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INFLUENCE OF ZEOLITE CRYSTALS EXTERNAL SURFACE MODIFICATION ON TOLUENE *PARA*- DISPROPORTIONATION SELECTIVITY

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Abstract. On the basis of HZSM-5 a series of catalysts with the deactivated external surface have been prepared by extracting aluminium atoms from zeolite crystals or by covering this zeolite's surface with the tetraethoxysilane thermal destruction products. It has been discovered that the external surface deactivation is not the main factor of the *para*-selectivity increasing in the toluene to benzene and *p*-xylene disproportionation reaction. It is decreasing of the diffusion of *o*- and *p*-xylene from the catalyst pores on the external surface of zeolite crystals that seems to be the determinant.

Key words: Toluene disproportionation, HZSM-5 zeolite catalysts, *para*-selectivity, external acid sites, external surface deactivation, diffusion.

1. Introduction

Today the toluene disproportionation is one of the important ways of producing benzene and particularly *p*-xylene. Two main methods of improving the disproportionation *para*-selectivity on zeolites are known: reduction of catalyst diffusive-kinetic characteristics to enlarge the residence time of *m*- and *o*-xylenes in the catalyst pores, thereby promoting their transformation into *para*-isomer [1, 2] and deactivation of external surface acid sites to prevent the undesirable isomerization of *p*-xylene to *m*- and *o*-isomers [3, 4]. There is no generally accepted opinion concerning the priority of one of these two approaches. Industrial processes involve, as a rule, the techniques of the pre-coking or surface silica deposition to increase the most desirable *p*-isomer content in xylene mixture. However the question is open where the formed coke species are located [4, 5]. Both of the methods have shortcomings [6]: intensification of cracking processes and partial loss of catalyst activity, respectively.

We have not found the reports about deactivation of the catalysts external surface by removing active sites.

The aim of this work is synthesis of HZSM-5 samples with the deactivated in different ways zeolite crystals external surface, and investigating of their properties in the toluene to benzene and xylenes disproportionation.

2. Experimental

To attain the above aim we have used 2, 4, 6-trinitrophenol (TNPh, or picric acid), tetraethoxysilane (TEOS), and silicon tetrachloride, the last as a vapour.

ZSM-5 (SiO_2/Al_2O_3=41) H-form has been obtained by the ion exchange of parent Na^+ cations for NH_4^+ cations with further calcination (sample 1).

Dealumination was performed by treating the initial zeolite samples with correspondent amount of aqueous (samples 2, 3, 5, 6) or spirituous (ethanol) (sample 4) solutions of TNPh at 373 K (water bath) or ambient temperature, respectively.

Modifying HZSM-5 by thermo destruction of tetraethoxysilane has been realized in the air-dry (sample 7) or dehydrated (sample 8) states, the samples being added to the definite volume of TEOS hexane solution (solid to liquid phase ratio 1:3). The suspension has been stirred for 15 min. Then hexane has been vaporized, and the samples have been calcined at 773-823 K for 3 h. The temperature was being raised with the speed of 3 degrees per min. SiO_2 deposits have been determined to be as 6,5 and 2,3 wt.% for samples 7 and 8 correspondingly, sample 7 being double modified.

Catalyst 9 was synthesized by treating ZSM-5 with $SiCl_4$ vapour in autoclave under static conditions at 623 K with further washing and obtaining H-form under the above mentioned conditions.

The catalytic properties of the samples (100 mg of each) have been investigated at 773 K in micro pulse set-up assembled on the base of "TSVET -500" chromatograph (capillary column 50 mm in length with 0.5 mm inner diameter, tvin-60 as the stationary phase, flame ionizing detector) using hydrogen as carrier gas (10-120 cm^3/min) under low surplus pressure. The toluene pulse volume was 2 ml.

3. Results

3.1. Acid treatment of the ZSM-5

Due to having molecules of large size, theoretically picric acid can extract aluminium atoms from the zeolite external surface only. Furthermore, rather external dealumination is known [7] to take place when sodium form of a mordenite is subjected to acid treatment. Therefore in addition to its H-form Na-form of ZSM-5 was used as catalyst basis.

