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Influence of Catalyst Pretreatment on *n*-Hexane Transformations on Platinum Black

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The hydrogenolysis and skeletal isomerization reactions of *n*-hexane on Pt-black have been studied as a function of thermal pretreatments of catalysts in different atmospheres. The catalytic behavior of platinum, particularly concerning the selectivity towards the above reactions, was found to be very sensitive to the presence of hydrogen or helium in the atmosphere. The mechanistic implications of the results obtained are discussed.

INTRODUCTION

The study of hydrocarbon transformations on platinum has been the object of extensive investigations in which both the reaction mechanism and the influence of the nature of solid have been taken into account.

Most of the studies have been performed on films and supported metals and excellent reviews have been recently reported (*1*,*2*). In the presence of hydrogen both skeletal isomerization and hydrogenolysis reactions occur.

Other work also appeared (*3*–*7*) using platinum black as a catalyst: in this case there are difficulties in performing the reaction in a system which undergoes a rapid change. Actually the employment of such systems allows the possibility of analyzing the behavior of catalysts completely free of the influence of the support and with a structure more close to the one of supported metals.

For these reasons a research has been performed on *n*-hexane isomerization and hydrogenolysis on platinum black in which attempts have been made to correlate the behavior of the reacting system with the treatment given to the solid materials.

EXPERIMENTAL METHODS

Catalyst Preparation

The same procedure has been followed for preparing different batches of catalysts. The procedure was in all cases the one suggested by Brown and Brown (*8*), with the small difference that in some cases a more concentrated H_2PtCl_6 solution was used for precipitating platinum black by sodium borohydride, as reducing agent. Substantially two kinds of catalysts were obtained. One prepared according to (*8*), and the other with the cited modification. The details of the preparations are reported below:

Catalyst No. 1: Two solutions were prepared, one containing 8 g of Pt in 100 cc of mixture H_2O-CH_3OH (50%), and another containing 8 g of sodium borohydride in 100 cc of CH_3OH. The two solutions were cooled to 0°C and then mixed in the presence of an ultrasonic field. Finally treatment

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with a solution of HCl was performed to decompose the excess of borohydride.

Catalyst No. 2: This catalyst was prepared according to the procedure suggested in (*8*).

Chemical analysis of the prepared catalysts revealed no impurities. The areas of the catalysts, measured with the classical BET method were: No. 1, $s = 10.3$ m^2/g; No. 2, $s = 16.0$ m^2/g for fresh catalysts; and No. 1, $s = 1.0$ m^2/g; No. 2, $s = 0.8$ m^2/g for used catalysts which had been subjected for about 1 hr to a hydrocarbon stream in the presence of hydrogen.

Before use, both catalysts were subjected to a pretreatment, called P_2, the details of which are given below.

Apparatus and Operative Conditions

The scheme of the apparatus employed for performing the runs is shown in Fig. 1.

The amount of platinum black used as catalyst was normally 0.5 g. It was diluted with 2 g of alundum granules (40–60 mesh), placed in the reactor and kept at isothermal conditions by a sand fluidized bed system. The temperature was measured by a thermocouple placed at the top of the catalytic bed.

n-Hexane feed was provided by a normal syringe driven by a motor, injecting into the hydrogen stream. The ratio (H_2/*n*-hexane) was about 6.

Analyses were performed with a Perkin-Elmer 880 gas chromatograph with FID detector. Gas chromatographic columns (6 m length) of 10% of the mixture bentone–diisodecylphthalate (1:1) on Chromosorb W were used.

The sampling valve and the exit tubes from the reactor were heated to avoid the products condensing, as is shown in Fig. 1.

The products recognized and analyzed were: methane, ethane, propane, butane, pentane, 2-methyl pentane (2-MP), 3-methyl pentane (3-MP), methyl cyclopentane (MCP). The identification was made by using the Kovats index system (*9*) while the quantitative analyses were performed taking into account the FID relative molar responses of hydrocarbons (*10*).

All the kinetic runs were performed at 300°C.

