

Alkylation of Benzene with 1-Alkenes over Zeolite Y and Mordenite

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Abstract

Influence of reaction temperature, molar ratio of benzene to 1-alkenes, weight of catalyst and length of hydrocarbon chain of 1-alkenes were tested in alkylation of benzene by 1-alkenes. The liquid-phase alkylation was carried out in autoclave at autogeneous pressure. Synthetic zeolites of Y-type and mordenite in H-forms were tested as solid catalysts. Zeolites were characterized by XRD, N₂ adsorption, FTIR with pyridine adsorption and NH₃-TPD. The influence of the reaction conditions (temperature, molar ratio benzene to 1-alkenes and weight of catalyst) on the conversion and selectivity to 2-phenyl isomer was studied with different 1-alkenes from C₆ to C₁₈. The activity of Y-zeolite was greater than that of mordenite but the selectivity to 2-phenyl isomer was much better in the case of mordenite catalyst.

Keywords: Alkylation, aromatics, 1-alkenes, zeolites

Introduction

The alkylations of aromatic hydrocarbons with different 1-alkenes or alcohols are applied on a large scale in the chemical industry. Reaction rate and mechanism are influenced with structure of alkylation agent, polarity, solvation ability of solvent and character of catalyst. As alkylation catalysts mainly Friedel-Crafts type liquid-phase catalysts as mineral acids are frequently used (H₂SO₄, HCl, H₃PO₄...). Because of problems with corrosion and high requirements on feed drying there is an effort to replace FC-catalysts with solid acids. Among solid acid catalysts mainly amorphous aluminosilicates and zeolites are the subjects of research.

In 1942 started the use of an amorphous aluminosilicate in alkylation of benzene with ethylene and propylene (Franck 1988; O'Kelly 1947). Later it was shown, that zeolites of type X and Y were effective for alkylation of aromatics with olefins (Ventuto 1966). In 1989 company Lumus, UOP, Unocal opened plant for the production of ethylbenzene in liquid phase by zeolite of type Y.

Advantages of alkylations in liquid phase are longer lifetime of catalyst and simply thermal control of process (Wang 1996; Da 2001). In the production of ethylbenzene also catalysts of type MSA, MCM and BEA were used (Bellussi 1991; Le 1992, Perego 1999).

The most used alkylating agents are alkenes and alkylhaloids, predominantly cheap alkenes (ethylene, propylene, and linear alpha alkenes up to C₂₀). As alkylating agent are used also alcohols, ethers, aldehydes, ketones. To the most important alkylation of aromatic hydrocarbons belongs alkylation of benzene with ethylene to ethylbenzene or with propylene to cumene, and alkylation of benzene with C₁₂ to produce dodecylbenzene as intermediate in surfactants production. In all these alkylation the liquid FC catalysts started to change into solid acids, mainly zeolite catalysts.

In this work we studied the alkylation of benzene with 1-alkenes over Y zeolite and mordenite from the point of view of the effect of zeolite pore size, reaction conditions and alkyl chain length of 1-olefin in range of C₆-C₁₈ on the catalytic activity and selectivity to 2-phenyl isomer.

Experimental

Sodium forms of zeolite Y with Si/Al ratio 2.24 and mordenite with Si/Al ratio 6.40 were obtained from Research Institute of Petroleum and Hydrocarbon Gases, Bratislava. Ammonium forms of zeolites were prepared by repeated ion exchange with ammonium nitrate, Na₂O content decreased to 0.55 wt. % in Y-zeolite and < 0.02 wt. % in mordenite. H-form of zeolites were prepared before the reaction by calcination of ammonium form 4 h at the temperature 450 °C and cooled in exicator.

Benzene (Lachema Brno, 99.8%) and commercial 1-alkenes - LAO (Linear Alpha-Olefins, Spolana Neratovice, purity about 95.9%) with alkyl chain C₆-C₁₈ were used for alkylation tests.

The surface area and pore properties were analyzed by physical adsorption of nitrogen at the temperature of liquid nitrogen using ASAP-2400 (Micrometrics). Before analysis, calcined samples were evacuated overnight for 8 h at 623 °K under vacuum of 2 Pa. Surface area was

obtained using conventional BET isotherm ($p/p_0 = 0.05 - 0.3$). External surface area and volume of micropores were calculated from t-plot using Harkins-Jura master isotherm. Total pore volume was determined from adsorbed nitrogen at relative pressure 0.98.

Infrared spectra were recorded with a FTIR Genesis (Unicam) spectrometer. The Brønsted and Lewis acidity of zeolite Y was analyzed by infrared spectroscopy using pyridine as basic probe molecule on self-support wafers with the density of about 7 mg/cm^2 . The samples were activated at 723 °K for 90 minutes under vacuum of 10^{-4} Pa . The infrared spectra of the samples were recorded at room temperature. After recording of FTIR spectra of OH-region $3600\text{-}3750 \text{ cm}^{-1}$, pyridine was adsorbed for 30 minutes at a room temperature and after desorption at 423 °K for 30 minutes under vacuum of 10^{-4} Pa FTIR-spectra of adsorbed pyridine in range of $1450\text{-}1550 \text{ cm}^{-1}$ were recorded.

The total acidity of zeolite Y and mordenite was determined by TPDA - Temperature Programmed Desorption of Ammonia. 300 mg of sample was calcinated at 723 °K in a flow He (1.2 ml.s^{-1}). NH_3 was adsorbed at 493 °K from a gaseous mixture NH_3 in He (1.2 ml.s^{-1}) up to saturation of the surface for 20 minutes. The excess of NH_3 was eliminated with flow of He of 2.7 ml.s^{-1} for 110 minutes. Desorption of NH_3 was initiated by continuous heating of the sample in a flow He (2.7 ml.s^{-1}) up to 823 °K at a heating rate of $14.07 \text{ °K.min}^{-1}$. The desorbed amount of NH_3 was determined by absorption in surplus of sulphuric acid (0.05 mol.dm^{-3}) followed by back titration with a NaOH solution.

