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CONTINUOUS CONVERSION OF FRUCTOSE INTO METHYL LACTATE OVER SnO2–ZnO/Al2O3 CATALYST

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Abstract

The conversion of fructose into methyl lactate on SnO_2–ZnO/Al_2O_3 catalyst in a flow mode was carried out. The supported $10SnO_2$–$5ZnO/Al_2O_3$ catalyst was obtained by a simple impregnation method of granular γ-Al_2O_3 with the aqueous solution of $SnCl_4$ and $Zn(OAc)_2$. The data on structural analysis, textural and acid-base parameters of synthesized samples. are presented. The following optimal conditions for obtaining 70 % methyl lactate yield at 100 % fructose conversion were found: use of 4.8 wt.% fructose solution in 80 % aqueous methanol as reaction mixture, reaction temperature of 180 °C at 3.0 MPa. Addition of Zn ions to catalyst content allows to use the initial fructose mixture without potassium carbonate. $10SnO_2$–$5ZnO/Al_2O_3$ catalyst provides full fructose conversion at 70 % methyl lactate selectivity for 6 h on stream. Spent catalyst after regeneration by washing with water at 120 °C restores initial activity.

Keywords: fructose conversion; heterogeneous catalysis; methyl lactate; Sn-containing oxides; supported catalyst.

КОНВЕРСІЯ ФРУКТОЗИ В ПРОТОЧНОМУ РЕЖИМІ ДО МЕТИЛЛАКТАТУ НА SnO2–ZnO/Al2O3 КАТАЛІЗАТОРІ

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Анотація

Проведено перетворення фруктози в метиллактат на SnO_2–ZnO/Al_2O_3 каталізаторі в проточному режимі. Нанесений $10SnO_2$–$5ZnO/Al_2O_3$ каталізатор було одержано простим методом просочення гранульованого γ-Al_2O_3 водним розчином $SnCl_4$ та $Zn(OAc)_2$. Представлено дані щодо структурного аналізу, текстурних та кислотно-основних параметрів синтезованих зразків. Знайдено наступні оптимальні умови для отримання 70 % виходу метиллактату при 100 % конверсії фруктози: використання 4.8 мас.% розчину фруктози у 80 % водному метанолі в якості вихідної суміші, температура реакції 180 °C при 3.0 МПа. Допування каталізатора SnO_2/Al_2O_3 іонами Zn дозволяє використовувати вихідний розчин фруктози без додавання карбонату калію. Каталізатор $10SnO_2$–$5ZnO/Al_2O_3$ забезпечує повну конверсію фруктози за 70 % селективності за метиллактатом протягом 6 год в проточному реакторі. Витрачений каталізатор після регенерації промиванням водою при 120 °C відновлює початкову активність.

Ключові слова: конверсія фруктози; гетерогенний каталіз; метиллактат; Sn-вмісні оксиди; нанесений каталізатор.

КОНВЕРСИЯ ФРУКТОЗЫ В ПРОТОЧНОМ РЕЖИМЕ ДО МЕТИЛЛАКТАТА НА SnO₂–ZnO/Al₂O₃ КАТАЛИЗАТОРЕ

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Аннотация
Проведено превращение фруктозы в метиллактат на SnO₂–ZnO/Al₂O₃ катализаторе в проточном режиме. Нанесенный 10SnO₂–5ZnO/Al₂O₃ катализатор получен простым методом пропитки гранулированного γ-Al₂O₃ водным раствором SnCl₄ и Zn(OAc)₂. Приведены данные структурного анализа, текстурных и кислотно-основных параметров синтезированных образцов. Найдено следующие оптимальные условия получения 70 % метиллактата при 100 % конверсии фруктозы: использование в качестве исходной смеси 4.8 мас.% раствора фруктозы в 80 % водном метаноле, температура реакции 180 °C при 3.0 МПа. Допирование SnO₂/Al₂O₃ катализатора ионами Zn позволяет использовать исходный раствор фруктозы без добавления карбоната калия. Катализатор 10SnO₂–5ZnO/Al₂O₃ обеспечивает полную конверсию фруктозы при 70 % селективности по метиллактату в течение 6 часов работы. Отработанный катализатор после регенерации промывкой водой при 120 °C восстанавливает исходную активность.

