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Kinetics of Catalyst Poisoning during Capillary Condensation of Reactants

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Abstract—The influence of the capillary condensation of reactants on the poisoning of Pt/SiO_2 catalysts by thiophene is studied experimentally for *p*-xylene hydrogenation at $T = 60$ and 80°C. The poisoning kinetics is independent of a catalyst and its rate decreases with a decrease in temperature. Poisoning during capillary condensation is 1.5–6 times slower than that in the gas phase, depending on the fraction of surface platinum in the pores filled with a liquid. The poisoning of the catalyst active sites in the pores filled with a liquid requires less sulfur at the same deactivation degree. The number of sulfur atoms per one platinum atom necessary for the complete poisoning of platinum in the gas phase is higher than that in the case of capillary condensation by a factor of 1.4–1.5.

INTRODUCTION

Capillary condensation during a catalytic reaction has only been studied so far by a few researchers. Gurfein and Danyushevskaya [1] theoretically substantiated the limits of capillary condensation in the porous grain of a catalyst and its effect on reactant transformations. Kim and Kim [2] experimentally observed several steady-state regimes of cyclohexene hydrogenation on Pt/Al_2O_3 and explained them by the capillary condensation of reactants at a certain temperature and hydrogen pressure. The detailed analysis and interpretation of these experiments are given in [3].

In our previous papers [4–7], we analyzed possible consequences of capillary condensation for catalytic reactions and estimated the influence of various factors on the efficiency of the catalyst grain during capillary condensation [5]. In [7], we reported the results of our experiments (with and without capillary condensation) on *p*-xylene hydrogenation on Pt/SiO_2 catalysts in steady-state and transition regimes and their computer simulation. Capillary condensation of some of the reactants may strongly affect the catalytic process because of the different kinetics and dynamics of the reaction in the catalyst pores filled with either a liquid or a gas. The low solubilities of hydrogen and other noncondensing components (H_2S) in the liquid phase play an important role in the processes involving hydrogen (hydrogenation and hydrorefining). This is especially important for deactivation because hydrogen acts as an agent that ensures the partial self-regeneration of a catalyst.

In this work, we experimentally studied the influence of the capillary condensation of reactants on the poisoning of Pt/SiO_2 catalysts with sulfur (thiophene). The catalysts, reaction, and experimental conditions chosen allowed us to compare catalyst poisoning both in the gas phase and under conditions of partial capillary condensation of the reactants in pores. Henceforth, the terms gas- and liquid-phase reactions imply that the reactions occur on the surface of a solid catalyst, whereas reactants and products are gaseous or liquid.

EXPERIMENTAL

Catalysts. Experiments were conducted on model Pt/SiO_2 catalysts with nearly the same parameters, except for their porous structures (Table 1). The SiO_2 support was used in two modifications: with narrow (KSM-5) and large (KSK-1) pores. The size distribution of pores (Fig. 1) was determined by the capillary condensation of nitrogen (Carlo Erba Sorptomatic 1900). The platinum distribution between the pores of different sizes was measured using the adsorption method [8].

Reaction. *p*-Xylene hydrogenation was chosen as a model. This allowed us to conduct the experiments under mild conditions both in the gas phase and during partial capillary condensation.

Conditions. Experiments were carried out in a gradientless flow-circulation reactor. This prevented catalyst overheating, the effect of the internal and external diffusion, and the gradients in the concentrations and temperature along the length and radius of the catalyst. Moreover, this substantially simplified the processing and interpretation of experimental data.

Experiments were performed at atmospheric pressure. The size of catalyst particles (0.25–0.5 mm) ensured the kinetics control of the reactions. Upon loading into the reactor, the catalyst was reduced by hydrogen for 3 h at 300°C and for 1 h at 150°C before

