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Short Communication

Selective conversion of dihydroxyacetone–ethanol mixture into ethyl lactate over amphoteric ZrO_2–TiO_2 catalyst

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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_2 oxide whereas hemiacetal and acetal of pyruval were the main products obtained over the acidic ZrO_2–SiO_2 catalyst and Amberlyst 15. Amphoteric ZrO_2–$3TiO_2$ oxide provides 89% yield of ethyl lactate at 140 °C and 1.0 MPa under the feed rate of 4 mmol $C_3H_6O_3/g_{cat}/h$.

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] provides the selective conversion of dihydroxyacetone to the lactates. We have studied amphoteric ZrO_2–TiO_2 and ZrO_2–Al_2O_3 oxides in the transformation of dihydroxyacetone–ethanol mixture into ethyl lactate.

2. Experimental

2.1. Catalyst preparation and characterization

Sulforesin Amberlyst 15 and acidic ZrO_2–SiO_2 oxide prepared according to [11], amphoteric ZrO_2–Al_2O_3 oxide obtained by the sol–gel method [12], and ZrO_2–TiO_2 mixed oxide were tested as catalysts. The ZrO_2–TiO_2 samples with different molar ratios ($0.17 \leq Ti/Zr \leq 6$) were prepared by a co-precipitated sol–gel method using $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$. Calculated quantities of $ZrOCl_2$-water solution (209 Zr mg/g) and ~2.2 M $TiCl_4$ 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 with rate 2°/min to 450 °C, 2 h. Sample codes ZrTi2 and 2ZrTi mean that Ti^{4+} content in the catalysts is two times higher or less than Zr^{4+} content, respectively.

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_2 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_α radiation).

The acidic and basic site content in ZrTi3 sample was determined by the inverse titration in the presence of bromothymol blue indicator using n-butyl amine and 2,4-dinitrophenol, respectively. 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^2) 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.

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The activity of ZrO_2–TiO_2 samples was determined in a TPR test reaction of 2-methyl-3-butyne-2-ol (MBOH) transformation according to the procedure described in [14].

2.2. Catalytic experiments

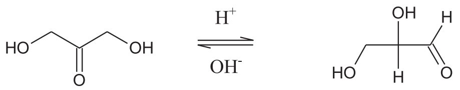
8 wt.% solution of dihydroxyacetone (>98%, Merk) in anhydrous ethanol was used as a reaction mixture. The experiments were carried out in a rotated autoclave (60 rpm) at 100–160 °C for 2 h. Usually, 0.5 g of dihydroxyacetone, 5.6 g of ethanol and 0.3 g (5 wt.%) of a catalyst were placed into a 25 ml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

The process was also studied in a flow regime using a fixed bed reactor. As rule, 2 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^{-1}) using a Waters-590 pump. The experiments were performed in Ar flow (15 cm^3/min) at 1.0 MPa preventing liquid to gaseous phase transfer.

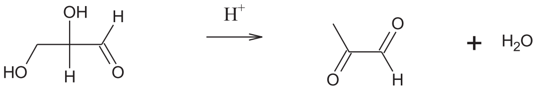
The reaction products were analyzed using ^{13}C NMR spectroscopy (Bruker Avance 400) and gas chromatography (Chrom-5 with 50 m capillary column) methods. The conversion values and selectivity (mol %) were calculated from ^{13}C NMR spectra.

3. Results and discussion

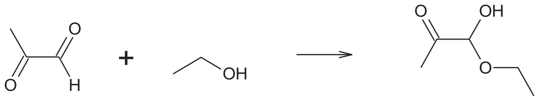
The transformation of 1,3-dihydroxy-2-propanone into ethyl lactate, taking into account the properties of hydroxy-aldehydes and hydroxyketones [15], could be described as follows. Firstly, Lobry de Bruyn–Van Ekenstein rearrangement proceeds:



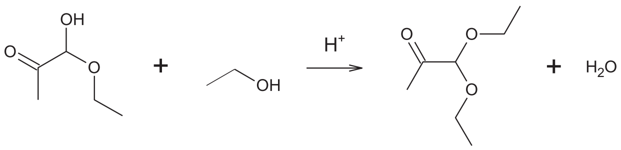
In acidic medium, the equilibrium shifts to gliceral formation. Further, gliceral dehydration occurs with the formation of pyruval:



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:

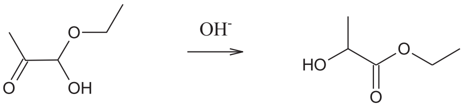


Table 1
Textural parameters of prepared oxides.

Sample	XRD	BET surface area, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm
ZrT 6	am. + anat.[a]	170	0.35	8.3
ZrT 3	am. + anat.	260	0.35	5.4
ZrT 2	am. + anat.	295	0.26	3.5
ZrT	am.	300	0.26	3.4
2ZrT	am.	270	0.23	3.4
ZrAl2.5	am.	310	0.37	4.9
ZrSi2	am.	315	0.44	5.6
ZrO_2	m + t	30	0.06	8.3
TiO_2	anat.	150	0.53	14.2
Al_2O_3[b]	γ	280	0.82	10.7

[a] am. — amorphous, anat. — anatase, m — monoclinic, and t — tetragonal phase.
[b] Industrial product (Alvigo, Ukraine).

The obtained results confirm this scheme of dihydroxyacetone transformation. The analysis of products obtained on typical solid acids Amberlyst 15 and ZrO_2–SiO_2 (Table 1) show that at 100% dihydroxyacetone conversion the main products are acetal and hemiacetal (Table 2). Individual TiO_2 and ZrO_2 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 — $Mg_6Al_2(OH)_{16}CO_3$ 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 is required for selective transformation of dihydroxyacetone–ethanol mixture into ethyl lactate.

The mixed ZrO_2–TiO_2 and ZrO_2–Al_2O_3 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_2O_3 oxides [12]. The same situation is observed for the mixed ZrO_2–TiO_2 oxides with Zr/Ti < 1 (Fig. 1). The dehydration occurs at lower temperatures than MBOH destruction (Fig. 1). Usually, solid acids catalyze dehydration of MBOH, and solid bases participate in MBOH destruction only.

Table 2
Effect of catalyst on ethyl lactate synthesis.[a]

Catalyst	T, °C	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
ZrT 2	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
Amberlyst 15	100	100	–	11	84	–	5
ZrO_2	130	66	7	57	26	5	5
TiO_2	130	100	27	47	12	14	–
Al_2O_3	100	19	29	71	–	–	–

[a] Reaction conditions: rotated autoclave; X, conversion of dihydroxyacetone; EL, ethyl lactate; HAc and Ac, hemiacetal and acetal of pyruvaldehyde; LA, lactic acid; NP, nonspecified products.