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# Hydrogen production from raw bioethanol over $Rh/MgAl_2O_4$ catalyst Impact of impurities: Heavy alcohol, aldehyde, ester, acid and amine

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ABSTRACT

The effect of various impurities added in a pure ethanol + water mixture was studied. The impurities chosen were acetic acid, diethylamine, butanol, butanal, ethyl acetate and diethylether. It was shown that the addition of diethylamine or butanal increases the ethanol conversion, compared to that obtained with a pure ethanol + water mixture, without changing the product selectivity. In the presence of the other impurities, butanol, ethylether and ethyl acetate, a strong deactivation of the catalyst with a decreased ethanol conversion was observed. Moreover, the selectivity in hydrogen was also strongly decreased, whereas an increase in intermediate products especially ethylene was observed. The deactivation was explained in terms of coke deposition at the catalyst surface. The poisoning effect induced by the presence of impurities can be classified in the following increasing order: diethylamine $\sim$ butanal $<$ no impurity $<$ acetic acid $<$ butanol $<$ diethylether $\sim$ ethyl acetate.

## 1. Introduction

The production of renewable energy sources with a drastic decrease of greenhouse gas emissions is key-challenge to a sustainable development for the 21st century. In this respect, PEMFC fuel cells supplied with hydrogen have attracted more and more attention. The steam reforming of different fuels is a less expensive process for the production of hydrogen on a large scale. However, this process is mainly applied to the transformation by steam of fossil hydrocarbons (natural gas or naphtha) [1–3] or oxygenated compounds [4–7]. Biomass-derived oxygenated compounds can also be used as feedstocks for the steam reforming reaction. In particular, bioethanol, much less toxic than methanol, is interesting for $H_2$ production since it can be produced by biomass fermentation (corn, beet sugar, straw ...) on a large scale, which makes it a renewable source of energy. Moreover, its transport, storage and distribution are relatively simple.

The main products of ethanol steam reforming (ESR) are $H_2$, $CO_2$, CO (Eqs. (1) and (2)), whereas the hydrogenation of ethanol is responsible for the formation of methane (Eq. (3)).

$$C_2H_5OH_{(g)} + 3H_2O_{(g)} \rightarrow 2CO_{2(g)} + 6H_{2(g)}, \quad \Delta H^{\circ}_{298} = +174\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$C_2H_5OH_{(g)} + H_2O_{(g)} \rightarrow 2CO_{(g)} + 4H_{2(g)}, \quad \Delta H^{\circ}_{298} = +256\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$C_2H_5OH_{(g)} + 2H_{2(g)} \rightarrow 2CH_{4(g)} + H_2O_{(g)}, \quad \Delta H^{\circ}_{298} = -157\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

However, the steam reforming reactions are generally preceded by a rapid transformation of ethanol into acetaldehyde (dehydrogenation, Eq. (4)), ethylene (dehydration, Eq. (5)) or methane, CO and $H_2$ (cracking, Eq. (6)).

$$C_2H_5OH_{(g)} \rightarrow CH_3CHO_{(g)} + H_{2(g)}, \quad \Delta H^{\circ}_{298} = +68\,\mathrm{kJ\,mol^{-1}} \tag{4}$$

$$C_2H_5OH_{(g)} \rightarrow C_2H_{4(g)} + H_2O_{(g)}, \quad \Delta H^{\circ}_{298} = +45\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

$$C_2H_5OH_{(g)} \rightarrow CO_{(g)} + CH_{4(g)} + H_{2(g)}, \quad \Delta H^{\circ}_{298} = +49\,\mathrm{kJ\,mol^{-1}} \tag{6}$$

Acetaldehyde, ethylene and methane may thus be considered as important intermediates in the formation of hydrogen from ethanol [8,9]. Once formed, methane is difficult to be reformed by steam, which penalizes the $H_2$ yield. The ethanol dehydration reaction occurs mainly on the acid sites of the support. The formation of ethylene involves a deactivation of the catalyst, the ethylene being a coke precursor [3], at the origin of the catalyst deactivation. The ethanol dehydrogenation yields acetaldehyde. This reaction depends not only on the basicity of the supports but also on the