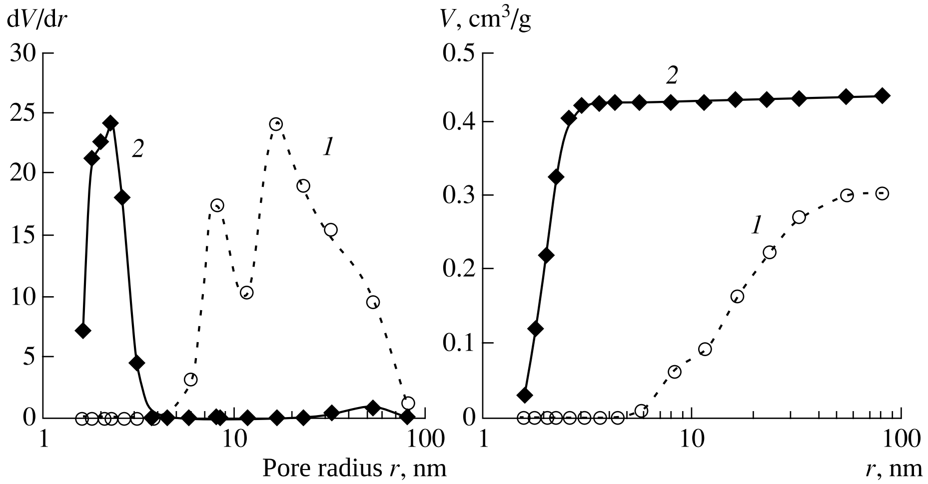

Fig. 1. Differential (d*V*/d*r*) and integral (*V*) size distribution of pores of (*1*) Pt/KSK and (*2*) Pt/KSM [7].

each experiment. The catalyst samples weighed ~0.2–0.3 g.

The catalysts were poisoned with a *p*-xylene solution of thiophene (3.3%) in the pulse regime (by adding 1-μl portions). The initial activity of the catalysts was examined at different reaction temperatures (60, 80, and 100°C) and the initial pressures of *p*-xylene (0.058 and 0.134 torr) [7]. The catalysts were poisoned at the constant reactant consumption at 60 and 80°C and the same initial pressures of *p*-xylene.

Table 2 presents the conditions of experiments on poisoning, where r_{cap} is the radius of pores, in which capillary condensation occurs at temperature T and the inlet partial pressure of *p*-xylene P^0_{xyl}. The r_{cap} values were calculated by the Kelvin equation (1) with due regard to the thickness of the adsorption film $\delta = 0.4$–1.0 nm [9]:

$$r_{\text{cap}} = -\frac{2\sigma V_{\text{M}}}{RT\ln(P_{\text{xyl}}/P^{\text{sat}}_{\text{xyl}})} + \delta, \qquad (1)$$

where σ and V_{M} is the surface tension and the molar volume of liquid *p*-xylene, respectively; $P^{\text{sat}}_{\text{xyl}}$ is the pressure of the saturated vapor of *p*-xylene at temperature T; and R is the universal gas constant.

The condensation of hydrogenation products (*cis*- and *trans*-1,4-dimethylcyclohexane) in catalyst pores were not taken into account because they have much lower boiling points (124 and 119°C, respectively) than *p*-xylene (138°C).

Table 1. Catalyst parameters [7]

Parameter	Pt/KSK-1	Pt/KSM-5
[Pt], wt %	1.0	0.9
Average pore radius, nm	10.0	3.0
Bulk density, g/cm^3	0.4	0.55
Dispersity of Pt	0.51	0.70
Grain size, mm	0.25–0.50	0.25–0.50
Pore volume, cm^3/g	0.35	0.47
Specific surface area (BET), m^2/g	130	370

RESULTS AND DISCUSSION

Reaction Kinetics

Kinetic experiments were performed as described in [10]. Under conditions unfavorable for capillary condensation, that is, during the gas-phase hydrogenation of *p*-xylene on Pt/SiO$_2$, the Langmuir kinetic curves are observed for both catalysts (Fig. 2a), and the dependence of the reaction rate on the partial pressure of *p*-xylene is described by the equation [7]

$$w_{\text{gas}} = \frac{k_{\text{gas}}P_{\text{xyl}}}{1 + bP_{\text{xyl}}}, \qquad (2)$$

where w_{gas} is the rate of gas-phase hydrogenation, k_{gas} ($\text{l}_{\text{gas}}\ \text{l}^{-1}_{\text{cap}}\ \text{s}^{-1}\ \text{torr}^{-1}$) is the rate constant for the gas-phase hydrogenation of *p*-xylene on Pt/SiO$_2$; b (torr^{-1}) is the adsorption coefficient of *p*-xylene; and P_{xyl} (torr) is the partial pressure of *p*-xylene.

