

## Synthesis of mesoporous $ZrO_2$ - $SiO_2$ and $WO_3/ZrO_2$ - $SiO_2$ solid acids\*

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The method for preparation of mesoporous  $ZrO_2$ - $SiO_2$  and  $WO_3/ZrO_2$ - $SiO_2$  oxides with silicic acid sol is proposed. It was shown that these acidic oxides demonstrate high activity in the reaction of tetrahydrofuran oligomerization.

### 1. INTRODUCTION

Solid acid catalysts are widely used in oil refinery and organic synthesis, especially medium acidic catalysts on the basis of zeolites and mixed oxides [1]. During the last 25 years, significant attention has been devoted to synthesis and study of stable solid superacids, such as sulphated [2] and tungstated [3] zirconia. These oxides effectively catalyze many important reactions at average temperatures, for instance isomerization of linear alkanes and acylation of aromatic compounds [2, 3]. However, at present the synthesis of solid acids which occupy the intermediate position between zeolites with their acidity function value ( $H_0 \geq -8$ ) and the superacid catalysts ( $H_0 \leq -12$ ) is of interest. High surface area and suitable texture parameters are also important for oxide material (see, for instance [4]).

Relatively low specific surface area, which is lower than  $100 \text{ m}^2/\text{g}$  [3], is a certain disadvantage of superacids on the basis of zirconia. This is connected with the high coordination number for  $Zr^{4+}$  ions (7 and 8) and, correspondingly,

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\*This article is dedicated to Professor Roman Leboda on the occasion of his 65<sup>th</sup> birthday

with dense packing of O<sup>2-</sup> ions in the ZrO<sub>2</sub> lattice. At the same time, it is known that joining of silicon-oxygen tetrahedrons allows to obtain silica materials as silicagel, with high surface area and considerable pore volume.

The synthesis of mixed ZrO<sub>2</sub>-SiO<sub>2</sub> oxide is described in literature [5-10], but there is almost no information on the preparation of ternary WO<sub>3</sub>/ZrO<sub>2</sub>-SiO<sub>2</sub> system. As starting reagents, water solutions of hexafluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) and hexafluorozirconic acid (H<sub>2</sub>ZrF<sub>6</sub>) [5], tetraethoxysilane, zirconium isopropylate [6, 7] and nitrate [8], sodium silicate and zirconium chloride [9] or a zirconium carbonate complex [10] were used to prepare ZrO<sub>2</sub>-SiO<sub>2</sub> samples. In the present work ZrO<sub>2</sub>-SiO<sub>2</sub> and WO<sub>3</sub>/ZrO<sub>2</sub>-SiO<sub>2</sub> oxides are prepared on the basis of silicic acid sol.

## 2. EXPERIMENTAL

Zirconyl chloride octahydrate ZrOCl<sub>2</sub>·8H<sub>2</sub>O, ammonium meta-tungstate (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O, potassium silicate K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, nonionic surface active substance Triton CF-10 (Dow Chemical), and carbamide were used as starting substances.

Water sol of oligomers of silicic acid was obtained treating potassium silicate with the cation-exchange resin KU-2 (sulfuretted styrene and divinylbenzene copolymer) [11, 12]. In order to synthesize mixed ZrO<sub>2</sub>-SiO<sub>2</sub> oxide, zirconium oxychloride solution in a small amount of water was added to 1 L of polysilicic acid solution (SiO<sub>2</sub> concentration equal 0.4 M) with the mole ratio Zr:Si=1:2 according to [10]. Then 48 g of carbamide and 10 g of Triton CF-10 were added. The resultant solution was heated to boiling and kept at this temperature for 2 h while stirring to transform sol into gel. The obtained gel was dried at 120<sup>0</sup>C for 48 h.

Further treatment of xerogel was performed in two ways:

- Dry method.  
The obtained xerogel was heated (2<sup>0</sup>C/min) up to 700<sup>0</sup>C and kept at this temperature for 2h. During the treatment, volatile and combustible compounds (carbamide and its transformation product, ammonium chloride) were eliminated. The resultant sample of mixed ZrO<sub>2</sub>-SiO<sub>2</sub> oxide is named ZrSi(dry).
- Wet method.  
The obtained xerogel was washed with water several times to eliminate chloride ions, dried, and then thermally treated in air for 2 h at 700<sup>0</sup>C. This sample is further coded as ZrSi(aq).

