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Selective Deactivation of Platinum Black Catalyst Caused by Retained 3-Methylpentane

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The deactivation of two platinum black samples caused by pulses of 3-methylpentane introduced into atmospheres with different hydrogen pressures was determined by relating yields obtained in subsequent pulses to those observed over freshly regenerated catalyst. The remaining catalytic activity could be related to the amount of hydrocarbon retained on the surface as determined by radiotracer studies. The selective deactivation for isomerization and C_5-cyclization as well as hydrogenolysis was interpreted in terms of multiple sites for these processes deactivated by their partial covering with carbonaceous residues formed in the first moment of reaction with hydrocarbons.

INTRODUCTION

The catalytic activity of platinum black is generally influenced by several factors. The reactions observed in the presence of different amounts of hydrogen may be very different (*1*, *2*). With low hydrogen pressures hydrocarbons gradually deactivate the catalyst (*3*). The platinum may be regenerated using air and/or hydrogen treatment (*4*, *5*); different treatments lead to different catalytic activities and selectivities (*6*).

Taylor *et al.* (*7*) and Reid *et al.* (*8*) have shown that the reactions of hydrocarbons over various metals are accompanied by their partial "retention" on the surface. It has been suggested (*9*) that the presence of carbonaceous species has a considerable influence on the catalyst activity and selectivity. It seemed to be reasonable to combine the study of the change of catalytic activity and selectivity of Pt during its contact with hydrocarbons with hydrocarbon retention studies under similar conditions in order to get a deeper insight into the behavior of the platinum–hydrogen–carbon catalytic system.

EXPERIMENTAL METHODS

Apparatus, Catalysts and Materials

Experiments were carried out in a pulse-microcatalytic system as described before (*10*). Radioactivity measurements were performed by using a proportional counter (*11*).

The catalyst was precipitated from H_2PtCl_6 with HCHO in KOH (*11*); two catalyst samples were used: more sintered, aged Pt(A) had a surface of 1.1 m^2/g, not quite fresh but still rather active Pt(B) 1.6 m^2/g (BET, N_2).

The nonradioactive 3-methylpentane was practically of 100% purity. The radioactive sample contained 1.05% isopentane and 1.0% 2-methylpentane as radiochemical impurities.[1]

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Procedure

The catalysts were regenerated by introducing 10 ml air into pure helium. Then the gas stream was switched over to pure hydrogen and after about 15 min a pulse of 3-methylpentane was introduced. This pulse was denoted by H-1.

After Pulse H-1, the catalyst was regenerated again as described above, but after the air pulse, the helium carrier gas was substituted by a gas stream containing $n\%$ of hydrogen admixed with helium ($n = 0$, 5, 20, 35%, respectively). The first pulse introduced into this gas mixture was denoted by n-I. Subsequently, the carrier gas containing $n\%$ of hydrogen was substituted again by pure hydrogen without any air treatment and a 3-methylpentane pulse was introduced (H-2). After Pulse H-2, the carrier gas was switched back to that containing $n\%$ H_2 and another pulse was introduced which was denoted by n-II. This was followed by further pulses, n-III, n-IV $\cdots n$-i, in some cases.

The remaining activity can be evaluated by comparing yields obtained in the second pulse to those observed over freshly regenerated catalysts. The above sequence of experiments allows one to define two quantities. The ratio,

$$Y_n = \frac{\text{yield}_{\text{H-2}}}{\text{yield}_{\text{H-1}}},$$

was taken as a measure characteristic of the remaining activity of the catalyst shown in pure hydrogen after one single pulse of 3-methylpentane introduced into a medium containing $n\%$ of hydrogen. In order to eliminate the effect of eventual long-term deactivation, the conversion in hydrogen was always determined before using various carrier gases and thus each series has its own H-1 reference value. The ratio,

$$Z_n = \frac{\text{yield}_{n\text{-II}}}{\text{yield}_{n\text{-I}}},$$

measures the remaining catalytic activity measured in carrier gases containing $n\%$ hydrogen, after a single pulse of 3-methylpentane. Special experiments have shown that the hydrogen carrier gas between n-I and n-II did not affect the catalytic activity to a noticeable extent.

