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CONVERSION OF n-BUTANOL TO n-BUTYRALDEHYDE - SCREENING OF COPPER CATALYSTS

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n-Butanol, a mass product of chemical industry, is a molecule with remarkable transformation potential. It may also be obtained from renewable resources via fermentation, making it more tempting as green molecule for chemistry. The present paper is focalized on conversion of n-butanol to butyraldehyde, one of the very useful transformations, over copper supported catalysts. In the screening stage various supports to generate cheap and innovative copper catalysts were used: TiO_2, CeO_2, ZrO_2, Al_2O_3, Celite22, MnO_2 and SiO_2. The main reaction products were monitorized by gas chromatography to determine the best conversion and selectivity in the characteristic compound: n-butyraldehyde.

Keywords: n-butanol, copper-supported catalyst, ultrasound, n-butyraldehyde

1. Introduction

In the current context in which organic chemistry gathers its forces for a new offensive, catalysis is undergoing a period of revitalization in its attempt to produce new catalysts with improved performance.Thesupported catalysts obtained through conventional wet impregnation methods [1, 2] begin to be replaced with supported catalysts prepared by innovative, nonconventional techniques [3, 4] involving ultrasounds [5-8] and/or microwaves [9]. The latter have the potential to provide conversions and selectivities in useful products which are superior to the supported catalystsachieved by conventional methods. The catalystsprepared by conventional wet impregnation method differs from the catalysts prepared by innovative, nonconventional technique in that in the contacting phase ultrasounds are applied.

n-Butyraldehyde, is a key intermediate [10] in chemical industry to obtain valuable products such as: plant protection products, accelerators for

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vulcanization of rubber, textiles auxiliaries, odorant/flavourings, pharmaceuticals or fuel components/additives [11, 12]. n-Butyraldehyde is for the moment conventionaly made by a well-known industrial process involving the conversion of propene by a hydroformylation reaction, over rhodium-phosphyne catalysts [13, 14]. Butyraldehyde could be also obtained by catalytic dehydrogenation of n-butanol (Fig. 1). n-Butanol could be available from synthetic pathway or from natural resources [15], usually via fermentation, making it a regenerable source for butyraldehyde.

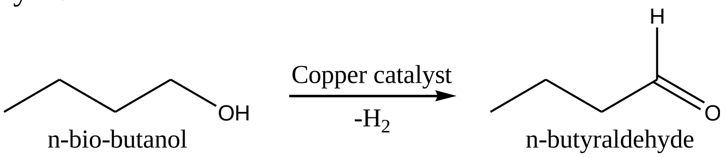


Fig.1 – Catalytic dehydrogenation of bio-n-butanol to n-butyraldehyde in presence of coppercatalysts

In this paper we are presenting the results of experimental work focused on production of n-butyraldehyde from n-butanol (from synthetic pathway) over a catalytic process to select those catalysts that may offer higher conversion, selectivity and yield. Similar processes could be applied to natural origins green n-butanol, using selected catalysts, experiments that are under investigations.

2. Experimental section

2.1. Material and equipment used

During the experiments the following materials were used: titanium oxide(Degussa, 99.9%), cerium oxide (Biddle Sawyer, 99%), zirconium oxide (Aldrich, 99%), alumina(Merck, 99%), Celite22 (Carlo Erba, 98%), manganese oxide (Merck-Emplura, ≥ 89%,), silica (Fluka, 99.9%), copper acetate monohydrate (Merck-Emplura, ≥ 99.0%), copper nitrate trihydrate (Merck Emsure, ≥ 99.5%), n-butanol (Merck, 99.9%, Honeywell, 99.98%), hydrogen (Linde, 5.0), 2-propanol (Riedel-de Haën, 99.8%), butyraldehyde (Union Chimique Belge, 99.9%), n-dibutyl ether (Veb Berlin Chemie, 99.9%) and iso-amyl alcohol (Union Chimique Belge, 99.9%).