Ключевые слова: конверсия фруктозы; гетерогенный катализ; метиллактат; Sn-содержащие оксиды; нанесенный катализатор.

Introduction

Now esters of lactic acid are widely used as a non-toxic solvents or intermediates in pharmaceutical, agrochemicals, coatings and food production [1; 2]. The common esters are methyl lactate, ethyl lactate and butyl lactate. So, methyl lactate is of interest as a starting material to produce a monomeric lactide [3] instead of lactic acid [4]. In an industry lactates are currently produced via esterification of lactic acid with appropriate alcohol [5]. Alternatively, the study on the catalytic conversion of renewable carbohydrates, as well as lignocelluloses, to alkyl lactates has accelerated [1]. As rule, the Sn-contained zeolites and oxides as Lewis acid catalysts were used [6-15]. Also the Sn(IV)-grafted mesoporous carbon-silica composite as effective bifunctional catalyst for the transformation of glucose, fructose and sucrose in methanol to methyl lactate was proposed [7]. However, the preparation of Lewis acid zeolites is complicated, time-consuming and energy-intensive [10; 11]. Therefore many researchers look for catalysts that are easier to synthesize. The authors [13] have found that alumina-supported Sn catalysts, easily prepared by impregnation, efficiently promote the conversion of trioses into ethyl lactate at mild reaction conditions.

Usually, the experiments on the carbohydrate conversion to lactates were carried out under stationary conditions using highly dilute solutions (∼ 3 wt.%) [7–9; 12]. In our previous work [14] more concentrated 13 % solution of fructose in ethanol was used, at that 50 % ethyl lactate yield on SnO_2/Al_2O_3 catalyst at 160 °C was obtained.

It is known that commercial potential of the catalyst depends on the ability of the system to operate continuously during long time. Therefore, we decided to further investigate the continuous conversion of concentrated methanolic solutions of fructose over SnO_2–ZnO/Al_2O_3 catalyst. Not numerous articles [16; 17] were devoted to the continuous conversion of carbohydrates into lactates.

In this communication the reaction conditions used during continuous conversion, especially the selection of initial reaction mixture, temperature, pressure and load on a catalyst are described. The results on catalyst doping by Zn^{2+} and Mg^{2+} ions for increasing methyl lactate selectivity are presented also.

Results and Discussion

The structural analysis by XRD shows that all reflections of xSnO₂–yMeO/Al₂O₃ samples are due to a poorly developed crystalline phase of γ-Al₂O₃ ($2\theta = 36.5°$, 46.1°, 66.6°, corresponding to the (311), (400), (440) crystal planes, respectively). No characteristic peaks assigned to SnO₂, ZnO or MgO were observed, indicating Sn, Zn and Mg species are highly dispersed (Fig. 1).

Fig. 2 shows the scanning electron micrographs (SEM) of the alumina mixed tin oxide granules surface at different magnifications. It can be observed that SnO₂ particles were homogeneously distributed all over the surface. The EDS analysis proved the presence of Sn, Al and O atoms with little Cl atoms.
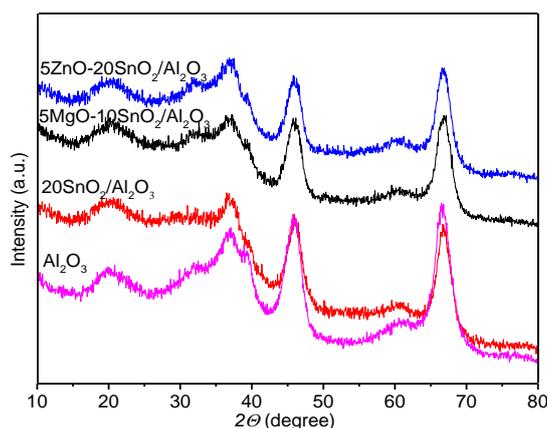
Fig. 1. XRD patterns of xSnO$_2$–yMeO/Al$_2$O$_3$ samples after calcinations at 550 °C for 2 h.