Sintering

On heating platinum black undergoes a sintering process accompanied by a loss of area. Actually such a process is strongly affected by the presence of different gas-

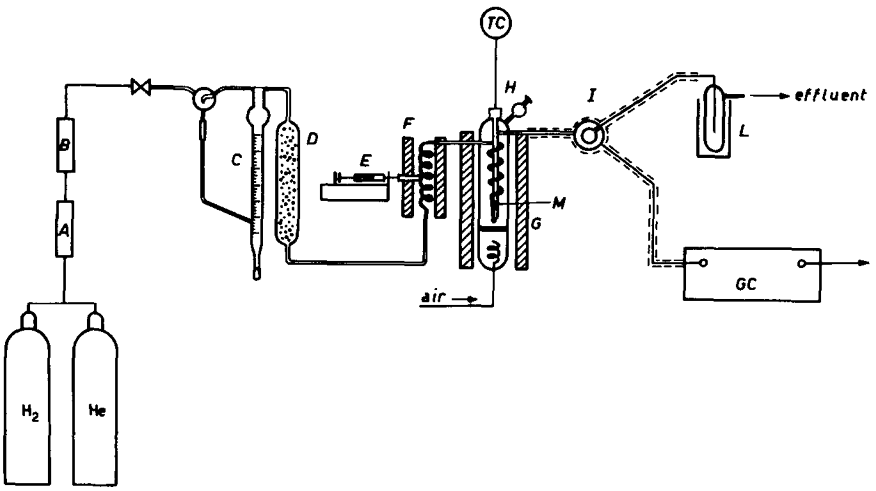


FIG. 1. Apparatus scheme for runs: (A) Deoxo unit; (B) dryer; (C) flow measuring system; (D) silica gel trap; (E) syringe driven motor; (F) preheater; (G) heater; (H) isothermal reactor with fluidized bed of sand; (I) sampling valve; (L) frozen trap; (M) catalytic bed; (GC) Perkin-Elmer gas chromatograph Model 880 with FID detector.

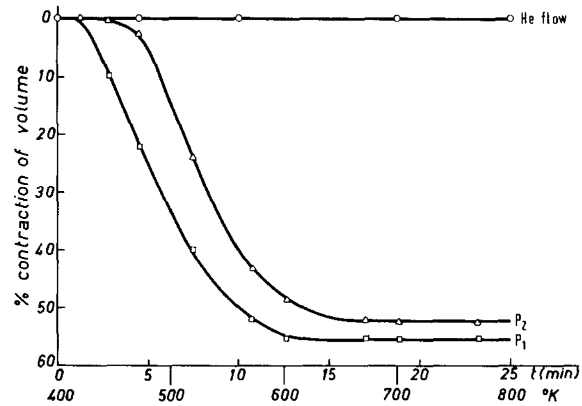


FIG. 2. Contraction of volume of Pt catalyst for heating treatment in several gaseous atmospheres. These runs were performed in a differential scanning calorimeter in which the platinum black samples were heated in an aluminum pan at a constant rate of 16°K/min. The contraction of volume was measured photographically.

eous atmospheres; helium causes negligible sintering while hydrogen has a significant influence on increasing the sintering rate (*5–7*). These findings have been confirmed by a photographic study of the phenomenon by analyzing the rate of volume contraction of the solid. The results are reported in Fig. 2. From the curves it appears that, in the presence of hydrogen, the maximum of the percentage contraction in volume is reached in about 10–15 min of heating at 16°K/min. No transformation has been observed in the presence of helium. On the other hand, if the sample had been previously treated at room temperature with hydrogen, sintering occurred on thermal treatment with helium. The observation (*5*) that the interaction with hydrogen plays an important role in platinum black sintering confirms that the system Pt/H_2 may behave as a very mobile solid system.

From these results it was concluded that, in normal runs, the heating time to reach 300°C in the reactor was sufficient to sinter the platinum black completely.

