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Research article

Transformations of n-undecane–indole model mixtures over the cracking catalysts resistant to nitrogen compounds

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ABSTRACT

Additives to a zeolite-containing cracking catalyst were synthesized and studied in order to enhance the resistance to the poisoning effect of nitrogen compounds (in particular indole) upon cracking of n-undecane as the model FCC hydrocarbon. The additives were represented by acid-activated clays and mixed oxides. The activation of clays in the catalyst by 5% sulfuric acid solutions was shown to enhance the resistance to nitrogen. The introduction of Mg, Al – mixed oxides in the catalytic system in the amount of 10 wt% increased its activity and resistance to indole. The highest resistance was observed for the systems containing magnesium-aluminum oxides with a Me^{2+} to Me^{3+} molar ratio equal to 0.5: 1. Cobalt modification of these mixed oxides enhanced the activity and nitrogen resistance of the cracking catalysts. Use of such nitrogen-resistant catalysts will allow cracking of heavy raw materials.

1. Introduction

An urgent task for producing countries and consumers of petroleum products is increasing the efficiency of processing heavy feed into light oil products. Catalytic cracking is the main process for deep oil refining. Both the vacuum gasoil with a broad fractional composition and the heavy residual stock are employed as a feed for the process. Along with hydrocarbons, the feed contains organic compounds of metals, oxygen, sulfur and nitrogen [1–3].

Nitrogen-containing compounds are adsorbed by the catalyst acid sites, thus decreasing the catalytic activity, which in its turn substantially affects the material balance of cracking [4–15]. Total nitrogen content in the cracking feed reaches 0.3 wt%.

The main methods for reducing the deactivating effect of nitrogen compounds are as follows [3]:

1. Adsorption uses acidic solid adsorbents such as bentonite, kaolinite, which sorb the nitrogen compounds.

2. Liquid extraction uses immiscible solvents to extract nitrogen compounds.

3. The most well-known hydrotreating method is used to reduce the nitrogen content in the feedstock. But the observed nitrogen removal rate does not exceed 30%, even at high sulfur removal rates, of > 98%.

The realization of these processes requires significant investment and operating costs.

4. A possible way to diminish the deactivating effect of nitrogen-containing compounds on a cracking catalyst is the use of special additives [4,11–13,14]. The action of additives consists in either the selective adsorption of nitrogen compounds or the transformation of organic nitrogen compounds into less basic compounds, for example, nitrogen. Thus, the additives prevent blocking of acid sites of the catalyst active component (ultrastable zeolite of type Y) and maintain its high catalytic activity in cracking reactions. An additive should possess the pronounced acidic properties and be stable at the temperature of the catalyst regeneration, which is above 700°C.

The activity of Mg, Al – mixed oxides as well as the systems modified with Zn, Co, Cu or Ce have been shown in SOx and NOx removal [16–18]. These additives can serve for increasing the stability of catalysts to the action of nitrogen compounds in the cracking process. A possible mechanism of the reaction.

$$R - N + [H] \rightarrow R - H + NH_3$$
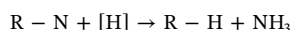
is based on the reactions of hydrogen transfer and aromatization, which result in the formation of intermediate hydrogenated nitrogen derivatives, which readily undergo cracking with the formation of ammonia [19,20]. In addition, it is very difficult to monitor the complete cycle of nitrogen compounds transformations under catalytic

Nomenclature		HTC	hydrogen transfer coefficient
		WHSV	weight hour space velocity, h^{-1}
MM	montmorillonite	c/o	catalyst-to-oil mass ratio
PG	palygorskite	C_{11} + ind	n-undecane + indole
TID	thermionic detector	XRD	X-ray diffraction
FID	flame-ionization detector		

cracking conditions, in comparison with sulfur compounds. First of all, this is due to the existence of a very large number of possible directions of transformations and as a consequence a wide variety of nitrogen-containing compounds in reaction products.

Acid-activated clays can also be used as the additives. It is known [21,22] that treatment of clay minerals with hot acids significantly enhances their catalytic and adsorption activity.

Nitrogen resistant catalytic systems show high activity and allow processing raw materials more efficient, therefore to obtain a greater yield of gasoline.

The goal of the work was to synthesize and investigate additives to the zeolite catalyst for cracking of hydrocarbons in order to improve their resistance to poisoning by nitrogen compounds (indole and quinoline), as well as the solution of such problem as processing of heavy feed in light oil products.

