PERSPECTIVES OF THE SLURRY-REACTOR TECHNOLOGY IN THE LIGHT OLEFINS SYNTHESIS FROM DIMETHYL ETHER

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Abstract

The innovative synthesis of light olefins from dimethyl ether (DME) with using the slurry-reactor technology is developed. DME conversion occurs in silicone oil, on a flow type installation, at 300-320°C under atmosphere pressure in the presence of ultra-dispersed zeolite catalysts obtained by the original method from the commercial zeolite (type MFI) produced in Russia. The perspectives of this newest technology are under discussion.

Keywords: *slurry-reactor, dimethyl ether, light olefins, ultra-dispersed catalysts, MFI-type zeolite catalysts*

1. INTRODUCTION

Light olefins such as ethylene, propylene and butylenes are valuable feedstocks for the petrochemical and organic synthesis industry. As considered, these chemicals are main raw materials for the production of numerous plastics materials, synthetic fibers, rubbers, oxygen compounds (Nikolaev et al. 2009). The major fields of ethylene application are large-scale processes for manufacturing polyethylene, polyvinyl chloride, ethylene oxide, ethanol, acetaldehyde, vinyl acetate, ethyl benzene and others goods. Propylene is the base for the production of polypropylene, other new polymers, in syntheses of propylene oxide, acrylonitrile, isopropyl alcohol, etc. Butylenes are co-monomers for obtaining the linear polyethylene of a low density and the reagents in the syntheses of butyl alcohol, maleic anhydride, polybutylene and others.

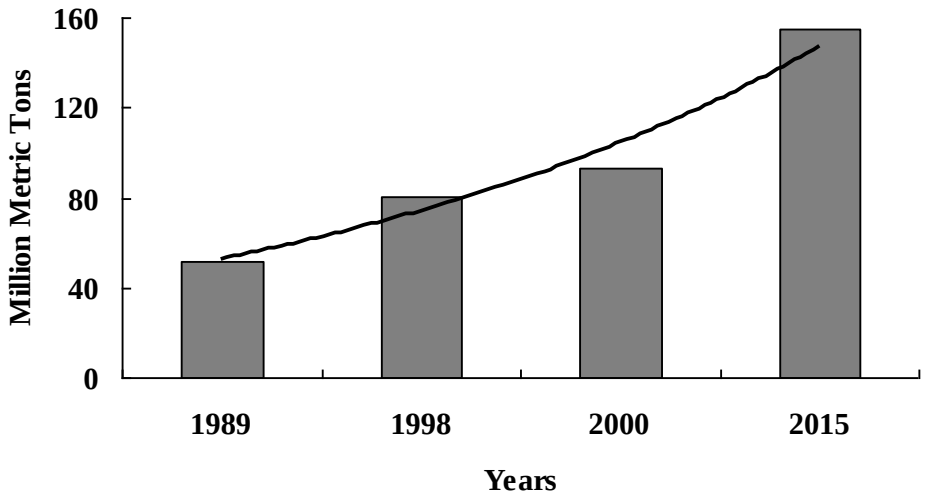


Figure 1. Ethylene world market
(Khadzhiev, Kolesnichenko & Ezhova 2008; Nikolaev et al. 2009; Sadrameli 2016).

Almost all industries consume these chemical goods on the olefins base (building, mechanical engineering, energy, electronics, medicine, agriculture and many others). Due to the rapid economic growth, there is a growing demand for goods produced from light olefins, especially, from ethylene and propylene. As a result, the world's production of these light olefins is continuously increasing (Fig. 1, 2). If in 1950 there were produced only about 1 million tons of ethylene (Kniel, Winter & Stark 1980), till 2000 ethylene market increased to about 93 million tons per annum (Khadzhiev, Kolesnichenko & Ezhova 2008), but the present demand by petrochemical and organic synthesis industry is over 155 million tons of ethylene per year (Sadrameli 2016). As to propylene market, in last years the demand for this olefin grew even faster than for ethylene (Brown 2002; Sadrameli 2016), and since the beginning of the century, the propylene world production has doubled (Fig. 2). The market of butylenes is continually increasing either.