Catalyst Pretreatments

On the basis of the facts described in the previous section our fresh catalysts were subjected to a pretreatment, in order to obtain sufficiently thermally stable systems. Two different pretreatments were performed:

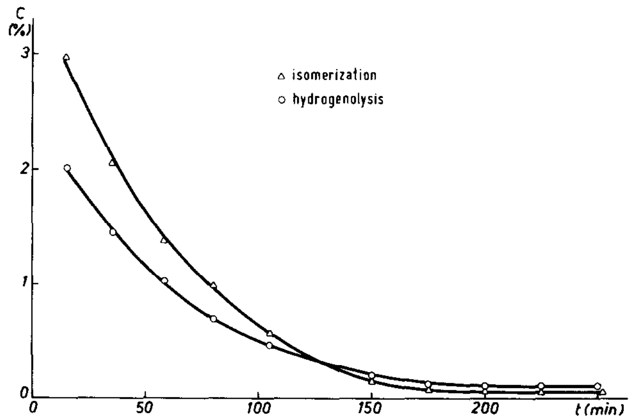


FIG. 3. Pretreatment P_1; activities for isomerization and hydrogenolysis, obtained at several times of catalyst exposure to hydrogen; C = conversion.

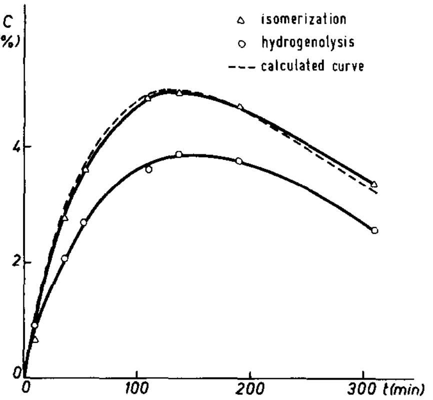


FIG. 4. Pretreatment P_2; activities for isomerization and hydrogenolysis, obtained at several times of catalyst exposure to hydrogen; C = conversion.

P_1 = heating in hydrogen flow to 300°C (about 0.5 hr);

P_2 = hydrogen adsorption at room temperature for 1 hr and then heating in a helium flow to 300°C (about 0.5 hr).

RESULTS

The catalysts 1 and 2 have been employed for a set of catalytic runs after the treatments P_1 and P_2. It emerged that the behavior of the catalysts was very sensitive to the type of pretreatment.

This is illustrated in Figs. 3 and 4 for catalyst 2, from which it appears that the P_1 treatment leads to a continuous deactivation of the catalyst, while the P_2 treatment leads to activity curves which start from about zero, go through a maximum and then slowly decrease.

Such a behavior was found to be reproducible for the large set of runs performed. Another important point arose from the analysis of selectivity versus time curves (Fig. 5). The comparison of such curves reveals that the ratio (rate of hydrogenolysis/rate of isomerization) decreases to a low value (about 0.5) for the catalyst subjected to P_1 treatment while it starts from low values and reaches an almost constant value (about 1.4) for the catalyst subjected to P_2 treatment.

In Fig. 5 the result of a run with an already employed catalyst, successively treated with oxygen to 300°C is given. In the latter case the behavior of the selectivity curve resembles the one for the P_2 catalyst.

A different kind of comparison of selectivities in isomerization reactions is reported in Fig. 6 in which the curves refer to the isomerization to 2-MP plus 3-MP and to MCP plus the preceding compounds, respectively. It appears that as the curves are extrapolated to zero time, the selectivities diverge in opposite directions.

