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## Equilibrium composition in the reaction of steam reforming of ethanol to produce H<sub>2</sub>

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## ABSTRACT

In order to compare the equilibrium composition of the reaction products in the steam reforming of ethanol to produce H<sub>2</sub> at various temperatures using the catalysts of Ni-hydrotalcite, Pt/hydrotalcite and Co/hydrotalcite, it was carried out the calculation of equilibrium composition of the reaction products. The equilibrium constants were calculated from thermodynamic properties in function of the temperature at 1 atm. The main reaction products were: H<sub>2</sub>, CO<sub>2</sub>, CH<sub>3</sub>CHO, CH<sub>4</sub> and CH<sub>2</sub> = CH<sub>2</sub>. These catalysts showed very low selectivity to CO. All the catalytic experiments were made at 450°C using a molar ratio H<sub>2</sub>O/ethanol of 4. This study demonstrates as a first approximation, if we are choosing a good catalyst for this reaction by the calculation of the equilibrium composition of six basic reactions.

## 1.- Introduction.

The reaction of ethanol with steam is strongly endothermic and it only produces H<sub>2</sub> and CO<sub>2</sub> if the ethanol reacts in the most desirable way. However, other undesirable products such as CO and CH<sub>4</sub> are also in general formed during the reaction [1]. Other reactions occur such as ethanol dehydrogenation to CH<sub>3</sub>CHO, dehydration to CH<sub>2</sub>=CH<sub>2</sub>, decomposition to CO and CH<sub>4</sub> or CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. The CH<sub>3</sub>CHO and the CH<sub>2</sub>=CH<sub>2</sub> are intermediary products that could be formed during the reaction at relatively low temperatures before the formation of H<sub>2</sub> and CO<sub>2</sub> and finally the formation of coke over the surface of the catalyst.

For this reaction, some authors [2-3] have demonstrated that an increase in temperature leads to an increase in H<sub>2</sub> and CO concentration and to a decrease in CH<sub>4</sub> at equilibrium [4]. They examined the thermodynamic equilibrium of this system and suggested operating temperatures greater than 650K, atmospheric pressure and a molar ratio of ethanol/steam of 10 in the feed to maximize the production of H<sub>2</sub>, minimize the formation of CO and CH<sub>4</sub> and avoid deposition of coke on the catalyst. Other authors [1] have also carried out a thermodynamic analysis of the system. They demonstrated that an increment in the total pressure led to decrease of H<sub>2</sub> and CO while the composition of the CH<sub>4</sub> in the equilibrium increased. However the system of H<sub>2</sub> production and its purification has been operated at low pressure when the level of CO is reduced and the gas is rich in H<sub>2</sub> using a metallic membrane of Pd.



Some authors carried out a thermodynamic analysis of the ethanol-water system applied to a fuel cell and suggested that a high water-to-ethanol ratio in the feed reduced the yield of undesirable products such as CO, CH<sub>4</sub> and carbon [5].

The catalytic process has been studied by developing catalysts where different metals such as: Rh, Pt, Ni, Co, Zn, Fe, Cu, Au, Pd and Ru have been proven, with diverse supports of metallic oxides such as Al<sub>2</sub>O<sub>3</sub> [6] CeO<sub>2</sub> [7], MgO [8], ZnO [9], SiO<sub>2</sub>, Sm<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> [10] La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> [11], CeO<sub>2</sub>-ZrO<sub>2</sub> [12] among other, some alkaline promoters as K, Na and Li have been proven [13].

From many investigations, it could be deduced that the activity and the distribution of products depended on the type and concentration of used metal, of the support type and the preparation method. The biggest interest is to find active catalysts that inhibit coke formation and especially of the CO that is harmful for fuel cells [14]. Catalysts containing Co have showed a significant enhancement of the catalytic performance in the steam reforming of ethanol [10].

Some studies of the chemical composition for this reaction in the equilibrium have been done[15-17].

