The Influence Of Coke Depositions On The Acidity Of FCC Catalysts

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Abstract

This paper presents the experimental results regarding the effect of coke deposition on the cracking catalyst acidity. It was investigate two to FCC catalysts, PREMIX and VISION fresh and coked by the vacuum distillate cracking reaction. It was established the total acidity and strength of acidity by adsorption and thermodesorption of NH_3. The increasing of coke contents on the catalyst involves to decreasing of total acidity and redistribution of acidity strength from the medium to wake strength.
The number of high strength acidity site remains practically constant.

Keywords: *coke, acidity ,catalyst*

Introduction

Catalytic cracking represents one of the most important secondary processes from refineries, which has as its main goal the conversion of heavy petroleum fractions, in gasoline with a high octane number and C_3-C_4 gases used in petrochemistry and for octane components production by alkylation, polymerization or etherification processes. [1,2,3].
Besides gases and gasoline the cracking reactions on zeolite type acid catalysts, also generate coke, a mixture formed of heavy compounds, with high molecular masses and condensed polycyclic structures. The coke formation determines the deactivation of the catalyst by decreasing of the active sites number, due to diffusion limitations generated by the total or partial blocking of the pores[2,3,4,5,6], which are accessible to reactants. Also, the coke deposit diminishes the acidity of the active sites with a direct effect in the decrease of its activity and selectivity.
The coke deposition on the active sites does not lead to loss of total acidity, but lead to diminishing of the density and acidity strength [7,8,9, 10].
The density and strength acid sites reduction decreases the carbocations formation rate and normaly the cracking reaction. The decrease of the acid sites density has a more severe effect on the selectivity of the catalysts, by reducing the gasoline yield, as a result of decrease in the hydrogen transfer rate reaction.
The experimental study developed in this paper, was focused to investigate the effect of coke deposits on total acidity and strength acidity distribution on the active sites of some cracking catalysts.

Experimental study

For the experimental, there have been used two industrial catalysts PREMIX (P) and VISION (V), in equilibrium conditions and with different coke content. The main characteristics of catalysts are presented in table 1. The coked catalyst samples have been obtained on a catalyst micro pilot testing installation, MAT, (Microactivity Test) [11]), taking into account the shown method in [12], using vacuum distillate as feed, at a 500°C, a 16 h^{-1} space velocity and an experiment time of 75, 110 and 150 s.

Table 1. The main characteristics of the equilibrium catalysts,

Catalyst characteristics	PREMIX	VISION
	Valori la echilibru	
Chemical composition % mass		
Al_2O_3	42,1	32,54
SiO_2	54,2	64,90
Fe_2O_3	0,6	-
Na_2O	0,34	0,17
Re_2O_3	1,6	1,34
SiO_2/Al_2O_3	1,28	1,994
Physical properties		
- The specific surface	203	219
Pore volume, cm^3/g	0,34	0,34
The unit cell diameter, a_o, Å	24,42	24,30
The Al atom number unit cell,*	26,38	12,55
Micro activity, % wt. conversion	78	78

* The Al atom number can be calculated with the relation $N_{Al} = 115,2 (a_o-24,191)$ [13]:

In order to determine the acidity, we have used the volumetric method due its constructive simplicity and the precision of the determinations. NH_3 was used for adsorption. The adsorption apparatus used is made of a conventional static-volumetric system, a vacuum distillation (constituted of a preliminary vacuum pump, a Hg diffusion pump, and a traps with liquid nitrogen), that allows obtaining a pressure of 10^{-5}mm Hg, sufficiently low enough to ensure "the cleaning" of the catalytic surface. The installation is completed by a heater used for the samples degaseification to removing the impurities from the catalysts. In order to dry and purify the adsorbent, an additional $CaCl_2$ and KOH traps has been inserted.

