Production of Pure Hydrogen by Ethanol Dehydrogenation

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Abstract

Hydrogen production from bio-ethanol is one of the most promising renewable processes to generate electricity using fuel cells. In this work, we have studied the production of pure hydrogen as by product of ethanol dehydrogenation reaction. This reaction is promoted by copper based catalysts and according to the catalyst used and the operative conditions gives place to acetaldehyde or ethyl acetate as main products. We studied in particular the performance of a commercial copper/copper chromite catalyst, supported on alumina and containing barium chromate as promoter that has given the best results. By operating at low pressure and temperature with short residence times, acetaldehyde is more selectively produced, while, by increasing the pressure (10-30 bars), the temperature (200-260°C) and the residence time (about 100 (grams hour/mol) of ethanol contact time) the selectivity is shifted to the production of ethyl acetate. However, in both cases pure hydrogen is obtained, as by product, that can easily be separated. Hydrogen obtained in this way is exempt of CO and can be directly fed to fuel cells without any inconvenience. In this work, runs performed in different operative conditions have been reported with the scope to individuate the best conditions. A carrier of H_2 6% in N_2 has been used. The studied catalyst has also shown a good thermal stability with respect to sintering phenomena, that generally occurs during the dehydrogenation on other copper catalysts. Hydrogen productivities of 8-39 mol_{H2} $(gcat)^{-1}(h)^{-1}$ have been obtained for the explored temperature range 200-260°C.
At last, the most accredited reaction mechanism is reported and discussed on the basis of the obtained results.

Keywords: Bioethanol, hydrogen production, Cu based catalyst

Introduction

The shortage of fossil fuels in the near future will cause energy problems. However the necessity of reducing the greenhouse gases emission (measured in CO_2 equivalents) as established by Kyoto protocol, has required deep studies to develop new renewable feedstock derived from biomasses, for the production of biofuels alternative to the traditional fossil fuels [1]. The hydrogen production with the eventual separation is becoming a topic of growing interest, because, hydrogen is a clean energy source [2]. Hydrogen in the long-term will simultaneously reduce dependence on foreign oil and emissions of greenhouse gases and pollutants [3]. Its demand as a fuel for fuel cells is growing in the last years, in fact fuel cells are a promising technology for efficient and clean power for vehicles, residential units, offices, and commercial buildings. A variety of technologies, such as steam reforming (SR), partial oxidation (POX), and auto-thermal reforming (ATR) can be used to produce hydrogen from light organic compounds such as methanol, propane or by fuels like gasoline, diesel, LPG. However the use of fuels produced by biomasses, such as bio-ethanol, are preferred, because, considered environmentally sustainable [4]. As a renewable fuel, ethanol generates far fewer greenhouse gases than conventional fuels such as gasoline or natural gas, since the CO_2 produced in combustion is the same consumed by plants and drawn from the environment via chlorophyll synthesis.

Actually, bio-ethanol production is growing in the world as a possible energy vector instead of petroleum. In Brazil ethanol produced from sugar cane residues fermentation, is currently used as fuel for cars, as an octane booster, directly or in mixture as oxygenate blended with gasoline. The use of ethanol as fuel increases the availability of this substance at low price.

Therefore, ethanol can become a building block for producing other chemicals like: ethylene, ethyl ether, acetaldehyde, ethyl acetate and hydrogen. Steam reforming of ethanol has been proposed for the production of hydrogen for fuel cells [5,6,7,8]. The steam reforming reaction, in the presence of copper catalyst, is endothermic and produce mainly H_2 and CO_2. However, sub-products such as acetaldehyde and ethyl acetate are also formed [9,10]. This process presents some disadvantages, such as the formation of by-products, the presence of CO that poison the fuel cell catalyst and catalytic deactivation.