Alkylation was realized in an autoclave (batch reactor) at the temperature 120 °C for zeolite Y and 200 °C for mordenite at autogeneous pressure that was from 0.27 MPa at 120 °C up to 1.21 MPa at 200 °C . Before reaction, NH_4 -forms of zeolites were activated at 450 °C for 3 h and added to the reaction mixture as H-form after cooling in an exicator. 80 g of the reaction mixture was used for each experiment. Liquid samples were taking from reactor during experimental conditions from the bottom of reactor via sampling valve. The reaction products at selected temperature after the pressure release after outlet from the valve were cooled in ice trap.

Samples of products for analysis were taken in following way: the first sample was taken at reaching the reaction temperature 120 °C (200 °C mordenite) in 30 min. The next samples were taken after each 30 minutes of reaction time up to 240 min.

Analysis of feed and the reaction products was carried out with gas chromatograph Hewlett-Packard 5890 A, Series II with FID, capillary column HP-1 $25\text{m} \times 0.2\text{mm} \times 0.32\mu\text{m}$ under following conditions: Inj. Temp. 350 °C , Det. Temp. 350 °C , Oven temperature for LAO C_6 -

C₁₀: 35 °C for 5min, 4 °C/min to 250 °C and isothermically to the end of analysis; Oven temperature for LAO C₁₂-C₁₈: 100 °C for 5 min, 4 °C/min to 280 °C and isothermically to the end of analysis.

Structures of olefins and alkylbenzenes in reaction mixtures were verified by GC-MS using MS25RFA Kratos, Manchester equipment. Small quantities of di-alkylbenzenes were observed and traces dimers of 1-alkenes were detected mainly in the case of small benzene: olefin ratio in feed and higher conversion. At high conversion besides linear alkylbenzenes also traces of branched alkylbenzenes were observed.

Conversion was calculated as a percentage of alkylbenzenes in sum of 1-alkenes and alkylation products - alkylbenzenes, eventually also di-alkylbenzenes and dimers. Selectivity was calculated as a percentage of 2-phenylalkylbenzene, which is the most biodegradable and consequently the most desired alkylation product, in all linear alkylbenzenes.

Results and Discussion

The alkylation of benzene with long chain 1-alkenes goes through a typical Friedel-Crafts reaction. It is a complex process consisting of possible various side reactions, besides the main reaction, alkylation. The formation of various phenyl isomers is likely by the electrophilic substitution of carbenium ion, which is formed upon chemisorption of 1-alkene on the catalyst surface. The results showed that, except for the desire products - a series of isomers of monoalkylated benzene, dimmers and dialkylbenzenes were created.

Characterization of used catalyst

X-ray diffraction confirmed that the both zeolites had a single-phase high crystallinity. The main characteristics of the zeolite samples are given in Table 1. Nitrogen adsorption results show that both zeolites have standard pore structure characteristics for these zeolite structures – micropore volume of 0.323 cm³.g⁻¹ for Y-zeolite and 0.145 cm³.g⁻¹ for mordenite. Values of external surface areas indicate smaller zeolite crystals for Y-type zeolite. The total acidity as determined using ammonia TPD is also given in Table 1. FTIR-spectra of adsorbed pyridine in Fig. 1, shows that Y-zeolite has acidity in both Brønsted (1543 cm⁻¹) and Lewis acid sites (1450 cm⁻¹) while the mordenite catalyst contains only Brønsted acid sites. This fact indicates the mordenite as possible more suitable catalyst for alkylation reaction, because Lewis acid centers are believed to support the dimerisation-polymerisation reactions.

Table 1 Physico-chemical characteristics of used catalyst

Sample	Si/Al	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	S_t ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$)	Acidity by TPDA *($\text{mmol}(\text{a.c.}) \cdot \text{g}^{-1}$)
H-Y zeolite	2.24	693	37.0	0.323	0.409	2.14
H-Mordenite	6.4	327	12.6	0.154	0.178	1.82

* a.c. – acid centre

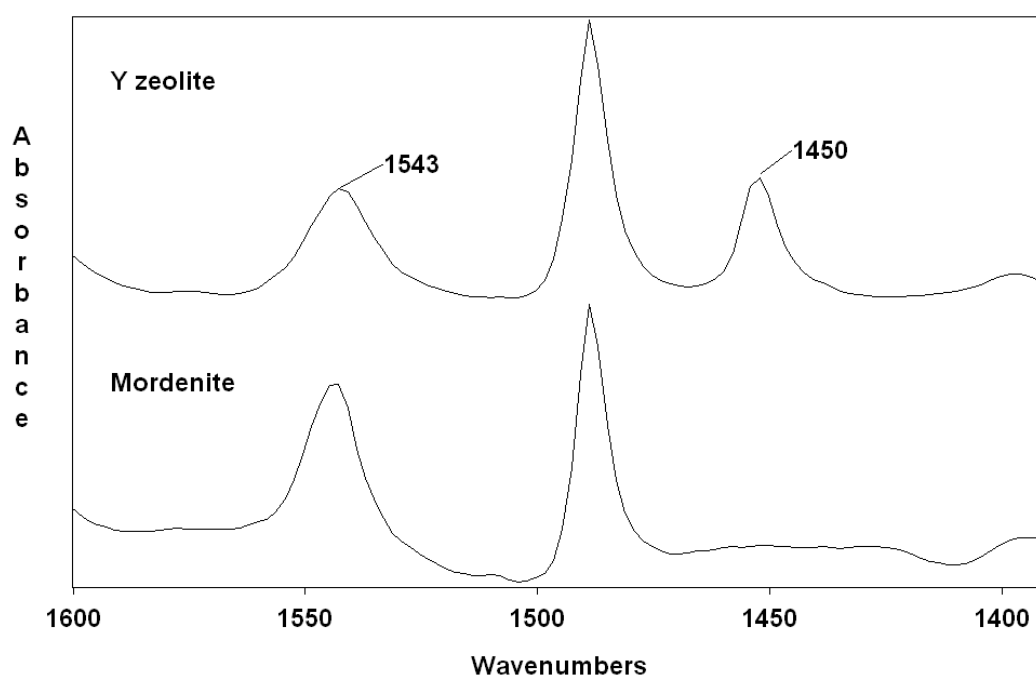


Fig. 1 FTIR-spectra of adsorbed pyridine on H-forms of Y-zeolite and mordenite

Effect of reaction temperature on the alkylation of benzene

To investigate the effect of temperature on the conversion of 1-hexadecene and on the product selectivity, the alkylation of benzene over Y zeolite was carried out in the temperature range of 80-120° C. As it is seen from Fig.2, by the increase of temperature from 80 to 120 °C the conversion of 1-hexadecene increased from 28.1% to 95.3%.