The equilibrium pressure was measured in the apparatus volume, before and after establishing the adsorption equilibrium, in order to determine the adsorption isotherm. It was successively feed amounts of gas at increasing pressures, the adsorption equilibrium point is reached. The chemosorption isotherms are the Langmuir model and the surface saturation being achieved at a 300mm Hg pressure.

To reduced the physical adsorption, as well as, eliminating a multi-layered adsorption, after reaching the chemosorption equilibrium, a supplementary degasification has been made. The amount of adsorbed was corrected by ratio to the degassed volume.

The total amount of adsorbed ammoniac, expressed in weight or volume in standard conditions, in relation with the weight unit of the catalyst is a measure of the global acidity of the adsorbent.

In these conditions, the total acidity is: $a = (V_{ads} - V_d) / 22,4$, MechivNH$_3$/gr. cat.

where: Vads - is the total NH_3 adsorbed volume; Vd – the degassed NH_3 volume.

The number of acid centers is calculated with the following formula:

N c.ac.=a*N=a*6,023 10^{23}

The distribution of the acidity strength of active catalytic sites was made through the thermodesorption by heatinjg with the 3 °C/ minute rate between the 200-450° C .

The thermal level of the desorption, depends on the strength of acid site, so that, proportionally to the amount of NH_3 desorbed/weight unit of catalyst at a certain temperature, we can establish the acidity, as it follows:

> weak acidity for the desorption t<200°C
> average acidity for the desorption $200\,^{\circ}C < t < 450\,^{\circ}C$;
> high acidity for the desorption temperature $t > 450\,^{\circ}C$;

Results and discussions

The total acidity and its strength distribution for the PREMIX (P) and VISION(V) type catalysts, at equilibrium point and different content of coke is presented in Table 2

Table 2. The acidity and distribution of acidity strength for the PREMIX and VISION type catalyst samples.

Catalyst		Fresh		Equilibrium		Coked, after a period of experimental time					
						75, s		110, s		150, s	
		P	V	P	V	P	V	P	V	P	V
Coke/catalyst/catalizator, % weight		0	0	0,2	0,2	1,53	1,19	2,84	2,00	4,60	3,29
Total acidity	MechivNH$_3$ gr.cat,	0,597	0,385	0,21	0,15	0,040	0,031	0,026	0,021	0,018	0,012
	Acid sites number x 10^{20}	3,60	2,32	1,27	0,903	0,24	0,186	0,16	0,125	0,11	0,072
Acidity's strength distribution %	weak	3	3	13	12	15	14	17	17	21	20
	Medium	72	67	58	57	55	54	53	52	50	50
	Strong	25	30	29	31	30	32	30	31	29	30

As it can seen in Table 2 and Figure 1, the variation mode of total acidity quantified by total number of acid sites is similar for the two catalysts, PREMIX and VISION, used in the experimental study developed in this paper.

We can be able to see a fast decrease of total acidity in the domain of small coke deposits, less than 0.2% weight, characteristics that are specific for the equilibrium catalysts. At higher amounts of coke deposits, we can say that the total acidity decreases lower

Adding an acid sites to each Al atom , the rapid decrease of acidity, from the fresh catalyst to the equilibrium catalyst, is mainly the cause of dealuminization zeolite by the hydrolysis reactions which take place in the regenerator at a temperature between 720 - 740°C. This effect increases by the coke deposit on the catalyst, which determines decreasing the acidity, either directly, through the covered of the acid sites with coke, or by isolation the uncontaminated active sites as result of the access pores blockage. The slow decrease of acidity in the domain of high coke deposits on the catalyst is justified by keep the acid character of the active site, even if coke has been deposited on it. [7, 8, 12, 14].

