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Regulation of the Chlorine Content on Pt/Al_2O_3 Catalyst

The catalytic properties of the Pt/Al_2O_3 catalyst used in naphtha reforming depend both on the characteristics of the metal and on the acidity of the Al_2O_3 support. Besides, a correct balance of the metallic and acidic functions must be kept during the process (*1*) in order to optimize its performance. The metallic function can be modified by means of the deposition technique and by thermal treatments, while the acidity can be modified by the incorporation of halogens (*2*).

During the preparation of the catalyst, chlorine is incorporated to the support in the impregnation step. It comes from the chloroplatinic acid and from the hydrochloric acid used to control the metal deposition. But in the following calcination and reduction steps, part of this chlorine is lost. Moreover, it is not possible to achieve simultaneously high metal dispersions and the desired final acidity level through the amount of HCl added during the impregnation. This shows the need of an adjustment of the chlorine content during the thermal treatments. The water present in the naphtha feed removes chlorine from the catalyst but it can be restored by the addition of chlorinated compounds to the feed. Therefore it is possible to regulate or to control the chlorine content of the catalyst through the simultaneous presence of water and chlorinated compounds, such as HCl, in the gases used in the thermal treatments during the catalyst preparation. This technique is quoted in several patents. (*3, 4*).

Owing to the importance that the chlorine content has on the catalyst performance in the reforming process, the control of this content during the preparation of the catalyst was studied in this paper. The regulation of the chlorine content was carried out in the calcination step by passing a vaporized mixture of HCl and H_2O in the air stream. Besides, in order to ascertain whether or not the metal plays a role in the chlorine regulation, studies were also made on the Al_2O_3 support.

EXPERIMENTAL

A commercial γ-Al_2O_3 (Cyanamid Ketjen CK-300) was used as a support; this material was calcined before use at 650°C in a stream of dry air.

The Pt/Al_2O_3 samples were obtained by impregnating 10 g support with 14 ml of an aqueous solution of HCl and H_2PtCl_6. The HCl and H_2PtCl_6 concentrations in the solution were 0.6 and 0.0142 mol/liter, respectively, obtaining samples with 0.38% Pt. The support was left for 6 h at 30°C in the impregnating solution and then the samples were drained off and dried for 12 h at 120°C. Then, they were heated in air from room temperature to the temperature at which the control of the chlorine content was carried out. At this temperature the chlorine concentration on the sample was fixed passing 1800 ml/h g of a gaseous mixture of HCl–water–air obtained by vaporizing a HCl aqueous solution in an air stream. Then the samples were purged with passage of a dry N_2 stream at 600 ml/h g during 30 min and finally reduced with flowing hydrogen at 600 ml/h g for 6 h, at the same temperature.

The experiments were carried out in an apparatus which has gaseous feed lines, a syringe pump for injection of the HCl–H_2O solution, a vaporizer, a reactor inside an oven, and a sampling device downstream of the reactor. The evolution of chlorine content on the samples during the different

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treatments was calculated from the chlorine content of the effluent and the mass balance.

All these studies were performed at atmospheric pressure and four temperatures: 400, 450, 500, and 550°C, using molar ratios H_2O/HCl, R, between 10 and 200, and HCl concentrations in air from 80 to 550 ppm. Other experiments with dry air and with wet air (4700 ppm H_2O) were carried out.

Ten-gram aliquots of the Al_2O_3 support were impregnated with 14 ml of a solution containing 0.6 mol/liter of HCl. The remaining treatments and conditions were equal to those used for the Pt/Al_2O_3 samples, but without the reduction with hydrogen.

Pt was determined by photocolorimetry and the metallic dispersion by the method of Benson and Boudart (*5*). Specific surface areas were measured by the BET method and pore volumes by the Hg–H_2O pycnometer. Chlorine in the reactor effluent was analyzed by adsorbing the gas in a NaOH solution, 0.1 mol/liter, and titrating it with $AgNO_3$. The chlorine content in the solid samples was determined by attacking them with H_2SO_4 and titrating the HCl.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of chlorine on Pt/Al_2O_3 samples during the calcination and reduction steps at 500°C. The results show a strong influence of the molar ratios R, while the HCl concentration does not play an important role. Besides, it can be seen that the chlorine concentration on the sample is stabilized at around 4 h from the beginning of the regulation step. This was confirmed by longer experiments; the differences were within the range of experimental error. Therefore it may be concluded that the chlorine content at 4 h of regulation corresponds to the equilibrium value, C^*_{Cl}.

