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NOTES

Surface Acidity and Acid Strength Distribution of Modified Alumina Support and Platinum Reforming Catalysts

Catalytic reforming is one of the most economical and widely accepted processes for upgrading motor gasoline by the production of aromatic hydrocarbons from paraffins and cycloparaffins. Isomerization and hydrocracking proceed on acid sites via a carbonium ion mechanism. These carboniogenic sites are developed by incorporating a suitable amount of halide (*1*) on the support, but if the halide concentration becomes too high, excessive undesirable hydrocracking takes place (*2*). A compromise has to be worked out by impregnating an optimum amount of halide in order to make the catalyst selective for isomerization with least hydrocracking.

The influence of fluorine on the activity of alumina-supported catalyst has been a subject of intense study (*3–5*). Fluorinated aluminas impregnated with platinum salts have high hydrocracking activity, whereas on chlorided aluminas it is low. The acidic properties of chlorided alumina–platinum reforming catalysts have not been studied in detail. We have therefore studied the uptake of chlorine by alumina support, its subsequent impregnation with platinum and iridium metals and have also correlated the chlorine content with the acidity and acid strength distribution.

Sample A was prepared from boehmite by calcination at 550°C for 24 hr in air and consisted of γ-alumina as confirmed by XRD patterns. Chlorided aluminas were prepared from γ-alumina using an excess of 0.067 *N* HCl solution. The first sample was taken out after 2 min (sample B) while the subsequent ones were removed after every 1 hr. The samples B_1, B_2, B_3, B_4, B_5, and B_6 were taken out of the solution after allowing 1, 2, 3, 4, 5, and 6 hr of impregnation, respectively. After depositing stable chlorine (0.68 wt%) on sample A, simultaneous impregnation of H_2PtCl_6 and H_2IrCl_6 solutions was made in order to obtain 0.35 and 0.04 wt% of platinum and iridium, respectively (sample C). All the samples were first dried at 110°C for 24 hr and finally activated at 550°C for 4 hr in air. Reduction of sample C in a stream of hydrogen at 450°C yielded sample D. Sample E was obtained by impregnation of H_2PtCl_6 and H_2IrCl_6 on sample A. Sample F was a product of simultaneous impregnation of HCl, H_2PtCl_6 and H_2IrCl_6 on sample A. Each of the samples E and F contained 0.35 wt% platinum and 0.04 wt% iridium.

The acid amount and acid strength distribution were determined by following nonaqueous titrations (*6, 7*) using *n*-butylamine as a base, benzene as a dispersant and Hammett indicators as the neutralization point detector.

Alumina exhibits acidity when heated to temperatures above 450°C (*8*). Pines and Haag (*9*) have found that the total number of acid sites responsible for the dehydration of *1*-butanol and the number of strong acid sites corresponding to the isomerization of cyclohexane are 10×10^{12} and 8×10^{12} sites/cm², respectively. They have further reported that alumina displays

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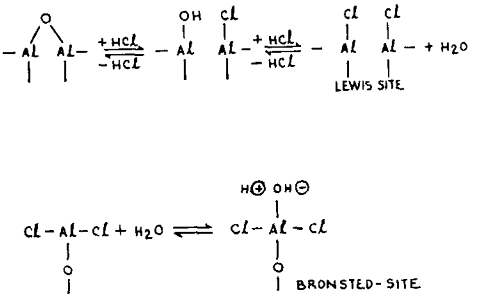

FIG. 1. Formation of Lewis and Brønsted sites on chlorided alumina.

Lewis acidity. The concept of Lewis and Brønsted acidity can also be extended to chlorided aluminas and the formation of acid sites can be postulated as shown in Fig. 1.

Data on the acidity/acid strength distribution of alumina support, chlorided aluminas and Pt—Ir—Al_2O_3 reforming catalysts are summarized in Table 1. The entire acid strength distribution spectrum can be divided into three parts, comprising weak ($-3.0 < pK_a \leqq +5.0$), medium ($-5.6 < pK_a \leqq -3.0$), and strong ($-8.2 < pK_a \leqq -5.6$) acid sites. A perusal of the results indicates that γ-alumina (sample A) exhibited a total population of 39 acid sites/10^4 Å^2 of the surface, all representing medium acid strength. Incorporation of 0.25 wt% chlorine on alumina (compare samples A and B) generate a fresh 36 acid sites/10^4 Å^2 out of which 15 sites each of weak and strong acid strength are produced and 6.0 sites correspond to medium acid strength. The impregnation of chlorine on alumina thus has not only increased the concentration of total acid sites but has also improved the strength of the sites. On further increasing the chlorine concentration from 0.25 to 0.53 wt% (sample B_1), the concentrations of weak and strong acid sites have not been affected, but 15.0 fresh acid sites/10^4 Å^2 of medium strength are generated. On still further increasing the chlorine concentration, the population of strong acid sites remains practically constant but the sites of weak and medium acid strength continue to increase until the total population of acid sites reaches a maximum value of 126 sites/10^4 Å^2. This chlorine concentration (0.68 wt%) also happens to be the