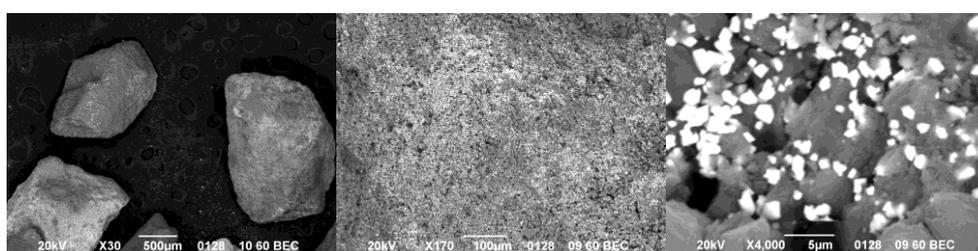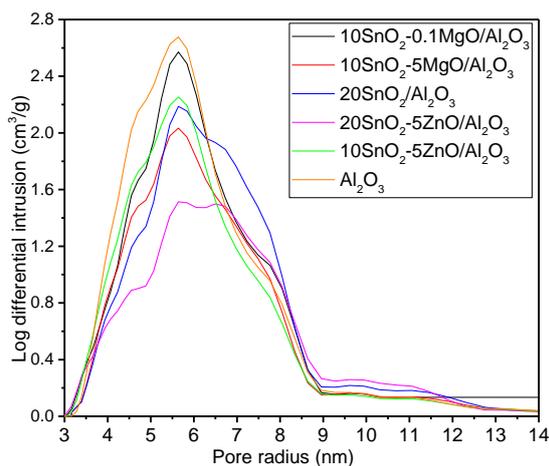**Fig. 2. SEM micrographs of 20SnO$_2$/Al$_2$O$_3$ sample.**

Table 1 summarized textural and acidic parameters of synthesized samples. All the alumina-supported samples presented slightly lower values of the specific surface area and mesopore volume than pure γ-Al$_2$O$_3$. As seen from the pore size distribution curves (Fig. 3), derived from the desorption branches of the isotherms using the DFT method, the deposition of dopants on alumina surface leads to decrease in pore content with $r \leq 5$ nm and insignificant decrease in pores volume. That could be explained by blocking of small pores after precipitated oxides loading during preparation procedures.

Table 1

Textural and acid-based characteristics of synthesized catalyst

| Sample	Specific surface area, (m²/g)	Pore volume (cm³/g)	Average pore diameter (nm)	Highest acid strength, H_o	Total content of acid sites (mmol/g)	Highest base strength H_-	Total content of basic sites (mmol/g)
10SnO$_2$-5ZnO/Al$_2$O$_3$	186	0.6	13/0	+3.3	0.6	+7.2	0.6
20SnO$_2$-5ZnO/Al$_2$O$_3$	147	0.5	12.9	+3.3	1.3	-	-
5SnO$_2$-10ZnO/Al$_2$O$_3$	215	0.7	13.0	-	-	+7.2	1.2
20SnO$_2$/Al$_2$O$_3$	178	0.6	13.5	+1.5	1.5	-	-
10SnO$_2$-5MgO/Al$_2$O$_3$	171	0.55	13.0	-	-	+9.3	0.2
10SnO$_2$-0.1MgO/Al$_2$O$_3$	195	0.6	13.0	+1.5	1.1	-	-
20SnO$_2$-0.3MgO/Al$_2$O$_3$	193	0.6	12.8	+1.5	1.3	-	-
Al$_2$O$_3$	208	0.7	13.6	+3.3	1.2	-	-

Fig. 3. DFT pore–size distributions of samples calcined at 550 °C.