When capillary condensation occurs in most of pores, the reaction kinetics cannot be described by the

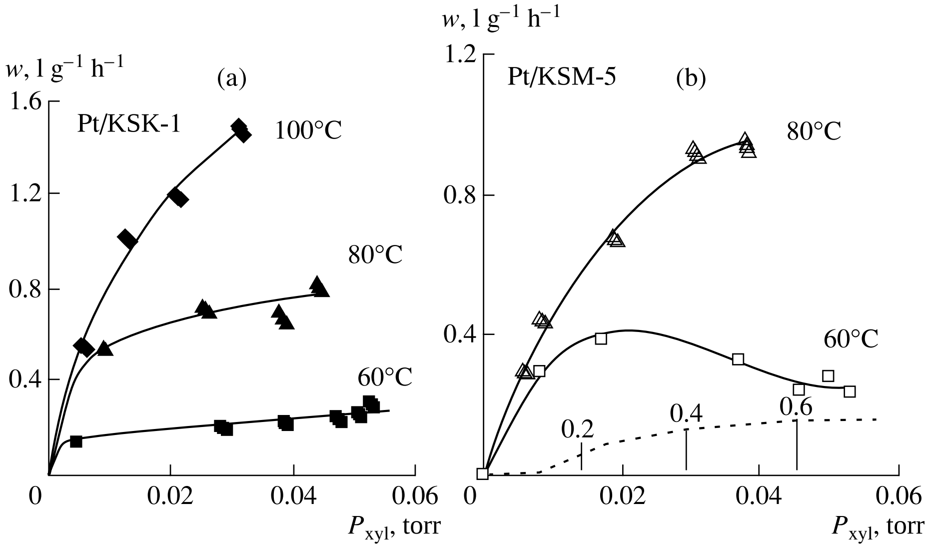

Fig. 2. Kinetic curves for the steady-state poisoning for (a) Pt/KSK and (b) Pt/KSM at P^0_{xyl} = 0.058 torr [7]. The platinum fraction in the pores filled with a liquid at 60°C is denoted with numbers and a dotted line.

Langmuir curves: the reaction rate decreases at high P_{xyl} values and the kinetic curve has a maximum (Fig. 2b, 60°C). The reaction rate in a capillary-condensed liquid w_{liq} can be expressed as follows [7]:

$$w_{\mathrm{liq}} = \gamma k_{\mathrm{liq}} P_{\mathrm{xyl}}, \tag{3}$$

where k_{liq} ($\mathrm{l_{liq}\ l_{cap}^{-1}\ s^{-1}}$) is the rate constant for the liquid phase hydrogenation of *p*-xylene on Pt/SiO_2 and γ ($\mathrm{l_{gas}\ l_{liq}^{-1}\ torr^{-1}}$) is the correlation coefficient between the dimensions of the rates of the gas- and liquid-phase hydrogenation of *p*-xylene on Pt/SiO_2 that takes into account the mole fractions of *p*-xylene in the condensate and its partial pressure.

Then the resulting rate of the reaction accompanied by capillary condensation is

$$\begin{aligned} w &= (1-\varphi_{\mathrm{liq}})w_{\mathrm{gas}} + \varphi_{\mathrm{liq}} w_{\mathrm{liq}} \\ &= (1-\varphi_{\mathrm{liq}})\alpha_{\mathrm{gas}}\tilde{w}_{\mathrm{gas}} + \varphi_{\mathrm{liq}}(\alpha-\alpha_{\mathrm{gas}})\tilde{w}_{\mathrm{liq}}, \end{aligned} \tag{4}$$

where

$$\tilde{w}_{\mathrm{gas}} = \frac{\tilde{k}_{\mathrm{gas}} P_{\mathrm{xyl}}}{1 + bP_{\mathrm{xyl}}}, \quad \tilde{w}_{\mathrm{liq}} = \gamma \tilde{k}_{\mathrm{liq}} P_{\mathrm{xyl}}, \tag{5}$$

Table 2. Conditions of the experiments on catalyst poisoning

No.	Catalyst*	T, °C	P^0_{xyl}, torr	Feed consumption, l/h	Concentration of surface Pt atoms, μmol/g	r_{cap}, nm	Fraction of pores of radius $r < r_{\mathrm{cap}}$, %	Platinum fraction in pores of radius $r < r_{\mathrm{cap}}$, %
1	Pt/KSK-1	60	0.058	0.59	26.2	15.0	30	60
2	Pt/KSK-1	80	0.058	2.27	26.2	2.5	0	0
3	Pt/KSM-5	80	0.058	2.27	32.3	2.5	70	38
4	Pt/KSM-5	80	0.134	2.17	32.3	15.0	98	70

* Catalyst samples were 0.21–0.26 g.

