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One Step Synthesis of Ethanol from Glycerol in a Gas Phase Packed Bed Reactor over Hierarchical Alkali-treated Zeolite Catalyst Materials

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The gas-phase conversion of glycerol into ethanol in a "green" one-step way over cesium metal-promoted zeolite catalyst has been reported for the first time. To our knowledge, the CsZSM-5 based catalyst presented in this work showed one of the best yields to ethanol in the gas-phase glycerol conversion. The catalyst samples structure, texture, and acid-base properties were characterized using numerous materials characterization techniques. The catalytic evaluation was carried out in a packed-bed continuous flow reactor. The highest ethanol yield achieved was 99.6 mol% over 20wt%CsZSM-5 catalyst with SiO₂/Al₂O₃ = 1500, 10 wt% glycerol feed concentration, 350 °C reaction temperature, and GHSVtotal = 625 h⁻¹. It was demonstrated that the best catalytic performance was related to the ample amount of surface basic sites, synergistic interaction between Cs species and HZSM-5 zeolite and to its smaller crystallite size obtained from XRD analysis. The achieved results exhibit a great potential of utilizing alkali-treated CsZSM-5 catalyst for the gas-phase conversion of glycerol into bio-based ethanol. The possible reaction route from glycerol to renewable ethanol was proposed based on direct glycerol conversion to ethanol *via* the thermal monodehydration, radical fragmentation, methylation and transfer hydrogenation reactions. Finally, for the first time, the methanol was directly converted into ethanol in the gas-phase continuous flow packed-bed reactor over 20wt%CsZSM-5 catalyst.

Introduction

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The depletion of fossil resources stimulated scientists to find sustainable alternative sources of energy. Therefore, substitutes of gasoline, natural gas, and diesel to such as bioethanol, biogas, and biodiesel are of high importance as a renewable and pollution-free solution. The biodiesel production from the transesterification of plant-derived triglycerides with methanol has experienced exponential growth in the last years, and according to the literature ¹, this positive trend will continue until 2020 with biodiesel production of 37 million metric tons. Glycerol is a byproduct in biodiesel production representing roughly 10% of the mass of the biodiesel produced, which led to a decrease of glycerol commercial price due to its high abundance on the world market. Glycerol can be used in cosmetics, soaps, pharmaceuticals, and personal care products, food, and tobacco industries ²⁻⁴. The commercial price of crude glycerol is in the range from 0.09 to 0.20 \$/kg, whereas the pure glycerol price is 0.60-0.91 \$/kg 5,6 .

Glycerol valorization can be carried out in gas–phase over heterogeneous catalysts. The most interesting products of this process are: acrolein ^{7,8}, acrylic acid ^{9–14}, dihydroxyacetone ^{15,16}, hydroxyacetone ^{17,18}, allyl alcohol ^{19,20}, epichlorohydrin ^{1,21}, lactic acid ^{22,23}, 1,2-propanediol ²⁴, 1,3-propanediol ^{5,25}, and very recently ethanol ^{26,27}. These products are important for industrial commercialization due to many applications and their high profitability on the world market.

Ethanol can be obtained by commercial routes (Scheme 1) through the hydration of ethylene over solid acid catalyst or by the fermentation of sugar, grain crops, and waste biomass ²⁶. The production of ethanol from ethylene has many disadvantages, the main of them are high production cost, non-environmentally friendly route, unsustainable production, and hazardous feedstock. Therefore, the fermentation way is more favorable. At the same time, the toxicity of ethanol to yeast limits the concentration of ethanol in fermentation reaction, and further distillation is necessary to obtain the high concentrated ethanol.



Scheme 1 Industrial processes of ethanol production.

In addition, ethanol can be obtained in the laboratory in different ways such as: *via* the reaction of dimethyl ether with CO₂ and H₂²⁸ (Scheme 2a); or from paraformaldehyde, CO₂ and H₂²⁹ (Scheme 2b); or by dry reforming of glycerol in two steps (Scheme 2c); or very recently 26,27 from glycerol in one step in a gas-phase packed-bed

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⁺ Footnotes relating to the title and/or authors should appear here.

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reactor over heterogeneous catalysts with H₂ participation (Scheme 2d).

$$O_+ 2CO_2 + 6H_2 \xrightarrow{Ru(PPh_3)_3Cl_2/Col_2} 2 \xrightarrow{OH} + 3H_2O$$

Dimethyl
ether (a)

$$(CH_{2}O)n + CO_{2} + H_{2} \xrightarrow{Ru(acac)_{3}-CoBr_{2}-Lil} OH + H_{2}O (b)$$
Paraformaldehyde
$$HO \xrightarrow{OH} OH \xrightarrow{Dry reforming} CO + H_{2} \xrightarrow{Catalyst} OH (c)$$

$$HO \xrightarrow{OH} OH \xrightarrow{Ni_{2,4}/Mg_{3,7}Cr_{2,0}O_{6,7}} OH (c)$$

$$HO \xrightarrow{OH} OH \xrightarrow{Ni_{2,4}/Mg_{3,7}Cr_{2,0}O_{6,7}} OH (c)$$

$$HO \xrightarrow{OH} OH \xrightarrow{CO/ZnO-ZIF} OH (c)$$

$$HO \xrightarrow{OH} OH \xrightarrow{CO/ZnO-ZIF} OH (c)$$

Scheme 2 Laboratory processes of ethanol production.

Ethanol has various applications such as a clean fuel, engine fuel, fuel additive, intermediate of manufacturing industries, feedstock, solvent, low-temperature liquid and etc. ^{26,30}. The global ethanol production is estimated to increase from 120 billion litters in 2017 to 131 billion litters by 2027, where a half of this increase is expected to originate from Brazil, and the other large contributors to the expansion in ethanol production are Thailand, China, India, and the Philippines with 12%, 10%, 9%, and 5%, respectively ³¹.

