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Gas-phase etherification of cyclopentanol with methanol to cyclopentyl methyl ether catalyzed by zeolites



Tomáš Soták ^a, Zuzana Magyarová ^a, Mariya Shamzhy ^b, Martin Kubů ^b, Kinga Gołąbek ^b, Jiří Čejka ^{b, *}, Milan Hronec ^{a, *}

^a Department of Organic Technology, Catalysis and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, Bratislava, 812 37, Slovakia

^b Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, Prague, 128 43, Czech Republic

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ABSTRACT

Symmetric ethers can be synthesized through the acid-catalyzed self-etherification of biomass-derived alcohols. However, synthesis of asymmetric ethers via catalytic cross-etherification of alcohols is limited by poor selectivity. Herein, we developed an efficient zeolite-catalyzed one-step synthesis of valuable asymmetric cyclopentyl methyl ether (CPME) using gas-phase reaction of bio-based cyclopentanol and methanol. Among different medium- (FER, MCM-22, ZSM-5) and large-pore (BEA, MOR, USY) aluminosilicate zeolites, commercial ZSM-5 catalysts with 2D system of intersecting channels are markedly more selective to CPME. The targeted CPME was produced with a selectivity of 83 % and a yield higher than 80 % over the ZSM-5 catalysts with Si/Al ratios ranging from 15 to 40. Decrease in Si/Al ratio in ZSM-5 enhanced the conversion value, while not affecting the selectivity. FTIR study of the step-by-step adsorption of both reactants in ZSM-5 evidenced the Rideal-Eley mechanism with cyclopentanol and methanol is a promising process for large-scale applications thanks to its mild operating conditions, high yields and selectivity when using commercial ZSM-5 zeolites as catalysts.

1. Introduction

Ethers are important chemicals for a wide range of processes. Moreover, these chemicals can be synthesized by catalytic upgrading of biomass materials, which enables their use as an alternative to conventional fuels and as lubricants, medical ingredients, solvents, fragrances and additives, among other applications [1-5]. In addition, they can be synthesized in both gas and liquid phases, using olefins and alcohols as raw materials, as well as acidic homogeneous and heterogeneous catalysts [2,3,6-8].

In general, acid-catalyzed bimolecular endothermic etherification of alcohols competes with unimolecular exothermic dehydration leading to alkenes [9,10]. Various solid acids, containing either Brønsted (e.g., ion-exchanged resins [11,12]) or Lewis (e.g., alumina [13,14]) or both types of acid sites (e.g., zeolites [15–18]) were shown as effective catalysts in the self-etherification of linear and branched alcohols, producing symmetric ethers. The main parameters recognized as crucial for the catalyst activity and selectivity are the number of acid sites and their

strength [9,10,19]. The activity usually increases with acid site density and strength, although the strongest acid sites facilitated undesired alcohol-to-olefin dehydration over zeolites [9,10] Facilitation of both external and internal mass transport is also crucial to achieve high yields in bimolecular etherification vs. dehydration especially when using bulky alcohols [10,20]. Usually, the proper balance between the strength, concentration and accessibility of acidic centers is a way to optimize the catalyst performance in etherification reaction [9,10].

In turn, catalytic etherification of alcohols for selective synthesis of asymmetric ethers is very rare because such reactions generally lead to one asymmetric and two symmetric ethers. Furthermore, although highly efficient cross-etherification reactions have been reported under homogeneous conditions, catalyst recycling is difficult [21–24]. Similarly, heterogeneous catalysts are seldom used for the synthesis of asymmetric ethers from alcohols, and sparse data on gas-phase heterogeneous catalysts are available yet [25–30]. However, various zeolite type catalysts have been used for gas-phase cross-etherification of methanol or ethanol with isobutene to the corresponding ethers [6,

* Corresponding authors. E-mail addresses: jiri.cejka@natur.cuni.cz, cejka@jh-inst.cas.cz (J. Čejka), milan.hronec@stuba.sk (M. Hronec).

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Received 3 November 2020; Received in revised form 24 February 2021; Accepted 21 March 2021 Available online 27 March 2021 0926-860X/© 2021 Elsevier B.V. All rights reserved. **31–33**]. Thus, developing a protocol for the heterogeneously catalyzed etherification of alcohols to prepare asymmetric ethers, such as cyclopentyl methyl ether (CPME), remains both a challenge and an important goal.