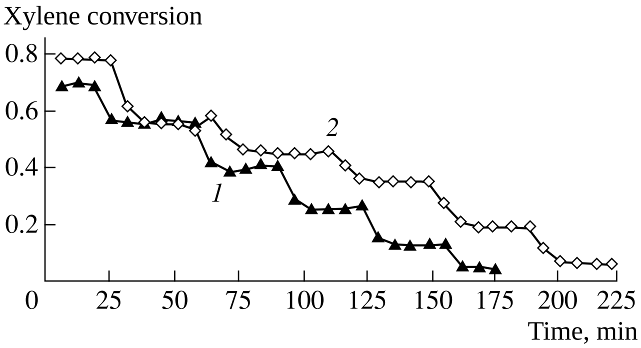

Fig. 3. Dynamics of catalyst poisoning (*1*) in the gas phase (Pt/KSK, 80°C, P^0_{xyl} = 0.058 torr) and (*2*) under conditions of capillary condensation (Pt/KSM, 80°C, P^0_{xyl} = 0.134 torr).

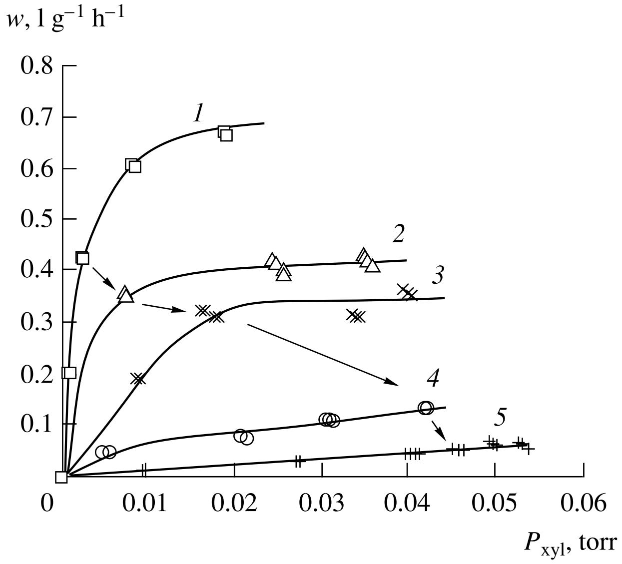

Fig. 4. Kinetic curves (*1*) for a fresh catalyst and (*2*–*5*) after its poisoning (after each pulse). Pt/KSK at 80°C, P^0_{xyl} = 0.058 torr. The arrows connect the points where poisoning occurs.

$\tilde{k}_{gas}$ (l_{gas} g_{Pt} s^{-1} $torr^{-1}$) and $\tilde{k}_{liq}$ (l_{liq} g_{Pt}^{-1} s^{-1}) are the rate constants for the gas- and liquid-phase hydrogenation of *p*-xylene on Pt/SiO_2, related to the weight of the active component in the catalyst, respectively; φ_{liq} (l_{liq}/l_{cat}) is the fraction of a liquid in the bulk of the catalyst; α (g_{Pt}/l_{cat}) is the weight fraction of platinum in the bulk of the catalyst; and α_{gas}, g_{Pt}/l_{cat} is the weight fraction of platinum that is not blocked with the catalyst.

Therefore, the fraction of platinum in the pores filled with capillary-condensed xylene increases with an increase in the P_{xyl} value. An increase in the contribution of the liquid-phase reaction causes a decrease in the overall rate of the reaction at high P_{xyl} pressures and the appearance of the maximum on the kinetic curve (Pt/KSM, 60°C) [7].

Catalyst Poisoning

Catalyst poisoning was conducted with a *p*-xylene solution of thiophene (3.3%) in a pulse regime (with 1-μl portions). Upon the addition of each thiophene portion, samples were withdrawn for analysis to determine the constant degree of *p*-xylene conversion. Then the next portion of the deactivating reactant was added. The poisoning pulses continued until the complete deactivation of the catalyst. Figure 3 illustrates the dynamics of the gas-phase poisoning of the Pt/KSK catalyst at 80°C and the inlet *p*-xylene pressure of 0.058 torr and of Pt/KSM poisoning during capillary condensation at 80°C and the inlet *p*-xylene pressure of 0.134 torr.

Figure 3 shows that poisoning occurs in the gas phase faster than during capillary condensation. However, under the conditions of capillary condensation after each thiophene portion, poisoning is obviously deeper if we take into account that the number of platinum atoms per 1 g of the Pt/KSK catalyst is 1.2 times lower than that for Pt/KSM (Table 2).