The aim of this work is to compare the calculated chemical composition in the equilibrium using two approaches (i) considering only the main reaction and (ii) considering six basic reactions versus experimental chemical compositions obtained from the catalysts: Ni, Pt and Co / Hydrotalcite-WOx [18-20].

## **2.- Experimental**

### **2.1- Composition of Ni, Pt and Co Catalysts**

Three series of Ni, Co and Pt supported on Hydrotalcites varying the concentration of WOx were studied previously [18-20]. In those studies, the best catalysts (Table 1), have been compared with the equilibrium mole fractions calculated from: (a) considering only the main reaction and (b) considering six basic reactions.

Table 1. Composition and surface area of the selected Ni, Pt and Co/hydrotalcite-WOx catalysts [18-20]

Catalysts	Ni (wt%)	Pt (wt%)	Co (wt%)	W (wt%)	Surface Area (m <sup>2</sup> /g)
HTN0.5W	1	0	0	0.5	197
HTP0.5W	0	0.35	0	0.5	227
HTC 1W	0	0	1	1	173

### **2.2. - Catalytic evaluation**

For the three series of catalysts, the catalytic evaluation was the same [18-20]. The catalytic ethanol steam reforming was made in a U-shaped stainless steel fixed bed reactor (7 mm internal diameter). The catalyst (1g, 100 US mesh) was charged for each of the reaction tests. The feed of the reactants comprised of a gaseous mixture of ethanol (Aldrich), water as steam and N<sub>2</sub> (purity 99.99%, Infra-Air Products) was supplied by a micrometric needle valve (1

ml/s). A constant mixture  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CH}_2\text{OH}$  (molar ratio of 4:1) in a  $\text{N}_2$  stream was supplied in gas flow using two glass saturators and this mixture was vaporized and kept at  $92^\circ\text{C}$  before it was feed to the reaction chamber.

The temperature of the catalyst was raised at  $450^\circ\text{C}$  in flow of  $\text{N}_2$  for 30 min to activate the catalyst and then the flow of reactants started at this temperature. The catalyst was held at that temperature for 30 min in order to have three analyses and for deactivation tests the catalysts were evaluated during 300 min.

The analysis of the reactants and all the reaction products was carried out online by gas chromatography. Inside an automated injection valve, the sample was divided into two portions which were then analyzed in a different way in order to obtain accurate, complete quantification of the reaction products. One of the portions was used to analyze  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ , using a packed column of silica gel 12 grade 60/80 (18'x 1/8") with a thermal conductivity detector (Gow-Mac 550 apparatus). The second portion was used to analyze  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_2\text{O}$  and  $\text{CH}_2=\text{CH}_2$  with a capillary column (VF-1ms, 15m x 0.25 mm) in a Varian chromatograph CP-3380 with a flame ionization detector (FID). Response factors for all products were obtained and the system was calibrated with appropriate standards before each catalytic test. The conversion (X) was calculated using the ethanol composition before and after of the reaction.

### **3.- Results and discussion**

#### **3.1.- Catalytic Product Distribution.**

Ethanol steam reforming for Ni/hydrotalcite- $\text{WO}_x$  catalysts (Figure 1), Pt/hydrotalcite- $\text{WO}_x$  catalysts (Figure 2) and Co/hydrotalcite- $\text{WO}_x$  catalysts (Figure 3) produced:  $\text{H}_2$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CH}_2=\text{CH}_2$ . These catalysts did not

produce another products and reaction 1 (see reactions below) was considered the main reaction.