According to OECD (Organization for Economic Cooperation and Development) the coarse grains and sugarcane will continue to be the dominant ethanol feedstock and the biomass-based ethanol is projected to account for about 0.3% of world ethanol production by 2027. At the same time the prediction of glycerol production is counted about 4.0 Mt/year by 2024¹. Mota et al. recently published ⁶ that the production of ethanol from glycerol could decrease the price of ethanol production by approximately 40%. On the other hand, all laboratory processes for ethanol production are needed to utilize H₂. Thus, the direct catalytic transformation of glycerol into concentrated ethanol in the gas-phase without an external H-donor could be a promising alternative.

Nowadays, only a few reports deal with the valorization of glycerol to ethanol in the gas-phase over heterogeneous catalysts. Haider et al. ³² studied the reactivity of glycerol using water as a potential hydrogen source. They established that the glycerol dehydration reaction could be carried out both on acid and base catalysts. As a basic or redox oxide catalysts, they used MgO, CaO, MgO/CaO mixture, and CeO₂ with reaction temperature at 227-327 °C, and glycerol concentration of 10 wt% in water. They observed methanol (with 60% selectivity) as the main product, where ethanol, acetaldehyde, hydroxyacetone, acrolein, ethylene glycol, propionaldehyde, 1-propanol, 2-propanol, allyl alcohol, 2,3butanedione, 2-hexanone, acetone, and CO₂ were byproducts. These unexpected product distributions support that the importance of catalyst basicity in the reaction of glycerol valorization. Very recently, Smith and coauthors ³³ investigated the conversion of 50 wt% glycerol solution over CeO₂ catalyst in the temperature range of 320-440 °C. They found out that acetaldehyde and methanol were the major products at 440 °C, at the same time hydroxyacetone was the main product at 320 °C with the highest glycerol conversion of 21%. Ryneveld et al. ³⁴ showed that Ni/SiO₂ Eatalyst With in proved reducibility achieved 69% total selectivity of propanol, ethanol, and methanol at 320 °C. The route of ethanol formation from glycerol through 1,2-propanediol compound was proposed. Sumari et al. 35,36 carried out the glycerol conversion to ethanol in a liquid phase over activated Cu/mordenite and Ag/Y catalyst assisted by ultrasound with the highest ethanol yield of 3.7% and 13.6%, respectively.

Zheng et al. ²⁶ recently reported the direct production of ethanol as the main product from glycerol in the gas-phase over heterogeneous catalyst for the first time. The synthesis route of ethanol from glycerol was achieved over a series of Ni-substituted stichtite derived Ni/MgCr₂O₄ catalysts in H₂ atmosphere under 2 MPa (Scheme 2d). The highest selectivity of ethanol was 63.3% with glycerol conversion of 99.6% over Ni_{2.4}/Mg_{3.7}Cr_{2.0}O_{6.7} catalyst after steady operation for 2 h. Recently, the same group with Zhao et al. ²⁷ synthesized a Co/ZnO catalyst with nano-sized Co particles incorporated into ZnO plates and used it for the synthesis of ethanol from glycerol at 210 °C with H₂/glycerol = 40 mol in a feed under high pressure (Scheme 2d). The maximum conversion of glycerol reached up to 98.8% with 57.9% ethanol selectivity over Co/ZnO-ZIF $([M(CH_3C_3H_2N_2)_2]_n, M = Co and Zn)$ catalyst after steady operation for 2 h. At the same time, the stability for both catalysts was not studied and an external H₂ source and high pressure were necessary for these reactions.

In this research work, we have investigated the "green" and onestep reaction of ethanol synthesis from glycerol without H_{2} in the gas-phase in a packed-bed reactor. The synthesis of the cesium zeolite catalysts with $SiO_2/Al_2O_3 = 30$ and 1500 molar ratios were obtained by the incipient wetness impregnation method and characterized by various physical-chemical methods. Cs alkali metal was chosen for modification of ZSM-5 zeolite due to the lowest electronegativity (0.79) of Cs atom and thus the highest basic strength (Li < Na < K < Rb < Cs) ³⁷. The influence of Cs species incorporation into ZSM-5 zeolite on the acidity-basicity and its catalytic performance was elucidated. The structural, morphology, acidic, and basic properties of alkali-treated zeolite catalysts were systematically investigated using thermogravimetric analysis (TGA), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS), powder X-ray diffraction (XRD), N₂ physisorption, scanning transmission electron microscopy – energy dispersive X-ray spectroscopy (STEM– EDX), scanning electron microscopy (SEM), CO₂-temperatureprogrammed desorption (CO₂–TPD), NH₃-temperature-programmed desorption (NH₃-TPD), and pyridine diffuse reflectance infrared Fourier transform (pyr-DRIFT) techniques.

Experimental

Materials and catalysts

 NH_4 -ZSM-5 zeolite (molar SiO₂/Al₂O₃ = 30, CBV 3024E) was purchased from Zeolyst International. HZSM-5 zeolite (molar SiO₂/Al₂O₃ = 1500, HSZ-890HOA) was obtained from Tosoh Corporation. Both commercial zeolites were calcined at 550 °C in air for 6 h to convert from the NH₄-form to its H-form and to completely remove any organic residues. Preparation of the CsZSM-5 catalysts involved the impregnation of zeolite using the incipient wetness

impregnation method with solution of 0.01 M CsNO₃ (Sigma-Aldrich, 99%). Briefly, cesium nitrate solution was added to the corresponding zeolite with vigorous stirring for 3 h at 80 °C. Thereafter, samples were dried overnight at 110 °C. Afterward, they were calcined for 6 h at 550 °C. Finally, all catalysts were prepared for catalytic evaluation in the packed-bed reactor by grounding and sieving to 250-400 μ m particle size.

Calibration curves were measured in the range of 0.1-10 wt% aqueous solutions for: glycerol (Merck, 99%), ethanol (Merck, >99.8%), acrolein (Fluka, >95%), allyl alcohol (Merck, >99%), hydroxyacetone (Alfa Aesar, 95%), glycidol (Merck, 96%), 2-methoxy-1,3-dioxalane (Merck, >99%), glycerol formal (Merck, 98%), acetaldehyde (Merck, >99.5%), propionaldehyde (Merck, 98%), acetic acid (Merck, >99.7%), acetone (Merck, >99.5%), propionic acid (Merck, >99.5%), acrylic acid (Merck, 99%), 1,2-propanediol (Merck, >99%), n-propanol (Merck, 99.5%), formaldehyde (Merck, 37wt% in H₂O), methanol (Merck, >99.9%).