However, the increase in conversion is connected with the decrease of selectivity to 2-phenyl isomer. This can be due to the increasing probabilities of rapid equilibration of the olefin isomer or easy diffusion of the bulkiest LAB isomers of the zeolite cavities at higher temperature. At the maximum conversion of 1-hexadecene (95.3%) in 90 min. of time-on-

stream at 120 °C were decreased the product selectivity for 2-phenyl isomer to about 20 %, and distribution of isomers was shifted more to the centre of hexadecane molecule.

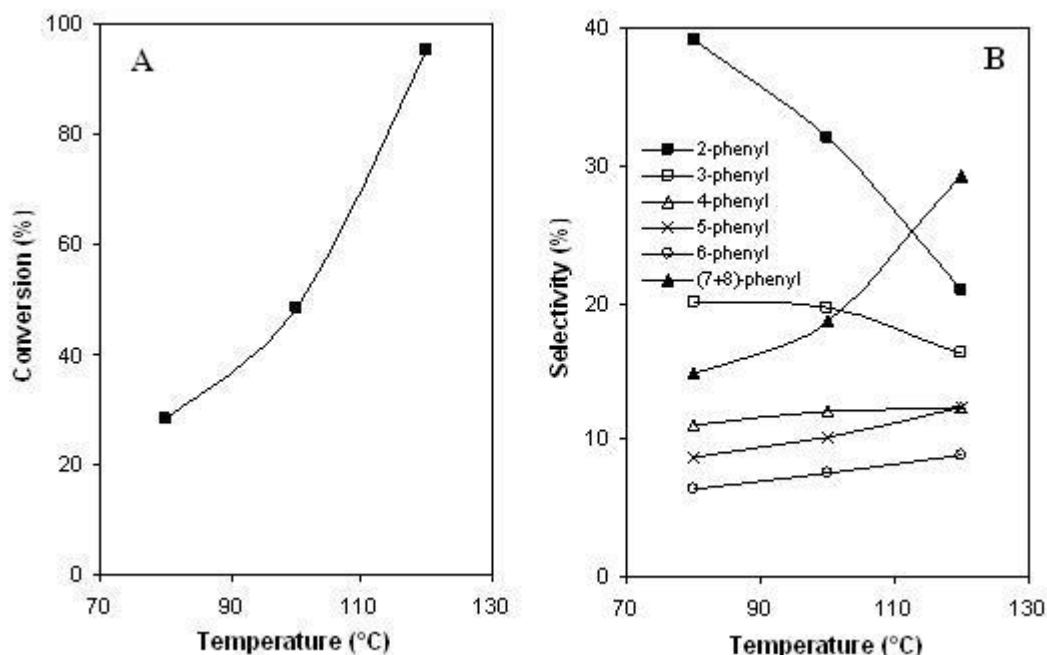


Fig. 2 Effect of reaction temperature on 1-hexadecene conversion (A) and product selectivity (B) over HY zeolite. Conditions: Be/C₁₆ = 8.6; catalyst weight = 2.0 g (2.5 wt. %); reaction time = 90 min.

On the base of detail analysis of alkylation products by GC-MS it was found that parallel and consequent reactions besides of primary alkylation of benzene proceed. The parallel one is double-bond shift from position 1 to inside of molecule with following alkylation of benzene, and consequent one is the isomerization of primary created 2-phenyl hexadecane isomer to others. The increase of temperature resulted in the increase of conversion not only in the desired primary reaction, but also in parallel reaction of double-bond shift to middle of the alkene molecule, and consequently the alkylation produced 3- to 8-phenyl isomers.

Effect of molar ratio of benzene:1-alkene on the alkylation of benzene

The effect of benzene:1-alkene molar ratio on the conversion of 1-hexadecene and product distribution at the temperature of 120 °C are presented in Fig. 3. The mole ratio of benzene:1-hexadecene was changed from 3.2 to 10, keeping other conditions the same.

