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On the Deactivation of Supported Pt Catalysts During the Hydrogenation of Cyclopropane

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Cyclopropane was hydrogenated to propane over an η-Al_2O_3 supported Pt catalyst between 50 and 75°C, in a single-pellet diffusion reactor. The catalyst was slowly poisoned by a self-poisoning process, involving both cyclopropane and propane as poison precursors.

Experiments showed a time delay in the poisoning if the catalyst was pretreated with H_2 for an extended time period, while the initial activity remained unchanged. Furthermore, part of the initial activity remained protected from poisoning, when a sintered catalyst was used, involving larger metal islands on the support.

NOMENCLATURE

c_A	concentration of species A (mole/cm^3)
$\psi_A(1)$	dimensionless concentration of species A at the center of the catalyst pellet, $= c_{A(\text{surface})}/c_{A(\text{center})}$
R	rate of the reaction (moles/sec)
R_0	rate of the reaction at zero time (moles/sec)
$\psi_A(\tau,1)$	dimensionless center-plane concentration of species A at time τ
$\psi_A(0,1)$	dimensionless initial center-plane concentration of species A
α	kinetic exponent of the active surface area = order of the poisoning process in terms of the surface area remaining unpoisoned
δ	order of the poisoning process in terms of the poison precursor concentration in the pores
k_3	heterogeneous rate constant of the series contributor to the triangular self-poisoning mechanism
k_2	heterogeneous rate constant of the parallel contributor to the triangular self-poisoning mechanism
h_1	initial Thiele parameter of the catalyst pellet, $$L\,(k_1a_0/D_A)^{1/2},$$ where k_1 is the heterogeneous rate constant of the main reaction (cm/sec), a_0 is the initially available surface area (cm^2/cm^3 catalyst), L is the thickness of the catalyst slab (cm), and D_A is the effective diffusivity of species A under reaction conditions (cm^2/sec)

$$\omega = \psi_A + \psi_B$$

INTRODUCTION

The hydrogenation of cyclopropane over Pt catalysts has been extensively studied (*1–18*). The reaction rate is especially convenient for experimental investigations in the temperature range of about 0 to 80°C. In the presence of a large excess of H_2, it is of first order in cyclopropane and of some negative order in hydrogen (*5, 11*). The reaction is irreversible and nearly isothermal over supported catalysts (*8, 11*), with an energy of activation of about *8* to

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10 kcal/mole. In addition, the large excess of H_2 allows a so-called "simple" reaction rate expression, whereby the constant H_2 concentration merges into the first-order quasihomogeneous rate constant (*11*).

All these properties make this model reaction a convenient tool to study Pt hydrogenation catalysts.

Many of the above-mentioned studies were complicated by the time-dependent decay of the catalyst activity. This poisoning was attributed to O_2 or H_2O traces (*9, 18*), to other trace impurities in the feed (*11, 15*), or to self-poisoning (*6, 10, 18, 19*). It was also shown that in diffusion-influenced single pellets the distribution of the poisoned surface is nonuniform along the distance parameter, between the extremes of pore-mouth and uniform poisoning (*11, 15, 18*).

After poisoning, the original activity could be regained by high temperature hydrogenation by part of the investigators (*18, 20*), while others (*8, 9, 11*) reported the irreversible loss of activity after the poisoning has taken place.

The aim of this study was to further investigate the nature of the poisoning of η-Al_2O_3 supported Pt catalysts during the hydrogenation of cyclopropane and to demonstrate the utility of the single-pellet diffusion reactor for this purpose. Experiments in the single-pellet diffusion reactor revealed some interesting aspects of the poisoning process. After discussing these, chemical arguments are considered to explain the observed phenomena.

Self-Poisoning Due to Skeletal Dehydrogenation of Hydrocarbons

In a previous paper by the authors (*21*) a single-pellet diffusion reactor technique (*22*) was applied to the problem of poisoning of a Pt/η-Al_2O_3 system during the hydrogenation of cyclopropane. The technique allows one to discriminate among impurity poisoning, parallel self-poisoning, series self-poisoning, and triangular self-poisoning, with poison precursors being, respectively, an impurity in the feed, the reactant itself, the product itself, or both the reactant and the product. A comparison of experimental data with these models (*20, 23*) indicated that the catalyst was poisoned by both the reactant cyclopropane (A) and product propane (B) (triangular self-poisoning), at temperatures between 50 and 75°C according to the

$$\begin{tikzcd}
A \arrow[r] \arrow[dr] & B \arrow[d] \\
& W
\end{tikzcd}$$

mechanism where W is the poison structure on the catalyst surface.