The synthesis of WO<sub>3</sub>/ZrO<sub>2</sub>-SiO<sub>2</sub> samples was performed in the same way, but ammonium metatungstate was added to sol at the atom ratio W:Zr=0.2:1.

Further treatment of corresponding gels was performed according to two routes described above for the  $\text{ZrO}_2\text{-SiO}_2$  samples. The samples of mixed oxides  $\text{WO}_3/\text{ZrO}_2\text{-SiO}_2$  would be referred to as WZrSi(dry) and WZrSi(aq).

X-Ray ( $\text{CuK}_\alpha$ ) patterns for all obtained samples were registered using a DRON-4-07 diffractometer. Nitrogen adsorption isotherms were measured using Nova 2200e Surface Area and Pore Size Analyzer. Reflectance spectra of the powdered samples were registered with a Specord M40 device. The reflectance coefficient  $R$  was calculated according to the  $\text{MgO}$  standard ( $R=R_{\text{sample}}/R_{\text{MgO}}$ ). The band gap width  $E_0$  was estimated from the reflectance spectra using the Kubelka-Munk equation  $\rho = (hv(1-R)^2/2R)^{1/2}$ . The  $E_0$  values were determined from the nearly linear long-wave segment of absorption band plot extrapolated to interception with the abscissa [13].

Total acid sites concentration was determined by the method of reverse titration using *n*-butylamine adsorbed on the surface of a sample from a solution in cyclohexane using bromthymol blue as an indicator. 20 ml of 0.1 M solution of *n*-butylamine in purified and dried cyclohexane were added to 300–400 mg of a sample. After stirring for 30 minutes, an aliquot of the solution was titrated with 0.05 M solution of hydrochloric acid. The strength of acid sites was estimated by the method of direct titration of the surface of synthesized samples with *n*-butylamine using the Hammett indicators: (benzalacetophenone ( $\text{pK}_a = -5.6$ ), anthraquinone ( $\text{pK}_a = -8.2$ ), 4-nitrotoluene ( $\text{pK}_a = -11.35$ ), 1-chloro-3-nitrobenzene ( $\text{pK}_a = -13.16$ ), 2,4-dinitrotoluene ( $\text{pK}_a = -13.75$ ) and 2,4-dinitro-1-fluorobenzene ( $\text{pK}_a = -14.52$ ). All samples were dried for 1 hour at  $500^\circ\text{C}$  before testing.

The activity of the samples was determined in the oligomerization reaction of tetrahydrofuran [14] and in the test reaction of 2-methyl-3-butyn-2-ol transformation [15].

### 3. RESULTS AND DISCUSSION

Figure 1 presents the X-ray patterns for ZrSi and WZrSi calcinated at  $700^\circ\text{C}$  and  $800^\circ\text{C}$ . As can be seen from the figure, the ZrSi samples are amorphous. Broad maxima around  $30^\circ$  and  $51^\circ$  approximately correspond to the most intensive peaks of zirconia. The formation of tetragonal crystalline  $\text{ZrO}_2$  phase was observed for the WZrSi(dry) sample after treatment at  $700^\circ\text{C}$  (curve 5). Zirconium dioxide crystals are observed in all WZrSi samples after calcinations at  $800^\circ\text{C}$ . Thus, insertion of  $\text{W}^{6+}$  ions promotes the crystallization of zirconia in this system. The  $\text{ZrO}_2$  crystallite size calculated from the peak half-width using the Sherrer equation is 4–5 nm for the WZrSi(aq) sample calcinated at  $800^\circ\text{C}$  and 9–10 nm for the WZrSi(dry) sample. Thus burning of the volatile templates without preliminary washing leads to crystallization of  $\text{ZrO}_2$  at lower

temperature and causes the formation of larger  $\text{ZrO}_2$  crystals. The crystalline  $\text{ZrO}_2$  phase does not appear under any synthetic conditions in the absence of tungstated ions. It is interesting that  $\text{WO}_3$  slows down crystallization of zirconia in the  $\text{WO}_3\text{-ZrO}_2$  systems not containing silicon [3, 15].

