CONVERSION OF C_6 HYDROCARBONS ON Zn/H(Na,K)L ZEOLITE

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abstract: Aromatization of C_6 hydrocarbons (hexane isomers and cyclohexane) was performed on a Zn/H(Na,K)L zeolite. Increasing temperature favors aromatization reactions, but leads to intense cracking. Zinc modifier promotes direct dehydrogenation leading to benzene, but reactions that lead to aromatics also take place on the acid sites remained in the zeolite. Cyclohexane is the reaction intermediate in the direct dehydrogenation pathway.

Keywords: L zeolite, Zn/L, hexane conversion, cyclohexane conversion

Introduction

Valorization of saturated hydrocarbons by transforming them into more valuable products is a topic widely covered in literature, aromatization of light alkanes being one of the processes that apply this concept [1-3]. Many types of zeolite structures were tested for this purpose, with ZSM-5 being most frequently used because of its acidic properties, pore structure and shape selectivity [2,4-6].

L zeolite has a structure composed of cylindrical 12-membered rings, with a pore diameter of 7.1 Å that allows an easy access of hydrocarbon molecules to the active centers [7]. KL zeolite modified with platinum was extensively studied for the aromatization of n-hexane with good selectivity for benzene, as an alternative method for obtaining aromatic hydrocarbons from alkanes and naphtha [3,8-18]. The high selectivity for benzene was attributed either to the structural parameters of this zeolite, or to its basic properties related to the alkaline cation [10]. Meanwhile, there is a consensus that the reaction mechanism is monofunctional and implies dehydrocyclization on the platinum clusters inside the zeolite channels, the zeolite support being non-acid in order to avoid secondary acid-catalyzed reactions [16-18].

For ZSM-5 zeolites, modification with Zn or Ga strongly increases the selectivity for aromatics, due to a change in the reaction pathways [1,2,4,19]. The modifiers promote dehydrogenation reactions leading to aromatics, instead of acid-catalyzed hydrogen transfer reactions that, besides aromatics, lead to large amounts of alkanes remaining in the reaction products. Due to the zinc beneficial effect in these processes, we intended to observe the role of zinc as modifier in aromatization of some C_6 hydrocarbons on L zeolite. We studied

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the activity of a LTL zeolite and that of Zn-modified LTL catalysts in the aromatization of n-hexane, 2-methylpentane, 3-methylpentane and cyclohexane. The catalyst was selective for obtaining a liquid fraction rich in aromatic hydrocarbons and C_5-C_8 oligomers.

Experimental

The LTL zeolites were analyzed and characterized at the "L.V. Pisarzhevsky" Institute of Physical Chemistry from the Ukrainian Academy of Sciences from Kiev, Ukraine. The as-synthesized parent sample, NaKL, had the following composition: $K_6Na_3[Al_9Si_{27}O_{72}] \cdot 21H_2O$. This parent sample was exchanged in the ammonium form and calcined at 450^oC for 2 h. Upon calcination, the composition was determined by atomic absorption spectroscopy to be $H_{3.33}Na_{2.79}K_{2.98}[Al_9Si_{27}O_{72}] \cdot 21H_2O$.

The calcined sample was obtained by impregnation of the parent zeolite with a $Zn(NO_3)_2$ solution, so that the final catalyst to have a 2.8% Zn concentration. The two catalyst samples were calcined in steps up to 550^oC.

All catalytic tests were performed in a fixed bed glass reactor, at atmospheric pressure and temperatures between 400 and 525^oC; the LHSV of reactant was $2h^{-1}$. Before the catalytic tests, the catalyst was heated at 550^oC in airflow, and then the temperature was lowered to the reaction temperature. After the reactor, reaction products were cooled and the liquid and gaseous fractions separately collected and analyzed by gas chromatography. Hexane (Merck, 99%), 2-methylpentane (Fluka AG, 99%), 3-methylpentane (Fluka AG, 99%) and cyclohexane (Merck, 99.7%) were used as raw materials. Total conversion was calculated as the amount of feed transformed into products divided by the amount of feed introduced into the reactor. Selectivity for aromatics was calculated as the amount of aromatics formed in the reaction divided by the amount of feed transformed into products.