There are several reasons to believe that the poisoning is due to strongly sorbed, partially dehydrogenated surface residues of cyclopropane and propane. Studying the adsorption, chemisorption and hydrogenation of cyclopropane over various Pt surfaces, such surface residues have been frequently observed (*12, 24, 25*). It is very likely that propane also loses hydrogen upon sorption, as do other alkanes (*24, 25*). The energy of activation of the series contributor to the triangular self-poisoning is about 12.4 kcal/mole larger than that of the parallel contributor, as it was calculated from the comparison of experimental data with theory (*20, 21*). This indicates that propane is a less severe poison precursor than cyclopropane, apparently due to the partially unsaturated character of the latter, causing a stronger sorption of cyclopropane on the Pt surface. Taylor, Thompson and Webb (*25*) compared the sorption strength of alkanes, cyclopropane, alkenes and acetylene over supported Pt and found that the above sequence corresponded to increasing sorption strength.

In some additional experiments by the present authors (*20*) it was observed that the poisoned catalyst can be readily reactivated to the initial activity by high temperature (400°C, 12 hr) hydrogenation, if the catalyst was previously exposed only a limited time to hydrocarbons, between about 50 and 75°C. The catalyst could also be reactivated by 2 hr calcining in 3 vol % O_2 in N_2 at 410°C and subsequent treatment for 10 hr in flowing H_2 at 300°C. Either method will regenerate the catalyst to approximately the same activity provided the catalyst was not severely deactivated prior to the activation procedure. Ten days exposure of the same Pt/η-Al_2O_3 catalyst to a cyclopropane (100 Torr)–hydrogen (800 Torr) mixture at 35°C resulted in the irreversible poisoning of the pellet: the initial activity could not be regained after 12 hr hydrogenation at 400°C. The explanation of these observations may be that if the dehydrogenation of surface residues proceeds beyond a certain point, the conditions of the reactivation are not any more sufficient to rehydrogenate the carbonaceous residues.

EFFECTS OF THE SUPPORT ON THE POISONING PROCESS

In order to study the effects of the support on the time scale, mechanism and kinetics of the poisoning process, experiments were carried out in a single-pellet diffusion reactor. The reactor is described by the authors elsewhere (*20, 22*). The essence of the technique is that it allows the experimental measurement of concentrations at the center of a catalyst pellet under reaction conditions, as well as the bulk concentrations outside the pellet. The additional information of the center-plane concentration allows one to determine the order of the reaction, the effective diffusivity of the reactive species, the Thiele parameter and the effectiveness factor of the catalyst pellet, and the quasihomogeneous rate constant. In the case of decaying activity (poisoning), the center-plane concentration approaches the bulk concentration as the poisoning progresses with time, and thus it serves as an indication of the momentary activity of the catalyst pellet.

The reactor scheme corresponds to a recirculated, batch, differential reactor with 10,977 cm^3 total volume. The pellet was pressed into a stainless steel cylinder under carefully controlled conditions, to insure uniform density distribution and to prevent bypassing near the wall of the cylinder (*22*). The catalyst contained 0.25 wt % Pt (dry basis) over η-Al_2O_3. The support was manufactured by Davison (research sample, 230 m^2/g specific surface area). After hydrogen treatment under reactivation conditions, the Pt-free support was found to be inactive for the hydrogenation of cyclopropane between 35 and 75°C. The metal was deposited by impregnation with $H_2[PtCl_6]$. The catalyst powder was dried but not calcined before pressing it into the reactor cylinder, in order to enhance the mechanical stability of the pellet. Once in the reactor, the pellet was calcined at 400–410°C in a mixture of 6% O_2 and 94% N_2 at a total pressure of 800 Torr for 2 hr. After this treatment, hydrogen was flowed past both pellet faces for 10 hr at 300°C. After the poisoning experiment, the pellet was reactivated by the same procedure as above, except that only 3% O_2 was used.

