Temperature hysteresis phenomena in heterogeneous catalysis

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Temperature hysteresis is observed only in exothermic heterogeneous catalytic reactions (*viz.*, oxidation and methanation of CO or propene hydrogenation) and is absent in the case of endothermic reactions (dehydrogenation of isobutane) or reactions with heat close to zero (*viz.*, 2-butene isomerization). Temperature hysteresis in hydrogenation reactions was discovered for the first time. The concept of local overheating of catalyst active sites caused by poor removal of the reaction heat is proposed to provide a noncontradictory interpretation of the appearance of hysteresis loops.

Key words: heterogeneous catalysis, temperature hysteresis, oxidation, hydrogenation, methanation.

Temperature hysteresis in heterogeneous catalysis belongs to the class of phenomena referred to as critical in theoretical kinetics.[1] The essence of this phenomenon is that some reaction parameter (for example, the rate or the degree of conversion of a reactant) measured during the change of temperature in one direction does not coincide with the same parameter measured during the change of temperature in the opposite direction. This produces the so-called hysteresis loop when the ascending and descending branches of the temperature dependence differ from each other.

An explanation of hysteresis is based on the view that several steady states exist in a catalytic system. In this case, it is assumed that during gradual temperature change, one steady state is replaced, at a particular instant, by another state submitting to different kinetic features. Therefore, the reaction proceeds at a different rate, although the temperature measured in the reactor remains the same.

This conclusion has been drawn, for example, after mathematical analysis of CO oxidation over platinum.[2] The possibility of existence of different steady states in this reaction proceeding over the 0.05%Pd/SiO_2 and (0.05Pd%+1%Cr_2O_3)/Al_2O_3 catalysts has been verified experimentally.[3] The appearance of hysteresis has been attributed[4] to the fact that CO oxidation over nickel catalyst occurs in the region of the Ni—NiO phase transition. It is believed[4] that the formation of the two-dimensional NiO phase is accompanied by substantial acceleration of the reaction, whereas the subsequent transition to the three-dimensional NiO phase results in its sharp retardation. In another study, the occurrence of hysteresis in CO oxidation over platinum was explained by the existence of different steady states.[5] Among the relevant publications, one can also mention studies in which this reaction was carried out at low pressures (10^{-2} Torr) over the CuO/SiO_2 and Pd catalysts, respectively.[6,7] The hypothesis of multiple steady states as a reason for hysteresis has been considered fairly comprehensively in a review.[8] The results of a systematic study of the mathematical models of chemical reactions, which can involve critical phenomena, are presented in a monograph,[1] in which the same CO oxidation is considered as an example.

Other interpretations of the reasons for temperature hysteresis have also been proposed; however, they describe particular cases. Thus hysteresis arising in CO oxidation over platinum foil was attributed to the slow change in the state of adsorbed oxygen and, hence, in the platinum surface when excess O_2 is present in the reaction mixture.[9] In this study, a smooth (*i.e.*, having intermediate points) pattern of the temperature dependence was fairly regarded as indicating the absence of transition of the system from one steady state to another. The appearance of a hysteresis loop in CO oxidation over a platinum wire that had not been preliminarily cleaned was interpreted as being due to the removal of sulfur and carbon impurities, which could retard the reaction, from the metal surface.[10]

The hysteresis kinetic effects observed in methane oxidation over the 5%Pd/Al_2O_3 and 2%$Pd/La_2O_3 \cdot Al_2O_3$ catalysts were explained[11] by the formation of the PdO oxide phase. A hysteresis loop was also observed[12] in CH_4 combustion catalyzed by PdO/Al_2O_3. These are perhaps the only examples of reactions other than CO oxidation in which temperature hysteresis effects were observed, although they are still oxidation reactions.

The temperature hysteresis in CO oxidation over various catalysts has also been noted in several recent publications.[13—17] However, the authors did not propose any original interpretation of this phenomenon.

The opinion has been expressed[18] that the presence of multiple steady states cannot be considered to be a necessary condition for hysteresis.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1379—1385, August, 2000.

