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C_2–C_4 ALKENES CONVERSION OVER ZVM+2 % Zn HIGH-SILICA ZEOLITE CATALYST AT HIGH VOLUMETRIC FLOW RATES

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Abstract. C_2–C_4 alkenes conversion over high-silica zeolite catalyst modified with 2 mas % of Zn has been investigated at the laboratory plant of flow type within temperatures ranges of 723–773 K and volumetric flow rates 1000–30000 h^{-1}. It has been shown that a propylene high conversion and high yield of liquid catalizate containing lower arenes are achieved at space velocities of 20000 h^{-1}.

Keywords: modified high-silica zeolite, propylene, volumetric flow rate, alkenes, arenes.

1. Introduction

C_2–C_4 alkenes are present in gases of thermal and thermocatalytic processes of oil refining. Alkenes content in gases of vacuum gas oil catalytic cracking is about 50 mas %. At refineries gaseous alkenes are used for the production of high-octane components of motor fuels as well as raw material for petrochemical synthesis. At some refineries, namely at Ukrainian ones, refinery gases including alkenes are mainly used as power-plant fuel. One of the ways of refinery gases conservation is arenes production *via* transformation of alkenes presented in the gases over high-silica zeolite catalysts.

A lot of experimental and theoretical works are dedicated to the catalytic conversion of gaseous hydrocarbons over high-silica zeolites [1-4]. The regularities of alkanes and alkenes C_2–C_4 were investigated within the temperature range of 573–873 K over high-silica zeolites of ZSM type, both non-modified and modified by various metals (Zn, Ga, Cd, Ni, Co).

During conversion of C_3–C_4 alkanes over high-silica zeolite catalysts modified with Zn or Ga liquid catalysate is formed, which contains mainly arenes C_6–C_8 and gaseous products H_2, CH_4, C_2H_6, C_2H_4, C_3H_8 and C_3H_6. The arenes yield is 40–50 % [5-7] at 823–873 K and space velocities 500–1000 h^{-1}. Volumetric flow rate (VFR) is a ratio of gas flow and the catalyst volume under normal conditions. During hydrocarbons conversion the coke is formed over the catalyst surface and after 5–6 h of the catalyst operation its activity decreases. After coke burning by air oxygen the catalyst activity renews completely [8, 9].

The process of lower arenes production from the components of the associated petroleum gas using their conversion over modified high-silica zeolite catalyst has been developed and implementd commercially [10]. Since a service cycle is short in such a process and space velocities are small the process is implementd in the reactor with fluidized catalyst.

At the conversion of C_2–C_4 alkenes over modified with metals high-silica zeolite catalyst gaseous products and liquid catalysate containing lower arenes are formed. Under mentioned conditions alkenes are converted almost completely. The liquid catalysate yield is 60–80 % [11, 12]. Obviously, the above-mentioned process of arenes production from the components of the associated petroleum gas may be used also for the production of arenes from refinery gases, *viz* gases after catalytic cracking, which contain alkanes and alkenes C_2–C_4. The technological process of arenes production from the raw material with olefines high content has been developed [13].

The development of plants for the production of arenes from refinery gases in the reactor with fluidized catalyst needs considerable capital outlays. Moreover, losses of the expensive catalyst are essential. Thus it would be interesting to implement such process in the reactor with a stationary catalyst. This work deals with the experimental results concerning C_2–C_4 alkenes catalytic conversion at high volumetric flow rates under which it is possible to implement the process of arenes production from refinery gases alkenes in the reactor with the stationary catalyst.

2. Experimental

In order to investigate C_2–C_4 alkenes catalytic conversion the high-silica zeolite of ZVM type modified with 2 mas % of Zn has been used as a catalyst. The

physico-chemical characteristics of the catalyst are represented in Table 1.