Another innovative way, to produce pure hydrogen, is the ethanol dehydrogenation to acetaldehyde [11] and/or ethyl acetate [12,13]. The production of hydrogen by this reaction is an innovative route and there are not papers in the literature devoted to this particular aspect but indirectly different papers have been published related to the production of both acetaldehyde and methyl acetate. The ethanol dehydrogenation is promoted by copper based catalyst. Cu is one of the most active transition metals and is highly selective for alcohols dehydrogenation. The copper based catalysts were been found to be excellent for ethanol dehydrogenation because of their ability to maintain the C-C bond intact while dehydrogenating the C-O bond. However, the copper catalysts, normally, have a relatively low activity and are susceptible to deactivation due to sintering phenomena.

The presence of promoters and of metal oxide, to increase the activity and selectivity, and the choice of the optimal operative conditions, allows to obtain a good selectivity to acetaldehyde or to ethyl acetate. The ethanol dehydrogenation to acetaldehyde or to ethyl acetate involves, in both cases, the production of pure hydrogen, that can be separated very easily from the effluents, being these liquids at room temperature. Hydrogen so obtained is, pure not containing in particular CO_x as it occurs for the hydrogen deriving from steam reforming. In this work, we focused our study on the ethanol dehydrogenation reaction to ethyl acetate and pure hydrogen [14,15] promoted by two commercial catalysts, one based on copper/alumina/zinc oxide and another one based on copper/copper chromite containing also alumina and barium chromate as promoters.

1. Experimental section

1.1 Employed catalysts

Two different commercial catalysts have been employed for the study of ethanol dehydrogenation reaction, supplied by BASF Companies, that are:

1) The catalyst BASF K-310 which contains $CuO/ZnO/Al_2O_3$ (40:40:20%$_{wt}$), this catalyst, is, normally, used for promoting low temperature gas shift reaction [16]. It is constituted by cylindrical pellets of regular size 0.5 cm of diameter and 0.5 cm of height.

2) A pre-reduced copper/copper chromite catalyst BASF Cu-1234-1/16-3F, supported on Alumina and containing $BaCrO_4$ as promoter. The catalyst composition is $Cu_2CrO_4/CuO/Cu/BaCrO_4/Al_2O_3$ (45:1:13:11:30%$_{wt}$) and is constituted by a cylindrical extrudate with a diameter of 1/8''.

Both the catalysts examined were previously pre-reduced in situ with hydrogen, for 16-18h, by using a flow of H_2 and N_2 (H_2/N_2=1:15.6) with a flow rate of 25 cm^3/min and a temperature of 200°C.

1.2 Catalytic Tests

The catalytic tests, related to the ethanol dehydrogenation to ethyl acetate/acetaldehyde, were performed in a stainless steel tubular packed bed reactor. Normally, about 10 g of the catalyst, in pellets were charged in the reactor and, before the catalytic test, the catalyst was submitted to a pretreatment with a flow stream of 25 cm^3/min of a mixture of H_2-N_2 (H_2/N_2=6:94) at a temperature of 200°C for 16-18h, with the aim to deeply reduce the catalyst. This pretreatment reduces CuO to Cu. After the pretreatment, the catalyst was heated to the desired reaction temperature. The liquid ethanol (Fluka 99.8%$_{wt}$) was vaporized in a gas stream of H_2 and N_2 (H_2/N_2=1:15.6), at 200°C, and preheated in a tube filled with inert material (glass balls). The reaction has always been conducted in the presence of a gas stream of hydrogen/nitrogen as carrier.

The reaction, normally, has been performed in the temperature range 200-260°C, at pressure of 10-30 bars and ethanol contact time of W/F=32-338 $ghmol^{-1}$, where W and F are respectively the catalyst weight and the ethanol flow molar rate.

