



Comparative study of TAME synthesis on ion-exchange resin beads and a fibrous ion-exchange catalyst

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Abstract

The reaction rates to *tert.*-amyl methyl ether (TAME) with the ion-exchange resin bead catalysts (A16, A35 and XE586) and a fibrous catalyst (SMOPEX-101) were measured as a function of temperature (323–353 K) with stoichiometric amount of reagents fed to a continuous stirred tank reactor. When the reaction rates were assessed against the weight or acid capacities of the catalysts, the activity order was A35 > A16 > SMOPEX-101 > XE586. When the rates were calculated versus the square of the acid capacity, the activities of the catalysts were similar. This indicated a dual-site mechanism. The rates of TAME formation and the isomerisation of isoamylenes as a function of temperature (333–353 K) and the feed MeOH/isoamylylene molar ratio (0.5–2.0), as well as the decomposition of TAME, were then measured in a batch reactor with the ion-exchange fibre (SMOPEX-101) as catalyst. Kinetic modelling results favoured a single-site mechanism for the isomerisation and a dual-site mechanism for the etherification. The activation energy was determined to be 116.7 kJ mol⁻¹ for the isomerisation of 2M1B to 2M2B, 92.7 kJ mol⁻¹ for the etherification of 2M1B to TAME and 93.0 kJ mol⁻¹ for the etherification of 2M2B to TAME.

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1. Introduction

The reformulated gasoline component TAME (*tert.*-amyl methyl ether, 2-methoxy-2-methylbutane) is commercially manufactured in liquid phase with use of strongly acidic macroporous ion-exchange resin beads as catalyst. The conventional ion-exchange catalysts are

copolymers of divinylbenzene (DVB) and styrene, where sulfonic acid is the active site (Bröndstedt acidity). The amount of divinylbenzene varies from 12 to 20 wt%, and determines directly the degree of crosslinking and rigidity of the structure. That is, the more DVB in the catalyst the more rigid is the resin and its macroporous structure. The bead catalysts have a bidisperse structure, however, with microporous gel phase present as well. The beads swell in polar solvents, those with less DVB swelling more than those with more DVB. The catalytic

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activity of the resins is determined by the amount of sulfonic acid; typically this varies from 4.8 (e.g. conventionally sulfonated Amberlyst 15) to 5.2 mmol g⁻¹ (e.g. hyper-sulfonated Amberlyst 35) [1].

The novel ion-exchange fibre catalyst SMOPEX-101, manufactured by Smoptech, is prepared by supporting sulfonic acids on poly-(ethylene-graft-polystyrene). The catalyst has been studied previously in our laboratory in the etherification of C₈-alkenes [2] and shown to have favourable properties in the synthesis of ethers bulkier than TAME. SMOPEX-101 was superior to Amberlyst 35 in the formation of 2-methoxy-2,4,4-trimethylpentane owing to its open structure and thus negligible mass-transfer limiting effect.

Several groups have studied the ion-exchange resins used as catalysts for etherification reactions. Parra et al. [3] compared the catalytic activity of 12 different ion-exchange resins as catalysts for MTBE synthesis in liquid phase. Experimental data showed that the ion-exchangers with higher acidic capacity were the most active; thus, the rate of MTBE formation was 29% greater with Amberlyst 35 than with Amberlyst 15. Different polynomials containing three variables (acid capacity, BET surface area and average pore diameter) were fitted to the data and the best one statistically showed that the acid capacity had a stronger influence on the catalytic activity than the other two variables. The authors concluded that the resins with greater density of the sulfonic groups were more active because the reaction of MTBE synthesis involves a concerted mechanism in which adjacent sulfonic groups participate. Pannemann and Beenackers [4] have reported initial reaction rate constants for MTBE synthesis with several macroporous resins and demonstrated significant differences between the resins. In their view, the catalytic activity depends on the three-dimensional structure of the resins (level of crosslinking, porosity, surface area) and on the sulfonic acid content and its distribution within the particles. The activation energies varied with

the feed composition and also were resin dependent. The kinetic measurements with partially neutralised resins showed that with Amberlyst 15 for example, the dependence of the rate constant on the concentration of sulfonic acid groups was almost third order, in agreement with the results of Ancillotti et al. [5].

Rhodes et al. [6] applied a flow microcalorimetric technique to characterise the acidities of macroporous and gel-type resin catalysts by ammonia adsorption from the gas phase. One of the test reactions was TAME synthesis. The results showed that catalytic activities were not related in a simple way to the *concentrations* of acid sites measured by ammonia adsorption, but there was a noticeable correlation between the *strengths* of the acid sites measured in this way and catalytic activities of the resins. They concluded that acid site strength can be a useful indicator of activity for this type of acid catalyst.