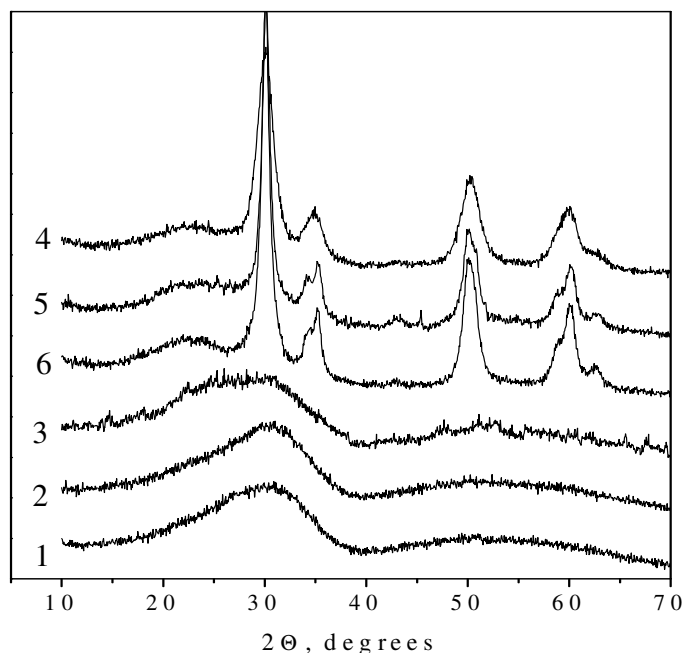


Fig. 1. XRD patterns ( $\text{CuK}\alpha$ ) for the  $\text{ZrO}_2\text{-SiO}_2$  and  $\text{WO}_3/\text{ZrO}_2\text{-SiO}_2$  samples: 1 –  $\text{ZrSi}(\text{aq})700$ , 2 –  $\text{ZrSi}(\text{aq})800$ , 3 –  $\text{WZrSi}(\text{aq})700$ , 4 –  $\text{WZrSi}(\text{aq})800$ , 5 –  $\text{WZrSi}(\text{dry})700$ , 6 –  $\text{WZrSi}(\text{dry})800$ .

Figure 2 shows the pore size distribution for the  $\text{WZrSi}$  samples, and Table 1 presents the texture data for prepared  $\text{WZrSi}$  and  $\text{ZrSi}$ . The values of specific surface area of the  $\text{WZrSi}$  and  $\text{ZrSi}$  samples in the range of  $200\text{--}350\text{ m}^2/\text{g}$ , that is 3–5 times higher than those for the  $\text{WO}_3/\text{ZrO}_2$  samples obtained by the coprecipitation technique ( $50\text{--}70\text{ m}^2/\text{g}$ ) [15]. Correspondingly, the pore volume for  $\text{WZrSi}$  and  $\text{ZrSi}$  exceeds three times the appropriate values for  $\text{WO}_3/\text{ZrO}_2$ . However, the average mesopore size for  $\text{ZrSi}$ ,  $\text{WZrSi}$  (Table 1) and  $\text{WO}_3/\text{ZrO}_2$  [15] remains approximately the same ( $1.8\text{--}2.2\text{ nm}$ ). It should be noted that  $\text{WZrSi}(\text{dry})$  obtained using burning out of organic template and ammonium chloride possesses larger size pores than the samples obtained from washed out xerogels. Probably, the products of thermal polymerization of carbamide and ammonium chloride perform the role of templates and pore-forming substances.

