ULTRA-DISPERSED SUSPENDED CATALYSTS AS THE INNOVATION IN THE CATALYTIC SYNTHESIS OF LIGHT OLEFINS FROM DIMETHYL ETHER

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Abstract

Highly dispersed zeolite catalysts have been obtained from commercial zeolite (MFI type) produced by AZKOS (Angarsk, Russia) by using the methods of the mechanical abrasion and the acoustic treatment. Ultra-dispersed samples of zeolite catalyst of (1%) Mg/MFI suspended in high boiling liquids have been shown to be promising catalysts for the innovative synthesis of light olefins from dimethyl ether (in slurry-reactor).

Key words: *zeolite catalysts, ultra-dispersed catalysts, catalysis in the dispersed phase, suspended catalysts, slurry-reactor, dimethyl ether, light olefins*

1. INTRODUCTION

Light olefins such as ethylene, propylene and butylenes are valuable feedstocks for the petrochemical industry. These chemicals are considered as main raw materials for the production of numerous plastics materials, synthetic fibers, rubbers, oxygen compounds. The production of light olefins is large-scaled and continuously increasing due to growing demand for these chemical goods (Khadzhiev, Kolesnichenko & Ezhova 2008). If in 2000 ethylene market was about 93 million tons per annum, the present demand by petrochemical industry is over 155 million tons of ethylene per year. As propylene market, in last years the demand for this olefin grew even faster than for ethylene (Brown 2002; Sadrameli 2016). The market of butylenes is continually increasing either. At present the growing demand for light olefins becomes covered by the steam cracking (SC) of naphta (Sadrameli 2015, 2016), fluidized bed catalytic cracking (FCC) (Awayssa et al. 2014; Corma et al. 2017), deep catalytic cracking (DCC), and MTO (methanol to olefins) (Tian et al. 2015) and MTP (methanol to propylene) (Koempel & Liebner 2007). The alternative to these industrially established processes of olefins production is the transformation of dimethyl ether (DME) to olefins (DTO) (Kolesnichenko 2011, 2013; Al-Dughaither & Lasa 2014; Perez-Uriarte et al. 2016a). DTO is considered to be the very perspective and the cheapest modern method of light olefins synthesis (Khadzhiev, Kolesnichenko & Ezhova 2008; Nasser et al. 2016; Perez-Uriarte et al. 2016b, 2016c).

DTO-way of light olefins synthesis is very attractive for the technology because the production of DME on a large scale can be realized through syngas performed from the large reserves of fossil sources alternative to oil (natural gas, coal), as well as form lignocelullosic biomass and wastes of the consumer society (plastics, tires, sewage sludge and others) (fig. 1). Among two possible ways of DME synthesis from syngas (in a single-step or through methanol), a single-step process has some advantages (such as a favorable thermodynamic, cost saving due to using only a single reactor, the lower requirement of H_2/CO ratio, the feasibility of co-feeding CO_2 with syngas and valorizing CO_2) (Olah, Goeppert & Prakash 2009; Sun et al. 2014). Nowadays the technology of DME synthesis in a single-step has acquired a remarkable development.

The light olefins production from DME synthesized by this way is in progress. 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 over a stationary heterogeneous catalyst. As catalysts, there are used either molecular sieves (like SAPO-34 (Li et al. 2014; Ghavipour et al. 2014) or SAPO-18 (Hirota et al. 2016; Perez-Uriarte et al. 2016b)) or zeolites (HZSM-5 (Al-Dughaither & de Lasa 2014; Perez-Uriarte et al. 2016a, 2016c) or dealuminated

mordenite (Nasser et al. 2016)). The best results have been achieved with using zeolite MFI type (ZSM-5 structure) modified with metals and agglomerated with a binder (γ-Al_2O_3 or it precursor). For the modification of MFI, there are used magnesium (Goryainova et al. 2011), rhodium (Kolesnichenko et al. 2011), lanthanum and zirconium (Biryukova et al. 2011). Over these catalysts, the light olefins are obtained with the high yield (more 88% mol.) at 340-360^oC and atmospheric pressure. The major products are ethylene and propylene (their selectivity was more 80% mol.)