Previously, we studied the kinetics of TAME formation with Amberlyst 16 (12% DVB, acid capacity 5.0 mmol g⁻¹) and introduced a kinetic model of the Eley-Rideal type [7] and a revised model of the Langmuir-Hinshelwood type [8] for the synthesis of TAME. In the present study we compare the activities of different commercial cationic ion-exchange resin beads from Rohm&Haas and a fibre catalyst from Smoptech. Kinetic modelling for the synthesis of TAME with SMOPEX-101 was carried out to compare the values of the kinetic parameters with those obtained with Amberlyst 16. Mechanistic conclusions are drawn on the basis of the experimental steady state reaction rates obtained with the different catalysts and the kinetic modelling results.

2. Experimental

2.1. Part I. Experiments with different catalysts

The reaction rates to TAME with bead catalysts (A16, A35 and XE586) and fibre

catalyst (SMOPEX-101) were measured at different temperatures (323–353 K) with reagents fed in stoichiometric amount to a continuous stirred tank reactor (CSTR).

2.2. Part II. Batch reactor experiments with SMOPEX-101

The rates of TAME formation and the isomerisation of isoamylenes with SMOPEX-101 as catalyst were measured as a function of temperature (333–353 K) and the feed MeOH/isoamylenes molar ratio (0.5, 1.0, 2.0) in a batch reactor. The decomposition of TAME to MeOH and isoamylenes was also measured. Isopentane was used as solvent. The experiments are presented in Table 1.

2.3. Chemicals

The following reagents were used in the experiments: p.a. grade 2-methyl-1-butene (2M1B, Aldrich, 99.8 wt%), redistilled 2-methyl-2-butene (2M2B, Aldrich, 99 wt%),

mixture of isoamylenes (Fluka Chemika, 2M2B, technical grade) with a composition of 2M2B 93 wt% and 2M1B 7 wt%, p.a. grade MeOH (Riedel-de Haën, 99.8 wt%), and p.a. grade isopentane (Fluka Chemika). The ether, TAME, was supplied by Fortum Gas&Oil and the purity was 98 wt%.

2.4. Catalysts

Commercial macroporous cation ion-exchange beads in hydrogen form (Amberlyst 16, Amberlyst 35, XE586 from Rohm&Haas) and ion-exchange fibre (SMOPEX-101 from Smop-tech) were used as catalysts in the experiments. SMOPEX-101 is prepared by grafting a polyethylene fibre with styrene and sulfonating the grafted fibre with chlorosulfonic acid. The SMOPEX-101 was ground to a very thin powder and ~0.7 g of the powder was placed in the reactor as slurry (0.33–0.35 g in the TAME decomposition experiments). Before the experiments, the catalysts were washed with methanol (bead catalysts) or ethanol (fibre catalyst). The

Table 1
Description of the batch reactor experiments carried out with SMOPEX-101

No.	T (°C)	Reactant	MeOH/alkene molar ratio	Molar fraction in the feed			
				MeOH	Alkene	Isopentane	Ether
1	60	IA	1	0.45	0.45	0.1	
2	70	IA	1	0.45	0.45	0.1	
3	80	IA	1	0.45	0.45	0.1	
4	60	IA	2	0.53	0.27	0.2	
5	65	IA	2	0.53	0.27	0.2	
6	70	IA	2	0.53	0.27	0.2	
7	80	IA	2	0.53	0.27	0.2	
8	60	IA	0.5	0.27	0.53	0.2	
9	65	IA	0.5	0.27	0.53	0.2	
10	70	IA	0.5	0.27	0.53	0.2	
11	80	IA	0.5	0.27	0.53	0.2	
12	60	TAME				0.5	0.5
13	70	TAME				0.5	0.5
14	80	TAME				0.5	0.5
15	60	2M1B	1	0.15	0.15	0.7	
16	65	2M1B	1	0.15	0.15	0.7	
17	70	2M1B	1	0.15	0.15	0.7	
18	80	2M1B	1	0.15	0.15	0.7	
19	60	2M2B	1	0.15	0.15	0.7	
20	70	2M2B	1	0.15	0.15	0.7	
21	80	2M2B	1	0.15	0.15	0.7	

bead catalysts were stored in methanol and the fibre catalyst was dried in an oven (100 °C) to remove moisture and other impurities and stored dry in a desiccator. The properties of the catalysts are summarised in Table 2.