In the case of  $\text{CH}_3\text{CHO}$  we found this product in all the catalytic analyses. The presence  $\text{CH}_3\text{CHO}$  suggested that these catalysts acted as dehydrogenation catalysts following the reaction (2). In accordance with the reaction mechanism proposed by Frusteri et al. [8].  $\text{CH}_3\text{CHO}$  is an intermediate product in reactions to produce  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2$ . The presence of  $\text{CH}_3\text{CHO}$  has been reported in ethanol steam reforming using several catalysts. For example in Ni-Mg-Al layered double hydrotalcites the selectivity was of 4% at  $450^\circ\text{C}$  [21], in Rh/MgO, Pd/MgO, Co/MgO and Ni/MgO reported among 5 and 19 %vol. [8]. The  $\text{CH}_3\text{CHO}$  selectivity was 4% and 3% on Ni/ $\text{Y}_2\text{O}_3$ , and on Ni/ $\text{La}_2\text{O}_3$  respectively [11]. Also similar selectivities of  $\text{CH}_3\text{CHO}$  have been observed in our catalytic results (average of 5%). If we choose the reaction mechanism proposed by Frusteri et al. [8], ethanol is firstly dehydrogenated to  $\text{CH}_3\text{CHO}$  which subsequently decomposes into  $\text{CH}_4$  and  $\text{CO}$ . These last ones by steam reforming of  $\text{CH}_4$  and water gas shift reaction of  $\text{CO}$  give rise to the formation of  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CO}$ . Frequently,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$  are reported as final products which are favored through the excess of water in the system [22].

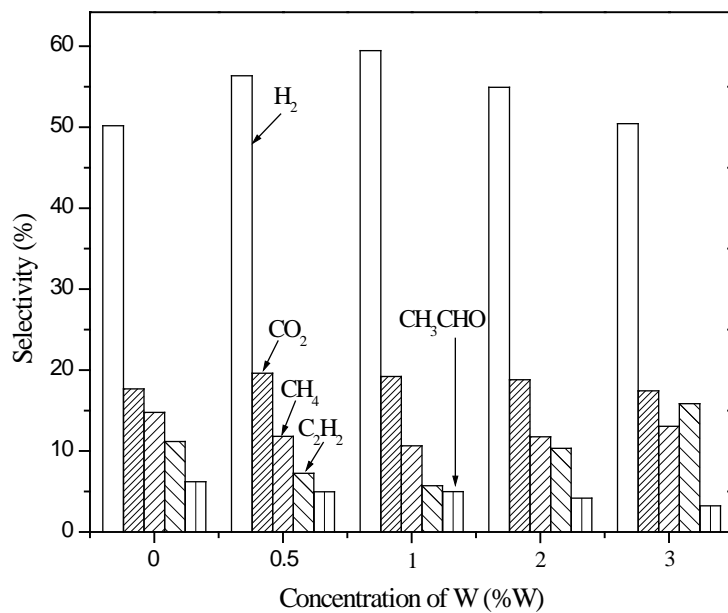


Figure 1. Reaction products from Ni/Hidrotalcite-WOx/catalysts at 450°

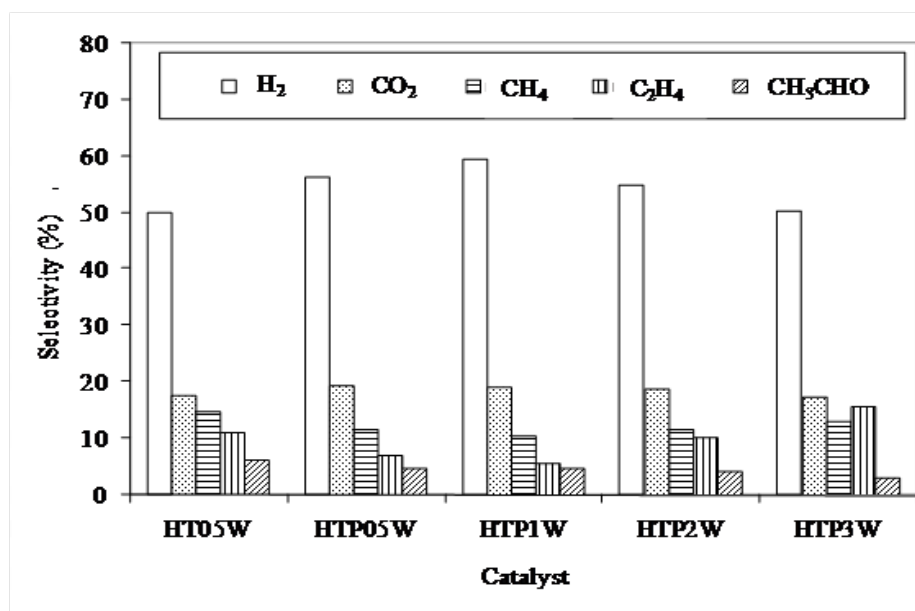


Figure 2. Selectivity of reaction products from ethanol steam reforming over Pt/WOx-Hydrotalcite catalysts at 450°C.