1066-5285/00/4908-1373 $25.00

Thus, the data obtained previously are scattered and the range of reactions used to study the hysteresis effect is very narrow. No data on the relationship between temperature hysteresis and the nature of the catalyst can be found in the literature either. We set ourselves the task to carry out a systematic study by a unified procedure of the temperature dependences for reactions of various classes using a wide range of catalysts of different natures. Some of the results reported here have been published previously.[19—23]

Experimental

The experiments were carried out at atmospheric pressure in a specially designed semiautomatic nongradient catalytic setup, which ensured (a) controlled supply of gaseous components of the reaction mixture; (b) maintenance of the measured temperature in the reactor and its change with a small step (down to 1 °C); (c) circulation of the reaction mixture at a flow rate of $\geq$180 L h^{-1} to create conditions without concentration gradients; (d) the possibility of taking samples for GLC analysis at the inlet and the outlet of the reactor.

The weight of the catalyst samples was usually 0.5 or 1 g.

The reaction mixture of CO oxidation was analyzed using a 1.5 m$\times$2 mm chromatographic column packed with the Porapak Q phase. In the case of CO and propylene hydrogenation, analysis was carried out on a 2 m$\times$2 mm column with 5A zeolite, and for isobutane dehydrogenation and 2-butene isomerization, an identical column with β,β′-oxydipropionitrile was used.

When the composition of the reaction mixture in the two or three successive measurements after transition to a next temperature had remained constant, the degree of conversion of the initial substrate (x) corresponding to this temperature was determined from the results of analysis.

The size of the hysteresis effect was conventionally estimated as the width of the hysteresis loop, equal to the difference between the temperatures corresponding to a degree of conversion, equal to 30%, on the ascending and descending branches (ΔT_{30}). To make sure that hysteresis is not a consequence of the change in the catalyst activity, several successive heating—cooling cycles were conducted and the degree of conversion x was measured not only during the temperature change in the forward direction (from low to high temperatures) but also during the temperature decrease. In all cases, the temperature dependences obtained were true in this sense.

Other necessary experimental details are mentioned below in the description of the corresponding experiments.

Results and Discussion

CO oxidation. Like our predecessors, we observed clear-cut temperature hysteresis in CO oxidation by atmospheric dioxygen. We attempted to find out whether the magnitude of this effect is related to the catalyst properties.

The following catalysts were tested: a copper-alumino-calcium catalyst prepared from the system containing 20 mol. % CuO and 80 mol. % talum (according to X-ray diffraction analysis, this was a mixture of calcium mono- and dialuminates)[24]; unsupported copper oxide of two types, namely, a chemically pure grade commercial preparation and the oxide prepared by thermal decomposition of copper hydroxocarbonate at 300 °C; supported palladium catalysts Pd/Al_2O_3 containing 0.03 or 0.3% (w/w) Pd; palladium black; the industrial platinum catalyst AP-56 (0.5% (w/w) Pt/Al_2O_3); supported platinum catalyst 0.6% Pt/Al_2O_3 prepared by impregnation of Al_2O_3 with chloroplatinic acid; platinum foil; the nickel-alumino-calcium catalyst NKM-4 (the NiO—$CaAl_2O_4$ system containing 35% (w/w) NiO)[25]; and the NTK-7 catalyst containing 12.7% Mn_3O_4, 64.3%Al_2O_3, and 23.1% CaO.

The flow rate of the CO—air reaction mixture was 6 L h^{-1}. The CO : O_2 ratio was ~1 : 1.5 unless otherwise specified.

In most cases, efficient CO oxidation takes place in the same temperature range, 100—150 °C, irrespective of the catalyst. Only in the presence of unsupported CuO prepared by the decomposition of Cu hydroxocarbonate, which is one of the most active catalysts for this reaction, does oxidation start somewhat below 100 °C (Fig. 1, *a*), whereas the reaction catalyzed by Pt foil exhibiting very low activity starts above 200 °C (Fig. 1, *b*).

The hysteresis loop obtained with highly active catalysts is much wider than that obtained with catalysts having low activities. For example, if we consider only the copper-containing catalysts, in the case of the active copper-alumino-calcium system, ΔT_{30} > 80 °C (Fig. 2, *a*), whereas with the low-activity commercial copper oxide, this value is at most 15 °C (Fig. 2, *b*) for close compositions of the reaction mixture (14.2 and 13.6% CO, respectively).

