

Synthesis of acetic acid from ethanol–water mixture over Cu/ZnO–ZrO₂–Al₂O₃ catalyst

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ARTICLE INFO

Article history:

Received 14 November 2012

Received in revised form 28 March 2013

Accepted 29 March 2013

Available online xxx

Keywords:

Ethanol

Acetic acid

Cu-containing catalyst

ABSTRACT

It was shown that acetic acid can be obtained from aqueous ethanol (6–40 mol%) solutions over Cu/ZnO–ZrO₂–Al₂O₃ catalyst at 250–320 °C and atmospheric pressure. Selectivity of 80–90% and space-time yield of acetic acid up to 9 mmol_{g_{cat}}⁻¹ h⁻¹ at 60–80% ethanol conversion were obtained while processing 14–37 mol% aqueous ethanol solutions. Hydrogen was generated in an amount ~2 moles per 1 mole of acetic acid as a co-product.

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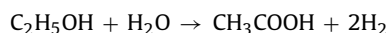
1. Introduction

Acetic acid is a large-scale chemical product (15.3 million tons in 2010 year [1]). Vinyl acetate and acetic anhydride producers are the main consumers for the product [2]. Currently, acetic acid is mainly produced via methanol carbonylation at 180–220 °C and 3–4 MPa using a methyl-iodine-promoted Rh catalyst (Monsanto process [3]). Other prospective processes such as methyl formate isomerization and vapor phase oxidation of ethylene were described recently [2].

During the last decade, Sato with colleagues [4,5] noticed the formation of acetic acid as a by-product of the conversion of ethanol into ethyl acetate over the Cu-containing catalyst. It was supposed that ethyl acetate hydrolysis was the reason for the acetic acid formation since the content of acid was proportional to water concentration in the studied range of 0.5–15 wt% [5]. We have repeated the direct synthesis of ethyl acetate from dried ethanol over Cu/ZnO–ZrO₂–Al₂O₃ catalyst with different Cu-content [6]. In the present work, data on the conversion of ethanol–water solutions to acetic acid over Cu/ZnO–ZrO₂–Al₂O₃ as well as over Cu/ZnO, Cu/ZrO₂ and Cu/Al₂O₃ catalysts are presented.

This route of acetic acid production from aqueous ethanol solutions [7] could be interesting to industry because today ethanol, as a biobased platform chemical [8], is a large renewable

feedstock (84.5 billion liters in 2011 year [9]) for liquid fuels and commodity chemicals. Also, hydrogen is formed as a valuable co-product according to the gross-reaction:



In contrast to microbiological or catalytic oxidative processes of acetic acid manufacturing, two moles of hydrogen on one mole of consumed ethanol are generated in this method.

2. Experimental

2.1. Preparation of catalysts

The bifunctional Cu/ZnO–ZrO₂–Al₂O₃ catalyst with atomic ratio of Cu:Zn:Zr:Al = 6:1:2:4, which showed the best selectivity towards ethyl acetate [6], was tested. Cu/ZnO, Cu/ZrO₂ and Cu/Al₂O₃ samples (Cu:Me = 3:2) prepared by the co-precipitation technique were tested also. Corresponding quantities of Cu(NO₃)₂·3H₂O, and, if necessary, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O or ZrO(NO₃)₂·5H₂O were dissolved in distilled water and stoichiometric quantity of 3 N NaOH solution was added under stirring for complete precipitation of metal hydroxides. The precipitate was aged for 20 h at room temperature and then filtered, washed and granulated. The granules were dried at 120 °C and finally calcined in air at 350 °C for 4 h. According to the XRF analysis (X-ray fluorescence spectrometer ElvaX, Ukraine), residual Na content in the samples was in the range of 0.1–0.05 mol%.

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Table 1
The textural parameters of studied catalysts.

