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Solvent-free ketalization of polyols over germanosilicate zeolites: the role of the nature and strength of acid sites

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Isomorphic substitution of silicon for germanium affords germanosilicate zeolites with weak acid centers capable of catalyzing key reactions such as Baeyer–Villiger oxidation of ketones and etherification of levulinic acid. Herein, we show for the first time that UTL (Si/Ge = 4.2) and IWW (Si/Ge = 7.2) germanosilicate zeolites are active and selective catalysts of polyol (e.g., ethylene glycol, glycerol and 1,4 butanediol) ketalization to dioxolanes. Large-pore IWW outperformed the extra-large-pore UTL zeolite in the ketalization of polyols, thus indicating diffusion limitations in bulky platelet-like UTL crystals. FTIR spectroscopy of adsorbed pyridine revealed the Lewis acidity of the UTL zeolite, whereas the more active IWW catalyst was characterized by water-induced Brønsted acidity. Increasing the activation temperature (200 – 450 °C) reduced the concentration of Brønsted acid centers in IWW germanosilicate (i.e., 0.16; 0.07 and 0.05 mmol/g for T_{act} = 200, 300 and 450°C, respectively) but increased the number of Lewis acid sites in both zeolites. Under optimized reaction conditions (e.g., acetone/glycerol = 25, T_{act} = 300 °C), almost total transformation of glycerol to solketal was achieved within 3 h of reaction time over the IWW zeolite at room temperature (>99% yield of target product). The results from the present study clearly show that weak acid centers of germanosilicate zeolites can serve as active sites in ketalization reactions.

Introduction

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Large- and especially extra-large-pore zeolites had been highly targeted but rarely obtained as synthesis products until researchers recognized the structure-directing ability of germanium towards the formation of frameworks with small d4r and d3r units.^{1,2} Following this strategy, new lowframework density structures such as $\text{BEC},^3$ $\text{IWS},^4$ -ITV^5 and UTL^{6,7}, among others, were successfully synthesized. However, germanosilicates have two significant limitations: the high cost of Ge and their low hydrothermal stability. ^{2,8,9} Nevertheless, the high lability of Si-O-Ge and Ge-O-Ge linkages in acid/neutral aqueous medium and the preferential location of Ge atoms in d4r units of UTL,^{10,11, 12} UOV,^{13,14} IWW^{15,16} and *CTH¹⁷ have been recently exploited for controllable framework disassembly, thereby enabling the top-down synthesis of 2D precursors of new 3D zeolites.¹ Moreover, the post-synthesis substitution of Ge by other three- 18,19 or tetravalent elements ^{20-23} combined with recovery and recycling of leached germanium²⁴ generates acid sites of

variable strength while enhancing the hydrolytic stability and reducing the cost of such zeolites. Thus, for Ge-poor zeolites (Si/Ge > 20), instability is no longer a critical issue.

Despite recent achievements in the design of germanosilicate zeolites, these prospective materials have only been used as catalysts in a limited number of applications. Among these materials, germanosilicate zeolites with UTL, IWW and EWO structures were found to catalyze the Baeyer-Villiger oxidation of 2-adamantanone,²² esterification of levulinic acid,²⁵ and hydration of ethylene oxide to ethylene glycol.²⁶ Notwithstanding these recent advances highlighting the catalytic activity of germanosilicate zeolites, our knowledge of the nature of active sites in these catalysts remains limited. In addition, the scarce information on the acidity of specific germanosilicate zeolites is controversial. For example, Kasian et al detected both Brønsted and Lewis acid sites in UTL zeolite,27 whereas other studies based FTIR on characterizations suggested only the presence of Lewis acidity.28,7

Glycerol acetalization with aldehydes and ketones is especially important for using overproduced biodiesel glycerol to synthesize cyclic acetals and ketals²⁹⁻³¹ being prospective fuel additives.³² Glycerol ketalization with acetone is generally performed in the presence of a Brønsted or Lewis acid catalyst (Scheme 1), yielding two products: the target 2,2-dimethyl-4hydroxy-methyl-1,3-dioxolane (solketal) and 2,2-di-methyl-1,3dioxan-5-ol.

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^c *E-mail: vasile.parvulescu@chimie.unibuc.ro #jiri.cejka@natur.cuni.cz Electronic Supplementary Information (ESI) available: S1: 1H and 13C NMR spectra of reaction product (Figure 8); S2: FTIR spectra of IWW zeolite subjected to doseby-dose adsorption of water, followed by saturation with pyridine; S3: Variation of conversion with molecule size. See DOI: 10.1039/x0xx00000x



Scheme 1: Glycerol ketalization with acetone.