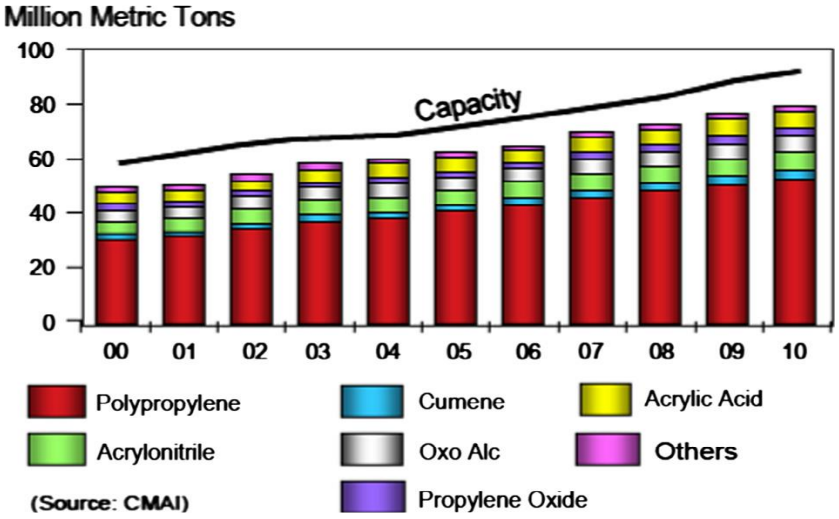


Figure 2. Propylene world market (Brown 2002; Sadrameli 2016).

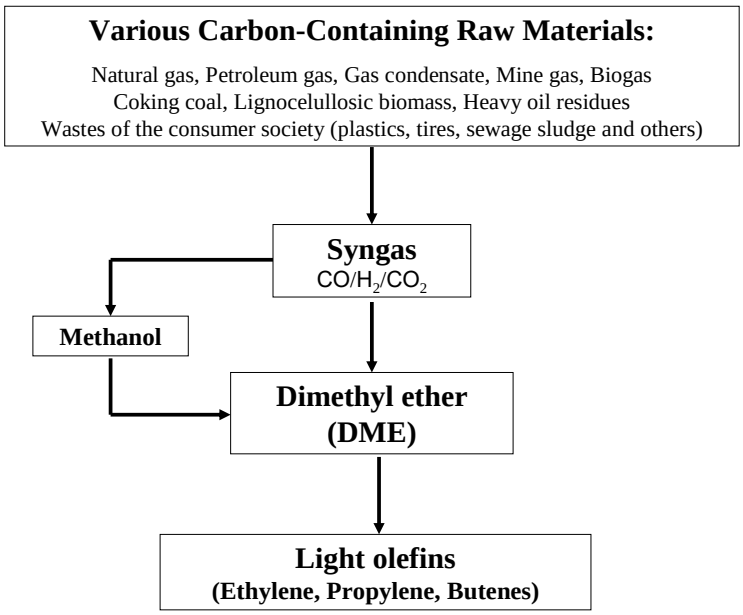


Figure 3. Light olefins production on the base of any carbon-containing raw material via syngas and dimethyl ether (DME)

Modern production of light olefins is processing naphta by the steam cracking (Sadrameli 2015, 2016), by fluidized bed catalytic cracking and by deep catalytic cracking (Awayssa et al. 2014; Corma et al. 2017). However, the growth rate of oil production is slowing, so today alternative raw materials are necessary for covering the light olefins growing demand. The possible production of light olefins via synthesis gas is considered as the most perspective way. Synthesis gas is the universal raw material which may be produced from any carbon-containing materials (including natural gas (Hickman & Schmidt 1993), charcoal (Wen 1980), biomass (Asadullah et al. 2002) and others) (Fig. 3), and nowadays, when the hydrocarbons market situation is unstable, this kind of feedstock is the most attractive. Some plants with light olefins production from synthesis gas via methanol- MTO (methanol-to-olefin) and MTP (methano-to-propylene) have been already built by a few companies (Exxon Mobil Corporation, UOP-Norsk Hydro, Lurgi, Japan Gasoline Company and Mitsubishi Chemical) (Koempel & Liebner 2007; Strizhak, Zhokh & Trypolskyi 2018; Tian et al. 2015). The alternative to these industrially established processes of olefins production via methanol is the transformation of dimethyl ether (DME) supplied from synthesis gas to olefins (DTO) (Fig. 3). As considered, this way of manufacturing olefins is the very perspective. This is the cheapest modern method of light olefins synthesis, because the unit cost of DME production from synthesis gas is much lower than the unit cost of methanol production (Gogate 2018). Nowadays DTO-process is in progress (Al-Dughaither & Lasa 2014; Kolesnichenko 2011; Perez-Uriarte et al. 2016).