The Table summarises the aluminium elimination data from the samples 2-6. The content of external acid sites has been taken as equal to 0.023 mmol/g [8].

Table

Dealumination of ZSM-5 zeolites by aqua (aq) and ethanol (EtOH) solutions of trinitrophenol

№	Initial form of zeolite	Amount of trinitrophenol, mmol/g	Amount of aluminium extracted, mmol/g
1	Hydrogen	-	0
2	Hydrogen	0.5 (aq)	0.08
3	Sodium	0.25 (aq)	0
4	Hydrogen	5 (EtOH)	0.03
5	Hydrogen	5 (aq)	0.12
6	Sodium	5 (aq)	0.12

The data obtained for the sample 2 show the amount of aluminium extracted to be greater than the number of external Al atoms. There are two possible reasons for this fact. The first one is extracting by the acid the extra framework aluminium generated during the H-form obtaining: only such aluminium or total, including that of external surface. The second reason is the ability of TNPh to dealuminate not only the external surface, as it may be expected due to comparably large picrate-anions sizes, but the internal surface as well.

Absence of Al in the filtrate from the sample 3 (NaZSM-5) seems to support the first assumption (Table). However, on the other hand, the absence of NaZSM-5 dealumination may be connected with the acting acid concentration decrease, as in the Na-zeolites the substitution of Na cations for acid protons occurs prior to the Al extraction from the zeolite structure [9]. Therefore we have increased the concentration of acid solution (samples 4-6), additionally using ethanol instead of water in case of sample 4 synthesis.

In spite of more concentrated ethanol solution (sample 4) we have failed to eliminate more aluminium atoms from the zeolite as compared to water solution conditions (samples 2, 3) which might be due to a small degree of TNPh dissociation in ethanol resulting from lower dielectric permeability of the latter. However increase in the amount of eliminated Al along with increased acid quantity in the cases of sample 5 and especially of

extraframework-Al-free sample 6 lets us suppose that dealumination of zeolite framework by the picric acid still takes place, and acid molecules can penetrate the deeper layers of zeolite crystals extracting the aluminium atoms also from the sites near the pores entrances as well.

3.2. Catalytic testing

The catalytic properties of the samples synthesized, in particular their *para*-selectivity (S_p), have been investigated in their dependence on the of carrier gas flow rate that effects the residence time of both reactive and product molecules within the catalyst cavities. We were interested to study the *para*-selectivity of the samples and their dependence on the preparation method at small residence time of both initial toluene and conversion products on the catalyst bed. Such testing method prevents further conversion of the primary reaction product, especially on the external surface of zeolite crystals, which excludes the undesired process selectivity decrease due to the above mentioned possible isomerization of *p*-xylene to *ortho*- and *metha*-isomers.

The data obtained (Figure) evidence that the preparation method is of great importance from the standpoint of *para*-selectivity. The curves 4, 5, 6 for acid
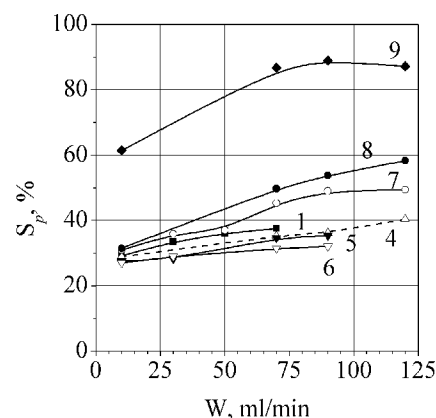

Figure. Dependences of selectivity for p-xylene (S_p) on carrier gas (W) flow rate for different catalysts (curve numbers coincide with the sample numbers in the text and in the Table)

treated zeolites are situated not far from the curve of the initial sample 1: S_p value does not exceed 40 % at the flow rate of the carrier gas up to 120 ml/min. The dependences for TEOS modified samples 7 and 8 start near the unmodified sample curve 1, shifting subsequently upwards to 50-60 % values. As was mentioned above, sample 7, unlike sample 8, has not been dehydrated before TEOS impregnation. Finally, sample 9 on the base of zeolite treated by $SiCl_4$ demonstrates the highest *para*-selectivity, originating from more than 60 % and reaching the highest value of about 90 % at carrier gas rate of 90 ml/min.