Solketal is used as 1) an additive to improve oxidation stability, and the octane number of liquid fuels, 2) a versatile solvent and a plasticizer in the polymer industry and 3) a solubilizing and suspending agent in pharmaceutical preparations, as recently reported.³² To date, different types of solid acids with strong acid sites such as aluminosilicate zeolites,³³ heteropolyacids³⁴⁻³⁶ and MOFs³⁷ have proved their ability to catalyze the acetalization of aldehydes and ketones.

The state of the art described above thus encouraged us to further investigate the catalytic performance of weakly acidic germanosilicate zeolites, including **IWW** and **UTL**. The surprisingly high catalytic activity of both germanosilicates in the liquid-phase ketalization of glycerol under solvent-free conditions prompted us to perform this detailed investigation of the zeolite structure and acidity effect on the reaction outcome. For this purpose, here we address the catalytic performances of **IWW** and **UTL** germanosilicates and of the commercial large-pore aluminosilicate zeolites beta (**BEA**) and mordenite (**MOR**) in the ketalization of different polyols in relation to the structural and acidic properties of the catalysts by XRD, N₂ ad-/desorption, SEM, and FTIR spectroscopy of adsorbed pyridine.

Experimental

Synthesis of zeolites

Structure-directing agents (SDA)

1,5-bis-(methylpyrrolidinium) pentane dihydroxide $(MPP(OH)_2)$ and (6R,10S)-6,10-dimethyl-5-azoniaspiro decane hydroxide (DMAD(OH)) were prepared according to Ref.^{38,39} *Hydrothermal synthesis*

The **IWW** zeolite sample was synthesized using MPP(OH)₂ as the SDA according to Corma et al.³⁸ The gel with a composition of 0.80 SiO₂:0.20 GeO₂ : 0.25 MPP(OH)₂:15 H₂O was transferred into a Teflon-lined autoclave and heated to 175 °C for 7 days.

The **UTL** zeolite was synthesized according to ref.⁴⁰ A gel with a composition of 0.67 SiO₂:0.33 GeO₂:0.25DMAD(OH):30 H₂O was heated to 175 °C for 7 days under agitation (60 rpm). The solid products were then recovered by filtration, washed out with deionized water, and dried overnight at 70 °C. Finally, the **IWW** and **UTL** zeolites were calcined in the air flow at 580 and 550 °C, respectively. The calcination time was 6 h, whereas the temperature ramp was 1 °C·min⁻¹.

Characterization

The phase purity of the zeolites was examined by X-ray powder diffraction (XRD) using a Bruker AXS-D8 Advance diffractometer with a graphite monochromator and a position-sensitive detector (Våntec-1) using CuK α radiation (λ = 1.5418 Å, 40 kV, 40 mA) in Bragg-Brentano geometry at a scan rate of 0.25° 20 min⁻¹ in the 3 - 40° 20 range. Samples were grinded

gently and carefully packed into the holder_{vib}efore_Othe DOI: 10.1039/D0CY01662D

The size and morphology of the zeolite crystals were examined by scanning electron microscopy (SEM, JEOL JSM-5500LV microscope). For these measurements, the crystals were coated with a thin layer of platinum (~ 10 nm) in a BAL-TEC SCD-050 instrument.

The chemical compositions of the zeolite samples were determined by ICP/OES (ThermoScientific iCAP 7000) analysis. In total, 50 mg of zeolite were mineralized in a mixture of 2 ml of HF, 4 ml of HNO₃, and 4 ml of HCl in a microwave oven. After cooling, the excess of HF was eliminated by complexation with 15 ml of a saturated solution of H₃BO₃, treating the final mixture in a microwave oven. Then, the solutions under analysis were collected and diluted in ultrapure water to a total volume of 250 ml. The leached species in the liquid phases was checked by ICP-OES (Agilent Technologies, Santa Clara, CA, USA, 700 Series) after calibrating the instrument with standard solutions.

Nitrogen adsorption/desorption isotherms were measured on an ASAP 2020 (Micromeritics) static volumetric apparatus at -196 °C. Before the sorption measurements, all samples were degassed with a turbo molecular pump at 300 °C for 8 h. The t-plot method⁴¹ was applied to determine the volume of micropores (V_{micro}).