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CPME is considered a key asymmetric ether in organic chemistry for its widespread use as an environmentally friendly solvent [34]. This hydrophobic solvent has low solubility in water and good stability under acidic and basic conditions. The Zeon Corporation has been producing CPME from cyclopentene, a raw material derived from the petroleum C_5 fraction, since 2005 [35]. However, CPME can only be a "green" and bio-based solvent if prepared from renewable raw materials. Nevertheless, biomass is a sustainable and renewable alternative to petroleum-derived specialty chemicals.

As we have recently shown, cyclopentanone and cyclopentanol are promising candidates for renewable CPME production because they can be efficiently prepared from biomass-based furfural [36–38]. Yet, to our best knowledge, no highly active and selective heterogeneous catalyst for direct cross-coupling of cyclopentanol with methanol has been published in the literature thus far. In this context, zeolites stand out as typical acid catalysts with numerous industrial applications and new emerging processes [39–41], which highlight their potential as candidates for selective heterogeneous catalysis. Moreover, their various micropore structures enable us to control the activity and selectivity of different reactions thanks to their shape-selective properties. Concurrently, new textural types of zeolites (two-dimensional, nanosponge and nanozeolites, among others) can be successfully used to optimize the outcome of different reactions [42].

Based on the above, this study aims to identify the characteristics of zeolites that are responsible for the activity and selectivity of these catalysts in the cross-etherification of cyclopentanol with methanol to CPME. For such purposes, we assessed the effect of the structural type of zeolites and of their Brønsted and Lewis acidity on the yield of this etherification reaction. In addition, FTIR adsorption experiments with methanol and cyclopentanol allowed us to propose a reaction Rideal-Eley mechanism for this etherification reaction.

2. Experimental

2.1. Materials and catalysts

Cyclopentanol (CYPol), methanol, CPME and cyclopentene (CYPen) were purchased from Sigma Aldrich. Commercial zeolites (USY (CBV 720 and CBV 500), ZSM-5 (CBV 3024E; CBV 5524 G; CBV 8014; CBV 1502), beta (CP 814E), mordenite (CBV 21A), ferrierite (CP 914)) were purchased from Zeolyst International. MCM-22 zeolite was synthesized according to a procedure described earlier [43], albeit with a 15/1 Si/Al ratio of the reaction gel. Ludox LS-30, sodium aluminate (50–55 % Al₂O₃ and 40–45 % Na₂O, Riedel-de-Haen), sodium hydroxide and hexamethyleneimine (HMI) were mixed with the following reactant ratios: OH–/Si = 0.18, HMI/Si = 0.55 and H₂O/Si = 53. The synthesis mixture was loaded into a Teflon-lined Parr reactor and placed in an oven on rollers (40 rpm). The hydrothermal synthesis was performed at 150 °C for 5 days. The product was isolated by centrifugation, washed with water, dried at 110 °C and then calcined at 540 °C for 6 h. Finally, MCM-22 was converted into NH⁴ by four-fold ion-exchange with a 1 M

NH₄NO₃ solution.

The catalysts were calcined at 500 °C for 5 h with a 5 °C min⁻¹ ramp and then pressed, crushed, and sieved into 0.3–0.7 mm grains. The screened catalysts are outlined in Table 1.

2.2. Catalyst characterization

Adsorption isotherms of nitrogen at -196 °C were measured on a Micromeritics ASAP 2020 volumetric instrument. To attain the necessary accuracy in the adsorption data collection, the ASAP 2020 was equipped with pressure transducers covering the 133 Pa, 1.33 kPa and 133 kPa ranges. Before the sorption measurements, all samples were degassed under a turbomolecular pump vacuum, starting at ambient temperature and increasing up to 110 °C until reaching a residual pressure of 0.5 Pa. After further heating at 110 °C, for 1 h, the temperature was increased to 300 °C and maintained for 6 h.

The surface area (S_{BET}) was calculated using adsorption data in the range of relative pressures $p/p_0 = 0.05-0.2$. The adsorbed amount at $p/p_0 = 0.97$ reflects the total adsorption capacity (V_{tot}). The *t*-plot method was used to calculate the external surface area (S_{ext}).