Obtained products and un-reacted ethanol were periodically analyzed on-line by a Gaschromatograph (HP 5890 instrument), withdrawing a small sample by on line sampling valve kept at 220°C. The gascromatograph is equipped by a Restek Rt-Q Plot 30m*0.32mm column and pure Helium as carrier. The conditions used for the analyses were as follow: the initial temperature was 40°C then increased at a rate of 10°C/min to 220°C and then maintained at this temperature for 10 minutes. A thermal conductivity detector (TCD) kept at (210°C) was used for the detection. The split-splitness injector was kept at 180°C. Three different sets of runs were performed to evaluate respectively the effect of the temperature, of the pressure and of the ethanol residence time on the catalysts performances. The feed rate of the gas mixture was kept constant during all the runs. Results are reported in terms of overall ethanol conversion and products selectivity. The ethanol conversion is defined as:

$$X = \frac{number\ of\ moles\ of\ ethanol\ reacted}{number\ of\ moles\ of\ ethanol\ fed} \quad (5)$$

while, the selectivities, determined effectuating a carbon balance on the different components, are defined as:

$$S = \frac{number\ of\ moles\ of\ product\ formed}{number\ of\ moles\ of\ reacted\ ethanol} * \frac{nC_i}{nC_{EtOH}} \quad (6)$$

Where n_{Ci} and n_{CEtOH} represent the numbers of carbon atoms respectively of the component i and of the ethanol fed.

2. Results and discussion

The ethyl acetate formation mechanism, on copper catalyst, probably starts with the nucleophilic addition of either ethanol or surface ethoxide to acetaldehyde to form an adsorbed hemiacetal specie, followed by dehydrogenation to ethyl acetate. The stepwise reactions via hemiacetal seems favored by relatively high pressure (10-30 bars) [17]. This behavior confirms the mechanism hypothesis suggested by Isawa et al.[18]. The possible reactions are:

1. $CH_3CH_2OH(g) \rightarrow CH_3CHO + H_2$

$$\Delta G^0_{298K} = 9302.9 \frac{Kcal}{Kmol} \qquad \Delta H^0_{298K} = 16420.5 \frac{Kcal}{Kmol}$$

2. $CH_3CH_2OH(g) + CH_3CHO(g) \rightarrow CH_3COOCH_2CH_3(g) + H_2$

$$\Delta G^0_{298K} = -7463.7 \frac{Kcal}{Kmol} \qquad \Delta H^0_{298K} = -\frac{10354.1 Kcal}{Kmol}$$

Ethanol dehydrogenation to acetaldehyde (1) is a relatively fast endothermic reaction occurring at temperatures higher than 100°C. One mole of hydrogen is released per mole of reacted ethanol. The reaction of ethanol with acetaldehyde to ethyl acetate (2) is an exothermic reaction occurring at relatively low temperature. In agreement with literature [19] data its formation is enhanced by increasing the residence time, the ethanol conversions and the pressure, because, the formation of ethyl acetate is thermodynamically favored over acetaldehyde up to 200°C. In addition, the ethyl acetate formation can be enhanced by increasing the size of the active metal particles on the catalyst surface. So the choice of the catalyst and of opportune operative conditions (temperature and pressure) favors the formation of ethyl acetate or acetaldehyde.
The overall reaction that produce one mole of ethyl acetate and two moles of hydrogen starting from two moles of ethanol is a relatively endothermic reaction.

3. $2\,EtOH \rightarrow AcOEt + 2H_2$

$$\Delta G^{\circ}_{298K} = -1839.2 \frac{Kcal}{Kmol} \qquad \Delta H^{\circ}_{298K} = 6066.4 \frac{Kcal}{Kmol}$$

In any case, hydrogen is obtained as by product and can easily be separated by un-reacted ethanol, ethyl acetate and acetaldehyde. Copper based catalyst are the most active to produce both ethyl acetate and acetaldehyde. The choice of a satisfactory catalytic system is fundamental to obtain high performances in the dehydrogenation reaction.
In Table 1, the results in terms of conversion, selectivities, and hydrogen productivity, at different time on stream of a kinetic run of ethanol dehydrogenation, performed on BASF K-310 catalyst, at atmospheric pressure, and at a constant temperature of 200°C, with a residence time of 338.7 ghmol^{-1} are reported. Ethanol was fed liquid with a flow rate of 0.1 cm^3/minute and was diluted in a flow stream of a nitrogen (4 cm^3/min). From the data reported in this table it can be seen that the mentioned catalyst is subjected to a progressive deactivation. Another observation is that at atmospheric pressure acetaldehyde is the main reaction product.

