Study of the Chemisorption and Hydrogenation of Propylene on Platinum by Temperature-Programmed Desorption

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(Received September 2, 1977)

The temperature-programmed desorption (TPD) chromatograms of propylene from platinum black comprised four peaks: A, B, C, and D, with peak maxima at about 260, 380, 570, and higher than 720 K respectively. Peaks A and B were identified as the mixtures of propylene and propane. Peaks C and D were methane formed from chemisorbed propylene by decomposition as the temperature was raised during the subsequent TPD. The reactivities of various types of chemisorbed hydrogen previously detected by TPD were also investigated with regard to the hydrogenation of propylene. Two types of chemisorbed hydrogen, presumed to be present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms and in the bridge form of molecular hydrogen, were found to react with propylene.

Four different types of chemisorbed hydrogen (α, β, γ, and δ) were previously found on the platinum surface, with the temperature-programmed desorption (TPD) peak maxima at about 170, 250, 360, and 570 K respectively.¹⁾ Their participation in the H_2–D_2 exchange reaction was also examined;²⁾ only α and γ, were found to readily undergo surface exchange at low temperatures.

The present work has been carried out in order to obtain more information on the differences in the reactivities of the forms of chemisorbed hydrogen, and on the chemisorption and hydrogenation of propylene.

Experimental

Apparatus. The apparatus used for the present study was essentially the same as that used previously,²⁾ except for minor modifications. It consisted basically of two parts: an adsorption and reaction system, in which the adsorption and reaction were measured in a conventional manner, and a TPD system, in which adsorbed gas was later desorbed into a carrier-gas stream (N_2 or He) by means of the programmed heating of the catalyst. The concentration of the desorbed gas was measured and recorded by means of a thermal conductivity detector. When the ambient gas consisted of hydrocarbons, a gas chromatograph equipped with a thermal conductivity detector instead of a Pirani gauge was employed to estimate the pressure. A mercury manometer and a McLeod gauge were occasionally used to calibrate the detector, but they were then isolated from the reaction system by means of a stopcock to avoid the contamination of the catalyst by mercury vapor. An oil-diffusion pump behind the rotary oil pump was used for the evacuation of the system.

Materials. The catalyst used in the present investigation was a platinum black obtained from Wako Pure Chemical Industries, Ltd., it was pressed into tablets about 2-mm thick and 4 mm in diameter. Atomic absorption spectrophotometric analysis showed that the largest metallic impurity was Fe (130 ppm), followed by Rh (80 ppm) and Pd (20 ppm). The catalyst was first reduced in a hydrogen stream at atmospheric pressure for 35 h at 520 K, and then for 5 h at 720 K. Its surface area, as estimated by the BET method, was 3.2×10^3 cm^2/g.

Cylinder hydrogen (99.975%) supplied by the Osaka Hydrogen Co. was stored in a reservoir for use as a reactant after having been passed over platinized silica at 720 K and then through a liquid nitrogen trap. The same cylinder hydrogen could also be fed through to the reactor for the reduction of the catalyst. Matheson's deuterium (99.5%) passed through a liquid nitrogen trap was also used as a reactant. Propylene obtained from Takachiho Chemical Industry Co., Ltd., was purified by repeated distillation with liquid nitrogen traps; its gas chromatographic analysis indicated a purity of 99.9%. High-purity helium (99.995%) and high-purity nitrogen (99.999%), obtained from the Seitetsu Kagaku Co., Ltd., were used as carrier gases for TPD after having been passed through a molecular sieve trap cooled in liquid nitrogen.

Procedure. Before each run, the catalyst was treated with hydrogen for 4 h at 680 K and under atmospheric pressure, and then heated up to 820 K in the stream of carrier gas; all the hydrogen chemisorbed on the catalyst was removed by this desorption. The catalyst was then cooled to a selected temperature in the carrier gas, and the reactor was evacuated for 30 min, unless otherwise stated, using the oil-diffusion pump to remove the carrier gas. The catalyst activity fell at first, but became reasonably stable after about fifty runs. All the data reported here were obtained with the stabilized catalyst.

