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Artur M. Mylin, Svitlana.I. Levytska, Mykhailo E. Sharanda, Volodymyr V. Brei

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### Short Communication

Selective conversion of dihydroxyacetone-ethanol mixture into ethyl lactate over amphoteric ZrO<sub>2</sub>–TiO<sub>2</sub> catalyst

Artur M. Mylin, Svitlana. I. Levytska, Mykhailo E. Sharanda, Volodymyr V. Brei\*

Institute for Sorption and Endoecology Problems of the National Academy of Science of Ukraine, 03164 General Naumov str.13, Kyiv, Ukraine

ABSTRACT

The conversion of dihydroxyacetone in ethanol solution into ethyl lactate over several acidic and amphoteric oxides at 100-160°C was studied. The formation of ethyl lactate with 80-90% selectivity was observed on amphoteric  $ZrO_2$ -TiO<sub>2</sub> oxide whereas hemiacetal and acetal of pyruval were the main products obtained over the acidic  $ZrO_2$ -SiO<sub>2</sub> catalyst and Amberlyst 15. Amphoteric  $ZrO_2$ -3TiO<sub>2</sub> oxide provides 89% yield of ethyl lactate at 140°C and 1.0 MPa under the feed rate of 4 mmol C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>/g<sub>cat</sub>/h.

Keywords: ethyl lactate, dihydroxyacetone, lactic acid, amphoteric catalyst

\* Corresponding author. Tel.: 38 044 4520127; fax: 38 044 4525417.

*E-mail address*: brei@ukr.net

### **1. Introduction**

Currently, ethyl lactate is quite widely used as an environmentally acceptable solvent instead of chlorinated hydrocarbons [1]. Ethyl lactate is produced from renewable raw materials - lactic acid and ethanol [2]. Recently, methyl lactate [3] and ethyl lactate [4, 5] have been synthesized from dihydroxyacetone and alcohols over solid acid catalysts. Dihydroxyacetone, obtained from accessible glycerol, is considered as a low-cost precursor for the production of lactic acid and its esters [3-10]. Dealuminated fauzasite (H-USY-6) [3], ion-exchanged Sn-montmorillonite [4], and titanium-containing silicates (TS-1, Ti-MCM-41, TiSil-HPB-60) [5] were applied as catalysts. The authors [3-5] supposed, that the acid B-sites [3, 4] or a combination of L- and mild B-sites [5] provide the selective conversion of dihydroxyacetone to the lactates. We have studied amphoteric  $ZrO_2$ -TiO<sub>2</sub> and  $ZrO_2$ -Al<sub>2</sub>O<sub>3</sub> oxides in the transformation of dihydroxyacetone ethanol mixture into ethyl lactate.

#### 2. Experimental

### 2.1. Catalyst preparation and characterization

Sulforesin Amberlyst 15, acidic ZrO<sub>2</sub>-SiO<sub>2</sub> oxide prepared according to [11], amphoteric ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> oxide obtained by the sol-gel method [12], and ZrO<sub>2</sub>-TiO<sub>2</sub> mixed oxide were tested as catalysts. The ZrO<sub>2</sub>-TiO<sub>2</sub> samples with different molar ratios ( $0.17 \le \text{Ti/Zr} \le 6$ ) were prepared by a co-precipitated sol-gel method using ZrOCl<sub>2</sub>•8H<sub>2</sub>O and TiCl<sub>4</sub>. Calculated quantities of ZrOCl<sub>2</sub>-water solution (209 Zr mg/g) and ~ 2.2 M TiCl<sub>4</sub> water solution (103 Ti mg/g) were mixed at stirring. Excess of hydrochloric acid was neutralized with ammonia solution (pH ~ 1.5). Then, stoichiometrical quantity of urea was added and the solution was aged at 110°C for 24 h. The obtained gel was washed and dried at 120°C. Finally, the samples were heated to 450°C for 2 h at 2°/min. Sample codes ZrTi2 and 2ZrTi mean that Ti<sup>4+</sup> content in the catalysts is two times higher or less than Zr<sup>4+</sup> content correspondingly.