DISCUSSION

A comparison of the two kinds of catalysts 1 and 2 is reported in Table 1, which shows that the former is less active and

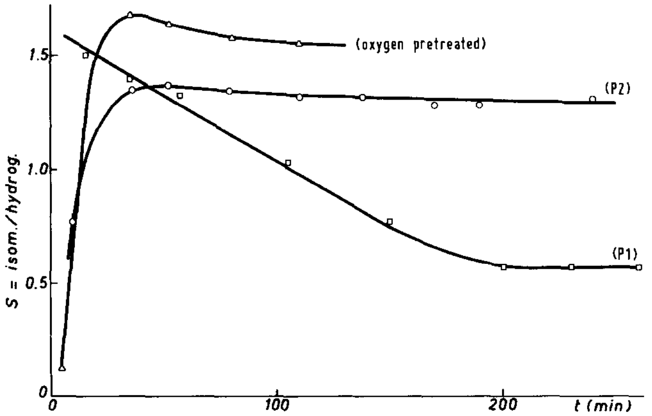


FIG. 5. Selectivity versus time for P_1 and P_2 pretreatment and for oxygen pretreatment.

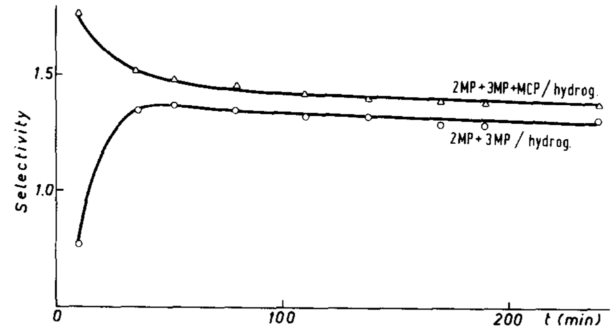


FIG. 6. Selectivities with respect to (2-MP + 3-MP) and (2-MP + 3-MP + MCP).

less stable. Both catalysts have been employed for a set of kinetic runs. It has been observed that the behavior with time of the activity and selectivity towards hydrogenolysis and isomerization was similar.

In the following discussion the analysis will be restricted to the data obtained with the more stable catalyst 2.

The modification of the catalyst implies the intervention of the chemical factors involved in the process under examination and these are connected with the different atmospheres in which the pretreatments were made. Hydrogen chemisorption affects the modifications of the catalyst structure and such a process in our runs was persisting also during the catalytic phenomenon. This fact seems to be confirmed by the continuous decreasing of the catalytic activity towards both the reactions, while the decrease of the selectivity seems to imply also a continuous modification of the active centers involved. Catalyst deactivation must be attributed in part to reactions leading to the formation of carbonaceous deposits on the catalyst surface. The detection of particles of carbon black by electron microscopy confirms this fact.

Traces of cyclohexane and benzene have been found in the reaction products. The fact that benzene was present only in traces is justified by the low probability of dehydrocyclization into benzene as a consequence of the high coverage of the catalyst surface by hydrogen. On the other hand, the catalyst subjected to P_2 treatment needed an activation period. The similarity of the curves (oxygen pretreated P_2) reported in Fig. 5 seems to indicate that activation must be attributed to the removal of presorbed oxygen from the surface which was not removed with helium. However, the thermal treatment with helium seems to favor the formation of a more stable configuration in that the selectivity after the activation period remained