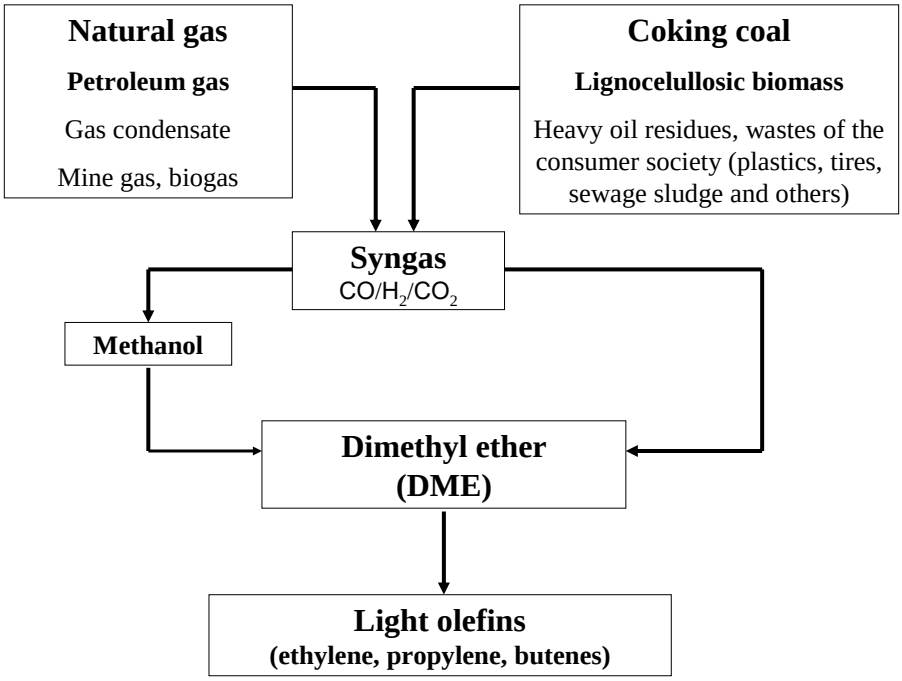


Fig. 1. Light olefins production through dimethyl ether (DME) and syngas

The recent tendency in DTO-process is the application of nano-scaled zeolite catalysts (Hirota et al. 2010; Hajjar et al. 2016). As known from other processes of petroleum synthesis, the application of nano-sized zeolites facilitated increasing the catalytic activity and extending the catalytic lifetime, as a result of decreasing intracrystalline diffusion limitations and improving mass and heat transfers (Popov, Pavlov & Ivanova 2016). As nano-scaled catalysts, there are usually used either nano-crystallines synthesized by a laborious method (as a rule, with the application of expensive templates) (Hu et al. 2009; Li et al. 2009) or nano-sized particles of zeolites obtained by any mechanical treatment of natural or commercial zeolites (Kazantseva et al. 2014; Kolesnichenko, Ezhova & Yashina 2016). As shown by Kolesnichenko et al. (2017), nano-scaled particles of MFI zeolites are the most stable, if the fine zeolite catalyst is suspended in a highly boiled liquid medium. Nevertheless, at present only a few examples of using suspended zeolites in catalysis are reported (Khadzhiev et al. 2015; Konnov et al. 2016).

In this study we aimed to obtain suspended zeolite catalysts for synthesis of light olefins from DME. Highly dispersed samples of zeolite MFI modified with magnesium have been obtained from the commercial zeolite by using different methods of the mechanical abrasion and the acoustic treatment. After dispersing these fine samples of Mg/MFI in high boiling liquids, the suspended catalysts have been tested in DME conversion (in a slurry-reactor). As a result, the most effective method of preparing ultra-dispersed suspended zeolite catalyst has been chosen.

2. MATERIALS AND METHODS

Suspended zeolite catalysts Mg/MFI were prepared from the commercial zeolite (trade mark ZVM) supplied by AZKOS (Angarsk, Russia). This zeolite MFI type, SiO_2/Al_2O_3= 37, is produced in ammonium form. First, the commercial sample was subjected to calcination at 550^oC for 5 hr in order to transform ZVM into proton-form. Then, obtained HMFI zeolite was modified with magnesium by the method described in the paper of Goryainova et al. (2011). As a result, there was obtained the initial sample of the catalyst Mg/MFI, with a coarse dispersion, containing 1% w. of magnesium. This coarsely dispersed sample was comminuted with using several methods. For shredding the initial sample of Mg/MFI, there were applied the handle mechanical grinding (in the agate mortar), an abrasion in a planetary mill (PULVERISETTE 7 premium line, FRITCH, Германия) for 5 min and for 20 min, the acoustic treatment in water (in the ultrasonic bath Elmasonic P30 H). As a result, four samples of comminuted catalyst Mg/MFI were obtained (table 1, samples I-IV). Another sample of the fine zeolite (table 1, sample V) was prepared by a prolonged acoustic treatment of HMFI in aqua solution of magnesium nitrate (in this case, the procedures of shredding zeolite and it modification with magnesium were combined). All comminuted samples were dried at 110-120^oC for 10-12 hrs, then, they were calcinated at 500-550^oC for 5 hrs. As a result, five powders of the comminuted catalyst of Mg/MFI were obtained.