To study the influence of capillary condensation on catalyst poisoning in more detail, we compared certain pulses during poisoning in the gas phase and under conditions of capillary condensation. We assumed in this case that *p*-xylene hydrogenation follows the first-order kinetics in all the experiments on poisoning. This assumption is valid because the initial conversion of *p*-xylene X_0 before poisoning was 0.7–0.9 in all the experiments and the reaction rate is $w \approx kP_{xyl}$ at these partial pressures of the reactant (Fig. 2, Eqs.(2)–(4)). This simplification is also true during poisoning. Figure 4 shows the representative kinetic curves obtained during poisoning upon each thiophene pulse for the Pt/KSK catalyst. The arrows in Fig. 4 connect the points corresponding to the reaction rates, at which poisoning occurs. The reaction is still first-order upon catalyst poisoning but occurs at a lower rate and remains first-order over a wider range of the partial pressures of *p*-xylene.

For the reversible deactivation of the catalyst, independent of the reactant concentrations, the only first-order reaction can be described by the following equations in the gradientless flow reactor [11, 12]:

$$X = k\tau(1-X)a, \quad \frac{da}{dt} = -k_pP^0_{xyl}\frac{a-a_{st}}{1-a_{st}}. \qquad (6)$$

Here $a = \frac{1-X_0}{X_0}\frac{X}{1-X}$, $\quad a_{st} = \frac{1-X_0}{X_0}\frac{X_{st}}{1-X_{st}}$, $\qquad$ (7)

where P^0_{xyl} is the initial concentration of the initial substance; t is time; τ is the contact time; k is the reaction

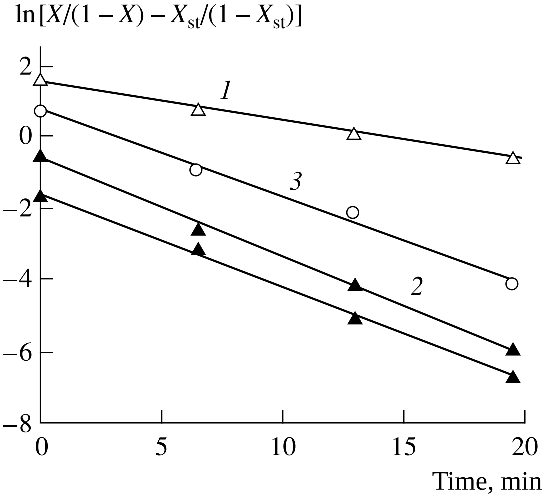

Fig. 5. Plots of linearized dependence (9) used to determine the rate constant for the gas-phase poisoning of the catalyst (P^0_{xyl} = 0.058 torr): (*1*) Pt/KSK at 60°C, (*2*) Pt/KSK at 80°C (two pulses), and (*3*) Pt/KSM at 80°C.

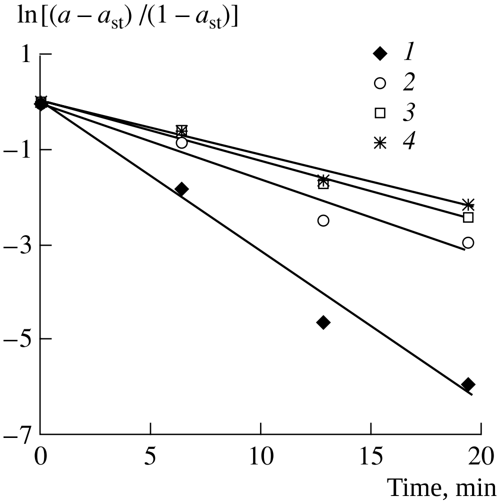

Fig. 6. (*1–4*) Plots of linearized dependence (8) used to determine the rate constant for catalyst poisoning under capillary condensation conditions for different pulses. Pt/KSM at 80°C, P^0_{xyl} = 0.134 torr.

rate constant; k_p is the rate constant of poisoning; X, X_0, and X_{st} are the current, initial, and steady-state degrees of conversion, respectively; and a and a_{st} are the relative activity and its steady-state value, respectively.

After integration, Eq. (7) for the relative activity is

$$\ln\left[\frac{a-a_{st}}{1-a_{st}}\right] = -\frac{k_p P^0_{xyl}}{1-a_{st}}t \tag{8}$$

or, in terms of the conversion,

$$\ln\left[\frac{X}{1-X}-\frac{X_{st}}{1-X_{st}}\right] = \ln\left[\frac{X_0}{1-X_0}-\frac{X_{st}}{1-X_{st}}\right]-\frac{1-X_{st}}{1-X_{st}/X_0}k_pP^0_{xyl}t. \tag{9}$$

In the $\left(\ln\left[\frac{a-a_{st}}{1-a_{st}}\right],\ t\right)$ or $\left(\ln\left[\frac{X}{1-X}-\frac{X_{st}}{1-X_{st}}\right],\ t\right)$ coordinates, this equation describes a straight line, and the rate constant of poisoning k_p can be determined from its slope [11, 12]. The choice of the coordinates is determined by the convenience of processing the graphic data and their description.