For the preparation of catalysts used in catalytic process there were used two types of US processors with sonotrode: Dr. Hielscher - UP 50H, 125 W, 20-22 kHz and Sonics - Vibracell 750 W, 20 kHz. Hydrogen, introduced at constant flowrate in reactor to protect the catalyst and as gas carrier for reagents, was measured with a Sierra type SmartTrak50 mass flow controller for gases. Also the reagent, n-butanol, was pumped at a constant flowrate in gas-liquid mixer through a Cole Parmer type MasterFlex C/L peristaltic pump. For the quantitative analysis of liquid or non-condensable gaseous samples taken during the operation of the laboratory installation, two gas chromatographs were used as follows: a) for liquid samples - HP6890 in the following configuration: column: HP-INNOWAX 19091N-133 crosslinked PEG, 30 m x 250µm; carrier gas - helium: pressure - 84 psi, flow– 1 ml/min (constant); injector: split, split ratio – 1:50, split flow – 20 ml/min, temperature -250 ºC, gas saver – ON, flow saver – 20 ml/min, saver time - 1 min; temperature program: level 1 - 2.5 min, 50 ºC – ramp 1 - 10 ºC/min to 250 ºC – level 2 – 5 min, 250 ºC, total time: 27.36 min; detector: flame ionization detector at 250 ºC, hydrogen flow – 40 ml/min, air flow – 450 ml/min, signal: range – 3, attenuation – 0; data acquisition software: Clarity 7.3 and b) for non-condensable gaseous samples - Buck Scientific 910 in the following configuration: two columns: (1) – Molecular sieves 13X for separation of atmospheric gases – nitrogen, oxygen, CO, CO_2, 6”x 0.53 mm and (2) – Silicagel 6”x 0.53 mm for separation of light hydrocarbons – methane, ethane, ethene, propane, propene, butanes, isobutanes, butenes, isobutene; carrier gas - helium: pressure - 84 psi, helium flow – 30 ml/min (constant); multiport valve: loop – 1 ml, 40 ºC; temperature program: level 1 – 4 min, 40 ºC, ramp 1 – 20 ºC/min to 220 ºC, level 2 – 10 min, 220 ºC; detectors: flame ionization detector – with metanizer at 350 ºC, hydrogen flow – 25 ml/min, air flow – 250 ml/min and thermal conductivity detector at 150 ºC, curent – 255mA; data acquisition software: Peak Simple 3.11.

2.2. Procedures

2.2.1. Catalyst preparation

The catalyst precursor amount (copper acetate or nitrate) was calculated to obtain the desired catalysts with a load of 10% copper. Catalysts with a load of 5% copper (M5 experiment) or with a load of 20% copper (M6 and S9 experiment) were also prepared in some cases as shown in Table 1. Two types of catalysts were prepared by wet impregnation with excess solution method: conventional and ultrasonic. In the case of the conventional preparation the precursor and the material used as support for the catalyst were introduced in distilled water and mechanically stirred at room temperature (2 hours, 400 rpm), followed by slow evaporation of the water on rotary evaporator under vacuum (12 hours, 90 rpm, 40 ºC with progressive raise of temperature up to 80 ºC in the last 4 hours), drying in the oven (12 hours, 110 ºC) and calcination of the catalyst (4 hours, 300 ºC or 350 ºC). In the case of ultrasonic preparation the precursor and the material used as support for the catalyst preparation were introduced in liquid media (water:ammonia 10:1, 2-propanol:water 4:1 or glycerol:water 2:1). A reductive reagent was added and then ultrasonically irradiated at room temperature. For each reductive reagent used the sonication time was different. The temperature in the preparation vessel was maintained by external cooling with an ice bath. The rest of the preparation steps are the same as for the case of conventional preparation. Four reductive reagents were used for preparation of catalysts using ultrasound: a) *ascorbic acid*, ultrasound irradiation using a Dr. Hielscher processor UP50H (15 minutes- continuous, 50% amplitude; 3 hours – pulse:5 s – ON, 1 s – OFF, 50% amplitude); b) *2-propanol*, ultrasound irradiation using a Sonics Vibracell processor VCX750 (15 minutes - continuous, 30% amplitude; 6 hours – pulse: 5 sec ON, 2 sec OFF, 30% amplitude); c) *2-propanol:ammonia solution*, using a Sonics Vibracell processor VCX750 (15 minutes - continuous, 30% amplitude; 3 hours – pulse: 5 sec ON, 2 sec OFF, 30% amplitude); and d) *glycerol:water solution*, using a Sonics Vibracell processor VCX750 (15 minutes - continuous, 30% amplitude; 3 hours – pulse: 2 sec ON, 2 sec OFF, 30% amplitude).

In all cases, before testing the catalytic activity the catalysts were reduced to metallic form (which is the active form) in the installation used for experimental work for 2 hours, at 400 ºC, in a hydrogen stream, at a flow rate of 10 cm^3/min and gas hourly space velocity of 0.160 s^{-1}. The catalysts prepared according to the above described procedures are presented in Table 1.

