Transformation of Propylene on Molybdenum Oxide Supported on Alumina

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The transformation of propylene in the presence of molybdenum oxide on alumina was studied in a flow system over the range of temperatures 250–500°C and contact times of 6–60 sec. Hydrogen, propane, butenes, and a highly unsaturated complex deposited on the catalyst surface were found to be the main reaction products. The decomposition of propylene as well as the formation of the major reaction products were shown to be of the first order. The rate constants and activation energies have been determined. The reaction mechanism has been postulated, involving dissociative adsorption of propylene, hydrogenation of propylene with chemisorbed hydrogen, addition of the methyl group to the complexes formed, and desorption of the products. Kinetics of the process based on this reaction scheme was discussed. Two empirical equations for the catalyst deactivation process have been proposed.

INTRODUCTION

Among the reactions of catalytic transformation of olefins not much attention has been paid to their self-hydrogenation. This reaction has been studied only marginally with regard to ethylene in the course of investigation of hydrogenation of ethylene to ethane (1, 2). Only a few papers have been devoted specifically to the study of self-hydrogenation, its kinetics, and mechanism (3, 4, 5). The work by Popov and Mardeleishvili (3) concerned the self-hydrogenation of ethylene and propylene on evaporated films of palladium, platinum, and nickel. An absence of hydrogen among the reaction products has been stated, and the mechanism of hydrogen transfer among the adsorbed radicals proposed. According to McKee (4), who used nickel as a catalyst, there is evidence supporting the Beeck's dissociative mechanism (2). Hirota and Teretani (5) were investigating the self-hydrogenation reaction of ethylene on nickel. They suggested the existence of at least two regions of different activity on the nickel surface: one which makes ethylene dissociate into an acetylenic complex and hydrogen atoms and the other in which hydrogenation of associatively adsorbed ethylene proceeds by means of migrated hydrogen. The structure of the complexes deposited on the surface of the catalyst as a result of the chemisorption and transformation of ethylene has been also examined (6).

All reported works dealt mainly with ethylene and were carried out, as a rule, at low temperatures and pressures in a static system in the presence of metal films.

The object of our investigation is to examine the processes of transformation of olefins at 200–500°C in a flow system in the presence of some metals and metal oxides supported on alumina. In our preliminary report (7) it has been shown that all olefins investigated undergo the same kind of specific transformation in the presence of many different catalysts. In the present paper a detailed study concerning the transformation of propylene on molybdenum oxide supported on alumina is reported.

EXPERIMENTAL

Catalyst. The catalyst was prepared by impregnation of 40 g of commercial γ-Al_2O_3 (surface area, 280 m^2/g; particle size, 0.5–1.2 mm) with a solution of 12 g of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in 100 ml of water. After 24 hr the excess of the liquid was filtered out and the solid washed with distilled water. The catalyst was dried at room temperature for about 24 hr, at 60° to 110°C for 8 hr, and calcined in a stream of dry air for 6 hr at 500–530°C. Then it was reduced for 6 hr at 530°C with hydrogen. The same sample of catalyst of the weight of 5.0 g was used in all experiments. Prior to each run the catalyst was regenerated by calcining for 3 hr at 500–530°C, reducing for 3 hr at 530°C with hydrogen, and finally blowing with nitrogen in order to remove hydrogen remaining on the catalyst. Before reduction the catalyst contained 14.5 wt % MoO_3. Porosimetric analysis (mercury porosimeter Carlo Erba AG-60) indicated that the majority of pores were in the 50–75 Å region. The surface area of the catalyst was 270 m^2/g as determined by BET with nitrogen. X-Ray examination of the catalyst both fresh and after use in the reaction (Guinier Camera "Nonius," Delft, Netherlands) showed an absence of metallic molybdenum and MoO_3. Only the lower molybdenum oxides, mainly MoO_2, were detected.

Apparatus and procedure. The apparatus used (8) consisted of a glass tubular reaction vessel inserted into a vertical resistance electric furnace and fitted with the necessary measuring devices, as well as facilities for introducing reactants (accuracy ±1%). The outlet of the reactor was connected with a modified Janak gas chromatograph, so the stream outgoing from the reactor was directly admitted to the analyzer. A reaction vessel was filled with a catalyst bed of a volume of 9.7 cc (5.0 g) and maintained at constant temperature (±0.5°C). For the chromatographic analysis the alumina columns (length, 1.7 m) and the active coal columns (length, 2 m) were used. Carbon dioxide (99.995% purity) was used as carrier gas. The accuracy of analysis was ±0.01% or ±0.05% for the components of the concentration less than 20 vol % or more than 20 vol %, respectively.

All experiments were carried out at atmospheric pressure. Propylene – nitrogen mixtures of a composition previously determined by analysis were used. The gaseous reaction products were analyzed, usually, every 20 min. After each run (about 2 hr) the catalyst was regenerated, and thus its previous activity was practically restored even after a great many regenerations.

