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Influence of the Reactor System on the Transformation of Methanol to Gasoline over H-ZSM-5

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In the current investigation, we studied the influence of reaction conditions on the liquid products formation and catalysts stability in methanol to gasoline synthesis process. Methanol to gasoline synthesis was carried out in continuous mode regime. Main reaction products were found to be gases including methane, ethylene, propylene, isobutene, and liquid hydrocarbons including cyclopropane and methylcyclopropane, as well as the aromatics - benzene, toluene, xylene, cresol, durol, naphthalene, methylnaphthalene, ethylnaphthalene, isopropylnaphthalene, methylisopropylnaphthalene etc. The optimal reaction conditions were found to be as the following: 5 bar of the total pressure in the system, 330 ºC process temperature, and methanol feed rate 5 mL/min. The optimal reactor size was found to be 30 cm length and 5 mm diameter. Under the established conditions the yield of the liquid strained hydrocarbons was the maximal and reached about 35 wt. %, while the aromatic content was only 3 wt. %.

1. Introduction

The decrease in traditional fuel sources leads to the research intensification in the field of synthetic fuel production. Modern methodologies of liquid fuels obtaining from biomass include Fisher-Tropsch route, biomass to methanol transformation followed by methanol to gasoline process, biomass pyrolysis with the further upgrading of obtained liquid fuel and cellulose liquefaction process (Anggoro et al., 2017). Among such techniques, methanol to gasoline process can be considered as one of the most prospective methods for biomass transformation to liquid fuels.

The formation of various types of hydrocarbons from methanol has been studied since the beginning of 20th century. This process implies the methanol dehydration into dimethyl ether (DME) with its further transformation into hydrocarbons (Sadehi et al., 2015). The earliest report of hydrocarbon formation from methanol was done by LeBel and Greene in 1914.The report was devoted to the decomposition of methanol in molten $ZnCl_2$. Hexamethylbenzene (HMB) and light gases were identified as the main reaction products. The formation of HMB was explained by LeBel and Green (1914) by the condensation of carbene (CH_2) with benzene molecule, followed by the benzene ring methylation by Friedel-Crafts reaction with CH_3Cl generated in situ. In 1914 Sernagiotto reported the decomposition of methanol over P_2O_5. The reaction yielded a mixture of unsaturated hydrocarbons. Propene and butene were identified as the main products. However, the formation of hexene and hexane, along with unidentified solid products, was also observed.

The further works in methanol transformation to hydrocarbons were done in 1950s. A patent granted to Grosse and Snyder (1950) described the conversion of methanol and DME to hydrocarbons over $ZnCl_2$, at 375 - 675 °C and high pressures. Topchiev and Ballod (1950) compared the activity of silica, alumina, and silica-alumina (Al_2O_3 30 wt. %, SiO_2 70 wt. %), in methanol conversion to DME. The aluminosilicate catalyst, after adsorbing methanol at 20°C, was heated up to 400 °C and yielded CO, C_2H_4, CO_2, and C_2H_6 in addition to DME and unreacted methanol. Gorin (1948) studied the reaction of a mixture of DME (18.2 mol. %) and isobutane over amorphous silica-alumina at 370 ºC, 150 psig, and 6.8 h^{-1} GHSV. The conversion of DME to hydrocarbons was 94 %, while no net change in isobutane was occurred. In the absence of isobutane, at a higher temperature, lower pressure, and higher space velocity, considerable amount of methane, CO, and carbon was produced,

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while the yield of C_5 hydrocarbon was less than 15 %. Although no explanation of the role of isobutene was proposed, one can surmise that it served to moderate the large reaction exotherm. A patent issued to Fawcett and Howk (1953) claims the direct conversion of methanol to hydrocarbon wax in the presence of a metal molybdite catalyst, e.g., $CoMoO_2$, modified with nickel chromite at 100-350°C at 70-100 atm. In that work, methanol served as a source of synthesis gas through dissociation process, and therefore hydrocarbons were formed in Fischer-Tropsch reaction.

A new age of methanol to gasoline synthesis began with the application of various zeolites. According to the literature, zeolites are porous materials (Sujeerakulkai and Jitkarnka, 2014), with a crystalline framework composed by tetrahedric AlO_4 and SiO_4 (Maihom et al., 2009), coupled through the shared oxygen atoms, forming a three-dimensional framework. Since oxygen in such structure is shared by two tetrahedra, the framework possesses a net negative charge (Palumbo et al., 2008). Nowadays, methanol to gasoline (MTG) synthesis is mainly provided over a zeolite-based catalyst in order to obtain light olefins (Al Naimi and Garforth, 2015). It has been found that the liquid hydrocarbon formation typically takes place in the temperature range of 300-400 °C (Perez-Uriarte et al., 2016). H-ZSM-5 zeolite can be considered as the most commonly applied catalyst in this process (Sun et al., 2014).