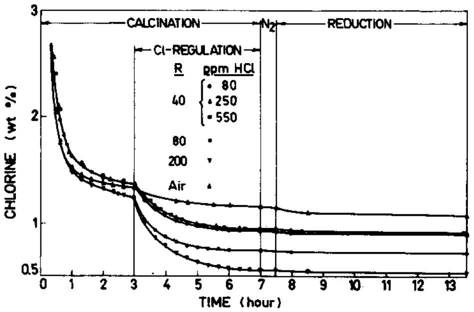


FIG. 1. Chlorine content as a function of time during treatment of Pt/Al_2O_3 samples. Zero- to one-hour heating step from room temperature to 500°C; then, isothermal treatments at 500°C.

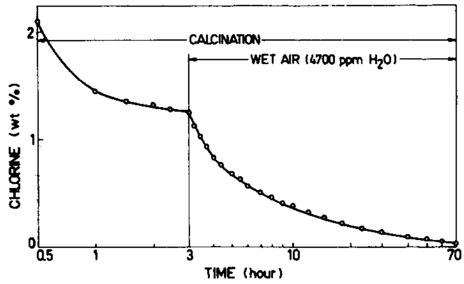
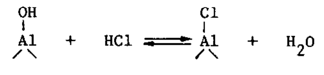


FIG. 2. Chlorine content as a function of time during the calcination of Pt/Al_2O_3 samples in wet air (4700 ppm H_2O), 500°C.

In order to find out whether it was possible to completely eliminate the chlorine of the samples, an experiment was carried out using air with water (4700 ppm). The results are shown in Fig. 2. They suggest that the total removal of chlorine is feasible, although the removal rate slowed down as the chlorine content decreased.

Table 1 shows the chlorine content at the end of the regulation step, for Pt/Al_2O_3 samples at temperatures between 400 and 550°C and different molar ratios H_2O/HCl. Experiments in which dry air was used are also included. Table 2 shows the results obtained for Al_2O_3 samples at 500°C.

The acidity of alumina can be promoted by means of different types of chlorinated compounds, organic or inorganic (*1*, *6–8*). When HCl is used, its interaction with the Al_2O_3 surface can be pictured as follows (*7*):



$$\underset{\wedge}{\overset{\overset{OH}{|}}{Al}} + HCl \rightleftharpoons \underset{\wedge}{\overset{\overset{Cl}{|}}{Al}} + H_2O \qquad (1)$$

TABLE 1

Equilibrium Chlorine Concentration on Pt/Al_2O_3

Expt. No.	Temp. (°C)	$\frac{\text{moles } H_2O}{\text{moles HCl}}$	C^*_{Cl} (wt%)	Expt. No.	Temp. (°C)	$\frac{\text{moles } H_2O}{\text{moles HCl}}$	C^*_{Cl} (wt%)
1	400	Air	1.37	17	500	40	0.93
2	400	20	1.38	18	500	40	0.97
3	400	60	1.22	19	500	40	0.94
4	400	60	1.29	20	500	60	0.89
5	400	120	1.16	21	500	60	0.87
6	400	200	0.94	22	500	60	0.82
7	450	20	1.15	23	500	80	0.69
8	450	60	1.06	24	500	80	0.75
9	450	200	0.78	25	500	80	0.74
10	500	Air	1.12	26	500	120	0.73
11	500	Air	1.06	27	500	120	0.63
12	500	Air	1.15	28	500	200	0.54
13	500	10	1.04	29	550	Air	0.92
14	500	40	0.96	30	550	40	0.75
15	500	40	0.98	31	550	80	0.51
16	500	40	0.97	32	550	200	0.40

Due to the low Pt concentration, the metal covers less than 1% of the Al_2O_3 surface (*9*). Thus, it is possible to suppose that its presence does not interfere with the equilibrium chlorine of the support. Therefore the treatment of Al_2O_3 or Pt/Al_2O_3 with streams which simultaneously contain HCl and H_2O would allow the regulation of the chlorine content as reaction 1 shows.

The dehydration degree of γ-Al_2O_3, and therefore the density of surface OH groups, depends on the thermal treatment (*6*, *10*).