Table 1: Behavior of K-310 catalyst at low pressure of 1 bar, at temperature of 200°C, during the run performed. The residence time was kept constant 338.7 ghmol^{-1}. The tubular reactor was charged with 0.58g. The liquid ethanol and nitrogen flow are respectively of about 0.1 and 4 cm^3/min. The Conversions and the selectivities are reported for different times on stream.

	Time (min)	F_{EtOH} (cm^3/min)	F_{N2} (cm^3/min)	X (%)	S_{AcOEt} (%)	S_{AcH} (%)	P_{H2} (g_{H2})/(Kg_{cat}*h)
BASF K-310	60	0.1	4	72.7	10.9	89.1	255.05
	90	0.1	4	64.3	10.7	89.3	225.58
	120	0.1	4	56.9	11.5	88.5	199.62
	160	0.1	4	55.3	12.1	88.0	194.01
	190	0.1	4	52.7	12.5	87.5	184.88
	210	0.1	4	48.1	13.9	86.1	168.75
	240	0.1	4	46.9	14.3	85.7	164.54
	280	0.1	4	41.7	15.6	84.4	146.29
	310	0.1	4	40.2	16.2	83.8	141.04
	350	0.1	4	40.2	16.2	83.8	141.03

Moreover, it is interesting to show the dependence of the ethylacetate/acetaldehyde selctivities on the reaction time (see Figure 1).

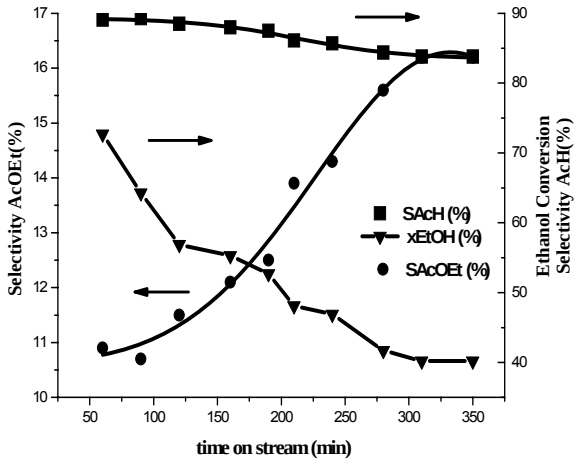

Figure 1: ethyl acetate and selectivity profiles vs time reaction. The reaction was conducted to 200°C, at atmospheric pressure and for a contact time of 338.7ghmol^{-1}.

The ethyl acetate selectivity increases with time, while, the one to acetaldehyde decrease. This behaviour suggests that the formation of ethyl acetate proceeds stepwise via acetaldehyde, which is a reaction intermediate. As mentioned, the catalyst rapidly deactivates as it can be appreciated in Figure 1, probably for the sintering effect favored by the relatively low copper Tamman temperature (300°C). The use of promoters and supports could prevent metal sintering maintaining constant activities and selectivities toward the desired product. At this purpose the catalyst BASF Cu-1234-1/16-3F, containing alumina, barium chromate and copper chromite as promoters, has given good results and for this reason has been studied in a more details.
The reactor has been charged also in this case with 10 g of catalyst. The kinetic runs have been performed by changing the ethanol contact time from 34.71 to 208.26 g mol h^{-1}, the temperature from 200 to 260°C, the pressure from 10 to 30 atm. The obtained results of ethanol conversion, ethyl acetate and acetaldehyde selectivities and hydrogen productivities are reported in Table 2. As it can be seen, the best results for the ethylacetate obtainment have been obtained at 220 °C, 20 atm and 104.13 g mol h^{-1} of ethanol contact time. In these conditions an ethanol conversion of about 70 % and a selectivity to ethyl acetate of 99.8% have been obtained, while, the best hydrogen productivity (38 g_{H2}/Kg_{cat}*h) has been obtained at 30 bars, 260°C and 104.13 g mol h^{-1} of ethanol contact time. By the results reported in Table 2 arises that operating under moderate pressure, with copper based catalysts, ethyl acetate is the most favored reaction product with respect to acetaldehyde.