The MTG reaction over a ZSM-5-based catalyst is always came amid by the coke formation, which leads to the partial or full deactivation of the catalyst surface. The deactivation takes place through the blocking the access to the active acid sites by coke, either by deposition of carbonaceous compounds directly on the acid sites and in the micropores channels of the zeolite. Also, catalyst deactivation can take place by blocking the access to the micropores, preventing the diffusion of methanol molecules into the zeolite structure (Teketel et al., 2012). The loss in the activity due to the coke formation is partly reversible (Wu et al., 2012), and the catalytic activity can be restored by a coke gasification that removes the deposited coke. The typical procedure of catalyst regeneration consists of the burning off the coke with oxygen at 500 – 600 °C (Zaidi and Plant, 2008). However, the regenerated catalysts show lower activity compared with the initial ones, due to the dealumination of the zeolite, which typically occurs at temperatures higher than 500 ºC in the presence of water (Aguayo et al., 2012).

In the past 30 years, the investigations have been focused on modification of HZSM-5 using various metals, such as Mo, Cu, Zn, and Ga (Meng et al., 2016). These catalysts showed even higher selectivity towards the undesired aromatics than the HZSM-5 catalyst. Literature reports indicate that the HZSM-5 catalyst with the large pore volumes but narrow pore sizes, external surface areas and the high amount of the external active sites, possesses good stability but high selectivity to aromatics. High aromatic content in gasoline is undesired, because a complete lack of aromatics is not good. Recent advances in the synthesis of composite micro/mesoporous materials are interested in the development of new MTG catalysts due to their enhanced (compared with zeolite) mass transfer properties and reduced diffusion limitations (Chen et al., 2016). It was hypothesized that the micro/mesoporous composite materials allow simultaneously moderation the pore size distribution and the overall acidity of the pore surfaces, thus, improving the selectivity towards alkanes and reducing the formation of aromatics and carbon deposition (Fattahi et al., 2016).

In spite of the various works in the field of MTG reaction, numerous issues can be arisen. Thus, the technology mainly used in MTG process implies the application of fluidized bed reactor with the catalyst circulation that operates at 400 °C and 12.8 bar (Baliban et al., 2012). However, to the best of our knowledge, there is a few works devoted to the use of fixed-bad continuous reactors. E.g. Castilla et al. (1998) studied MTG process in an Isothermal Fixed-Bed Reactor, Aguayo et al. (2001) proposed the use of pseudoadiabatic reactor for the transformation of methanol into hydrocarbons. The development and modification of novel reactors in MTG process is limited by its complex reaction scheme. Moreover, during the reactor design, numerous factors must be studied. Here we report the study devoted to the design of novel two-step reactor unit for MTG process. In the current work, we studied the influence of the reactor characteristics and the reaction conditions on the formation of strained cyclic C_3-C_4 liquid products. The following factors were investigated: reactor length, reactor internal diameter, process temperature and pressure and methanol feed rate. The data obtained were used for the kinetic modeling of the process.

2. Experimental

Methanol to gasoline synthesis was carried out in continuous mode. The scheme of the laboratory set-up is presented in Figure 1. Before the experiment, the system was purged with nitrogen for 40 min, and then the reactors were heated to the required temperature.

After stabilization of reaction temperature,high-pressure methanol pump purge system with methanol and reaction starts. The condensers (Figure 1, position 10) temperature was maintained constantly by thermostat for proper separation of reaction products. In a typical experiment, 5 g of the catalyst of methanol to DME(γ-Al_2O_3) was taken for methanol to dimethyl ether reactor filling (Figure 1, position 9) and 5 g of H-ZSM-5 was taken for DME to hydrocarbons reactor (Figure 1, position 12) filling. The nitrogen feed rate was maintained at

10 mL/min. In order to study the reaction parameter influence the following conditions were varied: methanol feed rate 1-10mL/min, reaction temperature 270-370°C, overall system pressure 5-30 bar.

The reaction mixture was analyzed by gaseous chromatography using the state-of-the-art analytic complex including gas chromatograph (Crystall 2000M, MetaChrom, Russia) equipped with the flameionization detector and thermal conductivity detector. Main reaction products were found to be gases including methane, ethylene, propylene, isobutene, and liquid hydrocarbons including benzene, toluene, xylene, cresol, durol, naphthalene, methylnaphthalene, ethylnaphthalene, isopropylnaphthalene, methylisopropylnaphthalene etc.