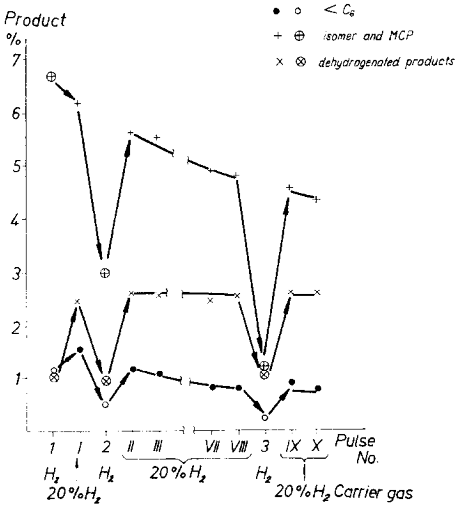

FIG. 1. A typical sequence of experiments applying pure hydrogen and 20% hydrogen + 80% helium mixture. Catalyst: 0.4 g Pt(A), $t = 360°C$.

RESULTS

Figure 1 shows a typical run with 20% H_2. It is striking that yields obtained in pure H_2 and those observed in 20% H_2 are more or less independent of each other. A slow deactivation is observed in 20% H_2, which is apparently not influenced by switching over hydrogen from time to time. On the other hand, a dramatic drop in activity was observed in pure hydrogen. The activity increases again by changing back to 20% H_2. The first pulse brought about the most abrupt change, further deactivation being slower.

Table 1 shows various yields and calculated Y_n and Z_n values for both catalysts ($n = 5$). It is seen that, in spite of the much higher activity of Pt(B), similar relative deactivation was observed for both catalysts. Therefore, further on, data for Pt(A) will be used for detailed evaluation.

TABLE 1

Yields of Various Products Observed over Two Types of Platinum Black in Different Atmospheres[a]

Catalyst	Characteristic value	Product			$\left(\frac{<C_6}{\text{Sat. } C_6}\right)$
		$<C_6$	Sat. C_6[b]	Unsat. C_6[c]	
Pt(A)	Yield (%)				
	in Pulse H-1	1.42	6.09	0.81	0.23
	n-I	1.31	2.05	4.00	0.64
	H-2	0.49	1.73	0.96	0.28
	n-II	1.03	1.39	3.89	0.74
	Ratio of yields				
	Y_n	0.35	0.28	1.18	
	Z_n	0.81	0.68	0.97	
Pt(B)	Yield (%)				
	in Pulse H-1	8.50	17.14	0.62	0.49
	n-I	5.86	3.67	3.68	1.60
	H-2	2.12	6.73	0.65	0.32
	n-II	4.26	2.35	3.15	1.81
	Ratio of yields				
	Y_n	0.25	0.39	1.04	
	Z_n	0.73	0.64	0.86	

[a] Catalyst, 0.4 g Pt; $t = 360°$; carrier gas: $n = 5\%$ H_2 (+95% He); 3 μl 3-methylpentane pulses.

[b] Hexane isomers + methylcyclopentane.

[c] 3-Methylpentene isomers + 1-methylcyclopentene + benzene.

Data on remaining activity (as characterized by Y_n and Z_n values) obtained in different carrier gases are summarized in Table 2. The activity loss depended on the hydrogen content of the carrier gas: as judged from Y_n values, it could reach 97% in helium, but even in 35% hydrogen, only about one half of the original activity remained. On the other hand, Z_n data indicate that deactivation is considerable only in helium, but even in this case, the Z_0 value is higher than Y_0. All these data show that different types of reaction are not equally sensitive to deactivation. The yields of saturated C_6 products drop most rapidly in the course of deactivation; hydrogenolysis was less affected and the yield of unsaturated products even increased in some cases.