Characterizations

The BET surface area, pore size, and pore volume of catalyst samples were measured by N2 adsorption-desorption isotherms on Micromeritics ASAP 2020, with the degassing under vacuum at 200 °C overnight with 150 mg of sample. After pretreatment, the sample tube was weighed and thereafter the specific surface area was measured. The pore-size distributions were calculated using the BJH method applied to the desorption branch of isotherms. Hierarchy factor (HF) was calculated as HF = $(S_{ext}/S_{BET}) \times (V_{micro}/V_{total})$. Powder X-ray diffractograms of synthesized catalyst samples were recorded using a PANalytical XpertPro diffractometer, equipped with a CuK α 1radiation (1.54056 Å) in reflection geometry. Diffractograms data were collected over 2 theta range of 5-70°, with a step size of 0.034°. Crystalline phases were identified with utilizing the Match! 2.0 software and the Crystallography Open Database (COD). Crystallinity was calculated based on the intensity of the characteristic peaks in the two 2 theta ranges such as 7.5-9.5° and 22.5-25.0°, respectively ^{38,39}.

Scanning electron micrographs were collected in FE–SEM SUPRA 35-F (Carl Zeiss) electronic microscope. Transition electron micrographs were recorded on a JEOL ARM 200 CF microscope equipped with a cold field-emission gun, probe spherical aberration corrector and Jeol Centurio EDXS system with 100 mm² SDD detector. Prior to the observation, the samples were prepared in ethanol, sonicated and finally deposited onto commercial Ni grids. ICP-AES analysis was performed using Varian model 715-ES after successful samples dissolution in HF and HClO₄ and/or in a mixture of HCl and H₃BO₃ if the residues were detected. ICP-MS analysis was carried out using Agilent Technologies model 7500ce for the Cs quantification in the studied catalyst samples.

The acid properties of the catalysts were determined by ammonia temperature-programmed desorption in Micromeritics Autochem 2920 II system with a thermal conductivity detector (TCD) and an on-line mass spectrometer (Pfeiffer Vacuum, ThermoStar™ GSD301T). Previously, 100 mg of sample was positioned inside a quartz U-tube reactor and purged under He flow up to 500 °C and cooled down to 100 °C. Thereafter, the sample was saturated with 10 vol% NH₃/He flow of 20 ml/min at 100 °C for 30 min. The

physisorbed NH₃ from the catalyst surface was removed by flushing He at 100 °C for 60 min. The chemisorbed NH₃ profiles were recorded from 100 to 600 °C with a heating rate of 10 °C/min.

The basic strength of studied catalysts was determined using CO_2 temperature-programmed desorption analysis carried out on an Autochem II 2920 instrument, equipped with a TCD detector and connected to a mass spectrometer (ThermoStarTM GSD320). About 100 mg of catalyst was preactivated at 300 °C for 10 min in 5% O_2 /He stream with flow rate of 20 ml/min to remove adsorbed moisture and other volatile species from the surface of catalyst sample and then, a quartz U-tube reactor was cooled to 10 °C. Thereafter, 50 vol% CO_2 /He flow of 20 ml/min was passed through the catalyst surface for 20 min. The weakly adsorbed CO_2 was removed in He flow at 10 °C for 30 min. The CO_2 desorption profiles were recorded from 10 to 800 °C with a ramp of 10 °C/min in He flow at 20 ml/min and monitored by a mass spectrometer.

Diffuse reflectance infrared spectra of adsorbed pyridine were obtained by using a Perkin Elmer Frontier IR spectrometer, equipped by DiffusIR® accessory from Pike Scientific. The samples (~10 mg) were pretreated at 500 °C for 30 min in N₂ flow at 50 ml/min to remove the physisorbed water and other impurities. Then, the catalyst sample was cooled to 125 °C and saturated with pyridine vapors for 10 min, followed by degassing in a vacuum (2 \Box 10⁻⁵ mbar) for 30 min. The IR spectra were recorded with 8 accumulations and spectral resolution of 4 nm between 800 and 4000 cm⁻¹. Thermogravimetric analysis data in the spent catalysts were collected on a TGA (DynTHERM, Germany) instrument from 40 to 700 °C with a heating rate of 10 °C/min in an air stream of flow rate 100 mL/min.

Catalytic activity performance

The catalytic activity tests for the gas-phase conversion of glycerol into ethanol were carried out in the Microactivity-Reference setup (PID Eng&Tech) using a stainless steel packed-bed reactor (9 mm internal diameter, 305 mm long) under atmospheric pressure. The catalyst sample (0.5 g, sieve fraction 250-400 μ m) was loaded between two layers of quartz wool and set up over a porous frit. The water solution of glycerol (10 wt%) was fed at room temperature by HPLC Piston Pump 307 to the hot box at 140 °C. The N₂ gas was used as a carrier gas and managed by a mass flow controller. The inlet gas mixture went through a six-port VICI reactor standard bypass valve and introduced into the reactor. The temperature of the packed-bed was measured with a thermocouple connected the TIC controller. After leaving the reactor tube, the outlet liquid sample was collected into the Peltier cell cooled vessel kept at 0 °C. Thereafter, the product mixture was moved to the condenser below the reactor.

The collected liquid products were analyzed using an Agilent GC-7890A gas chromatograph equipped with a flame ionization detector and a capillary column (DB-WAX Ultra Inert 30m \times 0.25mm \times 0.25µm). To obtain effective product separation, the column was held at 40 °C for 4 min, then temperature was increased to 200 °C at a rate of 12 °C/min and kept at this temperature for 10 min. Hydrogen was used as a carrier gas with a flow rate of 1 ml/min. Split mode with ratio of 1:150 was applied. For the quantification of reaction products in the obtained samples, an external calibration method with 6-point-level was used. The products were confirmed

 $SiO_2/Al_2O_3 = 30$ and 1500.