RESULTS

Preliminary runs revealed that propylene passed at 350°C over the catalyst undergoes some transformation. The major reaction products were found to be hydrogen, propane, and butenes (mainly isobutylene)

TABLE 1

TYPICAL CONCENTRATION OF REACTION PRODUCTS FROM
A SINGLE RUN (350°C, CONTACT TIME 20 SEC)

Component	Concentration (vol %)						
	Initially	23 min	45 min	65 min	86 min	106 min	126 min
Hydrogen	—	6.07	4.92	4.21	3.71	3.09	2.87
Nitrogen	38.10	43.40	42.10	41.05	40.60	39.90	39.80
Methane	—	0.63	0.54	0.51	0.55	0.49	0.42
Ethane	0.04	0.27	0.21	0.18	0.14	0.15	0.14
Ethylene	0.05	0.48	0.38	0.32	0.25	0.24	0.24
Propane	0.04	15.33	10.92	9.15	7.95	6.92	6.43
Propylene	61.75	31.50	39.20	43.15	45.60	48.05	49.05
Butanes	—	0.61	0.44	0.27	0.20	0.24	0.23
1-Butene	—	0.50	0.38	0.40	0.29	0.31	0.22
Isobutylene	—	0.97	0.58	0.56	0.50	0.42	0.43
2-Butene	—	0.24	0.33	0.20	0.21	0.19	0.17

as well as highly unsaturated residue ("complex") deposited on the catalyst surface. In the gaseous products some very small amounts of methane, ethylene, ethane, and butanes were also detected. The detailed investigations were carried out in the temperature region 250–500°C, with contact time of 6–60 sec, and the concentration of propylene in its mixture with nitrogen from 20 to 80 vol %. Under the reaction conditions the conversion of propylene was in the range of 10–85%.

As time went on, a rapid decrease in catalytic activity (propylene conversion)

was observed, but in spite of it the yields of all gaseous products in relation to converted propylene appeared to be practically constant. Some typical results obtained for a single run are given in Table 1 and illustrated by Fig. 1. The effect of propylene concentration and the reaction order were studied at 250°C and 350°C over the range of propylene concentration in its mixtures with nitrogen of 20 to 80 vol %. The results obtained are presented in Fig. 2.

The effect of temperature was studied over a wide range from 250° to 500°C using the propylene-nitrogen mixture
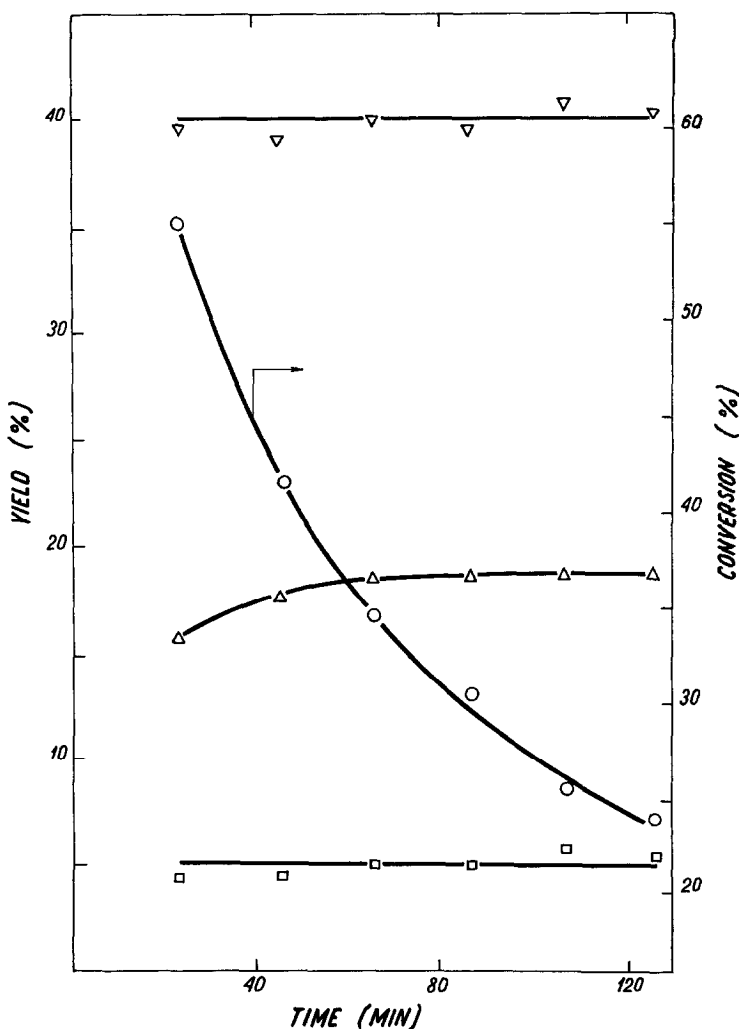