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activity of supported metals in dehydrogenation. Noble metals, especially Rh and Pt [8–16], were investigated in ESR. It was shown that Rh was the most active metal in the ethanol steam reforming, as for the steam reforming of many hydrocarbons. The choice of the support is a key factor for a good stability of the catalyst. It has a very strong effect on both the activity and the selectivity of the metal. The support plays a crucial role in the steam reforming reaction: (i) it may favor water splitting into OH groups and promote the migration of these reactive species toward the metal particles, where the final step of the $CO_x$ and hydrogen formation occurs [2,3]; (ii) it may catalyze reaction (4) and/or (5) and affect the selectivity in the final products [8,17,18]; and (iii) it may finally contribute to the stabilization of the metal particles at high temperature under steam [19–21]. Alumina is a support with a mobility of OH groups starting from 400 °C and it is very often used for hydrocarbon steam reforming ($400\ °C < T < 500\ °C$) [2,3]. However for reactions carried out at higher temperatures, typically higher than 600 °C, one reports a phenomenon of diffusion of the metal ions in the support and even the formation of aluminates starting from 700 °C [22–25]. This is not easily reversible and leads to the deactivation of the catalyst. Auprêtre et al. [26] tested several catalysts, and the results obtained with the $MgAl_2O_4$ spinel support allowed a strong limitation of deactivation by the aluminate formation.

Some papers dealt with the use of crude bioethanol for hydrogen production [27–29], but a majority of studies reported in the literature on bioethanol steam reforming deals with the use of a mixture of water and pure ethanol. However, the use of a raw bioethanol feed, limiting the purification steps, is of a major importance for a cost effective industrial application. But the presence of impurities in the feed may induce the deactivation of the catalyst. Then, the aim of this study is to show the effect of impurities present in raw bioethanol, such as esters, aldehydes, higher alcohols or acetic acid, on the stability of the 1%Rh/$MgAl_2O_4/Al_2O_3$ catalyst during bioethanol steam reforming for hydrogen production.

## 2. Experimental

### 2.1. Catalyst preparation

The starting materials used for the catalyst preparation were γ-alumina beads (~200 $m^2\ g^{-1}$, 1–2 mm in diameter) provided by Axens. The support was prepared by modification of the alumina beads by impregnation of magnesium acetate $Mg(CH_3COO)_2 \cdot 4H_2O$ (Alpha Aesar) in order to obtain 5 wt% of Mg in the support. The spinel was formed via a high-temperature solid–solid reaction between magnesium oxide (ex-acetate) and the γ-alumina beads. Acetate was chosen in order to obtain a better control on the acidity of the support [26]. The rhodium catalyst (~1 wt% Rh) was prepared by wet impregnation of rhodium chloride $RhCl_3$ (Acros) for 48 h at ambient temperature. This metal precursor was chosen because it favors a good dispersion of rhodium at the support surface without a significant increase in the solid acidity [26]. The impregnated support was evaporated under stirring at 45 °C during 24 h and dried at 120 °C for 15 h. The catalyst was finally calcined under a 30 $cm^3\ min^{-1}$ air flow at 700 °C for 4 h (ramp 2 °C $min^{-1}$) to stabilize the solid before reaction. The complete experimental procedure and the characteristics of the catalyst are described in detail in ref. [26]. The nomenclature of the catalyst is Rh(1%)/$MgAl_2O_4/Al_2O_3$.

