

Transesterification of methyl *tert*-butyl ether with ethanol over acidic ZrO₂–SiO₂ oxide and Dowex DR-2030 sulphoresin catalyst

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Alcoholysis of methyl *tert*-butyl ether with ethanol over Dowex DR-2030 sulphoresin catalyst and acidic ZrO₂–SiO₂ oxide at 60–120 °C using flow reactor has been studied. Effect of the ratio of methyl *tert*-butyl ether and ethanol on the ethyl *tert*-butyl ether yield was investigated. It was shown that the more active Dowex DR-2030 catalyst provides 61 % methyl *tert*-butyl ether conversion with 97 % selectivity towards ethyl *tert*-butyl ether at 80 °C in double excess of ethanol and LHSV = 1 h⁻¹.

Ethers are quite stable compounds commonly used as solvents at organic synthesis. However CH₃CO⁺ ions, generated from acetic anhydride in the presence of acid catalysts, are capable to cleave ether C–O–C bonds [1, 2]. The production of polytetramethylene acetate from tetrahydrofuran with acetic anhydride additive over the acidic ZrO₂–SiO₂ catalyst [1] is based on this property. Recently, acylation of methyl *tert*-butyl ether by acetic anhydride to *tert*-butyl acetate was performed on ZrO₂–SiO₂ and Amberlyst 15 catalysts [2].

In this work we have prolonged the comparable study on an activity of sulphoresin catalyst and acidic ZrO₂–SiO₂ oxide in the reaction of methyl *tert*-butyl ether (MTBE) transesterification with ethanol.

Currently, ETBE is considered [3, 4] as alternative, instead of MTBE, high-octane additive to gasoline due to its lower water solubility and volatility, and easily biodegradation also.

Experimental

Dowex DR-2030 sulphoresin catalyst (Supelco) and ZrO₂–SiO₂ oxide (Si/Zr = 2, atom) prepared by the sol-gel method [5] were tested as acid catalysts. Dried ethanol and 98 % MTBE were used as reagents. Total acidity of the samples was determined by the inverse titration using *n*-butyl amine solution in cyclohexane with bromothymol blue as an indicator. The strength of ZrO₂–SiO₂ acid sites was measured employing the standard indicator method [6].

The textural parameters of ZrO₂–SiO₂ were calculated from the nitrogen adsorption-desorption isotherms recorded on a Quantachrome Nova 2200e Surface Area and a Pore Size Analyzer.

The experiments were carried out in a flow stainless steel reactor with fixed bed of granulated (1–2 mm) catalyst (3 cm³) at 60–120 °C under 5 bar preventing liquid to gaseous phase transfer. The reaction mixture was introduced into reactor using a Waters-590 pump with LHSV = 0.5 – 4 h⁻¹, that correspond to load on a catalyst of 2,1–13,6 mmol MTBE g_{cat}⁻¹h⁻¹.

The reaction products were analyzed using ¹³C NMR spectroscopy (Bruker Avance 400) and gas chromatography (Chrom-5 with 50 m capillary column) methods. The conversion and selectivity values (mol %) were calculated from ¹³C NMR spectra.

Results and discussion

The textural parameters and concentrations of acid sites on the surface of synthesized ZrO₂–SiO₂ (ZrSi) and Dowex DR-2030 are presented in Table 1. ZrSi sample in comparison to the sulphoresin is characterized by a higher surface area (360 m²/g) and strong acid sites (H₀ ≥ -11.35). However, Dowex DR-2030 contains three times as many acid sites as the synthesized ZrSi.

The data on activity of studied catalysts in the transesterification reaction are presented in Table 2. According to the ¹³C NMR spectra, methyl *tert*-butyl ether (27,1; 49,4; 72,8 ppm), ethanol (18,1; 57,8 ppm), ethyl *tert*-butyl ether

Table 1. Textural parameters and acidity of catalysts

Catalyst	SA (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	R _p (nm)	[BH] (mmol g ⁻¹)	H _{0 max}
ZrSi	360	0,27	1,6	1,7	-11,35
Dowex DR-2030	30	0,10	6,6	4,7	-5,6

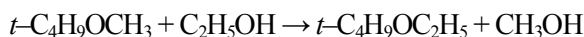
SA – specific surface area measured by BET; V_p – pore volume; R_p – average pore radius