FIG. 1. Effect of time on conversion of propylene and the yields of the major reaction products related to converted propylene: O, C_3H_6 (converted); ∇, C_3H_8; △, H_2; □, C_4H_8.
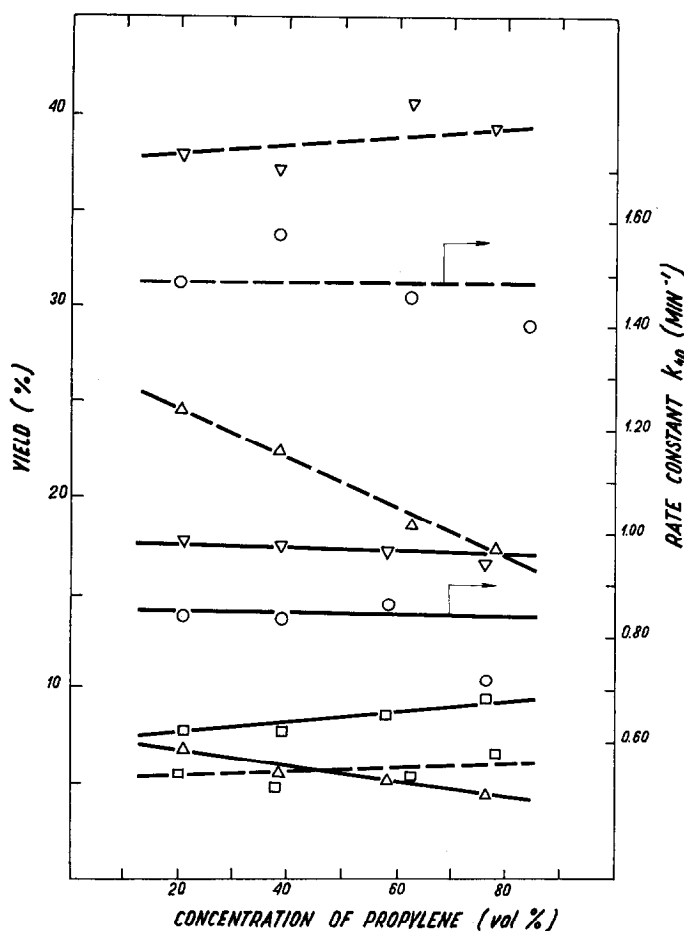
FIG. 2. Effect of the percentage of propylene in its mixture with nitrogen on the yields of the major products related to converted propylene and on the rate constant of propylene decomposition at 250°C (solid lines) and 350°C (broken lines): $\bigcirc$, k_{40}; $\triangledown$, C_3H_8; $\triangle$, H_2; $\square$, C_4H_8.

(about 60% propylene). The results are shown in Figs. 3 and 4. The activation energies for propylene decomposition and product formation were determined from an Arrhenius plot (Fig. 5). In Table 2 are collected some values of the activation ener-

gies obtained after 40 min of a run, as well as the pre-exponential factors.

In order to determine the degree of unsaturation of a complex deposited on the catalyst, the contents of carbon and hydrogen in it were determined by elemental

TABLE 2

KINETIC PARAMETERS FOR TRANSFORMATION OF PROPYLENE

	Temperature range (°C)	E (kcal mole^{-1})	log A (A, min^{-1})
Propylene decomposition	250–400°	4.6	1.76
	400–500°	14.5	5.00
Hydrogen formation	250–400°	12.8	3.90
	400–500°	21.4	6.73
Propane formation	250–500°	10.7	3.53
Butenes formation	250–350°	Rate constant $(7.1 \pm 0.9) \times 10^{-2}$ min^{-1}	
	350–500°	4.0	0.28
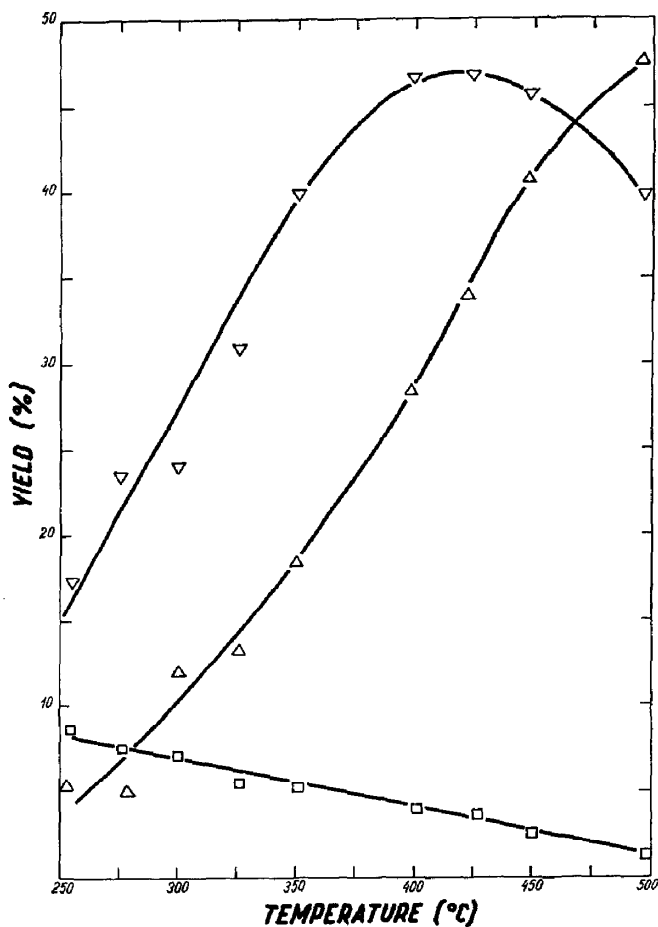
FIG. 3. Effect of temperature on the yields of the major reaction products related to converted propylene: ∇, C_3H_8; $\triangle$, H_2; $\square$, C_4H_8.
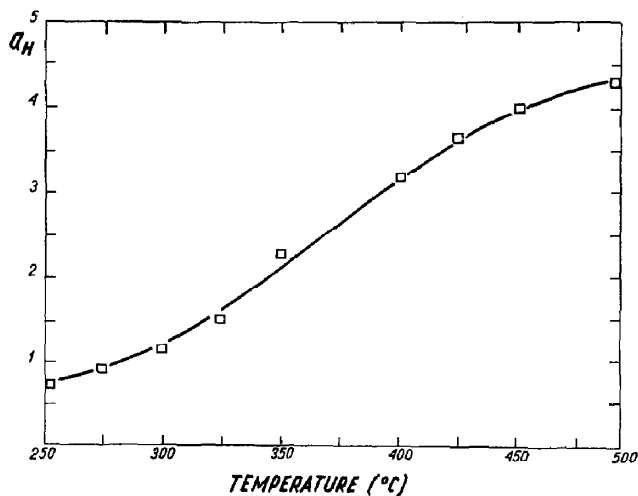

