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Conversion of propane-butane fraction to arenes on zeolite catalysts modified by gallium oxides

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Abstract

The main industrial technologies used currently for the conversion of natural and associated petroleum gas (APG) are steam reforming of methane and APG into synthesis gas on alum-nickel catalysts which is carried out at 860–950 ° C and the Fisher-Tropsch process. The synthesis gas is further processed into hydrocarbons on iron and cobalt catalysts. The high temperature (860–950 ° C) in the processes, especially at the first stage of synthesis gas production and the low selectivity of the target products in the Fischer-Tropsch process are major drawbacks of these technologies for the processing of natural gas (methane) and APG. The paper provides the comparative analysis of the activity and selectivity of microporous high-silica zeolites of the ZSM-5 type, synthesized using various additives, during the conversion of natural associated gas.

Keywords: Conversion, zeolite, associated petroleum gas, propane, temperature, catalyst;

1. Introduction

In the 70s of the 20th century microporous high-silica zeolites (VCC) of the ZSM-5 family were discovered, and due to their unique microporous structure (pore size 0.5-0.8 nm), they have been widely used in many petrochemical processes including cracking, paraffin isomerization, alkylation, isomerization and disproportionation of aromatic hydrocarbons, as well as the conversion of low molecular weight alcohols and synthesis gas into higher hydrocarbons. This discovery enabled the development of effective catalytic systems and technologies making use of these compounds to convert lower alkanes C1-C4 to higher hydrocarbons. Recently industrial technologies for chemical processing of APG without its preliminary separation into separate components have not been developed yet. A possible use of APG is to convert C2-C4 gases into liquid hydrocarbons and "dry gas" [1-5]. Zeolite catalysts can be the most efficient for this purpose.

2. Discussion

ZSM-5 high-silica zeolites were obtained by synthesis with a silicate module 50 from alkaline silica gel using an organic structur-forming additive of hexamethylenediamine (CKE-G) and alcohol fraction (CKE-SF), a by-product of caprolactam production, for 2-4 days at 175-180 ºC, as described in. [6-7]. After being synthesized, the obtained zeolite powders were washed with water, dried for 8 hours at 110 ºC and calcined for 8 hours at 600 ºC. H-CKE-G and H-CKE-SF zeolites

were modified to the active form by 25% aqueous NH4Cl solution at 90° C and continuously stirring with a mechanical stirrer for 2 hours. The obtained substance was dried at 110°C and calcined at 600°C for 6 hours. A physicochemical study of the obtained zeolites was performed using IR spectroscopy (Nicolet 5700 FTIR spectrometer), X-ray phase analysis (DRON-3 X-ray unit, Mo-anode, Ni filter and electron microscopy (Jem electron microscope) -100-CX). The X-ray patterns of synthesized H-CKE-G and H-CKE-SF zeolite show lines with interplanar distances (d, Å): 11.05, 10.19, 4.26, 4.07, 3.87, 3.83, 3.73, 3.66, characteristic of high-silica ZSM-5 type zeolites. In N-CKE-G micrograph zeolite particles are of globular shape10–15 μm in size. They are composed of a large number of smaller crystals, which are 0.5–1.0 μm or less in size. The micrograph of N-CKE-SF zeolites, indicate that the particles are of three shapes: globular (10–15 μm), composed of a large number of smaller crystals (0.5–1.0 μm); hexagonal and quadrangular prism. The IR spectra of the obtained H-CKE-G and H-CKE-SF zeolites have absorption bands at 1000–1200, 795–800, 450, and 540 cm – 1. The strong absorption band at 1000–1200 cm-1 corresponds to antisymmetric stretching vibrations of TO4 tetrahedra, the absorption band at 795 cm refers to stretching vibrations involving mainly SiO4 tetrahedra. The position of this band is influenced by the silicate module (SiO2 / Al2O3) of the zeolite. The absorption band at 541 cm-1 corresponds to the 5-membered rings in the framework of the zeolite and indicates that the synthesized zeolite belongs to the ZSM-5 type. According to X-ray phase analysis and IR-spectroscopy all the obtained N-CKE-G and N-CKE-SF samples refer to zeolites of the ZSM-5 type.

3. Research Methods

Modification of the initial N-CKE-G and H-CKE-SF zeolite with 1-3% wt. Ga2O3 wasconducted by impregnation method. For this, H-CKE-G and H-CKE-SF zeolite granules (granule size is 2-3 mm) were impregnated with aqueous solutions of gallium nitrate considering the moisture capacity of the zeolites, then the catalysts were dried at 110 0C and calcined for 8 hours at 600 0 C.