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by a gas chromatography-mass spectrometer (Shimadzu, GC/MS-QP2010) with the capillary column Zebron ZB-WAX-Plus (30m × 0.25mm × 0.5um). All samples were filtered through 0.25 μ m filter prior to injection. In addition, the gas phase was analyzed online by micro GC Fusion Inficon with Rt-Molsieve 5A, Rt-Q-BOND and Rt-U-BOND capillary columns. The small amount of CO₂ and H₂ were identified in the gas phase.

The conversion of glycerol, the product selectivity, and the product yield were calculated according to the following equations:

$$Glycerol conversion (mol\%) = \frac{moles of glycerol converted}{moles of glycerol fed} \times 100$$
 (1)

$$P \text{ roduct selectivity}(mol\%) = \frac{\text{moles of carbon in the product}}{\text{moles of carbon in glycerol converted}} \times 100$$
 (2)

Product yield (mol%) =
$$\frac{\text{moles of carbon in the product}}{\text{moles of glycerol fed}} \times 100$$
 (3)

The mass balance of liquid product mixture collected was always above 96%. The obtained results of conversion, selectivity, and yield were calculated based on the values of at least three experiments.

Results and discussion

Catalyst characterization

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Morphology, composition, and textural property of the HZSM-5 and CsZSM-5 catalysts

Fig. 1 shows the XRD patterns of the HZSM-5 and CsZSM-5 catalysts with SiO₂/Al₂O₃ molar ratio of 30 and 1500. The intensity of diffraction peaks assigned to MFI framework was changed and also the lattice parameters were modified after alkali-treatment. The peaks ascribed to CsNO3 are observed in Fig. 1(a, d) for the 20CsZSM-5(30) and 20CsZSM-5(1500) catalysts at around 2θ = 19.8, 28.2, 34.8, 40.4, 45.4, 50.0, 62.3, 66.3 and 69.9° (COD № 96-200-1972) 40. The peaks related to HZSM-5 framework are decreasing with the loading of CsNO₃ to HZSM-5. As shown on the XRD diffractograms this CsNO₃ addition has an impact on the framework of HZSM-5 which is also supported by SEM results below. In Fig. 1(c, d, f) the patterns represent distinct sharp diffraction peaks in 20 ranges of 7.5-9.5 and 22.5-25.2°, where all samples exhibit the typical diffraction peaks of HZSM-5 original structure ⁴¹⁻⁴³. The XRD patterns of the studied catalysts showed that the intensity of the Si diffraction peaks at 2θ = 7.9°, 8.8°, 23.0°, 23.3°, 23.7°, 23.9°, 24.4° have decreased after

Table 1 Surface	properties of the	zeolite catalyst
		Leonice caraijee



addition of CsNO₃ compared with parent zeolite catalysts with

Fig. 1. XRD patterns of the HZSM-5(30), 20CsZSM-5(30), and CsNO₃ – (a, b); HZSM-5(1500), 20CsZSM-5(1500), and CsNO₃ – (c, d). The reference lines on the 2 θ axis correspond to the materials present and were obtained from the COD database.

Catalyst	Csª (wt%)	S _{BET} b (m²/g)	S _{micro} b (m²/g)	S _{meso} b (m²/g)	V _{micro} c (cm³/g)	V _{total} c (cm³/g)	V _{meso} c (cm³/g)	PD ^d (nm)	HF ^e	Crystallite size ^f (nm)	Crystallinity ^f (%)
HZSM-5(30)	-	347.8	229.7	118.1	0.121	0.254	0.133	6.4	0.162	57.4	100
20CsZSM-5(30)	19.0	27.2	14.8	12.4	0.008	0.071	0.063	24.6	0.051	61.6	33.4
HZSM-5(1500)	-	321.6	282.1	39.5	0.148	0.179	0.031	3.9	0.102	91.5	100
20CsZSM-5(1500)	15.3	125.1	96.5	28.6	0.048	0.077	0.029	3.4	0.143	78.7	34.6

^aICP-AES. ^bBET method. ^ct-plot method. ^dAverage pore diameter measured from the desorption branch according to the BJH method. ^eHierarchy factor (HF) = $(S_{meso}/S_{BET}) \times (V_{micro}/V_{total})$. ⁱThe crystallite size and crystallinity were calculated from XRD data. Standard deviations of surface areas were measured to be between 0.5 and 1.5 m²/g, where the larger errors related to the catalyst samples with the highest surface areas measured.

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Table 1 shows the cesium loading, BET surface area, microporous surface area, external surface area, microporous volume, total pore volume, mesoporous volume, average pore diameters, hierarchy factor, and crystallite size.

Presented results show that the incorporation of Cs metal species to the parent HZSM-5(30) and HZSM-5(1500) zeolites decreased the BET surface areas, microporous and mesoporous surface areas, and pore volumes. Only the pore diameter was increased in the case of 20CsZSM-5(30) catalyst compared to the HZSM-5(30), namely from 6.4 to 24.6 nm. This observation can be explained by the higher dissolution of zeolite frameworks caused by interaction between alkali metal - zeolite support with lower SiO_2/Al_2O_3 ratio. In addition, the crystallite size, calculated from different individual reflections in XRD patterns by the Scherrer equation, exhibited a decrease from 91.5 to 78.7 nm for the CsZSM-5(1500) catalyst. According to the literature data, ⁴⁴ zeolites crystallite size decreasing can lead to improvement of catalytic activity and selectivity. At the same time, CsZSM-5(30) catalyst showed negligible trend of the crystallite size increase from 57.4 to 61.6 nm. The crystallinity of the CsZSM-5(30) and CsZSM-5(1500) catalysts was decreased from 100 to 33.4% and 34.6%, respectively. These results can be explained by desilication of ZSM-5 zeolite framework.



Fig. 2. N_2 -adsorption and desorption isotherms (a, b); BJH pore size distribution (c, d) of the catalyst samples.