Table 2: Catalytic results obtained for Cu-1234 catalyst. The reactor was charged with 10.70g of catalyst. The dehydrogenation reaction were conducted at different pressure (atm), residence time (ghmol-1) and temperature (°C).

Catalyst Type	RUN	Catalyst (g)	W/F (g h mol^{-1})	T (°C)	P (atm)	FEtOH (cm^3min^{-1})	FH_2 6%$_{wt}$ in N_2	X (%)	SAcOEt (%)	SAcH (%)	Sal. (%)	P_{H2} (g_{H2})/ (Kg_{cat}*h)
BASF Cu-1234-E-1/16 - 3F	2	10.70	34.71	200	10	0.3	5	44.86	84.5	14.58	16.65	8.75
	3	10.70	34.71	220	10	0.3	5	54.42	79.9	12.74	7.38	10.16
	4	10.70	34.71	240	10	0.3	5	68.23	77.9	19.26	2.85	9.92
	5	10.70	34.71	260	10	0.3	5	73.29	73.3	20.99	5.72	11.70
	6	10.70	34.71	200	20	0.3	5	50.05	89.0	10.20	0.8	11.38
	7	10.70	34.71	220	20	0.3	5	49.59	87.7	11.36	0.91	10.67
	8	10.70	34.71	240	20	0.3	5	58.42	86.8	9.076	4.14	8.97
	9	10.70	34.71	260	20	0..3	5	64.20	87.6	9.54	2.83	13.44
	10	10.70	104.13	200	10	0.1	5	46.85	87.3	10.90	1.81	13.86
	11	10.70	104.13	220	10	0.1	5	57.62	87.7	5.05	7.27	10.37
	12	10.70	104.13	240	10	0.1	5	53.79	88.2	8.72	3.02	13.81
	13	10.70	104.13	260	10	0.1	5	59.04	86.3	17.94	6.04	13.59
	14	10.70	104.13	200	15	0.1	5	60.20	98.2	1.2	0.63	13.40
	15	10.70	104.13	220	15	0.1	5	72.09	95.6	2.38	1.96	13.63
	16	10.70	104.13	200	20	0.1	5	55.53	97.0	1.11	1.82	15.19
	17	10.70	104.13	220	20	0.1	5	72.84	98.9	0.76	0.3	13.21
	18	10.70	104.13	240	20	0.1	5	72.84	96.6	1.71	1.61	12.90
	19	10.70	104.13	260	20	0.1	5	79.07	97.6	3.43	0.05	12.38
	20	10.70	104.13	270	20	0.1	5	73.35	86.7	7.93	5.31	12.94
	21	10.70	104.13	260	20	0.1	10	72.43	81.2	12.42	6.33	12.99
	22	10.70	104.13	200	30	0.1	5	65.84	95.9	2.96	1.12	14.41
	23	10.70	104.13	220	30	0.1	5	68.84	95.7	3.09	2.85	25.37
	24	10.70	104.13	240	30	0.1	5	70.39	91.9	5.06	2.98	28.75
	25	10.70	104.13	260	30	0.1	5	78.71	90.1	6.13	3.7	37.82