### 2.2. Ethanol steam reforming reaction (ESR)

The experiments were performed at 2 bar, controlled by a back pressure regulator (Swagelock). The steam reforming reaction was carried out in a flow reactor ($L = 550$ mm; $\varnothing_{int} = 12.5$ mm) made of refractory steel (TP 310 Z15CNS25). The ethanol/water mixture was injected with a liquid pump (Gilson 307) and preheated at 130 °C before entering the reactor. The molar ratio $R$ between ethanol and water was chosen equal to 4. The catalyst sample (typically 250 mg) was diluted in carborundum (SiC) (2.75 g), with roughly the same particle size. The resulting weight hourly space velocity (WHSV), calculated by dividing the ethanol flowrate (g $h^{-1}$) by the mass of catalysts (g) was equal to 19.5 $h^{-1}$. The product gases were first analyzed on line in a gas chromatograph (GC) equipped with a FID detector (Varian) after separation on an AT$^{TM}$-aquawax column (30 m, 0.25 mm) (Alltech). This analysis allowed us to determine the amount of organic compounds present in the reaction flow (ethanal, ethanol, ethanoic acid, ethyl ethanoate, etc.). The reaction gases were passed through a condenser at −2 °C to collect water and organic compounds mentioned above. The flow of non condensable gases ($H_2$, CO, $CO_2$, $CH_4$, $C_2H_4$, $C_2H_6$, $C_3H_6$, and $C_3H_8$, etc.) was measured on line using a gas meter (Ritter) and acquired in the computer. These gases were analyzed on line by a TCD (Varian) with helium carrier ($N_2$, $O_2$, CO and $CO_2$), by a GC with a FID detector (Varian) with helium carrier (hydrocarbon compounds) and by an external GC with a TCD detector (Perichrom) with nitrogen carrier ($H_2$). These analyses allowed us to determine every 15 min the exact composition of the product gas and of unconverted reactants (water and ethanol).

Before each catalytic test, the catalyst sample was reduced at the reaction temperature (675 °C) for 14 h under $H_2$ (9 $dm^3\ h^{-1}$) after having been heated from ambient temperature with a temperature ramp of 10 °C $min^{-1}$ and flushed under $N_2$ (9 $dm^3\ h^{-1}$) in order to remove hydrogen. The temperature of 675 °C was chosen because at this temperature and with the chosen WHSV, the ethanol conversion is not total. It reaches 78% after 8 h of time-on-stream with pure ethanol while keeping a good $H_2$ yield. These reaction conditions allowed us to discriminate the possible effects of the compounds present in bioethanol. Various types of impurities were studied on model mixtures by adding 1% (molar percentage) of the chosen impurity in the water and ethanol mixture.

If $n_X^{in}$ and $n_X^{out}$ are the molar flow rates of the product $X$ at the inlet and the outlet of the reactor, respectively, the catalyst performance is characterized by:

- the product yield (mole of $X$ per mole of introduced EtOH):

$$Y_X = \frac{n_X^{out}}{n_{EtOH}^{in}}$$

- the ethanol conversion:

$$X_{EtOH} = \frac{n_{EtOH}^{in} - n_{EtOH}^{out}}{n_{EtOH}^{in}} \times 100$$

- the selectivity for CO/$CO_x$ compounds:

$$S_{CO/CO_X} = \frac{n_{CO}^{out}}{n_{CO}^{out} + n_{CO_2}^{out}} \times 100$$

To give the efficiency of the overall process, including steam reforming and water gas shift (WGS), a theoretical hydrogen yield is also calculated (supposing a total conversion of $C_2H_5OH$ into $H_2 + CO_2$) according to:

$$Y_{H_2 th} = \frac{n_{H_2}^{out} + n_{CO}^{out}}{n_{H_2}^{out}} \times Y_{H_2}$$

## 3. Results

### 3.1. Performance of the catalyst for the ethanol steam reforming

The ethanol steam reforming was first performed using a pure ethanol and water mixture, i.e. without impurity, in presence or absence (blank experiment) of the Rh(1%)/$MgAl_2O_4/Al_2O_3$ catalyst. Results are summarized in Table 1 where they are compared to the thermodynamic values at the equilibrium.

In absence of catalyst (blank reaction), an initial 66% conversion is observed. As the same result was obtained using a quartz reactor, it can be inferred that this conversion is due to the homogeneous gas phase thermal decomposition. The main products are $H_2$, CO and $CH_4$ (reaction (6)). Ethylene, produced by dehydration, acetaldehyde, resulting from dehydrogenation, and ethane are also observed. The amount of water is higher than the amount introduced indicating that water does not react with ethanol in the absence of catalyst, it is produced during the reaction by the dehydration of ethanol. It is important to note that, in absence of catalysts, the reaction is rapidly stopped, the tubes being blocked by the coke produced.