According to the titration results, $20SnO_2/Al_2O_3$ is weakly acid oxide with $H_0 \leq +1.5$ (Table 1). Numerous studies showed that a combination of Lewis and Brønsted acidity catalyzes the selective conversion of monosaccharides to lactates [6; 7; 13; 14]. The base sites inhibited alternative reactions that lead to the formation of undesirable by–products [18–21]. It is also known that the addition of Zn^{2+} ions enhanced both the amount of Lewis acid and base sites [14; 15; 21]. As for magnesium, in article [20] showed that Mg^{2+} in the framework MOF can provide Lewis acidity and in the framework site of silicate molecular sieve can induce strong basicity

of framework oxygen atoms. We have doped SnO_2/Al_2O_3 with ZnO or MgO for decreasing acidity of studied oxide. As a result, with a simultaneous increase in zinc and decrease in tin oxides the weak base sites with $H_- = +7.2$ are appear (Table 1). The $10SnO_2-5ZnO/Al_2O_3$ sample has optimal combination of acidic and basic sites. At addition of small amount of MgO to $xSnO_2/Al_2O_3$ (0.1 wt.% MgO) no changes in the acidity of the samples are observed. With an increase in MgO content traces of weak base sites with $H_- = +9.3$ are detected, while acid sites disappear (Table 1).

According to the UV–*Vis* data all synthesized samples show maximum intensity near 200 nm that has previously been assigned to isolated tetrahedrally coordinated [IV]Sn^{4+} ions [14]. Fig. 4 illustrates the optical band gap (E_g) for synthesized samples. It is known, that E_g value for massive SnO_2 is near 3.55 eV [22]. ZnO is a high and direct bad gap semiconductor with band gap ~3.4 eV [23]. Band gap energy of bulk MgO is 7.8 eV [24]. In paper [14] for $20SnO_2/Al_2O_3$ sample the shift of E_g to 4.8 eV indicates the nanosized SnO_2 species with [IV]Sn^{4+} ions that absorb *UV* light at 200 nm. Only for $10SnO_2–5ZnO/Al_2O_3$ sample E_g value is near 4.7 eV (Fig. 4b). For all other synthesized doped SnO_2/Al_2O_3 samples, two values of the band gap are observed in the intervals of 4.5–4.7 eV and also 3.0–3.5 eV (Fig. 4). This indicates the agglomeration of SnO_2 particles occurring in $xSnO_2–yMeO/Al_2O_3$ samples at doping.
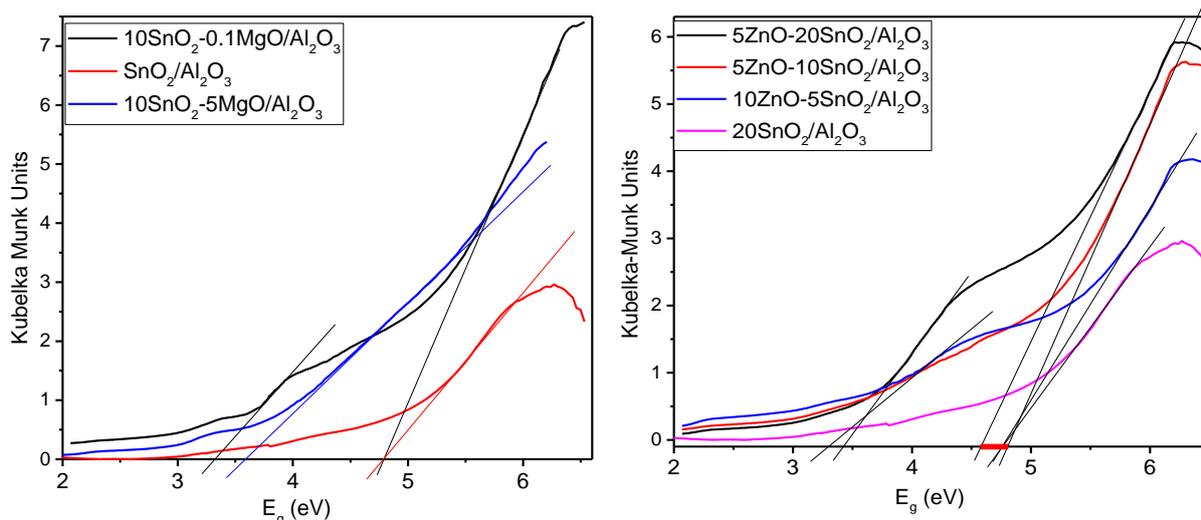
Fig. 4. Optical energy band gap from UV-*Vis* diffuse reflectance spectra of $xSnO_2–yMeO/Al_2O_3$ samples: a – MgO doped SnO_2/Al_2O_3, b - ZnO doped SnO_2/Al_2O_3.