Table 1

Catalysts prepared and tested in heterogenous gas/solid phase reaction

Catalyst	Experiment code	Support	Precursor	Metal load	Preparation mode	Solvent
Cu/TiO_2	T1	TiO_2	$Cu(CH_3COO)_2$	10%	conventional	distilled H_2O
Cu/CeO_2	Ce1	CeO_2				
Cu/ZrO_2	Z1	ZrO_2				
Cu/Al_2O_3	A3	Al_2O_3	$Cu(CH_3COO)_2$			
	A3R		$Cu(NO_3)_2$			
Cu/SiO_2	C2R	Celite22	$Cu(CH_3COO)_2$			
	C3		$Cu(NO_3)_2$			
Cu/MnO_2	M2R	MnO_2	$Cu(CH_3COO)_2$			
	M2R1					
	M4		$Cu(NO_3)_2$			
	M5			5%		
	M6			20%		
	M7		$Cu(CH_3COO)_2$	10%		
Cu/SiO_2	S3R	SiO_2				
	S3R1					
	S3R2					
	S5		$Cu(NO_3)_2$			
	S6		$Cu(CH_3COO)_2$		US – NH_3	distilled H_2O + NH_3
	S7				US	2-propanol: H_2O4:1

	S8					Glycerol : H_2O 2 :1
	S9			20%		2-propanol: H_2O4:1

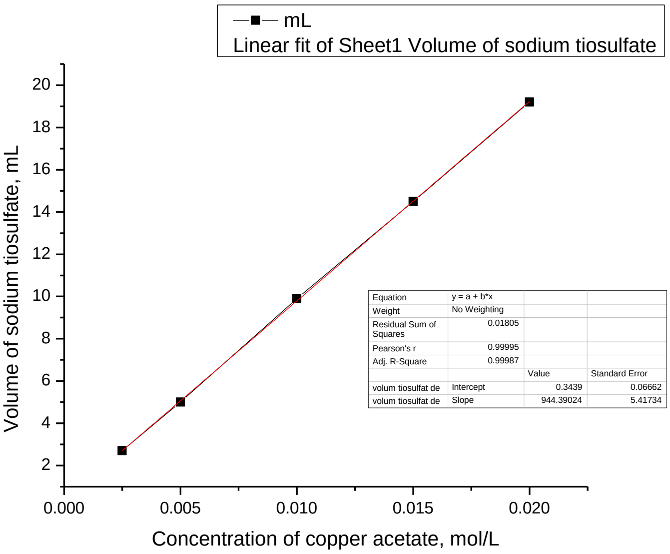
US - impregnation in presence of ultrasounds.

2.2.2. Determination of global Cu content of the catalysts by titration

The copper concentration of the catalysts was tested by a chemical method with insignificant deviations from the proposed values.

A quantity of unreduced catalyst (0.5 g) was reacted with an aqueous solution of acetic acid (50%). After catalyst desintegration with acetic acid, the pH of the solution containing copper acetate was verified with pH paper. Then the solution containing the cation was titrated with a solution of sodium thiosulfate (0.01 M) in presence of potassium iodide and sulfuric acid (0.1 N) until the color turns to light yellow. After this first step potassium thiocyanide (0.1 mol/L) and starch was added and the titration continued until the color turns to incolor [16].

The results were determined using the calibration curve described in eq.1 and in Fig. 2.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.01805		
Pearson's r	0.99995		
Adj. R-Square	0.99987		
		Value	Standard Error
volum tiosulfat de	Intercept	0.3439	0.06662
volum tiosulfat de	Slope	944.39024	5.41734

Fig.2 – Parameters of the calibration curve described in equation 1

$$V_{Na2S2O3} = 944.39024x + 0.3439 \tag{1}$$

Where:
x – quantity of Cu^{2+} in solution, mol/L;
$V_{Na2S2O3}$– volume of the $Na_2S_2O_3$ solution (0.01 M), used for titration;
944.39024 – slope of the line described in eq.1;
0.3439 – interception of the V_{Na2SO3} axis.

2.2.3. Experimental setup and procedure

The prepared catalysts were submitted to tests. The test reactions were carried out in the laboratory installation (Fig. 3) in the downward vapour stream over a fixed bed catalytic reactor loaded with catalyst for testing.