2. Experimental

The model compounds were represented by n-undecane (Haltermann; 95 wt%), cumene (Acros Organics; 98.0 wt%), decalin (Acros Organics; 98.0 wt%) which are classical representatives of the main hydrocarbon groups – paraffins and arenes, respectively. Indole (Acros Organics; 99.0 wt%) and quinoline (Alfa Aesar; 97.0 wt%) were chosen as the model nitrogen compounds. Nitrogen compounds were introduced into the feed in the amount of 500 ppm as referred to nitrogen. At the indicated concentration of a nitrogen compound, a decrease in activity of the cracking catalyst is observed [23].

Cracking of the model feedstock was carried out using laboratory samples. Particles size of cracking catalyst samples was in range 50–250 μm (middle size – 80 μm). The catalysts comprised the HREUSY

zeolite (ultrastable zeolite of type Y) and the matrix consisting of amorphous aluminosilicate, aluminum hydroxide and bentonite clay. The synthesis method and properties of the equilibrium catalyst (e-cat) are reported elsewhere [24]. The composition of catalytic systems and the way of additive introduction are listed in Table 1.

Acid activation of clays was performed using 5 and 15% sulfuric acid solutions at room temperature under constant stirring for 1 h with subsequent holding at 100 °C for 2 h. After the activation, the clay was washed to pH 7. The alkaline-earth forms of montmorillonite and palygorskite served as the initial clays. Me, Mg, Al – mixed oxides (Me = Co, Zn, Cu, Ce) were prepared by the technique reported in [16–18].

The synthesized samples were dried at 100 °C for 12 h with subsequent calcination at 550 °C under static atmosphere in an oven. Before testing, all the samples of model catalysts were treated in 100% water vapor at 760 °C for 5 h.

Catalytic testing was performed on a lab-scale unit with the fixed-bed catalyst (12.0 g) at a weight hour space velocity of 7.4 h^{-1} and at a catalyst-to-oil mass ratio equal to 2.70 in accordance with ASTM-D 3907. The model feed was tested at a temperature of 450 °C. The relatively low process temperature is due to the type of used feed - n-undecane. The study of the catalytic cracking at this temperature allows doing a more qualitative comparison of the activity of the catalytic systems presented in the paper.

The composition of the gaseous cracking products was analyzed on a Chromos GH-1000 gas chromatograph equipped with a capillary column (SiO$_2$, 30 m × 0.32 mm) and a flame-ionization detector to determine the composition of hydrocarbon gases (C_1–C_{5+}); a packed column (CaA zeolite, 2 m × 3 mm) and a thermal conductivity detector to measure the content of inorganic components in the gas, such as N_2,

Table 1
Tested catalytic systems.

Sample	ZT, wt%	Al$_2$O$_3$, wt%	Al-Si, wt%	Clay**, wt%	Additive, wt%	Additive type	Additive introduction
e-cat	18	20	40	22	–	–	–
l-cat-1*	18	20	40	22	–	MM NH$_4$+**	At the stage of the composition preparation
l-cat-2	18	20	40	–	22	MM 5% H$_2$SO$_4$***	
l-cat-3	18	20	40	–	22	MM 15% H$_2$SO$_4$***	
l-cat-4	18	20	40	–	22	PG NH$_4$+****	
l-cat-5	18	20	40	–	22	PG 5% H$_2$SO$_4$****	
l-cat-6	18	20	32	20	10	Mg: Al = 0.32: 1	
l-cat-7	18	20	32	20	10	Mg: Al = 0.49: 1	
l-cat-8	18	20	32	20	10	Mg: Al = 1.90: 1	
l-cat-9	18	20	32	20	10	Mg: Al = 2.58: 1	
l-cat-10	18	20	32	20	10	Mg: Al = 4.30: 1	
l-cat-11	18	20	32	20	10	Mg: Al = 2.94: 1	
l-cat-12	18	20	32	20	10	(Mg + Cu): Al = 3.51: 1	
l-cat-13	18	20	32	20	10	(Mg + Co): Al = 3.51: 1	
l-cat-14	18	20	32	20	10	(Mg + Zn): Al = 3.25: 1	
l-cat-15	18	20	32	20	10	(Mg + Ce + Cu): Al = 3: 1	
l-cat-16	18	20	32	20	10	(Mg + Co): Al = 1: 1	
l-cat-17	18	20	32	20	10	(Mg + Co): Al = 1: 2	
l-cat-18	18	20	32	20	10	(Mg + Co): Al = 1: 3	
l-cat-19	18	20	32	20	10	PG 5% H$_2$SO$_4$****; (Mg + Co): Al = 0.50: 1	

* l-cat-1 – the laboratory sample, which is an analog of e-cat;
** Montmorillonite (MM) treated with a solution of ammonium nitrate;
*** Montmorillonite (MM) treated with 5 and 15% solutions of sulfuric acid, respectively;
**** Palygorskite(PG) treated with solutions of ammonium nitrate and 5% sulfuric acid, respectively.