Table 2. Effect of catalysts on transesterification of MTBE with ethanol*

Catalyst	T, °C	LHSV, h ⁻¹	MTBE:EtOH, mol	X, mol %	S, mol %
ZrSi	60	1	1:2	39	94
	80	1	1:2	55	90
	90	1	1:2	58	92
	100	1	1:2	63	92
	110	1	1:2	66	95
	120	1	1:2	67	95
	100	1	1:3	64	92
	100	1	1:4	69	93
	100	1	1:6	72	94
	100	0.5	1:3	68	89
	100	2	1:3	46	92
	100	4	1:3	34	81
	Dowex DR 2030	60	1	1:2	58
70		1	1:2	61	96
80		1	1:2	61	97
90		1	1:2	61	97
100		1	1:2	61	92
100		1	1:3	86	92
100		2	1:3	64	95
100		4	1:3	62	94

*) X – MTBE conversion; S – selectivity towards ETBE

(ETBE) (16.4; 27.7; 56.8; 72.55 ppm) and methanol (50.1 ppm) were identified in the reaction product that corresponds to proceeding of such reaction:



Diethyl ether is formed in minor quantities also as by-product.

MTBE is characterized by the higher proton affinity value (PA = 842 kJ/mol) than ethanol (PA = 776 kJ/mol), therefore its molecules would be protonated with H-sites of a catalyst predominately forming intermediate *tert*-butyl

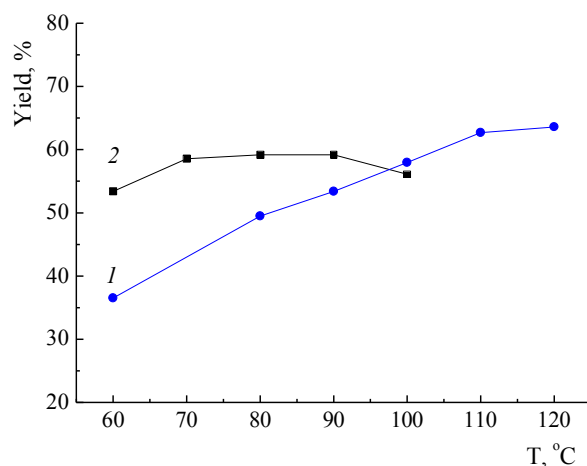
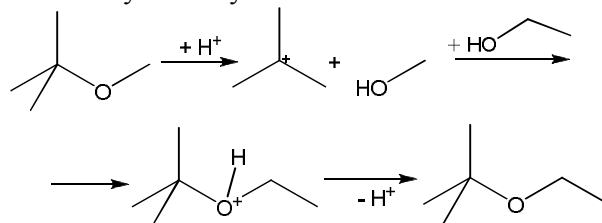


Fig. 1. Yield of ethyl *tert*-butyl ether on ZrSi (1) and Dowex DR-2030 (2) at different temperatures (LHSV = 1 h⁻¹, MTBE/EtOH = 1:2)

ions. The addition of these cations to ethanol molecules results in ethyl *tert*-butyl ether formation:



Alcoholysis of MTBE with ethanol is a reversible reaction. At increasing EtOH/MTBE ratio from 2 to 3, MTBE conversion raises from 61 up to 86 % on Dowex DR-2030 at 100 °C (Table 2). However in the case of ZrSi, only 9 % rise of conversion was observed at EtOH/MTBE ratio changing from 2 to 6 (Table 2).

The data on yield of ETBE, obtained on studied catalysts at different temperatures, are presented in Fig. 1. Higher ETBE yield at a level of 59 % was observed on sulphoresin catalyst in comparison with ZrSi oxide at 70–90 °C (Fig. 1).