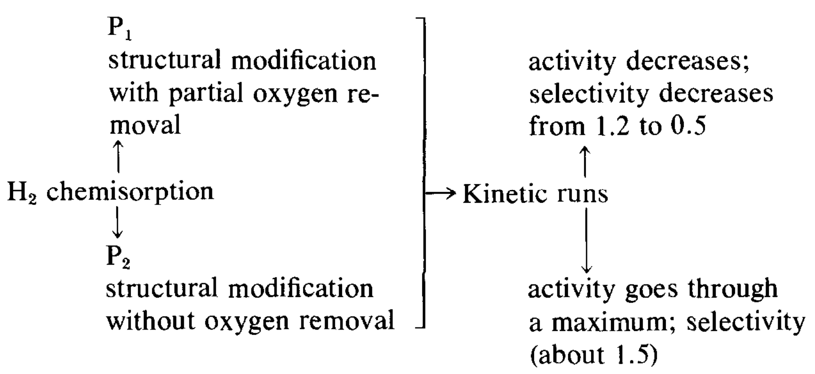
TABLE 1

A COMPARISON OF THE CATALYSTS USED IN THE RUNS

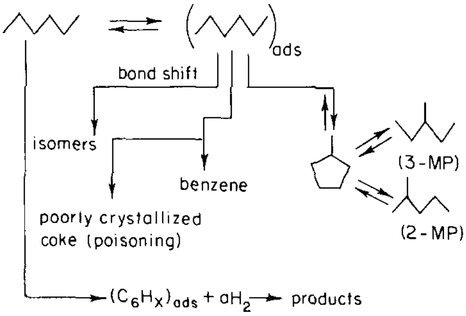
Catalyst	Surface area (m^2/g)		Initial activity (moles/hr g) × 100		Initial selectivity	Stability r/r_{init} referred to isomerization
	Initial	Final	Isomerization	Hydrogenolysis		
No. 1. From H_2PtCl_6 concn	10.3	1.0	0.125	0.09	1.39	0.01
No. 2. From H_2PtCl_6 dil as Ref. (*8*)	16.0	0.8	0.562	0.321	1.75	0.22

constant. On these catalysts the deactivation must be essentially attributed to the poisoning of active centers with carbonaceous deposits.

Since treatments P_1 and P_2 result in different sintering an influence of particle sizes on catalytic properties can be operative. Such a fact seems to be more important for catalyst subjected to P_1 treatment in which on the basis of Fig. 5, the ratio (isomerization/hydrogenolysis) decreases continuously with time. On the whole, the preceding analysis can be summarized by means of the following scheme:



In order to discuss the reaction behavior on the basis of previous research (*11*) and of the data of Table 2, the following reaction scheme can be employed:



The formation of carbonaceous deposits probably occurs through *trans*-polyolefins (*12*).

The kinetics of the hydrogenolysis reaction has been interpreted by means of the well-known equation:

$$r = k\, P_E{}^n P_{H_2}{}^{(1-na)},$$

where P_E and P_{H_2} are the *n*-hexane and hydrogen partial pressures, respectively. According to (*2*) a value of 3 has been attributed to the parameter *a*. A plot of $\ln(r/P_{H_2})$ vs $(\ln P_E - 3 \ln P_{H2})$ is given in Fig. 7 for different sets of runs. From this a value of *n* of about 0.85–0.90 is obtained, consistent with the values obtained with supported platinum. This fact reveals that the nature of the support does not affect the kinetics of the hydrogenolysis reactions.

The observed product distribution in hydrogenolysis reveals that in such a process a scheme of consecutive reactions is operative. In fact the experimental distribution

TABLE 2

2-MP/3-MP RATIO IN SEVERAL RUNS, AND A COMPARISON WITH SOME LITERATURE DATA

2-MP/3-MP (ratio)	Catalyst	Pretreatment	Run (Ref.)
2.08	1	P_1	Present work
1.92	2	P_2	Present work
2.10	2	P_2	Present work
1.94	2	P_1	Present work
2.61	Film	—	(*1*)
2.18	Film	—	(*1*)
2.20	Pt–Al_2O_3	—	(*1*)
2.05	Film deps.	—	(*1*)

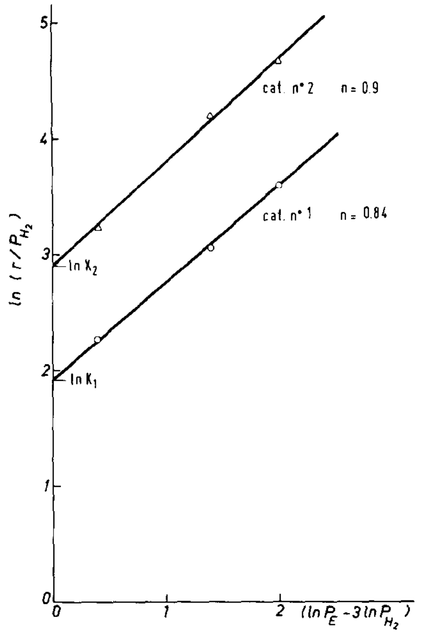


FIG. 7. A kinetic plot for the hydrogenolysis reaction.