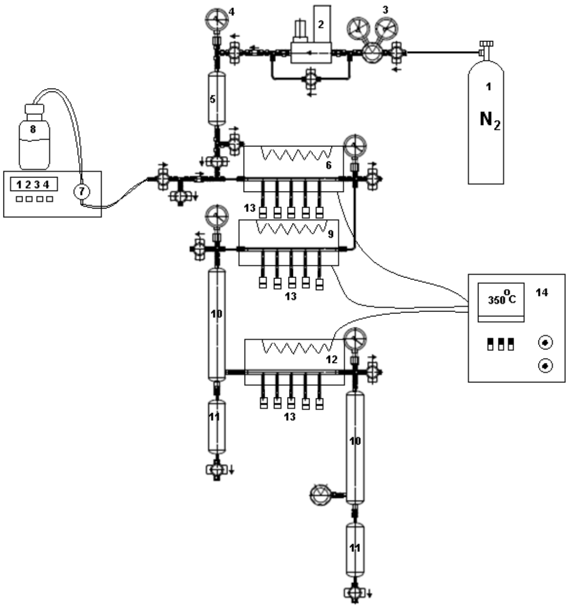

Figure 1: The scheme of laboratory set-up of methanol to gasoline synthesis process

3. Results and discussion

In order to study the reactor length and diameter influence on methanol to hydrocarbons transformation process the experiments were done using different lengths of the reactor tubes. The obtained results on methanol transformation rate are presented in Figure 2. 5 consecutive tests were done for each process conditions. The standard deviation was found to be ±3 %.

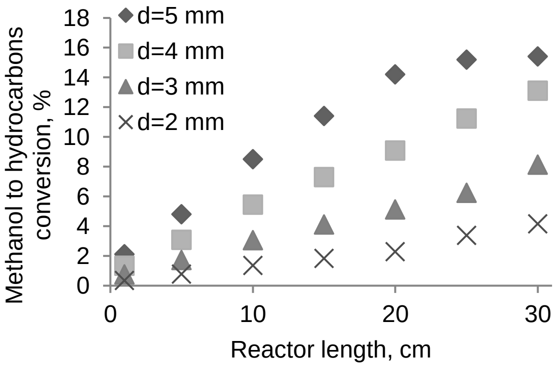

Figure 2: Effect of the reactor length and diameter on methanol to hydrocarbons conversion

It is well seen that the increase in both reactor length and reactor diameter increases the methanol molar conversion. This can be explained by the higher time of methanol presence in the reaction zone as well as the higher area of external surface of the catalyst allowing increasing the access of the substrate to the catalyst external active sites. The optimal reactor size was found to be 30 cm length and 5 mm diameter.

In order to estimate the influence of the reaction temperature the experiments were done varying the temperature in the range of 270-370 °C. The increase in temperature increases the rates of the transformation of both methanol and DME into hydrocarbons (Figure 3). It is well seen that while temperature increases, the formation of the strained hydrocarbons also increases. Meanwhile the amount of gaseous products changes insufficiently having a maximum at 330 °C. The significant increase in the content of aromatic hydrocarbons was observed at temperatures above 330 °C due to the transformation of the olefins adsorbed on the catalyst surface. Thus, the optimal temperature for the formation of gasoline-range hydrocarbons from methanol was found to be 330 °C allowing obtaining over 35 % yield. Moreover at this temperature the minimal formation of aromatics is observed.

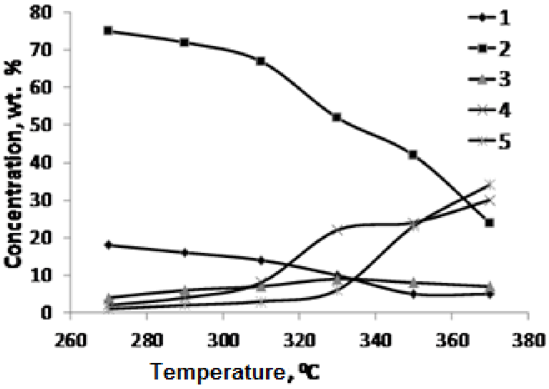

Figure 3: Effect of temperature on the composition of the resulting vapor-gas mixture. (1 - CH_3OH, 2 - CH_3OCH_3, 3 - CH_4, CO, CO_2, H_2, H_2O, 4 –cyclic C_3H_6, C_4H_8, 5 - C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, $C_6H_3(CH_3)_3$): methanol feed rate 5 mL/min, total system pressure 5 bar

In order to study the influence of the overall pressure on both methanol transformation rate and product formation the experiments were done varying the pressure in the range of 5-30 bar (Figure 4). It was found that the pressure practically does not affect the rates of methanol and DME conversion rates, which even slightly decrease at the pressure above 5 bar. However, the increase in total pressure in the system from 5 to 30 bar leads to the increase in the content of aromatic hydrocarbons. At the same time, when the total pressure in the system is 5 bar, the content of aromatic hydrocarbons does not exceed 3 wt. % and the content of light olefins is 36 %. Thus, the optimal reaction pressure was found to be 5 bar.