The concentration of Brønsted (BAS) and Lewis (LAS) acid sites was determined after d_3 -acetonitrile (ACN) adsorption by FTIR spectroscopy. FTIR spectra were recorded on a Nicolet 6700 FT-IR Spectrometer equipped with an AEM module with a resolution of 4 cm^{-1} . Zeolites were pressed into self-supporting wafers with a density of $8.0-12 \text{ mg cm}^{-2}$ and activated by degassing at 450 °C in the IR cell under vacuum. The experiments were performed at room temperature for 20 min and at a partial pressure of 5 Torr followed by desorption for 20 min. Before adsorption, ACN was degassed by freezing and thawing cycles. Spectra were recalculated at a wafer density of 10 mg cm⁻². The type and concentration of acid sites were evaluated using the molar absorption coefficients of d_3 -acetonitrile adsorbed on Brønsted $(\epsilon B = 2.05 \pm 0.1 \text{ cm } \mu \text{mol}^{-1})$ and Lewis $(\epsilon L = 3.6 \pm 0.2 \text{ cm } \mu \text{mol}^{-1})$ acid sites according to Ref. [44]. For the determination of the strength of acid sites, pyridine adsorption was carried out at 150 °C and a partial pressure of 3.5 torr for 20 min followed by FTIR-monitored desorption at 150, 250, 350 and 450 °C. Number of Lewis and Brønsted acid sites were evaluated from the integral intensities of bands at 1454 cm^{-1} (cL) and 1545 cm⁻¹ (cB) using the molar absorption coefficients, $\epsilon L = 2.22 \text{ cm } \mu \text{mol}^{-1}, \epsilon L = 1.67 \text{ cm } \mu \text{mol}^{-1}$ [45].

To clarify the first step of CPME formation (i.e., adsorption of either both alcohols or only one onto acid sites), the FTIR qualitative adsorption studies of increasing dose of cyclopentanol (or methanol) on H-form ZSM-5(40) zeolite was performed. Prior to alcohol adsorption, ZSM-5 (40) sample was pressed into self-supporting wafer ($\sim 8-12 \text{ mg/cm}^2$) and activated at 450 °C in FTIR *in-situ* cell. An excess of cyclopentanol (or methanol) was adsorbed in zeolite sample at p =3.5 Torr, T =75 °C for 20 min; subsequently the cell was outgassed for 3 min at 75 °C, followed by FTIR-monitored dose-by-dose adsorption of 0.09 mmol/g of methanol or CYPol on zeolite samples pre-loaded with CYPol (CYPol@ZSM-5(40)) or methanol (MeOH@ZSM-5(40)), respectively. FTIR spectra were recorded on a Nicolet iS50 FTIR Spectrometer equipped with DTGS detector at a resolution of 2 cm⁻¹.

Chemical composition was determined by X-ray fluorescence analysis on a Philips PW 1404 spectrometer equipped with an analytical program UniQuant. The samples were mixed with dentacryl as a binder and pressed on the surface of cellulose pellets.

2.3. Catalytic tests

The catalytic tests were performed in a stainless steel fixed-bed reactor (i.d. 6 mm, 250 mm), usually at a temperature of 100 °C and under atmospheric pressure, using 2 g of the catalyst (with a grain size of 0.3–0.7 mm) and nitrogen flow (10 mL min⁻¹). The solution of the cyclopentanol and methanol mixture (1:5 g g⁻¹) was fed continuously, using a syringe pump, to a preheating zone of the reactor containing

Table 1

Chemical composition and textural properties of zeolites.

	Zeolite	Si/Al	Pore system		$s = m^2 a 1^{-1}$	$m^2 a^{-1}$	$V = am^3 a^{-1}$	$V = am^3 a^{-1}$
			Size of the pores, nm	Dimensionality	S _{BET} III g1	S _{ext} III g	v _{micro} ciii [°] g	v _{tot} cm ⁻ g
Large-pore zeolites	USY (2.6) USY (15)	2.6 15	12-ring: 0.74×0.74 Cavity: 1.22 nm	3D	685 745	84 190	0.27 0.28	0.38 0.51
	BEA	12	12-ring: 0.66×0.67 12-ring: 0.56×0.56	3D	531	187	0.16	0.56
	MOR	10	12-ring: 0.65×0.70 8-ring: 0.26×0.57	2D	404	29	0.17	0.21
Medium-pore zeolites	ZSM-5(15)	15	10-ring: 0.51 \times 0.55 10-ring: 0.53 \times 0.56	3D	386	47	0.15	0.22
	ZSM-5(25)	25			369	62	0.15	0.27
	ZSM-5(40)	40			449	47	0.16	0.25
	ZSM-5(75)	75			375	38	0.16	0.20
	MCM-22	15	10-ring: 0.40 \times 0.55 10-ring: 0.44 \times 0.51 Cage: 0.71 \times 1.82	2D	547	158	0.19	0.43
	FER	27.5	10-ring: 0.42 \times 0.54 8-ring: 0.35 \times 0.48	2D	316	32	0.13	0.18