TABLE 2

Equilibrium Chlorine Concentration on Al_2O_3 at 500°C

Expt. No.	$\frac{\text{moles } H_2O}{\text{moles HCl}}$	C^*_{Cl} (wt%)
1	Air	0.95
2	Air	0.97
3	20	0.92
4	60	0.84
5	60	0.83
6	60	0.85
7	120	0.71
8	200	0.54
9	200	0.56

The equilibrium chlorine concentration on alumina in reaction 1 will be given by

$$C^*_{Cl} = KL(1/R)/(1 + K(1/R)), \quad (2)$$

where R is the partial pressure ratio or molar ratio H_2O/HCl, K is the reaction equilibrium constant, and L the sum of the surface concentrations of OH and Cl, considered as constant. Equation 2 indicates that the equilibrium chlorine concentration depends on the ratio and not on the absolute concentrations, as was found experimentally (Fig. 1).

The values of the coefficients K and L

TABLE 3

Total Number of Sites and Equilibrium Contants

Sample	T (°C)	L^a (sites/cm²)	K	r^2 (correlation coefficient)
Pt/Al_2O_3	400	1.45×10^{14}	418	0.95
Pt/Al_2O_3	450	1.26×10^{14}	388	0.99
Pt/Al_2O_3	500	1.19×10^{14}	157	0.94
Pt/Al_2O_3	550	0.96×10^{14}	150	0.99
Al_2O_3	500	1.10×10^{14}	207	0.87

[a] For a specific surface area of 165 m²/g.

TABLE 4

Physical Properties of Al_2O_3 and Pt/Al_2O_3

Property	Al_2O_3 calcined at 650°C	Pt/Al_2O_3 without Cl regulation[a]	Pt/Al_2O_3 with Cl regulation[b]
Specific surface area (m^2/g)	175	165	164
Pore volume (cm^3/g)	0.48	0.46	0.47
Average diameter (Å)	110	112	114
Metal dispersion (%)	—	82	80

[a] Calcined and reduced at 500°C.

[b] Calcined and reduced at 500°C. Regulation treatment with $R = 80$.

were calculated by linear regression and are shown in Table 3. By assuming a linear variation of log K and L with $1/T$ and T, respectively, and using Pt/Al_2O_3 samples data, the following correlations were obtained:

$$\log K = -0.0364 + 1814/T(K);\quad \text{correl. coeff: } r^2 = 0.83, \tag{3}$$

$$L\ (\text{sites/cm}^2) = 2.68 \times 10^{14} - 3.1 \times 10^{11}\, T\ (°\text{C});\quad \text{correl. coeff: } r^2 = 0.96. \tag{4}$$

The enthalpy change for reaction 1 was estimated from Eq. (3), resulting in −8.3 kcal/mol. L is of the same order as that of the values of OH concentration on alumina quoted in the literature (*8, 10*).

In Fig. 3 the experimental equilibrium chlorine concentrations on the catalyst are compared with the ones predicted by Eq. (2), calculating K and L according to Eqs. (3) and (4), respectively. Also in Fig. 3 the results for Al_2O_3 are shown; they are similar to those of Pt/Al_2O_3. The values of K and L for Al_2O_3 at 500°C differ from those of Pt/Al_2O_3 calculated by Eqs. (3) and (4) as 1.3 and 2.7%, respectively.

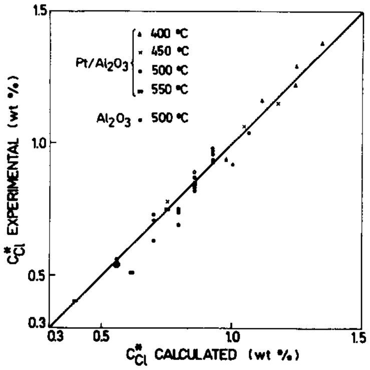


FIG. 3. Comparison of equilibrium chlorine concentrations, experimental vs calculated by Eq. (2).

This paper shows that the presence of Pt in low concentrations does not modify the equilibrium chlorine level on the support and the same correlation (Eq. (2)) can be used to calculate the chlorine concentration on Al_2O_3 and on Pt/Al_2O_3, as a function of temperature and molar ratio H_2O/HCl.

It must be emphasized that with the chlorine regulation technique employed the metallic dispersion and the porous structure of the support do not suffer great changes, as Table 4 shows.

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