Sample	SA (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	R _p , nm
Cu/ZnO	7	–	–
Cu/ZrO ₂	75	0.1	2.6
Cu/Al ₂ O ₃	160	0.3	7.5
Cu/ZnO–ZrO ₂ –Al ₂ O ₃	180	0.26	3.2

SA, specific surface area measured by BET; V_p, pore volume; R_p, average pore radius.

2.2. Characterization

Surface area, pore size distribution and pore volume were measured by N₂ adsorption at 77 K using Nova 2200e Surface Area and Pore Size Analyzer. Before the analysis, the samples were treated at 120 °C under vacuum for 0.5 h (Table 1).

The TPR spectra of ethanol and 2-methyl-3-butyn-2-ol (MBOH) transformation over the studied catalysts were recorded using a monopole mass-spectrometer MX7304A (Ukraine) according to the procedure described in [10]. Usually, 8–15 mg of a preliminarily reduced catalyst was evacuated at 300 °C, cooled to 30 °C, and then alcohol was adsorbed. After vacuumization of the sample, the TPR mass-spectra (sweep rate 2 a.u.m./s) were recorded at heat rate of 8 °C/min.

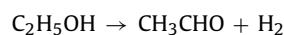
2.3. Catalytic experiments

Catalytic experiments were performed in a down-flow stainless steel reactor with a fixed bed of catalyst at 250–320 °C under atmospheric pressure. Prior to the reaction, the sieved fraction (0.5–2 mm) of a catalyst (3 cm³, 3.1 g) was reduced in hydrogen flow (50 ml min⁻¹) at 180–200 °C for 2.5 h. After the reduction, initially black catalyst became copper-brown.

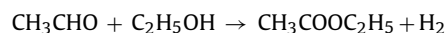
Ethanol–water mixture was introduced (0.6–12 ml h⁻¹) into the reactor using Water Systems model 590 pump. The ethanol content in water was varied from 10 to 60 mol%. The LHSV values were varied from 0.4 to 2.0 h⁻¹. The experiments were performed at 250–320 °C. Hydrogen formed in the reaction functioned as the carrier gas. Reaction products were entrapped in a condenser at 0 °C and analyzed using gas chromatography (Chrom-5 with 50 m capillary column) and ¹³C NMR spectroscopy (Bruker Avance 400) methods. Selectivity to acetic acid (mol%) was calculated as a ratio of acetic acid content (in moles) to the sum of all products content with allowance that one mole of aldol condensation by-products (butanol, methyl ethyl ketone) is formed from two moles of ethanol.

3. Results and discussion

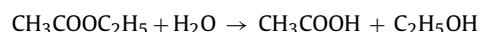
The assumed pathway for acetic acid formation includes three stages. Firstly, ethanol is dehydrogenated into acetaldehyde over Cu-sites:



Then adsorbed acetaldehyde and ethanol react on the oxide surface forming ethyl acetate [5]:



Final stage is hydrolysis of the formed ethyl acetate with participation of the base sites of the catalyst that gives one mole of acetic acid and recovers half of ethanol involved in this cycle:



So, the conversion of ethanol per one cycle cannot exceed 50 mol%.

The calculated equilibrium component contents in “ethanol–water–acetaldehyde–ethyl acetate–acetic acid–hydrogen” mixture