quartz wool at the weight hour space velocity (WHSV) of cyclopentanol, mostly 0.25 g_{cyclopentanol} g_{cat}⁻¹ h⁻¹. The temperature was controlled by the thermocouple placed in the center of the catalyst bed. The gaseous reaction products were cooled down and collected in the flask.

The reaction products and unreacted raw materials were analyzed by gas chromatography every hour using the external standard method and response factors of the corresponding standard compounds. A gas chromatography-mass spectrometry (Shimadzu) was used to identify the organic compounds. The yields of the reaction products (Y) were calculated based on the amount of cyclopentanol dosed into the reactor. The conversion of cyclopentanol was calculated according to the following Eq. (1):

$$X_{CYPol} = \frac{m_{CYPol,0} - m_{CYPol,1}}{m_{CYPol,0}} \times 100$$
 (1)

where $m_{CYPol,1}$ is the amount of unreacted cyclopentanol and $m_{CYPol,0}$ the amount of cyclopentanol charged into the reactor.

The selectivity to CPME was calculated as follows (2):

$$S_{CPME} = \frac{Y_{CPME}}{X_{CYPol}} \times 100$$
⁽²⁾

The reaction rates of the reaction products were calculated as moles of product per hour per g_{cat} (3):

reaction rate_{product} =
$$\frac{n_{product}}{\tau \cdot m_{catalyst}}$$
 (3)

3. Results and discussion

3.1. Catalyst characterization

To study the effect of the pore system of a zeolite on its catalytic performance in cross-etherification of cyclopentanol and methanol, a set of zeolites with close number of acid sites, but different textural characteristics was chosen (Tables 1 and 2). It includes commercial large-pore USY (Si/Al = 15, 3D channel system), BEA (Si/Al = 12.5, 3D) and MOR (Si/Al = 10, 2D) and medium-pore ZSM-5 (Si/Al = 40, 3D), FER (Si/Al = 27.5, 2D) and MCM-22 (Si/Al = 15, 2D) zeolites. In turn, the effect of zeolite chemical composition was investigated using the most selective (*vide infra*) ZSM-5 catalysts with Si/Al = 15–75 and USY zeolites with Si/Al = 15 and 2.6. The XRD patterns of zeolite catalysts confirm their phase purity (Fig. S1), while ad-/desorption nitrogen isotherms (Fig. S2) exhibit type I typical of microporous materials according to IUPAC classification [46].

The texture characteristics of catalysts agree well with individual zeolite frameworks. For BEA, USY(15) and MCM-22 zeolites, the increased uptake at higher relative pressures ($p/p_0 > 0.80$) reflects the interparticle adsorption. The micropore volume increased with pore size of cage-free FER, ZSM-5, MOR and BEA zeolites, while reached the

Table 2	2	
Acidic	properties	of zeolites.

			Acid am			
	Zeolite	Si/ Al	BAS μmol g ⁻¹	LAS µmol g ⁻¹	BAS+LAS, $\mu mol g^{-1}$	BAS/ LAS
	USY (2.6)	2.6	480	1010	1490	0.5
Large pore zeolites	USY (15)	15	200	340	540	0.6
	BEA	12	140	390	530	0.4
	MOR	10	350	420	770	0.8
	ZSM-5 (15)	15	620	200	820	3.1
	ZSM-5 (25)	25	360	110	470	3.3
Medium pore	ZSM-5 (40)	40	250	70	320	3.6
zeolites	ZSM-5 (75)	75	150	30	180	5.0
	MCM- 22	15	390	310	700	1.3
	FER	28	440	60	500	7.3

^a Measured by FTIR spectroscopy of adsorbed CAN.

maximal value for cage-based MCM-22 and USY: FER < ZSM-5(15) < BEA < MOR < MCM-22 < USY (15). In turn, with decreasing size of zeolite crystals (Fig. S3), external area S_{ext} increased in the following sequence: MOR \approx FER < ZSM-5 (40) < MCM-22 < BEA \approx USY (15) (Table 1). The micropore volume and external area in a set of ZSM-5 zeolites with Si/Al = 15–75 varied in the narrow ranges 0.15 - 0.16 cm³ g⁻¹ and 38–62 m² g⁻¹, respectively.