FIG. 4. Variation in the number of hydrogen atoms abstracted from the propylene molecule (a_H) with temperature.
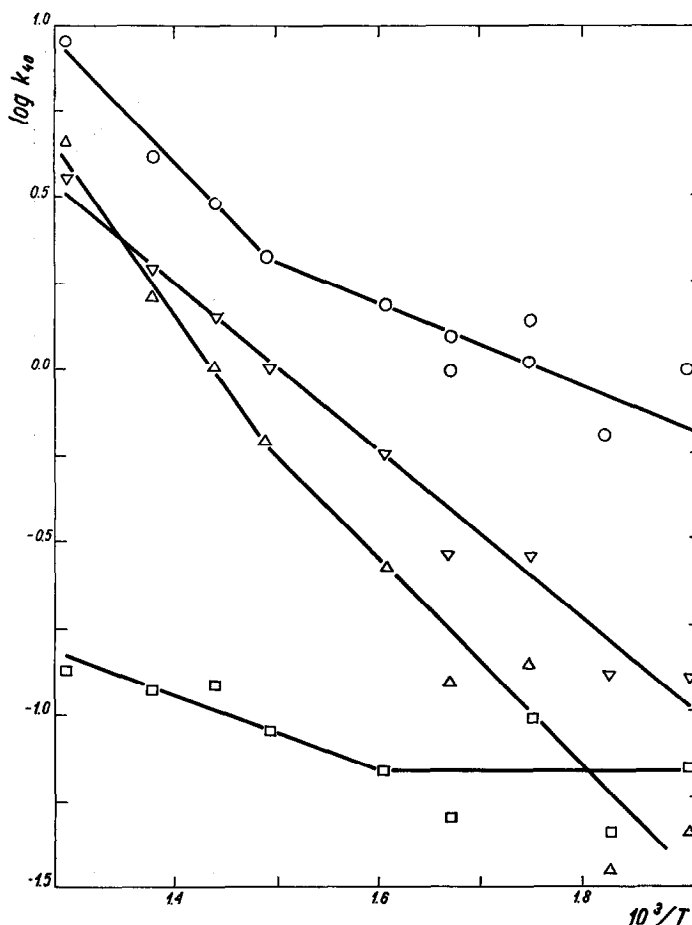
FIG. 5. Arrhenius plot for the decomposition of propylene (O), and formation of hydrogen (△), propane (▽), and butenes (☐) after 40 min of the run.

analysis. The results obtained (in one case the H/C ratio, 0.103–0.106 by weight; the calculated number of hydrogen atoms abstracted from the propylene molecule a_H = 2.20–2.25), were in a full agreement with those based on the carbon and hydrogen balance in the feed and gaseous products (in the same case a_H = 1.9–2.3). The attempts to reveal the structure of the complexes by analysis of the gaseous products of their thermal decomposition are the subject of a special study. As a result of the deposition of the complexes on the catalyst, its activity considerably falls in the course of a run. The experimental results fit well each of the two subsequent empirical equations (correlation coefficient 0.98–0.997):

$$\log y = a_1 - b_1 \tau^{1/2}$$
$$\log k = a_2 - b_2 \tau^{1/2}$$

where y represents conversion of propylene; k, the rate constant; τ, time of the catalyst work; and a_1, a_2, b_1, and b_2 are constants.

The examples are presented in Fig. 6. From these relationships the value of the rate constant after 40 min of the run, k_{40}, was computed and then applied to compare the results of the experiments carried out under different reaction conditions.