In presence of catalyst, the initial conversion is of 93%. The hydrogen yield is lower than the value predicted by the thermodynamic. This result is due in part to the incomplete conversion of ethanol and to (i) a relatively high methane yield, which is indicative of ethanol cracking (reaction (6)) and (ii) a non negligible amount of C2 compounds.

Fig. 1 presents the evolution of the dry gas flowrate and ethanol conversion as a function of time on stream (8 h) during the steam reforming of pure ethanol. It shows that these two parameters are dependent and decrease linearly as a function of time on stream, except during the first hour corresponding to the start-up of the reaction. The comparison between the initial values of yields measured after 1 h (Table 1) and those after 8 h of time on stream (Table 3) shows that during the reaction, the yields of $H_2$, CO and $CH_4$ decrease as a consequence of the decrease of the ethanol conversion. On the contrary, the yield of other products, especially intermediate products such as ethylene and acetaldehyde, can be considered as unchanged. It is known that acetaldehyde can easily undergo decarbonylation to form $CH_4$ and CO [30] or be converted by steam reforming. On the contrary, ethylene is an undesired product since it is a coke precursor at the origin, in part, of the deactivation observed. It should be noted that the deactivation may also result from the sintering of rhodium, involving a decrease in accessible metal surface, even if Frusteri et al. [31] have shown that Rh, when supported on MgO, is not sensitive to sintering during the ethanol steam reforming reaction compared to Ni, Co or Pd.

### 3.2. Influence of impurities on the ethanol steam reforming

The composition of crude bioethanol is presented in Table 2. The main impurities are alcohols accounting for 87% of the impurities contained in crude ethanol, the most important being propan-1-ol (27%) and methyl-3 butanol-1 (27%). One can also note the presence of esters, aldehydes, acetic acid and nitrogen-containing bases. In order to study the impact of each type of impurity on the ESR, "model" crude ethanol feeds were prepared by addition of 1 mol% of one impurity (0.01 mol $mol^{-1}$ of ethanol) It is important to note that the quantities of impurities taken for the tests are much higher than the values mentioned in Table 2. This choice was made to better see the role of each impurity on ESR during a short time on stream. The catalytic performances obtained with the "model" crude ethanol mixtures will be compared to those obtained with the pure ethanol mixture, considered as a reference.

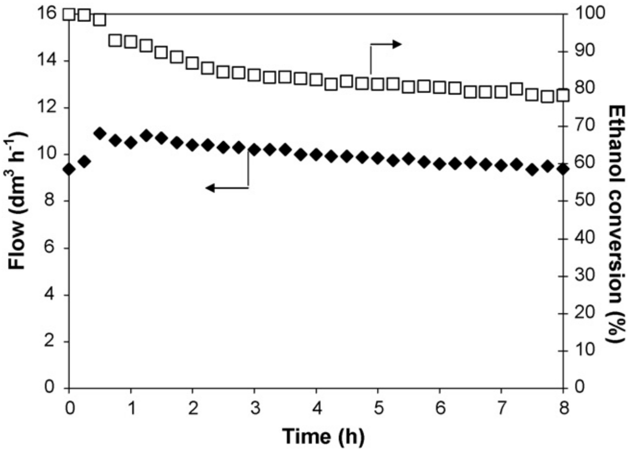

**Fig. 1.** Dry gas flowrate and ethanol conversion as a function of time on stream obtained during pure ethanol steam reforming (675 °C, 2 bar, $R = 4$) in the presence of the Rh/$MgAl_2O_4/Al_2O_3$ catalyst.

Two series of impurities have been studied, the first one corresponding to molecules with four carbon atoms and different functions (butanal, diethylether, butanol, ethylacetate) and the second one to molecules with acidic and basic properties (acetic acid and diethylamine).