DME conversion to olefins proceeds according to the scheme:

$$n(CH_3)_2O \rightarrow 2C_nH_{2n} + nH_2O$$

This reaction is usually carried out at 350-450^{o}C under 0.1 MPa in the fixed bed reactor. As catalysts, there are used either molecular sieves (like SAPO-34 (Ghavipour et al. 2014; Li et al. 2014) or SAPO-18 (Hirota et al. 2016)) or zeolites (like HZSM-5 (Al-Dughaither & de Lasa 2014; Bakare et al. 2018; Perez-Uriarte et al. 2016) or dealuminated mordenite (Nasser et al. 2016)). The best results have been achieved using zeolite MFI type (ZSM-5 structure) modified with metals and agglomerated with a binder (γ-Al_2O_3 or its precursor). Metals such as magnesium (Goryainova et al. 2011; Magomedova et al. 2017), rhodium (Kolesnichenko et al. 2011), lanthanum and zirconium (Biryukova et al. 2011), lanthanum and calcium (Bakare et al. 2018) were used for the modification of the MFI. Light olefins yield is very high over these catalysts at 340-360^{o}C and atmospheric pressure. Nevertheless, there are a few problems discouraging the DTO commercialization. Among them, not enough high ethylene/propylene selectivity and a very short catalyst life-time (as a consequence of secondary transformations of olefins and a high thermal effect of these reactions) are. At present, chemists are searching ways for the solution of these problems.

One possible way for the solution of DTO process problems could be an application of the technology based on a slurry-reactor. The main feature of this modern technology is using a fine dispersed catalyst, when micro-sized or nano-sized catalytic particles are as a suspension in a liquid medium. The application of micro-sized and, especially, nano-sized zeolites facilitated increasing the catalytic activity, selectivity and extending the catalytic lifetime as result of decreasing intracrystalline diffusion limitations and improving mass and heat transfers. The liquid medium is required for stabilizing of small catalysts particles and for removing heat and reaction products from the grain of the catalyst.

The slurry-technology has already used successively in some chemical, petrochemical and biochemical catalytic processes (Buisson et al. 2009; Chen, Liu & Soares 2016; Deng et al. 2016; Krupka, Dluhoš & Mrózek 2017; Pintar et al. 2004; Stamatiou & Muller 2017). However, a slurry-reactor application in DTO process is an innovation. This progressive DTO method started in Russia a few years ago (Kolesnichenko et al. 2017, 2018a). Recently, the original method for preparing micro-sized and nano-sized catalysts from commercial zeolites (type MFI) produced in Russia has been proposed in Topchiev Institute of Petrochemical Synthesis (RAS), and ultra-dispersed catalytic suspensions for DTO in a slurry-reactor were obtained (Kolesnichenko, Ezhova & Yashina 2016; Kolesnichenko et al. 2018b).

In this article we discuss the perspectives for using ultra-dispersed suspensions of MFI-zeolites in the light olefins synthesis from DME in a slurry-reactor. We compare the innovative technology of DTO in a slurry-reactor with the known method of DME conversion to light olefins in a fixed bed reactor. In this research MFI-zeolites modified with magnesium were as a catalyst (as the most effective known DTO catalysts).