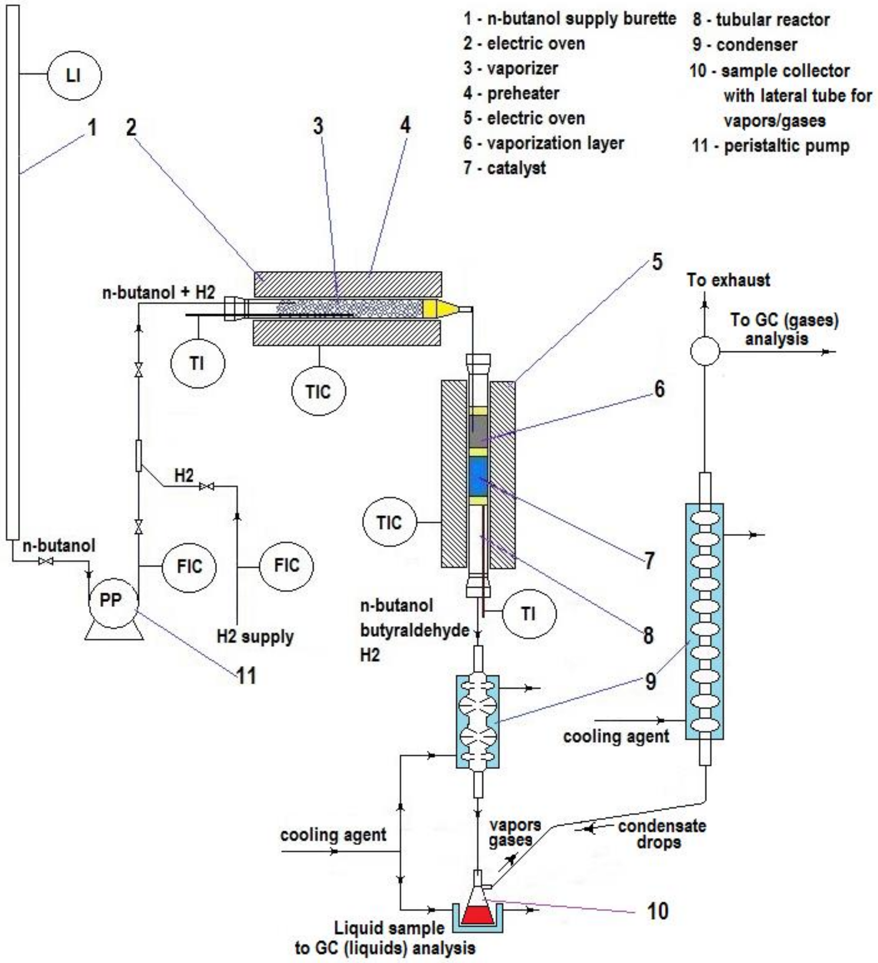


Fig.3 – Laboratory installation for testing of supported Cu catalysts (L – level, T – temperature, F – flow, I –indication, C – control, PP – peristaltic pump, GC – gas chromatograph)

The catalyst was protected with a hydrogen stream at atmospheric pressure; the hydrogen also acted as carrier for reagents. The reactor was filled with catalyst mixed with a solid inert (glass powder 100 – 300 µm) at a mass ratio of 1:1 and arranged between two layers of glass wool within a tubular glass reactor (ø 10 x 170 mm). The vaporization layer and catalyst layer heights were kept constant at 70 mm and respectively 30 mm for all tested catalyst formulations. The reactor was mounted then inside a vertical tubular oven (2) and the catalyst was activated for 2 hours, at 400 ºC, in a hydrogen stream, at a flow rate of 10 cm^3/min and gas hourly space velocity of 0.160 s^{-1}. The temperature in the reactor was maintained constant with a proportional-integral-derivative type temperature controller with an accuracy of ± 3ºC. The hydrogen flowrate was controlled with a mass flow controler.

The n-butanol was introduced in reactor via a peristaltic pump (11) at a constant flow rate of 0.1 g/min, the liquid passing through a gas-liquid mixer where hydrogen was inserted. The n-butanol/hydrogen mixture then enters into a preheater (3), filled with glass balls, acting as vaporizer. The preheater temperature was maintained constant throughout the experimental work at 325 ± 3 ºC. The reaction outcomes were condensed using two gas-liquid condensers cooled with a ethylene glycol – water mixture having -20ºC temperature. A recipient with lateral tube for gases/vapors (10) for collection of liquid samples was placed between the two condensers (9). The materials that remain in vapour phase after the first condenser enter in the second condenser where additional liquid phase is condensed and collected in the same sample collector (10). The condensed liquid was collected and was weighed at 30 minutes intervals to be used in determination of overall conversion of n-butanol and selectivities. Non-condensable gases were sampled after the second condenser at 30 minutes intervals and the samples were analyzed in a gas chromatograph specially configured for the analysis of gas phase compounds (Buck Scientific 910).