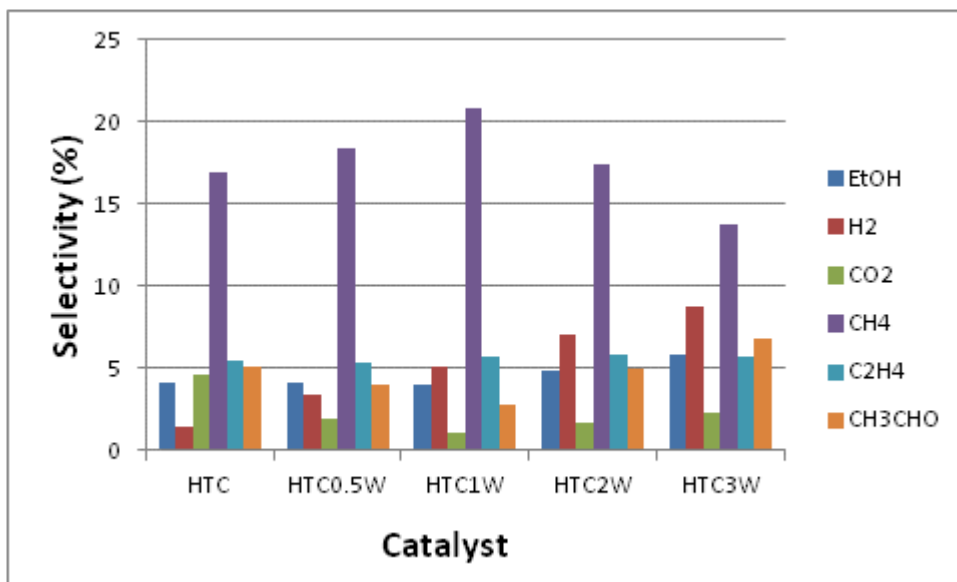


Figure 3. Selectivity of reaction products from ethanol steam reforming over Cot/WO<sub>x</sub>-Hydrotalcite catalysts at 450°C.

We did not find CO in the products distribution. CO formation is not negligible during the steam reforming of ethanol and under our reaction conditions (450°C). The presence of 16 % of CO selectivity has been reported in the homogeneous (non-catalytic) reaction Laosiripojana [23]. Using several catalysts the presence of CO has been reported by Comas et al. [24], these authors obtained 14% using a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Another example was made by Homs et al. [9], using the Co-Cu-ZnO<sub>2</sub> catalyst (at 723K). They obtained a CO selectivity of 1%. Another example using noble metals (Ir, Ru, Pd, Pt) supported on Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> was made by Erdoheily et al. [25]. They reported CO selectivities between 5 and 11%.

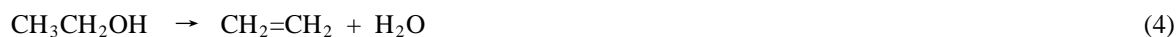
The ethanol dehydration to the olefin, (see the reaction 4) was affected by the presence of Pt. In accordance with Frusteri et al.[8], ethylene and acetaldehyde are intermediate products formed from ethanol dehydration and dehydrogenation respectively, reaction (4) and reaction (2). These products can promote coke formation [26].

The difference in H<sub>2</sub> selectivity between the HTP05W catalyst and the others was very small. It is known, that the H<sub>2</sub> production comes from several reactions; dehydrogenation, water-gas shift conversion of CO and decomposition of oxygenated compounds. In this way, infrared studies have showed that dehydrogenation of molecularly adsorbed ethanol was proposed as a key reaction step [25].