Conversion of propane-butane fraction was carried out on N-CKE-G and H-CKE-SF zeolite catalysts, modified by 1-3% wt. Ga2O3, using a flow-through catalytic unit with a fixed-bed catalyst at 500-600 ºC, raw space flow rate of 240 h-1 and atmospheric pressure. The the products of propane-butane fraction conversion into arenas were analysed using gas chromatography. The analysis of gaseous hydrocarbons was carried out using a stainless steel printed column (column length 3 m, internal diameter 3 mm) filled with 5% NaOH / γ-Al2O3 (fraction 0.25- 0.50 mm), liquid hydrocarbons using (on) a quartz glass capillary column (100 mx 0.25 mm x 0.25 μm) with a fixed ZB-1 phase. The quantitative analysis of the products of the conversion process of straight-run gasolines was carried out on a hardware-software complex based on the Chromatek-Crystal 5000 gas chromatograph version 1 using the Chromatek-Analytic processing program. The error in the determination of gaseous and liquid hydrocarbons is ± 2.5%. According to the hydrocarbon composition, the propane-butane fraction of PNG contains (% by weight): methane - 0.2%, ethane - 2.8%, propane - 81.1%, butanes - 15.9%.

It is known that zeolites of the ZSM-5 type possess strong acidic properties, which determine the reactions of aromatization of light alkanes. Due to these properties, the reactions of dehydrogenation, dehydrocyclization, and cracking of lower alkanes C3 – C4 mainly occur on zeolite catalysts [1].

The studies of the temperature effect showed that with the increase in the process temperature from 525 to 600 ºC and the volumeflow rate of PBF 240 h-1 to H-CKE-D, the yield of liquid products (arenes) increases from 26.4 at 525 ºC to 39.7% at 600 ºC, and the yield of gaseous products decreases from 73.6% at 525 ºC to 60.3% at 600 ºC. The degree of PBF conversion

(propane) increases from 54 to 92% with the increase in temperature from 525 to 600 °C. Benzene, toluene and xylenes are common among the arenes, the yield of benzene with the process temperature increase rises from 10.8% at 525 ° C to 23.9% at 600 ° C. The main gaseous products of the PBF conversion process are methane and ethane, which can be used for fuel purposes or as a source of hydrocarbons for petrochemical and gas chemistry processes. The total content of these products increases from 45.3 to 76.9% with an increase in process temperature from 525 ºC to 600 ºC among gaseous products The addition of 1% Ga2O3 to N-CKE-G zeolite with the increase in PBF conversion temperature from 525 to 600 ° C results in a significant increase in the yield of liquid products (arenes) from 40.2 to 60.1% compared to H-CKE-G zeolite. With the temperature increase from 525 to 600 ° the degree of PBF conversion increases from 76 to 98%, the arenes are dominated by C6-C9 hydrocarbons. The addition of 3% Ga2O3 to N-CKE-G zeolite leads to a further increase in the yield of liquid products from 50.8 to 64.1% compared to H-CKE-G zeolite, and the degree of PBF conversion increases from 89 to 99%, with an increase in temperature from 525 to 600 ° C; C6-C9 hydrocarbons are the main products among the arenes. 3% Ga2O3 / 97% H-CKE-G catalyst is the most active among the synthesized catalysts the maximum content of arenes on this catalyst is 64.2% at 600 ° C.

The analysis of the temperature effect indicated that with an increase in the process temperature from 525 to 600 ºC and a volume flow rate of PBF 240 h-1 to H-CKE-SF zeolite, the yield of liquid products significantly increases from 41.6 at 525 ºC to 51.4% at 600 ºC compared to N-CKE-G. The degree of PBF conversion increases from 77 to 89% with temperature rise from 525 to 600 ° C. C6 –C9 arenas prevail among the liquid products, while methane and ethane are the main gaseous products of PBF conversion. The addition of 1 and 3% Ga2O3 to N-CKE-SF zeolite leads to a significant increase in the yield of liquid products from 52.1 and 51.6% at 525 ° C to 60.1 and 63, with an increase in the temperature of PBF conversion process from 525 to 600 ° C. 3% at 600 ° C, respectively, compared to N-CKE-SF zeolite.