Figure 5 illustrates how the $\ln[X/(1-X) - X_{st}/(1-X_{st})]$ value changes with time upon a single thiophene pulse during gas-phase poisoning. The effective rate constants for catalyst poisoning k_p^{gas} were determined from the slopes of these curves illustrating the dynamics of poisoning. Figure 5 shows that, in the absence of capillary condensation, the slopes of the curves are virtually the same for both catalysts at 80°C and slightly different at 60°C. The average rate constant for gas-phase poisoning is ~2.44 min^{-1} torr^{-1} at T = 80°C and is lower by a factor of ~1.4 at 60°C (Table 3).

Figure 6 illustrates how the $\ln[(a - a_{st})/(1 - a_{st}]$ value decreases with time upon a single thiophene pulse under conditions of capillary condensation. In this case, it is more convenient to use these coordinates to rule out the random intersection of the curves in the plot because of changes in their slopes on passing from one pulse to another. The rate constant for gas-phase poisoning was determined from the slope of the curve. Table 4 summarizes the rate constants of poisoning under conditions of capillary condensation k_p as func-

Table 3. Rate constants for the gas-phase poisoning of catalysts

Catalyst	Poisoning conditions	k_p^{gas}, min^{-1} torr^{-1}
Pt/KSK	80°C, P^0_{xyl} = 0.058 torr	2.41
		2.37
		2.50
		2.61
Pt/KSM	80°C, P^0_{xyl} = 0.058 torr	2.31
Pt/KSK	60°C, P^0_{xyl} = 0.058 torr	1.69

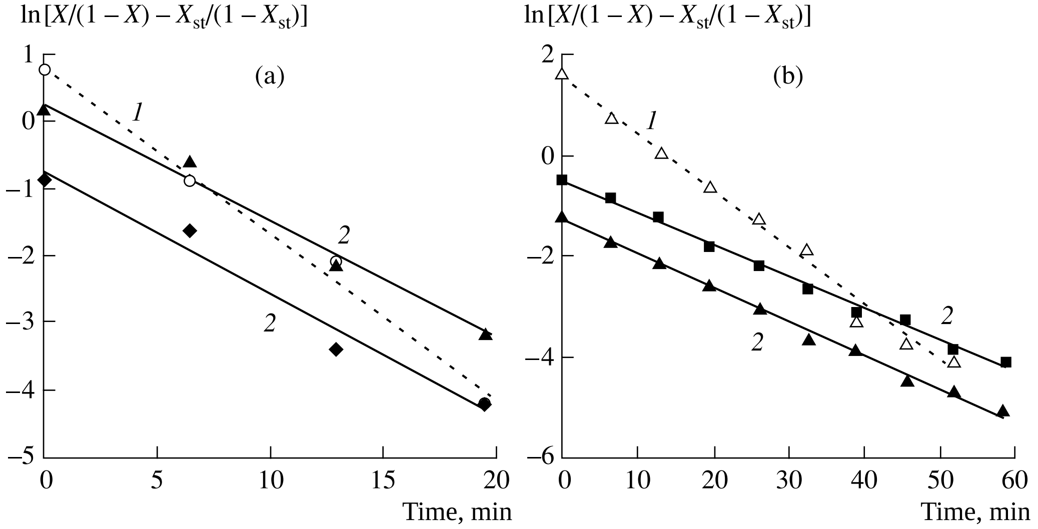

Fig. 7. Retardation of catalyst poisoning in the case of capillary condensation: (a) Pt/KSM, T = 80°C, P^0_{xyl} = 0.058 torr and (b) Pt/KSK, T = 60°C, P^0_{xyl} = 0.058 torr. (*1*) Gas phase and (*2*) capillary condensation.

tions of the platinum concentration in the pores filled with a liquid before the next thiophene pulse. Judging from the relative rate constant of poisoning $k_{\mathrm{p}}^{\mathrm{rel}}(T) = k_{\mathrm{p}}/\langle k_{\mathrm{p}}^{\mathrm{gas}}(T)\rangle$, catalyst poisoning during capillary condensation is slower than in the gas phase because the process is obviously limited by diffusion in the liquid. In this experiment, the fraction of the surface platinum atoms in the pores filled with a liquid before poisoning (q) is 0.33. In this case, the rate constant for catalyst poisoning is lower than that in the gas phase by a factor of ~1.6. Upon the first thiophene pulse, the q value increases to 0.48 and then remains virtually unchanged. The rate constants calculated for the second, third, and forth pulses were also close. For this extent of surface platinum blocking by the liquid condensed in capillaries, poisoning is 5–6 times slower than in the case of gas-phase poisoning.