Individual  $TiO_2$  and  $ZrO_2$  oxides were prepared from  $ZrOCl_2$  and  $TiCl_4$  water solutions in the same way as  $ZrO_2$ -TiO<sub>2</sub> samples.

The textural parameters of the samples were calculated from the adsorption-desorption isotherms of nitrogen using the BET method (Quantachrome Nova 2200e Surface Area and Pore Size Analyser). XRD patterns of samples were recorded with DRON-4-07 diffractometer ( $CuK_{\alpha}$  radiation).

### Table 1. Textural parameters of prepared oxides

The acidic and basic site content in ZrTi3 sample was determined by the inverse titration in the presence of bromthymol blue indicator using n-butyl amine and 2,4-dinitrophenol correspondingly. The strength of these sites was measured employing the standard indicator method [13].

The IR spectra of pyridine and pyrrole adsorbed on ZrTi3 sample were recorded according to the following procedure. The milled oxide was pressed into thin (10-12 mg/cm<sup>2</sup>) pellets. A pellet was placed into a heated quartz cuvette with KBr windows. After vacuumization of the sample at 350°C, the adsorption of pyridine or pyrrole (Sigma Aldrich, 99%) was performed at room temperature. The IR spectra were recorded (Specord IR-75 spectrophotometer) after repeated vacuumization of the sample at 100-150°C.

The activity of ZrO<sub>2</sub>-TiO<sub>2</sub> samples was determined in a test TPR transformation reaction of 2-methyl-3-butyne-2-ol (MBOH) according to the procedure described in [14].

### 2.2. Catalytic experiments

8 wt.% solution of dihydroxyacetone (>98%, Merk) in anhydrous ethanol was used as a reaction mixture. The experiments were carried out in a rotated autoclave (60 rpm) at 100-160°C for 2 h. Usually, 0.5 g of dihydroxyacetone, 5.6 g of ethanol and 0.3 g (5wt.%) of a catalyst were placed into a 25 ml teflon can.

The process was also studied in a flow regime using a fixed bed reactor. As rule,  $2 \text{ cm}^3$  of a granulated (0.5–1 mm) catalyst was placed into a steel reactor (d=8 mm). The catalyst was

trained at 120°C for 1 h in Ar flow. Feed rate was varied in 2–10 mmol  $C_3H_6O_3/g_{cat}/h$  interval (LHSV = 2.2–0.9 h<sup>-1</sup>) using a Waters-590 pump. The experiments were performed in Ar flow (15 cm<sup>3</sup>/min) at 1.0 MPa preventing liquid to gaseous phase transfer.

The reaction products were analysed using <sup>13</sup>C NMR spectroscopy (Bruker Avance 400) and gas chromatography (Chrom-5 with 50 m capillary column) methods. The conversion values and selectivity (mol %) were calculated from <sup>13</sup>C NMR spectra.

### 3. Results and discussion

The transformation of 1,3-dihydroxy-2-propanone into ethyl lactate, taking into account the properties of hydroxy-aldehydes and hydroxy-ketones [15], could be described as follows. Firstly, Lobry de Bruyn - Van Ekenstein rearrangement proceeds:



In acidic medium, the equilibrium shifts to gliceral formation. Further, gliceral dehydration occurs with the formation of pyruval+:



Catalyst acidic sites catalyze this stage also. Pyruval is a key semiproduct. Methyl glyoxal easily reacts with ethanol to form hemiacetal:



Hemiacetal can react with ethanol to form acetal in acidic medium:



However, the acetal formation is not a desirable process in our case. Alkali medium promotes the isomerization of hemiacetal to ethyl lactate:



The obtained results confirm this scheme of dihydroxyacetone transformation. The analysis of products obtained on typical solid acids Amberlyst 15 and  $ZrO_2$ -SiO<sub>2</sub> (Table 1) show that at 100% dihydroxyacetone conversion the main products are acetal and hemiacetal (Table 2). Individual TiO<sub>2</sub> and ZrO<sub>2</sub> oxides (Table 1) also catalyze the transformation of dihydroxyacetone into mainly acetals (Table 2). We have placed the product obtained on the acid catalyst with 12% ethyl lactate content into an autoclave and added typical base catalyst – Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub> hydrotalcite. After the reaction at 100°C, ethyl lactate content increased to 40% with corresponding decrease of the hemiacetal content. Thus, an amphoteric oxide with acid and base surface sites can catalyze selective the transformation of dihydroxyaxetone-ethanol mixture into ethyl lactate.

#### Table 2. Effect of catalyst on ethyl lactate synthesis

The mixed  $ZrO_2$ -TiO<sub>2</sub> and  $ZrO_2$ -Al<sub>2</sub>O<sub>3</sub> oxides were used as amphoteric catalysts. The mixed oxides possess an ability to catalyze both dehydration of 2-methyl-3-butyn-2-ol (MBOH) test substance to methyl-3-butene-1-in (m/e=66) over the acidic sites and the destruction of MBOH to acetylene (m/e=26) and acetone (m/e=58) on the base sites. It has been determined earlier for the mixed  $ZrO_2$ -Al<sub>2</sub>O<sub>3</sub> oxides [12]. The same situation is observed for the mixed  $ZrO_2$ -TiO<sub>2</sub> oxides with Zr/Ti < 1 (Fig. 1). However, the dehydration occurs at lower temperatures then

MBOH destruction (Fig. 1). Usually, solid acids catalyze dehydration of MBOH, and solid bases participate in MBOH destruction only.

Fig. 1. TPR profiles of 3-methyl-3-butene-1-in (66 a.u.m. ●), acetone (58 a.u.m. ▼) and acetylene (26 a.u.m. ■) formation from 2-methyl-3-butyn-2-ol adsorbed on ZrTi3.

The presence of acid and base sites on ZrTi3 surface is confirmed by the IR spectra of absorbed pyridine and pyrrole (Fig. 2). Namely, the bands at 1445, 1490 cm<sup>-1</sup> and at 1540 cm<sup>-1</sup> (Fig. 2 a) correspond to pyridine adsorbed on acidic L- and B-sites [13]. These acidic sites are weak because the absorbed pyridine can be removed after evacuation at 150°C (Fig. 2 a).

Fig. 2. IR spectra of pyridine (a) and pyrrole (b) adsorbed on ZrTi3; a- after evacuation at  $25^{\circ}C$  (1),  $100^{\circ}C$  (2) and  $150^{\circ}C$  (3); b - thin film of liquid (1), adsorbed on ZrTi3 (2).

In IR spectrum of pyrrole absorbed on ZrTi3, a board band  $v_{N-H}$  at 3410 cm<sup>-1</sup> is observed (Fig. 2 b). This band is shifted by 10 cm<sup>-1</sup> comparing to liquid pyrrole (3420 cm<sup>-1</sup>, Fig. 2 b) because of the absorbed pyrrole proton interaction with base sites on the ZrTi3 surface. Such a small shift corresponds to weak base sites [16].

Employment of amphoteric  $ZrO_2$ -TiO<sub>2</sub> and  $ZrO_2$ -Al<sub>2</sub>O<sub>3</sub> oxides resulted in the ethyl lactate content increase in the reaction products (Table 2). The best results were obtained on catalysts with metal ratio Ti<sup>4+</sup>/Zr<sup>4+</sup>=3 (ZrTi3 sample). This sample has predominantly amorphous structure, but weak anatase signals are registrated in the XRD pattern (Table 1). The weak-acid sites (H<sub>0</sub> ≥+1.5; 0.7 mmol/g) and weak-base sites (H<sub>-</sub> ≤ + 7.2; 0.5 mmol/g) were determined on the catalyst surface using an indicator method.