In a typical experiment on propylene, a known amount of propylene was adsorbed for 15 min at the experimental temperature. The reactor was then cooled to 238 K with the propylene present in the gas phase, and kept for 15 min. Following this, the carrier gas, helium, was diverted from the bypass into the reactor in order to remove the propylene in the gas phase, and then after 5 min, the catalyst was heated in a programmed manner. Before heating, hydrogen was sometimes admitted to react the adsorbed propylene after the helium had been removed by five minutes' evacuation. The reaction time in these cases was 30 min.

TPD chromatograms were obtained on the recorder chart and showed peaks due to the gas desorbed from the catalyst at different temperatures. A more detailed desorption of the TPD method has been given elsewhere.³⁾ The heating was stopped at about 800 K, after which the catalyst was kept in the helium stream for 20 min at the same temperature before cooling. Reproducible results were usually obtained by this procedure. When the results were not reproducible, however, the catalyst was treated with 20 to 30 kPa of oxygen for 1 h at about 770 K to oxidize any organic contamination, and was then again reduced by hydrogen as has been described above. This treatment improved the reproducibility considerably.

In the hydrogenation of propylene, various types of chemisorbed hydrogen were first prepared by the TPD technique described previously,¹,²⁾ and then propylene was admitted to

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the reaction system to start the reaction. Before the propylene was admitted, however, ten minutes' evacuation was done and the α-hydrogen weakly adsorbed on the surface was removed. Helium was added to dilute the propylene when the circulating pump in the reaction system was operated. After the reaction, all the system except for the reactor was evacuated through a liquid nitrogen trap to collect any condensable hydrocarbons, which were transferred to a sampler for analysis. The carrier gas was then diverted into the reactor, and any materials adsorbed on the catalyst were removed by TPD.

Analysis. The reactants, the reaction mixtures, and the desorption products were identified by gas chromatography. The deuterio-hydrocarbons obtained after the reaction were analyzed by means of a JEOL JMS D-100 mass spectrometer. Before subjecting the reaction mixture to mass-spectrometric analysis, they were separated gas chromatographically to avoid any mutual interference of the mass spectra.

Results and Discussion

Temperature-Programmed Desorption. Figure 1 shows some typical TPD chromatograms taken after the propylene had been adsorbed on the platinum black in the absence or presence of hydrogen as indicated, with helium used as the carrier gas. The pressure of the propylene or hydrogen admitted was 6.1×10^2 Pa, and the reaction temperature was 238 K. These four TPD chromatograms resemble each other, characteristically being composed of four peaks appearing at about 260, 380, 570, and higher than 720 K. These peaks are referred to as A, B, C, and D in the order of appearance with increase in the temperature. By gas chromatographic analysis, Peaks A and B were identified as the mixtures of propylene and propane, while Peaks C and D were methane. It is suggested that the propane was formed by the self-hydrogenation of chemisorbed propylene, where hydrogen was absent. The methane may be formed by decomposition from the chemisorbed propylene heated by TPD, as was previously suggested[4] for the ethylene-platinum system. In order to observe the desorbing hydrogen more clearly, nitrogen was used as the carrier gas for the TPD; only δ-hydrogen was observed in the TPD chromatogram. The other form of hydrogen may have been removed from the surface when propylene was admitted, probably by the displacement in the adsorption and/or in the surface hydrogenation to propane. On the surface, accordingly, only the admitted propylene along with δ-hydrogen was adsorbed in the form of propylene and/or propane. The results suggest that propylene is more strongly adsorbed on platinum than hydrogen.

It is not very clear at this stage whether the propane in the Peaks A and B, where hydrogen was present, is a result of the self-hydrogenation, or of the desorption of propane formed by hydrogenation, or both.