Also it was found that presence of water lowered the temperature at which the acetate species appeared and increased the stability of monodentate ethoxide species and the dehydrogenation of ethanol proceeded on the Pt metal producing H<sub>2</sub> and carbonyl-hydride surface species.

### 3.2.- Selected reactions.

These catalysts produced the following products of reaction:  $H_2$ ,  $CH_3CHO$ ,  $CO_2$ ,  $CH_4$  and  $CH_2=CH_2$ . The presence of  $CH_3COOH$ ,  $CH_3CH=CH_2$  or other oxygenates was not confirmed. For the all the catalysts, the presence of  $CO$  was very small or was not detected using the conductivity detector. Therefore we have selected the reactions that include only the chemical products detected in our experiments. The fewest number of reactions were:



### 3.3.- Equilibrium calculations

In order to get the first approach to equilibrium mole fraction, we performed calculations considering only the reaction (7) which represents the equilibrium constant of the main reaction. Also this constant in function of the reaction temperature was calculated for the 6 reactions as it is shown in Figure 4.

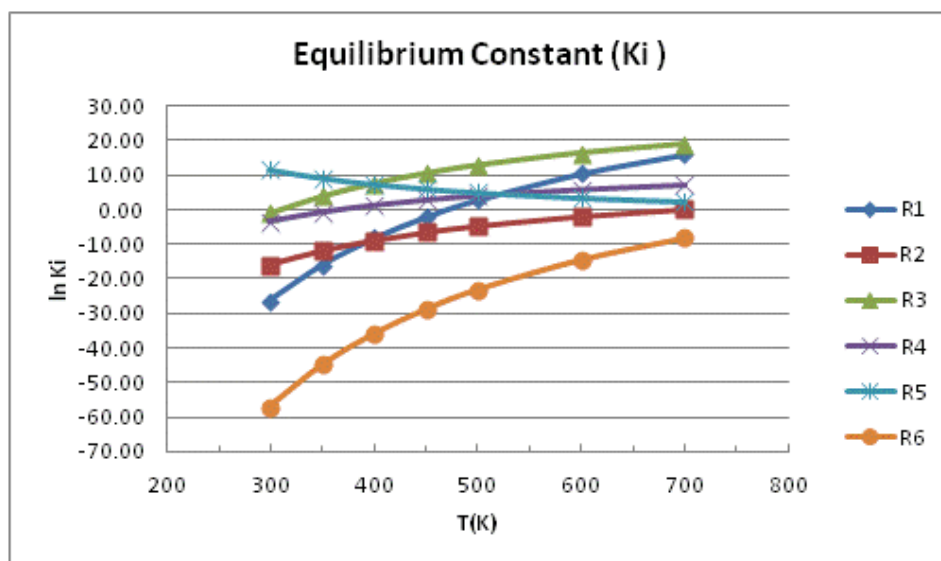


Figure 4. Calculated equilibrium constant  $K_i$  in function of temperature for the reactions that were proposed (equations from 1 to 6)

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The Figure 5 shows the equilibrium mole fractions calculated from equation 7. We considered a molar flow ratio of water to ethanol 4:1, where  $N_{OH}^{\circ} = 1$  mol (moles of ethanol fed to the reactor).

$$K = \frac{y_{CO_2}^2 y_{H_2}^6}{y_{H_2O}^3 y_{OH}} \quad (7)$$

The mole balance of the reaction (1) where X is conversion as follows:

$$N_{OH} = (N_{OH}^{\circ} - N_{OH}^{\circ} X) \quad (\text{moles of ethanol not converted}) \quad (8)$$

$$N_{CO_2} = N_{OH}^{\circ} 2X \quad (\text{moles of CO}_2 \text{ produced}) \quad (9)$$

$$N_{H_2} = N_{OH}^{\circ} 6X \quad (\text{moles of H}_2 \text{ produced}) \quad (10)$$

$$N_{H_2O} = (N_{H_2O}^{\circ} - N_{OH}^{\circ} 3X) \quad (\text{moles of water produced}) \quad (11)$$

$$N = \text{Total moles} = N_{OH}^{\circ} + 4N_{OH}^{\circ} X + N_{H_2O}^{\circ} \quad (12)$$

