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EVALUATION OF THERMAL STABILITY OF SOME REFORMING CATALYSTS

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ABSTRACT

This paper discusses the evaluation of the thermal stabilities of some reforming catalysts of the platinum–γ-alumina type commonly used in reforming processes and in the catalytic conversion of low straight-chain paraffins into branched-chain isomers Data obtained from this thermoanalytical investigation, which was performed in a differential scanning calorimeter and thermogravimetrically under atmospheres of nitrogen and oxygen gases, provided useful information on the thermal stabilities and properties of these catalysts which are usually subjected to elevated temperatures during isomerization and conversion processes

INTRODUCTION

The conversion of low straight-chain paraffins into branched-chain isomers and catalytic reforming of low-octane heavy naphthas, which are rich in paraffins and naphthenes, to high-octane reformates, which are rich in aromatics, are important refining processes used to improve the octane number of gasoline and in preparing aromatic intermediates [1–3]. It is gaining wide acceptance in the industry especially with the need for lead-free gasolines

These reactions are catalyzed mostly by bifunctional catalysts consisting of noble metals combined with an acidic oxide [4–6] Platinum–γ-alumina catalysts represent one of the most important types of industrial catalysts and have been widely used [7]

It is well known that platinum reforming catalysts work in a bifunctional sense [4] The hydro-dehydrogenation reactions take place on the noble

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metal sites, while the acid sites on the alumina support provide the acidic function required for isomerization, cyclization and cracking reactions The acidity of the catalyst is usually promoted by the incorporation of chlorine as chloride which acts as suitable acidic components of the catalyst [5,8,9]

Thermoanalytical techniques have been used recently [10,11] in studying the behavior of reforming catalysts under a hydrogen atmosphere and in determining impurities deposited on them

Since reforming and isomerization catalysts are usually subjected to elevated temperature (250–550 °C) for prolonged periods during the conversion processes, which could lead to the loss of some of the important chlorine acidic sites and eventually to lowering the percentage conversion and depletion in selectivity and activity, it is of scientific and economic importance to evaluate the thermal stabilities and to gain knowledge of the thermal properties of these catalysts, employing mainly differential scanning calorimetric and thermogravimetric techniques

EXPERIMENTAL

Apparatus

Differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) measurements were carried out on a Heraeus TA 500 thermal analyzer

In the DSC measurements, samples weighing 10–20 mg were heated at a rate of 10 °C min^{-1} in an aluminum crucible under the chosen atmosphere The reference cell was filled with pure and dried powdered aluminum oxide

TG and DTG curves were recorded simultaneously by placing a sample weighing 20–30 mg in a platinum crucible and heating at a rate of 10 °C min^{-1} under a flowing atmosphere of ultra high pure (grade 6) nitrogen or oxygen gas In all thermal measurements the gas flow rate was 6 l h^{-1}

Materials

Four types of fresh reforming catalysts were obtained from the Société Française de Produits pour Catalyse Some properties of these catalysts are

TABLE 1

Some properties of reforming catalysts

Type	Composition	Chlorine content (wt %)
RG 402	0 6% Pt/Al_2O_3	1 11
RG 412	0 35% Pt/Al_2O_3	1 14
RG 422	0 6% $(Pt+Ir)/Al_2O_3$	1 03
RG 432	0 35% $(Pt+Ir)/Al_2O_3$	1 27

shown in Table 1 The chlorine content of these catalysts was determined according to Mohr's method [12] by slurrying the catalyst in distilled water, filtering and titrating with 0 1 N $AgNO_3$ solution

RESULTS AND DISCUSSION

A typical DSC curve recorded between room temperature and 550 °C under nitrogen gas for the reforming catalysts is shown in Fig 1. The presence of a broad endothermic peak due to volatilization of adsorbed moisture was observed between about 75 and 200 °C This transition was followed by a weak endothermic offset from the baseline commencing at about 400 °C, which could be attributed to the loss of chlorine

The DSC traces of the same catalysts recorded in oxygen in the same temperature range were of a similar pattern to those recorded under the inert atmosphere

Representative TG and DTG traces performed between room temperature and 750 °C under nitrogen and oxygen gases for different catalyst samples are shown in Fig 2

The weight loss under both atmospheres indicated the presence of two transitions, the first ($T_i = 85$ °C, $T_{max} = 160$ °C and $T_f = 220$ °C) is related to the loss of adsorbed moisture and the second with a T_i commencing at about 415 °C is related to the slow and steady removal of the chlorine content incorporated in the reforming catalysts as chloride The initial temperatures of these weight-loss transitions were close to the initial temperatures of transitions recorded in their corresponding DSC traces