2. MATERIALS AND METHODS

Suspended zeolite catalysts were prepared from two samples of commercial high-silica zeolites (type MFI). One of them is supplied by OAO 'AZKOS' (Angarsk, Russia) with the molar ratio SiO_2/Al_2O_3 of 37. It is marked as MFI (1). The second zeolite is supplied by OAO 'Nizhegorodskye Sorbents' (Nizhniy Novgorod, Russia) with the molar ratio SiO_2/Al_2O_3 of 77. It is marked as MFI (2). Both of the commercial zeolite samples are in the ammonium form. At first, these samples were calcinated at 550ºC for 5 hr for their transform into the proton form. After obtaining H-MFI (1) and H-MFI (2), they were modified with magnesium by the method described in the paper of Goryainova et al. (2011). As a result, samples of the catalyst (Mg-MFI (1) and Mg-MFI (2)) having a coarse dispersion, containing 1% wt. of magnesium were obtained. Then Mg-MFI (1) sample coarsely dispersed was comminuted using several methods. Among them, the handle mechanical grinding in the agate mortar and shredding in a ball mill (a vibration-mechanical mill marked KM-1, equipped with an agate mortar and an agate grinding ball, time of fine grinding was 15 min) were applied. The others were an abrasion in a planetary mill (PULVERISETTE 7 premium line, FRITCH, Германия) for 10 min and the ultrasonic treatment in water (in the ultrasonic bath Elmasonic P30 H) for 1 hr. The Mg-MFI (2) sample coarsely dispersed was comminuted by the ultrasonic treatment in water. All comminuted samples were dried at 110-120ºC for 10-12 hr, then calcinated at 500-550ºC for 5 hrs. As a result four samples of comminuted Mg-MFI (1) zeolite and one sample of comminuted Mg-MFI (2) zeolite (Table 1, samples I-V) were prepared. Consequently, the comminuted zeolite samples were dispersed in silicone oil (trade mark Syltherm 800, Dow Chemical Co.) at room temperature for 1.5 hr using ultrasonic bath. In this way ultra-dispersed suspended catalysts were produced The dispersion of suspensions was determined by dynamic light scattering using the particle analyzer Malvern Zetasizer NANO SZ.

Table 1. The dispersion of the suspended zeolite catalysts comminuted by different grinding methods

Zeolite catalyst	Shredding method	Sample	Average dispersion of suspended catalyst, μm
Mg-MFI (1)	Handle mechanical grinding	I	1.5-1.7
	Shredding in a ball mill	II	1.0-1.2
	Abrasion in a planetary mill	III	0.6-0.8
	Ultrasonic treatment in water	IV	0.3-0.4
Mg-MFI (2)	Ultrasonic treatment in water	V	0.3-0.4

Catalytic properties of the suspended catalysts during conversion of dimethyl ether to hydrocarbons were tested using a stainless steel flow reactor (a slurry-reactor, autoclave type) equipped with a mechanical stirrer. The reaction was run at temperatures 300-320ºC and pressure 0.1 MPa. DME was diluted with nitrogen gas up to 10% vol. The gas products were analyzed by the gas chromatography using *CP*-PoraPLOT-Q capillary column (27.5 m/0.32 mm/10μm) connected to a flame ionization detector.

The experiments of DME conversion in the fixed bed flow reactor over the stationary catalyst of Mg-MFI (1)/γ-Al_2O_3 were carried out by the technique described in the paper of Goryainova et al. (2011).

3. RESULTS AND DISCUSSION

3.1. The influence of the dispersion of suspended catalyst Mg-MFI (1) on DME conversion in the slurry-reactor

Due to use a few various methods for shredding commercial zeolites, suspended catalysts Mg-MFI (1) with the different dispersion were obtained (Table 1). Their catalytic properties were investigated during DME conversion in the slurry-reactor. The research results are shown in Fig. 4-7.