DISCUSSION

On the basis of a constancy of the yield of products in relation to the converted propylene, independently of the time (Fig. 1) one can conclude that the character of
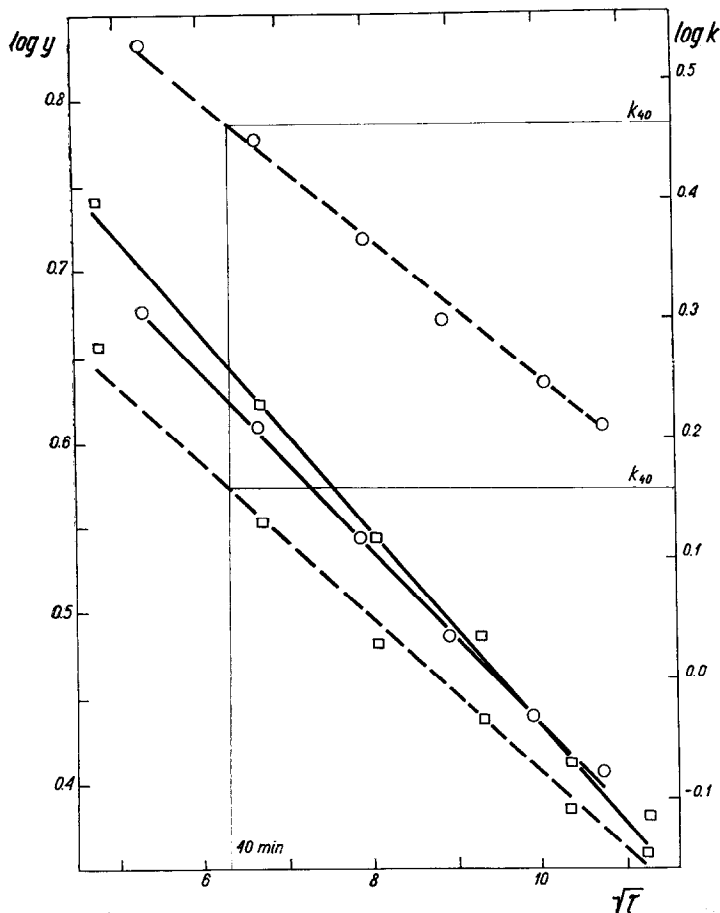
FIG. 6. Plots of log y against $\tau^{1/2}$ (solid lines) and log k against $\tau^{1/2}$ (broken lines): $\square$, 350°C, contact time 20 sec, propylene concentration 61.7 vol %; $\bigcirc$, 421°C, contact time 10 sec, propylene concentration 58.5 vol %.

the process is not affected by the changes in the catalyst activity. Only at 450°C or above, were there observed some slow changes in the yields of the main reaction products. It therefore appears that the catalyst sites, despite their different energies, are uniformly blocked. A reason for somewhat lower hydrogen yield at the initial stage of a run could be a consumption of a part of it for saturation of the catalyst with hydrogen.

The rate constant of the decomposition of propylene calculated as for the first order reaction was found to be independent of the propylene concentration (Fig. 2). The yields of all main products as well as propylene conversion observed for the same time of catalyst life are practically inde-

pendent of propylene concentration, the reactions of the transformation of propylene and formation of the products being, therefore, of the first order. A slight decrease of the hydrogen yield observed when propylene concentration is raised is undoubtedly caused by a secondary reaction of hydrogenation of propylene with gaseous hydrogen formed in reaction.
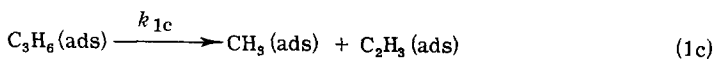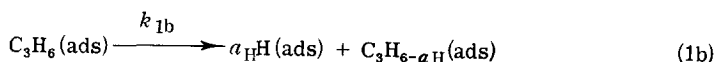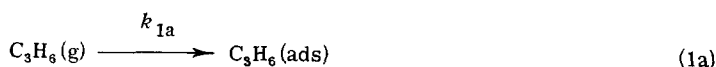
It follows from our results (Fig. 3) that the formation of molecular hydrogen becomes increasingly important as the temperature is raised. The reaction of self-hydrogenation of propylene leading to hydrogen and propane is the most important process over the whole temperature region studied. The yield of butenes formed simultaneously rapidly decreases with the rise of

temperature. The experiments carried out over unreduced catalyst (MoO_3/Al_2O_3) indicated that essentially identical transformation proceeds but in this case a decrease in the hydrogen yield was observed, clearly due to consumption of some hydrogen for reducing catalyst. With the carrier itself (Al_2O_3) a low conversion of propylene was observed. The composition of the products was quite different from that obtained in the presence of catalyst. Only negligible yields of propane related to converted propylene have been obtained.

Reaction Mechanism

The reaction scheme which accounts for the products and the observed kinetics is postulated as follows.