#### 3.2.1. Effect of acidic and basic impurities

The impact of the acid–base properties of the impurities on the ESR was studied using model impurities as present in crude ethanol, namely, acetic acid and diethylamine. Acetic acid is a relatively weak acid whereas diethylamine is a strong base. The catalytic activity of the support for ethanol dehydration is associated with its acid-base properties. Then, it can be expected that both acid and basic substances will have an effect on ethanol dehydration [32]. For example, it was shown that basic molecules like pyridine may compete with alcohol molecules for the acidic sites, whereas acetic acid may either promote olefin formation or inhibit it while favoring the esterification of the alcohol by acetic acid, depending on the structure of the alcohol used [33]. On the

**Table 1**
Initial performances in steam reforming of pure ethanol with or without Rh(1%)/$MgAl_2O_4/Al_2O_3$ catalyst after 1 h of time on stream (T = 675 °C, P = 2 bar, R = 4)

| | Yield (mol $mol^{-1}$) | | | | | | | | C balance (%) | $X_{EtOH}$[a] (%) | $S_{CO/CO_x}$[b] (%) | $H_2$ yield with WGS[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $CH_3CHO$ | $H_2O$ | | | | |
| Thermodynamic estimation | 4.07 | 0.88 | 0.86 | 0.26 | 0 | 0 | 0 | 2.4 | 100 | 100 | 50 | 4.95 |
| Blank reaction | 0.55 | 0.30 | 0.00 | 0.28 | 0.11 | 0.04 | 0.08 | 4.1 | 86 | 66 | 100 | 0.85 |
| Rh(1%)/$MgAl_2O_4/Al_2O_3$ | 2.58 | 0.69 | 0.35 | 0.34 | 0.08 | 0.06 | 0.02 | 3.4 | 92 | 93 | 66 | 3.27 |

[a] Ethanol conversion.

[b] Selectivity for $CO/CO_x$.

[c] Taking into account the amount of CO, considering that all the CO produced reacts with $H_2O$ to give $CO_2$ and $H_2$.

**Table 2**
Composition of rectified and crude alcohol

| Characteristic of the feed | Unities | Rectified alcohol | Raw alcohol |
|---|---|---|---|
| Alcohol percentage | %vol. (at 20 °C) | 96.3 | 92,9 |
| Total acidity (acetic acid) | g m$^{-3}$ | 0.8 | 04 |
| Dry extract | g m$^{-3}$ | 20 | 39 |
| Esters | g m$^{-3}$ | <1 | 123 |
| Aldehydes | g m$^{-3}$ | <1 | 108 |
| Methanol | g m$^{-3}$ | 42.5 | 94 |
| Butan-2-ol | g m$^{-3}$ | <0.5 | <10 |
| Propan-1-ol | g m$^{-3}$ | <0.5 | 581 |
| Methyl-2 propanol-1 | g m$^{-3}$ | <1 | 304 |
| Propen-2 ol-1 | g m$^{-3}$ | n.d. | <10 |
| Butan-1-ol | g m$^{-3}$ | <0.5 | <10 |
| Methyl-2 butanol-1 | g m$^{-3}$ | n.d. | 273 |
| Methyl-3 butanol-1 | g m$^{-3}$ | n.d. | 582 |
| Methyls-butanol-1 | g m$^{-3}$ | <0.5 | 855 |
| Total higher alcohols | g m$^{-3}$ | <1 | 1746 |
| Total sulphur | mg dm$^{-3}$ | <0.2 | <0.2 |
| Volatile nitrogenated bases | mg kg$^{-1}$ | <0.2 | 1.2 |

Analysis performed by the alcohol distillers union (n.d.: non detected).

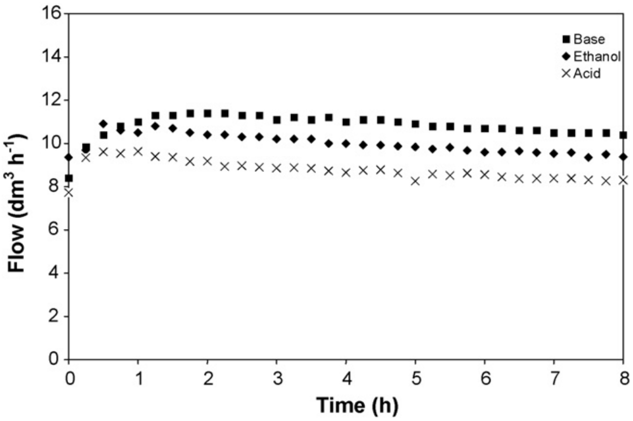

**Fig. 2.** Dry gas flowrate as a function of time on stream obtained during pure ethanol steam reforming (◆) or with 1% of diethylamine (■) or acetic acid (×), in the presence of the Rh/$MgAl_2O_4$/$Al_2O_3$ catalyst (675 °C, 2 bar, $R = 4$).

other hand, the adsorption of acidic molecules on the surface causes the acidity of the surface to increase [33] and then may favor the catalyst deactivation.