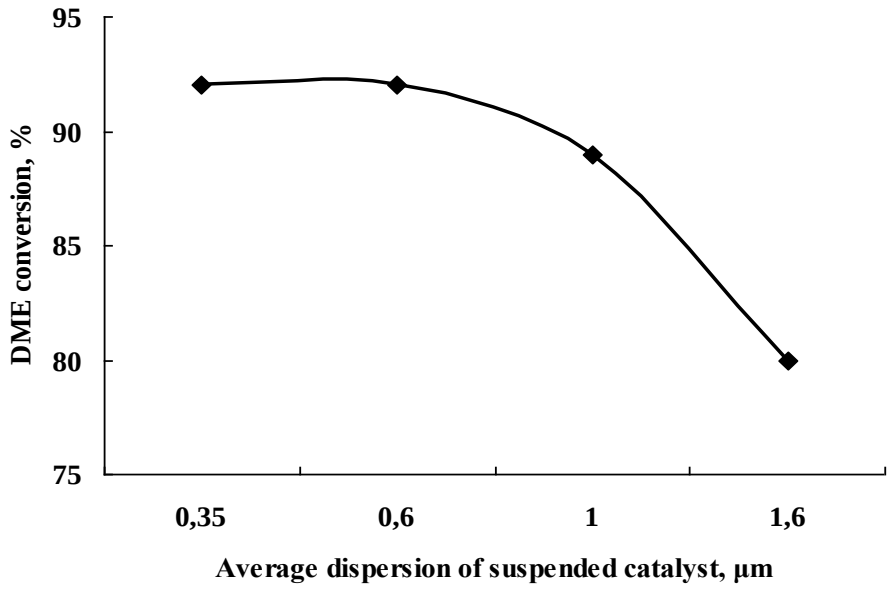


Figure 4. The effect of the suspended catalyst dispersion on DME conversion in the slurry-reactor

(Reaction conditions: Mg-MFI (1) (6.7% wt.), 0.1 MPa, 300°C, WHSV- 0.14 hr^{-1}, 10% vol. DME, gas flow rate- 2.8 l/hr, time on the flow- 2 hr)

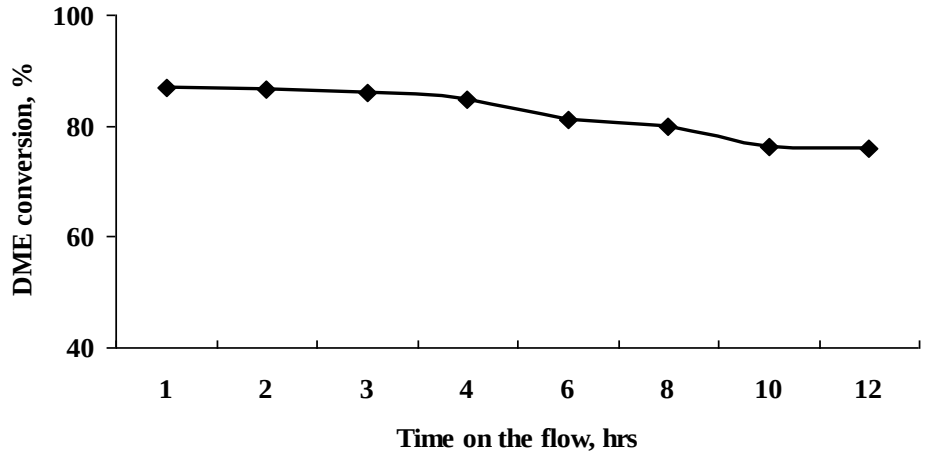


Figure 5. The dynamics of DME conversion into hydrocarbons in the presence of ultra-dispersed suspended catalyst in the slurry-reactor

(Reaction conditions: Mg-MFI (1) (the suspended catalyst dispersion- 0.6 µm), 6.7% wt. in the suspension, 0.1 MPa, 320°C, WHSV- 0.25-28 hr^{-1}, 10% vol. DME, gas flow rate- 4.7-5.6 l/hr, time on the flow- 2 hrs)

As seen from the data of Fig. 4, when decreased the particle size of the suspended catalyst, DME conversion was increased. The dynamics of DME conversion in the slurry-reactor with ultra-dispersed suspended zeolite catalysts was the rather stable. After 12 hours on the flow, a loss of the reaction rate was insignificant (Fig. 5). Thus, decreasing the scale of suspended catalyst particles could improve the catalytic activity and stability.