Results

The effect of temperature on the activity and selectivity for aromatics in the conversion of n-hexane on Zn/H(Na,K)L zeolite is shown in fig. 1 and table 1. The conversion has low values on the entire temperature range (400-525^oC) that increase slowly with temperature up to 10%. The selectivity for aromatics also increases with temperature, reaching a maximum of 45% at 500^oC. This increase is expected since many of the reactions that might lead to aromatic hydrocarbons (cyclization and dehydrogenation) are endothermic. At 525^oC, the slightly lower value for the selectivity for aromatics could be due to more intense cracking reactions and coking.

A very small volume of gas fraction is obtained at all temperatures, suggesting that cracking does not play an important role in the process. Due to its low Si/Al ratio and to the presence of Na and K in the structure, the acidity of this zeolite is smaller that in other zeolites used in hydrocarbon conversions, such as ZSM-5, so cracking is low in our catalyst.

Among gaseous hydrocarbons (table 1), propene and butenes have almost equal shares, larger than ethene's one, showing that cracking leads mainly to $C_3H_8 + C_3H_6$ and $C_4H_8 + C_2H_6$ hydrocarbons. Hydrogen was also observed in the reaction products, proving dehydrogenation reactions that presumably take place on zinc oxide.
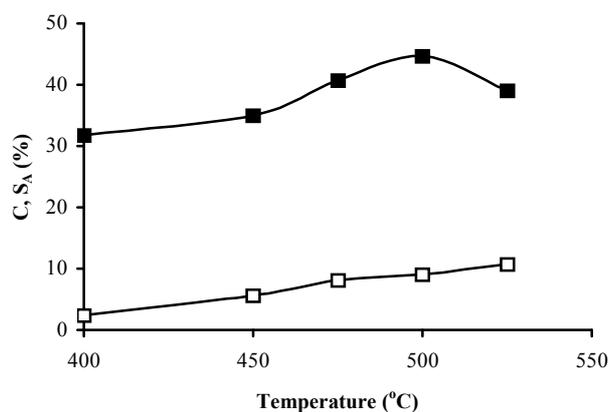
Fig. 1. *Influence of temperature on the activity and selectivity for aromatics in n-hexane aromatization on Zn/H(Na,K)L zeolite (LHSV = 2 h⁻¹; □ – n-hexane conversion; ■ – selectivity for aromatics.*

Table 1. Composition of reaction products in the aromatization of n-hexane on Zn/H(Na,K)L zeolite (LHSV = 2h⁻¹)

Products	400°C	450°C	475°C	500°C	525°C
Hydrogen	0.4	0.1	0.1	0.2	0.3
Methane	2.6	0.2	1.1	1.0	1.1
Ethane	9.2	0.5	2.1	0.8	2.6
Ethene	2.6	0.4	1.8	0.9	2.6
Propane	19.9	1.6	6.4	0.7	1.4
Propene	12.0	10.3	8.9	3.4	3.7
Butanes	1.3	0.2	0.4	0.2	0.3
Butenes	7.9	10.8	10.0	2.6	2.8
Oligomers	12.3	30.4	28.6	45.4	46.2
Benzene	11.9	28.7	8.9	9.8	4.2
Toluene	4.0	4.9	2.1	4.1	2.5
Ethylbenzene + Xylenes	13.4	9.1	12.1	12.9	10.2
C_{9+} aromatics	2.5	2.8	17.5	18.0	22.1

The main reaction products are oligomers, consisting in C_5-C_8 hydrocarbons among which hexane isomers, cyclohexane, methylcyclopentane and cyclohexene were identified. On acidic zeolites, aromatics are usually formed from alkanes by a succession of reactions on the acid sites, starting with cracking or dehydrogenation in order to obtain an alkene. This initial step is followed by oligomerization or alkylation of the alkene with an alkane, cyclization and dehydrogenation, leading to an aromatic hydrocarbon. If the catalyst is bifunctional (with a dehydrogenation component besides the acid function) and the starting alkane has at least six carbon atoms, then direct dehydrogenation is also possible. From the data in table 1, the first pathway seems to be active on Zn/H(Na,K)L. The large concentrations of C_5-C_8 oligomers that are formed, particularly at higher temperatures, show that the first succession of reactions is favored in these conditions. At lower temperatures, benzene is formed in large amounts, at 450°C being the main aromatic in the reaction products. This fact suggests that direct dehydrogenation also plays an important role, the presence of cyclohexane, methylcyclopentane and cyclohexene in the products supporting this hypothesis. As temperature increases, ethylbenzene, xylenes and C_{9+} aromatics become increasingly important, their formation being favored in the relatively large (7.1 Å diameter) circular pores of the zeolite.