In order to make the study more quantitative, pulses of radioactive 3-methylpentane have been introduced onto both catalysts. Calculation of a material balance was attempted from the amount of radioactivity introduced, the total radioactivity of the catalysate and the amount of radio-

TABLE 2

Y_n and Z_n Values Measured for Various Products Formed on Platinum Black with Different Carrier Gas Compositions[a]

Ratio of yields	*n*, % hydrogen in the carrier gas	Product		
		$<C_6$	Sat. C_6[b]	Unsat. C_6[c]
Y_n	0	0.054	0.03	0.28
	5	0.35	0.28	1.18
	20	0.44	0.42	0.92
	35	0.37	0.49	0.95
	100[d]	0.94	0.87	0.99
Z_n	0	0.30	0.25	0.68
	5	0.81	0.68	0.97
	20	0.74	0.90	1.06
	35	1.00	0.93	1.08

[a] Catalyst: 0.4 g Pt(A); $t = 360$; 3 μl 3-methylpentane pulses.

[b] Hexane isomers + methylcyclopentane.

[c] 3-Methylpentene + 1-methylcyclopentene + benzene.

[d] In this case "*n*-I" (i.e., the second pulse) was also introduced into pure H_2.

TABLE 3

Material Balance of Radioactive 3-Methylpentane Pulses Introduced into Different Atmospheres

Catalyst:	Pt(A)		Pt(B)	
Carrier gas:	He	5% H_2	He	5% H_2
Input: 3 μl 3 MP (counts)	36,900 ± 200			
Output: 3 MP (plus impur.)	33,870	31,890	31,760	31,800
Products	1320	3960	3790	4540
Total catalysate	35,190	35,850	35,550	36,340
Swept off by air	1350	330	1580	350
Total output	36,490	36,180	37,130	36,690
Surface atoms, 10^{15}	3630		5280	
Input, 10^{15} molecules	13,800			
Product, 10^{15} molecules	518	1524	1471	1724
Retained, 10^{15} molecules	468	123.6	591	131
Percentage of surface atoms blocked by retained species:				
One C_6 species/(Pt-atom)	12.9	3.40	11.2	2.48
One C_1 species/(Pt-atom)	77.4	20.4	68.4	14.9

activity swept off from the platinum by means of a pulse of regenerating air after the hydrocarbon pulse. It was checked that a second air pulse brought off no more radioactivity from the catalyst. Data in Table 3 show that, taking into account the statistical and other errors, a surprisingly good material balance was obtained.

Table 3 shows that the retained amount from a single pulse depends on the amount of hydrogen present in the carrier gas. With 35% H_2 and even more with pure H_2, the amount of radioactivity removed with the regenerating air pulse was near to the background variations and could not be evaluated.

By using the value of Boudart *et al.* (*13*) for the number of surface platinum atoms, the fraction of the surface covered by retained molecules was also calculated. Table 3 contains two hypothetical values which can be regarded as probable limiting cases: one C_6 species per surface atom may be assumed as the lower limit, whereas the assumption of one C-atom per surface platinum atom (with or without dissociation of the initial C_6-species) can be taken as an upper limit of coverage. Both values shown in Table 3 are comparable with the total platinum surface.

DISCUSSION

The most striking observation of this study is the different deactivation of the catalysts measured in different atmospheres in addition to the different selectivity observed earlier (*1–3*). It was proposed by the authors that hydrogen (as an astoichiometric component) generates active centers for C_5-cyclization and isomerization (*2*); at the same time, however, its active participation in C_5-ring closure (similarly to ring opening) as suggested by Liberman (*14*) cannot be excluded. On the other hand, Rooney and Clarke (*9*) emphasized the role of "carbonization" in determining the selectivity of platinum catalysts.