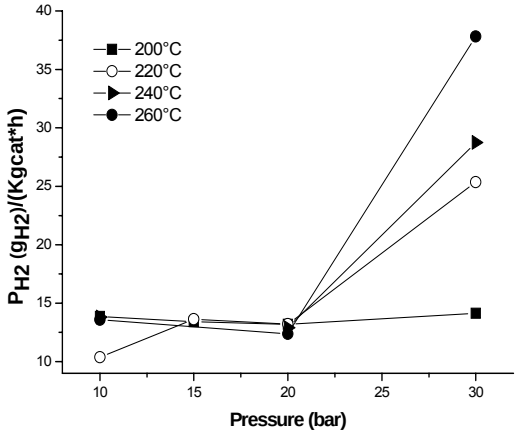

Figure 2: effect of pressure on the hydrogen productivity. The reaction was conducted to different temperature, and at contact time of

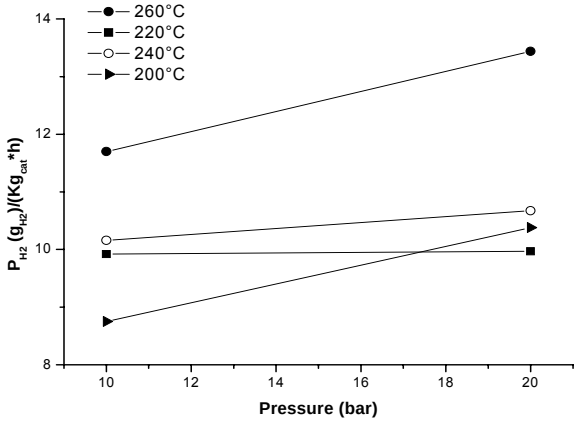

Figure 3: effect of pressure on the hydrogen productivity. The reaction was conducted to different temperature, and at contact time of W/F=34.71ghmol^{-1}.

In Figure 2, the effect of pressure on hydrogen productivity, at four different values of temperature for an ethanol contact time of 104.13 gmol h^{-1}, is reported. The profiles of Figure 2 underline that for low pressure reaction, the hydrogen productivity $g_{H2}/(Kg_{cat}*h)$ does not change significantly. The increasing of pressure from 20 to 30 bars determines an evident increment of the hydrogen productivity from 15 to 38 $g_{H2}/(Kg_{cat}*h)$.

In Figure 3, the effect of temperature on respectively the conversion and selectivity for three different values of the pressure at for the ethanol contact time 32.48 gh mol^{-1} is reported. By examining the profiles of Figure 3 it arises that the increase of pressure and temperature have a significant effect on the hydrogen productivity in the dehydrogenation reaction. In Figure 4 the dependence of the profiles of ethanol conversion and ethyl acetate selectivity on the temperature at two different pressures are reported. The runs were performed at constant contact time of 34.71ghmol-1. As it can be seen, conversion continuously increases with temperature, while, selectivity is poorly affected by the temperature but pressure has a dramatic effect. In Figure 5 a similar plot of ethanol conversion and ethyl acetate selectivity for a different contact time of 104.13 gmol h^{-1} , by considering three different values of the pressure, is reported. Again the conversion increases continuously with the temperature at the different pressures of 10, 20 and 30 bar, although the slope of the increase is lower for the runs performed at the highest pressure. Again selectivities are poorly affected by the temperature and are sensitive to the increase of the pressure in particular from 10 to 20 bars.

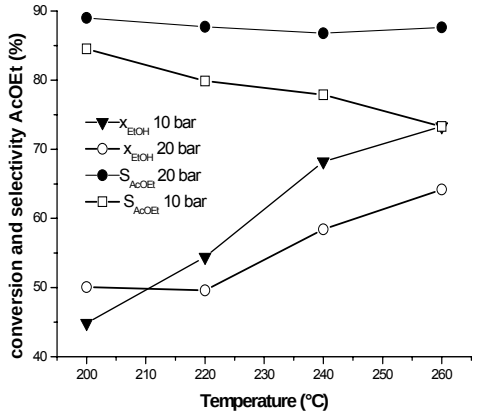

Figure 4: conversion effect of temperature and pressure on catalytic activity and selectivity of the copper chromite based catalyst Cu-1234. The catalytic test are conducted at residence time of W/F=34.71 ghmol^{-1}.