Because the maximum selectivity for aromatics was obtained at 500°C, the rest of the catalytic tests were performed at this temperature.

The influence of the starting hydrocarbon was investigated on the Zn/H(Na,K)L zeolite, using n-hexane, 2-methylpentane (2MeP), 3-methylpentane (3MeP) and cyclohexane (CH) as feed. 2MeP and 3MeP were tested because their formation was observed in the first series of experiments, and CH was tested in order to confirm the direct dehydrogenation pathway to benzene, that has CH as an intermediate. Results are shown in fig. 2 and table 2.
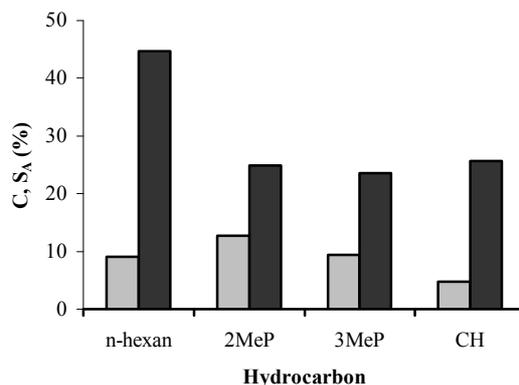
Fig. 2. *Influence of hydrocarbon nature on the activity and selectivity for aromatics in C_6 hydrocarbons aromatization on Zn/H(Na,K)L zeolite (LHSV = 2 h^{-1}; ■ – conversion; ■ – selectivity for aromatics.*

Among hexane isomers, results are similar, with a slightly higher conversion for 2MeP. The selectivity for aromatics has much lower values for 2MeP and 3MeP compared to n-hexane, probably because they can not be directly dehydrogenated to benzene and, in order to transform in aromatics, they have to pass through an isomerization step at one time of the reaction. For 2MeP and 3MeP, benzene is the main aromatic hydrocarbon, that can be formed by either isomerization to hexane and then dehydrogenation, or by cyclization to methylcyclopentane then isomerization to cyclohexane and dehydrogenation.

Oligomers were again present in high concentrations in the reaction products. Isomerization of hexane, 2MeP and 3MeP takes place on the acid sites that still exist in the zeolite, and the composition of hexane isomers is similar in the catalytic tests. The similarity of reaction products distribution among C_6 aliphatic hydrocarbons suggests that reaction pathways are the same, leading to the same intermediates and products. Both direct dehydrocyclization and the cracking - oligomerization - dehydrocyclization succession seem to be co-operating for these hydrocarbons.

CH has a more stable molecule and is less reactive on acid sites than hexanes, so its conversion has lower values than those obtained for the other hydrocarbon feeds. The fact that benzene concentration is double compared to that obtained for hexanes and that hydrogen is present in larger amounts confirm that in this case conversion takes place mainly by direct dehydrogenation.

Table 2. **Composition of reaction products in the aromatization of some C_6 hydrocarbons on Zn/H(Na,K)L zeolite (LHSV = 2h^{-1})**

Products	n-hexane	2MeP	3MeP	CH
Hydrogen	0.2	0.5	0.3	1.6
Methane	1.0	0.7	1.9	3.3
Ethane	0.8	2.1	4.0	4.9
Ethene	0.9	1.9	3.8	2.7
Propane	0.7	1.2	0.9	0.5
Propene	3.4	8.5	8.7	5.5
Butanes	0.2	0.9	1.3	6.0
Butenes	2.6	8.9	9.4	12.0
Oligomers	45.4	50.9	46.2	37.2
Total aromatics	44.8	24.4	23.5	26.3
Benzene	9.8	12.9	11.6	19.7
Toluene	4.1	2.1	1.9	2.2
Ethylbenzene + Xylenes	12.9	9.4	5.9	2.2
C$_{9+}$ aromatics	18.0	-	4.1	2.2

The influence of the promoted catalyst is discussed compared to the parent zeolite, H(Na,K)L. The results are shown in figs. 3-5 for n-hexane, 2MeP and CH feeds.