To quantify the reaction products two offline gas chromatographs have been used, one for the analysis of the liquid products (HP 6890 equipped with a flame ionization detector, internal calibration using iso-amyl alcohol as internal standard) and the other for the analysis of non-condensable products (Buck Scientific 910 equipped with a flame ionization detector and a thermal conductivity detector, calibrated for butene). The calibration curves for n-butyraldehyde, n-butanol, n-dibutyl ether as they appear in chromatographic software Clarity 7.3 and for butene are described in Figs. 4 – 7.

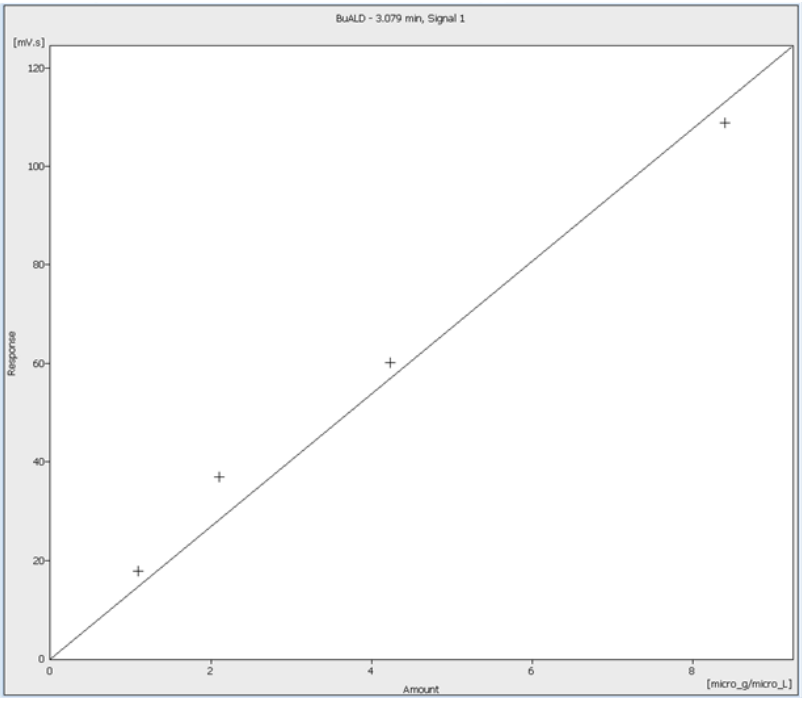


Fig. 4 – Calibration line for n-butyraldehyde – retention time – 3.079 min Correlation factor: 0.9955584, Residuum: 4.75804 [mV.s]

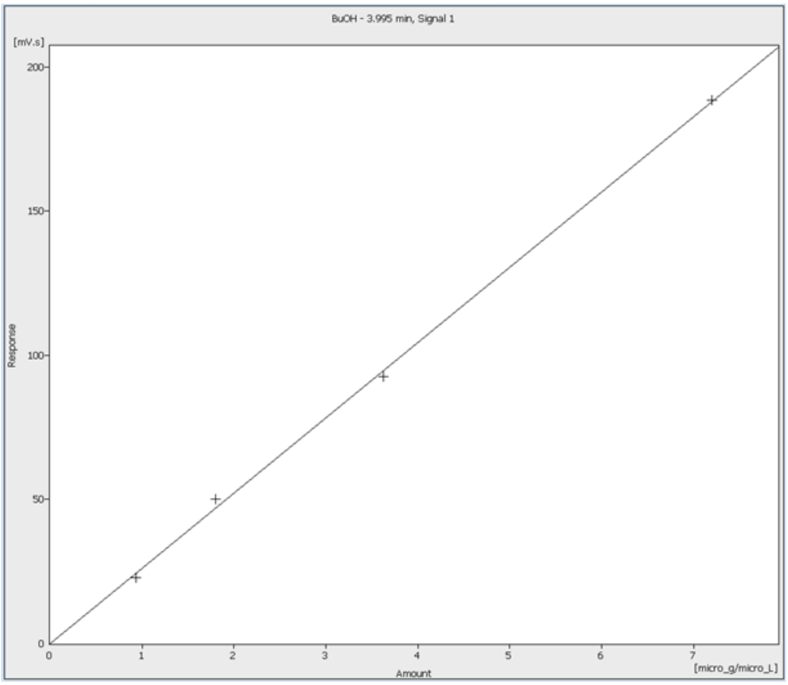


Fig. 5 – Calibration line for n-butanol - retention time – 3.995 min Correlation factor: 0.9996461, Residuum: 1.76565 [mV.s]