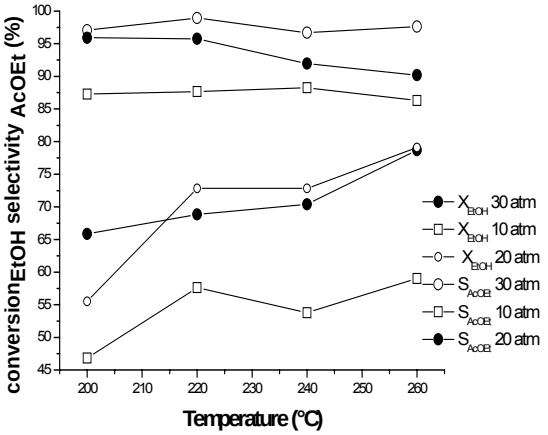

Figure 5: conversion effect of temperature and pressure on catalytic activity and selectivity of the copper chromite based catalyst Cu-1234. The catalytic test are conducted at residence time of W/F=104.13 ghmol^{-1}.

In Table 3, the performances obtained by the copper chromite based catalyst Cu-1234 for runs respectively performed at atmospheric pressure and at 20 bars on 50 g of catalyst are reported.

Table 3: Comparison of the commercial copper chromite catalyst Cu-1234 performances operating respectively under pressure and at atmospheric pressure. The runs were performed at constant contact time of 97.55 ghmol^{-1}. The reactor was charged with about 50g of catalyst. The liquid ethanol and gas mixture of H26% N2 feed was respectively of 0.5 cm^3/min and 25cm^3/min.

	RUN	T (°C)	P (atm)	FEtOH (cm^{3}min^{-1})	FH_2 6%wt in N_2 (cm^3/g)	X (%)	SAcOEt (%)	SAcH (%)	Sal. (%)	P_{H2} (g_{H2})/ (Kg_{cat}*h)
BASF Cu-1234 E 1/16	26	220	1	0.5	25	49.80	56.20	16.21	28.49	7.33
	27	220	20	0.5	25	57.33	99.33	0.66	0.01	11.50

From the results reported in Table 3 it is possible to confirm that the choice of the pressure level is fundamental for the selectivity to ethyl acetate (under pressure) or to acetaldehyde (atmospheric pressure). However, in both cases hydrogen with a relatively high productivities of 7.3-11.5 (g_{H2})/ (Kg_{cat}*h) are obtained.

3. Conclusions

As it has been seen the ethanol dehydrogenation promoted by copper based catalysts is an interesting process to obtain acetaldehyde by working at low pressure (atmospheric) and low residence time. By increasing the pressure (10-20 bars) and the residence time always keeping the temperature in a range of 200-250°C the selectivity is completely shifted to the production of ethylacetate. Both these chemicals are of great interest for the industry. Both the reactions give place to the production of pure hydrogen that can easily be separated by the reaction mixture. This hydrogen is exempt of CO_x and can, therefore, used directly for feeding fuel cells. A commercial copper/copper chromite based catalyst supported on alumina and containing $BaCrO_4$ as promoter resulted active, selective and stable to sintering in the mentioned reaction. The best results in the production of ethyl acetate on this catalyst has been obtained at 220 °C, 20 atm and 104.13 g mol h^{-1} of ethanol contact time. In these conditions an ethanol conversion of about 70 % and a selectivity to ethyl acetate of 99.8% have been obtained. The best productivity of hydrogen (38 g_{H2}/Kg_{cat}*h) has been obtained at 30 bars, 260°C and 104.13 g mol h^{-1} of ethanol contact time.

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