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SULFURIZATION OF Pt/Al_2O_3-Cl CATALYSTS

I. ADSORPTION ISOTHERMS

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The sulfurization of Pt/Al_2O_3-Cl is partly reversible (on support and metal) and partly irreversible (on metal) and the latter is independent of H_2S concentration. The surface with irreversible S has an atomic ratio S/Pt = 0.5 and its H_2 adsorption capacity is 65% of the one of the fresh catalyst.

Введение серы в Pt/Al_2O_3-Cl является частично обратимым процессом (на носителе и металле) и частично необратимым (на металле). Последний является независимым от концентрации H_2S. Поверхность с необратимой S имеет атомную долю S/Pt = 0,5 и ее адсорбционная емкость для H_2 составляет 65% от емкости чистого катализатора.

Naphtha reforming catalysts are sulfurized to improve stability. The effects of sulfur are reversible /1,2/ and some amount of it remains on the catalyst /2,3/. In this paper Al_2O_3, Al_2O_3-Cl and Pt/Al_2O_3-Cl were sulfurized in order to study the S coverage of Pt.

EXPERIMENTAL

The Pt/Al_2O_3-Cl catalyst (0.37% Pt, 0.79% Cl) was prepared by impregnation of a very pure γ-Al_2O_3 (Cyanamid Ketjen CK 300 with a BET-N_2 surface area of 199 m^2/g and a total pore volume of 0.48 cm^3/g) with a solution of H_2PtCl_6 and HCl. It was calcined in air and reduced with H_2 at 773 K in a flow reactor 40 mm

in height and 12 mm in diameter. Sulfurized catalysts were obtained in this reactor by passing for 90 min a stream of H_2S in H_2 at 773 K and atmospheric pressure. The H_2S concentrations were between 0.03 and 10%. After sulfurization, S was chemically analyzed according to the method of Svajgl /4/. The chemisorption of H_2 was made by titrating O_2 previously adsorbed on the catalyst, according to the method of Benson-Boudart /5/.

Chlorided alumina were obtained impregnating the γ-alumina with HCl solutions. These materials and the alumina were heated at 773 K and were sulfurized following the same technique used for the sulfurization of the catalyst.

RESULTS AND DISCUSSION

Figure 1 shows the sulfur adsorption isotherms. Alumina adsorbs more sulfur, the presence of chlorine decreases S deposition, as can be seen comparing curves 1, 2 and 5. The curves are of the saturation type and the data, interpreted as a Langmuir isotherm, give, upon linearizing the isotherms, a maximum S coverage of 4.0×10^{13} atoms/cm^2 for alumina. This value is similar to the number of exposed Al^{3+} ions at the alumina surface which are active for olefin isomerization, these values were obtained by poisoning this reaction with H_2S /6,7/. For the chlorided aluminas with 0.54% Cl and 1.41% Cl the maximum coverage is 2.5×10^{13}/cm^2 and 1.0×10^{13}/cm^2, respectively.

Curve 3, Figure 1, shows the amount of S adsorbed on the Pt/Al_2O_3-Cl catalyst. At low H_2S concentration the adsorption is higher than on alumina because of the influence of the amount deposited on the metal. Upon heating this sulfurized catalyst at 773 K in a H_2 stream for 30 h, some S desorbs very quickly (reversible, S_r), and the other part desorbs very slowly (irreversible, S_i). Curve 4 is the amount of S desorbed from the catalyst. The remaining sulfur, S_i, is constant and independent of the H_2S concentration, as shown by curve 6. The catalysts covered

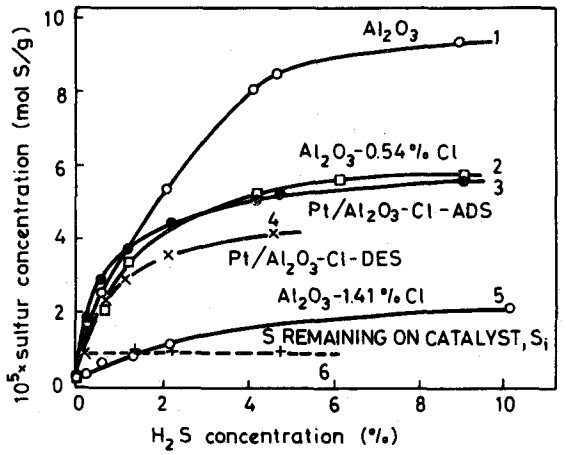

Fig. 1. Sulfur concentration on the solid as a function of H_2S concentration in H_2 at 773 K. 1 – alumina adsorption isotherm; 2 – chlorided alumina (0.54% Cl) adsorption isotherm; 3 – catalyst adsorption isotherm; 4 – sulfur desorbed from the catalyst in 30 h in H_2 at 773 K; 5 – chlorided alumina (1.41% Cl) adsorption isotherm; 6 – sulfur remaining on the catalyst after desorption

with irreversible sulfur have an H_2 adsorption capacity (titration method) equal to 65% of that of the nonsulfurized catalyst.

When a stream of H_2S is passed over the catalyst at 773 K and then cooled to room temperature, always passing H_2S, the amount of S retained (S_r and S_i) is very high. The H_2 adsorption capacity on this catalyst is zero or negligible. Upon heating these sulfided catalysts from room temperature in a stream of H_2, when reaching 673-703 K, the hydrogen adsorption capacity of the catalyst increases because of the desorption of S_r. The value of S_i is $7\text{-}9 \times 10^{-6}$ mol S/g cat (0.02-0.03 wt.%), and according to the Pt concentration and dispersity (93%), it corresponds to an atomic ratio of S/Pt = 0.5. One sulfur atom interacts with two platinum atoms. This result for supported Pt and atmospheric pressure is in agreement with the ones obtained on very definite Pt surfaces and very low pres-

sures. Heegemann et al. /8/ found that at around 653 K, part of the sulfur deposited on the (111) face of Pt is desorbed, and the sulfur adsorbed passes from a disordered structure to an ordered one which is stable between 723 and 1073 K. Fischer and Kelemen /9/ stated that the amount of sulfur adsorbed on a (100) Pt surface has the atomic ratio of S/Pt = 0.5 and is stable up to 1023 K.

Then, at the usual temperature of the naphtha reforming process, a stoichiometric surface compound Pt_2S covers all the metallic surface of supported Pt. This compound has a H_2 adsorption capacity and, according to the H_2S pressure, adsorbs some S reversibly, decreasing its H_2 adsorption capacity.

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