



Accumulation of condensation products on the catalyst surface and catalyst regeneration in the process of ethylene conversion over HZSM-5 Catalyst

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Abstract

In the presented work, the process of ethylene conversion over the HZSM-5 catalyst has been extensively investigated. It was determined that the mentioned catalyst has a sufficiently high activity in the ethylene conversion process. Analysis of the obtained products shows that the mechanism of this process is very complex. To clarify these issues, alongside studying the conversion of ethylene into gaseous and liquid substances at various temperatures over the HZSM-5 catalyst, special attention was paid to the kinetics of accumulation, the quantity of condensation products (CP) formed on the surface, and catalyst regeneration. It was determined that the catalyst's activity in this process is observed only after the formation of 6-8% CP on the surface within ~20 minutes from the start of the reaction.

Keywords: Catalysis, zeolite, ethylene, coking

Introduction

In recent decades, the HZSM-5 catalyst has been widely used in processes for the purposeful conversion of hydrocarbons into various substances. In this process, the activity of the zeolite-containing catalyst depends on many factors: the structure of the zeolite, thermal stability, Si/Al ratio, the nature of the exchange cation, the addition of various modifiers, etc [1, 3]. At the same time, one of the main factors affecting the activity of zeolite-containing catalysts is the formation of condensation products (CP) on the surface during hydrocarbon conversion. In general, there are contradictory opinions in the literature regarding the role of CP formed on the surface during the process. Although this factor is taken into account in some cases, in most works, any process is investigated without providing any information about the CP formed on the surface during the conversion of olefins over high-silica zeolite catalysts.

Literature Review

An analysis of studies in the literature shows that the oligomerization and conversion of hydrocarbons into aromatic hydrocarbons over a zeolite catalyst occur at the acid centers. It is known that condensation products formed on the surface of the zeolite also form at the acid centers. In this case, the following question arises: if CP accumulates at the acid centers within 20-30 minutes from the initial moment of the investigated process, then at which active centers does the conversion of gaseous olefins take place?

Experimental Part

The HZSM-5 catalyst has a sufficiently high activity in the ethylene conversion process. Analysis of the obtained products shows that the mechanism of this process is very complex. To clarify these issues in the research, alongside studying the conversion of ethylene into gaseous and liquid substances over the HSZ (high-silica zeolite) catalyst at various temperatures, special attention was given to the accumulation kinetics and quantity of CP formed on the surface, as well as the regeneration of the catalyst. Since the

formation of CP on the surface during the conversion of ethylene over the catalyst at various temperatures sharply darkened the color of the samples, it was considered more appropriate to study the acidic properties of these samples via NH₃ adsorption using a McBain balance. Before ethylene adsorption, the catalyst sample was regenerated in an air stream at a temperature of ~550°C and then purged with a nitrogen stream to remove oxygen. Before use, the nitrogen was completely purified of oxygen by passing it through a reactor containing a 20 cm³ layer of Cu catalyst.

Results

One of the main goals of researchers is the creation of catalytic systems that can remain active for a long time while demonstrating high selectivity and activity. Although HZSM-5 zeolites, which are widely used for this purpose, have high catalytic performance, their specific structure limits the formation of heavy hydrocarbons (middle distillate fractions) [4, 5]. The deactivation (loss of activity) of such catalysts is usually explained by two main reasons — the blockage of micropores and the shielding of active acid centers. The difficulty of the generated oligomers moving within the zeolite channels (weak diffusion) causes them to accumulate inside and subsequently undergo coking, leading to the rapid loss of catalyst activity.

To determine the nature of the CP formed during the conversion of ethylene over the HZSM-5 catalyst at various temperatures, the dependence of its quantity on temperature was investigated. The obtained results are given in Table 1.

Table 1: Dependence of the amount of CP on time during ethylene conversion over HZSM-5 catalyst at different temperatures

No.	Time, min	25°C	100°C	200°C	300°C	400°C	450°C
1	5	2.0	1.7	1.8	2.9	1.7	1.8
2	10	3.8	3.1	3.7	3.9	3.1	3.3
3	15	5.9	4.9	5.2	5.4	4.7	4.8
4	20	6.6	5.5	6.1	6.4	5.8	5.9
5	25	7.2	6.2	6.8	7.3	6.3	6.4
6	30	7.2	6.2	6.8	7.3	6.3	6.4

Table 1 shows the dependence of the amount of CP accumulated on the catalyst surface on time during ethylene conversion at different temperatures. As can be seen from the table, supplying ethylene over the HZSM-5 catalyst at 25°C for 20 minutes increases the catalyst weight by 7.2%. Naturally, physical adsorption of ethylene occurs on the

catalyst surface at room temperature. However, as the temperature rises during desorption, ethylene molecules adsorbed at various acid centers of the zeolite can undergo chemical transformation, including oligomerization, and for this reason, its complete desorption temperature using a nitrogen flow rises to 400°C (Table 2).

Table 2: Removal of CP accumulated during ethylene conversion over HSZ catalyst at different temperatures

No.	CP accumulation temperature, °C	CP removal temperature, °C	CP removal time, min	Fraction of CP removed by N ₂ flow, %	Fraction of CP removed by air flow, %
1	25	400	40	100	-
2	100	400	40-45	100	-
3	200	450	50	70.58	29.42
4	300	500	80-90	34.2	65.8
5	400	550	100-110	17.79	82.21
6	450	550	110-120	15.75	84.25

As seen from Table 1, the weight increase during ethylene adsorption over the HZSM-5 catalyst at 100°C is 6.2%. When the desorption of ethylene adsorbed at this temperature is carried out, due to the formation of oligomers in the channel as the temperature increases, similar to the previous case, the removal of ethylene is completed at a temperature of ~400°C with a nitrogen stream. During ethylene conversion at 200°C, the dependence of CP formed on the catalyst surface on time and the temperature of catalyst regeneration differs from previous cases. As can be seen, in this case, the formation of 6.8% CP is observed within 20-25 minutes of supplying ethylene. The desorption of ethylene adsorbed at 200°C has a complex character. Thus, when heated with a nitrogen stream, only 70.58% of the formed CP is desorbed. The remaining part is removed only by burning with the supply of air or oxygen. This indicates that at the specified temperature in the zeolite channel, both the conversion of ethylene into condensation products and the physical adsorption of the oligomers formed during this process occur. As can be seen from the results given in Table 1, at 300°C within 25-30 minutes, 7.3% condensation products accumulate on the catalyst, and the CP formed at this temperature also consists of two parts. In this case, although 34.2% of the formed CP is removed by heating with a nitrogen stream, the remaining part is dynamically removed only by burning with an air or oxygen stream.

References

1. Ono L, Nakatani H, Kitagawa H, Suzuki E. The role of metal cations in the transformation of lower alkanes into aromatic hydrocarbons. *Studies Surt. Sci. Catal.* 44 – Amsterdam Elsevier, 2007:44:279-290.
2. Del Campo P, Martínez C, Corma A. Activation and conversion of alkanes in the confined space of zeolite-type materials. *Chemical Society Reviews*, 2021:50(15):8511-8595.
3. Zaikovskii VI, Vosmerikova LN, Vosmerikov AV. Nature of the Active Centers of In-, Zr-, and Zn-Aluminosilicates of the ZSM-5 Zeolite Structural Type. *Russian Journal of Physical Chemistry*, 2018:92(4):689-695.
4. Ji Y, Yanga H, Zhang Q, Yan W. *J. Solid State Chemistry*, 2017:251:7.
5. Ji Y, Yang H, Yan W. *Catalysts*, 2017:7(12):367.