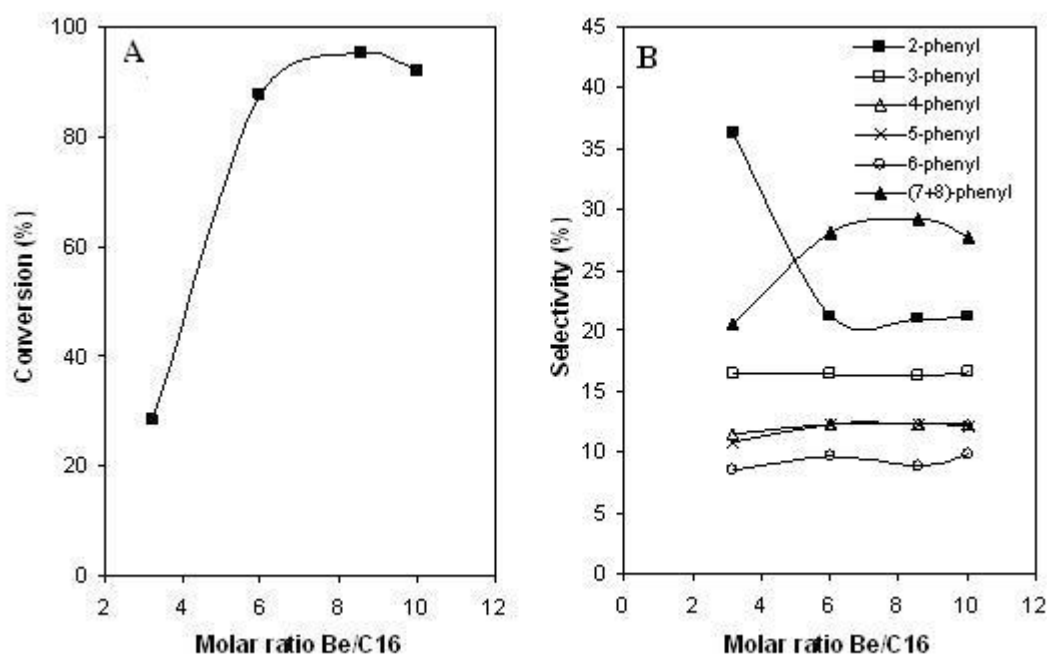


Fig. 3 Effect of molar ratio Be:C₁₆ on 1-hexadecene conversion (A) and product selectivity (B) over HY zeolite. Conditions: T = 120 °C; catalyst weight = 2.0 g (2.5 wt. %); reaction time = 90 min.

With the increasing molar ratio benzene to alkene the conversion in 90 min. of time on stream increased from 28.2 % to 95.2 % and then decreased to 91.9 %. The maximum conversion of 1-hexadecene (95.2 %) was obtained at molar ratio benzene: 1-hexadecene 8.6. At the low conversion of 1-hexadecene the highest selectivity to 2-phenyl hexadecane was observed. With the increase of benzene:1-hexadecene from 3.2 to 6-10 the conversion increased but the selectivity for the 2-phenyl isomer decreased from 36 to about 19-20 %. On the other side, at lower benzene:1-alkene ratio, higher probability to create dimers as well as di-alkyl benzenes was observed, as it is seen from Table 2. From this point of view the benzene: 1-alkene ratio seems to be better to keep higher. From this reason it was decided to use the ratio 8.6:1.

Table 2 Composition of products of alkylation of benzene with 1-hexadecene at different benzene: 1-hexadecene ratio at 120 °C, reaction time = 240 min.

Benzene:1-hexadecene (mol/mol)	Alkylbenzenes (wt. %)	Dialkylbenzenes (wt. %)	Dimmers (wt. %)
3.2:1	97.38	2.54	0.08
6:1	98.61	1.36	0.03
8.6:1	99.92	0.08	0.00
10:1	100.00	0.00	0.00

Effect of charge of Y zeolite catalyst on the alkylation of benzene

Effect of charge of Y zeolite catalyst on the alkylation of benzene with long chain 1-alkenes was investigated by varying the dosage from 0.625% to 2.5% expressed as the mass concentration of Y zeolite in the reaction mixture. The results are presented in Fig. 4 as conversion of 1-hexadecene vs. catalyst charge. It is seen that the conversion of 1-hexadecene in 90 min increased from 46.3% to 95.3%. At the same time, with the increase of the conversion, the selectivity to 2-phenyl isomer decreased to values about 20 %.

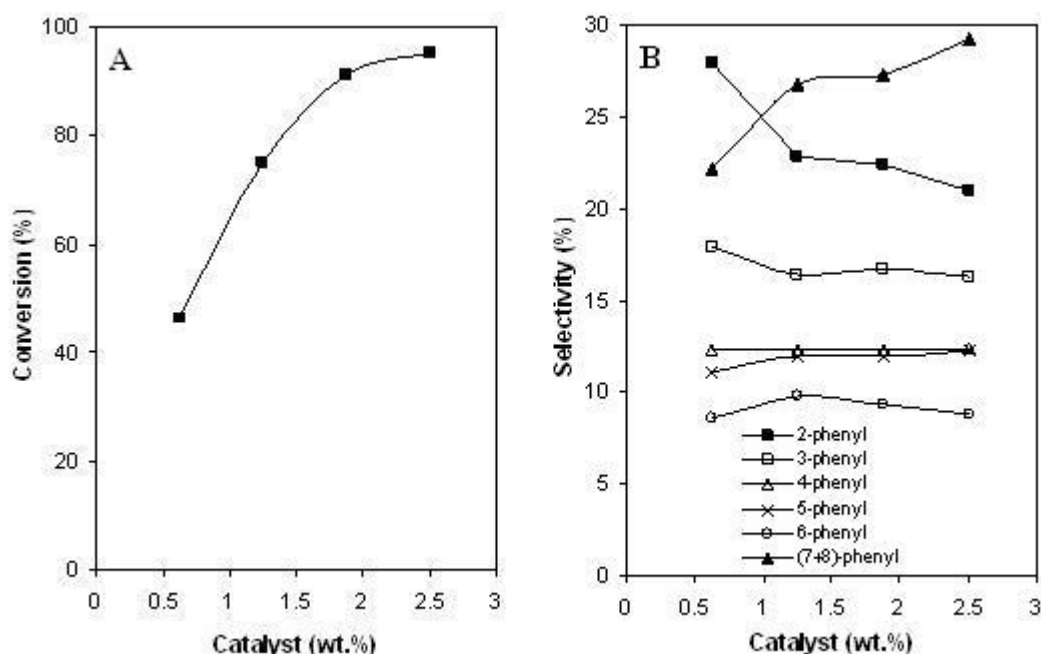


Fig. 4 Effect of charge of Y zeolite catalyst on 1-hexadecene conversion (A) and product selectivity (B). Conditions: T = 120 °C; Be/C₁₆ = 8.6; reaction time = 90 min.