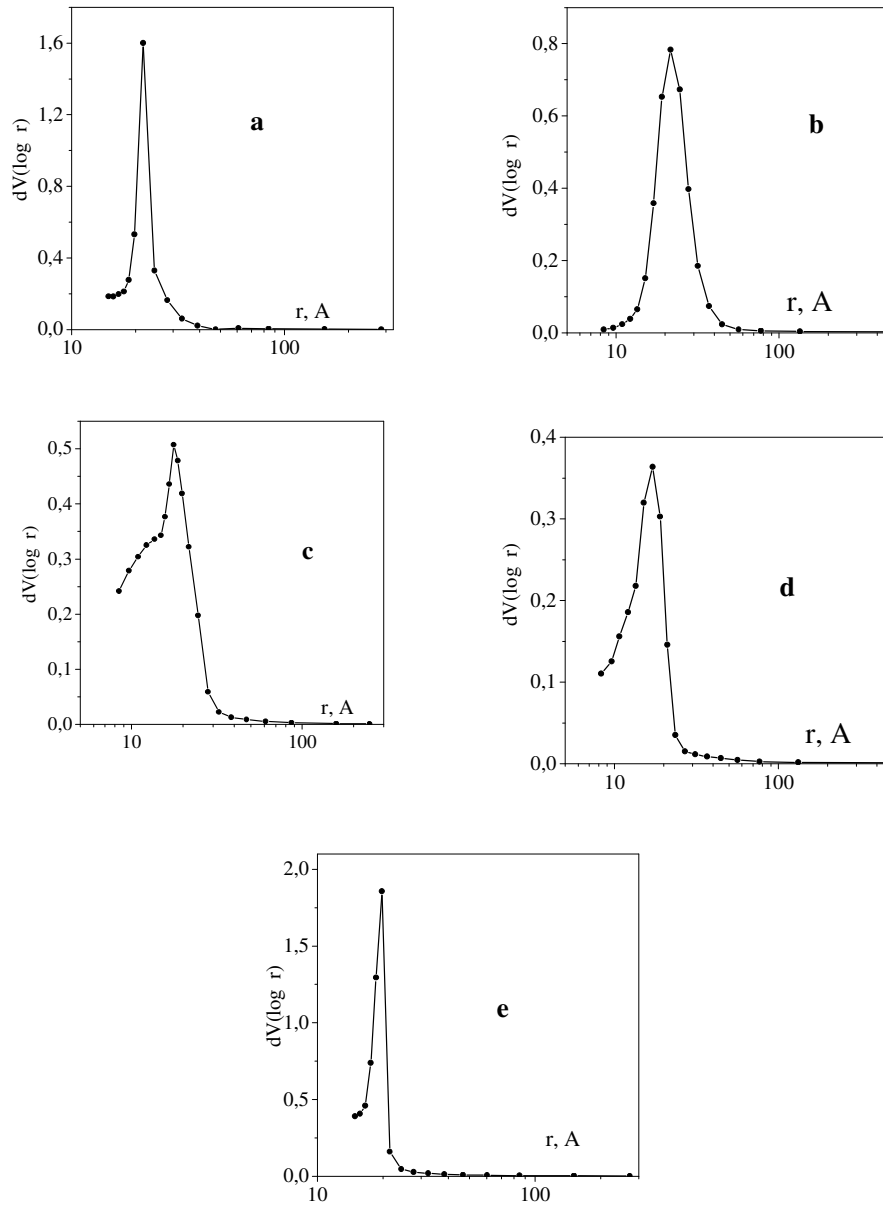


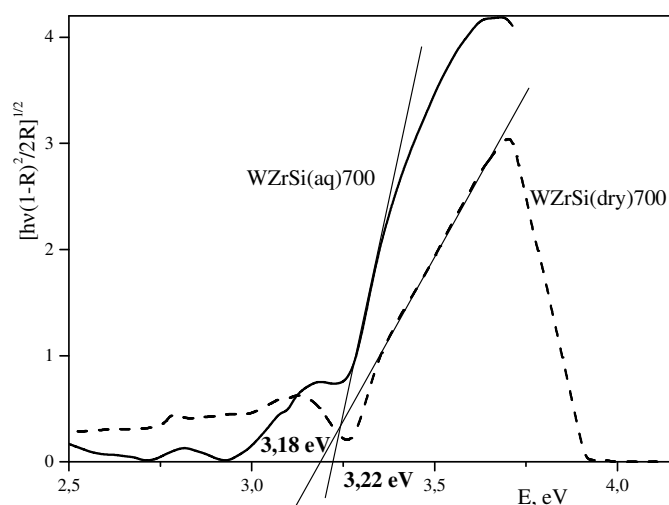
Fig. 2. BJH nitrogen desorption pore radius distributions for the  $ZrO_2$ - $SiO_2$  and  $WO_3$ - $ZrO_2$ - $SiO_2$  samples: a) WZrSi(dry)700, b) WZrSi(dry)800, c) WZrSi(aq)700, d) WZrSi(aq)800, e) ZrSi(aq)700.

Tab. 1. Texture parameters for ZrSi and WZrSi.

Sample	T, °C	Specific surface area, S, m <sup>2</sup> /g	Pore volume, V, cm <sup>3</sup> /g	Pore radius, nm
WZrSi(dry)	700	250	0.16	2.2
	800	140	0.19	2.2
WZrSi(aq)	700	270	0.17	1.8
	800	130	0.10	1.7
ZrSi(aq)	700	380	0.24	2.0

The effect of ammonium chloride as an ionogenic pore-forming agent is described in [14].

It is known that catalytically active WO<sub>3</sub>/ZrO<sub>2</sub> is characterized by surface tungstated clusters with the band gap width in the range  $E_0 = 3.0\text{--}3.2$  eV (individual ZrO<sub>2</sub> and WO<sub>3</sub> possess  $E_0 = 5.6$  eV and 2.6 eV respectively) [13]. The UV diffuse reflectance spectra for all WZrSi samples show that they are characterized by  $E_0$  values, which are very close to those for WO<sub>3</sub>/ZrO<sub>2</sub> (Figure 3).