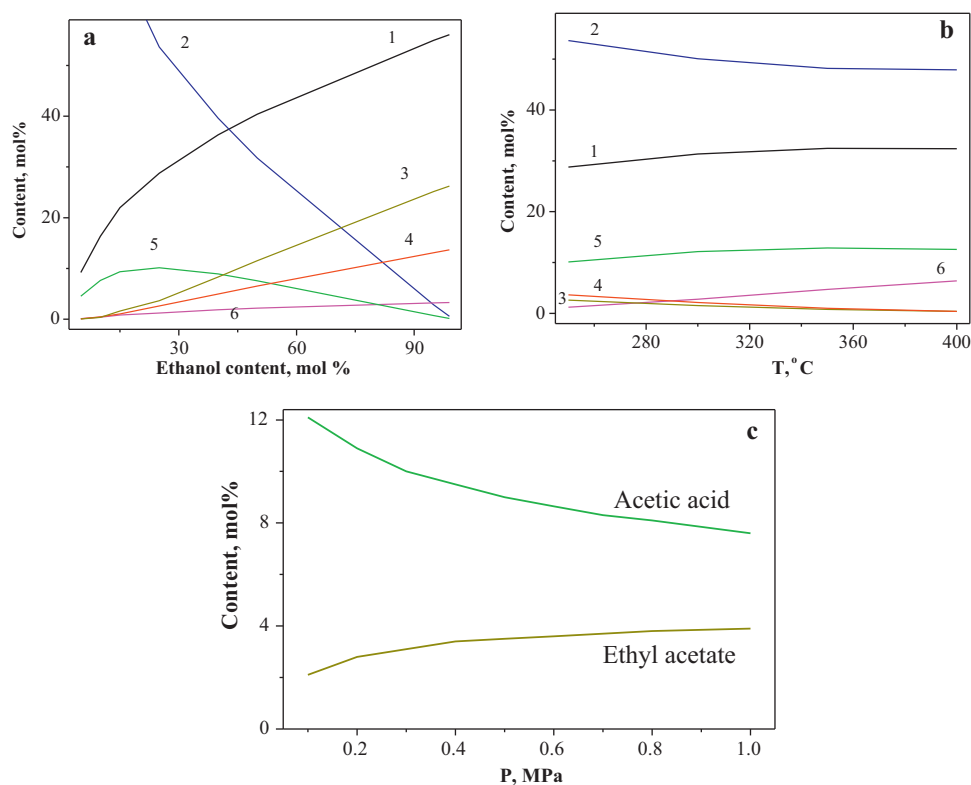


Fig. 1. Equilibrium content of components in the mixture “ethanol–water–acetaldehyde–ethyl acetate–acetic acid–hydrogen”: a – at different initial ethanol concentration (250 °C, 0.1 MPa); b – at different temperature; c – at different pressure (at 25 mol% ethanol concentration). 1 – hydrogen (–), 2 – water (–), 3 – ethyl acetate (–), 4 – ethanol (–), 5 – acetic acid (–), 6 – acetaldehyde (–).

Table 2
Effect of catalyst on the synthesis of acetic acid from 37 mol% ethanol–water mixture.

Catalyst	X (%)	Selectivity to products (%)				Yield AcOH (%)
		AcOH	AcOEt	AcH	AID	
Cu/ZnO	51	51.5	3.4	39.8	5.3	26.3
Cu/ZrO ₂	47	8.4	18.8	44.9	27.9	3.9
Cu/Al ₂ O ₃	70	26.6	20.0	27.6	25.8	18.6
Cu/ZnO–ZrO ₂ –Al ₂ O ₃	64	54.8	13.9	14.2	17.1	35.1

X, conversion of ethanol; reaction conditions: 300 °C; LHSV = 1.0 h⁻¹. AcOH, acetic acid; EtOH, ethanol; AcOEt, ethyl acetate; AcH, acetic aldehyde; AID, aldol derivatives (methyl ethyl ketone, butanol).

at different temperature and alcohol concentration are presented in Fig. 1. The highest content of acetic acid in the reaction products mixture may reach 13 mol%. It corresponds to 33 wt% concentration of acetic acid and it may be expected at initial ethanol concentration of 25 mol%. At that point, (ethanol):(acetic acid):(ethyl acetate) molar ratio should be equal to 0.4:1:0.3. The acetic acid content weakly depends on temperature with the smooth maximum at 280–360 °C (Fig. 1). Pressure depresses the acetic acid formation (Fig. 1). Therefore the experiments were carried out at ambient pressure.

The catalyst screening results of studied process are presented in Table 2. One can note that acetic acid yield increases in the order: Cu/ZrO₂ < Cu/Al₂O₃ < Cu/ZnO. However, Cu/ZnO–ZrO₂–Al₂O₃ demonstrates the highest selectivity towards acetic acid, not like a mixture of the above mentioned catalysts. The same order of catalyst activity in the acetic acid formation reaction was observed in [4].