Characteristics of initial ZVM zeolite

Index	Value
Silicate module ($SiO_2 : Al_2O_3$)	23
Specific surface, m^2/g	400–450
Static adsorption capacity, cm^3/g:	
– by water vapors	0.08
– by heptane vapors	0.16–0.18
Na_2O concentration, mas %	<0.01

The laboratory plant of continuous type was used. The quartz tube with diameter of 6 mm was a reactor. It was located in the electric oven. The length of isothermal area in the oven was approximately 20 cm (80 % of the total length). The temperature of the tube external wall was measured during the experiments. The layer of fine-grained catalyst by volume of 2 cm^3 was located inside the tube. The size of catalyst grains was 0.2–0.3 mm. Alkene was fed to the reaction tube through a flowmeter. After the tube the reaction products were cooled to 253 K in a special vessel where a liquid catalysate was collected. The amount of liquid catalysate formed for a definite period of time of alkenes transformation and corresponding reaction products was determined by a weight method. Then the volume of gaseous products was measured. The compositions of liquid catalysate and gaseous products were determined using a chromatographic analysis. Taking into account the measured gaseous flow rates, the amount of obtained liquid catalysate and the composition of reaction products we calculated the VFR (ratio between alkene and catalyst volume under normal conditions) and the conversion of alkene, liquid catalysate yield (to calculate for used alkene) and amount of obtained catalysate per time unit (to calculate for unit of a catalyst volume).

3. Results and Discussion

The VFR was changed within 1000–30000 h^{-1}. The temperature in the reaction zone was 723–773 K. At higher temperatures the catalyst coking was more intensive. The experimental results are represented in Table 2 and Fig.

Catalytic conversion of ethylene and butylenes was carried out at 773 K and 20000 h^{-1}. The experimental results are represented in Table 2 and Fig.

One can see from the obtained results that at 773 K the increase of VFR from 1000 to 20000 h^{-1} decreases the propylene conversion from 99 to 86.9 %, as well as a liquid catalysate yield from 64.0 to 53.3 %. The further increase of VFR to 30000 h^{-1} essentially decreases the catalysate yield to 42.1 %. At VFR 20000 h^{-1} and 723 K the catalysate yield decreases to 41 %.

The increase of VFR decreases hydrogen, methane and ethane concentrations in the gaseous products and increases ethylene, propylene, propane and C_4 hydrocarbons content. The composition of liquid products changes incidentally.

The increase of VFR increases the amount of formed catalysate to calculate for the catalyst volume unit per time unit. At 20000 h^{-1} and 773 K the catalysate yield is 20 g/cm^3 per hour or 20 t/m^3 per hour. The butylenes conversion and *pro tanto* liquid catalysate yield are greater than those of propylene, whereas the ethylene conversion is less.

It is shown in [12] that under atmospheric pressure and given conditions (temperature and VFR) of the conversion of C_2–C_4 alkenes over high-silica zeolites the conversion of initial compounds and yield of liquid catalysate do not depend upon alkenes concentrations in gaseous mixtures. The general yield of liquid catalysate is subject to additivity rule. On the basis of data from Table 2 one can accurately determine the liquid catalysate yield during alkenes conversion of catalytic cracking gases over modified high-silica zeolite catalysts.