An increase in the initial CO concentration over certain limits also increases the width of the hysteresis loop; for the copper-alumino-calcium catalyst, when the content of CO in air is 6.2% (CO : O_2 = 1 : 3.5), $\Delta T_{30} \approx$ 15 °C, and when [CO] = 14.2%, ΔT_{30} > 80 °C (see

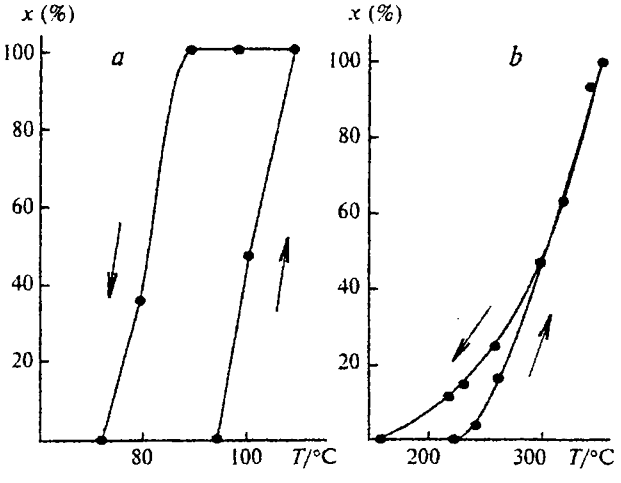

Fig. 1. Temperature dependence of the degree of CO oxidation over copper oxide prepared by thermal decomposition of copper hydroxocarbonate (*a*) and over Pt foil (*b*) (the arrows mark the increase and the decrease in temperature).

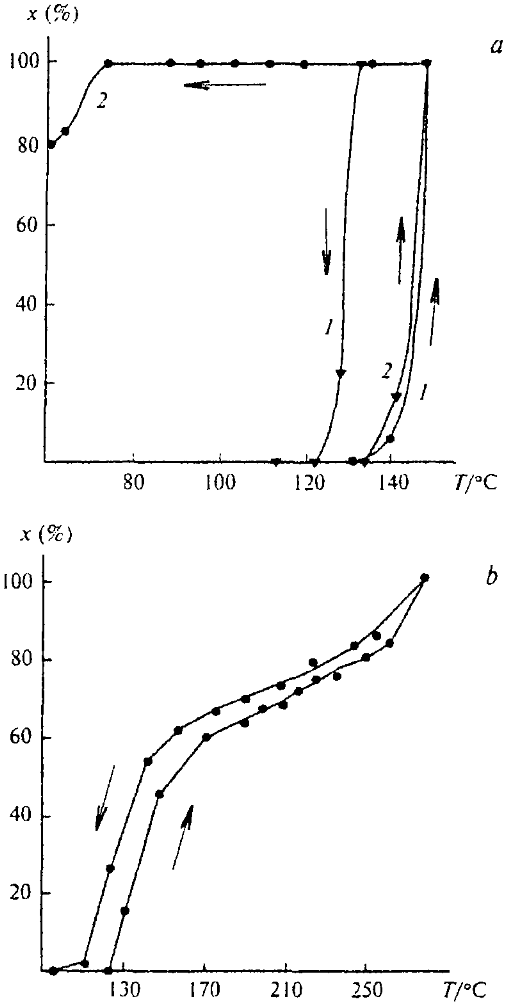

Fig. 2. Temperature dependences of the degree of CO oxidation over copper-alumino-calcium catalyst (*a*) at initial CO concentrations of 6.2 (*1*) and 14.2 (*2*) % (v/v) and over commercial copper oxide (*b*).

Fig. 2, *a*). In the latter case, a self-sustaining reaction mode was realized, *i.e.*, when the heat supply from the outside had been terminated, the measured temperature in the reaction was maintained at a level of ~60 °C by means of the reaction heat.

A similar and, in some cases, an even more pronounced hysteresis effect was observed in CO oxidation over three palladium catalysts (Fig. 3), the 0.6% Pt/Al_2O_3 and AP-56 catalysts (Fig. 4), NTK-7 (Fig. 5, *a*), and NKM-4 (Fig. 5, *b*).

