages of the given model are presented in Table 2.

Thus, under steady-state conditions the main contribution (up to 90 %) to the reaction rate is made by the transformation according to the associative mechanism. The transformations according to the oxidation-reduction mechanism determine the dynamics of transient regimes, in particular on a preliminary oxidized catalyst.

CONCLUSION

Dynamics of transient processes in the reaction of high-temperature steam CO conversion on carriers with general composition such as $\text{Ce}_{0.5-x}\text{Zr}_{0.5-x}\text{La}_{2x}\text{O}_y$ ($x = 0, 0.1$) and Pt-containing catalysts on their basis was investigated. It has been demonstrated that kinetic laws for both carriers are described by the simplest oxidation-reduction reaction scheme with the rate-determining stage of surface reoxidation by water. After applying platinum the CO conversion level increases to a considerable extent, and the reaction proceeds under the conditions close to thermodynamic equilibrium. Under steady-state reaction conditions at an equimolecular ratio between the reagents the condition of the catalyst is close to reduced one. The main contribution to the reaction rate is

made by the transformation according to the associative mechanism realized at the platinum-carrier interface which mechanism supposes direct interaction between CO adsorbed on platinum and hydroxyl groups of the carrier. At the same time, the dynamic features of transient regimes are determined by transformations according to oxidation-reduction mechanism, as well as by the rate of oxygen diffusion from the bulk of the carrier and the rate of oxygen transfer from the carrier to platinum.

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