2.5. Apparatus and procedures

2.5.1. Part I. CSTR

The reaction rates to TAME with the bead catalysts (A16, A35, XE586) and the fibre catalyst (SMOPEX-101) were measured at 323, 343 and 353 K. Reagents were fed in stoichiometric amount to a continuous stirred tank reactor (CSTR, 55.6 cm³, stainless steel) where the reaction mixture was magnetically stirred. The stirrer speed was set to 950 rpm to eliminate the influence of external diffusion control on the reaction rates [9]. The A16 (0.2951 g dry) and XE586 (0.2740 g dry) were placed in a metal gauze basket (60 mesh), and the fibre catalyst (0.7052 g dry) and A35 (0.3193 g dry) were introduced to the reactor as slurry. The temperature (323–353 K) was controlled within ± 0.2 K by immersing the reactor in a thermostated water bath. The pressure was kept constant at 0.7 MPa to ensure liquid-phase operation at all temperatures. The pulse-free flow rate (59.8–64.4 g h⁻¹) of the feed was controlled by a liquid mass flow controller. A Mettler PM 6000 balance was used to measure the actual flow at the outlet of the reactor system. The compositions of the feed and the reactor effluent were analysed on-line with a gas chromatograph equipped with an automated liquid sampling valve. During the experiments the effect of temperature was varied randomly. The stability

of the catalysts was checked by repeating the experiment at the first temperature after completion of the experiments at the other temperatures. The catalysts showed no deactivation. Depending on the temperature intervals, it took ~2–4 h to obtain a steady state in CSTR.

2.5.2. Part II. Batch reactor

The kinetic experiments with SMOPEX-101 were carried out in a batch reactor (80 cm³, stainless steel). The reaction mixture (~50 g initially) was stirred magnetically, and the temperature was controlled within ± 0.25 K by immersing the reactor in a thermostated water bath. To guarantee liquid-phase operation at every temperature, the pressure was set at 0.7 MPa. Vertical mixing baffles on the reactor walls ensured complete mixing. The samples (8 × 0.6 g) were removed manually via a sample valve from the top of the reactor. The valve and the sample were cooled with ice during the sampling in order to avoid evaporation. The samples were taken as a function of contact time (amount of catalyst × time), and experiments took from 3 to 6 h depending on the feed (shorter times for TAME decomposition).

2.6. Analysis

The products were analysed with a Hewlett-Packard gas chromatograph 5890 Series II, equipped with a flame ionisation detector and using a HP 3396A integrator. The compounds were separated in a glass capillary column DB-1 (length 60 m, film thickness 1.0 μm, column diameter 0.254 mm; J&W Scientific). During

Table 2
Properties of the catalysts

	A16	A35	XE586	SMOPEX-101
Crosslink level	Medium	High	Medium	
Exchange capacity (mmol g ⁻¹)	5.0	5.2	1.3	3.4
Surface area (m ² g ⁻¹)	35	45–50	75	
Average pore diameter (Å)	200	250–300	200	
Porosity	0.25	0.35	0.35	
Particle diameter (mm)	0.38–0.45	0.15–0.25	Mean: 0.7	Powder

the experiments, the response factors were regularly checked using calibration solutions.

3. Results and discussion

3.1. Part I. Comparison of catalysts

In a search for the kinetic mechanism of TAME formation, we carried out experiments with three types of beads and also with a powdered fibre catalyst. Steady-state measurements were carried out with Amberlyst 16, Amberlyst 35, XE586 and SMOPEX-101. The Amberlyst 16 was sieved and the Amberlyst 35 was crushed and sieved to very small particles (diameter 0.15–0.25 mm). The XE586 was used unsieved, because in this catalyst the acid sites are located solely in permanent macropores, whereas A35 and A16 have an active gel phase with micropores present too.

The catalyst weight based reaction rate r_{obs} ($\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$) to the product TAME was calculated from the measured amount of TAME (g) in the product stream (weight fraction of TAME in the outlet \times total mass of the stream (g s^{-1}), because $W_{\text{T,in}}$ is zero since TAME was not fed to the reactor) divided by the molecular mass of TAME and the weight of the dried catalyst according to Eq. (1):

$$\begin{aligned} r_{\text{obs}} &= \frac{(F_{\text{T,out}} - F_{\text{T,in}})}{W_{\text{cat}}} \\ &= \frac{(w_{\text{T,out}} - w_{\text{T,in}})\dot{m}_{\text{tot}}}{M_{\text{T}}W_{\text{cat}}} \end{aligned} \quad (1)$$

To compare the influence of the sulfonic acid concentration of the different catalysts on the observed reaction rates, the reaction rate to TAME (s^{-1}) was also calculated by further dividing Eq. (1) with the exchange capacity (mol kg^{-1}) of the studied catalysts according to Eq. (2) or with the square of the exchange capacity (mol kg^{-1})² according to Eq. (3):

$$\begin{aligned} r_{\text{obs}} &= \frac{(F_{\text{T,out}} - F_{\text{T,in}})}{W_{\text{cat}}[H^+]} \\ &= \frac{(w_{\text{T,out}} - w_{\text{T,in}})\dot{m}_{\text{tot}}}{M_{\text{T}}W_{\text{cat}}[H^+]} \end{aligned} \quad (2)$$

$$\begin{aligned} r_{\text{obs}} &= \frac{(F_{\text{T,out}} - F_{\text{T,in}})}{W_{\text{cat}}[H^+]^2} \\ &= \frac{(w_{\text{T,out}} - w_{\text{T,in}})\dot{m}_{\text{tot}}}{M_{\text{T}}W_{\text{cat}}[H^+]^2} \end{aligned} \quad (3)$$

These equations take into account the number of sulfonic acid groups in the different catalysts according to a first order (2) and second order (3) dependence. The activities of the catalysts are compared in Fig. 1a–c.