(Table 3) shows that pentane is subjected to a partial decomposition; the extent of this decomposition has been calculated and therefore the ratio of the rates of breaking different bonds, given in Table 4, has been derived. In Table 4 a comparison between our data and the results on other kinds of catalyst is given. It appears that on Pt-black a higher selectivity towards terminal bonds is operative with respect to ultra-thin Pt-films and to Pt supported on silica.

TABLE 3
MOLAR DISTRIBUTION PRODUCTS OF HYDROGENOLYSIS AT 300°C

Carbon atoms:	C_1	C_2	C_3	C_4	C_5
Exptl	27.47	13.10	29.00	13.66	16.75
Calcd	23.80	12.20	28.00	12.20	23.80

As to the isomerization reaction it has been stated that the process can occur through two mechanisms: one via bond shift and the other via C_5 ring closure and subsequent hydrogenolysis of the ring. It has also been suggested that the latter mechanism is favored by the presence of hydrogen in the gas stream. The occurrence of the C_5 ring closure mechanism should imply a correlation between the ring opening behavior of MCP and the distribution of reaction products. The data of Table 2 seem to support the existence of such a kind of correlation.

In Table 5 the relative amount of MCP in different runs is given. On the whole it seems that the reaction of hydrogenolysis and isomerization via C_5 should occur on different active sites.

Since the breaking of C_5 to 2-MP and 3-MP takes place through hydrogenolysis, it seems that in the P_2 treatment the formation of C_5 isomerization centers is favored also if the succeeding reaction implies an activation by means of hydrogen. This finding can be justified if one takes into ac-

TABLE 4
RELATIVE C–C BOND RUPTURE PROBABILITIES[a]

Catalyst	Reaction temp (°C)	Relative probabilities					Runs (Ref.)
		1–2	2–3	3–4	4–5	5–6	
Pt-black	300	0.24	0.12	0.28	0.12	0.24	Present work
Thick fringe free polycrystalline Pt-film	273	0.24	0.12	0.28	0.12	0.24	(*1*)
Ultrathin Pt-film	273	0.13	0.16	0.40	0.16	0.13	(*1*)
0.8% Pt/silica	295	0.12	0.17	0.42	0.17	0.12	(*1*)

[a] $\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$.

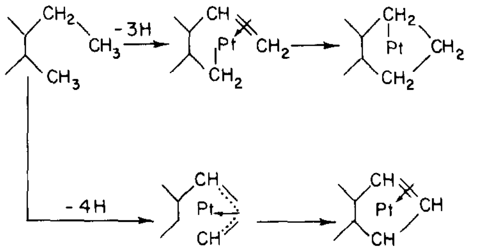
TABLE 5

ISOMERIZATION DISTRIBUTION PRODUCTS AT VARIOUS TIMES OF CATALYST EXPOSURE TO HYDROGEN[a]

Pretreatment	Time (min)	% MCP	% 2-MP	% 3-MP	Hexane flow (moles/hr)	Hydrogen flow (moles/hr)
P_2	15	49.14	29.90	20.96	0.0160	0.098
	37	10.50	59.90	30.50		
	54	7.20	61.80	31.00		
	80	7.58	61.50	30.92		
	110	7.20	61.41	31.39		
	190	7.05	67.80	25.15		
P_1	15	11.20	59.40	29.40	0.0160	0.098
	35	12.02	58.24	29.74		
	58	8.04	61.20	30.76		
	80	—	63.00	37.00		

[a] The catalyst employed was No. 2. The hydrogenolysis and isomerization conversion are those reported in Figs. 3 and 4.

count that probably the ring closure to C_5 derivatives can occur at a catalyst site consisting of a simple metal atom. For instance, Shephard and Rooney (*13*) proposed the two alternative mechanisms:



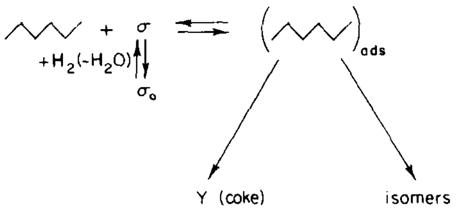
which resemble analogous processes occurring in organometallic chemistry.