In the <sup>13</sup>C NMR spectrum of the products obtained on ZrTi3 at 120°C signals from both ethyl hemiacetal of pyruval (202, 95, 63, 25, 15 ppm.), and ethyl lactate (176, (175), 67, 62, 20, 14 ppm.) were observed. Ethyl lactate content, obtained at different temperatures, passes over the

maximum at 140°C (Fig. 3). At higher temperature, dark-colored products are formed as result of aldol condensation of glyceral with dihydroxyacetone [15]. The ethyl lactate yield of 81% was observed after 2 h reaction in a rotated autoclave at 140°C. For comparison, 48% and 93% ethyl lactate yields were obtained using TiSil-HPB-60 (autoclave, 105°C, 6 h) [5] and Sn-montmorillonite (autoclave, 150°C, 15 h) [4] correspondingly while processing 3% solutions of dihydroxyacetone in ethanol.

Fig. 3. Conversion (X) of 1,3-dihydroxy-2-propanone and selectivity (S) towards ethyl lactate on ZrTi3 at different temperatures (rotated autoclave).

The results of experiments performed in a flow reactor at 140°C are presented in Table 3. At 100% conversion of dihydroxyacetone, raising its feed rate from 2 to 10 mmol  $C_3H_6O_3/g_{cat}/h$  decreases the selectivity towards ethyl lactate from 90% to 70%. Ethyl lactate high yield (90%) is observed at the load on a catalyst of up to 4 mmol  $C_3H_6O_3/g_{cat}/h$  (Table 3). The ZrTi3 catalyst ensures the ethyl lactate space time yield in 3.6 mmol/g<sub>cat</sub>/h at 89% selectivity. The comparison of the ethyl lactate yield values for the rotated autoclave (Table 2) with that for the flow conditions (Table 3) shows that a higher yield could be achieved under the flow regime where the liquid reaction mixture contact time with a catalyst is 0.25–0.5 h, being 2 h for the autoclave.

Table 3. Content of products (mol%) obtained at 140°C in flow reactor over ZrTi3 catalyst

Hemiacetal is the main by-product obtained under the flow conditions (Table 3). Water is also formed according to the gross-reaction

$$C_3H_6O_3 + C_2H_5OH = C_5H_{10}O_3 + H_2O_3$$

and reacts with methyl glyoxal forming lactic acid as a co-product (Tables 2, 3). It should be pointed out that the content of lactic acid increased when we employed 92% ethanol instead of anhydrous one (Table 3).

The ZrTi3 catalyst sustained 100% conversion of dihydroxyacetone during 7 h. However, ethyl lactate selectivity decreased by 15% over the time.

#### 4. Conclusions

The transformation of dihydroxyacetone into ethyl lactate in ethanol solution over acidic and amphoteric catalysts in batch and flow regimes has been studied. It was shown that the selective formation of ethyl lactate occurs on amphoteric  $ZrO_2$ -TiO<sub>2</sub> and  $ZrO_2$ -Al<sub>2</sub>O<sub>3</sub> oxides whereas ethyl hemiacetal and acetal of pyruvic aldehyde are the main products obtained over acidic Amberlyst-15 and  $ZrO_2$ -SiO<sub>2</sub> catalysts. The continuos process is preferable for ethyl lactate synthesis than the batch process. 90 % selectivity towards ethyl lactate has been achieved employing  $ZrO_2$ -TiO<sub>2</sub> catalyst under LHSV = 2.2–4.4 h<sup>-1</sup> at 140°C and 1.0 MPa.

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### **Figures and Tables captions**

**Fig. 1**. TPR profiles of 3-methyl-3-butene-1-in (66 a.u.m. ●), acetone (58 a.u.m. ▼) and acetylene (26 a.u.m. ■) formation from 2-methyl-3-butyn-2-ol adsorbed on ZrTi3.