Time on stream study over Y-zeolite

In order to study the effect of time on stream, alkylation reaction was studied as a function of time under optimized conditions and the results are demonstrated in Fig. 5. It can be seen that, the conversion for 1-alkenes increases from 41.1% at 30 min. to practically 100 % in 120 – 150 min. More than 95% of conversion can be obtained in reaction time 90 min. The selectivity to 2-phenyl hexadecane decreases with conversion to about 19%. It seems that this composition of alkylbenzenes is near to thermodynamic equilibrium, because over 90 min of TOS, representing more than 95 % conversion and the composition of alkylbenzenes practically did not change.

On the basis of the above studies, it is found that the optimum reactions for the Y zeolite enhanced alkylation of benzene with long chain 1-alkenes in liquid phase are 8.6:1 of benzene

to long chain 1-alkenes, 2.5 wt.% of catalyst charge at the temperature of 120 °C for 90-180 min.

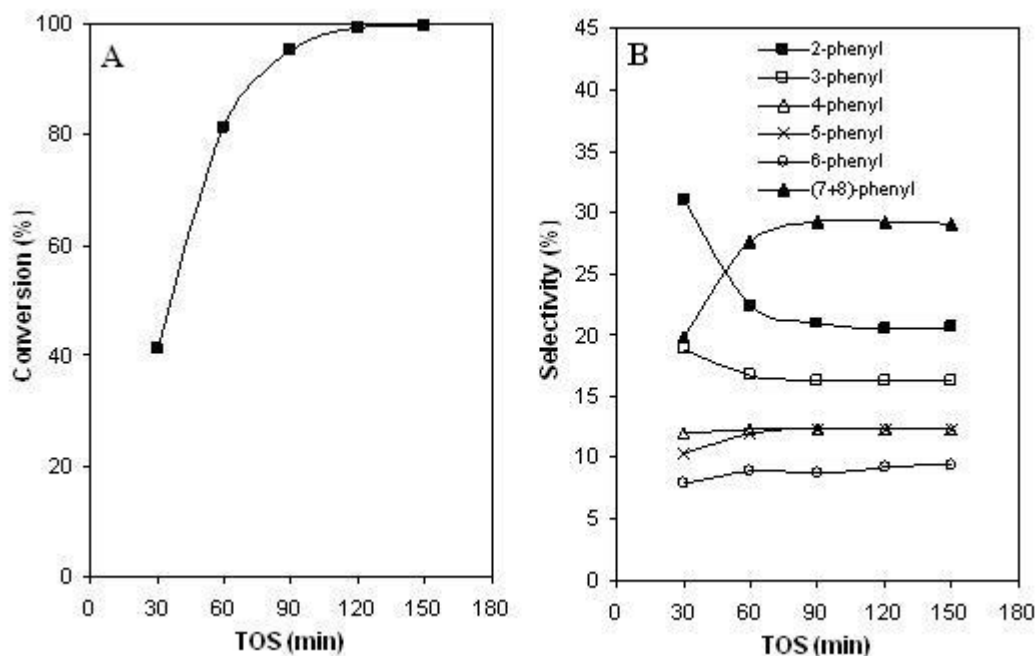


Fig. 5 Effect of reaction time on 1-hexadecene conversion (A) and product selectivity (B) over Y zeolite. Conditions: T = 120 °C; Be/C₁₆ = 8.6; catalyst weight = 2.0 g (2.5 wt.%);

Time on stream study over mordenite

The activity and product selectivity of mordenite catalyst as a function of time for the reaction of benzene alkylation with 1-hexadecene at the temperature of 200 °C, molar ratio Be/C₁₆ of 8.6:1 and 2.5 wt.% of catalyst is depicted in Fig. 6. The temperature 200 °C was chosen on the base of preliminary studies, because at 120 °C the conversion was very low even after 200 min of TOS. It can be seen that, the conversion of 1-alkene almost linearly increased with reaction time to 77.5% in 240 min. of TOS. The selectivity to 2-phenyl isomer was at low conversion very high – more than 80%, but with increased conversion only slightly decreased and even at almost 80% conversion the selectivity was more than 60%. The differences in conversion and selectivity between Y-zeolite and mordenite can be explained mainly by the differences in their pore structures. Y-zeolite having 3-dimensional pore structure with pore entrance windows of 0.74 nm allows good accessibility to great concentration of acid centers inside of zeolite crystals without restriction to formation of all phenyl-hexadecane isomers. Mordenite with lower concentration of acid sites as consequence of higher Si/Al ratio has only uni-dimensional pore system accessible to aromatics but with narrower pore size –

0.67x0.7 nm. Uni-dimensional and narrower pore system of mordenite in comparison with three-dimensional wide-pore system of Y-zeolite decreases the accessibility of acid centres inside of porous structure and consequently desires higher temperature to achieve comparable conversion. On the other side, the narrower pore system of mordenite ensures higher shape-selectivity towards the increase of selectivity to the most desired product isomer - 2-phenyl hexadecane.

Effect of alkyl chain length of 1-alkene on the alkylation of benzene

To investigate the effect of alkyl chain length of 1-alkene, the benzene alkylation was realized with 1-hexene up to 1-octadecene under similar optimized reaction conditions using Y zeolite and mordenite catalysts. The effect of reaction time on conversion of long chain 1-alkenes to alkylbenzenes over Y zeolite for a series of 1-alkenes is shown on Fig. 7. From this figure it is seen that the conversion of 1-hexene reached almost 100% in 90 min of reaction time. With the increase of chain length of 1-alkenes to C18 the reaction time for 100% conversion extends to 150 min. It means that the reactivity of 1-alkene in benzene alkylation slightly decreases with the alkyl chain, as it seen also from Fig. 8.