The concentration of Brønsted and Lewis acid sites in zeolites under study was determined based on the intensities of the bands at 2297 and 2315 – 2325 cm⁻¹ in FTIR spectra of adsorbed ACN (Fig. S4, Table 2). The total number of acid sites in a series of ZSM-5 and USY zeolites decreased with increasing Si/Al value, while Brønsted-to-Lewis acid sites ratio was in the range 3.1–5.0 and 0.5 – 0.6, respectively (Table 2). In turn, Brønsted-to-Lewis acid sites ratio increased from 0.4 to 7.3 in the following sequence of the studied commercial zeolites: BEA < USY(15) < MOR < MCM-22 << ZSM-5(40) << FER.

3.2. Gas-phase etherification

Direct gas-phase etherification of biomass-derived cyclopentanol over acid catalysts is an attractive, but not yet elaborated method for producing asymmetric ethers. Zeolites offer the possibility of controlling the acidity by varying the Si/Al ratio and reaction selectivity by adjusting the extent of molecular confinement [47]. Catalytic performance of various types of zeolites is further discussed for the conversion of cyclopentanol/methanol mixture at moderate temperatures where etherification prevails over alcohol dehydration [48].

3.2.1. Effect of the zeolite type

In screening catalysts for gas-phase etherification of cyclopentanol with methanol, we investigated different zeolites in protonated form. All zeolites were tested at the same WHSV = 0.25 $g_{cvclopentanol} g_{cat}^{-1} h^{-1}$ and different temperatures. For all zeolites, increasing the temperature resulted in enhancement of cyclopentanol conversion, while selectivity showed volcano-type dependence on the temperature (the results obtained for ZSM-5(40) are shown in Fig. 2 and discussed vide infra). As a result, the maximum yield of the targeted CPME product over zeolites with different structures was attained at different temperatures (i.e., 100 °C for ZSM-5; 120 °C for MCM-22, BEA, USY; 140 °C for FER and 150 °C for MOR). To address a role of zeolite topology on catalytic activity, the "best" performance of the tested zeolites was compared at different reaction temperatures in Fig. 1. The reaction rates of CPME and cyclopentene formation are summarized in Table S1. All tested zeolites were highly active in the conversion of cyclopentanol, except for MCM-22 and ferrierite, most likely due to the lower accessibility to active sites in their channel system, susceptible to a rapid coking. In turn, the most active zeolites exhibit significantly different selectivities of etherification to CPME. The highest selectivity for this reaction was found when using zeolites ZSM-5(40) (76.5 %) and USY(15) (64.8 %), and the lowest selectivity was assessed over the large-pore zeolites BEA (39.5 %) and MOR (25.2 %). The most selective catalysts feature either large (USY) or medium (ZSM-5(40)) micropores, substantially different strength of acid sites (Fig. S5) and Brønsted-to-Lewis acid sites ratios (3.6 and 0.6, Table 2). To shed the light on the effect of zeolite acidity on the catalytic performance in cross-etherification of CyPol with methanol, we studied the effect of Si/Al ratios on the performance of ZSM-5 zeolite in more detail, while further optimizing the reaction conditions (Section 3.2.2). Medium-pore zeolites MCM-22 and ferrierite were highly unselective, with a high formation of carbonaceous deposits on the catalyst surface. Under these reaction conditions, the competitive etherification of cyclopentanol to symmetric dicyclopentyl ether in the presence of these zeolites was usually not detected; only traces of this product were identified in the reaction mixtures. Conversely, dimethyl ether was formed in a parallel reaction in a yield of 10-15 %. However, due to its volatility, the measurement was determined with a high error. The presence of CPME and cyclopentene was not detected in the outgas.