4. Discussion

In spite of the expectations, the deactivation of external surface of the zeolites has not only failed to improve their *para*-selectivity but even somewhat decreased it. On the base of the chemical analysis results (Table) we arrived at a conclusion about the extraction of aluminium atoms from the sites near the pore entrances, which leads to the pore entrances diameters increasing. In consequence we have succeeded in external surface deactivating of samples 2, 4-6 when simultaneously increasing the ability of reaction products to diffuse from the zeolite channels, i.e. increasing the departure of the undesired *o*- and *m*-xylenes on the external surface of zeolite crystals.

On the other hand, we believe that during the HZSM-5 modification by TEOS, not only external surface inactivation occurs but also partial blocking of pore openings by the products of TEOS destruction takes place. The latter seems to be true especially for sample 8, in which SiO_2 cover might expend towards the pores mouths, reinforcing the molecular sieve effect, as zeolite channels of this sample were preliminarily emptied from water molecules. In case of sample 9, similarly to $SiCl_4$-treated Y-type zeolite [10, 11], some amount of extraframework species have probably formed in the channels of the catalyst thus hindering free movement of the molecules produced.

That is why the catalysts selectivity seems to be strongly dependent on the extent of the steric hindrances to the migration of more bulky *o*- and *m*-xylene isomers within the crystals of zeolite basis. One can assume that the absence of the sites for the secondary *p*-xylene isomerization on the external surface of a catalyst seems to be of some positive influence on the *p*-selectivity only for sample 4 with the smallest rate of the acid modification and the highest carrier gas rate (Figure). At the same time the larger the pores' openings the lower *para*-selectivity is observed regardless of the external surface deactivation (samples 5, 6). On the contrary, inhibition of the diffusion of more bulky isomers from the zeolite channels increases *para*-selectivity of samples 7, 8, and especially 9 in the whole carrier gas rate diapason.

Therefore, under applied micro pulse reaction conditions, deactivation of external surface by removing the active sites using picric acid does not enhance the selectivity of toluene disproportionation process. The effect is levelled down by zeolite pore entrances enlargement. The pore size restricting plays the dominant role in attaining the high *para*-selectivity in toluene disproportionation reaction. Taking into account that even the smallest applied carrier gas rate cannot decrease *para*-selectivity of sample 9 below 60 % (that is twice as much as the value for unmodified zeolite), the tendency observed may remain valid for the increased residence time of all the components on the catalyst bed. These aspects of disproportionation require additional investigation. What can be stated definitely is that the highest yields of *p*-xylene can be achieved by combining the lowest acidity of the external surface of zeolite crystals and maximum decreased diffusivity of zeolites.

Regarding the positive influence of the preliminarily zeolite catalyst coking upon the disproportionation results, mentioned in the introductory part of the paper, such an influence can be caused not only by narrowing the entrances to zeolite cavities by coke, but similarly to the TEOS action, deactivating the external surface of zeolite crystals by blocking external surface acid centres.

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ВПЛИВ МОДИФІКУВАННЯ ЗОВНІШНЬОЇ ПОВЕРХНІ ЦЕОЛІТНИХ КРИСТАЛІВ НА ПАРА-СЕЛЕКТИВНІСТЬ ДИСПРОПОРЦІОНУВАННЯ ТОЛУОЛУ

Анотація. На основі цеоліту HZSM-5 приготовано серію каталізаторів з дезактивованою зовнішньою поверхнею шляхом вилучення атомів алюмінію з цеолітних кристалів або покриттям цієї поверхні продуктами термічного розкладу тетраетоксисилану. Знайдено, що дезактивація зовнішньої поверхні не є основним фактором зростання пара-селективності в реакції диспропорціонування толуолу до бензолу й п-ксилолу: таким бачиться погіршення дифузії о- і м-ксилолу із пор каталізаторів на зовнішню поверхню цеолітних кристалів.

Ключові слова: толуолу диспропорціонування, HZSM-5 цеолітний каталізатор, пара-селективність, зовнішньо-поверхневі кислотні центри, дезактивація поверхні, дифузія.