Effect of VFR on the propylene catalytic conversion

| Temperature, K	VFR, h^{-1}	Composition of gaseous products, vol %							Composition of liquid catalysate, mas %					C_3H_6 conversion, %	Yield of liquid catalysate, mas %
		H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	$\sum C_4$	Aliphatic hydrocarbon	Benzene	Toluene	Xylenes	C_{9+}		
773	1000	67.86	14.52	6.44	3.08	6.48	0.93	0.7	3.2	21.7	45.9	26.1	3.1	99.0	64.0
773	10000	41.09	7.54	4.20	17.48	16.24	10.53	2.92	3.8	26.8	40.0	23.0	6.4	90.2	53.7
773	20000	42.54	4.62	2.55	18.35	13.78	13.33	4.83	3.9	27.1	42.4	21.8	4.8	86.9	53.3
773	30000	36.51	3.08	2.09	21.06	11.9	19.6	5.76	4.2	27.6	41.9	20.9	5.4	80.3	42.1
723	20000	21.8	4.76	3.5	22.9	18.09	20.4	8.55	11.1	20.1	40.4	21.2	7.2	78.6	41.0
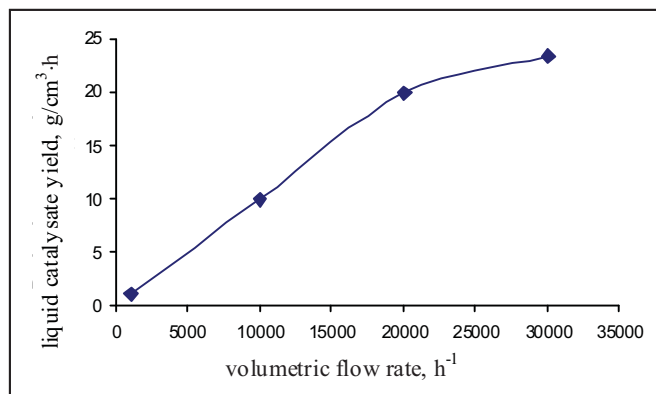
Fig. Dependence of liquid catalysate yield (to calculate for 1 cm^3 of the catalyst per 1 h) upon arenes VFR at 773 K

On the basis of the chemical composition of liquid catalysate and gaseous products presented in Table 2 the material and heat balances of the alkenes conversion over high-silica zeolite catalyst have been calculated. Under mentioned conditions alkenes are converted with slight heat evolution, *i.e.* the process is close to thermoneutral. At the implementation of industrial process of arenes production from refinery gases with their preheating to the necessary temperature the regime in the reaction zone will be close to the isothermal one.

At the refineries the gas flow of catalytic cracking plants (typical productivity by raw material is 1 million ton) equals to 10000 nm^3/h. Alkenes content in the gases is 50 mas %.

For the implementation of arenes production from catalytic cracking gases *via* their conversion over high-silica catalyst at VFR 20000 h^{-1} it is necessary to use 0.5 m^3 of the catalyst. Under such small catalyst volume and service cycle of 5–6 h it is possible to implement the process in the reactor with multi-stage arrangement of the stationary catalyst. So, the reactor block will consist of two reactors and the initial raw material would be feed to the every stage of every reactor by turns. The catalysts from all stages will be regenerated simultaneously by coke burning with air.

4. Conclusions

The high conversion of propylene and butylene (86 and 92 % respectively) and sufficiently high yield of liquid catalysate (53 and 59 %, respectively) containing mainly lower arenes are achieved at C_3–C_4 alkenes conversion at volumetric flow rate 20000 h^{-1} and 773 K over high-silica zeolite catalyst modified with 2 mas % of Zn. Under such conditions it is possible to implement the process of arenes production from catalytic cracking gases in the reactor with multi-stage arrangement of the stationary catalyst.

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ПЕРЕТВОРЕННЯ АЛКЕНІВ C_2–C_4 НА ВИСОКОКРЕМНЕЗЕМИСТОМУ ЦЕОЛІТОВОМУ КАТАЛІЗАТОРІ ЦВМ+2% Zn ПРИ ВИСОКИХ ОБ'ЄМНИХ ШВИДКОСТЯХ

Анотація. *На лабораторній установці проточним методом досліджено протікання реакції перетворення алкенів C_2–C_4 на висококремнеземистому цеолітовому каталізаторі, модифікованому 2 % мас. цинку в інтервалі температур 723–773 К і об'ємних швидкостях 1000–30000 год$^{-1}$. Показано, що за високої об'ємної швидкості 20000 год$^{-1}$ досягається висока ступінь перетворення пропілену і бутилену та високий вихід рідкого каталізату, який містить нижчі арени.*

Ключові слова: *модифікований висококремнеземистий цеоліт, пропілен, об'ємна швидкість, алкени, арени.*