Fig. 3. UV-Vis diffuse reflectance spectra for the WO<sub>3</sub>/ZrO<sub>2</sub>-SiO<sub>2</sub> samples.

Total concentration of acidic sites for ZrSi(aq) and WZrSi(aq) calcinated at 700<sup>0</sup>C is 1.3 mmol/g and 1.1 mmol/g, respectively. The results of determination of strength distribution for the acid sites of the ZrSi and WZrSi samples are

presented in Figure 4. It was found that both ZrSi and WZrSi samples change their color from white to light yellow in the presence of 4-nitrotoluene ( $H_0 = -11.35$ ). It can be seen (Figure 4) that concentration-strength acid site distributions are considerably different for the ZrSi and WZrSi samples. WZrSi is a stronger solid acid because about 80% of its medium-acid sites are characterized by the acidity function value  $H_0 = -8.2$ . The main contents of sites (60%) on the surface of the ZrSi sample are described by the value of  $H_0 = -5.6$ . For the  $WO_3/ZrO_2$  system, a wide range of acid strength is observed, from the medium ( $-5.6 \geq H_0 \geq -8.2$ ) up to superacidic values of  $H_0 = -14.5$  (~5%) [15].

Acidity of ZrSi, WZrSi correlates with their activity in the test reaction of 2-methyl-3-butyn-2-ol (MBOH) transformation (Figure 5). This molecule undergoes acid-catalyzed dehydration to 3-methyl-3-butene-1-yne (Mbyne,  $m/e = 66$ ) and isomerization into 3-methyl-2-butene-1-al (Prenal,  $m/e = 84$ ). The first reaction proceeds easily over weak acid sites of a catalyst, and therefore the maximum of Mbyne evolution appears at lower temperature (40–50<sup>0</sup>C). However, strong acid sites are required for the isomerization of MBOH into Prenal. The prenal peaks are observed at 110<sup>0</sup>C for the  $WO_3/ZrO_2$  samples [15]. For the less acidic WZrSi and ZrSi samples, these peaks are shifted to 130<sup>0</sup>C and 220<sup>0</sup>C, respectively (Figure 5).

The synthesized  $WO_3/ZrO_2-SiO_2$  and  $ZrO_2-SiO_2$  samples demonstrate high activity in tetrahydrofuran oligomerization reaction in a flow reactor (Table 2, Figure 6). It should be noted that an industrial catalyst for this process has been developed on the basis of  $ZrO_2-SiO_2$  [8]. The activity of ZrSi and WZrSi only slightly differs at low loading on the catalyst ( $L < 4$  mmol THF/ $g_{catal} \cdot h$ ), but higher yield of polytetramethylene ether (PTME) is observed for WZrSi at higher L values (Figure 6).

#### 4. CONCLUSIONS

Thus, the mesoporous  $ZrO_2-SiO_2$  and  $WO_3/ZrO_2-SiO_2$  oxides with high content of acidic sites have been obtained on the basis of silicic acid sol. It was shown that  $WO_3/ZrO_2-SiO_2$  is a suitable catalyst for the tetrahydrofuran oligomerization process.