3.2.2. Optimization of reaction conditions. Effect of the Si/Al ratio on the ZSM-5 catalyst

Based on a preliminary screening of zeolites in the gas phase (Fig. 1), we optimized the reaction conditions using the most promising ZSM-5 (40) zeolite. As mentioned above, the catalytic activity and mainly the distribution of reaction products significantly depend on the reaction temperature. The reaction temperature effect on cyclopentanol conversion and selectivity to CPME is presented in Fig. 2, which shows that both the yield of and selectivity to CPME significantly increase from



Fig. 1. Catalytic performance of various types of zeolites for the etherification of cyclopentanol to CPME at WHSV=0.25 $g_{cyclopentanol} g_{cat}^{-1} h^{-1}$.



Fig. 2. Effect of reaction temperature on the catalytic performance of ZSM-5 (40) zeolite at WHSV=0.25 g_{cyclopentanol} g_{cat}^{-1} h⁻¹.

13.0% to 53.1% and from 32.2% to 71.1%, respectively, when increasing the reaction temperature from 90°C to 100°C. Within this temperature range, the formation of cyclopentene increases from 6.6% to 12.8%. Further increasing the reaction temperature to 110-120°C leads to higher cyclopentanol conversion but adversely affects the selectivity to CPME. The lower selectivity to CPME can be explained due to coke deposition.

CPME yield can be further improved by optimizing the WHSV using the ZSM-5(40) catalyst. In the studied WHSV range, from 0.05 to 0.35 $g_{cyclopentanol} g_{cat}^{-1} h^{-1}$, the conversion of cyclopentanol steadily decreases, whereas the yield and selectivity to CPME peak at a WHSV of 0.10 $g_{cyclopentanol} g_{cat}^{-1} h^{-1}$ and then both values decline (Fig. 3). Under optimal conditions, 80.4 % yield and 82.5 % selectivity to CPME are reached at 97.5 % cyclopentanol conversion. Cyclopentene, the product of cyclopentanol dehydration, is formed in 15.6 % yield.

Fig. 4 shows the conversion of cyclopentanol, the yield of CPME and CYPen as a function of time on stream (TOS) using the catalyst ZSM-5 (40) at 100°C. Experimental results indicated that, under the aforementioned conditions, the catalyst was stable and exhibited high activity and selectivity at least for 6h of TOS.

After identifying the ZSM-5(40) zeolite as the most promising catalyst, providing CPME in high yield, we studied the effect of Si/Al ratios in ZSM-5 catalysts on the etherification of cyclopentanol in more detail (Fig. 5). Cyclopentanol conversion and CPME yield decrease steadily with the increase in Si/Al ratio (Fig. 5); from X = 92.9 % and Y = 67.3 % for ZSM-5(15) to X = 41.1 % and Y = 30.7 % for ZSM-5(75), respectively. In turn, the selectivity to CPME remains almost unchanged (72–76 %) among ZSM-5 catalysts with different Si/Al ratios. The maximum yield of cyclopentene, the product of cyclopentanol dehydration, is 16.5 % over the ZSM-5(25) zeolite. This co-product can be easily hydrogenated into cyclopentane, which is currently used as a substitute for environmentally harmful freons, for example, in refrigerants and freezers or as a blowing agent [49].

3.2.3. The path of cyclopentyl methyl ether formation over the ZSM-5 zeolite

Various mechanisms have been proposed for alcohol etherification



Fig. 3. WHSV effect on the catalytic performance of the ZSM-5 (40) zeolite at a reaction temperature of 100° C.



Fig. 4. Effect of time on stream on the catalytic performance of ZSM-5(40) zeolite at 100°C and WHSV= 0.10 $g_{cyclopentanol} g_{cat}^{-1} h^{-1}$.



Fig. 5. Effect of the Si/Al ratio in ZSM-5 zeolites on catalytic performance at 100° C and WHSV= 0.25 g_{cyclopentanol} g_{cal}⁻¹ h⁻¹.

over heterogeneous catalysts involving both Brønsted and Lewis acid sites as active sites [17,50–53]. Both Langmuir–Hinshelwood and Rideal–Eley mechanisms are reported in the literature for alcohol-to-dialkyl ether transformations (Scheme 1), depending on the catalyst used in these reactions [54,55].

To verify the path of CPME formation over the most selective ZSM-5 catalyst (either Langmuir–Hinshelwood or Rideal–Eley mechanism, Scheme 1), a subsequent adsorption of methanol and cyclopentanol in the ZSM-5(40) zeolite was monitored with FTIR spectroscopy.