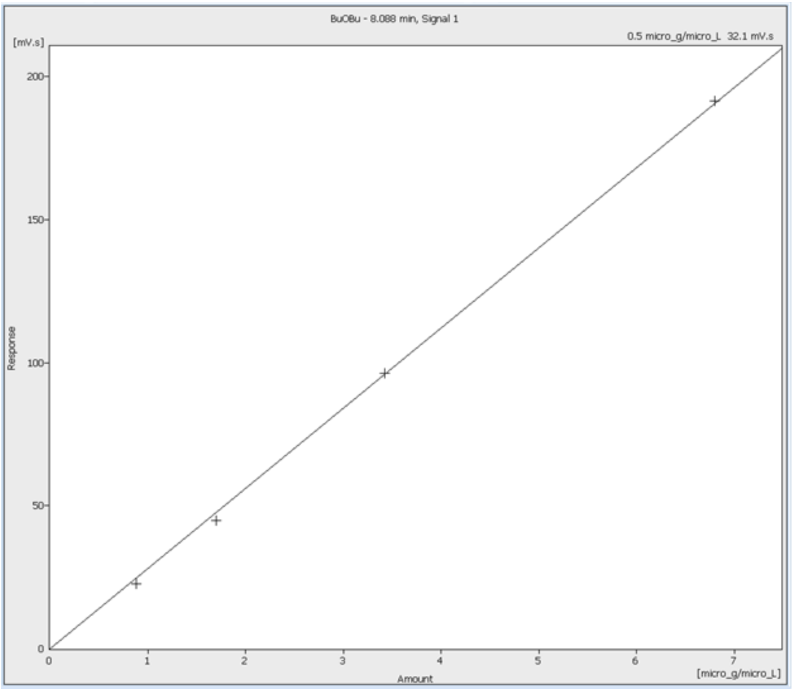
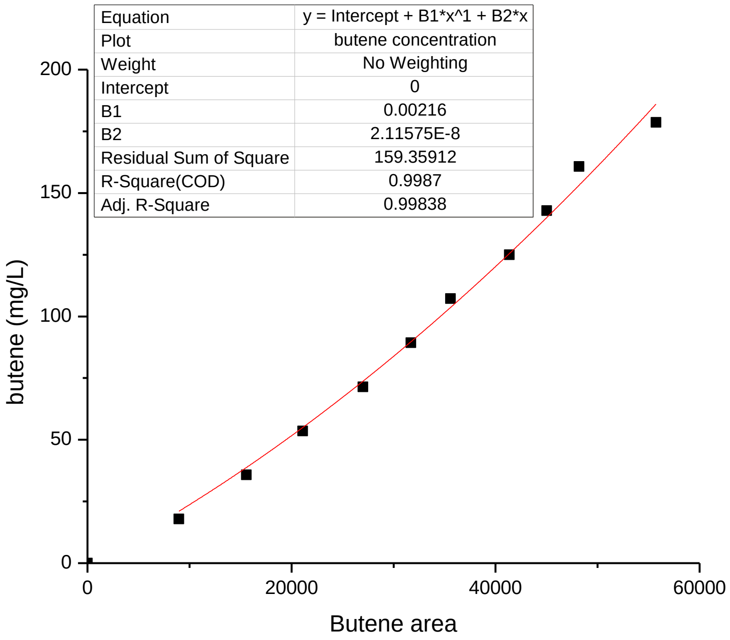


Fig. 6 – Calibration line for n-dibutyl ether retention time – 8.088 min
Correlation factor: 0.9998485, Residuum: 1.64524 [mV.s]



Equation	y = Intercept + B1*x^1 + B2*x
Plot	butene concentration
Weight	No Weighting
Intercept	0
B1	0.00216
B2	2.11575E-8
Residual Sum of Square	159.35912
R-Square(COD)	0.9987
Adj. R-Square	0.99838

Fig. 7 – Calibration curve for butene – retention time – 14.2 min

3. Results and discussion

3.1. Catalysts activity

The catalysts shown in the Table 1 were tested in gas/solid phase dehydrogenation reaction of n-butanol to n-butyraldehyde at three test temperatures (300 ºC, 325 ºC and 350 ºC, corresponding to a gas hourly space velocity of 0.621, 0.648 and 0.675 s^{-1} respectively and time on stream of 1 hour for each test temperature).