It is noteworthy that in all cases, without exceptions, transition to a high degree of conversion is not instantaneous. Even for very steep ascending branches of the temperature dependences, which are observed with the most active catalysts, intermediate points are always present on the curves. In order to detect these points, it was often necessary to raise the reactor temperature in tiny steps, literally, by 1 °C.

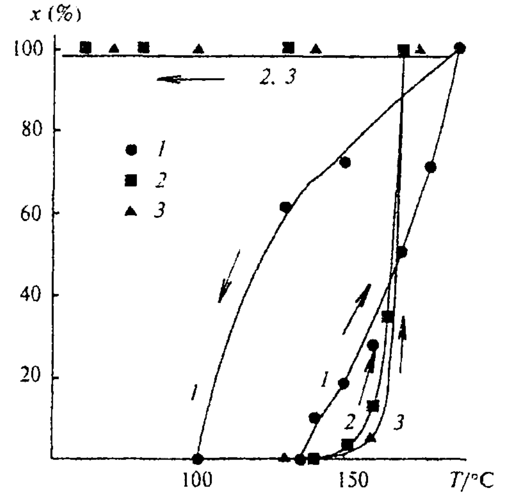

Fig. 3. Temperature dependences of the degree of CO oxidation over 0.03%Pd/Al_2O_3 (*1*), 0.3%Pd/Al_2O_3 (*2*), and Pd black (*3*).

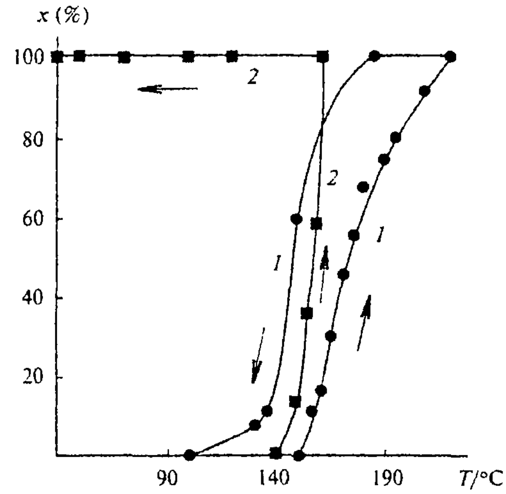

Fig. 4. Temperature dependences of the degree of CO oxidation over the AP-56 catalyst (*1*) and 0.6%Pt/Al_2O_3 (*2*).

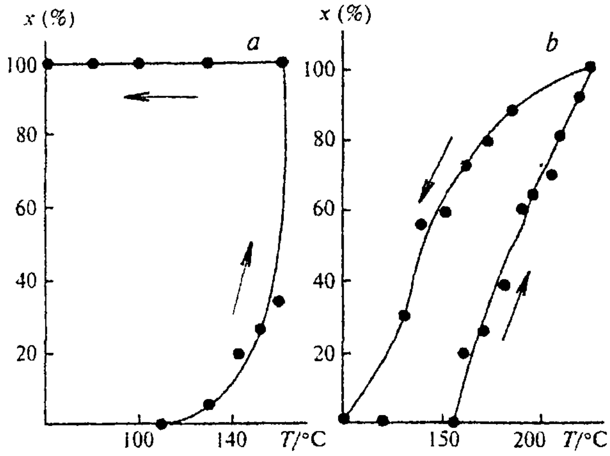

Fig. 5. Temperature dependence of the degree of CO oxidation over the NTK-7 (*a*) and NKM-4 (*b*) catalysts.

The temperature dependence of the degree of CO oxidation on Pt foil represents a somewhat specific case; in this case, hysteresis is virtually absent (see Fig. 1, *b*).

On the whole, the general patterns of temperature dependence with a hysteresis loop obtained with absolutely different catalysts (several copper-containing, platinum, palladium, nickel, and manganese-containing catalysts) are similar. It is significant that the temperature dependences obtained with catalysts of the same basic nature, the commercial "wire" copper oxide and the copper oxide prepared in a laboratory, which sharply differ in specific surface area (0.1 and 34 $m^2 g^{-1}$) and, hence, in activity, were absolutely different (see Figs. 1 and 2, *b*).