TABLE 1. HYDROGENATION OF PROPYLENE ON PLATINUM BLACK[a)]

Series	Surface reactant: Type of chemisorption and estimated amount[b)] (cm^3, STP)			Gas-phase reactant	
	β	γ	δ	Pressure of propylene (10^2 Pa)	Propane formed (cm^3, STP)
A	—	—	—	6.7	0.0022
B1	—	—	0.0358	6.5	0.0035
B2	—	—	0.0467	6.5	0.0046
C1	—	0.0383	0.0334	6.6	0.0314
C2	—	0.0383	0.0334	6.5	0.0296
D1	0.0078	0.0441	0.0332	6.5	0.0400
D2	0.0045	0.0246	0.0371	6.0	0.0196

a) Catalyst weight, 2.53 g. Reaction temp, 246 K, and reaction time, 20 min. b) Estimated from TPD chromatograms in comparable experiments.

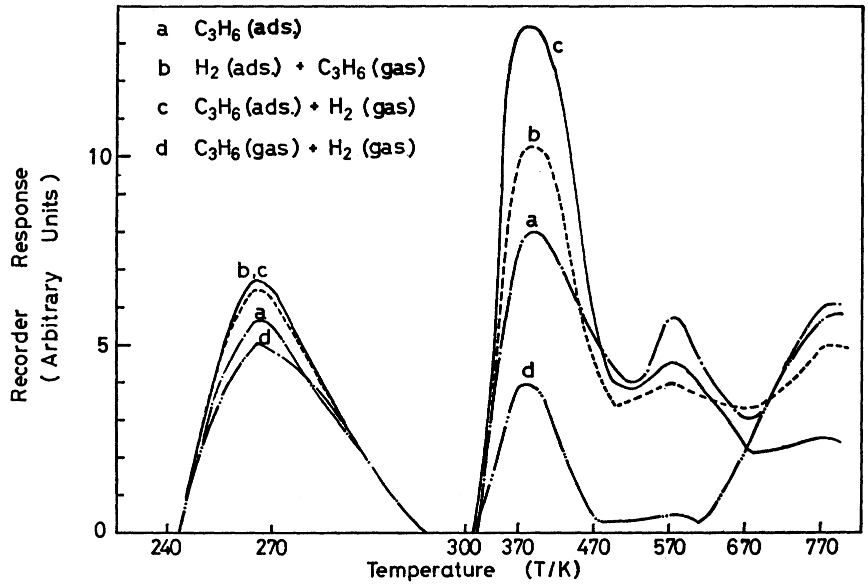

Fig. 1. TPD chromatograms of propylene on platinum. (a) C_3H_6 only was adsorbed. (b) H_2 was preadsorbed and C_3H_6 was subsequently admitted. (c) C_3H_6 was preadsorbed and H_2 was subsequently admitted. (d) C_3H_6 and H_2 were simultaneously admitted.

Table 2. Hydrogenation of propylene with labeled hydrogen chemisorbed on platinum[a)]

Type of surface used	Amounts of hydrogen preadsorbed[b)] (mm³, STP) β	γ	δ	Pressure of C_3H_6 (10^2 Pa)	Deuteriopropanes formed (mm³, STP) d_0	d_1	d_2	d_3	d_4
H-H-D	15.4	11.3	2.8	6.1	16.8	—	—	—	—
H-D-H	27.7	31.9	5.1	6.1	12.5	8.6	2.7	1.1	0.6
D-H-D	26.5	30.6	4.8	6.1	24.3	1.8	—	—	—
D-H-D	15.9	13.1	3.8	6.5	14.0	2.7	—	—	—
D-D-H	16.9	12.6	2.8	6.7	9.1	4.2	1.3	0.5	0.5

a) Catalyst weight, 1.80 g. Reaction temp, 238 K, and reaction time, 30 min. b) Estimated from TPD chromatograms in comparable experiments.

Reactivity of Chemisorbed Hydrogen. Table 1 shows the results of the surface hydrogenation experiments with hydrogen preadsorbed on the platinum black in various forms (the surface reactant), and with gaseous propylene subsequently admitted into the reaction system (the gas-phase reactant). The amounts of propane formed in Series B with δ-hydrogen agreed approximately with those in Series A, in which propane was formed by a self-hydrogenation reaction. Apparently, δ-hydrogen hardly reacts with the gas-phase reactant under the present experimental conditions.