Our previous test of $20SnO_2/Al_2O_3$ catalyst in conversion of 8% fructose solution at different temperature (160–190 °C) showed that the maximal methyl lactate (ML) yield was observed

at 180 °C [15]. Therefore, studied catalysts have been tested at this temperature, and the compositions of obtained products are presented in Table 2. Complete 100% conversion of fructose

is observed on SnO_2/Al_2O_3 and $xSnO_2$–$yZnO/Al_2O_3$ samples. Addition of MgO decreases fructose conversion to 85–82 % (Table 2). The maximal

methyl lactate yield of 71 % was obtained on $10SnO_2$–$5ZnO/Al_2O_3$ catalyst.

Table 2

**Product composition of fructose conversion on studied catalysts[a]**

Catalyst	X, %[b]	Products, mol%			
		ML	5-HMF	PADA	Others[c]
$10Sno_2$-$5ZnO/Al_2O_3$	100	71	5	23	1
$20SnO_2$-$5ZnO/Al_2O_3$	100	67	16	17	-
$5SnO_2$-$10ZnO/Al_2O_3$	100	65	0	7	29
$20SnO_2/Al_2O_3$	100	40	21	20	19
$20SnO_2/Al_2O_3$[d]	100	65	12	23	-
$10SnO_2$-$5MgO/Al_2O_3$	85	33	0	-	52
$10SnO_2$-$0.1MgO/Al_2O_3$	83	34	0	-	49
$20SnO_2$-$0.3MgO/Al_2O_3$	82	30	0	-	52

[a] Reaction conditions: 180 °C, 3.0 MPa. 4.8 % fructose solution, τ = 11 min (L = 1.5 мmmol $C_6H_{12}O_6$/ml$_{cat}$/h). [b] X – fructose conversion after 2 h. [c] Others: β–D–Fructopyranose, 5–methoxymethylfurfural, furfural, 3–hydroxy–2–butanone and no indentified products. [d] 0.03 wt% K_2CO_3 was added to initial reaction mixture.

The obtained by-products can be divided into two groups: acetals and furans. Namely, pyruvic aldehyde dimethyl acetal (PADA) is product of aldol decondensation of fructose. The fructose dehydration products are 5–hydroxyl-