Hydrogenation. Hydrogenation of CO (methanation) was carried out over the 10%Ni/ZrO_2, (10%Ni+3%La)/ZrO_2, 10%Ni/TiO_2, and NKM-4 catalysts and over a nickel wire, while propylene hydrogenation was performed on the 50%Ni/Kieselguhr catalyst. The CO : H_2 and C_3H_6 : H_2 ratios in the initial reaction mixtures were ~1 : 4 for an overall flow rate of 8 L h^{-1}. Prior to experiments, the catalysts were reduced in a flow of H_2 for 4 h at 400 °C.

It can be seen in Fig. 5, *b* that CO oxidation over the NKM-4 catalyst is accompanied by a substantial temperature hysteresis. An even more pronounced effect is observed in CO methanation over this catalyst (Fig. 6) in approximately the same temperature range. Hysteresis loops were also found in CO methanation over other supported catalysts (Fig. 7). The narrowest hysteresis loop was found in the case of Ni/TiO_2 (ΔT_{30} = 57 °C), which might be due to the strong metal—support interaction typical of this system, which may decrease the catalyst activity.[26,27] However, in CO hydrogenation, unlike oxidation, the self-sustaining mode was not detected with any of the catalysts.

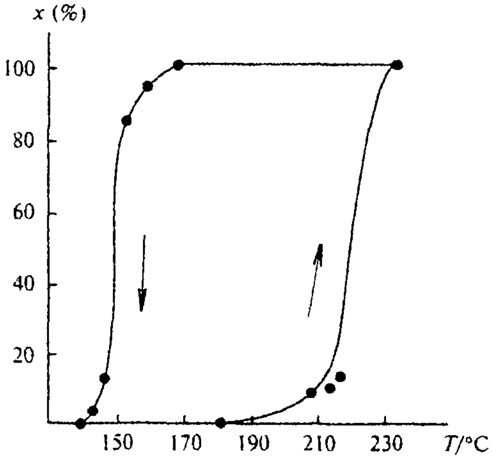

Fig. 6. Temperature dependence of the degree of CO methanation over the NKM-4 catalyst. The arrows indicate the points obtained in two successive heating—cooling cycles.

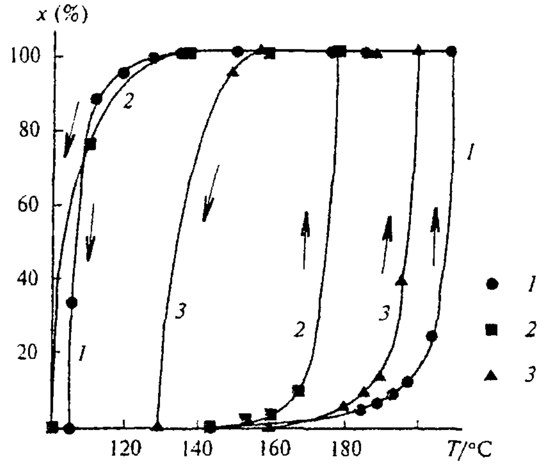

Fig. 7. Temperature dependences of the degree of CO methanation over (10%Ni+3%La)/ZrO_2 (*1*), 10%Ni/ZrO_2 (*2*), and 10%Ni/TiO_2 (*3*).

In the case of nickel wire (due to its low activity, a 10-g sample was used), the hysteresis loop is very narrow (ΔT_{30} = 17 °C), although it is still observed (Fig. 8, *a*).

A relatively small but obvious temperature hysteresis has been found in the hydrogenation of propylene (Fig. 8, *b*).

To the best of our knowledge, hysteresis temperature phenomena in hydrogenation reactions have never been studied previously. It can be seen from the above-presented figures that the temperature dependences for fundamentally different chemical reactions, *viz*., oxidation and hydrogenation of CO, follow similar patterns.

Isobutane dehydrogenation. All the reactions considered above, the oxidation and methanation of CO and the hydrogenation of propylene, are exothermic. It was of interest to compare the temperature dependences for these reactions with those for endothermic reactions and for reactions with slight thermal effects.