In Series C, with δ- and γ-hydrogen preadsorbed on the surface, however, relatively larger amounts of propane were produced than in Series B. The amounts of propane formed agreed with those of the preadsorbed γ-hydrogen. In the TPD chromatogram obtained after propylene was admitted to the preadsorbed hydrogen, where nitrogen was used as the carrier gas, the γ-hydrogen disappeared, while δ-hydrogen was still present in almost the same amount. It is, therefore, clear that γ-hydrogen is involved in the hydrogenation.

In Series D, in which β-, γ-, and δ-hydrogen were preadsorbed, the amounts of propane formed were again in approximate agreement with those of γ-hydrogen, suggesting that only preadsorbed γ-hydrogen reacted. The contribution of β-hydrogen to the hydrogenation, however, could not be observed, because the amounts of preadsorbed β-hydrogen were much smaller than those of γ-hydrogen. It was, accordingly, not clear at this stage whether or not only γ-hydrogen participates in the hydrogenation.

To elucidate the point, the preadsorbed hydrogen was partially displaced by deuterium before propylene was introduced, and the deuteropropanes formed by hydrogenation were then analyzed. The participation of the different types of chemisorbed hydrogen was consequently elucidated. For the sake of simplicity, the word "hydrogen" in the present paper will hereafter stand for both isotopes, protium and deuterium, and, where necessary, the individual isotopes will be designated as H and D. The types of surface used were as follows: (1) δ-Hydrogen was displaced by deuterium, and γ- and β-hydrogen were protium (H–H–D); (2) δ- and β-hydrogen were deuterium, and γ-hydrogen was protium (D–H–D); (3) δ- and β-hydrogen were protium, and γ-hydrogen was deuterium (H–D–H); (4) δ-hydrogen was protium, and β- and γ-hydrogen were deuterium (D–D–H). The method of preparation was described previously;[5)] the isolation of different types of chemisorbed hydrogen was confirmed by separate TPD experiments.

Table 2 shows the results of hydrogenation: the amounts of hydrogen preadsorbed and those of the individual deuteriopropanes formed by the hydrogenation are shown. The reactions were carried out at 238 K for 30 min. In the mass spectra of propylene, the reactant, the $m/e > 42$ could not be observed, the ^{13}C contribution having been corrected.

Obviously, propylene is deuterated to deuteriopropane over the H–D–H, D–H–D, and D–D–H surface, but not over the H–H–D surface. These results agree quite well with the above suggestions that δ-hydrogen does not, and γ-hydrogen does, participate in the hydrogenation. The results also suggest the participation of β-hydrogen, which was not detected before. The total amount of deuteropropanes formed over the H–D–H surface was larger than that over the D–H–D surface under similar experimental conditions, and it seems that γ-hydrogen is more reactive than β-hydrogen. Over the D–D–H surface, propane-d_0 was formed, suggesting that the self-hydrogenation of propylene took place even when hydrogen was present.

On the mechanism of the hydrogenation of olefins, extensive studies have previously been reported.[6)] It is premature at present to discuss the matter on the basis of our results and to add further conclusions to other than those already reported.

It has previously been presumed that γ-hydrogen is present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms, and that β-hydrogen is molecular hydrogen chemisorbed in a bridge form.[1)] The difference in the reactivity may, accordingly, be due to the chemisorbed state, whether or not the H–H bond has been split. In the H_2–D_2 exchange reaction, β-hydrogen is not reactive, but it is reactive in the hydrogenation of propylene. It is, accordingly, probable that a different tendency would be shown depending upon the sort of reaction; the explication of the other reactions awaits further investigations.

The authors are grateful to Mr. Shizuo Fujisaki of this faculty for obtaining the mass spectra, and also to Professor Tatsuaki Yashima and Dr. Nobuo Takahashi of Tokyo Institute of Technology for the atomic absorption spectrophotometric analysis of the catalyst. The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, for which the authors' thanks are due.

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