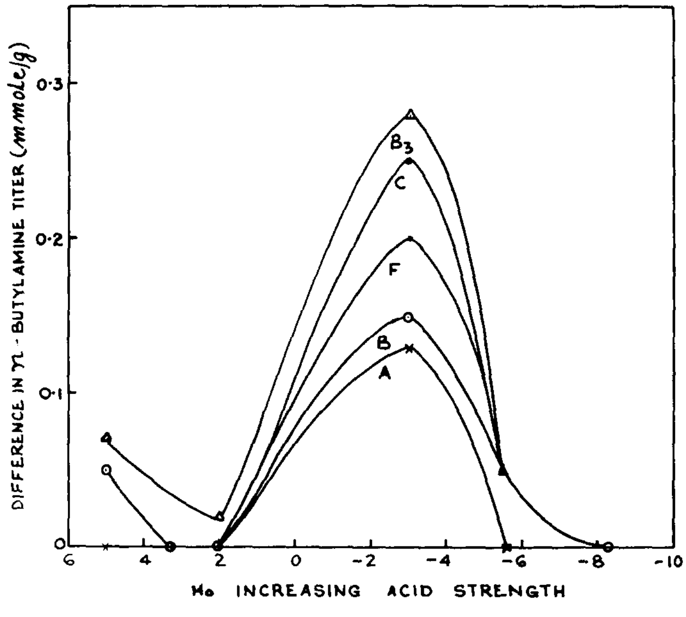

FIG. 2. Acid strength distribution spectrum of various samples: (A) sample A; (B) sample B, (B_3) sample B_3; (C) sample C; (F) sample F.

TABLE 1

Total Acidity and Acid Strength Distribution of Chlorided Aluminas and Platinum-Reforming Catalysts

Sample	Impregnation time (hr)	Chlorine content (wt%)	Difference in *n*-butylamine titer values[a] for indicators of various pK_a values				
			$+3.3 < pK_a \leq +5.0$	$+2.0 < pK_a \leq 3.3$	$-3.0 < pK_a \leq +2.0$	$-5.6 < pK_a \leq -3.0$	$-8.2 < pK_a \leq -5.6$
(A) Al_2O_3	—	—	0	0	0	39.0	0
(B) Al_2O_3-Cl	0.03	0.25	15.0	0	0	45.0	15.0
(B_1) Al_2O_3-Cl	1	0.53	15.0	0	0	60.0	15.0
(B_2) Al_2O_3-Cl	2	0.63	21.0	0	9.0	75.0	15.0
(B_3) Al_2O_3-Cl	3	0.68	21.0	0	6.0	84.0	15.0
(B_4) Al_2O_3-Cl	4	0.68	21.0	0	6.0	84.0	15.0
(B_5) Al_2O_3-Cl	5	0.68	30.0	0	0	90.0	15.0
(B_6) Al_2O_3-Cl	6	0.68	21.0	0	0	90.0	15.0
(C) Pt-Ir-Al_2O_3-Cl (fresh)		1.0	16.0	0	0	79.0	16.0
(D) Pt-Ir-Al_2O_3-Cl (reduced)		—	13.0	0	0	70.0	17.0
(E) Pt-Ir-Al_2O_3		0.36	0	0	0	57.0	16.0
(F) Pt-Ir-Al_2O_3-Cl (simultaneous)		1.0	16.0	0	0	64.0	16.0

[a] Number of *n*-butylamine molecules consumed by 10^4 Å^2 of the surface.

optimum stable uptake of chlorine by the alumina support and no substantial change in acidity has been observed thereafter.

The chlorided alumina support containing optimum chlorine (sample B_3) when impregnated with platinum and iridium salts to obtain sample C, displayed the same amount of strong acid sites as in the parent sample B_3 but the weak and medium strength sites have been suppressed presumably due to the occupation of some of the sites by the impregnated metal species. The catalyst reduced in a stream of hydrogen does not show much variation in the concentration and strength of acid sites, in agreement with the results reported by Hirschler and Schneider (*10*) in their studies on platinum reforming catalysts.

When platinum and iridium salts are impregnated on an unchlorided support yielding sample E, the medium and strong acidity is still found to be prevailing, but the homogeneity (dispersion of the metallic species on the surface of the support) has considerably deteriorated, thus making the catalyst less attractive from an industrial point of view. On the other hand, when HCl H_2PtCl_6 and H_2IrCl_6 are impregnated simultaneously on unchlorided alumina yielding sample F, the catalyst shows an excellent homogeneity and acidity also (compare samples C and F).

A graphical representation of our acidity determination results (Fig. 2) reveals that most of the acidity of the chlorided aluminas and Pt—Ir-Al_2O_3-Cl catalysts falls in the medium strength range ($-5.6 < pK_a \leqq -3.0$) and only a small amount of acidity corresponds to weak and strong acid sites.

Clark *et al.* (*3*, *4*) have reported that the acid catalyzed hydrocarbon reactions, viz, cracking, isomerization, etc., occur readily on relatively weak acid sites. Hirschler and Schneider (*10*) in their investigations on acidic properties of cracking and reforming catalysts concluded that acid sites stronger than $pK_a \leqq -3.0$ decreased the gasoline yield in a cracking process. On the other hand acid sites stronger than $pK_a \leqq -3.0$ have been proved favorable for the production of higher octane gasoline under reforming conditions. A decisive conclusion can thus be drawn on the basis of the above findings that the acid sites of strength $-5.6 < pK_a \leqq -3.0$, are of paramount importance for isomerization reactions in the reforming process. In conclusion it can be argued that our catalyst (sample F) prepared by simultaneous impregnations of HCl, H_2PtCl_6 and H_2IrCl_6 consisted of an appreciable concentration of sites of acid-strength $-5.6 < pK_a \leqq -3.0$ vital for isomerization activity in the reforming process. It is further pointed out that this route of preparation is less troublesome and more economical as it does not require the multi-impregnation procedure.

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