We may assume that the first hydrocarbon pulse after air regeneration meets the metal in a "clean" state where a certain hydrogen coverage corresponding to the temperature and the given hydrogen pressure is established. In helium, since only "retained" hydrogen is present (*15*), a rapid deactivation takes place (Table 2), but on the basis of the slow activity change in the presence of hydrogen (e.g., Fig. 1) it may be assumed that the catalytic activity is characteristic of the given hydrogen-containing atmosphere for a fairly long period [which can last for several minutes as shown by other experiments carried out in a circulation apparatus (*16*)].

Changing the hydrogen pressure reveals, however, that behind this there lies a considerable "hidden" deactivation of the catalyst which manifests itself at higher hydrogen pressure only. This must be caused by "retention" of some hydrocarbons by the catalyst. The presence of such species was directly verified by our radiotracer experiments both in helium and in hydrogen (Table 3).

The "retention" process presumably takes place during the first fractions of seconds of the contact of hydrocarbon with the metal. As a result, a "carbon pool" is formed on the surface [similarly to the "hydrogen pool" suggested earlier (*17*)]. The activity level of the catalyst shown in *n*% hydrogen corresponds to a given hydrogen *and* a given carbon coverage. The latter is formed in a kind of a displacement process of hydrogen by retained carbon-rich hydrocarbons. Obviously, the amount of displaceable hydrogen (and the amount of primary retained species) is controlled by the hydrogen pressure in the system. Further hydrocarbon pulses increase the carbonization only slowly, in a process obviously different from primary retention (*17*). Although for the time being we have no evidence to attribute any definite stoichiometry or structure to retained carbonaceous species, by comparing data in Tables 1 and 2 with the size of "free" surface as judged on the basis of radiotracer experiments it is seen that Z_n values are in very good agreement with the percentage of unblocked surface estimated on the basis of one C-atom per surface platinum atom (last row of Table 3). These data give a direct correlation between catalytic activity and the amount of retained species.

The much lower Y_n values can be interpreted in the following way. Hydrogen at higher pressures practically cannot remove retained species (*17*) but competes with gaseous hydrocarbons for the "free" (catalytically active) surface sites (*1, 3, 18*); therefore, the catalyst exhibits much less activity in pure hydrogen than expected on the basis of experiments carried out using lower hydrogen pressures.

The more rapid decrease of the yields of hydrogenolysis and saturated C_6-products as compared with dehydrogenation means that the surface sites for these reactions are either different or that the same sites show a different activity under different conditions.

The first possibility corresponds to the suggestion of Anderson and Shimoyama (*19*) proposing edges or corners as active sites for C_5-cyclic isomerization. The selective deactivation of platinum in the reactions of ethylene has also been previously interpreted tentatively in terms of the existence of different type of sites (*17*). With selectively poisoned edges and corners, however, the increase of the catalytic activity in Pulse *n*-II after a low value in H-2 (cf. Fig. 1) could hardly be possible.

We suggest, instead, that for hydrogenolysis and cyclization–isomerization sites are just geometric combinations (perhaps anywhere on the surface). The blocking of only one part of such combined sites by carbon and/or hydrogen would stop these reactions, at the same time when dehydrogenation could still proceed at the adjacent "free" fraction of the ensembles. This corresponds to the mechanistic suggestion for hydrogenolysis involving multiply bonded species (*20*) and is in agreement with our recent suggestion that C_5-cyclization (and the opening of the C_5-ring) occurs on particular "dual sites," keeping the C_5-cyclic structure (to be formed or destroyed) parallel to the surface (*18*).

The close Y_n and Z_n values for Pt(A) and Pt(B) are in favor of our suggestion and so is the fact that the initial selectivity (determined by the nature of the catalyst sample and the hydrogen pressure) is only slightly affected by accumulation of retained species (Table 1).

Our data underline the importance of carbonaceous species in determining the catalytic activity and selectivity [cf. (*9*)]. Although the role of hydrogen may be more indirect than suggested earlier, its two aspects should be stressed here, namely, its ability to govern surface hydrocarbon retention and its competition for the remaining "free" surface sites; the first effect is an irreversible factor and the second a reversible one determining catalytic activity in a given moment.

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