= LETTER TO THE EDITOR =

Selective Oxidation of CO under Conditions of Catalyst Surface Ignition

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The oxidation of CO in the presence of hydrogen (selective oxidation of CO) has been intensely studied in recent years in the context of hydrogen purification for fuel cells (for example, see [1, 2] and references therein). Many researchers observed a rapid increase in the conversion of CO with temperature. This phenomenon was usually defined by the term ignition. Note that, as a rule, ignition cannot be implemented in heterogeneous catalysis. However, the spontaneous change of a reaction to an outer-diffusion region (Frank-Kamenetskii [3] named it catalyst surface ignition) can be observed. According to Frank-Kamenetskii [3], this change is observed in exothermic reactions in the case that the positive heat flow q^+ due to the reaction becomes equal to the negative heat flow q^- related to heat removal, $q^+ = q^-$. In combination with the constraint $dq^+/dT > dq^-/dT$, this condition becomes crucial, and the reaction abruptly changes to an outer-diffusion region as the temperature is increased; this is accompanied by a spontaneous increase in the reaction temperature [3] (see also [4]).

To understand the essence of the above processes, we studied the selective oxidation of CO on a platinumcontaining catalyst in an excess of hydrogen in the presence (and in the absence) of CO_2 and water vapor in flow reactors with dramatically different conditions of heat removal.

Reactor 1 (with a high rate of heat removal) was close to an isothermal reactor. The reaction was performed in a cylindrical metal reactor with a coaxially placed metal tube. A catalyst sample was diluted with an inert material in a ratio of 1 : 10 and loaded in an annular gap between the tube and the reactor walls.

Cylindrical quartz reactor 2 (with a low rate of heat removal) approached an adiabatic reactor, so that the temperature of a gas mixture increased as the mixture moved along the axis of the reactor. A catalyst sample was placed in the reactor without dilution with an inert material. The temperature of the gas mixture was measured to within 0.1 K at the inlet and outlet of the catalyst bed (thermocouples in a thin metal jacket in the catalyst bed). The furnace temperature was specified with the use of a special programmer.

The residual concentration of CO in a dried gas mixture was measured (and recorded) in an on-line mode with the use of a BINOS 100 IR analyzer (error of <1 ppm).

We found that the oxidation of CO in reactor 1 occurred in a kinetic region. In reactor 2, the ignition of a catalyst surface was observed, and the reaction abruptly changed to an outer-diffusion region. Figure 1 illustrates the ignition and quenching of the surface. At a low temperature, the reaction occurs in a kinetic region; the temperature in the catalyst bed increased in parallel with the temperature of the furnace until the critical temperature of surface ignition was reached. On reaching a critical value, the catalyst bed temperature spontaneously increased at a constant furnace temperature with a simultaneous decrease in the residual concentration of CO. Once the surface ignition mode was established, a change in the furnace temperature only slightly affected the gas temperature in the catalyst bed and the residual CO content of the gas mixture until the critical temperature of surface quenching was reached (with decreasing temperature). On reaching this critical value, the temperature in the catalyst bed abruptly decreased, and the CO content increased; both of these parameters changed to a level that occurred before ignition. In this case, a hysteresis was observed, which is characteristic of the phenomenon of surface ignition (Fig. 1).

The apparent activation energy was determined by two methods: from the dependence of the critical temperature of surface ignition on the space velocity of a gas flow (see [4, p. 193]) and from data obtained in an isothermal reactor using a traditional method. Both of the values were practically equal (13 and 14 kcal/mol).

It is of importance that in all cases the residual CO content under optimum conditions was much lower in a surface ignition mode than that in an isothermal reactor, where the reaction occurred in a kinetic region.

Figure 2 demonstrates the temperature dependence of the residual CO concentration in an isothermal reactor (curve 1) and in a "hot spot" at the outlet of the catalyst bed in reactor 2 (curves 2, 3). It can be seen that the residual CO concentration at the same temperatures and space velocities was lower by one order of magnitude under conditions of catalyst surface ignition.



Fig. 1. Hysteresis in the ignition and quenching of a catalyst surface. Space velocity: 66700 h^{-1} . Initial gas mixture composition (vol %): CO, 0.85; O₂, 0.85; CO₂, 17; H₂, 33; H₂O, 17; and the balance N₂.



Fig. 2. Dependence of the residual CO concentration on gas temperature (*I*) in an isothermal reactor and (2, 3) at the outlet of the catalyst bed in reactor 2. The initial gas mixture composition is specified in Fig. 1. Space velocity (h^{-1}) : (*I*) 13500, (2) 12800, or (3) 14200.

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Thus, the conditions of catalyst surface ignition are more favorable than isothermal conditions for the selective oxidation of CO in an excess of hydrogen.

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