The data on acetic acid formation over Cu/ZnO–ZrO₂–Al₂O₃ catalyst at different inlet ethanol concentrations and at different temperatures are presented in Fig. 2. The maximum content of the acid is observed at 25 mol% of alcohol that corresponds with the thermodynamic calculations (Fig. 1). However, the content of acetic acid in liquid product formed from 25 mol% ethanol solution at 250 °C was only 5.9 mol%, whereas equilibrium value is 14.4 mol%. The main by-products are acetaldehyde and methyl ethyl ketone, butanol, acetone as the result of aldol condensation of acetaldehyde (Table 3). These by-products are also formed during the conversion of anhydrous ethanol to ethyl acetate [5,6]. Hydrogen generation is observed at 1.9 moles per mole of consumed ethanol.

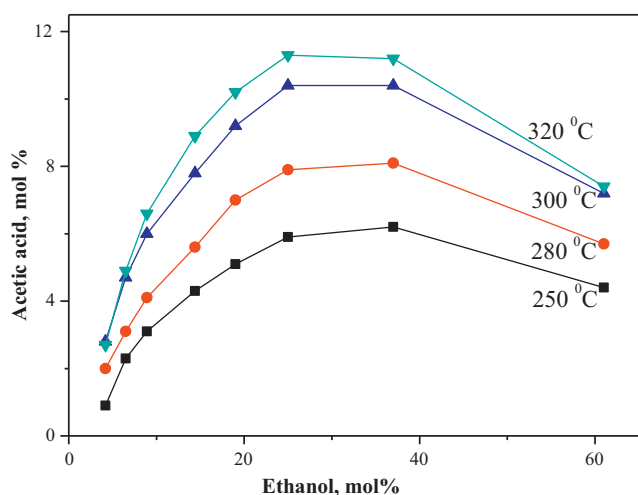


Fig. 2. Effect of temperature and inlet ethanol concentration on acetic acid content in liquid product (LHSV = 0.4 h⁻¹).

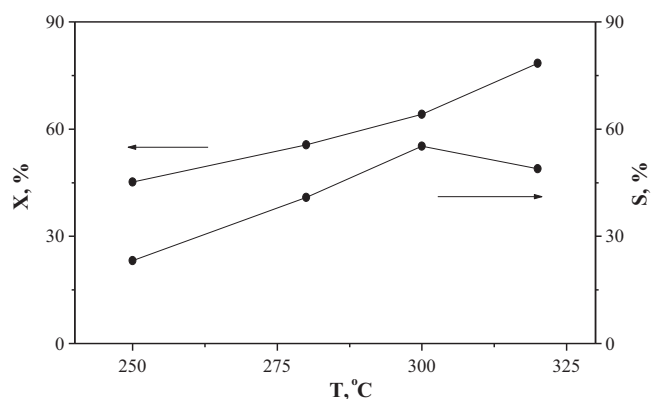


Fig. 3. Ethanol conversion and acetic acid selectivity at different temperatures ([C₂H₅OH] = 37 mol%, LHSV = 1.0 h⁻¹).

Ethyl acetate was formed with 90% selectivity during the conversion of anhydrous ethanol over the studied catalyst at 250 °C. When inlet ethanol was switched to ethanol–water mixture, the content of ethyl acetate decreased strongly, whereas the content of acetic acid increased, which corresponds to the thermodynamic calculations (Fig. 1). Thus, one could conclude that acetic acid was formed as a result of ethyl acetate hydrolysis.

We have treated ethyl acetate–water–acetone mixture over the catalyst at the same conditions (250 °C, LHSV = 1 h⁻¹). It has been found that ethyl acetate hydrolysis proceeds ineffectively: the conversion of ethyl acetate was only 33%. At 280 °C, the conversion of ethyl acetate was still low – 50% only. Therefore, the transformation of ethanol into acetic acid below 280 °C is not effective. The ethyl acetate conversion into acetic acid increases, as well as ethanol conversion, with raising temperature (Fig. 3). Acetic acid content at 300 °C becomes close to equilibrium values.