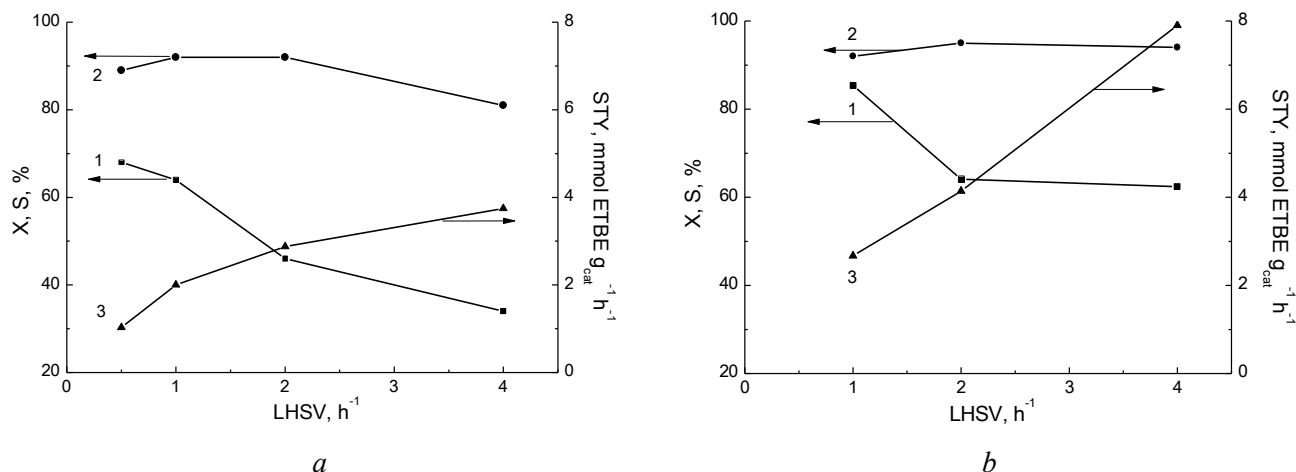


Fig. 2. Conversion (1), selectivity (2) and space-time yield (3) of ethyl *tert*-butyl ether on ZrSi (a) and Dowex DR-2030 (b) at different LHSV values (100 °C, MTBE/EtOH = 1:3)

The results on productivity of studied catalysts (space-time-yield) at different loads on a catalyst are shown in Fig. 2. At rising LHSV from 1 h^{-1} to 4 h^{-1} MTBE conversion decreases from 50 to 34 % on ZrSi and from 86 to 62 % over sulphoresin catalyst. Selectivity towards ethyl *tert*-butyl ether was not changed for Dowex DR-2030 and reduced by 10 % for ZrSi. Space-time yield (STY) of ETBE increases at LHSV rise and reaches values of 8 and 3.7 mmol ETBE $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ at LHSV = 4 h^{-1} for Dowex DR-2030 and ZrSi correspondingly (Fig. 2). At that, selectivity towards ethyl *tert*-butyl ether and methyl *tert*-butyl ether conversion are not changed significantly during 6 h of catalyst testing.

Lower ETBE yield over ZrSi mixed oxide can be attributed to a lower concentration of acid sites on its surface in comparison with Dowex DR-2030 sulphoresin catalyst (Table 1).

Conclusions

It was found that acid $\text{ZrO}_2\text{-SiO}_2$ oxide and sulphocationite Dowex DR-2030 effectively catalyze the alcoholysis of methyl *tert*-butyl ether with ethanol at 60–120 °C. More active Dowex DR-2030 catalyst provides 60 % methyl *tert*-butyl ether conversion with 97 % selectivity towards ethyl *tert*-butyl ether at 70–90 °C under a double excess of etha-

nol. Space-time yield of ETBE reaches values of 8 and 3.7 mmol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ on Dowex DR-2030 and on ZrSi correspondingly at 100 °C under liquid space velocity of 4 h^{-1} .

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Переэтерифікація метил-*трет*-бутилового ефіру з етанолом на кислотному ZrO_2-SiO_2 оксиді та Dowex DR-2030 каталізаторі

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Досліджено процес алкоголізу метил-*трет*-бутилового ефіру з етанолом на Dowex DR-2030 каталізаторі та кислотному ZrO_2-SiO_2 оксиді в проточному реакторі при 60–120 °С та 5 бар. Вивчено вплив співвідношення метил-*трет*-бутилового ефіру до етанолу на вихід етил-*трет*-бутилового ефіру. Показано, що більш активний Dowex DR-2030 каталізатор забезпечує 61% конверсію метил-*трет*-бутилового ефіру з 97 % селективністю по етил-*трет*-бутилового ефіру в подвійному надлишку етанолу при 80 °С і $LHSV = 1 \text{ год}^{-1}$.

Переэтерификация метил-*трет*-бутилового эфира с этанолом на кислотном ZrO_2-SiO_2 оксиде и Dowex DR-2030 катализаторе

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Исследован процесс алкоголиза метил-*трет*-бутилового эфира с этанолом на Dowex DR-2030 катализаторе и кислотном ZrO_2-SiO_2 оксиде в проточном реакторе при 60–120 °С и давлении 5 бар. Изучено влияние соотношения метил-*трет*-бутилового эфира к этанолу на выход этил-*трет*-бутилового эфира. Показано, что более активный Dowex DR-2030 катализатор обеспечивает 61% конверсию метил-*трет*-бутилового эфира с 97 % селективностью по этил-*трет*-бутилового эфиру в двойном избытке этанола при 80 °С и $LHSV = 1 \text{ ч}^{-1}$.