Cyclopropane was obtained from Matheson, containing less than 0.5% impurities. It was passed through an activated $MgClO_4$ U-tube, frozen out by liquid N_2, evacuated, melted, degassed and distilled. The middle fraction of the boiling range was admitted to the reactor.

The hydrogen was also from Matheson (ultrapure quality, containing 99.99970% H_2, <5 ppm N_2, <2 ppm H_2O and <1 ppm O_2). The gas was passed through an activated $MgClO_4$ U-tube to remove traces of water. Further purification of the hydrogen was carried out by other authors (*8, 9*), apparently without eliminating the poisoning problem. Previous experiments in the single-pellet diffusion reactor (*21*) did not indicate that any remaining impurities in the hydrogen contribute significantly to the poisoning process.

In the first two experiments to be considered here, cyclopropane was reacted with hydrogen over the Pt/η-Al_2O_3 catalyst pellet (*21*). The cylindrical pellet had a diameter of 0.93 cm and a length of 0.38 cm. Only the flat faces of the cylinder were exposed to the hydrogen–hydrocarbon mixture. The pellet was essentially isothermal.

The weight of the pellet was 0.2949 g, and it contained 0.04% Pt. This Pt concentration was achieved by diluting the 0.25% Pt catalyst with the inert η-Al_2O_3 support. Due to the small Thiele parameter of the individual grains, the procedure is permissible in this case (*26*).

Runs 2-43-a and 6-47 were carried out

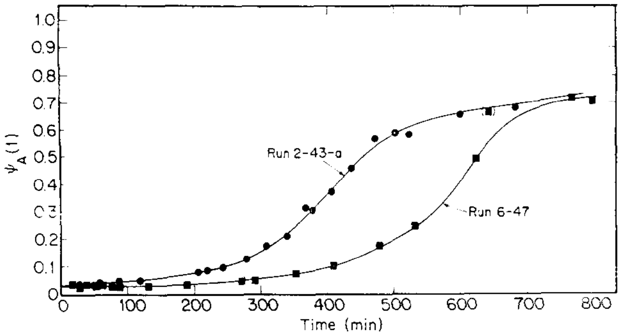

FIG. 1. Time delay in the poisoning process, caused by additional prehydrogenation of the catalyst.

at 75°C. The only difference between the two runs is that in the second case the hydrogenation lasted 13 hr at 300°C instead of 10 hr at the same temperature for the first run. Figure 1 shows the measured center-plane concentration versus the elapsed time for both runs. The initial Thiele parameter, effectiveness factor and the calculated quasihomogeneous rate constants are displayed in Table 1.

The comparison of these two experiments resulted in the discovery of a time delay in the poisoning process, when the supported catalyst was hydrogenated for a longer time (Fig. 1). It is important to point out that the initial activity and the initial Thiele parameter of both runs were the same, indicating that the extended hydrogenation did not increase the pellet initial activity, it merely delayed its poisoning.

It was shown earlier (*21, 23*) that eliminating time as a reaction variable and replacing it by the center-plane concentration enabled the mechanism and kinetics of the poisoning process to be studied independently of its time scale. Plotting the relative overall reaction rate versus the normalized center-plane concentration (Fig. 2) resulted in the superimposition of the data from Runs 2-43-a and 6-47, indicating that in both cases the mechanism (triangular self-poisoning) and kinetics ($\alpha = 1$, $\delta = 2$) of the poisoning process remained unchanged, and that only the time scale was altered by the extended prehydrogenation.

In Fig. 2, R/R_0 represents the ratio of the overall reaction rate at any time to its initial value. The nondimensional center-plane concentration of cyclopropane $\psi_A(\tau,1) = c_A(\tau,1)/c_A(\tau,0)$ is normalized in such a way that its value changes from zero (full activity at zero time) to one (completely poisoned catalyst). The Greek

TABLE 1
POISONING EXPERIMENTS IN THE SINGLE-PELLET DIFFUSION REACTOR

Run	$c_{H_2} \times 10^6$ (mole/cm³)	$c_{C_3H_6} \times 10^6$ (mole/cm³)	T (°C)	Calculated from data at zero time k_1a_0 (sec⁻¹)	h_1	ϵ	D_A (cm²/sec)	Pellet no.
2-43-1[a]	41.45	3.454	75	2.61	4.47	0.22	0.019	11
6-47[a]	41.45	3.454	75	2.48	4.36	0.23	0.019	11
1-44-a	41.45	3.454	50	0.85[b]	2.28	0.43	0.023	11
53	41.45	3.509	50	0.95[c]	3.56	0.28	0.017	14

[a] Refs. (*20, 21*).
[b] Pt (0.25%) on η-Al_2O_3, diluted to 0.04% Pt by η-Al_2O_3.
[c] Pt (0.25%) on η-Al_2O_3, sintered.