Acetic acid selectivity passes through a maximum at 300 °C (Fig. 3). At higher temperature, the acetaldehyde and ketones yields significantly increase as it was observed for anhydrous ethanol [6].

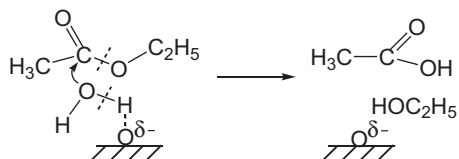
The TPR profiles of ethanol transformation products on preliminarily reduced Cu/ZnO–ZrO₂–Al₂O₃ catalyst show that the formation of H₂ (m/e = 2) and acetic aldehyde (m/e = 44, 29) is observed at 160–180 °C and at T > 240 °C (Fig. 4). In the TPR spectra for Cu/Al₂O₃, Cu/ZrO₂, Cu/ZnO samples, the first peak of acetaldehyde formation was recorded at T_m = 160–190 °C. However, acetaldehyde is formed at T > 250 °C on the acidic Cu/SiO₂. We use these T_m values for the estimation of the catalyst activity in the ethanol dehydrogenation reaction.

According to the TPR profiles of MBOH transformation, Cu/ZnO–ZrO₂–Al₂O₃ catalyst could be considered as a solid base because acetylene and acetone formation is observed (Fig. 4). The basic Cu/ZnO, Cu/Al₂O₃ and Cu/ZrO₂ samples also catalyze the decomposition of MBOH into C₂H₂ and (CH₃)₂CO at T_m = 70, 100, 140 °C, correspondingly. These T_m values correlate with the base site strength of ZnO (H₋ ≤ +18.4), ZrO₂ (H₋ ≤ +7.2) [10], and with the activity of Cu/ZnO, Cu/Al₂O₃ and Cu/ZrO₂ in the acetic acid formation (Table 2). The values of T_m = 90–110 °C allow one to characterize the strength of basic sites of Cu/ZnO–ZrO₂–Al₂O₃ catalyst by the value of H₋ ≤ +17.2 [10]. These quite strong basic sites provide effective hydrolysis of ethyl acetate. Obviously, Zn is an important component for the strong base sites formation in the amorphous Cu/ZnO–ZrO₂–Al₂O₃ mixed oxide structure. Water is a stronger acid than ethanol (ΔpK_{BH} ≈ 2). Therefore, water molecules are mainly activated via the interaction with the O²⁻ surface anions and react with ethyl acetate molecules forming acetic acid as shown in the scheme:

Table 3
Effect of inlet ethanol concentration on the synthesis of acetic acid from ethanol–water mixture at different temperatures.