Hydrogenolysis, instead, is believed to involve dissociatively chemisorbed hydrocarbon intermediates which are presumably multiply bonded to the surface.

Kinetic Model

In order to describe the time dependence of the isomerization reactions on P_2 catalysts, a simplified kinetic model has been devised. The model is based on the hypothesis that the activation of the isomerization centers occurs through water removal and that the deactivation is a consequence of the formation of amorphous coke.

The model can be described by means of the following oversimplified scheme; in which only the isomerizing active centers are taken into account:



that is:

$$\begin{aligned} &\text{a.} \quad \sigma + \mathrm{E} \rightleftarrows \sigma_{\mathrm{E}} \xrightarrow{k_1} \text{products} + \sigma, \\ &\text{b.} \quad \sigma_{\mathrm{O}} + \mathrm{H}_2 \xrightarrow{k_2} \mathrm{H_2O} + \sigma, \qquad (1) \\ &\text{c.} \quad \sigma_{\mathrm{E}} \longrightarrow \mathrm{Y}, \end{aligned}$$

where: σ = isomerizing active centers. Such centers could be hydrogenated platinum atoms with undefined stoichiometry (*14,15*). In fact these sites containing hydrogen have high catalytic activity and are responsible for isomerization. σ_{E} = active centers with *n*-hexane adsorbed; σ_{O} = active centers with oxygen adsorbed; Y = active centers deactivated by coke.

By assuming the adsorption process to be at equilibrium it follows that:

$$\begin{aligned} &\vartheta_{\mathrm{E}}/\vartheta P_{\mathrm{E}} = b_1, \\ &\frac{d\vartheta}{dt} = k_2\vartheta_{\mathrm{O}}P_{\mathrm{H}_2} + k_1\vartheta_{\mathrm{E}}, \qquad (2) \\ &\frac{d\vartheta_{\mathrm{Y}}}{dt} = k_3\vartheta_{\mathrm{E}}, \end{aligned}$$

ϑ_i being the fraction of active centers covered by i.

Since $\vartheta_0 + \vartheta + \vartheta_E + \vartheta_Y = 1$ it follows that:

$$\frac{d\vartheta}{dt} = k_2[1 - \vartheta(1 + b_1P_E) - \vartheta_Y] \times P_{H_2} + k_1\vartheta_E, \quad (3)$$

$$\frac{d\vartheta_Y}{dt} = k_3b_1P_E\vartheta.$$

A reasonable hypothesis is to assume that $\vartheta = 0$ both for $t = 0$ and $t = \infty$. The integration of Eq. (3) leads to:

$$\vartheta = C_1(e^{-\alpha_1 t} - e^{-\alpha_2 t}), \quad (4)$$

where C_1 is a constant and:

$$\alpha_{1,2} = (A \pm B^{1/2})/2, \quad (5)$$

where

$$A = k_2P_{H_2} - (k_1 - k_1P_{H_2})b_1P_E,$$
$$B = [k_2P_{H_2} - (k_1 - k_1P_{H_2})b_1P_E]^2 - 4k_1k_2b_1P_EP_{H_2}.$$

Besides:

$$r_{\text{isom}} = k_1\vartheta_E = k_1b_1P_E\vartheta. \quad (6)$$

From Eq. (6) the description of the isomerization conversion curves as a function of time can be derived:

$$(\text{conv. }\%)_{\text{isom}} = 0.842\,\frac{W}{F}\,(e^{-0.35t} - e^{-0.60t}), \quad (7)$$

where W = catalyst weight (g), F = hexane flow (moles/hr) and $8.42 \times 10^{-3} = k_1b_1P_EC_1$.

The calculated curves obtained with Eq. (7) are in agreement with experimental data, as shown in Fig. 4.

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