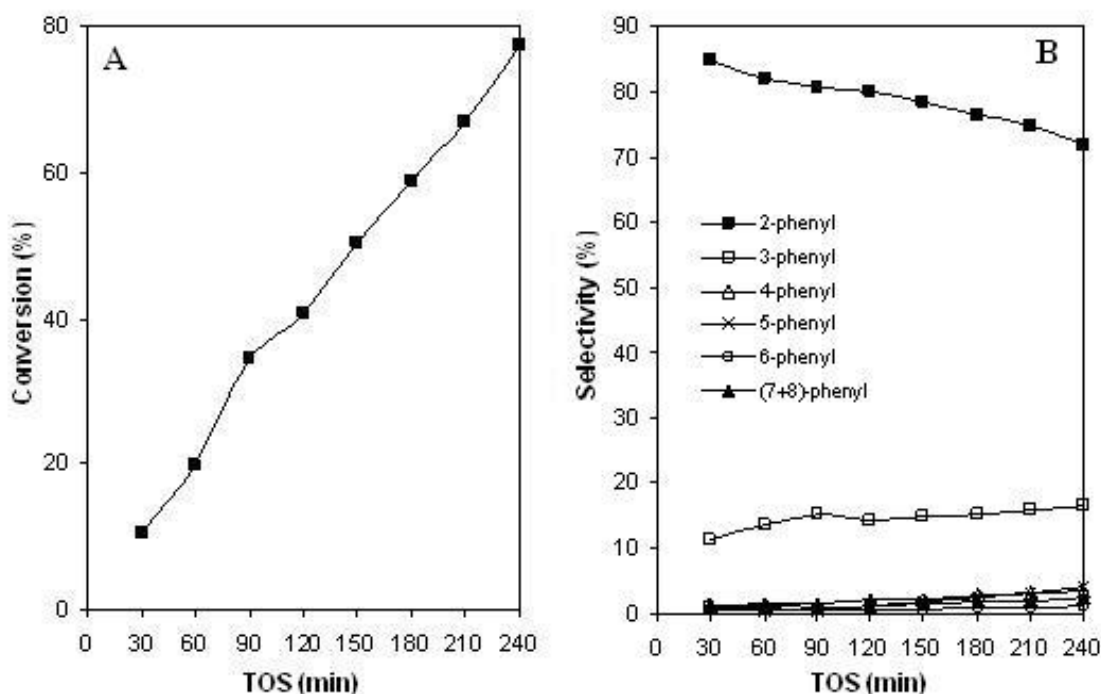


Fig. 6 Effect of reaction time on 1-hexadecene conversion (A) and product selectivity (B) over mordenite. Conditions: T = 200 °C; Be/C₁₆ = 8.6; catalyst weight = 2.0 g (2.5 wt.%)

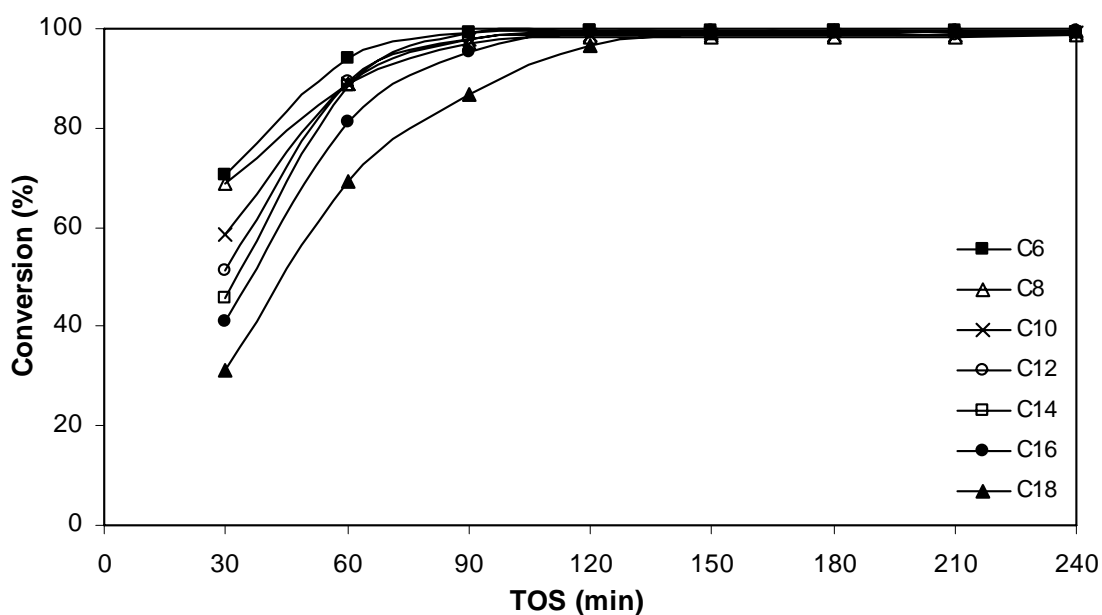


Fig. 7 The conversion of 1-alkenes C_6 - C_{18} over Y zeolite in dependence on time-on stream
Conditions: $T = 120\text{ }^\circ\text{C}$; $Be/1\text{-alkene} = 8.6$; catalyst weight = 2.0 g (2.5 wt.%)