methylfurfural (5–HMF), 5–methoxymethylfurfural (5–MMF) and others. As a whole, the studied transformation of fructose could be represented such Scheme:
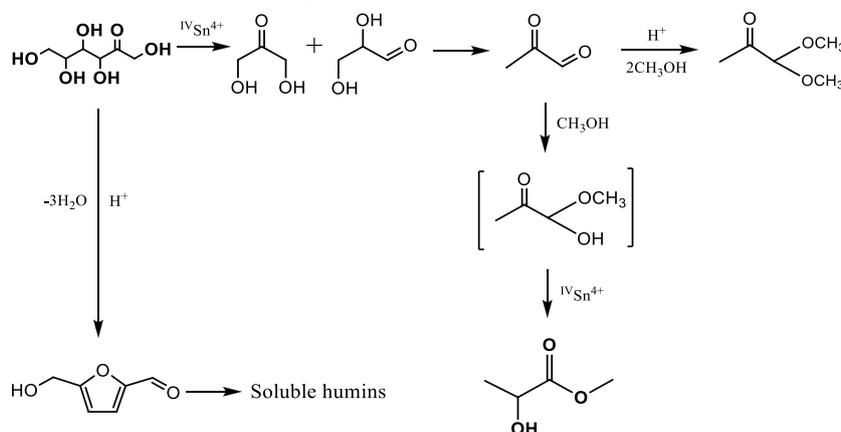
The $^{IV}Sn^{4+}$ ions in SnO_2/Al_2O_3 as Lewis acid sites promote retro-aldol fructose condensation and Cannizzaro reargerment of intermediate methyl pyvural hemiacetal into methyl lactate. But Brønsted acid sites on the SnO_2/Al_2O_3 surface catalyze the dehydration of fructose, mainly to 5–hydroxymethylfurfural.

It is well known that the main problem of catalytic transformations of C_6 carbohydrate solutions at elevated temperatures of 130–200 °C is the formation of polymeric dark brown compounds of complex structure and variable composition generally called humins [25; 26]. The

extensive formation of humins leads to decreasing selectivity and rapid deactivation of a catalyst. Many efforts have been made to suppress humin formation [26; 27]. Humin`s structure depends on reaction conditions, catalysts, etc. The article [27] hypothesizes that identified humin fragments are formed through aldol condensation between 5–HMF and its hydrated products and through condensation of furanic species.

One of the ways to solve this problem is inhibition of fructose dehydration reaction by addition of a small amount (0.03 wt.%) of potassium carbonate to reaction mixture [8; 14]. It

leads to an increase in selectivity towards methyl lactate from 40 to 65 mol% and the decrease inside 5–HMF from 21 to 12 mol% at 100% conversion of fructose (Table 2).

Another way is decreasing Brønsted acidity of a catalyst. Therefore, we have doped SnO_2/Al_2O_3 catalyst with ZnO and MgO oxides. For $10SnO_2$–$5ZnO/Al_2O_3$ catalyst methyl lactate yield achieves 71 % at 5 % content of 5-hydroxymethylfurfural (Table 2). This result is better than at K_2CO_3 adding to the fructose solution (Table 2). As seen from Table 1, with ZnO adding the content of Brønsted sites on $x$$SnO_2$–$y$MeO/$Al_2O_3$ samples is decreased, and the base sites are formed also. Using magnesia as a dopant, both fructose conversion and methyl lactate selectivity decrease (Table 2). At this, 5–HMF and PADA were not observed in ^{13}C NMR spectra.