The data extracted from the TG curves in nitrogen and oxygen atmospheres are shown in Table 2, indicating the percentage weight loss at 100 °C intervals The thermal data presented confirmed the fact that there is

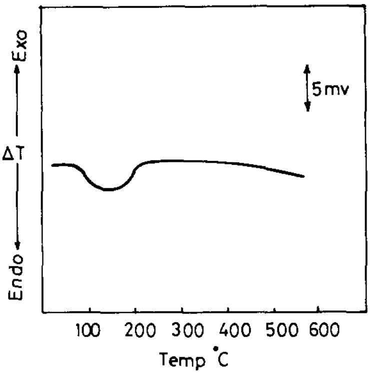

Fig 1 Representative DSC curve of the reforming catalysts studied

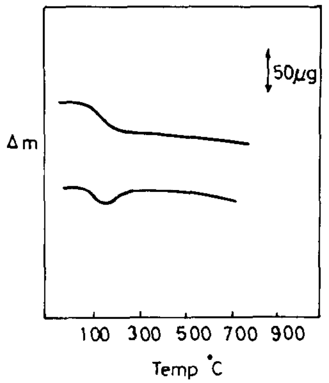

Fig 2 Representative TG and DTG curves of the reforming catalysts studied

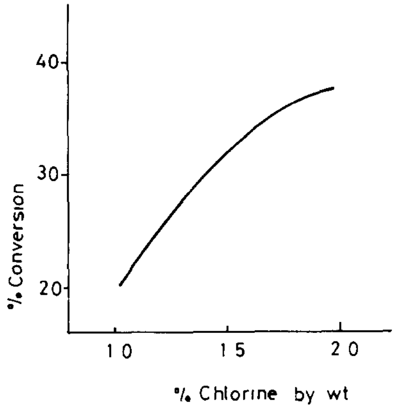

Fig 3 Influence of chlorine content of a reforming catalyst on n-hexane conversion

TABLE 2

Thermogravimetric data [a,b] on reforming catalysts studied

Temperature range (°C)	Percentage weight loss in nitrogen				Percentage weight loss in oxygen			
	402	412	422	432	402	412	422	432
25–225 [c]	3 8	4 3	4 2	5 3	3 9	4 4	4 2	5 4
225–325	0	0	0	0	0	0	0	0
325–425	0 05	0 05	0 05	0 05	0 06	0 06	0 05	0 06
425–525	0 26	0 26	0 27	0 29	0 28	0 28	0 30	0 31
525–625	0 29	0 30	0 29	0 32	0 31	0 31	0 31	0 34
625–725	0 34	0 34	0 31	0 36	0 35	0 36	0 33	0 37

[a] From TG curves

[b] Average of two determinations

[c] Loss of adsorbed moisture

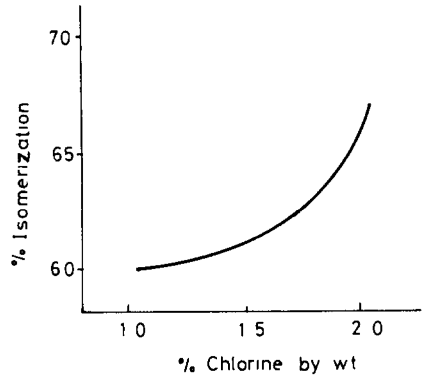

Fig 4 Influence of chlorine content of a reforming catalyst on n-hexane isomerization

a steady decrease in the chlorine content of the catalysts studied with increase in temperature over 400 ° C

Meanwhile, the effect of the chlorine content of a reforming catalyst on the mode of isomerization of, for example, *n*-hexane is displayed in Figs 3, 4 and 5, indicating the relationship between chlorine content and percentage conversion, isomerization and cyclization, respectively It is clear from these figures that the activity and selectivity of the reforming catalyst used for isomerization is closely dependent on its percentage chlorine content

The results achieved when using thermoanalytical techniques in studying the thermal properties of reforming catalysts, indicated that the useful life-time of these catalysts and their activity and selectivity, could be prolonged and preserved when the reforming and conversion processes are carried out at the lower end of the recommended temperature range employed in such catalytic processes

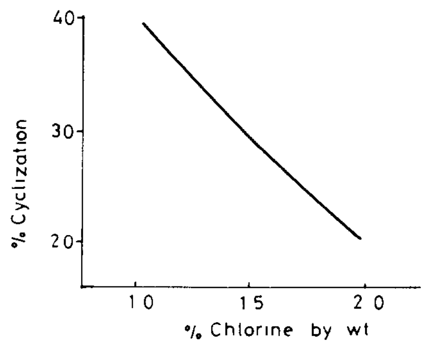

Fig 5 Influence of chlorine content of a reforming catalyst on n-hexane cyclization

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