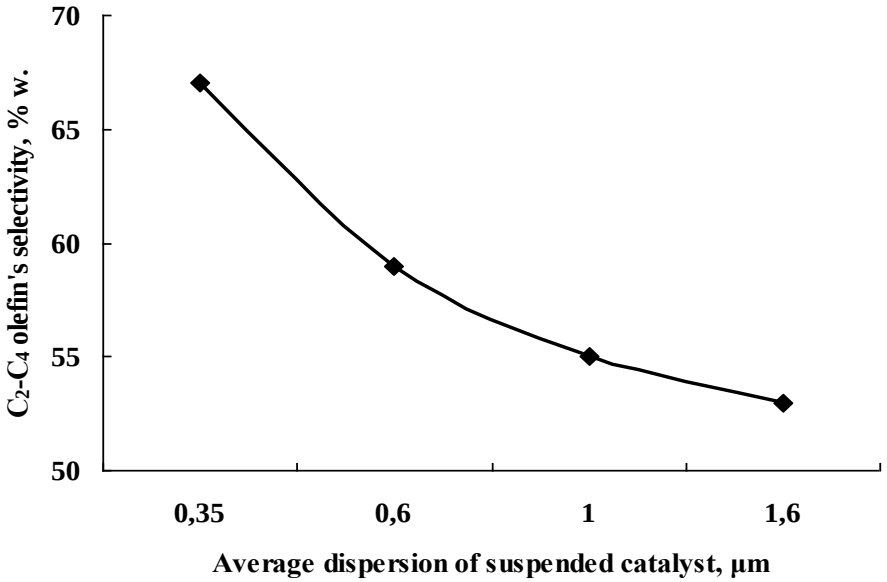


Figure 6. The effect of the suspended catalyst dispersion on light olefins selectivity during DME conversion in the slurry-reactor

(Reaction conditions: Mg-MFI (1) (6.7% wt.), 0.1 MPa, 300°C, WHSV- 0.14 hr^{-1}, 10% vol. DME, gas flow rate- 2.8 l/hr, time on the flow- 2 hrs)

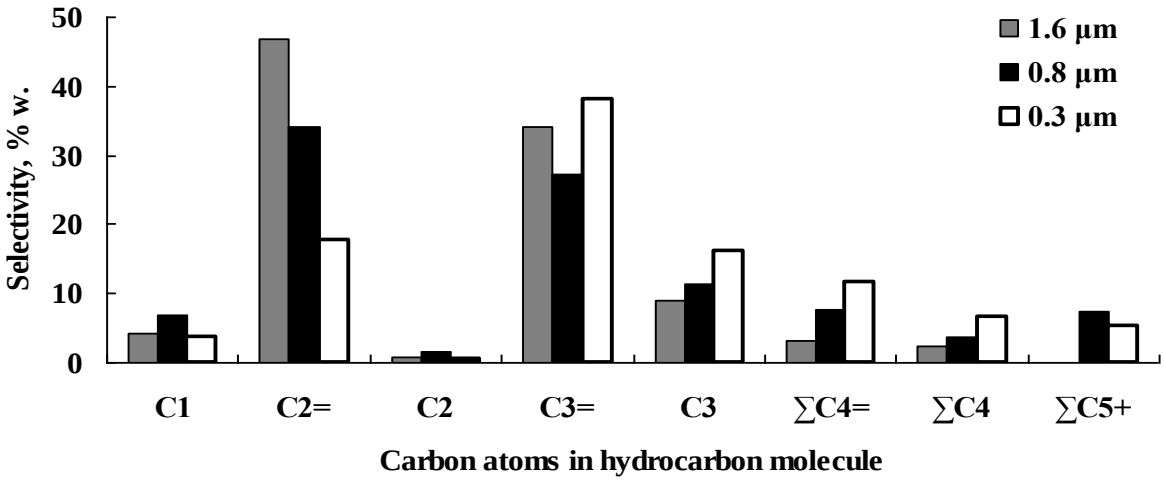


Figure 7. The effect of the suspended catalyst dispersion on hydrocarbons composition of the product of DME conversion in the slurry-reactor

