PETROLEUM AND GAS PROCESSING

THE CHANGE IN THE PROPERTIES OF PLATINUM-ALUMINA REFORMING CATALYST DURING PROLONGED USE

(UDC 665.534)

G. N. Maslyanskii, N. R. Bursian, and V. V. Shipikin

All-Union Scientific Research Institute of Petrochemistry
Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 1,
pp. 2-6, January, 1965

Platinum-alumina catalysts can be successfully used in reforming processes over long periods of time. According to the literature, the length of service of platinum-alumina catalysts may reach 2.5 years [1, 2].

However, gradual deterioration of the catalytic properties of a platinum-alumina catalyst is observed over the course of the operation—activity decreases and selectivity is impaired.

The change in activity and selectivity may be caused both by deposition of coke on the catalyst surface and by a change in the physicochemical properties of the catalyst under the influence of impurities present in the feed, and also as a result of the high temperatures. Recovery of the activity and selectivity of the catalyst is obtained by periodic oxidative regeneration. However, oxidative regeneration leads to a recovery of catalytic properties only when the change was due to coking of the catalyst.

The aim of the present work was to investigate platinum-alumina catalysts after prolonged use in a reforming process and to establish the effect of length of use of the catalyst on its physicochemical and catalytic properties.

Samples of catalysts described below were used in the work.

Sample 1. Platinum-alumina catalyst unloaded from reactors of a semiworks catalytic reforming plant. The catalyst had been operated under reforming conditions for 15,000 h. During this time, 35 m^3 of feedstock per kg of catalyst was fed [3].

Sample 2. Platinum-alumina catalyst recovered from the reactors of a catalytic reforming pilot plant.

Sample 3. Platinum-alumina catalyst recovered from the reactors of a commercial catalytic reforming plant. The catalyst had been in use for about 7500 h.

For purposes of comparison, Table 1 presents data on the physicochemical properties of the fresh and used catalysts, which were taken from reactors 1, 2, and 3 numbered in a downstream direction.

In order to exclude the effect of coke on catalyst activity, all samples were subjected to oxidative regeneration prior to testing. Catalytic activity and selectivity tests were conducted in a small-scale apparatus under hydrogen pressure [4]. The feedstock was an 85-180°C gasoline fraction from Romashkin crude, and was hydrotreated prior to use in the tests. Characteristics of the fraction are presented below.

Specific gravity, ρ_4^{20} 0.746
Composition by fractions, °C:
    ibp 110
    10% 116
    50% 132
    90% 162
    ep 182
Hydrocarbon composition, wt. %
    aromatic 11.3
    naphthenic. 27.2
    paraffinic 61.5
Sulfur content, wt. % 0.001
Octane number (motor method). 37.0

TABLE 1. Characteristics of Platinum-Alumina Catalysts

Property	Fresh	Sample 1			Sample 2			Sample 3		
		1	2	3	1	2	3	1	2	3
Bulk density, kg/liter	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61
Pellet dimensions, mm	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0	2.6 × 4.0
Content in catalyst, wt. %										
platinum	0.58	0.58	0.57	0.61	0.57	0.57	0.59	0.58	0.58	0.57
fluorine	0.36	0.06	0.04	0.09	0.05	0.23	0.25	0.25	—	—
chlorine	0.58	0.57	0.03	0	0.1	0	0	—	—	—
silicon	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Metal impurities, wt. %										
iron	0.01	1.0	0.17	0.14	0.53	0.09	0.06	0.24	0.17	0.058
sodium	0.012	0.4	0.2	0.21	—	0.10	0.016	0.05	0.03	0.03
copper	0.0002	0.015	—	—	0.015	0.015	0.002	0.0035	0.0005	0.0007
tin	0.0025	0.008	—	—	0.0025	0.0025	0.002	0.010	0.005	0.005
calcium	0.0015	0.007	—	—	0.009	0.009	0.0015	0.015	0.015	0.015
vanadium	0	0.009	—	—	0	0	0	0	0	0
bismuth	0	0.015	—	—	0.06	0.06	0	0	0	0
chromium	0	0.025	—	—	0.01	0.01	0	0.03	0.015	0.005
lead	0	0.100	—	—	0.05	0.05	0.0015	0	0	0
manganese	0.0001	0.002	—	—	0.002	0.002	0.00015	0.004	0.0015	0.001
magnesium	0.005	0.008	—	—	0.008	0.008	0.002	0.07	0.02	0.015
Surface area, m²/g (by benzene adsorption)	120	83	—	—	—	—	—	—	—	—

Note: Contents of metal impurities, with the exception of iron and sodium contents, were determined semiquantitatively by spectroscopy. The determinations were carried out by Ya. É. Shmulyakovskii.