The nature and strength of acid sites in germanosilicate zeolites were determined by FTIR spectroscopy of adsorbed pyridine (FTIR-Py). For this purpose, the zeolites were pressed into self-supporting wafers to a density of ~10 mg/cm² and in situ activated at T = 200, 300 or 450 °C and p = $5 \cdot 10^{-5}$ Torr for 4 h. In particular experiments, water calibrated aliquots were gradually introduced into the cell at 25°C, followed by pyridine adsorption. An excess of pyridine (Py) was adsorbed at 25°C for 20 minutes, followed by 20-minute desorption at the same temperature. Thermodesorption of Py was performed at 25, 50, 75, 100, 120 and 150 °C for germanosilicate and at 150, 250, 350, 450 °C for aluminosilicate zeolites for 20 min. FTIR spectra were recorded using a Nicolet iS50 spectrometer with a transmission MTC/B detector with a resolution of 4 cm⁻¹ by collecting 128 scans for a single spectrum at room temperature. The spectra were treated using Omnic 8.2 (Thermo Scientific) program. For baseline correction, the spectrum of activated wafer was subtracted from the spectra collected after Py adsorption/desorption. The concentrations of Brønsted acid sites in germanosilicate and reference aluminosilicate zeolites were evaluated from the integral intensity of the band at 1545 cm⁻¹ using the absorption coefficient ϵ =1.7 cm/µmol.⁴² The concentrations of Lewis acid sites in aluminosilicate zeolites were evaluated from the integral intensities of the bands at 1454 cm⁻¹ using absorption coefficient $\epsilon(L) = 2.2 \text{ cm}/\mu \text{mol}$,⁴² whereas the number of Lewis acid sites in germanosilicates was estimated based on the integral intensity of the band at 1611 cm⁻¹. To determine the area of the peak characteristic for coordinatively bonded (1611 cm⁻¹) and H-bonded (1596 cm⁻¹) Py, the resulting spectral curve was fitted using the Gaussian line shape. IR peak centers

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were fixed within ± 5 cm⁻¹, and the full widths at half maxima were constrained between 5 cm⁻¹ and 20 cm⁻¹.

The differential thermal and thermogravimetric analysis of neat and spent catalyst was carried out using a TG-DTA analyser (Shimadzu Apparatus) on 4–6 mg samples in nitrogen flow of 10 ml min⁻¹, under the heating rate of 10°C/min from room temperature to 600°C, using Al crucible and alumina as reference.

Catalytic tests

Before the catalytic tests, the germanosilicate zeolites were activated by heating to different temperatures (200, 300, 450 °C) with a rate of 10 °C/min and maintaining the selected temperature for 2 hours. Typically, 5mg of catalyst, 1mmol of glycerol, ethylene glycol or 1,4-butanediol were mixed with an excess of ketone (5 or 25 mmol). The catalytic tests were performed in glass vials with magnetic stirring at room temperature or 80 °C for 3 hours. After the reaction time elapsed, the reaction mixture was cooled, and a small amount of ethanol (up to total volume of 1ml) was added to solubilize the untransformed glycerol that usually formed a separate phase. The mixture was then centrifuged, filtered and dried over sodium sulphate. In total, 200 μ l of final solution were slowly evaporated at 45 °C overnight to remove the solvent. For recycle studies, after each catalytic cycle, the catalyst was immediately centrifuged, washed several times with ethanol and acetone, dried at 40 °C and subjected to another catalytic run, thus avoiding a longer contact with the moisture. To identify possible leaching of active species, the reaction mixture was removed after the 1-hour catalytic test, filtered off, and the separated liquid was investigated under the same reaction conditions for another 2 or 12 hours.

Silvlation of reaction products before the injection into chromatographic column was required to increase their volatility and to derivatize the free hydroxyls of polyols. For this purpose, 150 µL of derivatization agent (1 % w/w of trimethylchlorosilane in N.O-Bis(trimethylsilyl)trifluoroacetamide) was mixed with 50 μL of pyridine as catalyst. The derivatization occurred at 60 ºC for 30min. The derivatization agent-to-substrate molar ratio was 3:1. The final products were analyzed using a GC-MS (THERMO Electron Corporation, ISQ LT Single Quadrupole GC-MS system TRACE 1310, equipped with TG-5SilMS column 30m×0.25mm×0.25µm) and NMR spectroscopy (Bruker Advance III UltraShield 500 MHz spectrometer, operating at 500.13 MHz for ¹H NMR, 125.77 MHz for ¹³C NMR). For GC analysis, the injector was set up at 250 °C. The temperature in the oven was kept at 50 °C for 1 min and then increased to 250 ^oC at a rate of 7 ^oC min⁻¹.

Reference commercial aluminosilicate zeolites were used for comparison with **UTL** and **IWW** germanosilicate catalysts. Commercial **BEA** zeolites with different Si/Al included BEA-12.5 (Si/Al = 12.5, CP814E, purchased by Zeolyst), BEA-25 (Si/Al = 25, CP814Q, Zeolyst), BEA-75 (Si/Al = 75, CZB-150 from Clariant). The commercial **MOR** zeolite was MOR-10 (Si/Al = 10, CBV-20A, Zeolyst).