For all starting hydrocarbons conversion values are similar on the two catalysts, but the selectivity to aromatics is intensified when zinc is present in the catalyst, confirming its

promoting role. This finding is in line with literature data that prove the positive influence of zinc promoter in aromatization reaction on other zeolites.

On the parent zeolite, aromatic hydrocarbons are formed in very small amounts, and they consist in benzene, toluene and no xylenes except for the reactions with n-hexane. On the zinc-modified catalyst mainly benzene and xylenes concentrations increase.
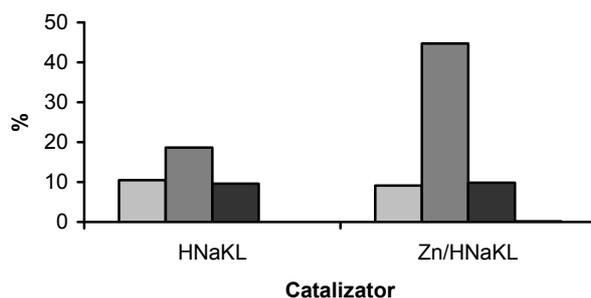
Fig. 3. *Catalytic activity and reaction products composition in n-hexane aromatization on H(Na,K)L and Zn/H(Na,K)L catalysts. LHSV = 2 h^{-1}, T = 500°C. ▪ –conversion; ▪– selectivity for aromatics, ▪-benzene concentration.*
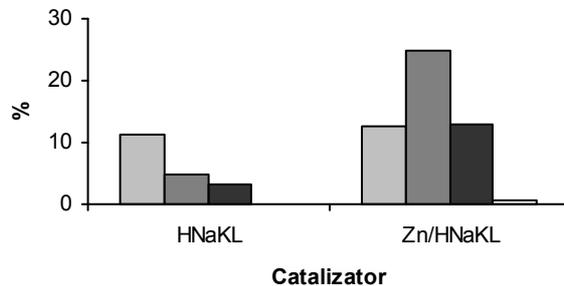
Fig. 4. *Catalytic activity and reaction products composition in 2MeP aromatization on H(Na,K)L and Zn/H(Na,K)L catalysts. LHSV = 2 h^{-1}, T = 500°C. ▪ –conversion; ▪– selectivity for aromatics, ▪-benzene concentration, □- hydrogen concentration.*
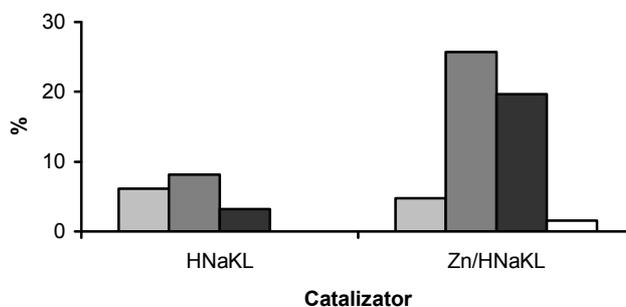
Fig. 5. *Catalytic activity and reaction products composition in CH aromatization on H(Na,K)L and Zn/H(Na,K)L catalysts. LHSV = 2 h⁻¹, T = 500ºC. ■ –conversion; ■– selectivity for aromatics, ■-benzene concentration, □-hydrogen concentration.*

Benzene is formed probably by dehydrocyclization, while xylenes result from coupling two butene molecules. Other differences are the higher hydrogen and methane concentrations in reaction products on zinc-modified catalyst. The higher hydrogen amount proves that zinc promotes dehydrogenation reactions and it correlates with the higher selectivity for aromatics and higher benzene concentration in the reaction products.The fact that methane is formed in larger amounts on zinc-modified zeolites was also observed in aromatization reactions on ZSM-5 [19], and it was explained by the hydrogenolysis activity of zinc ions.

Conclusion

The Zn/H(Na,K)L catalyst showed a good selectivity to aromatics compared to the parent HNaKL zeolite, the main aromatic hydrocarbon being always benzene. This proves that zinc promotes direct dehydrogenation reactions, but is not involved in the activation of the initial hydrocarbon. Increasing temperature favors the aromatization process, but at high temperatures cracking becomes dominant. The presence of acid sites in the zeolite promoted reactions that lead to large amounts of C_5-C_8 hydrocarbons, including cyclohexane, methylcyclopentane and cyclohexene.

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