The mole fractions were:

$$y_{OH} = (N_{OH}^{\circ} - N_{OH}^{\circ} X) / N \quad (13)$$

$$y_{CO_2} = (N_{OH}^{\circ} 2X) / N \quad (14)$$

$$y_{H_2} = (N_{OH}^{\circ} 6X) / N \quad (15)$$

$$y_{H_2O} = (N_{H_2O}^{\circ} - N_{OH}^{\circ} 3X) / N \quad (16)$$

The second approach to the calculation of the composition in the equilibrium has been made considering the six above mentioned basic reactions. We have calculated the  $K_i$  and made the six equilibrium equations as follows:

$$K_1 = \frac{[y_{CO_2}]^2 [y_{H_2}]^6}{[y_{OH}] [y_{H_2O}]^3} P^{\Delta n} \quad (17)$$

$$K_2 = \frac{[y_A] [y_{H_2}]}{[y_{OH}]} P^{\Delta n} \quad (18)$$

$$K_3 = \frac{[y_{CO_2}] [y_{H_2}]^2 [y_M]}{[y_{OH}] [y_{H_2O}]} P^{\Delta n} \quad (19)$$

$$K_4 = \frac{[y_{Et}] [y_{H_2O}]}{[y_{OH}]} P^{\Delta n} \quad (20)$$

$$K_5 = \frac{[y_{CO_2}] [y_{H_2}]}{[y_{CO}] [y_{H_2O}]} P^{\Delta n} \quad (21)$$

$$K_6 = \frac{[y_{CO}] [y_{H_2}]^3}{[y_M] [y_{H_2O}]} P^{\Delta n} \quad (22)$$

Where  $\Delta n = \Sigma(\text{stoichiometric coefficients of products}) - \Sigma(\text{stoichiometric coefficients of reactants})$

P = total pressure of the reaction (atm).

$y_A$  = mole fraction of acetaldehyde

$y_{Et}$  = mole fraction of  $\text{CH}_2=\text{CH}_2$

$y_M$  = mole fraction of  $\text{CH}_4$ .

$y_{CO}$  = mole fraction of CO

The calculated mole fractions for two temperatures at 177 and 450°C were made (Table 2) and we can distinguish the temperature effect on the molar composition. The mole fraction for  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CH}_2=\text{CH}_2$  were almost the same.

Table 2. Calculated mole fractions evaluated at 177°C and 450°C,  $P = 1$  atm and  $N_{OH}^\circ = 1$  mol (mole of ethanol fed to the reactor) and a molar flow ratio of water to ethanol of 4:1.

Temp.(°C)	$y_{OH}$	$y_{H_2}$	$y_{CO_2}$	$y_A$	$y_{Et}$	$y_{CO}$	$y_M$	$y_{H_2O}$
177	0.002	0.509	0.148	0.0239	0.024	0.0000006	0.00005	0.291
450	0.009	0.496	0.145	0.0214	0.024	0.0002	0.0003	0.30

### 3.4.- Experimental and calculated mole fractions

The experimental and equilibrium mole fractions for  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  were compared for the Ni/hydrotalcite-WOx catalysts (Table 3) for 78% of conversion. The calculated mole fractions for the products  $\text{H}_2$  and  $\text{CO}_2$  were higher than the experimental fractions. The reason could be related with the other experimental mole fractions of  $\text{CH}_3\text{CHO}$ ,



$\text{CH}_2=\text{CH}_2$  and  $\text{CH}_4$  that were not included. In the case of water, the differences between experimental and calculated mol fractions were small, because this reactant was in excess with respect to ethanol.