Detailed analysis of changes in the FTIR spectra after adsorption of cyclopentanol and methanol is presented in Supplementary information (Fig. S6, S7, S8), while the key findings can be summarized as follows:

1) Both cyclopentanol and methanol molecules tend to adsorption not only on zeolite strong Brønsted acid sites, but also on terminal Si–OH groups with negligible acidity. The adsorption of both alcohols on Lewis acid sites is expected based on the previously reported results [56,57], but could not be traced in FTIR spectra due to the lack of characteristic bands.

2) At low surface coverage, the formation of neutral alcohol adduct hydrogen-bonded with Si(OH)Al/Si–OH takes place over ZSM-5(40) for both methanol and cyclopentanol. The alcohol hydroxyl group in cyclopentanol molecule is not disturbed. Similar forms of alcohol adducts in dehydration of cyclohexanol were reported for BEA zeolite [58].

3) Increasing alcohol dosage leads to the formation of ionic methanol dimers, while the dimeric cyclopentanol adducts were detected in the presence of much higher alcohol loadings. These dimeric cyclopentanol adducts were probably formed only on the external surface of catalysts due to the limiting pore size of zeolite ZSM-5.

Further FTIR-monitored dose-by-dose adsorption of CYPol on zeolite sample pre-loaded with methanol (MeOH@ZSM-5(40)) provided several evidences supporting the Rideal–Eley mechanism (Scheme 1, bottom) operating upon MFI-catalyzed cross-etherification:

- the methanol molecules interacting with acid sites, both Brønsted and Lewis, in MeOH@ZSM-5(40) are gradually exchanged by the cyclopentanol molecules as shown by the steady increase in the intensity of the bands characteristic of cyclopentanol (i.e., at 2970 cm⁻¹ and 2883 cm⁻¹) (Figs. 6 and 7).

- in contrast to methanol, cyclopentanol is more strongly adsorbed not only on Brønsted acid sites (decreasing band at 3612 cm⁻¹ of Si(OH) Al groups in CYPol@ZSM-5(40) vs. activated ZSM-5(40), Fig. S8), but also on silanols (decreasing band at 3745 cm⁻¹, Fig. S8), easily accessible sites located on the external surface of the catalyst.



Fig. 6. Evolution of FTIR spectra of cyclopentanol adsorption at an increasing dosage on $CH_3OH@ZSM-5(40)$; the dark blue spectrum refers to the methanol excess after removing physisorbed molecules by evacuation; the red spectrum refers to cyclopentanol interacting with acid sites after methanol replacement (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).



Scheme 1. Langmuir–Hinshelwood (top) and Rideal–Eley (bottom) mechanisms of cyclopentyl-methyl ether formation over the ZSM-5 zeolite catalyst. Activation of CyPol molecule can occur on both BAS and LAS, while BAS (\equiv Al(O···H⁺)Si \equiv) are shown as active sites in this Scheme.



Fig. 7. Evolution of methanol (2957 cm⁻¹; brown) and cyclopentanol (2970 cm⁻¹; blue) band intensity at an increasing dosage of cyclopentanol on the CH₃OH@ZSM-5(40) sample (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

-when using small dosages or even an excess of methanol, the substitution of cyclopentanol molecules adsorbed on acid sites in CYPol@ZSM-5(40) sample was not observed (Fig. S8).

Based on the above, the plausible mechanism of CPME formation over ZSM-5(40) zeolite under conditions used in this study includes the following steps (Scheme 1, bottom): (i) cyclopentanol molecules are adsorbed on the acid sites; (ii) in the next step, the carbon atom of the neutral H-bonded intermediate is attacked by the OH group of methanol in the gas phase, forming the new C—O bond in the asymmetric ether; (iii) the formed CPME and water molecules are desorbed from the acid sites.

The FTIR-verified Rideal—Eley mechanisms of CPME formation over the ZSM-5 zeolite catalyst agrees with lacking correlation between the Brønsted-to-Lewis acid sites ratio and selectivity of cross-etherification, discussed in the following section.