The morphology and the texture of all obtained powder samples and the commercial sample ZVM were researched by scanning electron microscopy (SEM) (ZEISS; 10 40 SEM_SEI; Hitachi TM3030).

Suspended catalysts were obtained by dispersing powder's samples of comminuted Mg/MFI in silicone oil (trade mark Syltherm 800, DOW) in the ultrasonic bath at room temperature for 60 min. The dispersion of suspensions was determined by dynamic light scattering with using the particle analyzer Malvern Zetasizer NANO SZ.

The catalytic properties of suspended catalysts in the conversion of dimethyl ether to hydrocarbons were tested with using a stainless steel reactor (a slurry-reactor, autoclave type) equipped with a mechanical stirrer. The reaction was run at temperatures 220-300^oC under pressure 0.1 MPa, in a flowing gas mode. DME was diluted till 10% vol. by molecular nitrogen. The gas products were analyzed by the gas chromatography method with *CP*-PoraPLOT-Q capillary column (27.5 m/0.32 mm/10μm) connected to a flame ionization detector.

Table 1. Methods of MFI zeolite shredding for obtaining a comminuted zeolite catalyst of Mg/MFI

Shredding method	Duration, min	Sample of comminuted zeolite catalyst
Handle mechanical grinding Mg/MFI zeolite	60	I
Abrasion of Mg/MFI zeolite in a planetary mill	5	II
Acoustic treatment of Mg/MFI zeolite in water	60	III
Abrasion of Mg/MFI zeolite in a planetary mill	20	IV
Acoustic treatment of HMFI zeolite in aqua solution of magnesium nitrate (the combination of shredding zeolite and the modification of HMFI with magnesium)	>90	V

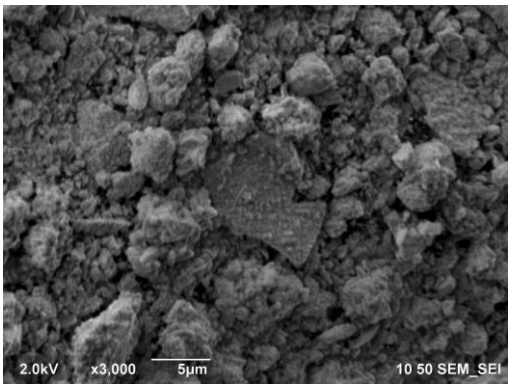
3. RESULTS AND DISCUSSION

As reported earlier (Kolesnichenko, Ezhova & Yashina 2016), the commercial zeolite ZVM was the rather coarse material, with layered inclusions, with large particles (till 3 μm). After handle crushing the initial sample of Mg/MFI, the dense layered structure of the zeolite didn't change, the size of the particles remained (sample I).

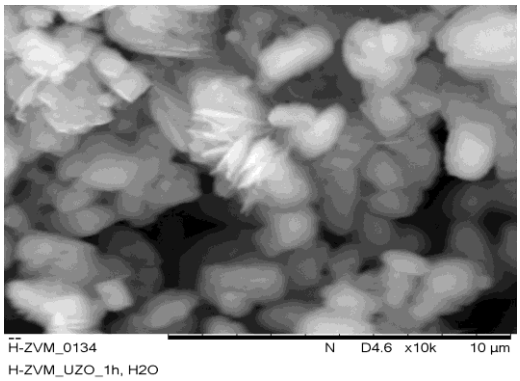
In the figure 2, there are shown SEM micro images of Mg/MFI comminuted by other methods (sample II-V). As seen, crushing the zeolite in a planetary mill for a short time (5 min) gave to destructing the layered structure and to partial reducing in size, but the texture of the zeolite was still dense (sample II). As a result of the acoustic treatment of Mg/MFI in water (for 60 min), the heterogeneous friable material was obtained (sample III). The uniform loose and friable material (particle size till 0.8 μm) was prepared by the abrasion of the initial Mg/MFI in a planetary mill for 20 min (sample IV). The most homogeneous material consisting from single crystals (till 0.5 μm) was formed by a long acoustic treatment of HMFI in aqua solution of magnesium nitrate (sample V).

