Conversion of Fructose into Ethyl Lactate

Subjects: Physical Chemistry

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The study is directed to the search of a simple effective catalyst for ethyl lactate obtained from fructose as renewable raw material. A series of SnO_2-containing oxides prepared by impregnation of alumina were characterized by several techniques in order to determine their textural and acid-base properties. The transformation of a 13% fructose solution in 98% ethanol over SnO_2/Al_2O_3 catalysts using autoclave rotated with 60 rpm at 160°C for 3 h was studied. It was found that doping SnO_2/Al_2O_3 samples with ZnO improves selectivity towards ethyl lactate. The supported SnO_2-ZnO/Al_2O_3 catalyst provides 100% fructose conversion with 55% yield of ethyl lactate at 160°C. A possible scheme of fructose transformation into ethyl lactate on L-acid $^{IV}Sn^{4+}$ sites is discussed.

Ethyl lactate obtained from lactic acid and ethanol is used mainly as green solvent, as well as in the food, cosmetic and pharmaceutical industries [1][2][3] . At present, ethyl lactate is considered as material for synthesis of monomeric lactide and ethyl acrylate [3]. Therefore, considerable attention is paid to the search for alternative methods for its preparation [4–8]. Some progress was made in the synthesis of alkyl lactates from dihydroxyacetone [4][5][6] and glycerol [7]. Holm with co-workers [8] found in 2010 that Sn-Beta zeolite directly catalyzes the transformation of mono- and disaccharides in methanol (0.1mmol/l) into methyl lactate at 160°C. However, the preparation of Sn-zeolites is rather complicated procedure. In this work, we have used several Sn-containing oxides obtained by a simple impregnation method as catalysts of one-pot conversion of fructose into ethyl lactate.

Alumina-supported Sn-catalysts containing 10-25 wt.% SnO_2 were prepared by incipient wetness impregnation of commercial γ-Al_2O_3 (Alvigo) with calculated aqueous solutions of $SnCl_4 \cdot 5H_2O$ (Aldrich, 98%). All synthesized samples were analyzed by several techniques in order to study their chemical, structural, textural and acid properties. The structural analysis by XRD indicates high dispersion of tin oxide on the alumina surface. Small peaks corresponding to tetragonal SnO_2 for $25SnO_2/Al_2O_3$ sample were detected. According to the titration results, γ-Al_2O_3 is weakly acid oxide with $H_0 \leq +3.3$. The addition of SnO_2 to alumina surface increases the strength of acid sites of supported SnO_2/Al_2O_3 samples to $H_0 \leq +1.5$. Also, at increasing SnO_2 content from 10 to 25 wt.%, the concentration of acid sites raises from 1.2 to 1.8 mmol/g. According to the UV-*Vis* data, $^{IV}Sn^{4+}$ or $^{VI}Sn^{4+}$ ions with different coordination are present in studied samples. So, UV−*Vis* spectrum of $25SnO_2/Al_2O_3$ sample shows a broad line around 260 nm, which is attributed to octahedral $^{VI}Sn^{4+}$ ions in SnO_2 phase. At the same time for $10SnO_2/Al_2O_3$ and $20SnO_2/Al_2O_3$ samples the maximum intensity is observed at 200 nm that attributed to isolated tetrahedral $^{IV}Sn^{4+}$ ions.

For catalytic experiments, 13 wt.% solution of D-fructose in anhydrous ethanol was used as a reaction mixture. The experiments were carried out in a rotated autoclave (60 rpm) at 160°C for 3 h. The formation of insoluble products at these conditions was not observed. The reaction products were analyzed using ^{13}C NMR spectroscopy (Bruker Avance 400, Karlsruhe, *Germany*).

Target ethyl lactate is formed with 34–53% selectivity at 95–100% fructose conversion on prepared SnO_2/Al_2O_3 samples. However, the significant amount of 5-hydroxymethylfurfural is also formed. The addition of a small amount (0.03 wt.%) of potassium carbonate to the fructose–ethanol initial mixture leads to increasing of ethyl lactate yield due to inhibition of hexose dehydration. Also we have doped SnO_2/Al_2O_3 with ZnO oxide for decreasing acidity of the catalyst. The highest acid strength of this catalyst decreases from +1.5 to +3.3. At that, in comparison with $10SnO_2/Al_2O_3$, for $10SnO_2$–$5ZnO/Al_2O_3$ sample the weak base sites with $H_0=+7.2$ at total content — 0.6 mmol/g were detected. As a result, ethyl lactate yield increased to 56% with significant decrease of 5-HMF content.

The obtained results show that acid $^{IV}Sn^{4+}$ L-sites catalyze aldol decondensation of fructose as the first stage of the ethyl lactate formation as well as initiate the isomerization of hemiacetal into ethyl lactate.

[1][2][3][4][5][6][7][8]

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Keywords

fructose;ethyl lactate;SnO2/Al2O3 catalyst