It is known that the hierarchical zeolite shows higher HF value (>0.1) ^{45–47}. In the case with the conventional zeolite, the HF has value ≤ 0.1 . The HF values of the HZSM-5(30) and HZSM-5(1500) zeolites are 0.162 and 0.102, respectively. This indicates the possessing mesoporosity for both studied zeolite catalysts. When the HZSM-5(30) catalyst was impregnated by CsNO₃, the HF decreased to 0.051 which indicates the absence of mesopores. This result can be explained by the high Al content (or low SiO₂/Al₂O₃ ratio) in the HZSM-5(30) zeolite support, which can lead to reduced mesopore formation. At the same time, the 20CsZSM-5(1500) catalyst exhibited increase of the HF from 0.102 to 0.143, which is 2.8 times higher in comparison with the 20CsZSM-5(30) sample. This behaviour can be attributed to the low Al content (or high SiO₂/Al₂O₃ ratio) in the HZSM-5(1500) zeolite.

The SEM images in Fig. 3 provide a view on the morphologies and particles sizes of the parent and CsNO₃ impregnated zeolites. Fig. 3C and Fig. 3D show the particles size less than 50 nm for the HZSM-5(30) and 20CsZSM-5(30) catalysts, while HZSM-5(1500) and 20CsZSM-5(1500) samples exhibit the particles size in the range 1-2 μ m (Fig. 3A and Fig. 3B). As can be seen from the SEM images, all crystalline zeolites are agglomerated and consisted of cube nanocrystals. Also, it is evident from the microphotographs that the framework of zeolite support has suffered from alkali dissolution after CsNO₃ impregnation (Fig. 3B and Fig. 3D).

Fig. 4 shows the TEM images and elements mapping of the 20CsZSM-5(1500) catalyst. It is clear that Cs species are homogeneously distributed into the zeolite framework and most of these species are located inside of the zeolite crystals (Fig. 4B).



Fig. 3. HRSEM images of the A – HZSM-5(30), B – 20CsZSM-5(30), C – HZSM-5(1500), D – 20CsZSM-5(1500).

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Fig. 4. HRTEM image and elements mapping of the 20CsZSM-5(1500) zeolite catalyst – (A, B).

Acid-base properties of the HZSM-5 and CsZSM-5 catalysts

Fig. 5 shows the CO₂-TPD results of the parent HZSM-5 and alkalitreated zeolites. It was found that CsNO₃ impregnated zeolites have relatively high basicity. The small desorption peak at the temperature of 45 and 135 °C is present for the HZSM-5(30) and HZSM-5(1500) zeolites, respectively. These peaks indicate on the presence of surface basic sites that was due to the interaction between the framework of HZSM-5 and CO₂ ^{48,49}. It is known ³⁷ that zeolites can include acid and basic sites, where the latter can appear from the negative charge in the Si-O-Al species. Zeolites basicity depends on their chemical composition (on framework and nonframework atoms) and the structure type influences the oxygen basicity. ZSM-5 alkali-promoted zeolites showed basic properties due to a high charge on oxygen, which relates to Cs⁺ cation with the lowest electronegativity (0.79) and thus, weak acidity ³⁷.



Fig. 5. CO_2 -TPD profiles of HZSM-5(30); HZSM-5(1500); 20CsZSM-5(30); 20CsZSM-5(1500) catalysts.

Table 2 Acid-base properties of the HZSM-5 and CsZSM-5 zeolite sam	ıples
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Fig. 6 shows the NH₃-temperature-programmed description (NH₃-TPD) signals of the HZSM-5 and CsZSM-5¹zéoMe data ysts²-FAB acidic sites for the Cs promoted zeolite catalysts were not detected by NH₃-TPD analysis. The NH₃-TPD profile clearly indicates that when CsNO₃ was loaded onto the zeolite framework, the surface acidity decreased (or totally disappeared) but the surface basicity increased, which is also in agreement with previous reports ^{50–52}.

The 20CsZSM-5(30) and 20CsZSM-5(1500) samples exhibit three main desorption peaks with representing weak (45-55 °C), medium (350-450 °C) and strong (\approx 640 °C) basic sites. These data clearly indicate that the addition of CsNO₃ to HZSM-5 increase the intensity of the CO₂ desorption peak and improve the surface basicity, which is in good agreement with the literature ^{53,54}. The total basicity increased from 0.9 to 18.2 µmol_{CO2}/g_{catalyst} (Table 2) after CsNO₃ impregnation to HZSM-5(30) zeolite and from 1.1 to 17.3 µmol_{CO2}/g_{catalyst} when HZSM-5(1500) zeolite support was impregnated.



Desorption temperature, °C **Fig. 6.** NH₃-TPD signals of the HZSM-5(30), HZSM-5(1500), 20CsZSM-5(30) and 20CsZSM-5(1500) catalysts as a function of temperature.

At the same time, HZSM-5(30) catalyst exhibits usual desorption spectrum with two distinct desorption peaks of the NH₃-TPD profile containing a low-temperature peak at 200 °C related to weak acid sites and a high-temperature peak at 400 °C corresponding to strong acid sites ^{41,42}. It was shown that with the rising SiO₂/Al₂O₃ ratio of HZSM-5 zeolites from 30 to 1500, the acid sites almost completely disappeared. This shows that HZSM-5(1500) zeolite has a very weak acidic character. Only a small peak was detected at 150 °C, which is related to weak acid sites and also correlated with Pyr-DRIFT analysis below.