Results and discussion

Physico-chemical properties of germanosilieate 20011100CY01662D

XRD patterns of both germanosilicate zeolites (Figure 1A) correspond to those reported in the literature^{6,7}, confirming their phase purity. Both **IWW** and **UTL** samples showed type I isotherms characteristic of microporous materials (Figure 1B). The micropore volume of the medium-pore **IWW** was lower than that of the extra-large pore **UTL** zeolite (0.11 versus 0.21 cm³·g⁻¹, Table 2).



Figure 1: XRD patterns (A) and nitrogen ad-/desorption isotherms (B) of IWW (-) and UTL (-) zeolites.

Table 1: Chemical composition and crystal sizes of germanosilicate zeolites.

	Sample	C	Crystal size,			
		mol.	%	mmol ⁻ g ⁻¹	Si/G	μm
		Si	Ge	Ge	е	
	IWW	87.8	12.2	1.9	7.2	0.5×0.5×0.5
	UTL	80.8	19.2	2.8	4.2	30×25×1

Figure 2 depicts the SEM images of **IWW** (A) and **UTL** (B) zeolites illustrating important differences between the two samples. **IWW** possesses homogeneous $0.5 \times 0.5 \times 0.5 \mu$ m-sized rectangular crystals, whereas **UTL** zeolite shows quite uniform thin rectangular 30×25×1 µm-sized crystals (Table 1).

In line with previously reported results, the FTIR spectra of both **IWW** and **UTL** zeolites (Figure 3 A) display characteristic bands of silanol (3740 cm⁻¹) and germanol (3660-3680 cm⁻¹) groups.^{28,43-45} The remarkably more intensive band at ca. 3740 cm⁻¹ in the spectrum of **IWW** sample is consistent with its smaller crystal size/higher external surface (Table 1, 2) bearing terminal silanol groups. A weak and broad band apparent at 3600–3400 cm⁻¹ in the spectra of zeolites activated at 200 and 300 °C is indicative of hydrogen-bonded OH groups attributed to adsorbed water.

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Figure 2: SEM images of IWW (A) and UTL (B) zeolites.

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The adsorption of pyridine on both **IWW** and **UTL** zeolites gave rise to absorption bands (a.b.) characteristic of: 1) pyridine coordinatively bonded to Ge Lewis acid sites, **LAS-Py**, at υ_{8a} = 1611 and υ_{19b} = 1452 cm⁻¹; 2) H-bonded pyridine, H-**Py**, at υ_{8a} =1596 and υ_{19b} =1443 cm⁻¹ and 3) physically adsorbed pyridine, **phys-Py**, at υ_{8b} =1577 and υ_{19b} =1438 cm⁻¹ (Figure 3B).^{46,47}



Figure 3: FTIR spectra of UTL and IWW zeolites after (A) activation at T_{act} = 200 (–), 300 (–), 450°C (–) and (B) ad-/desorption of Py at T = 25 °C. Region of OH- (A) and Py-ring (B) vibrations.

In agreement with Ref. 46, the υ_{19b} absorption bands of H-Py and LAS-Py overlapped, while respective υ_{8a} bands were well-resolved and thus used here for semi-quantitative estimation of Ge Lewis acid centers. Nevertheless, determination of the molar absorption coefficient for u_{8a} band and hence quantification of LAS in both IWW and UTL was precluded by unavoidable contribution of H-Py. The markedly higher intensity of the u_{8a} -LAS band in **UTL** vs. **IWW** (Figure 3B) suggested an enhanced number of Lewis acid sites in the former. Although Ref. 27 reported Brønsted acidity was characteristic of UTL germanosilicate, no sign of Brønsted acid centers was detected in the UTL zeolite activated at different temperatures (Figure 3B). In contrast to UTL, the FTIR-Py spectra of IWW germanosilicate indicated the presence of the Brønsted acid centers (a.b. of **BAS-Py** at v_{19b} = 1545 cm⁻¹ and u_{8a} = 1637 cm⁻¹). The evolution of the band at ca. 1545 cm⁻¹ with the temperature of pyridine desorption (Figure 4B) revealed that the Brønsted acid sites of IWW germanosilicate





Figure 4: Number of Brønsted acid sites in IWW zeolite vs. T_{act} (A) and of Lewis acid sites in UTL (B) and IWW (C) zeolite vs. T_{act} as determined from the desorption of pyridine at different temperatures. x% values correspond to the fraction of acid sites keeping adsorbed pyridine after desorption at 100 °C (A) or 150 °C (B).