Fig. 1a and b shows that A35 is the most active catalyst, especially at elevated temperatures ($\geq 70^\circ\text{C}$), when the reaction rates are calculated per catalyst mass or sulfonic acid concentration. This must be due to hyper-sulfonation [1]. The next most active catalyst is A16, and the fibre catalyst shows moderate activity. Activity was surprisingly low for the surface sulfonated XE586. Beforehand we had thought that XE586 might be very active since the active sites are located in easily accessible macropores and there should be no intraparticle diffusion limitations. Since it turned out that this was not the case, and since the fibre catalyst showed only moderate activity, we were forced to conclude that the *density* of the active sites is the key parameter in rendering a catalyst suitable for etherification, or for other acid-catalysed reactions in organic phase, such as dimerisation. The most interesting observation is that, when the rates are calculated according to Eq. (3), i.e. when the rate is expressed in inverse proportion to the square of the sulfonic acid concentration, all catalysts showed similar activity, except for XE586, which was slightly more active (Fig. 1c). This result suggests that the etherification reaction proceeds via a *dual-site mechanism*, at least in stoichiometric conditions. This is a finding that we surely did not

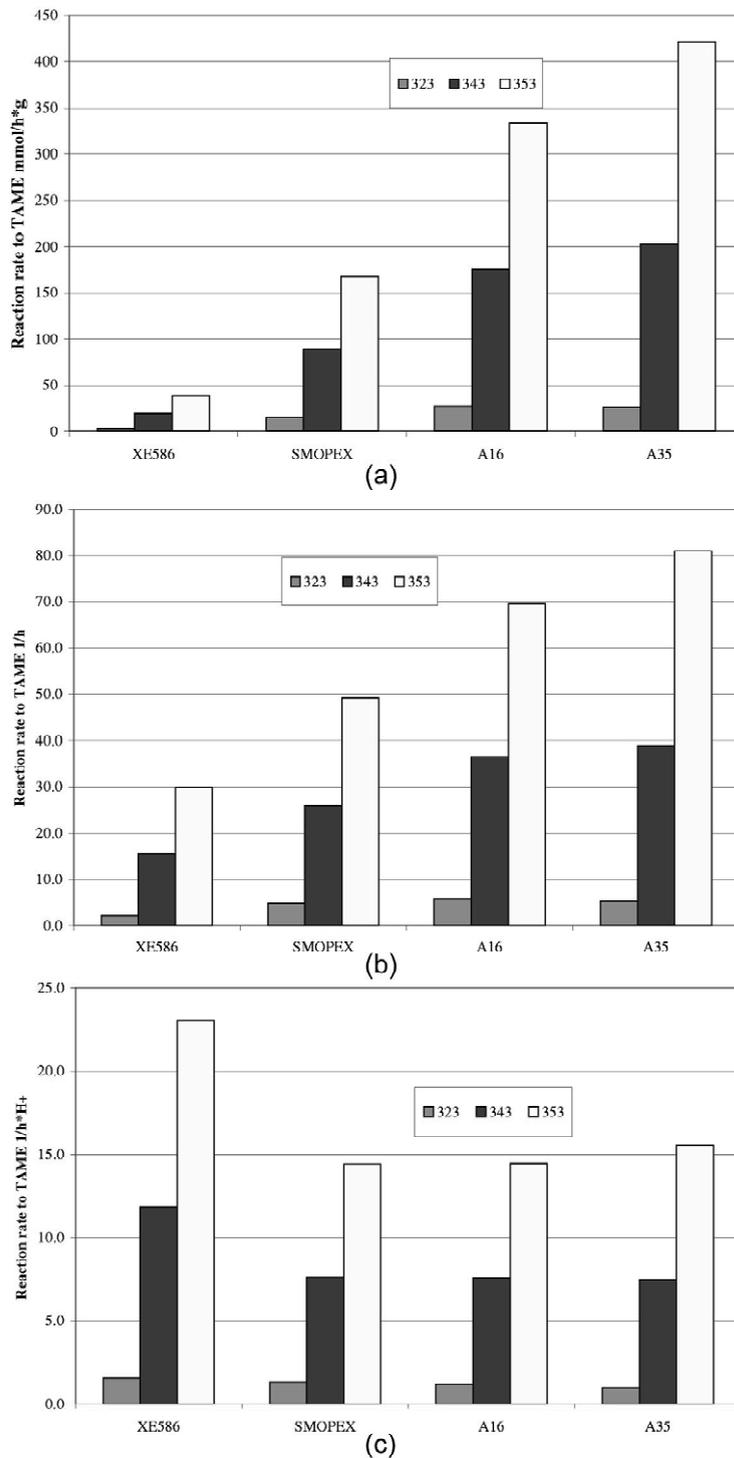


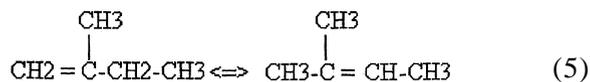
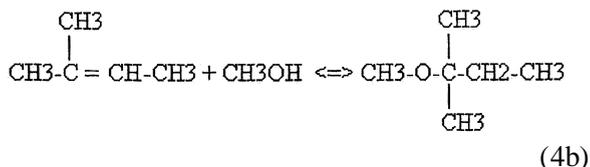
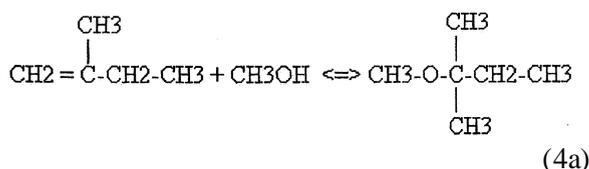
Fig. 1. Comparison of the catalysts: (a) weight-based reaction rate, (b) reaction rates against acid capacity, and (c) reaction rates against square of the acid capacity.

expect beforehand, and obviously it would be interesting to compare the catalysts also in other than stoichiometric conditions. In this study only the effect of temperature was studied, but temperature is kinetically were strong variable, so that these results in our opinion are very intriguing. This surely merits further study.

3.2. Part II. Batch reactor experiments with SMOPEX-101

3.2.1. General observations

Two types of main reactions of isoamylenes took place simultaneously in the experiments: the etherification with the alcohol and the isomerisation of the double bond between the α - and the β -positions (feed: 2M1B) or between the β - and the α -positions (feed: 2M2B). The same was also observed earlier with other catalysts [7,10]:



The calculation of the initial rates was made by regression from the slopes of the initial straight lines of the experimental ether and 2M*i*B ($i=1,2$) concentrations (mmol) as a function of contact time ($\text{h g}_{\text{dry cat}}^{-1}$). The calculated initial rates of the reactions at 333, 338, 343 and 353 K are presented in Table 3. At the temperatures studied, the initial rate of ether formation was about twice that of isomerisation, when an equimolar ratio of methanol and 2M1B was used as a feed, whereas the initial rate of etherification was ~ 10 times that of isomerisation when an equimolar ratio of methanol and 2M2B was used. The etherification of 2M1B was two to three times as fast as the etherification of 2M2B. The decomposition of TAME

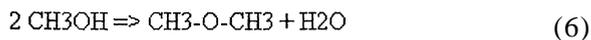
Table 3
Initial rates for the formation of products in main and side reactions and conversions of alkenes after 6 h

No.	Temp., K	TAME, $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	2M2B, $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	2M1B, $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	TAOH, $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	DIA, $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	Conv. (%) after 6 h
1	333	19.2			0.253		20
2	343	47.5			0.494		36
3	353	82.6			0.477		54
4	333	12.1			0.156		19
5	338	21.0			0.207		27
6	343	32.9			0.248		41
7	353	69.2			0.289		57
8	333	13.2			0.323		14
9	338	29.6			0.310		31
10	343	32.9			0.367	0.136	35
11	353	86.9			0.501	0.191	37
12	333	74.0					
13	343	142.8					
14	353	322.5					
15	333	8.8	3.8		0.157		47
16	338	13.8	6.2		0.187		60
17	343	21.6	10.7		0.155		77
18	353	57.7	30.8		0.268		80
19	333	3.7		0.36	0.053		13
20	343	9.0		0.94	0.080		32
21	353	17.9		1.73	0.134		43

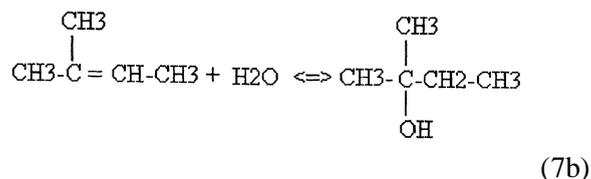
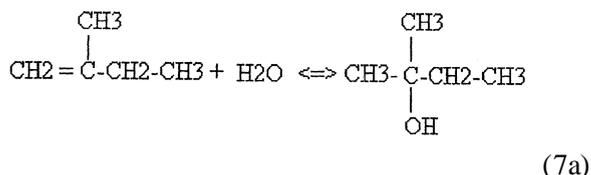
with dilution of 50 mol% of isopentane was about four times as fast as the formation of TAME at stoichiometric conditions with dilution of 10 mol% of isopentane. These general trends are in line with earlier observations by Rihko et al. [7] made with Amberlyst 16 as catalyst in TAME synthesis.