(Reaction conditions: Mg-MFI (1) (6.7% wt.), 0.1 MPa, 300°C, WHSV- 0.14 hr^{-1}, 10% vol. DME, gas flow rate- 2.8 l/hr, time on the flow- 2 hrs)

As established, the dispersion of suspended zeolite affects the reaction selectivity. As seen from the data of Fig. 6, the higher light olefins selectivity was achieved due to the smaller catalytic particle size. Moreover, as the scale of suspended zeolite was minimized ethylene amount of the reaction product was decreasing, but propylene amount was growing (Fig. 7). This feature gives a possibility for controlling the selectivity of DME conversion to light olefins. If ethylene is needed you should take micro-sized suspended zeolite Mg-MFI. On the contrary, if propylene is needed you should apply nano-sized suspended catalyst.

Thus, when minimized the scale of suspended zeolite catalyst all catalytic properties were improved. Nano-sized suspensions were the best catalysts for DTO in the slurry-reactor.

3.2. The comparison of DME conversion to light olefins in the slurry-reactor to the known DTO reaction in the fixed bed reactor

In the Table 2, the results of DME conversion in the slurry-reactor with nano-sized suspended zeolites (Mg-MFI (1) and Mg-MFI (2)) are compared to the indicators of the known DTO-process (in a fixed bed reactor with the stationary catalyst Mg-MFI (1)/γ-Al_2O_3) (Goryainova et al. 2011). The distribution of hydrocarbons in the reaction products is shown in Fig. 8.

Table 2. Indicators of light olefins synthesis from DME in the fixed bed reactor with the stationary heterogeneous catalyst (a flow mode I) and in the slurry-reactor with the suspended ultra-dispersed catalyst (a flow mode II)

Indicators	Fixed bed reactor with the stationary heterogeneous catalyst (a flow mode I) (Goryainova et al. 2011)	Slurry-reactor with the suspended ultra-dispersed catalyst (a flow mode II)	
Zeolite manufacturer	OAO 'AZKOS' (Angarsk)	OAO 'AZKOS' (Angarsk)	OAO 'Nizhegorodskye Sorbents' (Nizhniy Novgorod)
Molar ratio SiO_2/Al_2O_3	37	37	77
Catalyst	Granular Mg-MFI (1)/γ-Al_2O_3	Suspended Mg-MFI (1)/ Syltherm 800	Suspended Mg-MFI (2)/ Syltherm 800
Average size of particles, μm	2.7-15.0	0.3-0.4	0.3-0.4
Technological parameters:			
Pressure, MPa	0.1	0.1	0.1
Temperature, °C	320-360	300-320	300
Diluting gas	N_2	N_2	N_2
DME concentration in the flow gas, % vol.	10-20	10-20	40-50
WHSV, hr^{-1}	0.3	0.3	0.7-1.0
Productivity			
Olefins g/(g-cat·hr)	0.20-0.21	0.21	0.30-0.35

Stability			
Δ DME conversion, %/hr	-7.5	-1.4	-0.8
Selectivity:			
$C_{2=}$-$C_{4=}$ olefins, % wt.	63-78	54-75	80
Ethylene/propylene ratio, wt.	1.5-2.5	0.5-0.6	1.4-1.5
Major product	Ethylene	Propylene	Ethylene + Propylene

First, for the both technologies we researched DME conversion using Mg-MFI (1) zeolite (as a catalyst base) and DME diluted with N_2 up to 10% vol. As seen from the data of Table 2, to obtain the same productivity the higher temperature is required in the fixed bed reactor (320-360ºC) compared to the slurry-reactor (300ºC). The catalyst stability in the slurry-reactor was more than five times higher than in the fixed bed reactor. Propylene was the major product of the slurry-reactor, in contrast to, ethylene was the same in the fixed bed reactor (Fig. 8, lines I, II). In our opinion, all these differences observed are related to that fact that in the case of the slurry-reactor the nano-sized suspended catalysts are used while in the case of the fixed bed reactor micro-sized catalytic particles are used.