The following parameters were defined and monitored during the experimental work, equations 2 and 3:

$$\text{Conv} = \frac{m_2 - m_1}{m_2} \cdot 100 \qquad (2)$$

$$Sel_1 = \frac{M_{W1}}{M_{W2}} \cdot \frac{m_3}{m_2 - m_1} \cdot 100 \quad Sel_2 = \frac{M_{W1}}{M_{W3}} \cdot \frac{m_4}{m_2 - m_1} \cdot 100 \qquad (3)$$

in which:

Conv – overall conversion of n-butanol;
Sel_1 – selectivity in n-butyraldehyde (main product);
Sel_2 – selectivity in n-dibutyl ether (secondary product);
m_1 – mass of the unreacted n-butanol;
m_2 – mass of the n-butanol introduced in the system;
m_3 – mass of the n-butyraldehyde obtained;
m_4 – mass of the n-dibutyl ether obtained;
M_{w1} – molecular weight of n-butanol;
M_{w2} - molecular weight of n-butyraldehyde;
M_{w3} - – molecular weight of n-dibutyl ether.

3.2. Reaction pathways

The resulting gas and liquid phase from n-butanol catalytic reaction were passed through a condensation train, collected and analyzed. The main compounds detected in liquid phase were: n-butyraldehyde, di-n-butyl ether and unreacted n-butanol (1,1 dibutoxy-butane, n-butyl-butanoate, 2-ethyl-hexanol and 2,4,6 tripropyl-1,3,5 trioxane being detected in very small quantities by GC-MS). In gas phase, the main detected products were: butenes and hydrogen.

The main reaction pathways of *n*-butanol under our conditions are (Fig. 8):

- dehydration to produce butene;
- dehydrogenation to produce *n*-butyraldehyde;
- dehydration involving two *n*-butanol molecules to produce n-dibutyl ether.

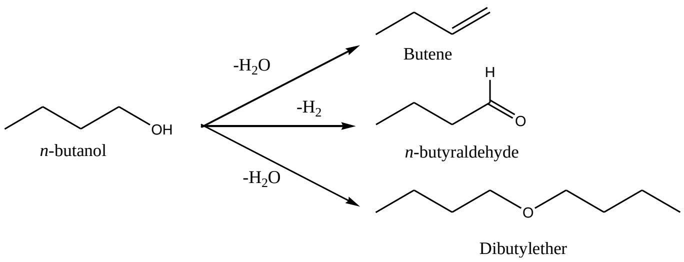


Fig. 8 – Reactions pathways for the catalytic conversion of n-butanol to main analyzed products

3.3. Results of catalyst screening

The catalysts shown in Table 1, were tested in the laboratory installation (Fig. 3) using the following working parameters: temperature of 300 ºC, 325 ºC and 350 ºC, corresponding to a gas hourly space velocity of 0.621, 0.648 and 0.675 s^{-1} respectively, time on stream of 1 hour for each test temperature, n-butanol flow rate of 0.1 g/min and hydrogen flow rate of 10 cm^3/min. The results are summarized in Figs. 9 and 10, Ox axis being the experiment code and Oy axis the parameters Conv, Sel1, Sel2 described in equations 2 and 3.

After this first trial of catalysts it is clearly shown that those selected in Fig. 10 are more promising catalysts from both overall conversion of n-butanol and selectivity in n-butyraldehyde (except T1 catalyst: low conversion, high selectivity).

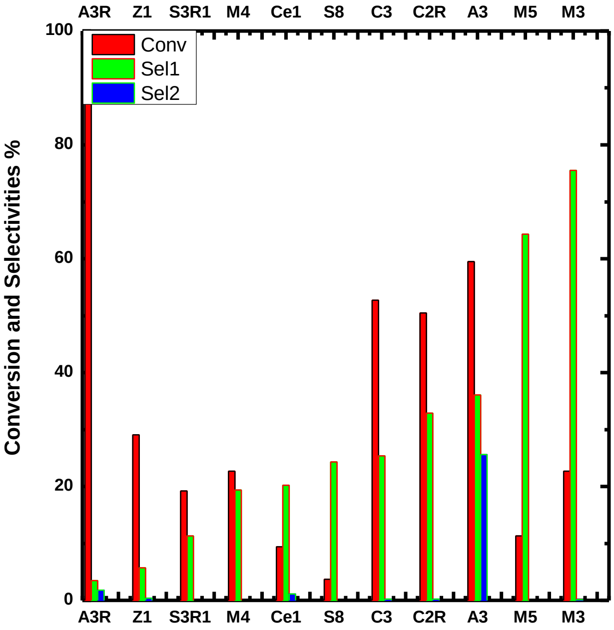


Fig.9 – Results of catalyst screening listed in Table 1 at temperature of 325 ˚C (catalysts with low selectivity to n-butyraldehyde)