Total basicity by CO ₂ -TPD		Pyr-DRIFT							
Amount (μmol _{c02} /g _{catalyst})	Total acidity (mmol/g _{cat})	BAS (mmol/g _{cat})	LAS (mmol/g _{cat})	BAS/LAS ratio					
0.9	0.63	0.5	0.13	3.8					
1.1	0.09	0	0.09	0					
18.2	0.23	0	0.23	0					
17.3	0	0	0	/					
	Total basicity by CO ₂ -TPD Amount (μmol _{CO2} /g _{catalyst}) 0.9 1.1 18.2 17.3	Amount Total acidity (μmol _{co2} /g _{catalyst}) (mmol/g _{cat}) 0.9 0.63 1.1 0.09 18.2 0.23 17.3 0	Total basicity by CO2-TPD Pyr-Di Amount (μmol _{C02} /g _{catalyst}) Total acidity (mmol/g _{cat}) BAS (mmol/g _{cat}) 0.9 0.63 0.5 1.1 0.09 0 18.2 0.23 0 17.3 0 0	Total basicity by CO2-TPD Pyr-DRIFT Amount (μmol _{co2} /g _{catalyst}) Total acidity (mmol/g _{cat}) BAS (mmol/g _{cat}) LAS (mmol/g _{cat}) 0.9 0.63 0.5 0.13 1.1 0.09 0 0.09 18.2 0.23 0 0.23 17.3 0 0 0					

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On Fig. 7, the effect of 20 wt% Cs addition on the acidity of HZSM-5(30) and HZSM-5(1500) zeolites is studied by Pyr-DRIFT technique. Acidity in CsZSM-5(1500) is totally lost, whereas in the case of aluminum-rich CsZSM-5(30) the BAS are totally eliminated and LAS are increased approximately in 2 times: from 0.13 to 0.23 mmol/g. The LAS peak of 20CsZSM-5(30) shifts to lower frequencies, indicating weakening of its total acidity (0.23 mmol/g) compared to pristine HZSM-5(30) with 0.63 mmol/g. This increasing of LAS over the 20CsZSM-5(30) catalyst can be explained by the weak Lewis acidity of Cs⁺ in combination with alumina interaction. This increase of LAS was also observed in the literature ⁵⁵, when the loading of CsNO₃ was above 10 wt%.



Fig. 7. FTIR spectra of pyridine chemisorbed on parent HZSM-5(30) and HZSM-5(1500) zeolites before and after modification with Cs.

Bisio et al. ⁵⁶ speculated that some leaching of the related tricoordinated extraframework Al species occurs after Cs impregnation of H-BEA material which resulted in the appearance of LAS. Also the Cs-Al₂O₃ interaction was studied earlier ^{57,58} where strong chemisorption bonds formation between Cs and alumina surface was confirmed. The absence of LAS over the 20CsZSM-5(1500) catalyst can be attributed to the very low content of alumina in the HZSM-5(1500) zeolite support.

Catalytic activity performance

Fig. 8 shows the example of ethanol, glycidol, allyl alcohol, hydroxyacetone, acrolein, acetaldehyde formation. These liquid products covered 100% of the total mass of product mixture. Fig. 9 shows the performance of glycerol conversion reaction over the 20CsZSM-5(30) catalyst with TOS = 52 h and GHSV_{total} = 625 h⁻¹. The results showed that over the 20CsZSM-5(30) catalyst the main product was hydroxyacetone with the highest achieved selectivity during time on stream of 55%. The glycerol conversion decreased from 38.7% after the first hour to 11.5% after 30 hours of time on stream and did not decrease further. Although there was a significant

drop in conversion during the reaction, the selectivity to hydroxyacetone increased from approximately 25% in the first few hours to 55% when conversion of glycerol stabilized, i.e. after 30 hours. This could be due to coking of the catalyst during time on stream and blockage of the pores ⁵⁹. Once the majority of pores are blocked, no significant deactivation is observed. Apparently, coke deposition has also a beneficial effect on hydroxyacetone selectivity. Again, the pore blockage could be the reason. If the reaction proceeds only on the outer surface of the zeolite (which is the case when all the pores are blocked) selectivity is shifted towards hydroxyacetone. Initially, glycerol conversion can occur also inside of the zeolite crystals, where shape selectivity of the zeolite and proximity of active sites and longer diffusion path lead a major role in the reaction.



Fig. 8. GC-FID traces for a typical run over the 20CsZSM-5(1500) catalyst. Rxn conditions: catalyst, 0.5 g, 250-400 μ m; TOS = 4 h; T_{reactor} = 350 °C; C(GL) = 10 wt%; FR(GL) = 1.0 ml/h; GHSV_{total} = 625 h⁻¹.



Fig. 9. Time course of products selectivity and glycerol (GL) conversion over 20CsZSM-5(30) catalyst.

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Fig. 10 shows the 20CsZSM-5(1500) catalyst evaluation under the same reaction conditions as the 20CsZSM-5(30) catalyst sample. Here the main reaction product was ethanol with 91.9% selectivity after TOS = 52 h. The reaction was repeated 3 times and the results were reproducible. The highest yield achieved was 99.6% after TOS = 2 h. The glycerol conversion decreased from 99.8% to 39.7% during the reaction period, which indicates that 20CsZSM-5(1500) catalyst is more coke resistant in comparison to the 20CsZSM-5(30) catalyst where conversion dropped to 11.5% at the same reaction conditions. This statement is also supported by TGA study. A tremendous difference between the two prepared catalysts shows just how important the support is in this reaction. Apparently, the HZSM-5(1500) support shifts the selectivity toward a totally different main product. Therefore, there must also be a difference in active sites in both catalysts. The most obvious difference between the two catalysts is a complete absence of BAS and LAS in the 20CsZSM-5(1500), whereas LAS were present in the 20CsZSM-5(30). Therefore, those acid sites could be the reason for completely different selectivity of the 20CsZSM-5(30). Besides the effect on the reaction, acid sites could also be responsible for more pronounced coking over 20CsZSM-5(30) than over 20CsZSM-5(1500) catalyst since it is known that BAS promote coking of the catalysts in many reactions ^{60,61}.



Fig. 10. Time course of products selectivity and glycerol (GL) conversion over 20CsZSM-5(1500) catalyst.

Thermogravimetric analysis (TGA)

Thermal analyses were performed on the catalysts after catalytic tests. Temperature ramp was set up to 650 °C. TGA was used to determine the amount of coke deposited on the catalyst samples after catalytic tests for 27 h under the same experimental conditions. The initial weight loss of the samples was observed in the temperature range of 50 to 250 °C (Fig. 11). This weight decrease can be related to the evaporation of physisorbed, chemisorbed water and volatile species ^{62,63}. The major losses of weight were observed above 255-280 °C for both samples due to the presence of coke.