The results obtained in the presence of the acidic and basic impurities, and in the presence of pure ethanol as a reference, are summarized in Table 3 and illustrated in Fig. 2. Fig. 2 shows that, except at the starting point of the reaction, the dry gas flowrate in the presence of the amine is definitely higher than that of the reference test. This may be directly linked to the higher ethanol conversion observed in the presence of the amine (Table 3). This highest ethanol conversion has a direct consequence not only on the hydrogen yield but also on the CO, $CO_2$ and $CH_4$ yields (Table 2), which are also slightly higher in the presence of the amine than with pure ethanol. On the contrary, the yields of intermediate products such as ethylene and acetaldehyde can be considered as identical in the presence of diethylamine compared to the pure ethanol/water mixture. If we look at the amount of water, it is also the lowest in the presence of diethylamine, which indicates that a more important amount of water has reacted in the presence of the base. These changes in the products yields, especially hydrogen, due to the addition of diethylamine in the ethanol/water mixture should be explained by the steam reforming of diethylamine even if only 1% of diethylamine was added to pure ethanol. Then, it is interesting to analyze the product distribution obtained with or without diethylamine at isoconversion of ethanol, i.e. at the same value of ethanol conversion. This can be performed by comparing the data obtained at 88% of ethanol conversion, corresponding to 8 h of time on stream in the presence of diethylamine (Table 3), to those obtained at 2 h of time on stream with pure ethanol (results not shown). In that case, the yields of the various products can be considered as identical. Consequently, it can be deduced that diethylamine does not modify significantly the reaction pathway during the ethanol steam reforming but it promotes the ethanol steam reforming by increasing its conversion. This promoting effect of diethylamine may be explained by the fact that this basic molecule may compete with the alcohol molecules for the acidic sites, in accordance with ref. [33], thus inhibiting the dehydration of ethanol on these sites. However, in the presence of diethylamine in the stream, (i) the yield of ethylene and (ii) the rate of deactivation, illustrated by the evolution of the gas flowrate versus time on stream (Fig. 2) are similar to those obtained with the pure ethanol and water stream Then it can be inferred that the diethylamine transformation also yields ethylene and does not limit coke production leading to catalyst deactivation. The promoting effect of diethylamine on ethanol conversion may also be explained by a modification of the metal electronic properties resulting from an electron transfer of the free nitrogen doublet toward the metal phase [34,35].

In the presence of acetic acid, the dry gas flowrate (Fig. 2) is lower than that obtained with the reference mixture (water + ethanol), which is due to the lower ethanol conversion observed in the presence of the acid. As a result, the hydrogen yield and the yield of other products strongly decreased. At 88% of conversion (obtained at the beginning of the reaction, after 1 h of time on stream) the hydrogen yield (2.37 mol mol$^{-1}$ of ethanol) is lower than that obtained with pure ethanol or with ethanol + diethylamine. The yield of CO, $CO_2$, $CH_4$ and acetaldehyde are also lower whereas the yield of ethylene and ethane are higher. Neither ester that may result from the reaction between ethanol and acetic acid nor acetone, as observed by Takanabe et al. [36,37] during acetic