The concentration of Brønsted acid sites in **IWW** zeolite evaluated from the integral intensity of the band at 1545 cm⁻¹ (Figure 3B) decreases with the increase in activation temperature: 0.16 mmol/g (T_{act} = 200°C), 0.07 mmol/g (300°C) 0.05 mmol/g (450°C). The weakness of Ge-associated Brønsted acid sites and the variation of their concentration as a function of the activation conditions may be related to the waterinduced nature of such acid centers. To validate this assumption, **IWW** zeolite activated at T=450°C was subjected to dose-by-dose adsorption of water, followed by saturation with pyridine monitored using FTIR spectroscopy. The gradual adsorption of water resulted in progressive diminishing a.b. of **LAS-Py** at υ_{8a} = 1611 cm⁻¹ with simultaneously growing intensity of **BAS-Py** a.b. at υ_{19b} = 1545 cm⁻¹ (Figure S2).

Similarly, the water-induced formation of Brønsted acid sites in Sn-BEA and their reactivity was recently reported.⁴⁷

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Decreasing a.b. of LAS-Py in the spectra of IWW zeolite with decreasing activation temperature/increasing water loading accompanying by the increase in the intensity of the absorption band of BAS-Py (Figure 3B, S2) may suggest a similar mechanism of Lewis-to-Brønsted acid site conversion for Sn- and Ge-containing zeolites: adsorption of water on tetrahedrally coordinated Ge atoms (Lewis acid centers, ≡Si-O-Ge(OSi)₃) followed by formation of bridging OH groups centers, \equiv Si-(OH)-Ge(SiO)₃(OH)(H₂O)). (Brønsted acid Conversely, the increase in activation temperature positively affected the number of Lewis acid sites in the UTL germanosilicate (~3 times higher integral intensity of u_{8a} = 1611 cm⁻¹ for zeolite activated at 450 vs. 200 ^oC, Figure 4B).

 Table 2:
 Chemical composition, textural and acidic properties reference aluminosilicate zeolites.

Sample	Si/Al	Concentration of acid sites, mmol/g			V _{micro} ,	S _{ext} , m ^{2·} g ⁻¹
		В	L	Σ	cm ³ ·g ¹	
BEA-12.5	12.5	0.31	0.32	0.63	0.16	220
BEA-25	25	0.33	0.19	0.52	0.25	210
BEA-75	75	0.05	0.07	0.12	0.20	220
MOR-10	10	0.56	0.35	0.91	0.14	70
IWW	-	0.16ª 0.07 ^b 0.05 ^c	n.d. ^d	n.d.	0.11	94
UTL	-	-	n.d.ª	n.d.	0.21	40

 ${}^{a}T_{act}$ = 200°C; ${}^{b}T_{act}$ = 300°C; ${}^{c}T_{act}$ = 450°C. ${}^{d}n.d.$ – not determined due to the restrictions of FTIR-Py.



Figure 5: XRD patterns (A) and concentrations of Brønsted (BAS) and Lewis (LAS) as determined from the desorption of pyridine at different temperatures (B) of the reference aluminosilicate zeolites. The samples were activated at T = $450 \text{ }^{\circ}\text{C}$ for 2 h

The result is in agreement with lower hydrolytic stability of **UTL** vs. **IWW** zeolite previously reported in Ref. 15-16.^{15, 16} Thus, the amount of Lewis acid sites detected by FTIR-Py in **UTL** activated at 450 °C and lacking adsorbed water (Figure 3A) reflects the number four-coordinated Ge atoms accessible for pyridine molecules. In turn, adsorbed water observed after **UTL** activation at 200 – 300 °C (Figure 3A) is expected to hydrolyze Ge-O-Si linkages decreasing the viewountoning framework Ge atoms and hence detecta

Noticeably, the number of acid sites detected by FTIR-Py (Figure 4) can hardly be correlated to the chemical composition of germanosilicates under the study (Table 1). The result can be explained, considering (i) sterical limitations for probe molecule interaction with neighboring acid sites located in close proximity to each other - the situation which is characteristic of germanosilicate zeolites known for preferential location of Ge atoms in d4r units of the framework;⁴⁸ (ii) low strength of Ge acid centers (i.e., the shift of pyridine adsorption-desorption equilibrium to the desorption even at low temperature).

The XRD patterns of reference commercial **BEA** and **MOR** zeolites highlight the lack of any crystalline admixtures (Figure 5A), whereas the results of N_2 ad-/desorption reveal reasonable values of micropore volumes characteristic of those materials (Table 2).

FTIR-Py showed the presence of both Brønsted and Lewis acid sites in aluminosilicate zeolites. The total number of acid centers decreased with the increase in the Si/Al ratio (Table 2). Importantly, all aluminosilicate zeolites had much stronger acid sites than **IWW** and **UTL** germanosilicates (Figure 5B shows the results of FTIR-Py for BEA-12.5 and MOR-10 to exemplify this general trend).

The crystal size of BEA-12.5, BEA-25 and MOR-10 samples was comparable to that of **IWW** germanosilicate, while BEA-75 showed bigger crystals (Figures 6 and 2).