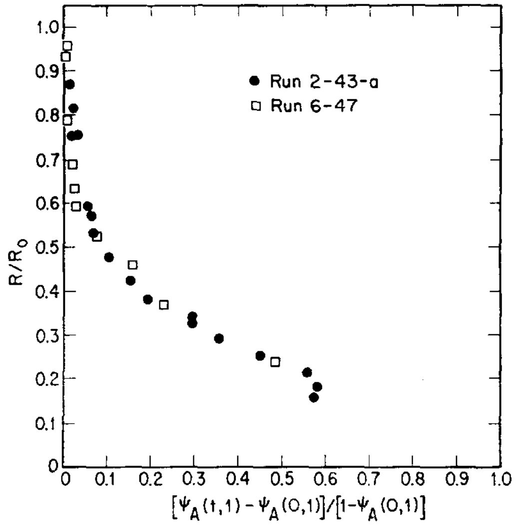

FIG. 2. Effect of the additional prehydrogenation on the mechanism and kinetics of the poisoning.

symbols α and δ indicate the kinetic order of the poisoning reaction in terms of the fraction of surface remaining active and the concentration of the poison precursor, respectively (*21*, *23*).

Another pair of experiments will now be considered in order to further investigate the role of the support in the poisoning process. Cyclopropane was hydrogenated at 50°C in the single-pellet diffusion reactor, using a Pt/η-Al_2O_3 catalyst containing 0.04% Pt. This catalyst pellet is identical to the one used for the previous experiments. According to the literature (*9*, *27*, *28*), the Pt is finely dispersed in the pores of pellets prepared in a way similar to our pellet. The initial results of this cyclopropane hydrogenation experiment are shown in Table 1.

A second catalyst pellet was prepared by sintering the catalyst (0.25% Pt over η-Al_2O_3) at about 600°C for 6 hr in flowing H_2, before the activation procedure was applied. This sintering procedure increases the size of the Pt islands on the support, with simultaneous reduction of the active surface area (*9*). For this reason, this catalyst was not diluted by the inert support. The surface area was not experimentally determined, since it was the aim of the experiment to cause only a relative change in it.

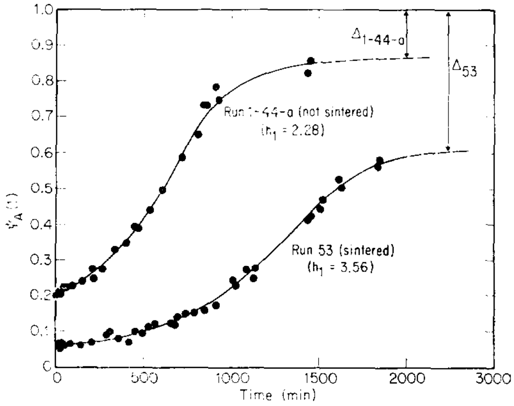

FIG. 3. Deactivation of a nonsintered (finely dispersed) and a sintered (less finely dispersed) catalyst.

Figure 3 displays the measured center-plane concentration versus the reaction time, for both of the last two experiments. The initial center-plane concentrations differ, since the initial Thiele parameters are not identical. Most interesting is that Run 53, employing the sintered catalyst, did not deactivate to the extent of Run 1-44-a, where a more finely dispersed catalyst was used; the distances indicated by Δ in Fig. 3 differ accordingly. In Fig. 3, Δ_{53} corresponds to about 15% of the initial reaction rate conserved.

To check if the mechanism and kinetics of the poisoning process changed upon sintering, the data of Run 1-44-a were fitted to the same triangular self-poisoning model (*21*) which described the earlier experimental data. The numerical solution of that model, employing the Thiele parameter of Run 53, coincides with the data of Run 53 (Fig. 4). This indicates that in comparing the two runs, the mechanism and kinetics of the poisoning process remained the same in both cases, and only the asymptotic limit of the extent of poisoning changed, apparently due to the sintering of Pt islands on the η-Al_2O_3 support.