In addition, reactions involving individual hydrocarbons were employed to compare the catalytic properties of fresh and used catalysts [5, 6]. Cyclohexane and n-pentane with the following constants were used in these experiments:

	Cyclohexane	n-Pentane
Boiling point, °C	80.5	36.5
Density, ρ_4^{20}	0.7780	0.6262
Index of refraction, n_D^{20}	1.4262	1.3577

It follows from the data presented in Table 1 that platinum content was practically the same in the fresh and used catalysts.

On the other hand, significant changes in halogen contents occurred during prolonged use of the catalysts: the fluorine content changed from 0.36 to 0.04-0.25%, and the chlorine content from 0.58 to 0.1-0.07%.

The content of metal impurities was significantly higher in the used catalysts. It should be pointed out that impurities in the catalysts were distributed nonuniformly among the reactors. The greatest amount of impurities was concentrated in the catalysts from 1, the upstream reactor.

The sharpest change was in iron content. Thus, the iron content of the catalyst taken from reactors of the semiworks plants after 15,000 h use was higher than that of the fresh catalyst by a factor of 100 in reactor 1, 17 in reactor 2, and 14 in reactor 3.
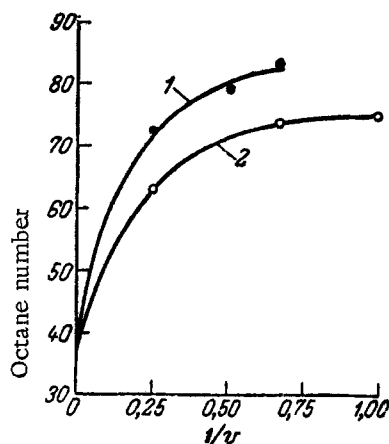
Fig. 1. Effect of feed space rate on anti-
knock properties of reformed gasoline.
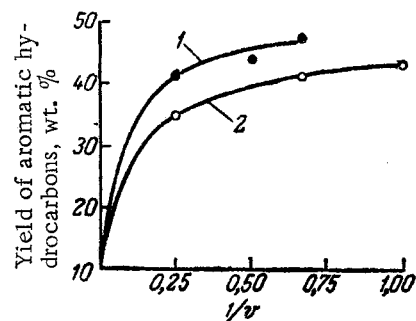Platinum-alumina catalyst: 1) fresh; 2) used.

Fig. 2. Effect of speed space rate on yield
of aromatic hydrocarbons (notation same as
in Fig. 1).

Moreover, accumulation of other metal impurities, particularly sodium, copper, and lead, also occurred, the contents significantly exceeding those in the fresh catalyst.

Prolonged use of the catalysts in catalytic reforming caused changes not only in chemical composition, but also in the physical properties of the catalysts. For example, the surface area of the catalyst obtained from reactor 1 of the semiworks catalytic reforming plant decreased from 120 to 83 m^2/g.

Further investigations employed the catalyst taken from reactor 1 of the semiworks catalytic reforming plant (Sample 1), since the physicochemical properties of this sample had undergone the greatest change.

Several experiments were carried out with each sample of the catalyst. The experiments were carried out at space rates (V) of from 1 to 4 h^{-1}, a temperature of 500°C, a pressure of 40 atm, and a circulation rate of hydrogen-containing gas of 1500 liters per liter of feed. The results obtained were employed to construct kinetic curves showing the dependence of change in octane number of the gasoline and of yield of aromatic hydrocarbons on the reciprocal of the space rate.

It is clear from Figs. 1 and 2, that the activity of the fresh catalyst decreased by a factor of 2-3 during prolonged use in the reforming process. The decreased activity of the used catalyst was reflected both in the change in octane numbers of the reformed gasolines and in the decrease in the yields of aromatic hydrocarbons.