It was shown (Fig. 11) that the highest coke formation was 14.7 wt% over 20CsZSM-5(30) catalyst, which can be related to the lower SiO_2/Al_2O_3 ratio and the acid sites presence ⁶⁴. The 20CsZSM-5(1500) catalyst showed a high coke resistance with the mass loss of 3.9 wt% in comparison to the 20CsZSM-5(30) sample. This observation can be explained by the high SiO_2/Al_2O_3 ratio of zeolite support and a complete disappearance of acid sites.



Fig. 11. TGA profiles for the 20CsZSM-5(30) and 20CsZSM-5(1500) fresh and spent (TOS = 27 h) catalyst samples.

We have found (Fig. 11) that TGA profiles of the 20CsZSM-5(30) and 20CsZSM-5(1500) fresh catalysts exhibited much lower weight decrease due to the absence of coke deposition. At the same time, it was observed on TGA profiles the decreasing trend of mass sample with increasing of temperature-programmed heating mode. These TGA results can be explained by the loosing of water molecules at a low temperature. At the higher temperature the catalyst weight decreasing is attributed to partial decomposition of CsNO₃, which is happens in the temperature range 400-750 °C ⁴⁰.

We have recovered based on the literature data ⁶⁵ our spent catalysts in the air at 550 °C for six hours. After the regeneration step, the CsZSM-5(30) and CsZSM-5(1500) (spent and fresh) catalysts were characterized by XRD analysis. The XRD patterns showed (Fig. 12) differences which related to CsNO₃ phase at $2\theta = 19.8$, 28.2, 34.8, 40.4, 45.4, 50.0, 62.3, 66.3 and 69.9°. We suppose based on the literature data ^{40,66,67} that CsNO₃ was decomposed during the regeneration procedure at 550 °C. It is known ^{40,66} that the melting temperature of CsNO₃ is in the range of 404-411 °C, but decomposition temperature can occur between 400 and 750 °C, where NO₂ and N₂O are decomposition products. Moreover, it was found ⁶⁷ that degree of CsNO₃ decomposition increased with increasing the number of calcinations.

At the same time, it was observed (Fig. 12b and 12d) that there is no difference between fresh and spent catalyst samples for the characteristic peaks (in 20 ranges of 22.5-25.2°) in MFI zeolite framework, which indicated that the crystalline phase of zeolite support remained unchanged. Thus, we can conclude that the catalytic activity of the studied catalysts can be changed after the regeneration procedure due to CsNO₃ decomposition.



Fig. 12. XRD patterns of the fresh and regenerated 20CsZSM-5(30) and 20CsZSM-5(1500) catalysts.

The 20CsZSM-5(1500) catalyst showed superior results in comparison to the literature data at the same time-on-stream (Table 3). The maximum ethanol yield achieved in this study was 99.6%.

On Scheme 4 the reaction pathways of ethanol formation from glycerol over 20CsZSM-5(1500) catalyst are proposed/file scheme includes 3 different ways: (1) direct glycerol conversion to ethanol via the thermal dehydration and radical fragmentation reactions to acetyl and hydroxymethyl radicals followed by both reduction into ethanol and methanol, respectively, where the latter is directly converted to ethanol through methylation by methyl carbene intermediates; (2) hydrogenation of acetaldehyde which was obtained from hydroxyacetone after glycerol dehydration; (3) decomposition of glycidol after glycerol dehydration. The first pathway is dominant when 20CsZSM-5(1500) catalyst is used. It was shown (Scheme 4) that glycerol conversion includes consecutive and/or parallel dehydration, transfer hydrogenation, radical fragmentation, and methylation reactions with the participation of basic sites.

Based on the Hutchings group study ⁶⁸, which used detailed isotopic labeling experiments to investigate the new chemistry of glycerol transformation into methanol, we propose our own reaction mechanism for ethanol production. For this reaction, the authors ⁶⁸ utilized 0.5 g basic or redox oxide catalysts (MgO, CaO, MgO/CaO mixture, CeO₂) with 10 wt% glycerol solution at 227-327 °C. 100% glycerol conversion and 60% methanol selectivity over CeO₂ catalyst was achieved, where ethanol was one of the main byproducts.

We suggest that in our study the thermal dehydration and radical fragmentation reactions are also dominant for glycerol transformation into ethanol. These reactions are carried out in a reductive atmosphere due to the presence of steam (hydrogen source) at our reaction conditions. We suppose that for the formation of ethanol the C-C bond cleavage and hydrogen source are required.

According to Bühler ⁶⁹ et al. the free radical degradation mechanism of glycerol into ethanol and/or allyl alcohol is favored when the pressure decrease from 45 to 25 MPa in the temperature range of 349-475 °C. This reaction temperature range is correlated with our experimental conditions but the high pressure existence has a significant difference. Similarly, Sumari et al. ^{35,36} proposed the pathway of ethanol production through the free radical mechanism at high temperature over activated Cu/mordenite and Ag/Y catalyst under atmospheric pressure.

A relative low amount of acrolein was obtained through double dehydration of glycerol over basic catalyst at high temperature, which is correlated with the literature data ⁶⁸.

Also based on the literature data ⁷⁰ we speculate that low amount of allyl alcohol was obtained directly from glycerol through the dehydration and transfer hydrogenation mechanism. Indeed, according to G. Sánchez et al. ⁷⁰ the formation of allyl alcohol can occur from glycerol dehydration to form intermediate and subsequent reduction of the latter. The authors utilized the following reaction conditions: atmospheric pressure; temperature: 340 °C; reactant: 35 wt% glycerol aqueous solution; GHSV = 1190 h⁻¹; catalysts: y-alumina/Fe, y-alumina/Fe/Li, y-alumina/Fe/Na, alumina/Fe/K, y-alumina/Fe/Cs and y-alumina/Fe/Rb. The direct synthesis of allyl alcohol from glycerol in the gas-phase packed-bed reactor was carried out by our group recently.