3.2.2. Side reactions

Formation of *tert.*-amyl alcohol (TAOH) from the isoamylenes and water was detected in the experiments. Because the catalyst was dry when placed in the reactor, the water needed for the formation of the *tert.*-amyl alcohol must have come from the condensation reaction of methanol:

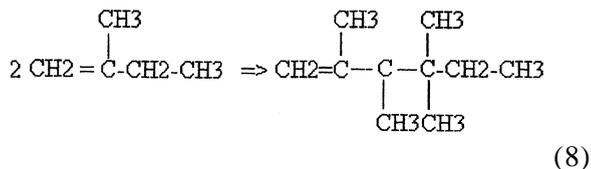


Thus, consequently:



The calculated initial rates are presented in Table 3. The *tert.*-etherification rate of isoamylenes was 40–240 times that of the hydration rate of the isoamylenes to form TAOH. With Amberlyst 16 the rate of *tert.*-etherification was 140–270 times that of the hydration in the study by Kiviranta-Pääkkönen et al. [11].

Dimerisation of isoamylenes was detected only at higher temperatures (≥ 343 K) and in the experiments where alkenes were fed in excess ($\text{MeOH}/\text{IA} = 0.5$):



The *tert.*-etherification rate of the isoamylenes was 240–450 times that of the dimerisation of the isoamylenes to form DIA. The dimerisation has been observed by Rihko et al. [12] with Amberlyst 16 only at low methanol/alkene ratios. The rates are collected in Table 3.

3.2.3. Conversions

Conversion of isoamylenes to TAME in experiments 1–11 (Table 3) was calculated according to Eq. (9):

$$\text{Conversion to TAME after 6 h} = \frac{n_{\text{TAME}}}{n_{\text{IA,feed}}} \quad (9)$$

Comparison of experiments 4–7 and 8–11 shows that the conversion to TAME is increased with excess methanol in the feed (Table 3). However, the initial etherification rate to TAME is decreased with excess methanol.

In experiments 15–21 conversions were also calculated by Eq. (10):

$$\begin{aligned} &\text{Overall conversion after 6 h} \\ &= \frac{n_{\text{TAME}} + n_{2\text{M}_j\text{B}}}{n_{2\text{M}_i\text{B,feed}}} \quad (i = 1,2 \text{ and } j = 2,1) \end{aligned} \quad (10)$$

Fractional conversion to TAME was greater from 2M1B than from 2M2B. Overall conversion of 2M1B was greater than the overall conversion of 2M2B (Table 3). These trends agree with the earlier results obtained with A16 as catalyst in the study of Rihko et al. [7] and A15 as catalyst in the study of Krause and Hammarström [10].

3.2.4. Kinetic modelling

Two kinetic models were tested against the data obtained with SMOPEX-101 in the batch reactor. The Eley-Rideal-type model in Eqs.

(11) and (12) assumes that only the alcohol and the ether but not the alkene are adsorbed on the *single* acid site of the catalyst [7]:

$$r_{\text{TAME}} = \frac{k_1 a_M a_{1b} \left(1 - \frac{a_T}{K_1 a_M a_{1b}}\right) + k_3 a_M a_{2b} \left(1 - \frac{a_T}{K_2 a_M a_{2b}}\right)}{\left(\frac{K_T}{K_M} a_T + a_M\right)} \quad (11)$$

$$r_{\text{ISOM}} = k_5 a_{1b} \left(1 - \frac{a_{2b}}{K_3 a_{1b}}\right) \quad (12)$$

The Langmuir-Hinshelwood-type model in Eqs. (13) and (14) assumes that the alcohol and the alkene are adsorbed on *two* adjacent acid sites, but the adsorption of alcohol is dominant [8,13,14]. The simple model derived from the dual-site expression states that the rate of etherification is proportional to the activity ratio of isoamylenes and methanol:

$$r_{\text{TAME}} = \frac{k'_1 a_{1b}}{a_M} \left(1 - \frac{a_T}{a_{1b} a_M K_1}\right) + \frac{k'_3 a_{2b}}{a_M} \left(1 - \frac{a_T}{a_{2b} a_M K_2}\right) \quad (13)$$

$$r_{\text{ISOM}} = \frac{k'_5 a_{1b}}{a_M} \left(1 - \frac{a_{2b}}{a_{1b} K_3}\right) \quad (14)$$