The humin content also can be reduced at decreasing contact time of methanolic fructose solution with $x$$SnO_2$–$y$MeO/$Al_2O_3$ catalyst from 33 min to 11 min [15]. Therefore, we studied the influence of load on a catalyst on fructose conversion and methyl lactate selectivity at constant contact time of 11 minutes. For this purpose, solutions of fructose with concentrations of 1.6, 4.8, 6.4, 8.0, 9.5 wt.% in 80% methanol were prepared to provide the required values of a load on $10SnO_2$–$5ZnO/Al_2O_3$ catalyst in 0.5, 1.5, 2.0, 2.5 and 3.0 mmol $C_6H_{12}O_6/ml_{cat}$/h, respectively. As shown on Fig. 5, at increasing catalyst load from 0.5 to 3 mmol $C_6H_{12}O_6/ml_{cat}$/h at constant contact time of 11 min, conversion of fructose and selectivity for methyl lactate decreases from 100 to ~80% and from about 70 to 44% respectively. At the same time a significant increase in by–products consisting of furan derivatives is observed (Fig. 6).
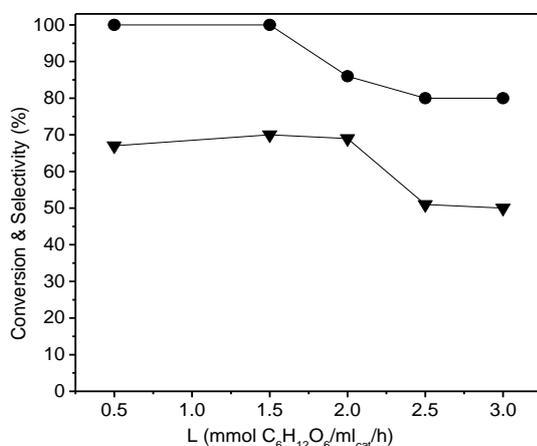
Fig. 5. Conversion (●) of fructose and selectivity (▼) for methyl lactate at different load (L) on 5ZnO–10SnO₂/Al₂O₃ (180 °C/3.0 MPa, τ = 11 min).

Thus, to ensure complete conversion of fructose the following process conditions were found: $10SnO_2$–$5ZnO/Al_2O_3$ catalyst, 180 °C, 3.0 MPa and 4.8% fructose solution in 80% methanol with load on a catalyst of 1.5 mmol $C_6H_{12}O_6/ml_{cat}$/h. At that the catalyst's productivity is 2.1 mmol ML/ml_{cat}/h. The main by-products under these conditions are PADA (23 mol%) and 5–HMF (5 mol%).
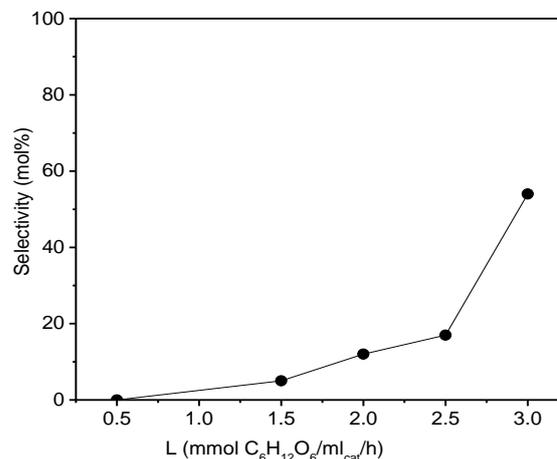
Fig. 6. The content of furan derivatives at different load on 5ZnO–10SnO₂/Al₂O₃ (180 °C/3.0 MPa, τ = 11 min).

The study of $10SnO_2$–$5ZnO/Al_2O_3$ activity from the time of stream shows that catalyst fast enough, during 6 h, loses more than 30 % of the initial activity. Regeneration of the spent catalysts carried out as follows: washing with running water at 120 °C, 1.5 MPa until the colour of the washing liquid disappears (~2–3 h). At this, the catalyst completely restored its activity after 3 cycles.

Experimental Section

A series of alumina-supported oxides was prepared by incipient wetness impregnation of commercial γ–Al_2O_3 (Ukraine) with an aqueous solution of Sn, Zn, Mg salts as describe in previous articles [14; 15]. Briefly, a fraction of 0.5–2.0 mm of γ–Al_2O_3 granules pre-treated at 250 °C (3 h) was impregnated by calculated aqueous solutions of $SnCl_4 \cdot 5H_2O$ (Aldrich, 98 %), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Sigma–Aldrich, ≥98 %) or $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich, 99 %). All supported precursors were calcined at 550 °C for 2 h. The samples were denoted as $x$$SnO_2$–$y$MeO/$Al_2O_3$, where x is SnO_2 content and y is MeO (ZnO or MgO) content expressed in wt.% in terms of Al_2O_3. Some physicochemical characteristics of obtained samples are summarized in Table 1.