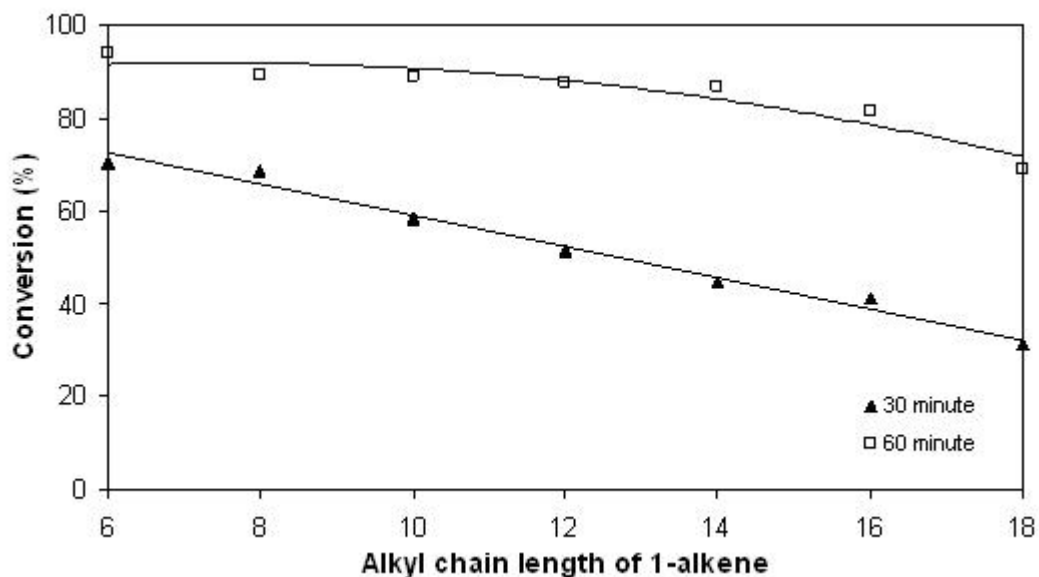


Fig. 8 The 1-alkene's conversion over Y zeolite – influence of alkyl chain length.
Conditions: $T = 120\text{ }^\circ\text{C}$; $Be/1\text{-alkene} = 8.6$; catalyst weight = 2.0 g (2.5 wt.%)

The highest increase of conversion of 1-alkenes for all alkenes was observed between 30 and 60 min of time-on stream and it is presented on Fig. 8. The conversion decreased with the increase alkyl chain length from C_6 to C_{18} but the conversion in 60 min has milder course of descent. The selectivity to 2-phenyl isomer decreased slightly between of 30 – 60 min of

reaction time and then was stable to the end of experiments. It is not so simple to compare the values of selectivity for different 1-alkenes, because with the increase of alkyl chain length the possible number of linear alkylbenzenes increases from 2 for phenyl-hexane to 8 for phenyl-octadecane, but very probably the composition of alkylbenzenes over Y-zeolite at higher conversion reached near thermodynamic equilibrium.

The effect of reaction time on the conversion of 1-alkenes to alkylbenzenes over mordenite for a series of 1-alkenes with carbon chain C₆-C₁₈ is shown on Fig. 9. Even at the reaction temperature of 200 °C the 100% conversion was achieved for C₆ after 150 min, for C₈ and C₁₀ after 210 min of reaction time. With the increase of the carbon chain the reactivity decreased more rapidly than in the case of Y-zeolite, and for the longest 1-alkene C₁₈ the conversion in 240 min. of time-on stream was only about 60%. The smaller conversion of 1-alkenes over mordenite catalyst could be ascribed to the different pore structure of mordenite in comparison with Y zeolite. While Y zeolite poses three-dimensional porous system with pore size 0.74 nm, porous system of mordenite contains only one dimensional porous system (0.65 x 0.70 nm) applicable to alkylation of benzene with 1-alkenes.

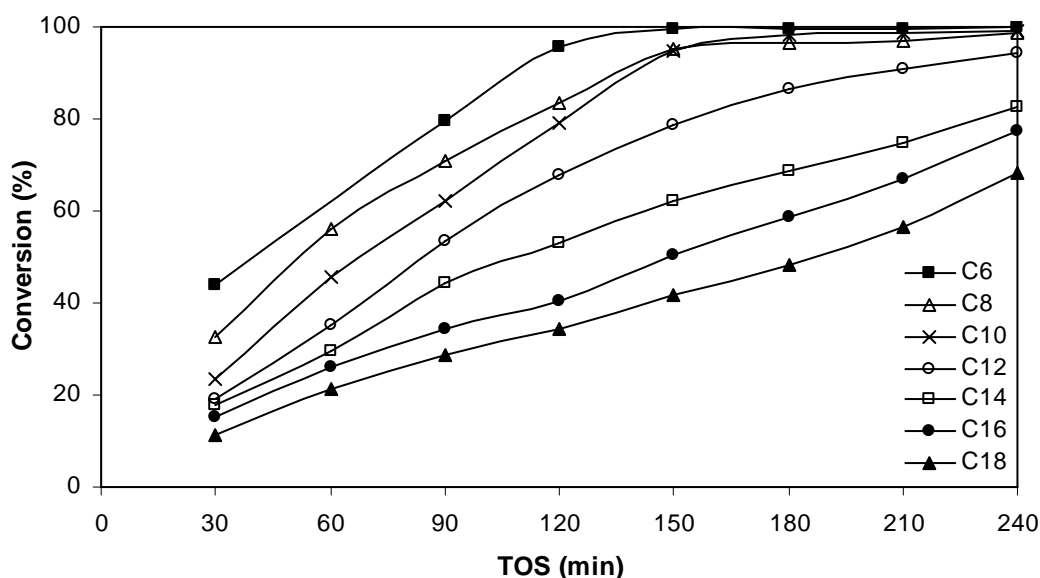


Fig. 9 The conversion of 1-alkenes C₆-C₁₈ over mordenite – influence of time-on stream. Conditions: T = 200 °C; Be/1-alkene = 8.6; catalyst weight = 2.0 g (2.5 wt. %)

As it can be seen in Fig. 10, the conversion of 1-alkenes over mordenite catalyst in 90 min of time-on stream decreased almost linearly with the chain length. On the other side, mordenite

catalyst is more suitable to increase a portion of 2-phenyl isomers of alkylbenzenes that are better biologically degradable.