The equilibrium compositions have been reported by Rihko-Struckmann et al. [15]. The temperature dependencies of the equilibrium constants are presented in Eqs. (15)–(17):

$$K_1 = \exp(-8.74435 + 4142.069/T) \quad (15)$$

$$K_2 = \exp(-8.24371 + 3219.118/T) \quad (16)$$

$$K_3 = K_1/K_2 \quad (17)$$

The estimation was carried out with the KINFIT estimation program by minimising with the Levenberg-Marquardt method the weighted sum of residual squares (WSRS) between the experimental and calculated compositions (mol)

at the outlet of the reactor. Altogether 141 samples (points of observation) were taken during the 21 experiments described in Table 1. Weight factor (w_i) 1 was used for all the compounds (Eq. 18).

$$\text{WSRS} = \sum (n_{\text{exp}} - n_{\text{calc}})^2 w_i \quad (18)$$

The activity coefficients were calculated by the Wilson method; the binary interaction parameters were taken from Rihko-Struckmann et al. [15]. The estimated parameters for the two mechanisms were the rate coefficients k_1 , k_3 and k_5 at 333 K ($\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$) and their corresponding Arrhenius-type activation energies E_1 , E_2 and E_3 (J mol^{-1}). In addition, the ratio of adsorption equilibrium constants K_T/K_M at 333 K was estimated for the Eley-Rideal-type model.

3.2.5. Modelling results and comparison with results obtained with Amberlyst 16

The estimated parameters for the two kinetic models are presented in Table 4.

The smaller residual sum of squares (RSS) for the dual-site mechanism than for the single-site mechanism shows that the dual-site mechanism is more appropriate. Also, for three of the parameter values the standard error (SE %) is one or two percentage points smaller with the Langmuir-Hinshelwood mechanism than with the Eley-Rideal mechanism. This is in line with the earlier results we obtained with Amberlyst 16 [8] and with the results presented in Part I of this study. The ratio of the adsorption equilibrium constants (K_T/K_M) for the ER mechanism has a value much smaller than one, which means that the alcohol is the dominant molecule to adsorb on the acid site of the catalyst. This is in contrast to the finding of Karinen and Krause [16] for C_8 -alkene etherification with the fibre catalyst. In C_8 etherification, the ratio obtained was the value of 2.5 in the parameter estimation procedure, which indicated that the ether adsorbs more readily than the alcohol on the fibre catalyst site.

Table 4
Modelling results with SMOPEX-101 as catalyst

Parameter	Eley-Rideal model,				Langmuir-Hinshelwood model,			
			95% confidence limits				95% confidence limits	
	Value	SE %	Lower	Upper	Value	SE %	Lower	Upper
k_1 (mol kg ⁻¹ s ⁻¹)	0.0134	8	0.0114	0.0153	0.0122	6	0.0109	0.0136
E_1 (J mol ⁻¹)	110 051	5	98 191	121 910	92 689	5	82 755	102 624
k_3 (mol kg ⁻¹ s ⁻¹)	0.0077	2	0.0074	0.0080	0.0055	2	0.0053	0.0057
E_2 (J mol ⁻¹)	89 446	2	86 267	92 625	93 040	1	90 404	95 675
k_5 (mol kg ⁻¹ s ⁻¹)	0.0092	14	0.0066	0.0117	0.0062	14	0.0045	0.0078
E_3 (J mol ⁻¹)	106 355	10	84 827	127 883	116 721	9	96 955	136 487
K_T/K_M	3.83×10^{-7}	21 766 006	-0.16318	0.163 184				
RSS				0.064				0.053

Since the etherification is a dual-site reaction and the isomerisation a single-site reaction, comparison of the dual-site results obtained with SMOPEX-101 as catalyst with the results obtained with Amberlyst 16 [8], requires the rate constants to be divided by the square of the acid capacity (k_1 , k_3) and the simple acid capacity (k_5) of the catalysts. The acid capacity of Amberlyst 16 was 5.0 mmol g⁻¹ and the acid capacity of the fibre was 3.4 mmol g⁻¹. The results are presented in Fig. 2. The figure shows that the values of the etherification rate parameters (k_1 and k_3) are approximately equal at lower temperatures of 333 K and 343 K. At 353 K the values with of the etherification rate parameters (k_1 and k_3) A16 are slightly smaller than the values with SMOPEX-101. The isomerisation rate parameter (k_5) is noticeably greater with the fibre than the bead catalyst at

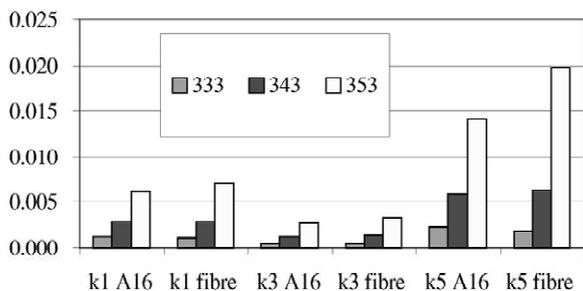


Fig. 2. Comparison of the etherification rate parameters (k_1 and k_3 ; H⁺)⁻¹ s⁻¹ and the isomerisation rate parameters (k_5 ; s⁻¹) with Amberlyst 16 [8] and SMOPEX-101 as catalyst. Temperatures 333, 343 and 353 K.