3.2.4. Correlation between catalytic performance and zeolites properties The etherification and dehydration of an alcohol can proceed on both

Brønsted and Lewis acid sites. Depending on the type of heterogeneous acid catalyst, some authors suggest that etherification or dehydration requires Lewis acid sites [59,60], whereas other authors correlate dehydration with the Brønsted acid sites [17,51,61]. To assess the effect of the acid properties of zeolite catalysts on the etherification reaction of formation of the asymmetric CPME, the correlation between the acidity of zeolites and their catalytic properties was investigated in detail. Fig. 8 presents the variation in cyclopentanol conversion and CPME yield as a function of the total concentration of acid sites (Brønsted and Lewis). The results suggest the increase of CyPol conversion and the yield of CPME with increasing total concentration of acid sites in ZSM-5 and USY catalysts (Fig. 8). Noticeably, while showing linear dependence of CyPol conversion vs acid site number for ZSM-5 catalysts with Si/Al = 40-75, the plot significantly departed from a linearity with decreasing Si/Al to 25 – 15. This trend reveals the diffusion control of the reaction rate over Al-rich ZSM-5 catalysts.

In turn, the selectivity to CPME was almost unchanged independently on Brønsted-to-Lewis acid sites ratio (Fig. S10, S11). Insensitivity of the studied zeolite-catalyzed gas phase cross-etherification reaction to the Brønsted-to-Lewis acid sites ratio distinguishes it from recently reported self-etherification occurring in a liquid phase over Brønsted/ Lewis acid tungstated zirconia [10,62,63]. Thus, the close proximity of Brønsted and Lewis acid sites seems not playing the role in the case of cyclopentanol etherification with methanol proceeding according to the Rideal–Eley mechanism.

When evaluating the product distribution, we assessed that cyclopentene is formed by parallel dehydration as a by-product, in addition to the desired CPME. The possibility of consecutive etherification of cyclopentene with methanol was examined using the ZSM-5(25) zeolite. Only approximately 3% of cyclopentene was converted into CPME under the reaction conditions given in Fig. 1 (the ratio of CYPen : methanol was 1:5 g g⁻¹). Thus, the results indicate that, over ZSM-5 zeolites, cyclopentene does not significantly react with methanol in the etherification to CPME.

4. Conclusions

We developed a new route for the efficient and highly selective transformation of bio-based cyclopentanol into the asymmetric



Fig. 8. Variation of catalytic properties as a function of the total concentration of acid sites in various zeolites in the gas-phase etherification of cyclopentanol. For conditions, see Fig. 1.

cyclopentyl methyl ether. Thus far, no synthesis of cyclopentyl methyl ether through heterogeneously catalyzed gas-phase etherification of cyclopentanol with methanol has been reported in the literature. A broad range of zeolites was investigated in the cross-etherification of cyclopentanol. Among all zeolites studied, ZSM-5 shows the highest selectivity most likely due to the combination of pore size effect with appropriate strength of the acid sites. In the 15-75 range, the Si/Al of MFI does not affect the selectivity to the asymmetric ether, which is formed via the Rideal-Eley mechanism, including the reaction of cyclopentanol adsorbed on zeolite surface with MeOH molecules. Conversion of cyclopentanol increases with the decrease in the Si/Al ratio as a result of the increase in the number of acid sites, although the results suggested a diffusion-controlled regime of a reaction over Al-rich ZSM-5 catalysts. Although the influence of Brønsted-to-Lewis acid sites ratio on ZSM-5 activity and selectivity was not observed in the ranges 3.1-5.0, the effect of this characteristic on the performance of a zeolite catalyst in both liquid and gas phase cross-etherification reaction leading to CPME should be a subject of a particular kinetic study.

At the reaction temperature of 100°C and at WHSV = 0.10 g_{cyclo-pentanol} g_{cat}⁻¹ h⁻¹, the yield of cyclopentyl methyl ether was > 80 %. The gas-phase cross-etherification of cyclopentanol with methanol described in this study is therefore a promising process for large-scale applications considering its mild operating conditions, high yields, selectivity and the use of bio-based cyclopentanol as raw material and of commercial zeolites as catalysts.

CRediT authorship contribution statement

Tomáš Soták: performed catalytic tests and prepared the first version of the manuscript. Zuzana Magyarová: performed catalysts and analyzed reaction products. Mariya Shamzhy: performed some FTIR test and corrected the manuscript. Martin Kubů: carried out adsorption investigations. Kinga Gołąbek: contributed to FTIR studies of the reaction mechanism. Jiří Čejka: supervised the research and finalized the manuscript. Milan Hronec: proposed this topic and contributed to writing and correcting of the manuscript

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118122.

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