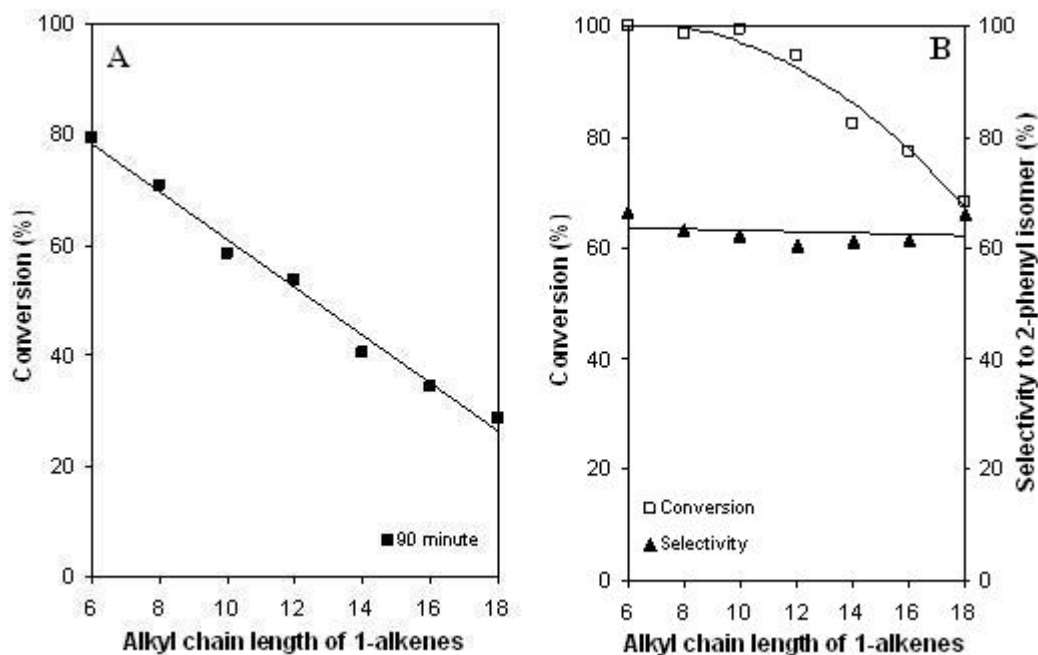


Fig.10 The 1-alkene's conversion (A) and product selectivity (B) over mordenite catalyst
Conditions: T = 200 °C; Be/1-alkene = 8.6; catalyst weight = 2.0 g (2.5 wt. %)

The comparison of the product selectivity to 2-phenyl isomer in benzene alkylation in Fig. 11 shows that the selectivity over mordenite catalyst is for all 1-alkenes much higher than over Y zeolite. When we take the product composition over Y zeolite as value near to equilibrium, the product selectivity decrease for mordenite with reaction time could be explained by approaching to the equilibrium. The differences are interesting mainly for longer chain length of 1-alkene, where the number of possible isomers of alkylbenzenes is much higher, and the selectivity keeps still over 60%.

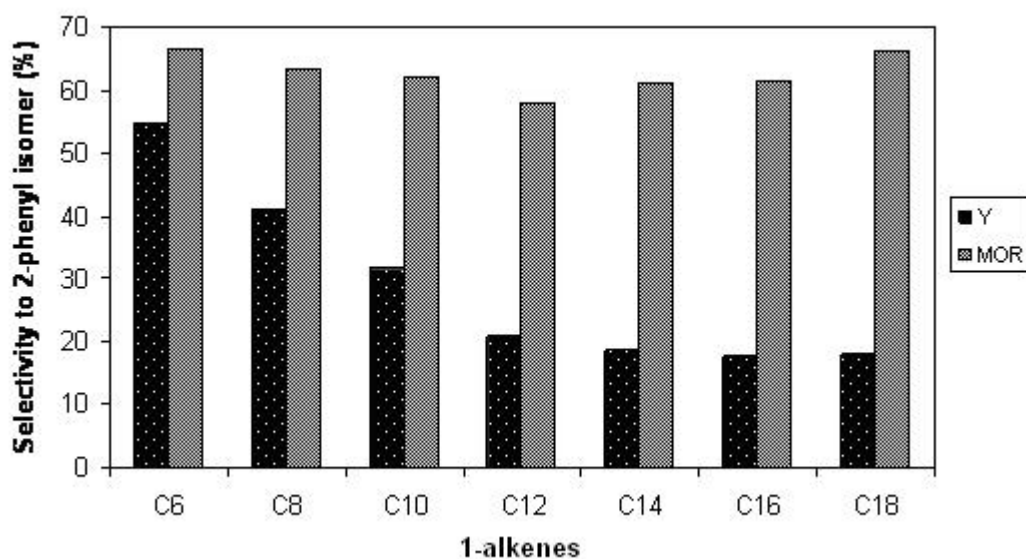


Fig. 11 Comparison of product selectivity over Y zeolite and mordenite catalyst

Conclusion

The liquid phase alkylation reaction of benzene with 1-hexadecene in batch reactor has been investigated over Y zeolite catalyst under autogenous pressure. Y zeolite exhibits good catalytic performances. The alkylation of benzene with 1-hexadecene leads to the formation of a mixture, including the desired products, a series of isomers of monoalkylated benzene, and some side-products - dimers from 1-alkenes and dialkylated benzene. The catalyst showed the highest catalytic activity at 120 °C with benzene:1-hexadecene molar ratio 8.6:1, and 2.5 wt. % dosage of catalyst.

Alkylation of benzene with linear 1-alkenes of chain length C₆-C₁₈ was studied under the optimized reaction conditions in liquid phase using Y-type (at 120 °C) and mordenite (at 200 °C) catalysts. The increase of chain length slightly decreased the conversion of 1-alkenes over Y-zeolite in the first 30-60 min but after 150 min for all 1-alkenes practically 100% conversion was observed. For mordenite catalyst even at 200° C the conversion of 1-alkenes increased with reaction time much slower and reached 100% only for C₆-C₁₀ after 240 min. Linear 1-alkenes with longer chain length C₁₄-C₁₈ achieved in this reaction time conversion only 65-70%. But mordenite catalyst has much better shape-selective properties towards to desirable 2-phenyl isomers in alkylation products. While the selectivity to 2-phenyl isomers over Y-zeolite is near to thermodynamic equilibrium for C₁₂-C₁₈ and it was about 20-22%, over mordenite catalysts was observed selectivity much higher – 60-65% for all 1-alkenes.

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