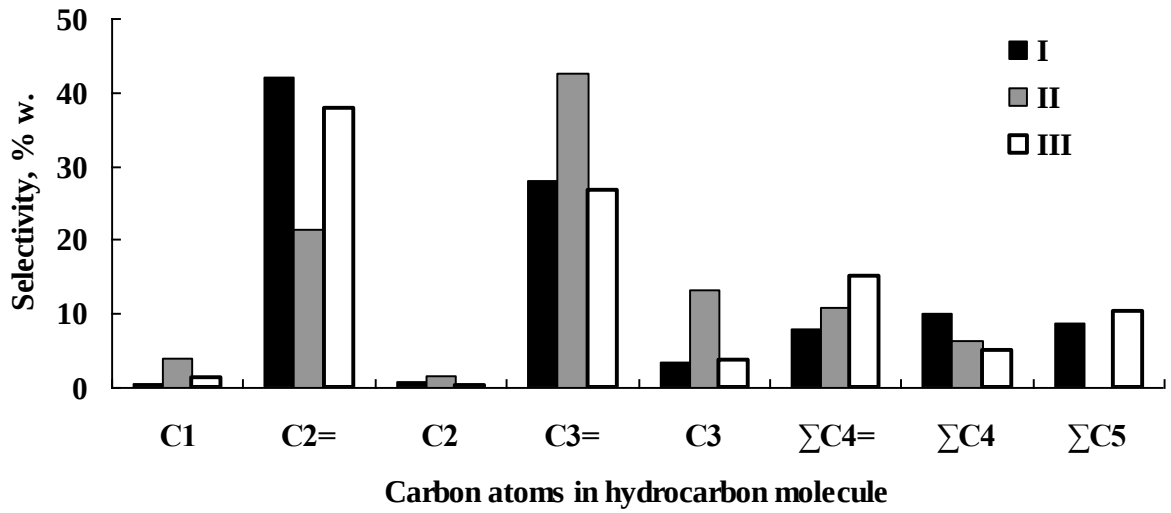


Figure 8. Hydrocarbons composition in the product of DME conversion in the fixed bed flow reactor with the stationary catalyst of Mg-MFI (1)/γ-Al_2O_3 (I) and in the slurry-reactor with suspended catalysts of Mg-MFI (1) (0.3 μm, 6.7% w.) (II) and Mg-MFI (2) (0.3 μm, 4% w.) (III).

(Reaction conditions: 0.1 MPa, 320ºC, WHSV- 0.25-28 hr^{-1} (I, II) and 0.7 hr^{-1} (III), 10% v. DME (I, II) and 50% v. (III), gas flow rate- 2.8 l/hr (I, II) and 3.5 l/hr (III), time on the flow- 2 hrs)

Then, taking into account the high catalyst stability in the slurry-reactor, we tried to raise DME concentration in the flow gas (to 50% vol.). As known (Goryainova et al. 2011), in the case of the conventional DTO technology, with a fixed bed reactor, the catalyst stability was failed as a result of some secondary transformations of olefins leading to reduced selectivity, coke formation and deactivation of the catalyst. However, in the case of the innovative slurry-technology, our attempt turned out to be successful. Productivity and C_2-C_4 olefins selectivity were increased as DME concentration raised. The deactivation rate decreasing was observed. Along with that, the distribution of hydrocarbons was somewhat changed, the ratio of ethylene to propylene was increased (probably, as a result of increasing WHSV) (Fig. 8, III).

4. CONCLUSIONS

1) Applying the slurry-technology for the light olefins synthesis from DME gives the possibility to improve the catalytic activity and stability. As a result, the reaction temperature of the slurry-reactor can be reduced compared to the known DTO-process using the fixed bed reactor, and DME concentration of the feed gas flow may be increased.
2) The smaller the size of catalytic particles is, the better the results are obtained for light olefins synthesis in the slurry-reactor.
3) Varying the dispersion of the suspended catalyst is a good tool for controlling the selectivity of DME conversion to light olefins. So, if ethylene is needed, micro-sized suspended zeolite Mg-MFI should be used. On the contrary, if you need propylene, nano-sized suspended catalyst should be taken.

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