At the same coke content, the PREMIX catalyst has a higher total acidity, because in contains a larger number of Al atoms in its structure (26,38), comparatively to the VISION catalyst, which contains only 12,55.
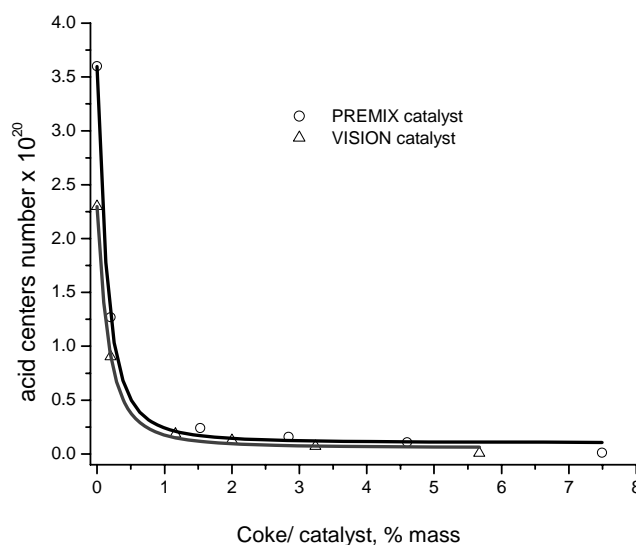
Figure 1. The variation of total acidity of fresh, equilibrium and coked PREMIX and VISION catalyst samples, as function with the coke/catalyst.

As a result of total acidity reduction, through dealuminisation, the distribution of acidity strength is modify, from the fresh to the equilibrium catalyst (Table 1, and figures 2 and 3) in the sense of increasing the ratio of the strong and low acidity sites and decreasing average acidity sites.

The aluminiums eliminated from the zeolite structure after regeneration process has the effect of changing from Al atoms surrounded by other 4 Al atoms (Lownestein's rule), to Al atom bordered by 3, 2,1 or even 0 Al atoms which generating very strong acid sites. Increasing the number of active sites, with low acidity can be explained by the presence of extra frame Al ions, which remain in the zeolite structure after dealuminisation.

After reaching an equilibrium, by increasing the coke content, we can observe an increase the concentration of active sites with low acidity, the decrease of the ones with an average activity, while the number of the highly acidity sites, is very little modified.

This process of acidity redistribution can be explained through the intervention of acid site types in the mechanism of the cracking reactions in general and especially in the case of coke formation.

This way, on the average acidity sites take place hydrogen [14] transfer reactions, which lead to polialchilaromatics formation that are strongly adsorbed on the catalyst surface, and further are convert in the final coke, through the condensation reactions.

As soon as the coke deposits formed by this reactions increase, the acidity of the active sites decreases and a most important part of the average acidity sites becames in weak acid sites.