Figure 6: SEM images of BEA-12.5 (A), BEA-25 (B), BEA-75 (C) and MOR-10 (D) zeolites.

Catalytic behavior of germanosilicate zeolites in the ketalization of polyols

The main issue of ketalization reaction is its low equilibrium constant and the need to remove the water produced in the reaction or to use an excess of ketone to shift the equilibrium to the product side. The research performed in this study used the second approach. Table 3 compiles comparative results assessed with **IWW** and **UTL** germanosilicates for the ketalization of different polyols.

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Table 3: Catalytic performance of IWW and UTL germanosilicates in ketalization of polyols.

	Polyol	Ketone	Main product	T℃	IW	IWW		UTL	
Nr.					Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	
1	ноОн	Ů	°×°	80	>99	>99	>99	>99	
2	ОН		\sim	80	69	>99	59	99	
3	но		ОСН	80	63	97	56	>98	
4	ноОн			80	96	>99	98	>99	
5	ОН			80	51	98	49	>99	
6	ноон		о сон	80	19	96	7	98	
7	НООН		ОН	25	56	98	27	97	
8	ноОН	$\overset{\circ}{\checkmark}$	\sim	25	89	>99	90	>99	

Reaction conditions: 1mmol polyol, 5mmol ketone, 3h, solvent-free, 5mg catalyst. The catalysts were activated at 300 °C.

Nr.	Polyol	Ketone	Main product	Catalyst (activation temperature)	Conversion (%)	Selectivity (%)
1				UTL (450)	17	96
2				IWW (450)	41	96
3				UTL (300)	27	97
4		0	ОН	IWW (300)	56	98
5	ОН	U II		UTL (200)	36	97
6 ⊦	ю С С С С С С С С С С С С С С С С С С С		ó vò	IWW (200)	46	98
7	• •		X	BEA-12.5 (450)	53	98
8				BEA-25 (450)	57	96
11				BEA-75 (450)	49	96
12				MOR 10 (450)	15	95

Table 4: Comparison of the catalytic performances of IWW and UTL activated at different temperatures with commercial aluminosilicate zeolites.

Reaction conditions: 1mmol polyol, 5mmol ketone, 3h, solvent-free, RT, 5mg catalyst.

Depending on the nature of the reagent, polyol conversion ranged from 7 to >99 % at T = 80 °C after 3 h, whereas selectivity was higher than 99 % for both catalysts in reactions with diols. When glycerol is used a side-product 2,2-di-methyl-1,3-dioxan-5-ol can be formed and as a result, in this case, selectivity vary between 96 and 99%. Increasing the ketone (e.g., 2-butanone vs. acetone) or polyol (1,4 butanediol vs. glycerol vs. ethylene glycol) size decreased the conversion for both germanosilicates (Table 3; S2). The result may indicate diffusion limitations for reagents in **IWW** and **UTL** germanosilicates; the trend was more pronounced for **UTL** featuring bigger crystals. Decreasing the reaction temperature to room temperature, as expected, decreased the conversion for both glycerol and ethylene glycol ketalization with acetone (Table 3, entry 7,8). Even at room temperature, ketalization proceeded with satisfactory conversions (Table 3).

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Table 4 compares conversions of polyols achieved with **IWW** and **UTL** germanosilicates activated at different temperatures and those of commercial aluminosilicate zeolites.

The internal diffusion effect on the rate of glycerol ketalization cannot be ruled out for **UTL** germanosilicate, which has the largest crystals (Figure 2B) and the lowest glycerol conversion values (16 – 39 %) *vs.* **IWW** and commercial aluminosilicate **BEA** zeolites (Table 4). Conversely, the conversions of glycerol achieved over **IWW** germanosilicate (40 – 50 %) were comparable to those of commercial aluminosilicate **BEA** (45 – 48 %) and exceeded the conversion over **MOR** (14 %) zeolite, which showed the highest concentration of strong acid sites, both Brønsted and Lewis (Table 2).