Inlet [EtOH] (mol%)	T (°C)	LHSV (h ⁻¹)	X (%)	Selectivity (%)				Yield AcOH (%)
				AcOH	AcOEt	AcH	AID	
98	250	2	59.0	0.7	86.6	9.9	2.8	0.4
61	250	2	44.3	5.8	38.9	21.5	33.8	2.6
37	250	4	33.0	9.6	35.2	28.0	27.2	3.2
37	250	2	36.0	14.3	30.3	21.2	17.1	5.2
37	250	1	44.0	26.6	37.1	19.3	17.1	11.6
37	280	0.4	54.6	46.8	30.0	10.9	12.3	25.6
37	280	1	55.6	40.9	32.2	14.7	12.3	22.7
37	300	1	64.1	54.8	13.9	14.2	17.1	35.1
37	300	2	55.4	45.0	25.6	17.2	12.3	24.9
37	320	2	68.0	56.4	19.8	10.4	13.4	38.3
37	320	1	78.4	48.9	14.7	10.9	25.5	38.3
20.7	320	2	77.5	64.5	14.1	13.2	8.2	49.9
20.7	300	2	56.1	64.6	14.9	12.9	7.6	36.2
20.7	300	1	65.0	77.8	6.5	4.5	11.2	50.6
20.7	300	0.4	68.9	78.4	7.1	4.1	10.3	54.1
14.4	300	2	58.0	77.1	8.9	7.8	6.2	44.7
14.4	300	1	72.0	83.7	7.6	4.6	4.0	60.3
14.4	300	0.4	81.0	88.5	4.4	3.1	4.0	71.6
14.4	280	1	62.3	66.5	10.2	10.2	13.2	41.4
14.4	250	1	60.0	30.8	23.5	16.2	29.5	18.5
8.9	300	0.2	82.0	88.0	2.8	1.4	7.8	72.2
8.9	280	1	76.0	91.5	3.1	3.0	2.4	69.5
8.9	300	1	80.0	91.7	3.0	3.1	2.3	73.3
6.5	280	4	33.2	64.7	5.6	28.7	1.1	21.5
6.5	280	1	60.6	78.4	0.0	11.2	10.4	47.5
6.5	280	0.4	80.9	82.8	9.9	3.2	4.2	67.0
6.5	250	0.2	77.7	86.8	2.8	4.3	6.0	67.5
6.5	300	0.2	79.6	90.5	5.1	1.3	3.1	72.1
4.2	280	4	47.0	89.7	3.9	4.2	2.2	42.2
4.2	280	2	60.0	88.2	3.2	7.1	1.5	52.9

X, conversion of ethanol; [EtOH], ethanol content; AcOH, acetic acid; EtOH, ethanol; AcOEt, ethyl acetate; AcH, acetic aldehyde; AID, aldol derivatives (methyl ethyl ketone, butanol).



The ethanol conversion and acetic acid selectivity increase when lowering the feed ethanol concentration (Fig. 5). The space-time yield (STY) of acetic acid does not considerably depend on the feed ethanol concentrations in the range of 14–37 mol% because higher conversion and selectivity are observed at lower ethanol content (Fig. 5).

Space-time yield of acetic acid increases at raising feed rate while ethanol conversion decreases as well as acetic acid selectivity (Fig. 5). The use of 14–21 mol% ethanol solutions at

LHVS = 0.2–0.4 h⁻¹ allows one to obtain high ethanol conversion (70–80%) and acetic acid selectivity of up to 90%, which is close to the calculated data. Under these conditions, the space-time yield and outlet concentration of acetic acid reach values of 6 mmol CH₃COOH g_{cat}⁻¹ h⁻¹ and 28–31 wt%, correspondingly. Cu/ZnO–ZrO₂–Al₂O₃ catalyst has worked quite stably in the experiments for at least 70 h. We have used one set of catalyst for all experiments. After that, ethanol–water solution was switched to pure ethanol. In 0.5–1 h, the product composition became the same as before introducing of an ethanol–water solution.

High acetic acid selectivity (>90%) is achieved at lower temperature 250 °C (LHVS = 0.2 h⁻¹), when more diluted ethanol solutions are used. At the same time, the STY values decrease significantly (<2 mmol g_{cat}⁻¹ h⁻¹). These conditions could be employed for the processing of low concentrated alcohol–water solutions, which are