When analyzing the poisoning kinetics, we took into account the following facts:

(a) Changes in the P_{xyl} in the course of the reaction;

(b) Filling the pores with xylene and the products of its hydrogenation;

Table 4. Rate constants for catalyst poisoning during capillary condensation k_{p}

Catalyst	Poisoning conditions	Platinum fraction in pores filled with a liquid	k_{p}, min^{-1} torr^{-1}	$k_{\mathrm{p}}^{\mathrm{rel}}(T)$
Pt/KSM	80°C, P^0_{xyl} = 0.134 torr	0.33	1.49	0.61
		0.48	0.50	0.20
		0.51	0.38	0.16
		0.55	0.54	0.22
Pt/KSM	80°C, P^0_{xyl} = 0.058 torr	0.26	1.69	0.69
Pt/KSK	60°C, P^0_{xyl} = 0.058 torr	0.30	1.07	0.63

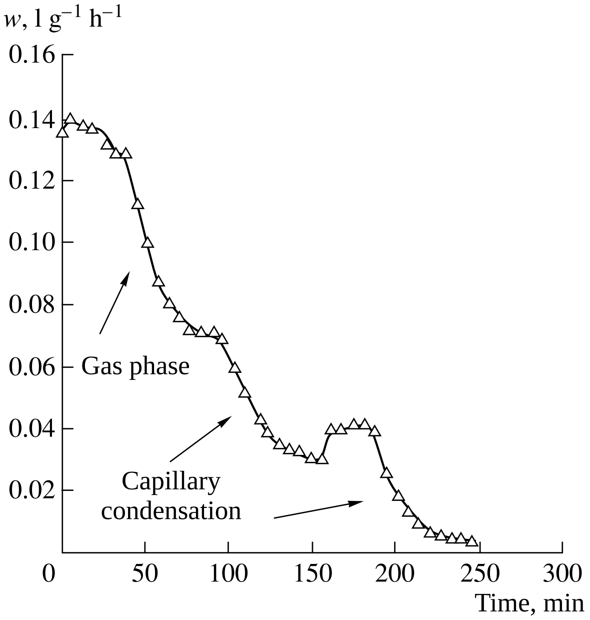

Fig. 8. Dynamics of Pt/KSK poisoning after the beginning of capillary condensation during poisoning (T = 60°C, P^0_{xyl} = 0.058 torr).

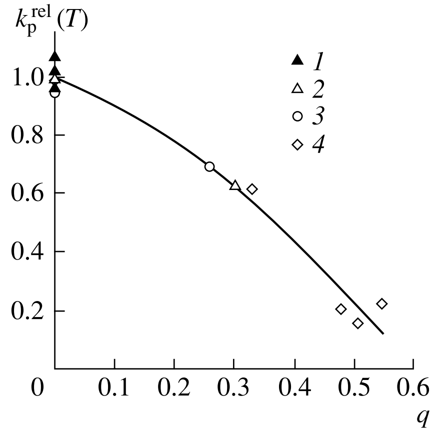

Fig. 9. Relative rate constant for catalyst poisoning $k^{\text{rel}}_{\text{p}}(T) = k_{\text{p}}/k^{\text{gas}}_{\text{p}}(T)$ as a function of the platinum fraction in the pores filled with a liquid (q): (*1*) Pt/KSK at 80°C, P^0_{xyl} = 0.058 torr; (*2*) Pt/KSK at 60°C, P^0_{xyl} = 0.058 torr; (*3*) Pt/KSM at 80°C, P^0_{xyl} = 0.058 torr; and (*4*) Pt/KSM at 80°C, P^0_{xyl} = 0.134 torr.

(c) The size distribution of pores; and

(d) The distribution of platinum in the pores of different sizes.

Our experimental results suggest that, under certain conditions, the reaction first occurs in the gas phase and then during capillary condensation (Figs. 7 and 8). In other words, the *p*-xylene conversion is initially high, its partial pressure is low, and poisoning occurs in the gas phase. Upon the next thiophene pulse, a decrease in the *p*-xylene conversion causes an increase in its partial pressure, which becomes sufficient for the capillary condensation of the reactant in the catalyst pores. Upon further thiophene pulses, poisoning occurs under conditions of capillary condensation. In two experiments, poisoning occurred as described above (Fig. 7). The behavior of the dynamic curves (on the rate-vs.-time plots) does not change in this case, but deactivation slows down (Figs. 7 and 8). The capillary-condensed liquid causes a decrease in the slope of the curves characterizing the poisoning dynamics; that is, the poisoning rate decreases. The rate constants of poisoning are listed in Tables 3 and 4 for these cases.