XRD patterns of the catalysts were recorded with DRON-4-07 diffractometer using CuKα monochromatized radiation.

The textural parameters of the samples were calculated from the N_2 adsorption–desorption isotherms at 77 K using Quantachrome Nova 2200e Surface Area and Pore Size Analyser.

UV-*Vis* diffuse reflectance spectra were recorded using a Perkin Elmer Lambda 40 spectrophotometer equipped with a diffuse reflectance chamber and integrating sphere (Labsphere RSA-PE-20). The UV–*Vis* data were transformed into an absorbance scale by Kubelka–Munk analysis and optical E_g values determined using the Tauc method [22].

To analyze sample morphology a scanning electron microscope (SEM JSM6490 LV, JEOL, Japan) with an integrated system for electron microprobe analysis INCA Energy based on energy-dispersive and wavelength-dispersive spectrometers (EDS + WDS, OXFORD, United Kingdom) with HKL Channel system was used.

Total number of acid or base sites was determined by reverse titration using n–butylamine or benzoic acid solution in cyclohexane, respectively, with bromthymol blue as an indicator. The highest acid or base strength was examined by the Hammett indicators method using 0.1 % solution of the corresponding indicators in cyclohexane [28].

The continuous catalytic experiments were performed in a flow stainless steel reactor (d = 8 mm) with a fixed bed of catalyst (3 cm^3). 1.6–9.5 % solutions of *D*-fructose in 80 % aqueous methanol were used as the initial reaction mixtures. The experiments were carried out at temperature of 180 °C in Ar flow (8–10 cm^3 min^{-1}) at pressure of 3.0 MPa preventing liquid to gaseous phase transfer. A pump Waters 590 was used for feeding the initial reaction mixtures under fixed LHSV = 5.6 h^{-1}, that corresponds to contact time of τ = 11 min. Aliquots of the reaction products were taken after 2 h from a sampling valve placed after the reactor.

The reaction products were identified by ^{13}C NMR spectra recorded on a Bruker Avance–400 spectrometer operating at 100 MHz at ambient temperature using a database of organic compounds (SDBS, National Institute of Advanced Industrial Science and Technology, Japan, www.aist.go.jp). A test solution was placed in a 5-mm NMR tube. The ^{13}C NMR data were obtained over 256 scans with a 30° flip angle (90° = 12 μs), an acquisition time of 1.3 s, a relaxation delay of 4 s and 32 k data points. Chemical shifts are reported relative to CH_3OH and converted to δ(TMS) using δ(CH_3OH) = 50.05 ppm. Fructose conversion (%) and product selectivity (mol%) were calculated from ^{13}C NMR spectra at appropriate signal plane ratios, e.g. fructose at δ = 101.9 ppm, methyl lactate at δ = 66.9 ppm, 5–hydroxymethylfurfural at δ = 57.2 ppm, pyruvic aldehyde dimethyl acetal at δ = 54.8 ppm. Pre-recorded calibration of ^{13}C NMR spectra of mixtures of ML : 5–HMF: methanol with molar ratios in 0.5: 1: 10; 1: 1: 10 and 1: 2: 10 was performed.

Conclusion

In this study we have been prepared SnO_2–ZnO/Al_2O_3 catalysts by a simple wet impregnation method and investigated their catalytic efficiency for the continuous conversion of fructose to methyl lactate in aqueous methanol solution. Under the optimized conditions 70 % yield of methyl lactate could be achieved over 10SnO_2–5ZnO/Al_2O_3 catalyst. Namely, the use of 4.8 wt.% solution of fructose in 80 % aqueous methanol at 180 °C, 3.0 MPa under the load on a catalyst of 1.5 mmol $C_6H_{12}O_6$/ml$_{cat}$/h and contact time 11 min. Treatment of spent catalyst with water at 120 ^{0}C was found to be an efficient method of restoring its activity.

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