Acetaldehyde traces can be obtained from glycerol through the retro-aldol reaction (reverse aldol mechanism) from intermediate product such as 3-hydroxypropanal and forms additional

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formaldehyde molecule. This hypothesis is correlated with literature data ^{71–74}, but formaldehyde was not detected in our product mixture. This can be explained by the high instability of formaldehyde ⁷² which can be easyly hydrogenated into methanol ³². At the same time, acetaldehyde can be synthesized directly from hydroxyacetone which is observed in the additional experiment below. Subsequent reduction of acetaldehyde to ethanol is not favorable reaction since high mass balance of the liquid product mixture was obtained and low concentration of gas products was detected in the reactor outlet.

One-step synthesis of glycidol *via* glycerol dehydration in a gasphase packed-bed continuous flow reactor was studied by our group recently. The reaction pathway (Scheme 4) to obtain ethanol from glycidol has low possibility due to the high mass balance and low amount of gaseous products and the absence of CO. Mahapatra et al. ⁷⁵ showed, using temperature-programmed desorption and reflection-absorption infrared spectroscopy, that glycidol can decompose on Pd(111) surface in two ways. The first way proceeds through the one C-O bond cleavage of the epoxide ring, which leads to the formation of a ketone or an aldehyde. The second way results in glycidol decomposition into ethanol, CO and H₂ after second $G_{\rm eff}Q$ bonds cleave in the epoxide ring. Based on the literature data we can assume that glycidol can be decomposed into ethanol but in our reaction conditions the favoured route of ethanol formation is the direct glycerol conversion *via* the thermal dehydration, radical fragmentation, methylation and transfer hydrogenation reactions as shown on Scheme 4.

Thus, the main reaction pathway is carried out by monodehydration of glycerol into enol, which undergoes enol-keto tautomerization into hydroxyacetone. The next step includes a radical fragmentation of hydroxyacetone through a Norrish type-1 process with acetyl and hydroxymethyl radicals. Then, one part of ethanol is produced after the reduction of acetyl radical. At the same time, another part of ethanol is obtained when hydroxymethyl radical reduced to methanol, which may then be transformed into ethanol. We suppose that this transformation was carried out *via* the methylation of methanol by methyl carbene intermediates, which is generated after dehydration of methanol. Hydroxyacetone, allyl alcohol, glycidol, acetaldehyde and acrolein were detected as byproducts when using 20CsZSM-5(1500) catalyst.



Scheme 4 Proposed reaction pathways from glycerol into ethanol.

Catalyst	Ethanol yield (mol%)	TOS (h)	FR _{GL} (ml/h)	T _{reaction} (°C)	C _{GL} (wt%)	m _{cat} (g)	Pressure (MPa)	External H-source	Year	Ref.
Ni _{2.4} /Mg _{3.7} Cr _{2.0} O _{6.7}	63.0	2	1.2	250	40	0.25	2.0	H ₂	2018	26
Co/ZnO-ZIF	57.2	2	1.2	210	40	0.10	2.0	H ₂	2018	27
20CsZSM-5(1500)	99.6	2	1.0	350	10	0.5	Atmospheric	No need	2019	This study

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To further investigate our hypothesis, we tested separately diluted methanol (J.T. Baker, 99.8%) (10 wt%) and hydroxyacetone (Alfa Aesar, 95%) at the same reaction conditions as when glycerol was utilized as a feed. It was found that in the case of methanol as a reactant the main and only one liquid product was ethanol (Fig. 13). At the same time, the conversion of methanol was quite low. The mass balance was always within 90 wt% even after 24 h. The detected gaseous products were low amount of CO_2 and H_2 . This data support our proposed hypothesis that methanol is intermediate on the way of ethanol production. Very recently Liu et al. ⁷⁶ carried out the direct catalytic methanol-to-ethanol photo-conversion *via* methyl carbine over GaN semiconductor. We assume that methanol transformation in our study exhibits a similar route *via* the methylation of methanol by methyl carbene intermediates, which were generated after dehydration of methanol.

When hydroxyacetone was used as a reactant many different reaction products were detected due to the fact that the reactant is very active feed. It was found that acetaldehyde is the main liquid product, which also confirms our proposed reaction pathway (Scheme 4). The mass balance was above 80 wt%. The detected gas products were only CO_2 and low amount of H_2 .



Fig. 13. GC-MS traces for a typical run over the 20CsZSM-5(1500) catalyst. Rxn conditions: catalyst, 0.5 g, 250-400 μ m; TOS = 20 h; T_{reactor} = 350 °C; C(MeOH) = 10 wt%; GHSV_{total} = 625 h⁻¹.

Conclusions

Two cesium metal-promoted ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios were prepared by incipient wetness impregnation method and studied in a packed-bed reactor. The results revealed that the 20wt%CsZSM-5(1500) is the most effective and promising catalyst for the gas-phase transformation of glycerol into ethanol. This catalyst showed a promising 91.9 mol% selectivity to ethanol after 52 h time-on-stream. To the best of our knowledge, this is the highest selectivity and stability reported for ethanol formation from

glycerol in the gas-phase packed-bed continuous-flow reactor until today. It was found that the significantly increased ethanol yield over the 20wt%CsZSM-5(1500) catalyst was achieved due to the presence of a suitable amount of basic sites, smaller crystallite size, absence of acid sites, and the strong synergetic interaction between CsNO₃ and HZSM-5 support. We speculate that water and/or glycerol was acting as a source of the hydrogen required for ethanol formation. Direct catalytic glycerol conversion to ethanol via the thermal monodehydration, radical transfer fragmentation and hydrogenation reactions was proposed, where the reaction pathway from methanol occurred through its methylation by methyl carbene intermediates, which were generated after methanol dehydration.

The reaction optimization and investigation of silicalite as a potential catalyst support and the loading amount and type of alkali metal need to be addressed in the near future for the most effective production of ethanol from glycerol in the gas-phase.

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Conflicts of interest

The authors declare no conflicts of interest.

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