The crystallite size of zeolites was earlier reported as one of an important factors for ghe glycerol conversion.⁴⁹ Smaller crystal sizes seam to improve the diffusion of reactants due to short path. Accordingly, diffusion limitation generated in mordenite (MOR) pores results in a lower glycerol conversion. According to data presented in Tables 1, 2 and 3, 4 a correlation between the volume of the micropores, surface area of the catalysts and conversion can be seen for commercial zeolites, especially the BEA ones. The conversions (Table 4) for commercial zeolites increase with increase of the volume of micropores and surface area. The surface area of germanosilicate zeolites is lower than for commercial ones, while the yields are comparable or even higher than for commercial zeolites. UTL catalyst has a higher surface area, larger crystals, but smaller volume of micropores comparative to IWW. In accordance, the conversion generated by UTL zeolite is comparable with that for **MOR** also possess smaller volume of micropores and larger crystals. However, only the textural properties of catalysts are not enough to explain the similar activity of germanosilicate zeolites, which have small surface area and weaker acid sites, with BEA. In this context, the acidic properties of the catalyst also play an important role and the collected results suggest that even the weak acid sites of germanosilicate zeolites serve as active centers in the ketalization reaction. Conversion values provided by commercial BEA zeolites (Table 4) cannot be correlated only with Si/Al ratio or with the overall concentration of acid sites. However, at some extent a correlation exists between Brønsted acid sites and conversion or B/L acid sites ratio. Varying from 0,97 to 1,7 and 0.7 B/L ratio in BEA zeolites lead to 53, 57 and respectively 49% conversion. The results suggest that even the weak acid sites of germanosilicate zeolites serve as active centers in the ketalization reaction. Consistently with the increase in the number of Brønsted acid sites of the IWW zeolite and with the enhanced strength of Lewis acid sites of UTL with the decrease in activation temperature (Figure 4), the optimal temperature for IWW is 300 °C, whereas the optimal temperature for UTL is 200 °C. The decrease in the activity of the zeolite catalyst with the increase in the concentration of aluminum acid centers (Table 2 and 4) is consistent with the high affinity of framework Al towards water formed in the reaction (Scheme 1), which may compete with reagents for adsorption on active sites.⁵⁰ Indeed, hydrophobization of Al-rich HY zeolite (CBV600, Si/Al ratio=2.6) with organosilane surfactant was recently reported to improve the

efficiency of solvent-free glycerol-to-solketal conversion at comm temperature.⁵¹ In the case of MFI Dzeolté939/Acrease660f hydrophobicity lead also to higher TOF.⁵² As result strong acidity in this type of biphasic reaction is not always an advantage. In contrast to AI, Ge incorporation into the frameworks of some silica zeolites decreased water uptake, thus allowing the preparation of weak solid acids characterized by moderate hydrophilicity.^{53,54} Moreover, water adsorption on Ge Lewis sites of both germanosilicate zeolite may promote the *in situ* generation of Brønsted acid centers, which are more active in the ketalization of glycerol than Lewis acid sites.⁵⁵



Figure 7: (A) Time-on-stream dependence of glycerol conversion (square) and solketal selectivity (circle) over zeolite catalysts. (B) appearance or reaction mixture after 15 and 60 minutes of reaction (B) *Reaction conditions:* 1mmol glycerol, 5mmol acetone, solvent-free, RT, 5mg catalyst.

Conversion to solketal in time for BEA-25, **IWW** and **UTL** catalysts is presented in Figure 7. For the germanosilicate zeolites the increase of the activity is more evident in the first two hours: for **IWW** the conversion increases from around 30 to more than 50% in the first two hours leading after that to slightly higher conversion than BEA-25. The same trend is observed for the **UTL** as well, although for smaller conversions. The commercial zeolite led to a 50% conversion in the first 15 minutes when it reaches a plateau. The single phase formation after 15 minutes of reaction (Figure 7 right). Taking into consideration the difference existing between the textural properties, Si/Ge ratio and acidity of **IWW** and **UTL** catalysts, the similar time needed to achieve a highest conversion



Figure 8: Ketalization of acetone to ketal. *Reaction conditions:* 5 mg catalyst IWW, RT, 3h magnetic stirring, solvent-free.

suggests that some induced species are responsible for increase of catalytic activity and the formation of those species is a time-factor. The concentration of Brønsted acid sites per surface unit is slightly higher in **IWW** zeolite, compared to BEA-

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25. However, the faster plateau reached in the presence of the **BEA** catalyst should be assumed to a larger surface area.

However, all catalysts provided similar selectivities after 2 h of reaction. The secondary product, acetal (2,2-dimethyl-1,3-dioxan-5-ol), is formed onto the **IWW** catalyst during the first hour, then subsequently glycerol converts only to solketal.



Figure 9: Catalyst recycling for solketal synthesis (*Reaction conditions:* 1mmol polyol, 5mmol ketone, 3h, solvent-free, RT, 5mg catalyst).

Noticeably, when increasing the ketone-to-alcohol molar ratio to 25, the solketal yield reached 99 % over the **IWW** catalyst, even at room temperature (Figure 8). In addition, no side-products, such as dioxane (2,2-dimethyl-1,3-dioxan-5-ol), or acetone condensation products (mesityl oxide) were identified when using **IWW** and **UTL** or even commercial zeolites under these conditions. This high selectivity is usually explained by a mechanism involving the rearrangement of dioxane to dioxalane, which is catalyzed by Brønsted acid sites and favored by an increase in pore volume and by a decrease in acidity. The literature on selectivity is, however, contradictory, increasing in some cases by dealumination⁵⁶ or desilication²⁹.