To elucidate the influence of capillary condensation on the rate of catalyst poisoning, we used the data of Tables 3 and 4 to study how the relative rate constant of poisoning $k^{\text{rel}}_{\text{p}}(T)$ changes with the platinum fraction in the pores filled with a liquid (q) (Fig. 9). We did not consider the intermediate pulses when the gas-phase poisoning transforms into the poisoning during capillary condensation.

The points obtained under different poisoning conditions (the inlet pressure of *p*-xylene and temperature) on various catalysts are close to each other if the platinum fraction in the pores filled with a liquid q is virtually the same. The rate constants for catalyst poisoning under conditions of capillary condensation at $q \sim 0.3$ are lower than those for the gas-phase poisoning by a factor of 1.4–1.6 at 80 and 60°C.

The number of pulses necessary for complete catalyst poisoning changes with temperature and depends on capillary condensation. The poisoning of the active sites in the pores filled with a liquid requires a smaller amount of sulfur at the same deactivation degree. For example, the complete poisoning of platinum in the gas-phase reaction and under conditions of capillary condensation requires 0.38–0.40 and 0.26–0.28 sulfur atoms per one platinum atom, respectively (Fig. 10). Capillary condensation causes deeper poisoning (by a factor of 1.3–3.1 at (S/Pt) = 0.05–0.25) at the same amount of sulfur (Fig. 10).

As noted above, the retardation of poisoning is due to both thiophene diffusion in the liquid and a change in the thiophene/*p*-xylene ratio near the active sites as compared to the gas phase. A decrease in the S/Pt ratio may be attributed to a dramatic decrease (by a factor of ~1000) in the hydrogen concentration in the liquid as compared to its concentration in the gas phase

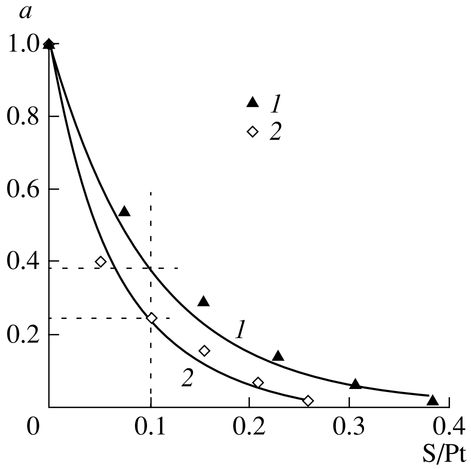

Fig. 10. Relative activity *a* as a function of the sulfur amount fed into the reactor per one platinum atom (S/Pt) for (*1*) the gas-phase poisoning (Pt/KSK at 80°C, P^0_{xyl} = 0.058 torr) and (*2*) poisoning during capillary condensation (Pt/KSM at 80°C, P^0_{xyl} = 0.134 torr).

because of its low solubility (the molar fraction of hydrogen in the liquid phase is ~10^{-3} mol/mol [13]).

CONCLUSIONS

Comparison of the catalyst poisoning in the gas phase and under conditions of capillary condensation suggests that:

1. Gas-phase poisoning is rapid and its kinetics is independent of the catalyst. Poisoning slows down with a decrease in temperature.

2. The effective rate constant of poisoning under the conditions of capillary condensation is lower than that in the gas phase because the process is obviously limited by diffusion in the liquid. The rate of poisoning during capillary condensation is also independent of the catalyst and is determined by the degree of capillary condensation. The rate constant for catalyst poisoning during capillary condensation is lower than that in the gas phase by a factor of 1.4–1.6 on the surface platinum fraction in the pores filled with a liquid $q \approx 0.3$, whereas, at $q \approx 0.5$ (both at 60 and 80°C), the rate constant ratio is $k_p^{gas}/k_p = 5–6$.

3. The poisoning of active catalyst sites in the pores filled with a liquid requires fewer sulfur atoms at the same deactivation degree. The complete poisoning of platinum in the gas-phase reaction requires 0.38–0.40 sulfur atoms per one platinum atom, whereas its complete poisoning during capillary condensation requires only 0.26–0.28 sulfur atoms per one platinum atom, which may be due to a dramatic decrease in the hydrogen concentration in the liquid (by a factor of ~1000) as compared to its concentration in the gas phase.

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