Fig. 2. SEM micro images of zeolite samples

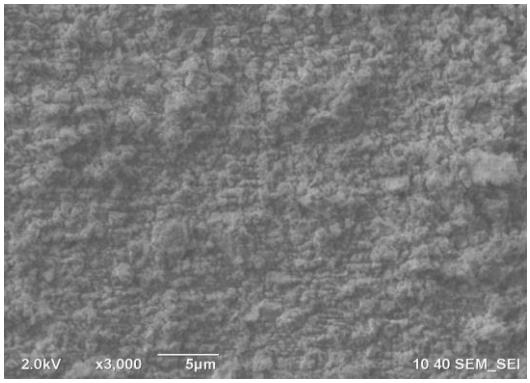
Sample II



Sample III



Sample IV



Sample V

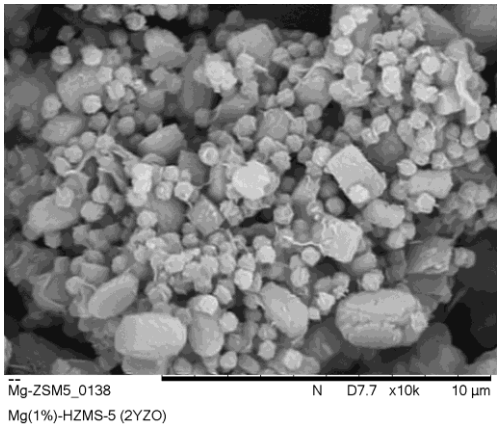


Table 2. Morphological features and dispersion characteristics of Mg/MFI comminuted samples

Mg/MFI sample	Morphological features	Average particle size of Mg/MFI in the powder, μm	Dispersion of Mg/MFI suspended, μm
I	A non-homogeneous material, dense layered texture	0.2-3.0	0.50-1.20
II	A non-homogeneous material, dense texture	0.2-1.5	0.60-0.80
III	Heterogeneous friable material	0.2-1.5	0.35-0.45
IV	Uniform loose and friable material	0.6-0.8	0.30-0.40
V	Homogeneous material, single crystals	0.2-0.5	0.25-0.30

When dispersing comminuted samples of Mg/MFI in the silicone oil, the reduction of the particle of zeolite in size was observed in all cases (table 2). The more uniform and the more friable was an initial powder material, the higher dispersion of the suspended zeolite was achieved. Suspension of the sample V formed from the most homogeneous and finest zeolite particles has the highest dispersion.

Table 3. The results of testing the catalytic properties of the suspended samples of comminuted Mg/MFI in dimethyl ether conversion into hydrocarbons in the slurry-reactor*

Zeolite catalyst sample	Dimethyl ether conversion, %	Light olefins C_2-C_4 yield, %	Hydrocarbon selectivity, %			
			Light olefins C_2-C_4	Alkanes C_2-C_4	Methane	Hydrocarbon C_5
I	80	42	53	30	6	11
II	84	46	55	33	6	12
III	89	49	55	33	5	7
IV	92	54	59	28	5	8
V	92	62	67	15	8	10

*Mg/MFI (1% w. magnesium) as a catalyst; 6.7% w. of the catalyst in the suspension; Syltherm 800 as a dispersion liquid medium; the temperature of dimethyl ether conversion of 300^{o}C; the pressure of 0.1 MPa; a gas flow as the mixture of dimethyl ether (10% vol.) and molecular nitrogen (90% vol.); a flow rate of 3.7 l/hr; weight hourly space velocity (WHSV) of dimethyl ether of 0.14 hr^{-1}; the time on stream of 2 hrs.