DISCUSSION

The hydrogen pretreatment and sintering experiments permit some speculations on

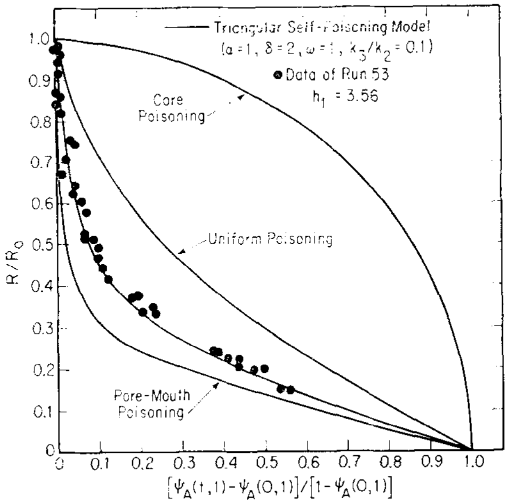

FIG. 4. Effect of sintering on the mechanism and kinetics of the poisoning.

the detailed nature of the poisoning process occurring in this system. These measurements provide clues to the formation of surface residues from adsorbed reactant and product molecules, to the role of hydrogen in the deactivation process, and to the effect of the support on it.

Strongly adsorbed surface species have been observed and studied in previous work (*12, 24, 25, 35*) and are believed to be dehydrogenated and sometimes polymerized hydrocarbon molecules. Local dehydrogenation and polymerization rates depend in part upon the hydrogen atom concentration, suggesting that poisoning should take place most rapidly in regions of lowest hydrogen atom concentration.

The spillover phenomenon has been reported in the literature (*29–31*) and is the name given to the process whereby hydrogen atoms are conducted from a metal to a support. Spillover is greatly enhanced by carbonaceous deposits (*32*) or by water (*30*) sorbed near the meal–support interface. Hydrogen atoms in the surface–(–OH) groups of η-Al_2O_3 readily exchange with hydrogen atoms activated by the metal (*33, 34*). If a concentration gradient is created by depleting the hydrogen atoms of the support surface–(–OH) groups by some process, the spillover phenomenon will be greatly enhanced, thus creating a region of lower hydrogen atom concentration near the Pt–support interface. The deposition of strongly sorbed carbonaceous residues in that region will in turn accelerate the spillover phenomenon, until finally the catalyst pellet loses its activity, due to the coverage of the active surface by strongly sorbed carbonaceous residues.

The formation of carbonaceous residues around the periphery of the Pt islands leads to a possible interpretation of the results from the sintering experiments. If we postulate that poisoning occurs in a ring of some specified width, then the larger islands of the sintered catalyst will retain upon poisoning a larger fraction of their original activity than the small islands of the unsintered catalyst, because the inner, protected area is a larger fraction of the original area in the case of the sintered catalyst.

The hydrogen pretreatment experiments suggest a capacitance effect and it is natural to suspect that the η-Al_2O_3 support serves as both a storage reservoir and a sink for hydrogen atoms. Alumina surfaces readily sorb hydrocarbons such as cyclopropane and propane, and the exchange between hydrogen atoms of the (–OH) groups and the sorbed hydrocarbons (*33, 34*) makes it conceivable that these hydrocarbons may lose or take up hydrogen from the support. The spillover of hydrogen atoms from the metal islands begins when the hydrogen is depleted to some extent on the alumina surface by the sorbed hydrocarbons. Longer initial hydrogenation of the catalyst at high temperatures increases the initial hydrogen concentration on the alumina surface and thus it delays the onset of the poisoning process.

The possibility is recognized that there are alternate explanations of the phenomena observed in the above experiments. The experiments showed, however, that the single-pellet diffusion reactor is sensitive to certain phenomena that cannot be easily studied in traditional reactors. In particular, the time delay phenomenon and the partial deactivation of the sintered Pt/η-Al_2O_3 system were revealed which suggest the important role of the support in the poisoning of this catalytic system. Further work is planned to study the exact nature of the "capacitance" properties of the support, and other details of the deactivation process.

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