1. Dissociative Adsorption of Propylene

species firmly adsorbed on the catalyst surface are formed apart from chemisorbed hydrogen atoms and methyl groups. The existence of so-called "complexes" deposited on the catalyst and formed by abstraction of one or two hydrogen atoms is generally admitted *(2, 8)*. The results of the present work have provided evidence that further steps of dissociation are also possible, up to abstraction of even four hydrogen atoms from the propylene molecule. As seen from Fig. 4 a_H depends on temperature, in such a way that the higher the temperature the more hydrogen atoms are abstracted and therefore the poorer the residual complex in hydrogen. The abstraction of the methyl group under the reaction conditions followed by its addition to the adsorbed

$$C_3H_6\,(g) \xrightarrow{\; k_{1a}\;} C_3H_6\,(ads) \tag{1a}$$

$$C_3H_6\,(ads) \xrightarrow{\; k_{1b}\;} a_H H\,(ads) + C_3H_{6-a_H}\,(ads) \tag{1b}$$

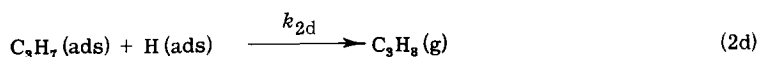$$C_3H_6\,(ads) \xrightarrow{\; k_{1c}\;} CH_3\,(ads) + C_2H_3\,(ads) \tag{1c}$$
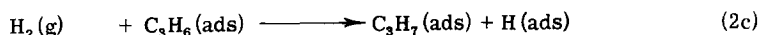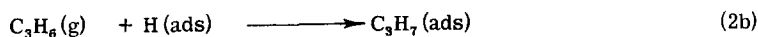
Propylene is first of all adsorbed associatively [reaction (1a)] on the active sites. Then a single-stage or many-stage process of dissociation follows through abstraction

species ("methylation") has not been postulated so far.

2. Hydrogenation of Propylene

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$$C_3H_6\,(ads) + H\,(ads) \xrightarrow{\; k_{2a}\;} C_3H_7\,(ads) \tag{2a}$$

$$C_3H_6\,(g) + H\,(ads) \longrightarrow C_3H_7\,(ads) \tag{2b}$$

$$H_2\,(g) + C_3H_6\,(ads) \longrightarrow C_3H_7\,(ads) + H\,(ads) \tag{2c}$$

$$C_3H_7\,(ads) + H\,(ads) \xrightarrow{\; k_{2d}\;} C_3H_8\,(g) \tag{2d}$$
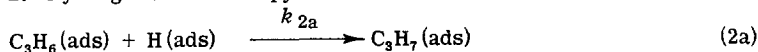
of hydrogen atoms [reaction (1b)] or a group of atoms, such as a methyl group [reaction (1c)] by the neighbor active sites. The abstraction of both hydrogen atoms and methyl group leading to the formation of C_2H_n(ads) complexes ($n < 3$) may also proceed. As a result of this reaction step, a number of highly unsaturated

Hydrogenation of propylene with hydrogen formed in reaction (1b) proceeds according to the generally accepted scheme of reactions (2a) and (2d). Apart from it, at low surface concentration of propylene (particularly at high temperatures) hydrogenation may proceed by another scheme [reactions (2b) and (2d)] and at high con-

centrations of hydrogen in the gas phase (in case of high conversion of propylene) by still another one [reactions (2c) and (2d)].

3. Transfer of Hydrogen to the Gas Phase

These reactions are not significant and some of them [reactions (5d) and (5e)] may be observed only at very high temperatures (500°C).

There are other plausible side reactions

3. Transfer of Hydrogen to the Gas Phase

$$C_3H_7(ads) + H(ads) \xrightarrow{k_{3a}} C_3H_6(ads) + H_2 \ (g) \tag{3a}$$

$$2 H(ads) \longrightarrow H_2(g) \tag{3b}$$

Hydrogen is transferred to the gas phase by reaction (3a), which is the reverse of the reaction (2c), or by desorption of hydrogen adsorbed on the catalyst surface.

4. Formation of C_4 Hydrocarbons

too, such as polymerization of the complexes (8).

Kinetics

The kinetics was based on the simplified

4. Formation of C_4 Hydrocarbons

$$
\begin{array}{c}
C_3H_6(ads) + CH_3(ads) \xrightarrow{k_{4a}} C_4H_9(ads) \xrightarrow{+H(ads)} C_4H_{10}(g) \\[2mm]
+H(ads) \updownarrow -H(ads) \qquad\qquad k_{4b} \ -H(ads) \updownarrow +H(ads) \\[2mm]
C_3H_5(ads) + CH_3(ads) \longrightarrow C_4H_8(ads) \longrightarrow C_4H_8(g)
\end{array}
\tag{4a, 4b}
$$

C_4 hydrocarbons are formed by addition of methyl group to propylene adsorbed associatively or to the adsorbed radical $C_3H_5(ads)$. A methyl is added predominantly to the β-carbon atom, forming finally isobutylene or isobutane.

5. Other Reactions

Some minor products of the reaction, i.e. ethylene, ethane, and methane, could be formed as follows:

version of the reaction scheme postulated above, including only reactions (1a), (1b), (1c), (2a), (2d), (3a), (4a), and (4b), which are decisive from the kinetics point of view.