The most important characteristic of platinum-alumina catalysts is their selectivity in the reforming process.
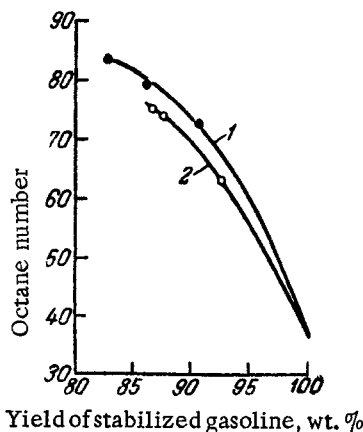

Yield of stabilized gasoline, wt. %

Fig. 3. Change in octane number of re-
formed gasolines as a function of yield
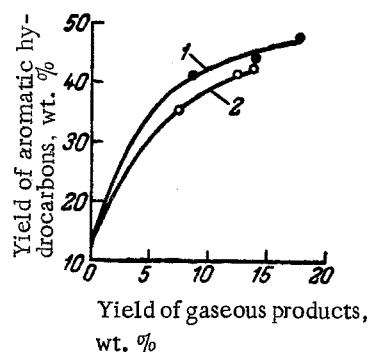(notation same as in Fig. 1).

Yield of gaseous products,
wt. %

Fig. 4. Change in yield of aromatic hydro-
carbons as a function of yield of gaseous prod-
ucts (notation same as in Fig. 1).

4

TABLE 2. Dehydrogenation Activity Tests on Platinum-Alumina Catalysts. Conditions: 470°C, 40 atm, inert gas circulation 40 liters per liter of catalyst, cyclohexane feed.

Expt. conds.			Composition, wt. %					
space rate, h^{-1}	mol. ratio hydrogen : cyclohexane	Refractive index of catalyzate, n_D^{20}	benzene	cyclohexane	methylcyclopentane	heptane	hexane	other hydrocarbons
Fresh catalyst								
63	8.9	1.4950	55.3	40.5	1.6	0.4	0.4	1.8
81	10.0	1.4568	53.9	43.7	1.1	0.4	0.2	0.7
121	9.0	1.4508	43.7	53.9	0.8	0.5	0.2	0.9
Used catalyst (Sample 1)								
53	10.2	1.4594	52.6	45.8	0.7	0.4	0.2	0.3
80	11.5	1.4512	44.6	54.3	0.5	0.3	0.2	0.1
114	12.0	1.4473	38.0	61.3	0.4	0.1	0.2	trace

TABLE 3. Isomerization Activity Tests on Platinum-Alumina Catalysts (Experimental conditions: 450°C, 40 atm, $V = 1.0$ h^{-1}, mol. ratio hydrogen:feed = 3:1, n-pentane feed)

Catalyzate composition, wt. %	Catalyst	
	fresh	used
$C_1 - C_4$	5.0	0.3
Isopentane	42.2	6.8
n-Pentane	52.8	92.9
Cyclohexane.	—	trace

Fig. 5. Effect of feed space rate on conversion of cyclohexane to benzene (notation same as in Fig. 1.)

Figure 3 shows the relationship between the octane number of the reformed gasoline and yield. The selectivity of the used catalyst was significantly below that of the fresh catalyst. The difference in yield of gasoline of the same octane number, Δ, from the fresh and used catalyst was:

Octane number	Δ, %
70	2.0
75	2.5
80	3.5

The difference in yield increased with an increase in the extent of reaction; i.e., the selectivity of the used catalyst deteriorated with an increase in the severity of the process conditions.

The decrease in catalyst selectivity is also confirmed by the data presented in Fig. 4.

Model reactions were used to evaluate the change in catalytic properties of platinum-alumina catalysts as a result of prolonged use.

The dehydrogenating ability of the catalyst, which is due to the platinum component, was characterized by dehydrogenation of cyclohexane.

The isomerizing activity of the catalyst, which is associated with acidity of the support (aluminum oxide promoted with halide), was measured by isomerization of n-pentane.
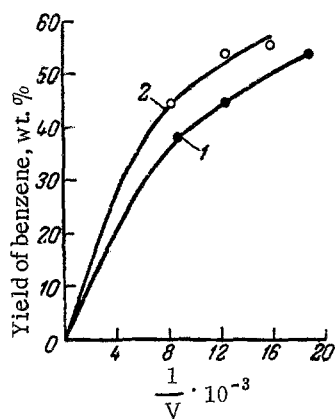
The results of tests of the catalysts in dehydrogenation of cyclohexane show that dehydrogenation activity of the used catalyst was approximately 1.5 times lower than that of the fresh catalyst (Fig. 5 and Table 2).

The results of isomerization activity tests on the fresh and used catalysts show that the isomerization properties of the catalyst deteriorate sharply over a prolonged period of use (Table 3). While the isopentane yield over the fresh catalyst was 42.2 wt. % under the conditions employed, that over the used catalyst was only 6.8%.