Two catalysts were chosen for the endothermic dehydrogenation of isobutane, namely, an alumino-pla-

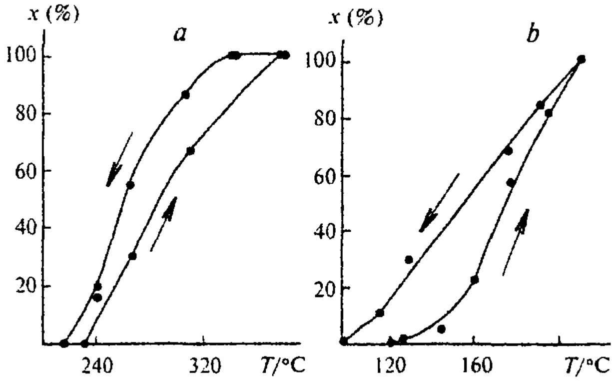

Fig. 8. Temperature dependences of the degree of CO methanation over Ni wire (*a*) and the degree of propylene hydrogenation over Ni/Kieselguhr (*b*).

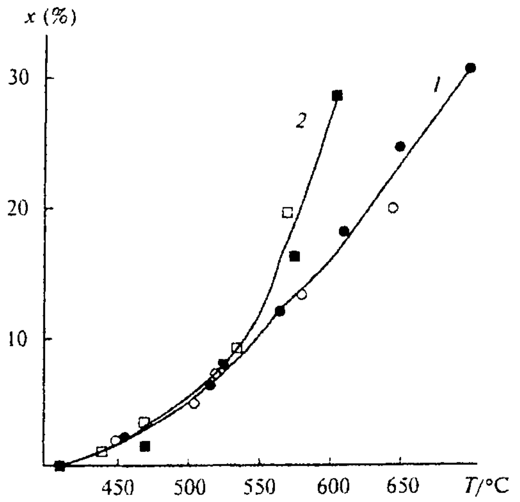

Fig. 9. Temperature dependences of the degree of isobutane dehydrogenation over (0.6%Pt+2%Sn+1%K)/Al_2O_3 (*1*) and over the alumino-chromium-potassium catalyst (*2*). Black dots were obtained during heating and light dots were obtained during cooling.

tinum catalyst with tin and potassium additives (0.6%Pt+2.0%Sn+1.0%K)/γ-Al_2O_3, which had proved to be efficient for this reaction,[28] and an alumino-chromium-potassium catalyst containing 6.5% Cr. The reaction mixture consisted of isobutane and H_2 in 1 : 1 ratio; the feed flow rate was 12 L h^{-1}.

Unlike oxidation or hydrogenation, no signs of hysteresis were found in the temperature curves in this case; the ascending and descending branches virtually coincided (Fig. 9).

2-Butene isomerization. As a reaction whose heat is close to zero, we chose the isomerization of 2-butene to 1-butene. The starting material contained *cis*- and *trans*-isomers. 2-Butene was fed to the reactor at a flow rate of 6 L h^{-1} without dilution with any gas. The process was catalyzed by γ-alumina.

The variation of the composition of the reaction mixture *vs.* temperature is shown in Fig. 10, while Fig. 11 shows the temperature dependence of the ratio of the total 1-butene concentration to 2-butenes concentration. The latter curve is actually equivalent to the temperature dependence of the degree of conversion of the starting hydrocarbon. It can be seen in Fig. 11 that no temperature hysteresis is observed in 2-butene isomerization.

Thus, the temperature hysteresis can be observed only in exothermic reactions; it does not show itself in reactions with a nearly zero or negative heat. Moreover, the width of the hysteresis loop tends to increase following an increase in the positive heat of reaction. Indeed, in the case of CO oxidation (ΔH = −283 kJ mol^{-1}), a self-sustaining reaction mode is established in some favorable cases. In CO methanation (ΔH = −206 kJ mol^{-1}), this mode cannot be attained even with the most active catalyst NKM-4, specially developed for this process,[24] and in propylene hydrogenation (ΔH = −124 kJ mol^{-1}), the hysteresis loop was relatively narrow. Note that 2-butene isomerization includes several reactions because both *cis*- and *trans*-isomers participate in it; however, the greatest heat of the reaction observed in the temperature range under interest is about 10 kJ mol^{-1}. In the case of isobutane dehydrogenation, the heat of reaction $\Delta H \approx$ 130 kJ mol^{-1} (the ΔH values were taken from the literature[29]).