Table 5
Activation energies obtained with A16 [8] and SMOPEX-101

	Amberlyst 16	SMOPEX-101
E_1 (kJ mol ⁻¹)	77.0	92.7
E_2 (kJ mol ⁻¹)	85.7	93.0
E_3 (kJ mol ⁻¹)	89.8	116.7

the highest temperature of 353 K. These results indicate that the diffusion of isoamylenes to the active site is less hindered with the fibre catalyst than within the bead catalyst.

The activation energies obtained earlier with A16 [8] and here with SMOPEX-101 are compared in Table 5 (LH model).

The activation energies obtained with the bead catalyst (A16) are marginally lower than the activation energies obtained with the fibre (SMOPEX) catalyst. This result further indicates that there were slight intraparticle mass-transfer limitations within the bead catalyst, because unsieved catalyst was used in the previous experiments [7,8]. It has been shown that no mass-transfer limitations are associated with the fibre catalyst [2,17].

4. Conclusions

Steady-state reaction rates for TAME synthesis were measured with three bead catalysts (A16, A35, XE586) and a fibre catalyst (SMOPEX-101) in a continuous stirred tank reactor. A35 was the most active catalyst,

especially at elevated temperatures ($\geq 70^\circ\text{C}$), when the reaction rates were calculated versus catalyst mass or sulfonic acid concentration. The next most active catalyst was A16, and the fibre catalyst showed moderate activity. The lowest activity was detected for the surface sulfonated XE586. When the rates were calculated against the square of the acid capacity, the four catalysts showed similar activity. This suggests that the reaction proceeds with a dual-site mechanism, at least in stoichiometric conditions.

The effects of temperature and molar ratio of the reagents on the synthesis and decomposition rates of TAME were measured in a batch reactor with the novel ion-exchange fibre SMOPEX-101 as the catalyst. Kinetic modelling results suggested a dual-site mechanism for the TAME synthesis. The rate parameters obtained in the earlier studies [8] with Amberlyst 16 (ion-exchange bead) as catalyst were the same as those obtained with SMOPEX-101 at 333 K and 343 K, but at higher temperature of 353 K the rate parameter values for SMOPEX-101 were higher than those for Amberlyst 16. The activation energies obtained for the isomerisation and etherification reactions of isoamylenes were 9–30% higher for the fibre catalyst than for the bead catalyst, indicating some diffusion limitations associated with the latter catalyst.

5. Notation

a_i	activity of a component $i = \gamma_i x_i$
E_a	activation energy, J mol^{-1}
F_i	molar flow of component i , mol s^{-1}
$[\text{H}^+]$	acid capacity of the catalyst, mol kg^{-1}
k	rate constant, $\text{mol kg}^{-1} \text{s}^{-1}$
K_i	adsorption equilibrium constant of component i
K_j	reaction equilibrium constant for a reaction j , $j = 1-3$
\dot{m}_{tot}	total flow, kg s^{-1}
M_i	molar mass of the component i
$n_{i,\text{calc}}$	amount of component i calculated by a model, mol

$n_{i,\text{exp}}$	amount of component i measured, mol
r_i	rate of reaction for component i , $\text{mol kg}^{-1} \text{s}^{-1}$
w_i	weight factor
W_{cat}	catalyst mass, kg
x_i	molar fraction of component i

Abbreviations

2M1B	2-methyl-1-butene
2M2B	2-methyl-2-butene
A15	Amberlyst 15 (Rohm&Haas)
A16	Amberlyst 16 (Rohm&Haas)
A35	Amberlyst 35 (Rohm&Haas)
CSTR	continuous stirred tank reactor
DIA	diisoamylenes, 2,3,4,4-tetramethyl-1-hexene
DME	dimethylether
IA	isoamylenes mixture (93 wt% 2M2B, 7 wt% 2M1B)
MeOH	methanol
TAME	<i>tert.</i> -amyl methyl ether, 2-methoxy-2-methylbutane
TAOH	<i>tert.</i> -amyl alcohol, 2-methyl-2-butanol
RSS	residual sum of squares
SE	standard error
WSRS	weighted sum of residual square

Greek letter

γ_i	activity coefficient for component i
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