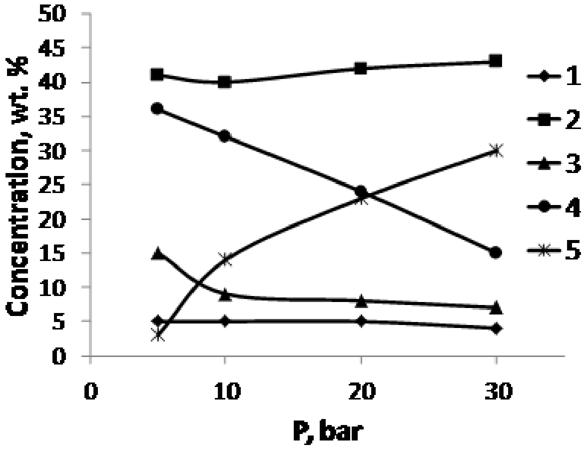

Figure 4: Effect of pressure on the composition of the resulting vapor-gas mixture (1 - CH_3OH, 2 - CH_3OCH_3, 3 - CH_4, CO, CO_2, H_2, H_2O, 4 –cyclic C_3H_6, C_4H_8, 5 - C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, $C_6H_3(CH_3)_3$): methanol feed rate 5 mL/min, process temperature 330 ˚C

Investigation of the influence of the methanol feed rate (Figure 5) on the composition of the resulting vapor-gas mixture was performed varying the substrate feed rate from 0.5 to 10 mL/min. The results show a significant decrease in the content of aromatic compounds with an increase in the methanol feed rate from 0.5 to 10 mL/min. In the same time, the increase in the concentration of strained hydrocarbons is observed, while the content of the gaseous products remains almost constant. However, the increase in the initial feed rate of methanol also leads to the increase in the methanol and DME content in the resulting vapor-gas mixture. The optimal methanol feed rate was found to be 5 mL/min allowing formation over 20 wt. % of gasoline-range hydrocarbons.

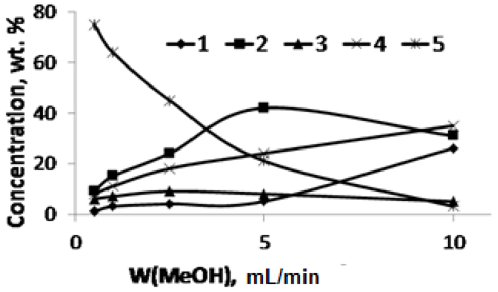

Figure 5: Influence of the methanol feed rate on the composition of the resulting gas-vapor mixture (1 - CH_3OH, 2 - CH_3OCH_3, 3 - CH_4, CO, CO_2, H_2, H_2O, 4 –cyclic C_3H_6, C_4H_8, 5 - C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, $C_6H_3(CH_3)_3$), overall pressure 5 bar, process temperature 330 °C

The study of the effect of methanol transformation time on the initial conversion of methanol (Figure 6) showed the decrease in the catalyst activity, which is the result of carbon deposition on the catalyst surface. It is noteworthy, that the loss in the catalyst activity is observed because the formation of a large amount of aromatics caused by the transformation of the formed olefins adsorbed on the catalyst surface and its further cocking.

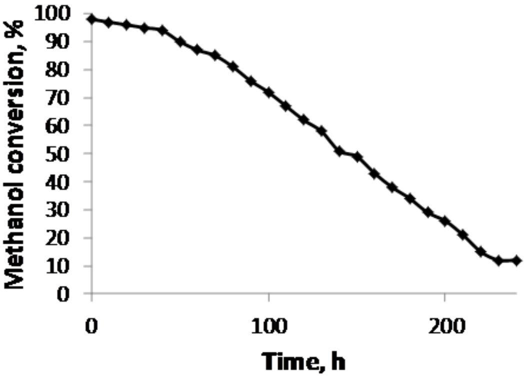

Figure 6: Study of the influence of the time of the methanol transformation process on methanol conversion: total pressure in the system 5 bar, process temperature 330 °C, methanol feed rate 5 mL/min.

4. Conclusions

The study of the influence of the operating conditions on methanol transformation to strained hydrocarbons showed that the optimal reaction conditions were found to be as the following: 5 bar of the total pressure in the system, 330 °C process temperature, and methanol feed rate 5 mL/min. The optimal reactor size was found to be 30 cm length and 5 mm diameter. Under the established conditions the yield of the liquid strained hydrocarbons was the maximal and reached about 35 wt. %, while the aromatic content was only 3 wt. %.

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