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REACTIVITY OF HYDROGEN CHEMISORBED ON PLATINUM FOR HYDROGENATION OF PROPYLENE

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The three types of chemisorbed hydrogen (β, γ, and δ) on platinum detected by the temperature programmed desorption were found to exhibit the different reactivity for the hydrogenation of propylene; γ-hydrogen was more reactive than β-hydrogen, and δ-hydrogen was not involved in the hydrogenation.

The existence of four different chemisorbed species of hydrogen on platinum surface was detected by the temperature programmed desorption technique (TPD),[1)] and their participation in the H_2-D_2 exchange reaction was examined.[2)] In the present work, we investigated the hydrogenation of propylene over platinum to obtain further information on the difference in the reactivity of chemisorbed hydrogen. For simplicity, the word "hydrogen" in the present paper will stand for both isotopes, protium and deuterium, and where necessary, the individual isotopes will be designated as protium (or H) and deuterium (or D).

The apparatus used for the present study was essentially the same as used previously,[2)] except for minor modification: instead of a Pirani gauge, the ambient pressures of propane and propylene were estimated by means of gas chromatography with a thermal conductivity detector. The catalyst (1.80 g) used was tabletted platinum black, and was reduced in a hydrogen stream for 35 hr at atmospheric pressure at 520 K, and then for 5 hr at 720 K. Its surface area estimated by BET method was 3.2×10^3 cm^2/g. Before each run, the catalyst was treated with hydrogen for 4 hr at 720 K at atmospheric pressure, and heated up to 820 K in a stream of carrier gas (helium or nitrogen); all the hydrogen chemisorbed on the catalyst were removed by desorption. The catalyst was then cooled down to a selected temperature in the carrier gas which was not flowing, and evacuated for 30 min by means of an oil diffusion pump to remove the carrier gas.

In the hydrogenation of propylene three different types of surface, H-H-D, H-D-H and D-H-D, on which hydrogen was adsorbed, were first prepared. As was previously reported,1) isolation of the different forms of chemisorbed hydrogen on the surface was confirmed by separate TPD experiments up to 770 K on samples prepared in analogous manner. Propylene was then admitted to the reaction system to start the hydrogenation reaction, where the ambient pressure of propylene was ca. 6×10^2 Pa during the reaction. To prepare the surface H-H-D, deuterium was first introduced and adsorbed on the surface, and the deuterium in the gas phase was evacuated. β- and γ-deuterium preadsorbed were then desorbed by subsequent TPD, and the catalyst was cooled down to 238 K. After the removal of the carrier gas protium was admitted and adsorbed, where the amount of δ-protium additionally adsorbed was extremely small as was previously reported.2) To prepare the surface H-D-H (or D-H-D), protium (or deuterium) was first adsorbed at 238 K, and the hydrogen in the gas phase was evacuated. Deuterium (or protium) was then admitted at ca. 13×10^2 Pa, and the H_2-D_2 equilibration reaction proceeded. As was previously observed,2) only γ-protium (or deuterium) was soon equilibrated, and it could actually be displaced by deuterium (or protium) because the sufficiently large amount of deuterium (or protium) was admitted. γ-Protium (or deuterium) remaining was less than 1 % of γ-hydrogen adsorbed after 10 min. Before propylene was admitted ten minutes' evacuation was made, and hydrogen in the gas phase as well as α-hydrogen weakly adsorbed on the surface were removed. After the reaction the system except the reactor was evacuated through a liquid nitrogen trap, in which any condensable hydrocarbons were collected, and they were transferred to a sampler for analysis. The carrier gas was then diverted into the reactor, and materials adsorbed on the catalyst was removed by TPD.

The reactant, the reaction mixtures and the desorption products were identified by gas chromatography. Mass spectra of the deutero-hydrocarbons obtained were taken with a JEOL JMS D-100 mass spectrometer at I. V. = 10 V. Before mass spectrometric analysis the hydrocarbon mixtures were separated gas chromatographically to avoid mutual interference of mass spectra.

Table 1 shows the typical results of hydrogenation: the amounts of hydrogen preadsorbed and those of the individual deuteropropanes formed by the hydrogena-

Table 1. Hydrogenation of Propylene on Platinum[a]

Type of surface employed	Amounts of hydrogen preadsorbed (ml, STP)[b]			Pressure of C_3H_6 (Pa)	Deuteropropanes formed (ml, STP)				
	β	γ	δ		d_0	d_1	d_2	d_3	d_4
H-H-D	0.0154	0.0113	0.0028	6.1×10^2	0.0168	---	---	---	---
H-D-H	0.0277	0.0319	0.0051	6.1×10^2	0.0125	0.0086	0.0027	0.0011	0.0006
D-H-D	0.0265	0.0306	0.0048	6.1×10^2	0.0243	0.0018	---	---	---

[a] Catalyst weight 1.80 g. Reaction temp. 238 K and reaction time 30 min.

[b] Estimated from TPD chromatograms in comparable experiments.

tion are shown. The reactions were carried out at 238 K for 30 min. In the mass spectra of propylene, the m/e > 42 could not be observed, ^{13}C contribution being corrected. Obviously, δ-hydrogen preadsorbed does not react with propylene admitted, because only d_0-propane was obtained, when the surface H-H-D was employed. Over the surface H-D-H and D-H-D, on the other hand, deuteropropanes were formed, showing that β- and γ-hydrogen preadsorbed reacted with propylene to form propane. The total amount of deuteropropanes formed over the surface H-D-H was larger than that over the surface D-H-D under similar experimental conditions, and γ-hydrogen is suggestively more reactive than β-hydrogen.

It has previously$^{1)}$ 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. The difference in the reactivity may accordingly be due to the chemisorbed state, whether or not the H-H bond was split. In the H_2-D_2 exchange reaction, β-hydrogen is not reactive, but is reactive in the hydrogenation of propylene. It is accordingly probable that the different tendency would be showed depending upon the sorts of reactions, and the informations on the other reactions still certainly await further investigations.

It is conclusively showed that with use of isotopes the individual species chemisorbed on the surface at the same time can be dyed in isotopically different color, and that each reactivity is separately measurable.

The method employed in the present study is a new development of the TPD, and is applicable to the usual catalytic research with a catalyst of powder or particle form. The flash-filament desorption widely used in surface science, can be used only for a metal filament in high vacuum, and it is hardly possible to interrupt the heating sharply to leave on the surface particular adsorbed species for further investigation.3) Accordingly, the present method can be used with advantage, while the information on the reactivity of the chemisorbed species could perhaps be obtained otherwise.

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