Let A, B, C, D, and F be the fractions of the active surface of the catalyst covered with C_3H_6, C_3H_7, H, C_4H_9, and CH_3, correspondingly. Then the rates of decomposition of propylene and formation of

5. Other Reactions

$$C_3H_6(ads) \xrightarrow{-CH_3(ads)} C_2H_3(ads) \xrightarrow{+H(ads)} C_2H_4(ads)$$

$$
\xrightarrow{\hspace{2cm}}
\begin{cases}
\xrightarrow{+2H(ads)} C_2H_6(g) \\
\xrightarrow{\hspace{1cm}} C_2H_4(g)
\end{cases}
\tag{5a}
$$

$$C_3H_7(ads) + CH_3(ads) \longrightarrow C_3H_6(ads) + CH_4(g) \tag{5b}$$

$$CH_3(ads) + H(ads) \longrightarrow CH_4(g) \tag{5c}$$

$$C_3H_6(ads) \longrightarrow C_2H_6 + C \tag{5d}$$

$$2 C_3H_6(ads) \longrightarrow 3 CH_4 + 3 C \tag{5e}$$

products could be represented by the following equations:

$$-\frac{d[C_3H_6]}{dt} = k_{1a}x_0\,(1-A-B-C-D-F)$$

$$\frac{d[H_2]}{dt} = k_{3a}BC$$

$$\frac{d[C_3H_8]}{dt} = k_{2d}BC$$

$$\frac{d[C_4H_8]}{dt} = k_{4b}D$$

where x_0 is the mole fraction of propylene in the gas phase.

Variations in the fractions of the surface covered with species are given by

$$dA/dt = k_{1a}x_0(1 - A - B - C - D - F) - k_{1b}A - k_{2a}AC + k_{3a}BC - k_{4a}AF - k_{1c}A$$

$$dB/dt = k_{2a}AC - k_{2d}BC - k_{3a}BC$$

$$dC/dt = a_H k_{1b}A - k_{2a}AC - k_{2d}BC - k_{3a}BC + k_{4b}D$$

$$dD/dt = k_{4a}AF - k_{4b}D$$

$$dF/dt = k_{1c}A - k_{4a}AF$$

When the steady state treatment is applied $(dA/dt = dB/dt = dC/dt = dD/dt = dF/dt = 0)$ the following expressions for the fractions of the surface covered with species are obtained:

$$A = \frac{k_{1a}bx_0}{c + k_{1a}hx_0}$$

$$B = \frac{k_{2a}}{k_{2d} + k_{3a}}\frac{k_{1a}bx_0}{c + k_{1a}hx_0}$$

$$C = \frac{a_H k_{1b} + k_{1c}}{2k_{2a}}$$

$$D = \frac{k_{1c}}{k_{4b}}\frac{k_{1a}bx_0}{c + k_{1a}hx_0}$$

$$F = \frac{k_{1c}}{k_{4a}}$$

where

$$b = 1 - \frac{a_H k_{1b} + k_{1c}}{2k_{2a}} - \frac{k_{1c}}{k_{4a}}$$

$$c = k_{1b}\left(1 + \frac{\frac{1}{2}a_H k_{2d}}{k_{2d} + k_{3a}}\right) + k_{1c}\left(2 + \frac{\frac{1}{2}k_{2d}}{k_{2d} + k_{3a}}\right)$$

$$h = 1 + \frac{k_{2a}}{k_{2d} + k_{3a}} + \frac{k_{1c}}{k_{4b}}$$

By substituting the expressions for A, B, C, D, and F into the equations given above the following expressions for the rates are obtained:

$$-\frac{d[C_3H_6]}{dt} = \frac{k_{1a}bcx_0}{c + k_{1a}hx_0}$$

Assuming $c \gg k_{1a}hx_0$

$$-\frac{d[C_3H_6]}{dt} \approx \text{const.} \cdot x_0$$

In a similar way

$$\frac{d[C_3H_8]}{dt} = \frac{1}{2}(a_H k_{1b} + k_{1c}) \times \frac{k_{2d}}{k_{2d} + k_{3a}}\frac{k_{1a}bx_0}{c + k_{1a}hx_0} \approx \text{const.} \cdot x_0$$

$$\frac{d[H_2]}{dt} = \frac{1}{2}(a_H k_{1b} + k_{1c}) \times \frac{k_{3a}}{k_{2d} + k_{3a}}\frac{k_{1a}bx_0}{c + k_{1a}hx_0} \approx \text{const.} \cdot x_0$$

$$\frac{d[C_4H_8]}{dt} = \frac{k_{1a}k_{1c}bx_0}{c + k_{1a}hx_0} \approx \text{const.} \cdot x_0$$

Assuming $c \gg k_{1a}hx_0$, i.e., $k_{1b} \gg k_{1a}$, the reaction scheme is seen therefore, to lead to the first order kinetics of propylene decomposition, as well as propane, hydrogen, and butenes formation, in agreement with what was found experimentally.

The assumption made above means that the associative chemisorption of propylene is the rate-determining step.

The ratio $d[H_2]/d[C_3H_8] = k_{3a}/k_{2d}$ should be independent of propylene concentration. Some small variations in this ratio observed in the course of the reaction or with high propylene concentrations can be attributed to the contribution of reaction (2c), usually of a minor importance.