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**Fig. 3.** Conversion (X) of 1,3-dihydroxy-2-propanone and selectivity (S) towards ethyl lactate on ZrTi3 at different temperatures (rotated autoclave).

### Table 1

Textural parameters of prepared oxides.

### Table 2

Effect of catalyst on ethyl lactate synthesis\*.

### Table 3

Content of products (mol%) obtained at 140°C in flow reactor on ZrTi3 catalyst\*.



a

Fig. 1

b

Fig. 3



Sample	XRD	BET surface area, m <sup>2</sup> /g	Total pore volume, cm <sup>3</sup> /g	Average pore diameter, nm
ZrTi6	am. $+$ anat. $*$	170	0.35	8.3
ZrTi3	am. + anat.	260	0.35	5.4
ZrTi2	am. + anat.	295	0.26	3.5
ZrTi	am.	300	0.26	3.4
2ZrTi	am.	270	0.23	3.4
ZrA12.5	am.	310	0.37	4.9
ZrSi2	am.	315	0.44	5.6
$ZrO_2$	m + t	30	0.06	8.3
TiO <sub>2</sub>	anat.	150	0.53	14.2
Al <sub>2</sub> O <sub>3</sub> **	γ	280	0.82	10.7

### Table 1

\* am. - amorphous, anat. - anatase , m- monoclinic, t- tetragonal phase

\*\* industrial product (Alvigo, Ukraine)

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Catalyst	T, ℃	X, %	Selectivity, mol %				
		-	EL	HAc	Ac	LA	NP
ZrTi6	100	85	7	83	10	-	-
ZrTi6	120	100	23	55	11	11	-
ZrTi6	130	100	33	51	6	10	-
ZrTi6	150	100	25	52	13	9	1
ZrTi3	100	84	14	73	13	-	-
ZrTi3	120	100	38	40	9	13	-
ZrTi3	130	100	61	18	6	15	-
ZrTi3	140	100	81	4	5	10	-
ZrTi3	150	100	72	6	9	11	2
ZrTi3	160	100	69	10	7	11	3
ZrTi2	130	98	46	31	9	14	-
ZrTi	100	65	13	67	12	5	3
2ZrTi	100	49	8	65	16	3	8
ZrAl2.5	100	52	11	38	42	-	9
ZrAl2.5	130	82	44	30	16	-	10
ZrSi2	100	69	12	35	45	-	8
ZrSi2	130	96	39	16	40	5	-
ZrSi2	140	100	42	4	45	3	6
Amberlyst15	100	100	-	11	84	-	5
$ZrO_2$	130	66	7	57	26	5	5
TiO <sub>2</sub>	130	100	27	47	12	14	-
Al <sub>2</sub> O <sub>3</sub>	100	19	29	71	-	-	-

### Table 2

Effect of catalyst on ethyl lactate synthesis\*.

\* reaction conditions: rotated autoclave; *X*, conversion of dihydroxyacetone; EL, ethyl lactate;

HAc and Ac, hemiacetal and acetal of pyruvaldehyde; LA, lactic acid; NP, non-specified products.

### Table 3

Load on a catalyst,	<b>FI</b>	II A		ТА
mmol C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> /g <sub>cat</sub> /h	EL	HAC	Ac	LA
2	90	10	-	-
4	89	11	-	-
6	85	7	4	4
8	78	10	4	8
10	70	20	3	7
8**	56	8	6	30
* 100% conversion of dihydroxyac	etone			
** 20% dihydroxyacetone solution	in 92% watered	ethanol		
		S		
$\mathcal{Q}$				
X				

### 1 Graphical abstract



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#### Highlights

- Ethyl lactate can be obtained with high selectivity from dihydroxyacetone in ethanol solution over ٠ amphoteric ZrO<sub>2</sub>-TiO<sub>2</sub> catalyst.
- 90% ethyl lactate yield was obtained at 140°C and 1.0 MPa. •
- Lactic acid is a co-product. •

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