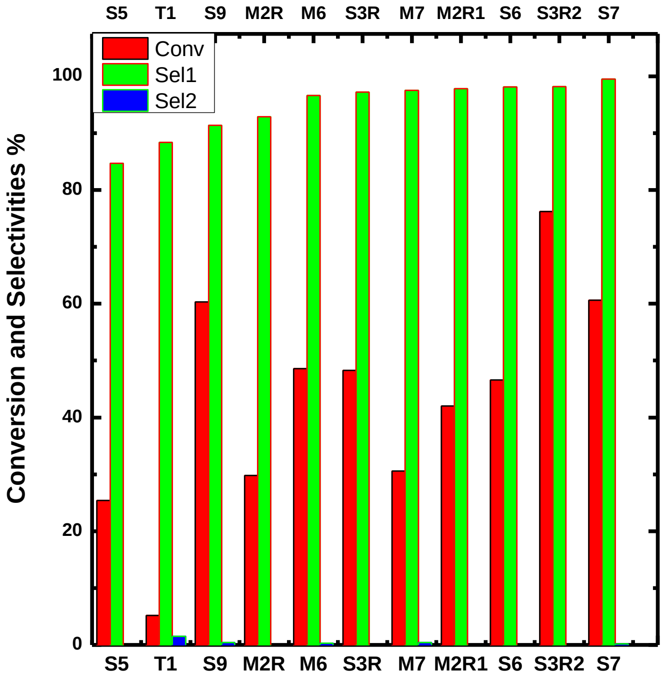


Fig.10 – Results of catalyst screening listed in Table 1 at temperature of 325 °C (catalysts with high selectivity to n-butyraldehyde)

The analysis of the data presented in Figs. 9 and 10 reveals the following aspects:

a) the catalysts deposited on Al_2O_3 support (A3 and A3R experiments from Fig. 9) have the highest conversion of n-butanol, but rather low selectivity in butyraldehyde (below 40%). However, a special case should be noted for A3R experiment in which butene selectivity was nearly 95% for n-butanol conversion of 91.2%, over a catalyst prepared from $Cu(NO_3)_2 \cdot 3H_2O$ precursor. This is not a desired reaction but could be an efficient potential method to produce butene from green n-butanol if it is the target product;

b) the catalysts deposited on ZrO_2 and CeO_2 support (Z1 and respectively Ce1 experiments from Fig.9) have a high coking tendency as in the S8 experiment (catalyst prepared by US impregnation in glycerol);

c) Cu/MnO_2 type catalysts (M5, M3, M2R, M6, M7 and M2R1 experiments) show rather good selectivities in butyraldehyde (more than 60%), but low conversion of n-butanol;

d) Cu/Celite22 type catalysts (C3 and C2R experiments from Fig. 9) offer reduced selectivities in butyraldehyde and rather low conversion of n-butanol;

e) Cu/SiO_2 type catalysts (S5, S9, S3R, S6 and S3R2 experiments from Fig. 10) exhibit very good selectivity in butyraldehyde (over 90%), with very little amounts of undesirable compounds;

f) the catalytic activity of the catalysts prepared from $Cu(NO_3)_2 \cdot 3H_2O$ precursor is significantly lower than that of the catalysts prepared from $Cu(CH_3COO)_2 \cdot H_2O$ precursor) (S5 experiment compared to S3R experiment);

g) in case of Cu/MnO_2 type catalysts, the metal loading of the support influences the catalytic activity which increases as the percentage of metal deposited on support increases: 5%, 10% and 20% (comparison between M5, M3 and M6 experiments). It is noteworthy that with conversion the selectivity increases, both due to the increase in the catalyst content of Cu as well as due to the increase in temperature over the studied range: 300 – 350ºC;

h) in the presence of the catalysts obtained in presence of US (S6, S7 and S9 experiments) the selectivities in butyraldehyde obtained are somewhat higher than those obtained in the presence of the conventional catalyst (S3R2 experiment).

In all considered cases, besides butyraldehyde, the quantities of other products are present in traces. The reduction of $Cu(CH_3COO)_2$ in the presence of NH_3 and US (S6 experiment) does not lead to better results than those obtained in the presence of catalysts prepared only in the presence of the US.

4. Conclusions

Several copper on support catalysts were prepared and tested in the process of n-butanol dehydrogenation to *n*-butyraldehyde.

The best catalytic activity and the best selectivity in butyraldehyde was obtained for catalysts deposited on SiO_2, precursor $Cu(CH_3COO)_2 \cdot H_2O$: S3R2 (Cu load – 10%, prepared by conventional impregnation), S7 (Cu load – 10%, prepared by US impregnation) and S9 (Cu load – 20%, prepared by US impregnation).

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