The first order kinetics of the propylene decomposition and product formation supports our view about the negligible role of direct desorption of hydrogen from the

catalyst [reaction (3b)]. The yield of butenes from converted propylene, $d[C_4H_8]/d[C_3H_6] = k_{1c}/c$, is independent of the concentration of propylene in the gas phase. The decrease of the butenes yield with the rise of temperature shows that activation energy for the abstraction of a methyl group is smaller than that for hydrogen abstraction by about 4 kcal mole^{-1}.

The change in activation energies for propylene decomposition and formation of hydrogen and butenes observed at about 400°C could be attributed to the change in mechanism of propylene adsorption. One can safely suppose that this is a result of the reduction of the active component of the catalyst to the form of lower molybdenum oxides, proceeding at the initial stages of the reaction.

Deactivation of the Catalyst

As shown above, the process of deactivation of the catalyst can be represented by two empirical equations.

An assumption that the fall in catalyst activity is simply an effect of the blocking of its surface by the deposition of the surface complexes seems unlikely. This is obvious from the comparison between the number of active sites necessary to combine complexes and the amount of the oxide molecules in a catalyst sample.

The number of active sites necessary to combine complexes formed when 1 mole of propylene is converted is given by

$$2\,\frac{W_1 + W_2}{a_H}\,c_kN = 2W_1\,\frac{1 + S}{a_H}\,c_kN$$

where W_1 and W_2 are the yields of propane and hydrogen related to converted propylene, S is the ratio of H_2/C_3H_8 yields, c_k is the number of active sites combining one complex and N is Avogadro's number.

The number of moles of propylene converted per unit of time is $V_0\,yx_0/V_M$, where V_0 is a flow rate of the reaction mixture, y is conversion of propylene, x_0 is mole fraction of propylene, and V_M is the molecular volume of propylene.

The number of active sites n blocked per unit of time is

$$\frac{dn}{dt} = 2W_1\,\frac{1 + S}{a_H}\,c_kN\,\frac{V_0yx_0}{V_M}$$

By insertion in the last equation of y eliminated from the empirical equation $\ln y = a_1 - b_1\,\tau^{1/2}$ and by integration from 0 to τ, one obtains finally

$$n = 4W_1\,\frac{1 + S}{a_H}\,c_kN\,\frac{V_0x_0}{V_M}\,\frac{\exp a_1}{b_1^{\,2}}$$
$$\times\,[1 - (1 + b_1\tau^{1/2})\exp(-b_1\tau^{1/2})]$$

Use of the values for a single run (one of those illustrated by Fig. 6), $W_1 = 0.402$, $S = 0.46$, $a_H = 2.3$, $V_0 = 12.4$ cm^3 min^{-1}, $x_0 = 0.617$, $V_M = 21\,960$ cm^3, $a_1 = 0.02$, $b_1 = 0.131$, $c_k = 1$, and $t = 50$ min gives rise to $n = 0.005\,N$. Similar values for n were obtained for other runs.

Comparing this result with the number of the molybdenum oxide molecules in a catalyst sample (5 g, 14.5% of MoO_3) equal to $0.005\,N$ it is clear that even if the smallest possible demand for the active sites ($c_k = 1$) is assumed, the molybdenum oxide should already be fully covered by the complexes and the catalyst completely deactivated after about 1 hr. However, the catalyst activity after this period, though less than initial, is still quite considerable. For thermodynamics reasons as well as because of an absence of certain products in a gas phase, it is difficult to suppose that under the reaction conditions the complexes could be desorbed. Hence we conclude that some part of the complexes migrates from the molybdenum sites to alumina.

CONCLUSION

The results of the present study clearly show that the process of self-hydrogenation observed in the past in the presence of some metal films as catalysts and regarded as being specific for metals proceeds also in the presence of some metal oxides. Because of the relatively lower catalytic activity of metal oxides, the reaction proceeds in this case at much higher temperatures. As a result, the reaction of self-hydrogenation over metal oxides is accompanied by some other reactions not observed by the authors studying similar processes at low temperatures in a static

system. Thus, at low temperatures no hydrogen was found in the reaction products, except by McKee (4). The amount of hydrogen formed at low temperatures is really very small and it is consumed for hydrogenation of olefins. On the contrary, at higher temperatures in a flow system, the amount of hydrogen produced is much larger and, as it is immediately removed from the reaction zone, the major part of it becomes a component of the reaction products. Some other reactions accompanying the self-hydrogenation of olefins could not be noticed before, as almost all studies were concerned only with ethylene. Using propylene as a substrate it was shown in the present work that the process of migration of a methyl group ("self-methylation") yielding C_4 hydrocarbons was proceeding too.

On the basis of present observations of specific transformation of propylene in the presence of molybdenum oxide on alumina as well as similar transformations in the presence of some other oxides, as reported in our preliminary report (7), one can postulate that such processes usually accompany many other catalytic reactions involving propylene.

The reaction mechanism proposed presently satisfactorily accounts not only for the transformation of propylene but of other olefins as well. A study of the transformation of other olefins will be a subject of a special report.

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