Referring to the distribution of acidity concentration, the data presented in Table 1, confirms the fact reported in literature [16], that the zeolyte with a lower number of Al atoms in its structure, the VISION catalyst, presents a higher density in strength acid sites, and a lower ratio of weak or average concentration acid sites than of the PREMIX catalyst with a higher aluminum content.
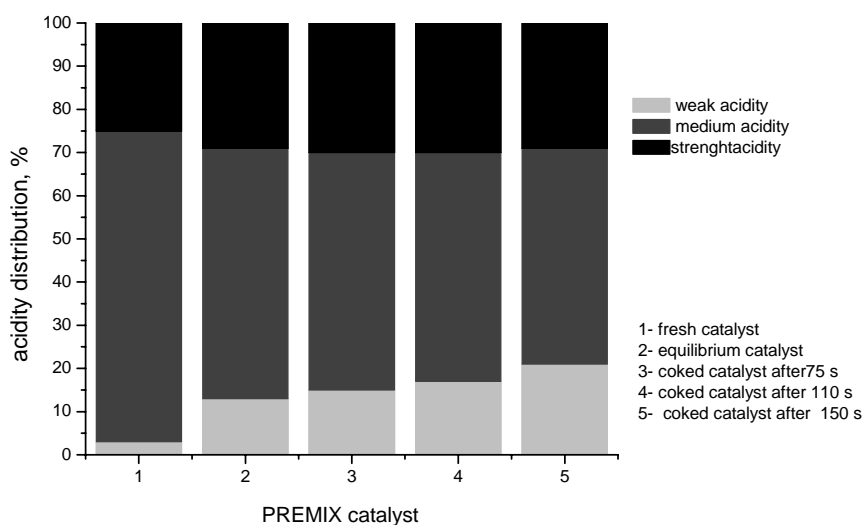
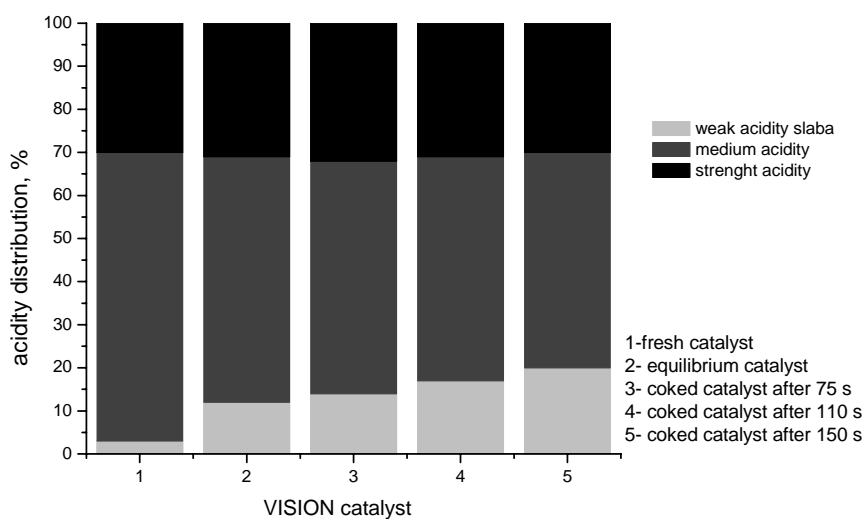**Figure 2**. The distribution of acidity strength of fresh, equilibrium and coked PREMIX catalyst samples.

Figure 3. The distribution of acidity strength of fresh, equilibrium and coked VISION catalyst samples

Conclusions

Total acidity decreases rapidly from the fresh to the equilibrium catalyst samples and after that the decrease is much slower with the increase of coke content on the catalyst.

The fast decrease of acidity is mainly the result of decreasing the Al atom number, due the dealuminisation of zeolite after hydrolysis reactions which take place in the regenerator at temperatures of 720-740 °C.

The coke deposit on the catalyst determines a decreasing the acidity, either directly, by covering the active sites with coke, either by isolation of the uncontaminated acid sites, as a result of the pores access blockage.

The increase of coke content on the catalyst determines the increase the density of weak acidity sites based on decreasing of number active sites with average acidity, while the strong acidity sites suffer very little modifications. On the active sites with an average acidity take place hydrogen transfer reactions which leads to coke formation. The coke deposited on the catalyst covers the active site and determine the decrease of acidity strength.

Acidity studies have shown that the zeolite with less Al atoms in its structure, the VISION catalyst, presents a higher density of strong acidity sites, and a lower density of medium and weak acidity, as compared to the PREMIX catalyst, where, the aluminum content is lower.

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Influenţa depunerilor de cocs asupra acidităţii catalizatorilor de cracare

Rezumat

Lucrarea prezintă rezultatele studiului experimental privind efectul depunerilor de cocs asupra aciditatii catalizatorilor de cracare. Au fost investigati doi catalizatori de cracare, PREMIX si VISION, proaspeti si cocsati in urma cracarii distilatului de vid. S-a determinat aciditatea totală şi tăria acidităţii folosind adsorbţia şi termodesorbţia amoniacului Creşterea conţinutului de cocs pe catalizator determină scaderea aciditatii totale, simultan cu modificarea distributiei tariei aciditatii in sensul creşterii ponderii centrilor activi cu aciditate slabă pe seama diminuării celor cu activitate medie în timp ce ponderea celor cu aciditate mare se modifică foarte puţin.