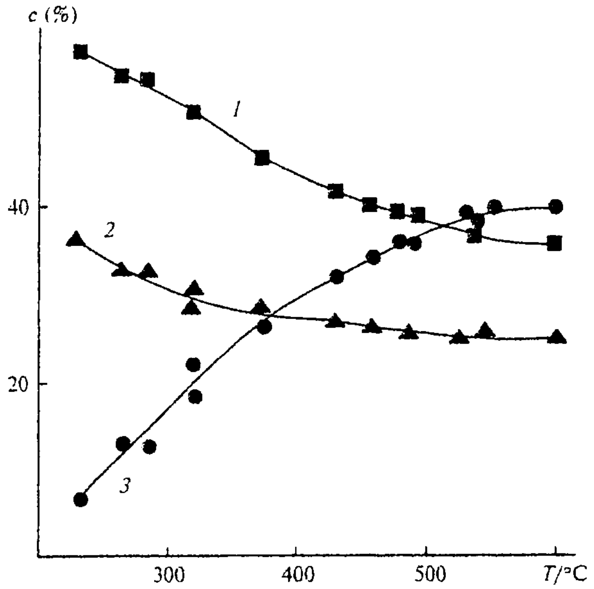

Fig. 10. Temperature dependence of the composition of the reaction mixture during 2-butene isomerization on Al_2O_3: (*1*) *trans*-2-butene, (*2*) *cis*-2-butene, (*3*) 1-butene.

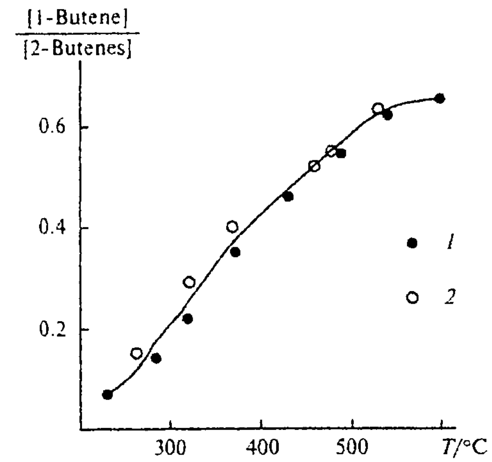

Fig. 11. Temperature dependence of the ratio of concentrations of 1-butene to 2-butenes during 2-butene isomerization on Al_2O_3: (*1*) temperature increase, (*2*) temperature decrease.

In addition, several other regularities can be followed:

— in none of the experiments, not even in the fastest reaction over the most active catalyst, is a "break" of the temperature curves with instantaneous transition to a higher degree of conversion observed; a cautious controlled raising of temperature with a step of 1 °C always provided intermediate points on both the ascending and descending branches;

— the character of the hysteresis temperature dependences follows no evident correlation with the type of reaction or the nature of the catalyst;

— only a slight hysteresis effect, if any, can be observed in the presence of bulk metal catalysts (*viz.*, foil, wire), unlike with supported dispersed catalysts;

— the higher the catalyst activity, all other factors being the same, the wider the hysteresis loop;

— the width of the hysteresis loop also depends on the reagent ratio.

Some of these facts obviously contradict the hypothesis of multiple steady states as the reason for hysteresis. As noted above, according to these views, at a particular instant during gradual temperature variation, the system would undergo a qualitative transition (leap) from one state to another state, in which other kinetic laws are effective, and, correspondingly, the reaction rate would change, although the temperature in the reactor remains the same. First of all, this fails to explain the sharp difference between exo- and endothermic reactions: in the former type of reaction, temperature hysteresis takes place, whereas in the latter type, it does not. In addition, transitions between different steady states should occur instantaneously; in this case, it would have been impossible to obtain any intermediate points on the temperature curves. It is this reason that has been regarded previously[9] as evidence against the explanation of the hysteresis effect by the existence of numerous steady states. Finally, this hypothesis is hardly consistent with the fact that reactions of absolutely different types occurring in the presence of catalysts different in both genesis and nature produce similar temperature hysteresis effects. Apparently, it could hardly be expected that different reaction systems would involve similar steady states and, moreover, that they would exist in roughly coinciding temperature regions.