In the case of Pt/ hydrotalcite-WOx the experimental and equilibrium mole fractions for  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  were compared (Table 4). The calculated mole fractions for the products  $\text{H}_2$  and  $\text{CO}_2$  were higher than the experimental fractions in a similar manner than the previous catalysts. Again the reason could be the same as it was previously mentioned because other experimental product mole fractions ( $\text{CH}_3\text{CHO}$ ,  $\text{CH}_2=\text{CH}_2$  and  $\text{CH}_4$ ) were not included.

Finally in the case of Co/hydrotalcite-WOx catalysts the experimental and calculated mole fractions for  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  were compared (Table 5) and small differences were found among the catalysts. These results suggested that these catalysts had high selectivity to  $\text{H}_2$  and  $\text{CO}_2$  and their composition values were very close to the equilibrium concentrations.

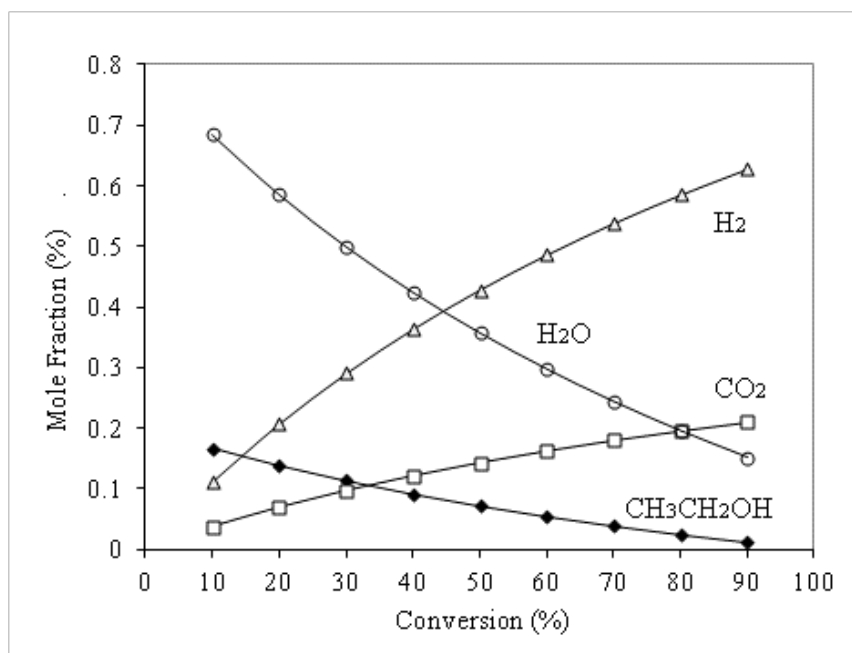


Figure 5. Mole fractions  $y_i$  for each reaction product in the equilibrium calculated from Equation (9).

Table 3. Experimental mole fractions of the ethanol steam reforming over Ni/hydrotalcite-WOx-catalysts at 450°C

Catalyst	$\text{C}_2\text{H}_5\text{OH}$		$\text{H}_2$		$\text{CO}_2$		$\text{H}_2\text{O}$	
	Exper.	Calculated	Exper.	Calculated	Exper.	Calculated	Exper.	Calculated
HT05W	0.026	0.04	0.50	0.592	0.17	0.20	0.14	0.20
HTN05W	0.033	0.04	0.56	0.592	0.19	0.20	0.15	0.20
HTN1W	0.042	0.04	0.59	0.592	0.19	0.20	0.17	0.20
HTN2W	0.051	0.04	0.54	0.592	0.18	0.20	0.17	0.20

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HTN3W	0.068	0.04	0.50	0.592	0.17	0.20	0.21	0.20
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<sup>1</sup> The experimental mole fractions of the CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> were not included.