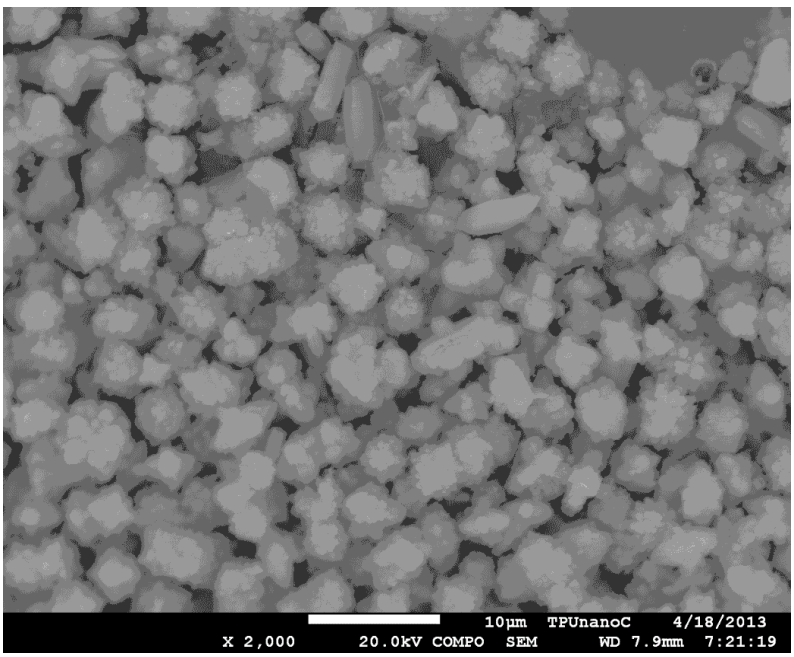

Figure 1. Micrograph of high-temperature zeolite N-CKE-G, synthesized using hexamethylenediamine as a structure-forming additive

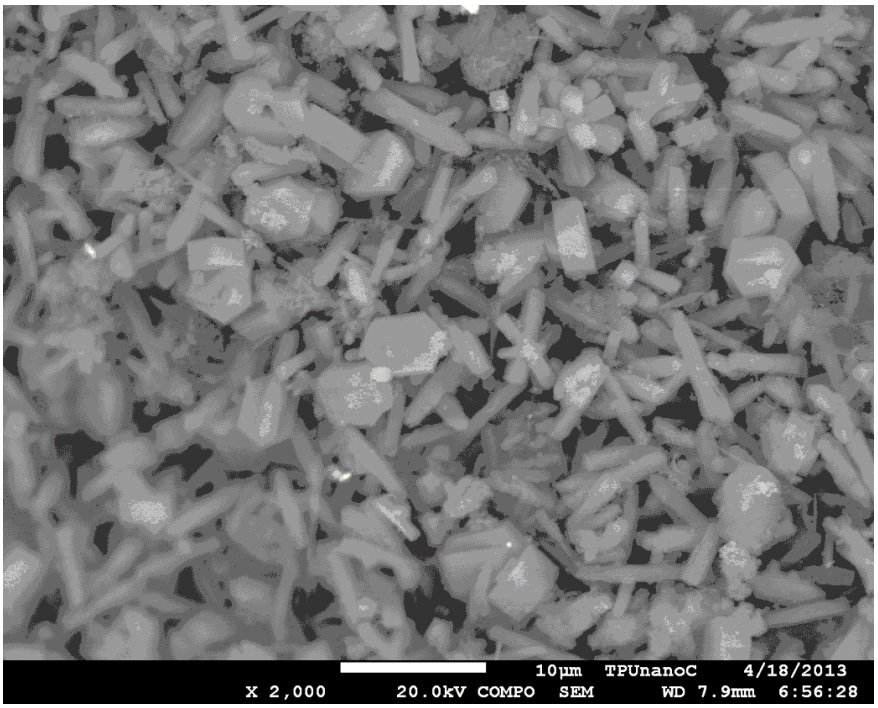

Figure 2. Micrograph of high-temperature zeolite H-CKE-SF synthesized using alcohol fraction as a structure-forming additive

4. Conclusion

The conducted analysis has shown that among the synthesized catalysts, 3% Ga2O3 / 97% H-CKE-G zeolite and 3% Ga2O3 / 97% H-CKE-SF zeolite are the most active and selective in the reactions of PBF arene formation, the maximum arene content on these catalysts is 64 , 2 and 63.3% at 600 ºC, respectively. It is important to note that 3% Ga2O3 / 97% H-CKE-SF catalyst largely corresponds to 3% Ga2O3 / 97% H-CKE-G catalyst in terms of catalytic activity and selectivity in formation of PBF arenes.

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