Our study of platinum-alumina catalysts taken from reactors of the catalytic reforming unit showed that prolonged use results in substantial changes in the physiochemical properties of catalysts: The content of metal impurities is increased, and the halide content is decreased.

Gasoline fractions charged to catalytic reforming units contain various impurities including metal impurities. When the reforming process does not include preliminary hydrotreating of the feed, the catalyst in the upstream reactor, reactor 1, accumulates the major portion of the impurities contained in the feed. Moreover, hydrogen sulfide corrosion of the apparatus and furnace coils occurs, and a significant portion of the corrosion products is carried to the reactor and deposited on the catalyst. Thus, the increase in the amounts of metal impurities in used catalysts is explained by the presence of metal impurities in the feed and by apparatus corrosion.

As indicated above, a sharp increase in sodium content was observed in catalysts obtained from the semiworks and pilot plants. At the same time, this increase was not observed in the catalyst obtained from the commercial plant. This circumstance is explained by the fact that in the semiworks and pilot plants removal of hydrogen sulfide from the circulating hydrogen-containing gas was accomplished by caustic solution. Entrainment of caustic from the wash column apparently explains the sharp increase in sodium content.

The sharp decrease in halide content of the catalysts is explained by the action of moisture contained in the feed and the circulating gas.

During prolonged use of the platinum-alumina catalyst there were significant changes in its dehydrogenation and isomerization activities. As was established in the experiments with cyclohexane, the dehydrogenation activity of the used catalyst was lower than that of the fresh catalyst by a factor of approximately 1.5. This is explained by a change in the state of the platinum in the catalyst; the amount of platinum in the used catalyst was unchanged from that in the fresh catalyst. The change in the state of the platinum could have been caused both by crystal growth [7] and by interaction of the platinum with iron and other metal impurities.

The sharp decrease in the isomerization activity of the catalyst is explained by a decrease in acidity owing to the significant increase in sodium content of the catalyst and by a decrease in the halide content [8-11]. However, a similar change in isomerization activity is not a characteristic of platinum-alumina catalysts used in commercial installations, since in this case the catalyst is not contaminated with large amounts of sodium.

Thus, the decrease in activity of platinum-alumina reforming catalysts during prolonged use is caused both by a change in the state of the platinum and by a change in the physicochemical properties of the support.

CONCLUSIONS

1. During the course of prolonged use of platinum-alumina reforming catalysts there are substantial changes in physicochemical properties of the catalyst. Thus, there is a significant increase in the content of metal impurities in the catalyst (particularly iron), a decrease in the halide content (fluorine and chlorine), and a decrease in the surface area of the catalyst.

2. The changes in physicochemical properties of the catalyst lead to a decrease in the dehydrogenation and isomerization activities of the catalyst. Activity and selectivity deteriorate simultaneously during the reforming process.

LITERATURE CITED

1. M. Sittig and W. Warren, Production of High-Octane Fuels [Russian translation], Gostoptekhizdat (1957).
2. Catalysis in the Petrochemical and Petroleum Refining Industries [in Russian], 2, Gostoptekhizdat (1961), pp. 600, 603.
3. G. N. Maslyanskii, N. R. Bursian, N. P. Mel'nikova, M. A. Podol'skii, and A. P. Fedorov, Khim. i tekhnol. topliv i masel, No. 2 (1962).
4. N. R. Bursian and G. N. Maslyanskii, Khim. i tekhnol. topliv i masel, No. 3 (1962).
5. A. A. Potapova, ZhOKh, 29, No. 2 (1959), p. 421.
6. N. R. Bursian and G. N. Maslyanskii, Khim. prom., No. 3 (1961).
7. US Patent 2,916,440 (1959).
8. A. Oblad, J. Messenger, and N. Brown, Ind. Eng. Chem., 39 (1947), p. 146.
9. G. Mills, H. Heinemann, T. Milliken, and A. Oblad, Ind. Eng. Chem., 45 (1953), p. 134.
10. P. B. Weiss and E. W. Swegler, Science, 126 (1957), p. 31.
11. G. N. Maslyanskii, N. P. Bursian, S. A. Barkan, V. A. Kobelev, and V. G. Telegin, Izv. vuzov, Ser.: Khim i khim. tekhnologiya, 3, No. 2 (1960), p. 359.