We propose an absolutely different concept of temperature hysteresis, which seems to be free from these contradictions. In our opinion, in the case of exothermic reactions proceeding over heterogeneous catalysts, an increase in the temperature results in an increase in the reaction rate in the catalyst active site up to a value at which the heat evolved has no time to dissipate due to heat transfer. The most efficient way of heat removal is heat conduction across the catalyst bulk.[30] However, in disperse solids, to which most of catalysts belong, contact heat conduction is hampered; the smaller the size of the particles of the grain material, the poorer the heat transfer.[31] In the case of less porous solids, the heat conductivity factor is greater than that for highly porous ones; bulk metals possess the greatest heat conductivities.

Due to the insufficient heat removal, the real "local" temperature of the active site at which the reaction actually proceeds becomes substantially higher than the average temperature in the catalyst bed measured by a thermocouple (which is usually referred to as the reaction temperature). Due to the local overheating of the active sites, the degree of conversion becomes greater than the value that should have been observed at the temperature measured by the thermocouple at a given instant. This enhances even more the heat evolution and, hence, the temperature of the active site. As a consequence, the degree of conversion in a very narrow measured temperature range swiftly increases. After the heat supply from the outside has stopped, *i.e.*, during cooling of the reactor, the excess heat that has not had time to dissipate due to insufficient heat removal makes the reaction proceed at a higher real temperature than the temperature recorded by the thermocouple. Thus, the degree of conversion is maintained at a higher level. The descending branch of the temperature curve would inevitably shift to the left along the scale of measured temperature with respect to the ascending branch, *i.e.*, a hysteresis loop would arise.

The possibility of substantial local overheating of the catalyst has been predicted theoretically[32] and observed experimentally[33] in CO methanation over a nickel bead catalyst; the measured temperature gradient reached 46 °C.

It follows from the foregoing that temperature hysteresis can be observed only in exothermic reactions over heterogeneous catalysts. It becomes clear why the pattern of the hysteresis curves is determined by the heat of reaction and by features of heat removal in this particular catalytic system rather than by the chemical nature of the reaction or the catalyst. Bulk metals are the best heat conductors; hence, their active sites are overheated to the least extent and, therefore, reactions over a metallic wire or foil exhibit the minimum temperature hysteresis (see Fig. 1, *b* and 8, *a*). In this connection, it should be noted that heat removal can be hampered not only by the support but also by the low-activity dispersed bulk of the catalyst itself. This might account for the fact that a wide hysteresis loop is observed in CO oxidation over Pd black (see Fig. 3), which is a finely dispersed powder. The increase in ΔT_{30} with an increase in the catalyst activity can also be understood. Indeed, the more active the catalyst, the greater the amount of heat evolved on the local sites (because the number of these sites is greater) and the higher their overheating. The dependence of the width of the hysteresis loop on the reactant ratio is explained in a similar way (see Fig. 2, *a*). When the ratio is favorable, the reaction rate increases, heat evolution is enhanced, and, correspondingly, the local overheating of the active sites is also enhanced.

In conclusion, we would like to note that taking into account the hysteresis effects can be directly related to the measurement of fundamental kinetic parameters such as the activation energy of reactions, catalyst activity, *etc.* The activation energy of a reaction in heterogeneous catalysis is by itself a complex value incorporating a series of elementary effects, for example, the heat of adsorption. In addition, measurement of the activation energy becomes meaningless without knowing the real temperature of the active sites, which can differ substantially from the measured temperature if hysteresis is involved. Just the same, it is difficult to estimate the catalyst activity in reactions in which hysteresis effects are possible.

This work was supported by the Russian Foundation for Basic Research (Project No. 00-03-32169).

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Received December 3, 1999;
in revised form March 27, 2000