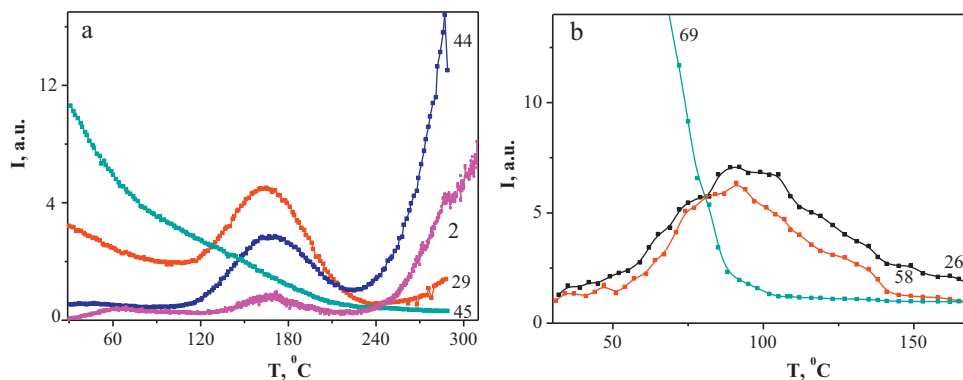


Fig. 4. TPR profiles of ethanol (a) and 2-methyl-3-butyn-2-ol (b) transformation on Cu/ZnO–ZrO₂–Al₂O₃ (C₂H₅OH – 45 a.u.m.; C₂H₄O – 44, 29 a.u.m.; H₂ – 2 a.u.m.; MBOH – 69 a.u.m., C₂H₂ – 26 a.u.m.; (CH₃)₂CO – 58 a.u.m.).

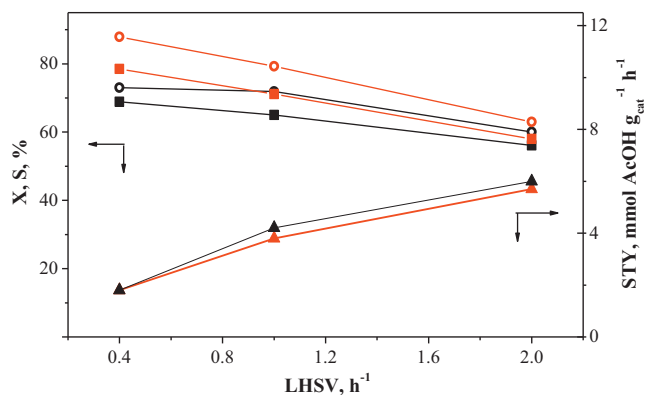


Fig. 5. Values of ethanol conversion (\square), selectivity to acetic acid (\circ) and space-time yield (Δ) at different feed rates at ethanol concentrations 14 mol% (—) and 21 mol% (---) (300 °C).

formed at fermentation of carbohydrates and also for the utilization of polluted water, resulted from the traditional ethyl acetate manufacturing.

The specificity of this process as well as the direct synthesis of ethyl acetate from ethanol is that some reactions should be realized on one catalyst, namely sequential formation of acetic aldehyde, ethyl acetate, and acetic acid. In a typical industrial process, each stage is realized in a separate reactor with a certain catalyst. The three-stage process can be performed at a significantly lower feed rate or load on the catalyst. So, we have used quite high LHSV = 4–5 h⁻¹ at obtaining of acetaldehyde from pure ethanol over the Cu-oxide catalyst, whereas LHSV = 0.4–2 h⁻¹ has been applied for acetic acid synthesis over Cu/ZnO–ZrO₂–Al₂O₃ catalyst only.

The studied process is realized at moderate temperature (250–300 °C), when reagent diffusion in catalyst pores usually limits the reaction rate. For the Cu/ZnO–ZrO₂–Al₂O₃ catalyst, the diffusion-control regime has been observed in the direct synthesis

of butyl butyrate from *n*-butanol at 180–280 °C [11]. Therefore, we have used quite thin cylindrical pellets (6 mm × 2 mm) of the catalyst while working with our experimental installation for ethanol processing (10 kg h⁻¹).

4. Conclusions

The formation of acetic acid from ethanol and water over the Cu/ZnO–ZrO₂–Al₂O₃ catalyst at 250–320 °C has been studied. The process includes the sequential formation of acetic aldehyde, ethyl acetate, and acetic acid as the result of ethyl acetate hydrolysis. Hydrogen is formed as a co-product. It was found that acetic acid yield reaches maximum values while processing of 21–37 mol% aqueous ethanol solutions.

Acknowledgment

Authors are grateful to Prof. A. Shmelev for rendering of SATRAPIS program for the thermodynamic calculations.

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