**Table 3**
Performances in steam reforming of ethanol with or without 1% of impurity using Rh(1%)/$MgAl_2O_4$/$Al_2O_3$ catalyst after 8 h of time on stream ($T = 675$ °C, $P = 2$ bar, $R = 4$)

| Impurity | Yield (mol mol$^{-1}$) | | | | | | | $X_{EtOH}$[a] (%) | $S_{CO/CO_x}$[b] (%) | $H_2$ yield with WGS[c] | $H_2O$ yield |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $CH_3CHO$ | | | | |
| – | 2.35 | 0.57 | 0.34 | 0.3 | 0.07 | 0.04 | 0.03 | 78 | 63 | 2.92 | 3.5 |
| Diethylamine | 2.53 | 0.67 | 0.37 | 0.38 | 0.06 | 0.04 | 0.02 | 88 | 64 | 3.2 | 3.45 |
| Acetic acid | 2.08 | 0.49 | 0.31 | 0.26 | 0.07 | 0.04 | 0.04 | 72 | 61 | 2.57 | 3.6 |
| Butanal | 2.6 | 0.67 | 0.39 | 0.35 | 0.06 | 0.04 | 0.02 | 86 | 62 | 3.27 | 3.41 |
| Diethylether | 1.2 | 0.34 | 0.13 | 0.29 | 0.11 | 0.05 | 0.05 | 59 | 72 | 1.54 | 3.89 |
| Butanol | 1.42 | 0.35 | 0.19 | 0.26 | 0.09 | 0.04 | 0.04 | 64 | 65 | 1.77 | 3.95 |
| Ethyl acetate | 0.97 | 0.31 | 0.09 | 0.29 | 0.13 | 0.04 | 0.05 | 57 | 77 | 1.28 | 4.06 |

[a] Ethanol conversion.
[b] Selectivity for CO/$CO_x$.
[c] Taking into account the amount of CO, considering that all the CO produced reacts with $H_2O$ to give $CO_2$ and $H_2$.

acid steam reforming over $Pt/ZrO_2$ catalysts, was observed. This result confirms that the presence of an acid such as acetic acid may favor the production of ethylene by dehydration reaction followed by the deactivation of the catalyst by coke deposition. It is also known that acetic acid forms acetate species at low temperature on clean noble metal surfaces and that acetate species decompose to yield $H_2$, $CO_2$ and adsorbed carbon on the surface [38,4].