Framework germanium atoms are able to not only change the local environment (reflected in the transformation of Lewis-to-Brønsted acid sites) but also leach to the liquid phase by coordination with water, as by-products of the ketalization reaction. The results from the recycling test showed that both **UTL** and **IWW** catalysts can be reused at least 3 times without selectivity and conversion losses, when 1:5 glycerol:acetone molar ratio is used (Figure 9). The type of acid sites and hydrolysis reaction are two factors affecting the most the selectivity to solketal.⁵⁶ During the recycle, the selectivity increases slightly for **UTL** and **BEA** catalyst. An enhancement can be explained by adsorption of some water on Brønsted acid sites during the catalyst recycle that can favour the rearrangement to solketal.⁵²

The commercial zeolite BEA-25 was also recycled 3 times without considerable changes in terms of conversion or selectivity. However, after the second recycle of BEA-25 it was noticed a change of the catalyst colour in yellow, persisting

after the catalyst washing. The differential thermal and thermogravimetric analysis of fresh and spender to the spender of the

After 3 catalytic cycles the weight loss for **IWW** catalyst is around 3% and for BEA-25 around 5% indicating larger deposits of coke. Also, for BEA-25 a new DTA peak occurs at temperatures between 120-130 °C related to these deposits. It was also observed a higher deactivation of **UTL** and **IWW** catalysts during recycle, when a higher amount of acetone was



Figure 10: The differential thermal and thermogravimetric analysis of fresh and spent BEA-25 and IWW catalyst (*Reaction conditions:* 1mmol glycerol, 5mmol acetone, solvent-free, RT, 5mg catalyst, 3 cycles).

used (reaction conditions from Figure 8). However, even for ultrastable Y zeolites, washing and drying did not prevent the decrease in catalytic activity.³¹

Leached Ge species in solution after 1h were under 0,1ppm as determined by ICP-OES. Nevertheless, the leached Ge species were not active during the ketalization reactions, as demonstrated for glycerol (Figure 11), with only a negligible increase in the conversion after removing the catalyst, even after 12 hours of reaction.



Figure 11: Results of leaching tests over the IWW and UTL catalysts (*Reaction conditions:* 1mmol glycerol, 5mmol acetone, solvent-free, RT, 5mg catalyst. The catalysts were activated at 300 °C).

The comparison of the performance of germanosilicate zeolites in ketalization reactions with the results reported in the literature shows that similar conversion/selectivity values were documented for glycerol ketalization with acetone when using other homogeneous or more complex heterogeneous catalysts, such as Lu(OTf)₃,⁵⁷ MoPO/SBA-15SiO2,⁵⁸ Re/SiO₂,⁵⁹ ZrO₂/SO₄⁶⁰ or **MOR**,³⁰ **MFI**, hydrophobic HY⁵¹ or **BEA** zeolites, ^{30, 56,49} which provided similar performances, sometimes even at higher temperatures.⁶¹

Conclusions

Weakly acidic germanosilicate zeolites IWW and UTL are active and selective catalysts of polyol (e.g., ethylene glycol, glycerol, 1,4 butyldiol) ketalization. Ketalization reactions with germanosilicate catalysts resulted in the exclusive formation of the targeted dioxolane products. The less active UTL catalyst presented a higher Ge content and a larger crystal size and volume of micropores than IWW. Based on FTIR spectroscopy of pyridine, the UTL zeolite exclusively had Lewis acidity, whereas the IWW catalyst was prone to water-induced formation of weak Brønsted acid sites. Increasing the activation temperature (200 - 450 ºC) reduced the concentration of Brønsted acid centers in IWW germanosilicate (i.e., 0.16; 0.07 and 0.05 mmol/g for Tact = 200, 300 and 450°C, respectively) but increased the number of Lewis acid sites in both zeolites. The IWW catalyst (40 - 50 % of solketal yield at Tact = 450 - 300 °C) outperformed not only the Lewis acidic UTL germanosilicate (16 - 36 % Tact = 450 -200 °C) but also the commercial aluminosilicate zeolites MOR (15 %, Si/Al = 10) and **BEA** (45 - 48 %, Si/Al = 12.5 - 75) with strong Brønsted and Lewis acid sites. Increasing the acetoneto-glycerol molar ratio to 25 led to a yield of >99% of the solketal product over the IWW catalyst, even at room temperature. The IWW catalysts were recycled 3 times without any conversion and selectivity losses. The IWW catalyst activity for solketal formation in terms of conversion, selectivity and recyclability is at least comparable with

commercial BEA-25 zeolite. Thus, the results of vithe resent study demonstrate the catalytic potential 1019 where the catalytic potential of the second seco

Conflicts of interest

There are no conflicts to declare.

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