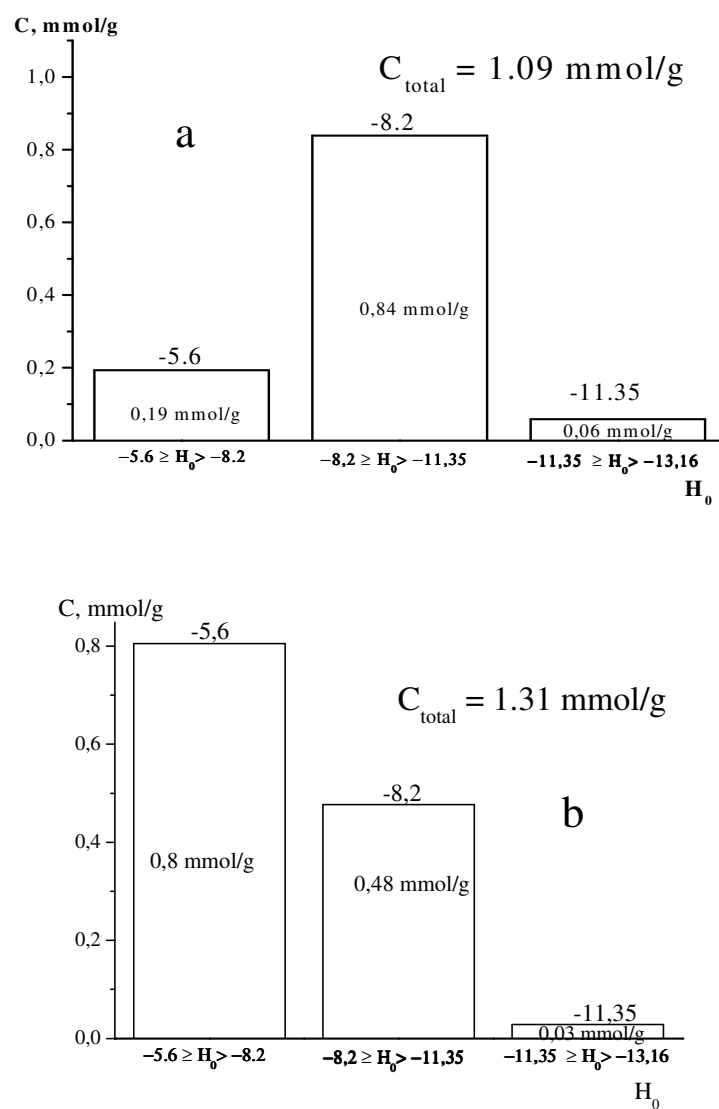


Fig. 4. Concentration-strength acid site distributions for the WZrSi(dry)700 (a) and ZrSi(aq) (b) samples.



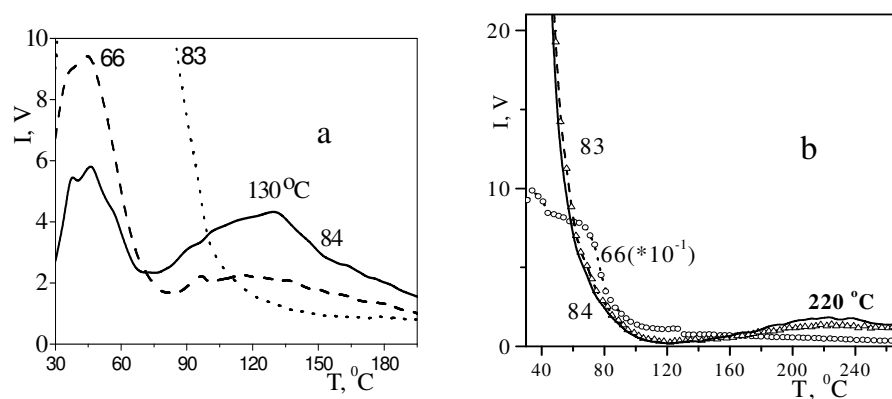


Fig. 5. TPR spectra of Mbyne and Prenal formation from MBOH adsorbed on WZrSi (a), ZrSi (b).

Tab. 2. Average number ( $M_n$ ), average weight ( $M_w$ ), and yield of PTME (THF:acetic anhydride = 8:1).

Catalyst	Load, mmol THF/g <sub>cat</sub> ·h	Yield, %wt	$M_n$	$M_w$	$M_w/M_n$
WzrSi	7.5	37	529	956	1.8
WzrSi	12.7	33	625	1205	1.92
ZrSi	7.5	30	487	723	1.48
ZrSi	12.7	21	489	962	1.97

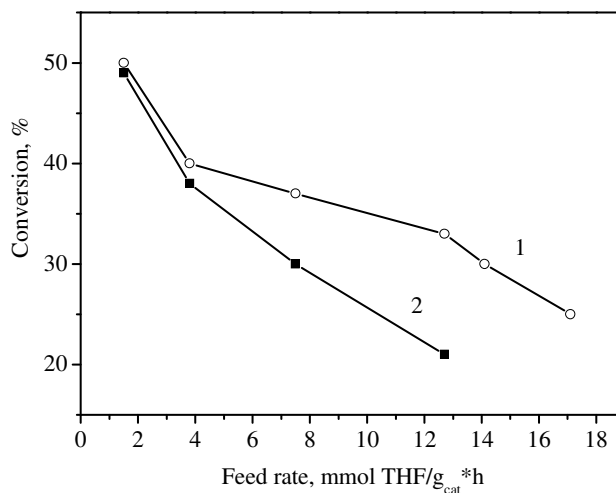


Fig. 6. Conversion of THF at different feed rates for WZrSi (1) and ZrSi (2).

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