### 3.2.2. Effect of the other types of impurities

Different molecules representative of raw bioethanol impurities were studied separately, namely an aldehyde, a heavier alcohol and an ester. An ether was also added in the series, although no ether was evidenced in raw bioethanol. In order to favor the comparisons, molecules with the same amount of carbon atoms were chosen, i.e. butan-1-al, diethylether, butan-1-ol and ethyl acetate. Results are presented in Table 3 and Fig. 3. In presence of butanal, results are similar to those obtained with diethylamine: the gas flowrate and the ethanol conversion are enhanced compared the reference test. The yields of the different products (Table 3) can also be considered as similar to those obtained with diethylamine. Conversely, the presence of the other impurities, i.e. the ester, ether, C4 alcohol, strongly affects the catalytic performance, especially the ethanol conversion. Furthermore, the conversion, measured after 8 h of time on steam, approaches the value obtained without catalyst by thermal decomposition (Table 1). Nevertheless, the yields of hydrogen are higher than that obtained by thermal decomposition thus proving that, even if the catalyst is strongly poisoned by the presence of these impurities, it is not totally deactivated. The poisoning effect of these impurities can be classified in this increasing order: butanol < diethylether < ethyl acetate. The yields of final products, i.e. hydrogen, CO, $CO_2$ and methane are strongly decreased compared to the reference test, whereas the yields of intermediate products, namely ethylene and acetaldehyde are higher than those obtained with the pure ethanol/water mixture. This proves that the presence of these impurities affects the overall kinetics of the reaction by probably decreasing the number of active sites. Then, it can be inferred that intermediate products are rapidly produced by ethanol dehydration or dehydrogenation on the catalyst but they are more slowly transformed. Moreover, the presence of high amounts of ethylene may enhance the deactivation of the catalysts by formation of carbonaceous products. It is difficult to compare the product distribution obtained in the presence of these various impurities to that obtained on the pure ethanol feed at isoconversion, the maximum of conversion reached with these impurities being much lower than that obtained in the reference test. Nevertheless, the calculation of the selectivity, calculated from the data given in Table 3 by dividing the amount of product (in mol) by the amount of ethanol converted (in mol), demonstrates that the selectivity for hydrogen formation is significantly decreased in the presence of these impurities: it is equal to 2.03, 2.2 and 1.7 in the presence of the ether, butanol and ester, respectively, whereas, it is equal to 3.01 with the pure ethanol feed. Then, it can be inferred that these impurities strongly poisoned the catalyst surface, but in a different way. In the case of diethylether, the enhanced production of ethylene may be explained by the dehydration of this impurity on the acidic sites of the support, as described by Knözinger and Köhne [39]. The deactivation observed in the presence of butanol may be linked to the production of butene, as intermediate product, by dehydration reaction. Although this olefin has not been detected in the reaction products, the formation of butene may contribute to the coke formation. Indeed, it can be inferred that butanol may be either dehydrated to olefin or dehydrogenated to aldehyde according to a similar mechanism to that proposed for ethanol [8,9]. However, the dehydrogenation of butanol, yielding butanal, is probably not favored on the $Rh/MgAl_2O_4/Al_2O_3$ catalyst, since butanal may promote the ethanol conversion. As far as the deactivation by the ester is concerned, it may be explained in part by the hydrolysis of ethylacetate on the acidic sites of the support, yielding ethanol and acetic acid [40], and then to the presence of acetic acid. However, the deactivation observed is much more important than that observed in the presence of acetic acid (see previous paragraph). Another possibility will be a competitive adsorption, where ethylacetate will be more strongly adsorbed on active sites of the catalyst than ethanol and/or water. It has been reported in the literature that ethylacetate is more strongly adsorbed on alumina than ethanol [40] and that this stronger adsorption leads to an inhibition of ethanol oxidation. As shown by results presented in Table 3, the yield of water obtained during the steam reforming of ethanol in the presence of ethyl acetate is equal to 4.06 mol $mol^{-1}$ of ethanol introduced, that is slightly higher than the water–ethanol molar ratio introduced ($R = 4$). Consequently, it can be deduced that the activation of water on the support is likely to be hindered when ethyl acetate is present; furthermore, the amount of water produced during the reaction is higher than the amount consumed, proving that the dehydration reaction yielding ethylene is predominant.

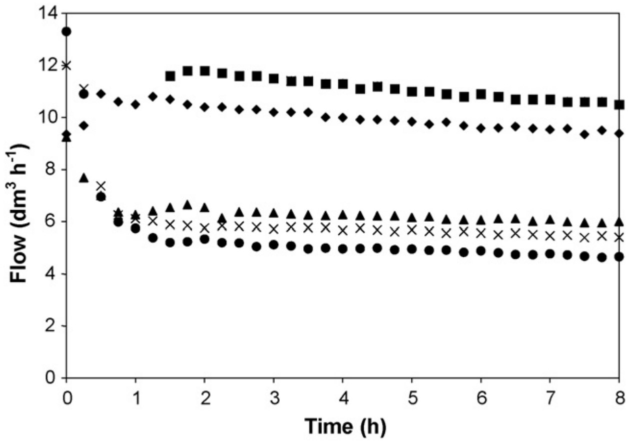

**Fig. 3.** Dry gas flowrate as a function of time on stream obtained during pure ethanol steam reforming (◆) or with 1% of butanal (■), butanol (▲), diethylether (×), or ethylacetate (●) in the presence of the $Rh/MgAl_2O_4/Al_2O_3$ catalyst (675 °C, 2 bar, $R = 4$).

## 4. Conclusion

The present paper aimed to evidence the effect of various impurities present in raw bioethanol on the catalytic performance of an $Rh/MgAl_2O_4/Al_2O_3$ catalyst for ethanol steam reforming. The impurities chosen were globally representative of those present in raw bioethanol, namely acetic acid, diethylamine and various type of molecules with the same number of carbon atoms, i.e. a higher alcohol, butanol, an aldehyde, butanal, an ester, ethyl acetate and an ether, diethylether. The impurities can be classified in two categories, corresponding to impurities with either a promoting effect (diethylamine and butanal) or a poisoning effect (butanol, diethylether and ethyl acetate). In the latter case the deactivation of the catalyst is mainly due to coke deposition.

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