Table 4. Experimental and equilibrium mole fractions of some reaction products over Pt/WOx-hydrotalcite catalysts at 78% conversion at 450°C. (considering only products of reaction (1))

Catalyst	C <sub>2</sub> H <sub>5</sub> OH		H <sub>2</sub>		CO <sub>2</sub>		H <sub>2</sub> O	
	Exper.	Calculated	Exper.	Calculated	Exper.	Calculated	Exper.	Calculated
HT05W	0.118	0.04	0.337	0.58	0.046	0.20	0.149	0.20
HTP05W	0.109	0.04	0.375	0.58	0.068	0.20	0.148	0.20
HTP1W	0.089	0.04	0.397	0.58	0.106	0.20	0.160	0.20
HTP2W	0.085	0.04	0.379	0.58	0.096	0.20	0.159	0.20
HTP3W	0.074	0.04	0.371	0.58	0.095	0.20	0.176	0.20

Table 5. Experimental and calculated mole fractions of the reaction products for the Co/Hydrotalcite/WOx catalysts at 78% of conversion at 450°C.

Catalyst	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
	Experimental	Experimental	Experimental	Experimental
HTC	0.054	0.51	0.16	0.216
HTC05W	0.055	0.56	0.16	0.22
HTC1W	0.051	0.59	0.16	0.204
HTC2W	0.050	0.47	0.16	0.20
HTC3W	0.034	0.37	0.15	0.136
Calculated	0.040	0.58	0.20	0.20

Table 6. Difference between experimental and calculated mole fractions of the reaction products of the selected catalysts of Ni, Pt and Co/Hydrotalcite/WOx.(First approach, only the main reaction) at 450°C

Catalysts	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Average
HTN0.5W	0.007	0.032	0.01	0.03	0.0197
HTP0.5W	- 0.069	0.205	0.132	0.052	0.080
HTC 1W	- 0.011	- 0.01	0.04	- 0.004	0.0037

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Table 7. Difference between experimental and calculated mole fractions of the reaction products of the selected catalysts of Ni, Pt and Co/Hydrotalcite/WOx.(Second approach, the six basic reactions) at 450°C

Catalysts	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Average
HTN0.5W	0.024	0.064	0.045	0.15	-0.004
HTP0.5W	0.10	-0.121	-0.07	-0.15	-0.062
HTC 1W	0.042	0.094	0.015	-0.096	0.061

The difference of molar fractions between the calculated and the experimental values (Table 7) showed that Ni/hydrotalcite catalyst was closer to the equilibrium.

#### 4. Conclusions

For six ethanol steam reforming reactions the equilibrium constants were calculated depending on temperature using the thermodynamic concepts. Calculated mole fractions of H<sub>2</sub>, CH<sub>3</sub>CHO, CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O and CH<sub>2</sub>=CH<sub>2</sub> were calculated by stoichiometric mass balance using six conversions.

By comparison, it was chosen six basic reactions of H<sub>2</sub> production and their equilibrium constants to calculate the mole fraction of each component versus the experimental mole fraction. The difference in molar fraction between the calculated and experimental values showed that the catalyst made of Ni achieved mole fractions near to the equilibrium ones. The catalysts made with Co and Pt produced similar differences with the equilibrium mole fraction however their average differences were larger than those found for the Ni catalysts.

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#### 6.- Nomenclature

Si (%) = Selectivity to product i

X = Conversion

Ni = Moles of product i

Nj = Moles of each product (included i)



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$K$  = Equilibrium constant

$y_{CO_2}$  = Mole fraction of  $CO_2$

$y_{H_2}$  = Mole fraction of  $H_2$

$y_{H_2O}$  = Mole fraction of  $H_2O$

$y_{OH}$  = Mole fraction of Ethanol

$N_{OH}$  = Moles of ethanol during reaction

$N_{OH}^{\circ}$  = Initial moles of ethanol

$N_{CO_2}$  = Moles of  $CO_2$  during reaction

$N_{H_2}$  = Moles of  $H_2$  during reaction

$N_{H_2O}$  = Moles of  $H_2O$  during reaction

$N_{H_2O}^{\circ}$  = Initial moles of  $H_2O$

$N$  = Total moles

$K_i$  = Equilibrium constant of the reaction “i”

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