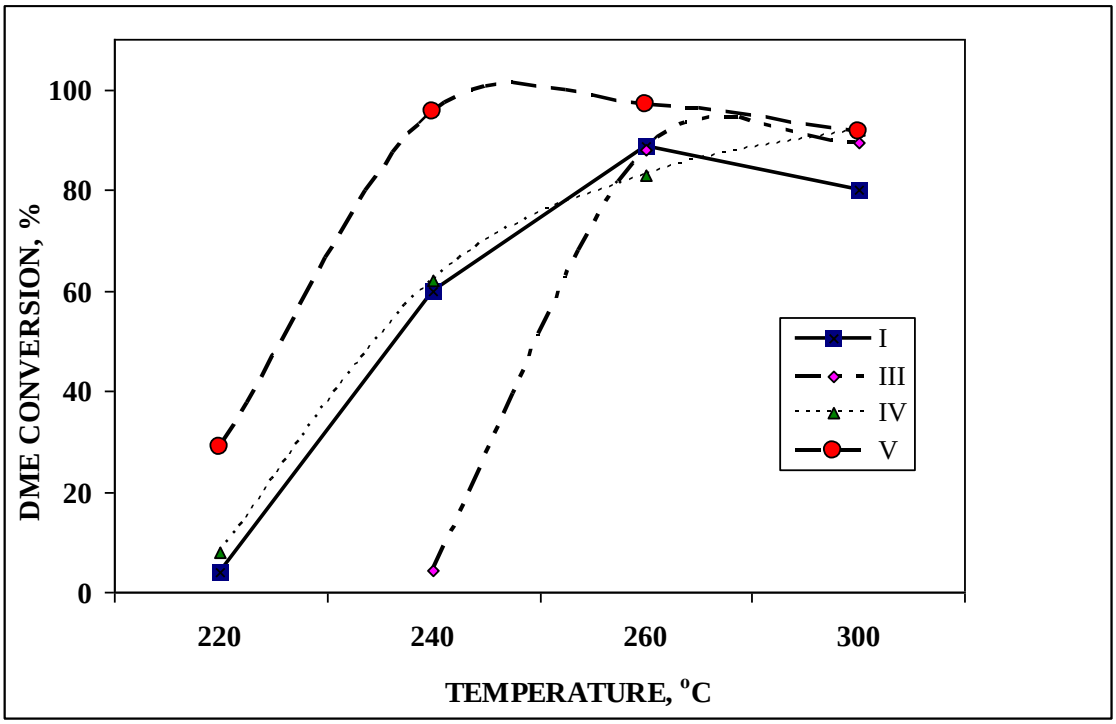
Fig. 3. The effect of temperature on dimethyl ether conversion in a slurry-reactor with using suspended samples of the catalyst Mg/MFI obtained by different shredding methods:

I. handle mechanical grinding (1%)Mg/MFI zeolite;

III. the acoustic treatment of (1%)Mg/MFI zeolite in water (1 hr);

IV. the abrasion of (1%)Mg/MFI zeolite in a planetary mill;

V. the acoustic treatment of HMFI zeolite in aqua solution of magnesium nitrate (for more 1.5hrs).



So, due to applying various methods for shredding commercial zeolite ZVM, five samples of the catalyst Mg/MFI comminuted with distinguished morphology and different dispersion were obtained. Suspensions of these catalytic samples were tested in the synthesis of light olefins from DME (in a slurry-reactor). The results are shown in table 3. According to data obtained, as increasing the homogeneity and the fineness of the catalyst, there was observed improving the catalytic properties. So, from sample I to sample V, you can see increasing DME conversion and olefins yield, decreasing the selectivity of undesirable C_2-C_4 alkanes (the major byproducts). When changing coarsely dispersed sample I for ultra-dispersed sample V, you can remark the increase in DME conversion more 10% and in olefin yield about 20%.

Thus, it can be argued that there is the dependence between the morphology and the dispersion of zeolite catalyst and its catalytic properties. The highest rates of the catalytic activity and selectivity were recorded for suspended sample V which is the finest dispersion catalyst, with the uniform morphology formed by single crystals. This catalyst led olefins synthesis with the high activity at temperatures 240-300^{o}C (figure 3). DME conversion remained at 91-97% over this temperature range. With using this suspended catalyst, C_2-C_4 olefins were obtained with a yield over 60% and with the improved selectivity to propylene. The rest catalytic samples didn't possess the same catalytic properties and lost the activity rapidly as decreasing temperature (figure 3).

So, on the base of data obtained, it may be concluded that the best method of preparing the effective suspended catalyst for the innovative light olefins synthesis from DME (in a slurry-reactor) is the combination of shredding zeolite HMFI and its modification with magnesium during prolonged acoustic exposure in aqua solution of Mg $(NO_3)_2$ (method V).

CONCLUSIONS

1. Ultra-dispersed samples of zeolite Mg/MFI suspended in high boiling liquids have been shown to be promising catalysts for the innovative synthesis of light olefins from dimethyl ether in a slurry-reactor.
2. From the commercial zeolite of MFI type (trade mark ZVM supplied by AZKOS, Russia, Angarsk), five samples of comminuted Mg/MFI with the various morphology and dispersion have been obtained. The uniformity of morphological structure and the fine dispersion of zeolite samples have been established to be the key factors determining the particle size of Mg/MFI in the suspension and the catalytic properties of the suspended comminuted zeolite.
3. The ultra-dispersed zeolite Mg/MFI, with the homogeneous texture, formed by monocrystals with the particle size 0.2-0.5 μm, has been shown to give the finest suspension and the most effective suspended catalyst. This catalytic sample was obtained by the method of the combination of shredding zeolite HMFI and its modification with magnesium during a prolonged acoustic exposure in aqua solution of Mg $(NO_3)_2$.

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